Atmospheric oxygen and the global carbon cycle. Observations from the new F3 North Sea platform monitoring station and 6 additional locations in Europe and Siberia

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Chapter 1
General Introduction

Abstract
This chapter gives a general overview of the context of this PhD research. It describes the carbon cycle, the greenhouse effect, the anthropogenic influence and global climate change. Furthermore the general topic of this thesis, atmospheric oxygen (O₂) measurements and the relation with the global carbon cycle is introduced and explained.
1.1. An introduction to the global carbon cycle*

1.1.1. The greenhouse effect: the basis of climate on earth

The climate on earth is shaped by the greenhouse effect. Thanks to the greenhouse effect, the average global surface temperature is about 14°C, whereas without the presence of greenhouse gases, it would be -17°C. The greenhouse gases therefore provide a substantial temperature precondition for life on earth as we know it. Nowadays, when the greenhouse effect is mentioned (e.g. in newspapers or political discussions), most often people refer to the enhanced greenhouse effect, disregarding the fact that the greenhouse effect is a natural phenomenon. Section 1.1.3 elaborates on the human influence on the greenhouse effect.

The influence of the greenhouse effect on the global average temperature is caused by the characteristics of the greenhouse gases in the atmosphere to absorb infrared radiation. The incoming short-wave solar radiation is absorbed by the earth’s surface, and subsequently re-emitted as long-wave thermal infrared radiation. The atmosphere, i.e. greenhouse gases and clouds, absorb a substantial part of this thermal infrared radiation, which is therefore not completely re-emitted into space. The absorption of this thermal infrared radiation leads to a higher global average temperature. The energy balance of the earth (including the greenhouse effect) is shown schematically in figure 1.1.

The major naturally occurring greenhouse gases are water vapour (H\textsubscript{2}O) and carbon dioxide (CO\textsubscript{2}). Additional (natural or anthropogenic) greenhouse gases with a smaller influence are CH\textsubscript{4}, N\textsubscript{2}O, chlorofluorocarbons (CFCs) and ozone. Water vapour plays a natural role in the global water cycle, and is only for a small part directly influenced by anthropogenic activities. Also CO\textsubscript{2} has been present in the atmosphere and acting as a major greenhouse gas before the start of industrialisation. In the tropics, the atmosphere contains a lot of water vapour, due to the high degree of humidity in these regions. Hence, the greenhouse effect there is already very large, which is why the addition of a certain amount of H\textsubscript{2}O has only a small effect. In the polar regions however, the small additional amount of H\textsubscript{2}O has a much larger effect. The role of CO\textsubscript{2} in the greenhouse effect and the processes it is involved in on earth are described in the following section.

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*This section is based on the content of the following books: IPCC (2007) and McKinney and Schoch (2003).
1.1.2. The global carbon cycle

Carbon is found in different reservoirs on earth, the major reservoirs which are directly interacting with the atmosphere are shown in figure 1.2. Fossil fuel is naturally not interacting with the atmosphere, except on millennial timescales (like other constituents of the earth’s crust containing carbon, such as carbonate minerals). The figure shows clearly that –from the given reservoirs– most of the carbon on earth is situated in the oceans.
In comparison with the other compartments, the atmosphere does not contain much carbon. CO$_2$ makes up only 0.04% of the atmosphere, besides the larger constituents N$_2$ (78.08%) and O$_2$ (20.95%). Natural variations in the carbon content of the atmosphere are caused by biological productivity and respiration and interaction with the ocean.

The exchange between the atmosphere and the ocean takes place in the surface ocean. CO$_2$ dissolves in the ocean water, subsequently undergoes a chemical reaction with the ocean water and forms bicarbonate ions (HCO$_3^-$) and carbonate ions (CO$_3^{2-}$), see equation 1.1.

$$\text{CO}_2 \text{ (dissolved)} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (1.1)$$

Together, CO$_2$, HCO$_3^-$ and CO$_3^{2-}$ are called the dissolved inorganic carbon (DIC) of the surface ocean. The exchange of DIC between the surface and the deep ocean is controlled by the solubility pump and the biological pump. The solubility pump is the sinking of heavy cold waters enriched in DIC at high latitudes from the surface ocean to the deep ocean, due to the high solubility of this water. The biological pump is the sinking of dead organisms and particles. Only a small fraction of this sinking biological material reaches the deep ocean as most is converted by bacteria and recirculated to the surface ocean. The mixing between the different layers in the ocean takes decades to centuries for the mixing between the intermediate waters and the surface ocean, and millennia between the intermediate and deep ocean.

The terrestrial biosphere is a smaller reservoir of carbon. The fluxes between the biosphere and the atmosphere are through the processes of photosynthesis and respiration as shown in equation 1.2 in a simplified form.

$$6\text{CO}_2 + 6\text{H}_2\text{O} \leftrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \quad (1.2)$$

The carbon from the atmosphere is included in plants. By decomposition through bacteria the remains are included in the soils and animals consume the vegetation. By means of river transport, there is also a flux from the terrestrial biosphere to the ocean.

Finally, carbon is also situated in the sediments in the form of carbonate rocks and also as fossil fuels. From 1750 the use of fossil fuels, firstly in the form of coal and later on also as petroleum and natural gas, has become an important energy source. The carbon gradually stored in the sediments during millions of years is now instantly (on a geological timescale) released back into the atmosphere. This is currently the major anthropogenic influence on
the global carbon cycle. In the 19th century land use changes in general and deforestation in particular were the most important anthropogenic contributors, and it still comprises about 25% of the anthropogenic influence on the carbon cycle. The effects of the human influence are described in the next section.

1.1.3. **Anthropogenic influence and global warming**

The combustion of fossil fuels releases huge and increasing amounts of CO$_2$ into the atmosphere every year. The interaction between the different carbon reservoirs on earth –atmosphere, land biosphere and oceans– determines the amount of CO$_2$ remaining in the atmosphere, as the rest is taken up by the other two compartments. The major fluxes and reservoirs have been described in the previous section and are shown in figure 1.3, together with the anthropogenic changes to the natural fluxes.

![Figure 1.3: The global carbon cycle, including the major reservoirs atmosphere, terrestrial biosphere, oceans and fossil fuels and the fluxes between the reservoirs. The numbers represent the global carbon cycle in the 1990s and shown in GtC/year. The natural fluxes and reservoirs are presented in black and the anthropogenic changes are shown in red (IPCC, 2007).](image-url)
Fossil fuel consumption patterns have lead to a carbon flux into the atmosphere of $7.2 \pm 0.3 \text{ GtC/year}$ over the period 2000 to 2005. The rising CO$_2$ concentration$^1$ in the atmosphere is a direct effect of the increasing global fossil fuel consumption levels. The rising CO$_2$ concentration is shown in figure 1.4 together with the increasing trends in the greenhouse gases CH$_4$ and N$_2$O. The anthropogenic influence on the composition of the atmosphere is also caused by land use changes. This consists mainly of deforestation and the related biomass burning as well as changes in agricultural practices.

![Concentrations of Greenhouse Gases from 0 to 2005](image)

**Figure 1.4:** The rising concentrations of three major anthropogenically influenced greenhouse gases CO$_2$, CH$_4$ and N$_2$O over the last two millennia (IPCC, 2007).

Figure 1.5 shows a closer look at the increasing trend in the global emissions of fossil fuels (b) together with the increasing atmospheric CO$_2$ concentrations (a) during the last decades. The figure includes also the decreasing atmospheric O$_2$ concentration, shown on a relative scale in per meg; the topic of this thesis. An introduction to atmospheric O$_2$ is included in the next section.

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$^1$ Throughout this thesis the more correct term mixing ratio has been substituted by concentration to avoid confusion with the term O$_2$/N$_2$ ratio.
The rising CO$_2$ concentrations—as well as the increases in the concentrations of other greenhouse gases—enhance the greenhouse effect. The enhanced greenhouse effect leads to warming of the global climate. Global mean surface temperature data confirms this change as it is increasing more rapidly during the last 100 years, from 0.07 $\pm$ 0.02°C per decade to 0.13 $\pm$ 0.03°C per decade and is predicted to increase even faster with 0.15 $\pm$ 0.03°C from 2009 to 2014 (Lean and Rind, 2009). Eleven of the twelve last years before 2006 rank among the 12 warmest years since the start of the measurements in 1850. The warming of the climate leads to other changes such as decreasing snow cover and melting of glaciers and ice caps. Together with thermal expansion due to the temperature increase, this melting leads to sea level rise. The sea level rise is estimated at 1.8 $\pm$ 0.5 mm/year between 1961 and 2003.
The continuing increase in global fossil fuel consumption patterns will lead to a stronger impact of the CO$_2$ emissions on the global climate. Even if all fossil fuel combustion would be halted today, a further temperature increase is expected of 0.6°C during the 21st century. This is mainly due to the delay in response of the oceans. Scenarios predict a further temperature increase between 1.8°C and 4.0°C in a low and high emission scenario respectively. Sea level rise is expected to increase further as well, with 0.2 to 0.6 meter (IPCC, 2007) or 0.75 to 1.90 meter (Vermeer and Rahmstorf, 2009) in the 21st century. Snow cover and sea ice are projected to shrink further.

Another effect of increasing CO$_2$ concentrations is an increased uptake by the oceans. The size of the fluxes between the reservoirs described in this section, is directly related to the size of the reservoirs. Increasing marine CO$_2$ uptake leads to a reduced global surface ocean pH, as can be seen from equation 1.1 in the previous section, since the reaction increases the amount of H$^+$ ions, which are a measure for the pH. Increasing dissolved CO$_2$ in the oceans leads to ocean acidification, which has impact on marine life, such as dissolution of corals and organisms like coccolithophores and foraminifera, which are at the base of the marine food chain. The size of the uptake of atmospheric CO$_2$ by the oceans currently includes large uncertainties. Concurrent measurements of atmospheric CO$_2$ and O$_2$ contribute to reducing these uncertainties. The next section will explain the use of atmospheric O$_2$ in the determination of the marine CO$_2$ uptake in detail.

### 1.2. Atmospheric oxygen

#### 1.2.1. Atmospheric oxygen and the global carbon cycle

Highly precise and accurate atmospheric O$_2$ measurements offer a significant contribution to our understanding of the global carbon cycle (Machta, 1980; Keeling and Shertz, 1992; Keeling et al., 1993; Bender et al., 1996). Specifically, combined measurements of atmospheric O$_2$ and CO$_2$ can be used to partition land and ocean CO$_2$ uptake (Keeling et al., 1996; Langenfelds et al., 1999). Most processes show an inverse relationship between O$_2$ and CO$_2$ (e.g. fossil fuel combustion, photosynthesis and respiration), but in the exchange between the ocean and the atmosphere O$_2$ and CO$_2$ are uncoupled. Marine CO$_2$ uptake leads to a chemical reaction with the ocean water, leading to a CO$_2$ buffer effect. The uptake of O$_2$ does not have this effect, as O$_2$ merely dissolves in water and this is independent of the CO$_2$ uptake process.
The difference in behaviour of \( \text{O}_2 \) and \( \text{CO}_2 \) in ocean-atmosphere exchange yields valuable information about the global carbon cycle in general and the ocean \( \text{CO}_2 \) uptake in particular, which cannot be acquired from measurements of the concentrations of \( \text{CO}_2 \) alone.

\[
\Delta \text{CO}_2 = F - B - O \\
\Delta \text{O}_2 = - \alpha_F \cdot F + \alpha_B \cdot B + Z
\]

**Figure 1.6:** The relationship between \( \text{O}_2 \) and \( \text{CO}_2 \) in the main compartments on earth (symbols defined in the text).

The processes on earth in which \( \text{CO}_2 \) and \( \text{O}_2 \) play a role take place in the main compartments—atmosphere, terrestrial biosphere and oceans—as shown in figure 1.6. The figure includes the following processes: the \( \text{CO}_2 \) emission from fossil fuel combustion (F), the net land biotic \( \text{CO}_2 \) sink (B), the oceanic \( \text{CO}_2 \) sink (O) and the net \( \text{O}_2 \) flux (Z) between the ocean and the atmosphere. In these processes \( \text{CO}_2 \) and \( \text{O}_2 \) are inversely related through their stoichiometric or molar oxidation ratio. This ratio determines the relationship between both gases. The average stoichiometric ratios (\( \alpha_B \) and \( \alpha_F \)) for processes involving \( \text{CO}_2 \) and \( \text{O}_2 \) are reasonably well-known. The average global fossil fuel combustion takes up 1.4 \( \text{O}_2 \) moles from the atmosphere for the release of 1 mole of \( \text{CO}_2 \) (Keeling, 1988b). For photosynthesis and respiration processes this ratio is on average 1.1 \( \text{O}_2 \) moles for each mole of \( \text{CO}_2 \) (Severinghaus, 1995). Marine uptake forms the exception, since the uptake of \( \text{CO}_2 \) is independent of \( \text{O}_2 \) and vice versa. On short timescales (weeks to months) the marine biosphere processes are visible in the atmospheric \( \text{O}_2 \) concentration. The \( \text{CO}_2 \) concentration however does not reflect the short-term ocean biosphere processes as these are buffered by the marine \( \text{CO}_2 \) processes. On short timescales the changes in the atmospheric \( \text{O}_2 \) concent-
tration can therefore be used to determine the (integrated) marine biological production. All processes involve gas exchange with the atmosphere. The changes in the CO₂ and O₂ concentrations in the atmosphere therefore reflect the processes in the other compartments. The long term situation is represented in equation 1.3 and 1.4 (all parameters in moles).

\[
\Delta CO_2 = F - B - O \\
\Delta O_2 = -\alpha_F F + \alpha_B B + Z
\]

On long timescales the net O₂ flux (Z) to the atmosphere is 0.5 PgC/year (Manning and Keeling, 2006). For CO₂ the long term flux (O) is significant, the marine CO₂ content increases over time. The difference in these processes enables us to use the changes in the atmospheric CO₂ and O₂ concentrations to partition the CO₂ uptake from the atmosphere between the land and marine sinks. The long-term situation is illustrated in figure 1.7.

**Figure 1.7:** A schematic overview of the relationship between the changes in the atmospheric O₂ and CO₂ concentrations.

The changes in the atmospheric O₂ and CO₂ concentrations, together with the statistics on fossil fuel combustion and the known stoichiometric ratio for land biological processes yield the average O₂ uptake by the world’s oceans. In case all combusted fossil fuel CO₂ would stay in the atmosphere, the atmospheric observations would reflect the known fossil fuel statistics as presented by the arrow indicated with F and \( \alpha_F F \) in figure 1.7. However, the atmospheric observations (dashed line) show a smaller O₂ decrease and a smaller CO₂ increase than expected from fossil fuel combustion alone. The CO₂ difference can partly be explained by the terrestrial biological activity (B) and the remaining difference is the combined marine uptake (O) and outgassing (Z).
1.2.2. Measuring atmospheric oxygen

The absolute variations of O\textsubscript{2} are in the same range as for CO\textsubscript{2}, but they are to be detected against a much higher background. Measuring atmospheric O\textsubscript{2} concentrations is therefore challenging. The atmospheric O\textsubscript{2} concentration is around 209392 ± 3 ppm (Tohjima et al., 2005), compared to around 380 ppm for CO\textsubscript{2} (e.g. IPCC, 2007). The first technique to measure atmospheric O\textsubscript{2} with the required precision of 1:10\textsuperscript{6} (WMO, 2009) was based on interferometry and was developed by R. F. Keeling (1988a; 1988b). Current techniques meeting the required precision include mass-spectrometry (Bender et al., 1994), a paramagnetic analyzer (Manning et al., 1999), vacuum ultraviolet absorption (Stephens, 1999; Stephens et al., 2003), gas chromatography (Tohjima, 2000) and a fuel cells-based technique (Patecki and Manning, 2007; Stephens et al., 2007; Thompson et al., 2007). Each of these has its specific advantages and disadvantages, mostly relating to the obtained precision or the possibilities to run the instrument automatically, remotely or in harsh conditions (e.g. shipboard).

Changes in the atmospheric O\textsubscript{2} concentration are usually reported as the changes in the ratio of O\textsubscript{2} to N\textsubscript{2}. As the atmospheric N\textsubscript{2} concentration is much less variable, the changes in the O\textsubscript{2}/N\textsubscript{2} ratio mainly represent changes in the O\textsubscript{2} concentration. Unlike the O\textsubscript{2} concentration, the O\textsubscript{2}/N\textsubscript{2} ratio is insensitive to the changes in other atmospheric gases, such as CO\textsubscript{2}. Changes in the O\textsubscript{2}/N\textsubscript{2} ratio of a sample are expressed as relative deviations from a known reference gas, as shown in equation 1.5 (Keeling and Shertz, 1992).

\[ \delta(O_2/N_2) = \frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1 \]  

(1.5)

For natural air, the \(\delta O_2/N_2\) values are relatively small and are therefore multiplied with 10\textsuperscript{6} and expressed in per meg. While mass spectrometers measure the O\textsubscript{2}/N\textsubscript{2} ratio directly, other methods measure the O\textsubscript{2} concentration. When measuring the O\textsubscript{2} concentration directly, dilution by changes in the CO\textsubscript{2} concentration requires a correction and therefore simultaneous measurements of the CO\textsubscript{2} concentration. Equation 1.6 (Stephens et al., 2003; Kozlova et al., 2008) shows the relationship between changes in the O\textsubscript{2} concentration and changes in \(\delta O_2/N_2\).

\[ \delta(O_2/N_2)_{\text{sample}} = \frac{\delta XO_2 + (\Delta CO_2 \cdot S_{O_2})}{(1 - S_{O_2}) \cdot S_{O_2}} \]  

(in per meg)  

(1.6)
Here $S_{O_2} = 0.20946$ (Machta and Hughes, 1970) represents the standard mole fraction of $O_2$ in air and $\delta X_{O_2}$, $\Delta CO_2$ and $\delta O_2/N_2$ are the changes in the $O_2$ mole fraction (i.e. $O_2$ concentration), the $CO_2$ concentration and the $O_2/N_2$ ratio respectively. A change of 1 ppm in the $O_2$ mole fraction without any concurrent change in $CO_2$ therefore causes a change of 6.04 per meg in $\delta O_2/N_2$ (see equation 1.7), while an exchange of a certain amount of $O_2$ molecules for the same amount of $CO_2$ molecules causes a change of 4.77 per meg in $\delta O_2/N_2$.

$$1 \text{ ppm} = \frac{1}{(1 - S_{O_2}) \cdot S_{O_2}} \approx 6.04 \text{ per meg} \quad (1.7)$$

Corrections for other atmospheric species, such as Argon, are not included in equation 1.6 since their variations in natural air are negligible. The amount of water vapour in a sample does however have a large influence on the $O_2$ concentration and the water vapour is therefore removed from the sample either by cryogenic methods or by using a drying agent.

The relationship between atmospheric $O_2$ in per meg and ppm is not difficult to understand but can be complicated. Therefore the calculation is illustrated by a series of examples which look at changes in the concentrations in actually occurring circumstances. In the following examples an air parcel is considered which consists of 1,000,000 molecules of which 209,460 molecules are $O_2$, 780,800 molecules are $N_2$ and 350 molecules are $CO_2$ (see also Stephens, 1999). If we add one molecule of $O_2$, the $O_2$ mole fraction changes by:

$$\left(\frac{209461}{1000001} - \frac{209460}{1000000}\right) = 0.79 \mu \text{mol} / \text{mol}$$

whereas the change in the $O_2/N_2$ ratio in per meg would increase by (equation 1.5):

$$\left(\frac{209461/780800}{209460/780800} - 1\right) \cdot 10^6 = 4.77 \text{ per meg}$$

which is the same as using equation 1.6:

$$\frac{0.79 + 0}{(1 - 0.20946) \cdot 0.20946} = 4.77 \text{ per meg}.$$

The relationship between per meg and ppm in that case is:

$$\frac{4.77}{0.79} = 6.04 \text{ per meg} / \text{ppm}.$$
In the case where one molecule of CO$_2$—instead of O$_2$— is added to the original air parcel, the O$_2$ mole fraction changes by:

$$\left(\frac{209460}{1000001} - \frac{209460}{1000000}\right) = -0.21\text{µmol/mol},$$

while the O$_2$/N$_2$ ratio does not change at all, which also results from equation 1.6:

$$\frac{-0.21 + 1 \cdot 0.20946}{(1 - 0.20946) \cdot 0.20946} = 0 \text{ per meg.}$$

Another example is the case in which one molecule of O$_2$ is added to the air parcel and at the same time, another molecule—e.g. Argon— is removed from the air parcel. In that case the O$_2$ mole fraction changes by:

$$\left(\frac{209461}{1000000} - \frac{209460}{1000000}\right) = 1\text{µmol/mol},$$

whereas the O$_2$/N$_2$ ratio changes by:

$$\left(\frac{209461/780800}{209460/780800} - 1\right) \cdot 10^6 = 4.77 \text{ per meg.}$$

However, when using equation 1.6, the change in δO$_2$/N$_2$ is:

$$\frac{1 + 0}{(1 - 0.20946) \cdot 0.20946} = 6.04 \text{ per meg.}$$

This example shows that the conversion from per meg to ppm does not take into account the changes in other gases than CO$_2$, resulting in different δO$_2$/N$_2$ values. When using the result of equation 1.6, the per meg/ppm relation is again:

$$\frac{6.04}{1} = 6.04 \text{ per meg/ppm.}$$

The same applies when there is a change in the N$_2$ concentration. Adding 1 molecule of N$_2$ and removing a molecule of O$_2$ gives a change in the mole fraction of:

$$\left(\frac{209459}{1000000} - \frac{209460}{1000000}\right) = -1\text{µmol/mol},$$

whereas the O$_2$/N$_2$ ratio changes by:

$$\left(\frac{209459/780801}{209460/780800} - 1\right) \cdot 10^6 = -6.05 \text{ per meg.}$$
Using equation 1.6 for this example gives:

\[
\frac{-1 + 0}{(1 - 0.20946) \cdot 0.20946} = -6.04 \text{ per meg}.
\]

The relation between per meg/ppm is therefore again:

\[
\frac{-6.04}{-1} = 6.04 \text{ per meg/ppm}.
\]

In the final example (5), this CO₂ correction is shown. One molecule of O₂ is added to the air parcel, while a molecule of CO₂ is removed. This leads to a change in the O₂ mole fraction of:

\[
\left(\frac{209461}{1000000} - \frac{209460}{1000000}\right) = 1 \mu\text{mol/mol}.
\]

The O₂/N₂ ratio changes again by:

\[
\left(\frac{209461}{780800} - \frac{209460}{780800}\right) \cdot 10^6 = 4.77 \text{ per meg},
\]

which is in this case equal to the result of equation 1.6:

\[
\frac{1 - 1 \cdot 0.20946}{(1 - 0.20946) \cdot 0.20946} = 4.77 \text{ per meg}.
\]

In this case however, the per meg/ppm relation is different:

\[
\frac{4.77}{1} = 4.77 \text{ per meg/ppm}.
\]

The four examples above clearly show that attention should be paid when dealing with atmospheric O₂ concentrations, the expression in per meg versus expression in ppm (µmol/mol) and processes involving both O₂ and CO₂ (due to the correction for CO₂ in equation 1.6).

Atmospheric O₂ can be measured by several different techniques (as described above). Only by mass spectrometry the O₂/N₂ ratio is obtained directly. Other techniques measure the O₂ concentration and therefore require a conversion to δO₂/N₂ in order to be able to compare the results. The measured O₂ concentration is in that case first expressed as the apparent mole fraction (δXO₂) and secondly converted to δO₂/N₂ by correcting for the dilution by the amount of CO₂ in the sampled air using equation 1.6.

Corrections for other atmospheric species, e.g. Argon, are not included since their variations in natural air are negligible and water vapour is usually removed from the air sample before the measurement.
In chapter 3, the fuel cell technique to measure atmospheric $O_2$ concentrations is presented, in which the sample gas is continuously measured together with a reference gas. To increase the measurement precision of the $O_2$ measurements, the reference and the sample gas are switched between the fuel cells at regular time intervals of 5 minutes. This yields a double differential $O_2$ signal, which is defined by equation 1.8 (Thompson et al., 2007).

$$\Delta(\Delta) = (S_1 - R_2) - (R_1 - S_2) \hspace{1cm} (1.8)$$

$S$ and $R$ are the $O_2$ concentrations of the Sample and the Reference gases in % $O_2$ (of the total measured air) and the subscripts indicate the respective fuel cells on which they were measured. The $\Delta(\Delta)$ symbol indicates that this is a double differential signal.

Figure 1.8 shows an example of a measurement by the two fuel cells. In this example, the sample gas and the reference gas are switched between the two fuel cells every two minutes. The first switch is shortly after 02:58. After that, the $O_2$ concentration of the sample gas is measured by cell 2 ($S_2$) and the reference gas is measured by cell 1 ($R_1$). After the next switch, this is reversed: $S_1$ and $R_2$.

**Figure 1.8:** The $O_2$ concentration of the sample air ($S$) and the reference gas ($R$) alternately measured by cell 1 (light blue squares) and cell 2 (dark blue squares).
Figure 1.9 shows the difference between the signals of both fuel cells (cell 1 - cell 2). So, by switching the reference gas and the sample gas between both fuel cells, this gives either \((R_1 - S_2)\) or \((S_1 - R_2)\). The \(\Delta(\Delta)\) value is then, following equation 1.8, the difference between these two differences, as indicated in figure 1.9.

\[
\Delta(\Delta) = (S_1 - R_1) + (S_2 - R_2) = m(S - R)
\]  

(1.9)

In the ideal case, where both fuel cells act exactly the same, \(m = 2\) and the \(\Delta(\Delta)\) value is then two times the difference between the measured sample and the known reference gas. Using equation 1.9, however, requires the \(O_2\) concentration of the reference gas to be perfectly known, which is why the \(\Delta(\Delta)\) value (i.e. the difference to the reference gas) is directly calibrated on a daily basis with a suite of calibration gases, as described in chapter 3 and appendix A.2 of this thesis.
1.2.3. **Atmospheric potential oxygen (APO)**

Stephens et al. (1998) have defined the tracer Atmospheric Potential Oxygen (APO), as shown in equation 1.10.

\[
\delta \text{APO} = \delta \text{O}_2 / \text{N}_2 + \frac{1.1 \cdot (\text{CO}_2 - 350)}{\text{S}_\text{O}_2} \quad \text{(per meg)}
\] (1.10)

APO is the sum of the O\textsubscript{2} concentration (\(\delta \text{O}_2 / \text{N}_2\)) plus 1.1 times the CO\textsubscript{2} concentration, with 1.1 being the global average stoichiometric ratio (\(\alpha_B\)) between O\textsubscript{2} and CO\textsubscript{2} in terrestrial photosynthesis and respiration processes (Severinghaus, 1995). \(S_{\text{O}_2}\) is the standard mole fraction of O\textsubscript{2} in air. An arbitrary reference of 350 ppm is subtracted from the CO\textsubscript{2} concentration, as used on the Scripps Institution of Oceanography (SIO) per meg scale for APO (Manning and Keeling, 2006). The definition implies that APO is unaffected by activity of land biota and is therefore sensitive principally to ocean-atmosphere exchange of O\textsubscript{2} and CO\textsubscript{2}, but also to changes in N\textsubscript{2} (Manning and Keeling, 2006) and still partly to fossil fuel combustion and its specific oxidation ratio (OR = O\textsubscript{2} : CO\textsubscript{2}). This is illustrated in figure 1.10.

![Figure 1.10](image)

**Figure 1.10**: The relationship between O\textsubscript{2} and CO\textsubscript{2} yield the Atmospheric Potential Oxygen (APO). APO does not include biological processes and therefore mainly represents the marine CO\textsubscript{2} uptake (and a residual part of the fossil fuel combustion).
The global average OR for fossil fuel in the 1990’s was $\alpha_F = 1.39 \pm 0.04$ (Marland et al., 2002; Manning and Keeling, 2006). Therefore the APO on average still includes 0.3 times the fossil fuel combustion contribution, which can be seen from the global budgets for CO$_2$, O$_2$ and APO (in moles) when combining equations 1.3 and 1.4 to 1.11 (Manning and Keeling, 2006).

\[
\Delta\text{CO}_2 = F - B - O \quad \text{(repeated 1.3)}
\]
\[
\Delta\text{O}_2 = -\alpha_F F + \alpha_B B + Z \quad \text{(repeated 1.4)}
\]
\[
\Delta\text{APO} = \Delta\text{O}_2 + \alpha_B \Delta\text{CO}_2 = \left( \alpha_B - \alpha_F \right) F - \alpha_B O + Z \quad (1.11)
\]

Where $\Delta\text{CO}_2$ and $\Delta\text{O}_2$ are the changes in the atmospheric concentration of CO$_2$ and O$_2$ respectively, expressed in moles. $F$ is the CO$_2$ emission to the atmosphere originating from fossil fuel. $B$ is the net uptake of CO$_2$ from the atmosphere by the terrestrial biosphere. $O$ is marine CO$_2$ uptake and $Z$ is the net marine O$_2$ exchange. As both the CO$_2$ fossil fuel source and the terrestrial biospheric CO$_2$ sink are directly coupled to the changes in the O$_2$ concentration, they are included in the relationship for O$_2$ with their respective molar exchange ratios ($\alpha_B$ and $\alpha_F$ respectively). The marine processes involving CO$_2$ and O$_2$ are not coupled, and they are therefore represented by different symbols (O and Z). The relationship for APO as represented in equation 1.11 shows that APO is unaffected by terrestrial biosphere activity (including anthropogenic effects such as deforestation).

As APO is defined to estimate marine CO$_2$ uptake, the small remaining influence of fossil fuel combustion should be accounted for. Sirignano et al. (2010) therefore suggest the use of a modified version of APO, named $\Delta\text{APO}^*$, which is represented in equation 1.12 and is truly only sensitive to ocean-atmosphere exchange.

\[
\Delta\text{APO}^* = \Delta\text{APO} - \left( \alpha_B - \alpha_F \right) F \quad (1.12)
\]

The oxidative ratio for fossil fuel combustion ($\alpha_F$) varies over the globe, depending on the types of fossil fuels that are used in each country. The average oxidative ratios for the individual fossil fuel types are: 1.17 for coal, 1.44 for oil and 1.95 for natural gas (Keeling, 1988a). Biofuels have the lowest OR, around 1.1, which is identical to the ratio for terrestrial biospheric release. Therefore combustion of biofuels is removed from the APO signal like the terrestrial biosphere. In the Netherlands the fossil fuel OR is higher than average (around 1.7), because of the higher share of natural gas which also significantly varies within the different seasons.
1.3. The aims of this research

1.3.1. A new atmospheric measurement station in the North Sea

To extend the existing data sets of atmospheric O$_2$ and CO$_2$, a new atmospheric measurement station was installed on the North Sea oil and gas production platform F3, 200 km north off the Dutch coast (54º51’N, 4º44’E). The first goal of this PhD research project was to design, develop and install this measurement system. The measurement system includes a set-up for the continuous monitoring of atmospheric O$_2$ and CO$_2$ concentrations on-site using the fuel cell technique (Oxzilla II) and infrared absorption respectively (Vaisala CarboCaps). Besides that it includes an automated flask sampler and an integrated air drying system.

The location of the station is favourable since local effects—except for sea-atmosphere exchange—are practically absent. Furthermore, atmospheric inversions (causing large variability at land based stations) practically do not occur at sea, resulting in stable and calm O$_2$ and CO$_2$ signals. It is therefore an ideal location for measuring atmospheric background concentrations and studying air-sea interaction of CO$_2$ and partitioning of CO$_2$ emissions between the land biosphere and oceans. This station is the first fixed sea based station with on-site continuous O$_2$ and CO$_2$ measurements and will yield valuable information about the CO$_2$ uptake in coastal marine regions, specifically about the North Sea. The data from this measurement station will be a valuable contribution to the existing European data sets of atmospheric O$_2$ and CO$_2$, since only few atmospheric measurements stations exist that are equipped to measure atmospheric O$_2$ continuously.

Further details on the measurement location and the set-up for the continuous monitoring of atmospheric O$_2$ and CO$_2$ are presented in chapter 2 and 3.
1.3.2. **Analyzing oxygen records from a flask sampling network**

Besides the contribution of a new continuous on-site measurement system for atmospheric O\(_2\) measurements, the Centre for Isotope Research (CIO) of the University of Groningen is also operating a flask sampling network in which flasks are filled with sample air in various locations, mainly in Europe. For this PhD project, the flask samples from several locations were analyzed, leading to improved insights in the atmospheric O\(_2\) trends, variability and gradients. Flasks samples from Lutjewad, the Netherlands, Mace Head, Ireland and the F3 North Sea platform were studied, as well as the samples from aircraft campaigns over four locations in Russia. The outcomes of these analyses are presented in chapter 4 and 5.

1.4. **Structure of this thesis**

Following this general introduction into the subject of atmospheric O\(_2\) and its context, this PhD thesis starts out with a general description of the measurement locations in chapter 2. Chapter 2 concentrates on the measurement station at the F3 platform, giving several significant characteristics; furthermore additional details on the other measurement sites are presented. After the general chapters 1 and 2, this thesis consists of three main chapters in which the analyzed data is presented.

Chapter 3 describes the measurement setup at the F3 platform for the continuous monitoring of atmospheric O\(_2\) and CO\(_2\) and presents the first on-site continuous data from August 2008 through June 2009, including interesting observations on a short temporal scale.

The CO\(_2\), \(\delta\)O\(_2\)/N\(_2\) and APO observations from the Lutjewad, Mace Head and F3 platform flask sampling network are presented in chapter 4. This includes the CO\(_2\) and O\(_2\) records from these three sites between 1998 and 2009 as well as APO. A comparison between the sites is given, including the gradients of CO\(_2\) and O\(_2\) between Lutjewad and Mace Head.

Chapter 5 presents the atmospheric CO\(_2\) and O\(_2\) records for flask samples collected from aircrafts over four different locations in Russia: Fyodorovskoye, Syktyvkar, Zotino and Ubs Nur.

A combined conclusion is presented in chapter 6, together with the perspectives for future research. Additional information on the calibration strategies used, are included in the appendix.
References


