Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites
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Chapter 5

Continuous and flask observations of atmospheric $\delta O_2/N_2$ and $CO_2$ at Lutjewad station, the Netherlands, and Mace Head station, Ireland

Abstract

This chapter presents an update of the flask-based observations of atmospheric $\delta O_2/N_2$ and $CO_2$ at the atmospheric monitoring stations Lutjewad, the Netherlands (53°24’N, 6°21’E), and Mace Head, Ireland (53°20’N, 9°54’W), and also includes the first continuous $\delta O_2/N_2$ observations from Lutjewad. The flask observations now cover a period of over 15 years for both stations, running from 1998 to 2014 for Mace Head and 2000 – 2015 for Lutjewad. The $\delta O_2/N_2$ ratio of all flasks is determined in the laboratory of the Centre for Isotope Research (CIO), University of Groningen, the Netherlands, on a Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) – as presented in chapter 3 of this thesis. Trends and (peak-trough) amplitudes for $CO_2$, $\delta O_2/N_2$ and the related tracer APO (Atmospheric Potential Oxygen) were determined for the flask measurements of the two stations, using only samples collected at baseline conditions (not influenced by local sources and sinks), for both the complete dataset as well as the most recent data running from 2009 to 2014 / 2015. The data record of Mace Head appeared to be very robust, with almost no need to remove data points from the dataset due to non-background measurements and almost no variation in the seasonal cycle throughout time. A large gap in the dataset in 2009 for the $\delta O_2/N_2$ observations did, however, cause problems in the determination of the trend for both $\delta O_2/N_2$ and APO at Mace Head. Lutjewad station included more locally influenced samples, with as a consequence a higher need for background condition filtering and more variation in the calculated seasonal cycles and trends. The new, continuous $\delta O_2/N_2$ measurement system running at Lutjewad since 2011 is not yet satisfactory, mainly because the current dataset contains many gaps, which causes problems in the – delicate – trend and seasonal cycle determination.

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5.1. Introduction

Human activities have a profound influence on the composition of the earth’s atmosphere. The largest known contribution is the emission of carbon dioxide (CO$_2$) to the atmosphere by burning of fossil fuels, deforestation and changes in land use practices, summarized as “anthropogenic emissions”. CO$_2$ is a greenhouse gas that absorbs infrared radiation – an effect that is called the greenhouse gas effect. CO$_2$ exists naturally in the atmosphere but since the industrial revolution humans have increased its concentration by over 40% from a background concentration of about 274 – 284 ppm in 1750 (Etheridge et al., 1996) to 395.2 ± 0.1 ppm in 2013 (Dlugokencky and Tans, 2015). It is extremely likely that this increase of the CO$_2$ concentration – together with the rise of other greenhouse gases such as CH$_4$ and N$_2$O – is causing warming of the global climate (IPCC, 2013).

The behavior of CO$_2$ in the atmosphere is not straightforward. Once released in the atmosphere, CO$_2$ can be absorbed by the oceans or taken up by the biosphere through photosynthesis. There is a continuous exchange of carbon between the different reservoirs of the earth and this entire dynamic system is known as the global carbon cycle. A considerable fraction of the anthropogenic CO$_2$ emissions is absorbed by the oceans and terrestrial biosphere, which is thus limiting the increase of CO$_2$ in the atmosphere and the warming of global climate. Current estimates indicate that of all the emitted anthropogenic CO$_2$ in the period 1750 – 2013 (equivalent to 580 ± 70 Gt Carbon) less than half has accumulated in the atmosphere (250 ± 5 GtC). The remaining emitted carbon has been taken up by the ocean (170 ± 20 GtC) and biosphere (160 ± 70 GtC) (Le Quéré et al., 2015). Estimating the sizes of these natural carbon sinks and understanding the processes involved has been subject to many scientific studies as this is crucial in predicting future climate change.

Combining atmospheric CO$_2$ measurements with measurements of atmospheric oxygen (O$_2$) can give valuable information about the global carbon cycle. In most processes – e.g. combustion of fossil fuels, biosphere respiration and photosynthesis – O$_2$ is consumed while CO$_2$ is produced or vice versa. The atmospheric concentrations of the two species are therefore closely coupled and show roughly mirrored patterns. In air-sea exchange, however, O$_2$ and CO$_2$ are uncoupled due to carbonate reactions in the seawater, which have a buffering effect on the atmospheric CO$_2$ but no effect on atmospheric O$_2$. The uptake of CO$_2$ by the oceans can therefore be studied by measuring the O$_2$ concentration in addition to the CO$_2$ concentration (e.g. Keeling and Shertz, 1992).

In the near future, the combination of atmospheric O$_2$ and CO$_2$ measurements can also play an important role in studying Carbon Capture and Storage (CCS) processes in the world. When CO$_2$ is captured and stored underground on a large scale this has an influence on the O$_2$ – CO$_2$ balance of the atmosphere, as O$_2$ will still be consumed during the burning of fossil fuels while the CO$_2$ counterpart will be missing (Keeling et al., 2011). In case of a leak of CO$_2$ from a storage site there will be an increase in the CO$_2$ concentration without a concurrent decrease in the O$_2$ concentration. This can distinguish a leak from other sources of CO$_2$ such as fossil fuel burning and biosphere respiration (Keeling et al., 2011) and see also chapter 4 of this thesis.
While atmospheric CO$_2$ measurements have become increasingly straightforward in the past decades, atmospheric O$_2$ measurements are still considered a challenge. Only about a dozen programs in the world are currently involved in those measurements (Keeling and Manning, 2014) – the Centre for Isotope Research (CIO) of the University of Groningen, the Netherlands, being one of them. Flask sampling for atmospheric O$_2$ measurements at the CIO started in December 1998 at Mace Head, Ireland, followed by Lutjewad station, the Netherlands, in October 2000. The CIO also measured flask samples from the F3 gas production platform in the North Sea, the Netherlands (van der Laan-Luijkx et al., 2010a), Jungfraujoch, Switzerland (van der Laan-Luijkx et al., 2013), aircraft samples from Fyodorovskoye, Russia (van der Laan et al., 2014), and very recently flask samples are also taken at Halley station, Antarctica. Continuous atmospheric O$_2$ – CO$_2$ measurements started in August 2008 at the gas production platform F3 (van der Laan-Luijkx et al., 2010b). In 2011 an almost identical copy of this instrument was built and placed at the atmospheric measurement station Lutjewad. Besides these long-term measurement programs at fixed stations, the CIO also developed a transportable O$_2$ – CO$_2$ instrument to aid in leak detection of CCS sites (see chapter 3 and 4 of this thesis).

In this chapter we present O$_2$ and CO$_2$ data from the measurement station Lutjewad, the Netherlands – both from our flask sampling record and our continuous O$_2$ – CO$_2$ measurement system – as well as data from the measurement station Mace Head, Ireland, for flask samples. Flask sample observations from both Lutjewad and Mace Head have been presented before by (Sirignano et al., 2010) and (van der Laan-Luijkx et al., 2010a) and this chapter gives an update of these data. Flasks observations are now reported here until January 2015. Data of our continuous O$_2$ – CO$_2$ measurement system in Lutjewad have not been presented before.

The measurements of the flasks and the operation principles and performance of the continuous instrument were presented in chapter 3 of this thesis. Here we first describe the atmospheric monitoring stations Lutjewad and Mace Head (section 5.2.1), present Atmospheric Potential Oxygen (APO – a defined tracer based on combined O$_2$ and CO$_2$ measurements) (section 5.2.2), and describe the flask sampling procedures at the two stations (section 5.2.3). In section 5.3 we present the observations of O$_2$, CO$_2$ and APO, first of the flask samples at Lutjewad and Mace Head (section 5.3.1) followed by the continuous system at Lutjewad (section 5.3.2). In section 5.3.3 we discuss the trends and seasonal cycles found for the different locations, measurement methods and time frames and compare them with other stations in the vicinity of Lutjewad and Mace Head. We end with a discussion and some conclusions.

5.2. Materials and methods

5.2.1. Site description

Figure 5.1 shows the locations of Lutjewad atmospheric monitoring station (53°24’N, 6°21’E) on the northern coast of the Netherlands and Mace Head atmospheric research station (53°20’N, 9°54’W) on the west coast of Ireland. The figure also shows other locations in Europe where atmospheric O$_2$ is (or has been) observed. The measurements of
these stations will be presented for comparison with our own measurements of Lutjewad and Mace Head.

The prevailing wind direction in the Netherlands is southwest, implying that continental air masses influenced by anthropogenic and biogenic sources and sinks are the most common at Lutjewad station. With northern wind the station measures background air coming from the sea. The station consists of a 60-meter tall tower and a building with a laboratory. Air is pumped from air inlets in the top of the tower to the laboratory, where the air is either analyzed by one of the continuous instruments or stored in flasks and analyzed later in the laboratory of the Centre for Isotope Research (CIO) in Groningen.

The station was opened in 2000 when the first measurements started. In time, several instruments were upgraded or added. Currently the station measures continuous records for CO$_2$, CO, CH$_4$, H$_2$O, SF$_6$, N$_2$O, O$_2$, $^{222}$Radon and COS. Flask samples are generally taken once or twice a week and are analyzed in the laboratory in Groningen for CO$_2$, CO, CH$_4$, O$_2$, $^{13}$CO$_2$, $^{18}$O and partially for $^{14}$CO$_2$. For $^{14}$CO$_2$, monthly-integrated samples (both continuous and wind-selected) are taken as well. In addition, the basic meteorological conditions are monitored. In the coming year, measurements of aerosols will be added to the station. More information about the station and most of the equipment can be found in (van der Laan, 2010).

At Mace Head atmospheric research station the prevailing wind direction is west, which means the station is mainly in background air coming from the Atlantic Ocean (“baseline
5.2.2. Atmospheric Potential Oxygen (APO)

The tracer Atmospheric Potential Oxygen (APO) is defined as the sum of the $O_2/N_2$ ratio and 1.1 times the $CO_2$ concentration, according to (Stephens et al., 1998):

$$\delta APO = \delta(O_2/N_2) + 1.1 \times \frac{(CO_2-350)}{SO_2}$$

Equation 5.1

In this formula $\delta APO$ is the APO concentration in per meg and 1.1 is the approximate global average $O_2:CO_2$ exchange ratio for photosynthesis and biosphere respiration as determined by (Severinghaus, 1995). $SO_2$ is again the standard mole fraction of $O_2$ in air as given before and 350 is an arbitrary consensus defined reference value defined by (Manning and Keeling, 2006). APO is, by definition, not sensitive for biosphere activity and thus only represents air-sea exchanges of $O_2$ and $CO_2$ and partly fossil fuel combustion, as the stoichiometric ratio between $O_2$ and $CO_2$ for fossil fuel combustion generally exceeds 1.1. The oxidative ratio is about 1.95 for natural gas, 1.44 for crude oil and 1.17 for coal (Keeling, 1988). The global average oxidative ratio for fossil fuels is roughly 1.4 but this number shows important differences between counties, and also changes with time, depending on the global fuel mix. It was for example estimated to be 1.391 and 1.378 for the time periods 1990 – 2000 en 2000 – 2010 respectively (Keeling and Manning, 2014).

5.2.3. Flask sampling

The flasks used in our flask-sampling network are 2.5-liter volume glass flasks with two Louwers Hapert Viton sealed valves. An automated flask sampler controls the filling of the flasks at Lutjewad station, which is able to fill up to 20 flasks. A flask is flushed for one hour before the sampler closes it and continuous to flush the next flask. Flasks can be blocked to remove them from the flushing sequence and store the sample (Neubert et al., 2004). Flasks are taken at various conditions, but for the record presented here, only flasks taken at “local background” conditions are considered, with $^{222}$Radon mixing ratio < 3 Bq m$^{-3}$ and the $CO_2$ concentration < 200 ppb. At Mace Head flasks are manually filled in pairs every week, almost exclusively at baseline conditions. Flasks with a $CO_2$ concentration > 200 ppb are removed, such that the remaining dataset strictly represents baseline conditions. At both stations, the air is first cryogenically dried and flasks are filled at ambient pressure. The flask samples are analyzed in the CIO laboratory and in this chapter we present the $CO_2$ and $O_2$ measurements of the flask samples. The $CO_2$ concentration of the flasks is determined on a HP Agilent HP6890N Gas Chromatograph (GC) while the $O_2/N_2$ ratio is determined on a Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS), as was presented in chapter 3 of this thesis. More information about the automated flask sampler and flask sampling records at Lutjewad and Mace Head can be found in Neubert et al. (2004), Sirignano et al. (2010) and van der Laan-Luijkx et al. (2010a).
5.3. Observations

Here we present the observations of O₂ and CO₂ at the Lutjewad and Mace Head atmospheric monitoring stations. First we present the results of our flask sampling records (section 5.3.1), which is a follow-up on the work presented earlier by Sirignano et al. (2010) and van der Laan-Luijkx et al. (2010a). Section 5.3.2 then presents the first results of the continuous O₂ – CO₂ instrument at Lutjewad and compares them with the flask measurements. In section 5.3.3 the trends and seasonal cycles that are determined from the different datasets are discussed.

5.3.1. Flask sampling records of Lutjewad and Mace Head

The flask sampling records of Lutjewad and Mace Head were updated since the last publication of the dataset which included flasks up until 23 March 2009 (van der Laan-Luijkx et al., 2010a). All new flasks (with a standard deviation of less than 15 per meg for the duplo measurements) were first filtered to represent background conditions (²²²Radon mixing ratio < 3 Bq m⁻³ and the CO concentration < 200 ppb for Lutjewad and CO concentration < 200 ppb for Mace Head – a strategy adopted from van der Laan-Luijkx et al. (2010a)). Flasks that could not be filtered because either ²²²Radon or CO was not available are kept in the dataset. For Lutjewad slightly more than 25% of all flasks were removed in this procedure while for Mace Head this was only about 1% of the flasks. The difference can be explained by two reasons. First, the flask filling procedure at Mace Head is strictly focused on sampling background air while at Lutjewad flasks are also filled for other reasons during for example field campaigns at the station. Second, Mace Head is measuring mainly background air from the ocean while Lutjewad measures mainly air from the continent, which makes it often more difficult to sample background air.

After the filtering for background conditions, a linear combination of a 3-harmonic seasonal component and a linear trend has been fitted to the datasets – in the same way as has been done by van der Laan-Luijkx et al. (2010a). The fit procedure involved three steps of fitting the trend and seasonal cycle and filter the dataset for outliers to the fit, using a 2.7 sigma exclusion filter. In this filtering procedure, the measurement with the largest residual from the fit is hypothesized to be an outlier. The average and standard deviation of the remaining residuals are then calculated and in case the hypothesized outlier is more than 2.7 times the new standard deviation away from the new average it is marked as an outlier and excluded. This procedure is repeated until all outliers are removed from the dataset. This outlier filtering removed another 10% (CO₂) and 6% (O₂) of the flasks from the Lutjewad dataset and 3% (CO₂) and 1% (O₂) of the flasks from the Mace Head dataset. Again, not surprisingly, the Mace Head dataset appeared to represent background conditions much better than the Lutjewad dataset.

The amount of flask measurements for both stations was more than doubled since the last publication of the data record in van der Laan-Luijkx et al. (2010a).
Observations of $\delta$O$_2$/N$_2$ and CO$_2$ at Lutjewad and Mace Head

Figure 5.2: Results of the flask sampling measurements from Lutjewad and Mace Head, for both $\delta$O$_2$/N$_2$ and CO$_2$. The axes have been scaled in a 1 ppm : 5 per meg ratio to be able to compare the two species on a mole to mole basis. The black dots are the actual flask measurements, filtered to represent background conditions and filtered for outliers to the fit. The black lines give the best-estimated combined trend and seasonal variation and the trends for the two gases of the complete dataset. The orange lines give the original fits as determined in (van der Laan-Luijkx et al., 2010a) while the red lines show the fits determined for only the new data.
Figure 5.3: APO records of Lutjewad and Mace Head. The black dots are the actual flask measurements, filtered to represent background conditions and filtered during the fitting procedure (of the complete dataset). The black lines give the best-estimated combined seasonal variation and trend and the trends of the complete datasets. The orange lines give the original fits as determined in (van der Laan-Luijkx et al., 2010a) while the red lines show the fits determined for only the new data.

For Lutjewad the total amount of flasks after background condition and outlier filtering is now equal to 616 and 611 for CO\(_2\) and O\(_2\) respectively. For Mace Head these numbers are 589 and 455 for CO\(_2\) and O\(_2\) respectively. Differences between the amount of data points included for CO\(_2\) and O\(_2\) at one station are caused by a combination of failure of one of the measurements and the outlier filtering procedure. The considerable difference in the amount of flasks for CO\(_2\) and O\(_2\) at Mace Head (589 versus 455) is caused by a long period of moisture contamination in the flasks collected in 2009. Due to the moisture, the flasks could not be measured on the DI-IRMS and thus no O\(_2\)/N\(_2\) ratio could be established. For CO\(_2\) the moisture contamination was not very important.

Figure 5.2 presents the O\(_2\) and CO\(_2\) flask sampling records of the atmospheric monitoring stations Lutjewad and Mace Head. The black dots in the figure represent the final flask measurements on which the fits are based. The fits of the complete dataset are added in
Observations of $\delta$O$_2$/N$_2$ and CO$_2$ at Lutjewad and Mace Head

black, while the existing fits as determined in (van der Laan-Luijkx et al., 2010a) are presented in orange. The red lines in the figure represent fits based on only the new data. Both the orange and red fits are based on about 50% of the dataset (considering the number of flasks). The large gap in the Mace Head O$_2$ data record around 2009 causes some problems in determination of the trend and seasonal cycle.

Figure 5.3 shows the APO records for Lutjewad and Mace Head calculated from the CO$_2$ and O$_2$ datasets (filtered to represent background conditions, but not filtered for outliers to the CO$_2$ and O$_2$ fits). Just as for CO$_2$ and O$_2$, a linear trend and 3-harmonic seasonal cycle has been fitted to the data. The procedure of fitting the data is the same as for CO$_2$ and O$_2$ and several outliers were excluded during the fitting procedure using the 2.7 sigma exclusion filter. The black dots in Figure 5.3 represent the final flask measurements on which the fits are based, which are 554 and 443 flasks respectively for Lutjewad and Mace Head. The black, orange and red lines represent again the fits on the total, existing and new dataset, respectively.

The fit parameters from Figure 5.2 and Figure 5.3 are summarized in Table 5.1. For the ease of comparison the fit parameters of the continuous dataset (presented in the next section) are also included in this table (5th column). The trends and seasonal cycles presented in the table will be discussed and compared to other stations in section 5.3.3.

5.3.2. Continuous O$_2$ – CO$_2$ record Lutjewad

From 21 July 2011 onwards, the continuous data record of the combined O$_2$ – CO$_2$ measurements is available for station Lutjewad. Figure 5.4 shows the hourly averaged data (both the grey and black data points) from the Oxzala Lutjewad gathered between 21 July 2011 and 13 January 2015. The $^{222}$Radon data from Lutjewad station was used to filter the continuous dataset to represent background conditions ($^{222}$Radon mixing ratio < 3 Bq m$^{-3}$). No $^{222}$Radon measurements were available for about 7% of the dataset; these measurements have been kept. In total 18% of the data points were removed, as they did not represent background conditions.

Just like for the flask measurements, a combination of a linear trend and 1-harmonic seasonal cycle has been fitted to the datasets. Because the dataset contains many gaps, a 1-harmonic fit was chosen instead of a 3- (or 2-) harmonic for the continuous dataset. The fit procedure involved again three steps of fitting the trend and seasonal cycle and filter the dataset for outliers to the fit, using the 2.7 sigma exclusion filter. The final fit parameters are presented in Table 5.1. The black data points in Figure 5.4 represent all the data that have been kept after removing the outliers, which is 76% and 73% of the original data (before any filtering is applied) for O$_2$ and CO$_2$ respectively and 93% and 89% of the background data (after filtering using $^{222}$Radon mixing ratio < 3 Bq m$^{-3}$) for O$_2$ and CO$_2$ respectively. The linear trend as well as the linear trend combined with a 1-harmonic seasonal cycle are added to the graphs in green. Flask measurements from the same time period are also added to the figure, just as the combined linear trend and seasonal cycle determined from the most recent flask measurements (2009 – 2015). These data are all marked in red.
Table 5.1: Parameters of the fits presented in Figure 5.2 and Figure 5.3 for both Lutjewad and Mace Head atmospheric monitoring stations. Data in the columns marked with "a" are from (van der Laan-Luijkx et al., 2010a) the other columns show new data.

<table>
<thead>
<tr>
<th></th>
<th>Lutjewad</th>
<th></th>
<th>Mace Head</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flasks</td>
<td>Continuous</td>
<td>Flasks</td>
<td></td>
</tr>
<tr>
<td>Trend CO₂ (ppm year&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>1.97 ± 0.07</td>
<td>2.94 ± 0.09</td>
<td>2.19 ± 0.03</td>
<td>2.20 ± 0.05</td>
</tr>
<tr>
<td>Trend δO₂/N₂ (per meg year&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>-21.0 ± 0.9</td>
<td>-20.8 ± 0.8</td>
<td>-20.5 ± 0.3</td>
<td>-24.4 ± 0.4</td>
</tr>
<tr>
<td>Trend APO (per meg year&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>-10.6 ± 0.7</td>
<td>-6.4 ± 0.5</td>
<td>-9.4 ± 0.2</td>
<td>-12.0 ± 0.2</td>
</tr>
<tr>
<td>Amplitude CO₂ (ppm)</td>
<td>12.0 ± 0.6</td>
<td>16.9 ± 0.8</td>
<td>14.5 ± 0.6</td>
<td>17.0 ± 0.2</td>
</tr>
<tr>
<td>Amplitude δO₂/N₂ (per meg)</td>
<td>114 ± 8</td>
<td>136 ± 8</td>
<td>130 ± 6</td>
<td>125.6 ± 1.5</td>
</tr>
<tr>
<td>Amplitude APO (per meg)</td>
<td>64 ± 6</td>
<td>49 ± 5</td>
<td>49 ± 5</td>
<td>43.0 ± 0.8</td>
</tr>
<tr>
<td>Day of maximum CO₂</td>
<td>72 (Mar 13)</td>
<td>64 (Mar 5)</td>
<td>67 (Mar 8)</td>
<td>56 (Feb 25)</td>
</tr>
<tr>
<td>Day of minimum CO₂</td>
<td>229 (Aug 17)</td>
<td>243 (Aug 31)</td>
<td>244 (Sep 1)</td>
<td>238 (Aug 26)</td>
</tr>
<tr>
<td>Day of minimum δO₂/N₂</td>
<td>90 (Mar 31)</td>
<td>83 (Mar 24)</td>
<td>92 (April 2)</td>
<td>61 (Mar 2)</td>
</tr>
<tr>
<td>Day of maximum δO₂/N₂</td>
<td>252 (Sep 9)</td>
<td>243 (Aug 31)</td>
<td>248 (Sep 5)</td>
<td>244 (Sep 1)</td>
</tr>
<tr>
<td>Day of minimum APO</td>
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<td>69 (Mar 10)</td>
<td>87 (Mar 28)</td>
<td>101 (Apr 11)</td>
</tr>
<tr>
<td>Day of maximum APO</td>
<td>255 (Sep 12)</td>
<td>238 (Aug 26)</td>
<td>254 (Sep 11)</td>
<td>219 (Aug 7)</td>
</tr>
</tbody>
</table>
Observations of $\delta$O$_2$/N$_2$ and CO$_2$ at Lutjewad and Mace Head

Figure 5.4: The continuous dataset from the Lutjewad Oxzala for both $\delta$O$_2$/N$_2$ and CO$_2$. The black dots are the actual measurements that have been used to determine the final fits of the trend and seasonal cycle. Combined with the grey data points they represent the complete continuous dataset. The green lines give the best-estimated combined seasonal variation and trend and the linear trends of the complete datasets. The flask measurements from the same time period are added to the graphs in red squares. The fits determined earlier based on the most recent measurements (2009 – 2015) are added in red as well. The axis have been scaled such that 1 ppm = 5 per meg to be able to compare the two species on a mole-to-mole basis.

The big gap visible in the graph from 2 September 2013 up till 18 March 2014 is caused by the rebuilding of the laboratory in Lutjewad in autumn 2013 followed by several starting-up problems after moving the system to the new laboratory. The flask record also shows a gap in this time period but here it is significantly smaller – lasting for only roughly one month for CO$_2$ (16 September – 23 October) and four months for O$_2$ (20 August – 21 December). The reason for this difference between CO$_2$ and O$_2$ is a campaign in autumn 2013 in which all Lutjewad flasks were only measured for CO$_2$.

The dataset contains many other gaps of different sizes, varying from several months to several minutes. Reasons for the system to shut down completely were, amongst others, power failures, broken CO$_2$ sensors (3 times) and empty reference cylinders that were not replaced on time. Smaller gaps are often caused by temperature disturbances in the laboratory of Lutjewad (e.g. very high or low temperature in the laboratory or very strong temperature fluctuations caused by an inadequate temperature regulation). In these cases...
data was gathered but contained too much noise for the \( \text{O}_2 \) measurements to be useful to include. In the first months of 2012 (18 January – 18 April) data was gathered, but \( \delta\text{O}_2/\text{N}_2 \) was much more negative than expected (\( \approx 100 \) per meg), causing problems in fitting the data of both \( \text{O}_2 \) and APO. All three calibration and target cylinders run empty in less than three months in this time period, which is a clear indication of a leak in the system, as they should in principle last for more than two years. During maintenance work on the system on 18 April 2012, several leaks were identified and repaired.

Figure 5.5 shows the APO record of the Ozzala system, calculated from the \( \text{O}_2 \) and \( \text{CO}_2 \) measurements that were filtered for background conditions (\( ^{222}\text{Radon mixing ratio} < 3 \text{ Bq m}^{-3} \)). Just as for the \( \text{O}_2 \) and \( \text{CO}_2 \) data records, a combination of a linear trend and 1-harmonic seasonal cycle has been fitted to the dataset. The fit procedure involved again three steps of fitting the trend and seasonal cycle and filter the dataset for outliers to the fit, using the 2.7 sigma exclusion filter. The black data points represent all the data that have been kept after the outlier filtering procedure, which is 94% of the original APO data. The fitting procedure is thus slightly more efficient for APO as it is for \( \text{CO}_2 \) and \( \text{O}_2 \), which can be explained by the fact that biosphere influences are completely removed when APO is calculated, leading to less noise in the signal compared to \( \text{CO}_2 \) and \( \text{O}_2 \).

A discussion about the trends and seasonal cycles of \( \delta\text{O}_2/\text{N}_2 \), \( \text{CO}_2 \) and APO of the continuous measurements and a comparison with the flasks measurements and data records from other stations can be found in section 5.3.3.

5.3.2.1. Comparison continuous measurements and flasks

After 21 July 2011 – the start of the continuous \( \text{O}_2 – \text{CO}_2 \) measurements – 205 flasks (with a standard deviation of less than 15 per meg for the duplo measurements) were analyzed for atmospheric \( \text{O}_2 \).

Depending on the flow rate of a system, there is a delay between the actual sampling at 60 meters altitude in the tower and measurement by an instrument or storage in a flask. For the
Oxzala (60 mL min\(^{-1}\)) and automated flask sampler (2 L min\(^{-1}\)) these delays were estimated to be roughly 25 and 5 minutes respectively.

A flask is flushed for one hour after which it is closed. In case the old air in the flask would be merely pushed out by the fresh air without mixing, the flask sample would represent the last 75 seconds of the hour that it was flushed. If, on the other hand, we assume perfect mixing in the flask (which is more realistic), the air in the flask is a time-weighted mean over the flushing period (Chen et al., 2012). Because our continuous measurements have an output frequency of 5 minutes it is not possible to do a very precise comparison between the flasks and the continuous data. Based on the flask size, flow and model outcome of (Chen et al., 2012), we assume the last 10 minutes of the flushing time as representative for the content of the flask, which means we compare with the average of two measurements from the Oxzala. Combining this estimate with the estimates of the delay times, this means that a flask closed at 12:00 o’clock represents air from 11:45 – 11:55 in the tower, which is measured by the Oxzala between 12:10 and 12:20.

Figure 5.6 shows the 120 flasks that overlap with the continuous measurements of the Oxzala system, plotted as the average measured value by the Oxzala (in 10 minutes) against the flask samples.

Figure 5.6: Comparison of the $\delta$O$_2$/N$_2$ measurements between the flask samples and the continuous O$_2$ – CO$_2$ system. Out of 205 flasks that were analyzed after the start of the continuous O$_2$ – CO$_2$ measurements, 120 could be linked to measurements of the continuous system and are plotted here. Applying the 2.7 sigma exclusion filter to the residuals of a linear fit resulted into two outliers, which are marked in red. The remaining 118 flask measurements are on average 6.2 ± 2.4 per meg (1σ standard deviation of the individual measurements was 25 per meg). The average difference between the flask and continuous measurements (n = 120) was found to be 6.2 ± 2.4 per meg, the flask measurements being higher than the continuous measurements. Applying the 2.7 sigma exclusion filter to the residuals of the fit gave two outliers, which are marked in red in Figure 5.6. Without these two outliers, the average difference between the flask and continuous measurements (n = 118) was found to be 4.9 ± 2.3 per meg (1σ standard deviation of the individual measurements was 25 per meg). The
difference is thus significant. The black line in Figure 5.6 represents the linear relationship (of the 118 flasks) with a slope of $1.02 \pm 0.04$ and a correlation coefficient ($R^2$) of 0.85. This slope is thus not significantly different from the ideal relationship between the two measurements, indicated by the dashed diagonal line in the figure. From that we conclude that the difference between the flask and continuous measurements is only an offset, most likely caused by a calibration difference. This is not very surprising in the light of the difficulties in the establishment of the scales, as was discussed before. The spread found in the individual comparisons, however, is larger than we would expect based on the measurement precisions of the two systems (based on that we would expect $\approx 12$ per meg as standard deviation). Contaminations during flask sampling, transport and storage are probably the reason for the additional variability. (Goto et al., 2013) found a correlation coefficient of 0.90 when doing the same comparison between their continuous and flask $O_2$ measurements and although their flask samples were also higher on average than the continuous measurements they found a difference that was on average only $1.8 \pm 5.5$ per meg.

5.3.3. Trends and seasonal cycle analysis

Both the Lutjewad and Mace Head $O_2$ – $CO_2$ flask sampling record now cover a period of about 15 years. In this section we will discuss the observed trends (section 5.3.3.1) and seasonal peak-trough amplitudes (section 5.3.3.2) of both the flask sampling and the new continuous data record at Lutjewad and compare them with observed trends and seasonal amplitudes at other stations in Europe.

5.3.3.1. Trends

Table 5.2 shows the trends that were determined in this chapter, as well as the values determined for other stations in the proximity of Lutjewad and Mace Head in Europe. Locations of these stations can be found in Figure 5.1. Unfortunately, most $O_2$ data records visible in Table 5.2 are not very recent, which makes it difficult to compare our newest data. Only a continuous dataset from Weybourne including measurements between 2009 and 2012 (Wilson, 2012) and the intercomparison project of Jungfraujoch flasks (van der Laan-Luijkx et al., 2013) show data later than 2009.

For both the Lutjewad and Mace Head flask sampling records, the most recent time frame shows the highest trend in the $CO_2$ concentration. For Lutjewad, however, the observed trend of $2.94 \pm 0.09$ ppm year$^{-1}$ for the period 2009 – 2015 is unrealistically high, which is caused by the irregularly distributed sampling, with especially a high sampling frequency in the winter of 2013-2014 (shown in Figure 5.2). The most recent observed trends for Mace Head ($2.41 \pm 0.04$ ppm year$^{-1}$) corresponds very well to the trend found at Weybourne for the period 2009 – 2012 ($2.41 \pm 0.07$ ppm year$^{-1}$). The trend found for the continuous dataset from Lutjewad ($2.20 \pm 0.05$ ppm year$^{-1}$) is lower but corresponds very well with the average global $CO_2$ trend, which is $2.17$ ppm year$^{-1}$ for the period 2010 – 2014 (Dlugokencky and Tans, 2015).
Observations of δO₂/N₂ and CO₂ at Lutjewad and Mace Head

Table 5.2: Estimated trends at different atmospheric measurement stations in the vicinity of Lutjewad and Mace Head atmospheric monitoring stations. The locations of these stations are shown in Figure 5.1. In this table, several flask measurements from stations other than Lutjewad and Mace Head were performed at the CIO as well (F3, Fyodorovskoye and one dataset from Jungfraujoch – all marked with “CIO” in the table).

<table>
<thead>
<tr>
<th>Location</th>
<th>Time period &amp; reference</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>Lutjewad (53.24°N 6.21°E)</td>
<td>2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)</td>
<td>1.97 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2009 – 2015 [Flasks – CIO] (this work)</td>
<td>2.94 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>2000 – 2015 [Flasks – CIO] (this work)</td>
<td>2.19 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2011 – 2014 [Continuous – CIO] (this work)</td>
<td>2.20 ± 0.05</td>
</tr>
<tr>
<td>Mace Head (53.20°N 9.54°W)</td>
<td>2000 – 2015 [Flasks – CIO] (this work)</td>
<td>2.19 ± 0.03</td>
</tr>
<tr>
<td>Weybourne (52.95°N 1.12°E)</td>
<td>Jan 2009 – April 2012 [Continuous] (Wilson, 2012)</td>
<td>2.41 ± 0.07</td>
</tr>
<tr>
<td>F3 (54.51°N 4.44°E)</td>
<td>2006 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)</td>
<td>2.11 ± 0.04</td>
</tr>
<tr>
<td>Shetland Islands (60.28°N 1.28°W)</td>
<td>2004 – 2008 (Kozlova et al., 2008)</td>
<td>2.17</td>
</tr>
<tr>
<td>Ochsenkopf (50.01°N 11.48°E)</td>
<td>June 2006 – December 2008 (Thompson et al., 2009)</td>
<td>1.6 ± 0.5</td>
</tr>
<tr>
<td>Jungfraujoch (46.33°N 7.59°E)</td>
<td>2006 – 2008 [Flasks] (Uglietti, 2009)</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – CIO] (van der Laan-Luijkx et al., 2013)</td>
<td>1.94 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – MPI] (van der Laan-Luijkx et al., 2013)</td>
<td>1.83 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – Bern] (van der Laan-Luijkx et al., 2013)</td>
<td>1.76 ± 0.17</td>
</tr>
<tr>
<td>Puy de Dôme (45.46°N 2.58°E)</td>
<td>2004 – 2008 [Flasks] (Uglietti, 2009)</td>
<td>1.2</td>
</tr>
<tr>
<td>Fyodorovskoye (56.27°N 32.55°E)</td>
<td>1998 – 2008 [Flasks 100 m– CIO] (van der Laan et al., 2014)</td>
<td>1.98 ± 0.15</td>
</tr>
<tr>
<td>Białystok (53.13°N 23.01°E)</td>
<td>Aug 2005 – Jun 2008 [Continuous] (Popa et al., 2010)</td>
<td>2.0 ± 0.5</td>
</tr>
</tbody>
</table>
The global average trend for $\delta O_2/N_2$ is estimated to be -18.8 per meg year$^{-1}$ for the period 1992 – 2009 (Scripps Institution of Oceanography, 2015). All stations within the globally spread Scripps oxygen program measure a very similar trend, which means that the trend is globally consistent. Table 5.2, however, shows strong variations in the trend, both for our own measurements as well as for other stations in Europe. For the Lutjewad flask record the trend is very constant throughout time, varying only within the error bars. At Mace Head strange differences are visible between the two different time periods and the total dataset. Looking at Figure 5.2 there is a clear break visible between the two time periods around 2009, which was the time frame where almost no samples could be measured for $O_2$ due to contamination issues. The big gap between the two time periods decouples the measurements and their fits of the first and second period, but it also seems that a downward scale shift occurs. The reason for this could be a change in the setup after the discovery of the problems that lead to moisture contamination in the flasks. It is very unlikely that this problem is caused by the DI-IRMS, as in that case the shift would also be visible in the intercomparison program and the Lutjewad data record. Due to the shift of the measurements to a lower level after 2009, the overall trend is significantly more negative than the trends of the separate time periods. This trend of $-21.4 \pm 0.3$ therefore has to be considered as too low. However, at Lutjewad station and also at Weybourne station, trends are found that are comparable to or even lower than the overall trend found at Mace Head. This is also the case for observations performed at a similar latitude in Sendai, Japan ($38^\circ N$, $140^\circ E$), where the trends found for the $O_2/N_2$ ratio were $-22.0 \pm 0.5$ per meg year$^{-1}$ for flask measurements between 1999 – 2010 (Ishidoya et al., 2012) and $-24.2$ per meg year$^{-1}$ for continuous measurements between 2007 – 2009 (Goto et al., 2013).

Both the differences in observed trends between the different stations, and the temporal trend variation of each station are considerable, even more so for $\delta O_2/N_2$ and APO than for CO$_2$. The reason for this is threefold. First, and foremost, year to year trend variability (due to inter-annual variations in the carbon cycle) is real and is also observed elsewhere: compare for example 2010 ($2.42 \pm 0.11$) with 2011 ($1.88 \pm 0.11$) at Mauna Loa (Tans and Keeling, 2015). This obviously causes differences when calculating trends for e.g. 2010 – 2014 or 2011 – 2015. Second, data gaps and irregular sampling can cause problems in determining a proper trend (and peak-trough amplitude), as it influences proper weighing over the seasonal cycle. Third, as was shown in an intercomparison study of three laboratories all measuring flasks from Jungfraujoch station (see the last three rows of this station in Table 5.2), difference beyond the errors in the fit coefficients can arise in both trend and seasonal cycle determination due to differences in the sample treatment (transport, storage) and measurements at the different laboratories (van der Laan-Luijkx et al., 2013).

Determining a simple, linear trend for the complete flask sampling record is becoming more and more unrealistic as the dataset grows. On the other hand, the longer a data record, the more reliable the (mathematical) determination of such a simple linear trend can be, especially when a dataset shows many gaps. This explains why the fits for the longest time series at Lutjewad and Mace Head give the smallest errors. A long data record also gives the possibility to determine the trend for different time periods, as we also did for our flask sampling records.
For APO the fitted trends vary even more for the different time periods and different locations than for δO2/N2. As APO is calculated from δO2/N2 and CO2, the data record of Mace Head suffers from the same problems as the δO2/N2 dataset does, with a significant change around 2009 when no flask samples were available. Next to fitting the APO data calculated from the O2 and CO2 data records, the trend of APO could also be determined from the separate O2 and CO2 trend fits. The results were found to be similar, varying only within error bars.

5.3.3.2. Seasonal cycles

The seasonal cycles of the different species, stations and time periods as visible in Figure 5.2 and Figure 5.3 are plotted as 1-year detrended cycles in Figure 5.7. The numbers are given in Table 5.3, together with amplitudes found at other stations in Europe.

![Figure 5.7: Seasonal cycles of δO2/N2, CO2 and APO at the stations Lutjewad (flasks and continuous) and Mace Head (flasks). The axes have been scaled in a 1 ppm : 5 per meg ratio to be able to compare the two species on a mole to mole basis.](image)
At Lutjewad station the seasonal amplitudes for O$_2$ and CO$_2$ previously found for the flask sampling dataset were considered to be too low due to an inadequate sampling frequency in the narrow trough periods (van der Laan-Luijkx et al., 2010a). Sampling in the narrow trough periods and therefore also the quality of the fit has been improved in recent years and the fits of the most recent flask data (2009 – 2015) show significantly higher, more realistic, amplitudes for both CO$_2$ and O$_2$. For APO the opposite occurs: the amplitude of the new fit is smaller than before. The fits of the total flask datasets are closer to the fits for the recent than for the older ones. Looking at Figure 5.7, the continuous measurements show a significantly different seasonal cycle for both δO$_2$/N$_2$ and CO$_2$, although the observed amplitudes in Table 5.3 are not very different. Part of the reason for their deviation is that only a 1-harmonic fit has been used. Although the (fit) errors of the amplitudes are much lower for the continuous data than for the flask sampling records (due to the large number of data), these fits are less reliable. The continuous dataset is very short and also contains many gaps.

At Mace Head the seasonal cycle of CO$_2$ is very consistent throughout time. For O$_2$ the variations are slightly bigger but also here the amplitude is the same for the different time periods within error bars. As a consequence, also the APO seasonal cycle is very robust throughout time. The gap in the O$_2$ record around 2009 only seems to influence the trend and not so much the seasonal cycle.

Looking at the complete dataset, we found that for CO$_2$ the seasonal (peak-trough) amplitude is the same within error bars for Lutjewad (14.5 ± 0.6 ppm) and Mace Head (14.1 ± 0.3 ppm). This also corresponds well to the seasonal cycle found at Weybourne (14.9 ± 0.8 ppm) for a continuous dataset from January 2009 to April 2012 (Wilson, 2012) and the 14 ppm found for the continuous dataset of Lutjewad from May 2007 to August 2008 (van der Laan et al., 2009). Also at the Japanese site in Sendai a very similar seasonal amplitude was found: 13.9 ± 2.5 ppm for the flask measurements between 1999 – 2010 (Ishidoya et al., 2012).

For δO$_2$/N$_2$ we find the same amplitude within error bars at Lutjewad (136 ± 8 per meg) and Mace Head (137 ± 6 per meg) when looking at the most recent datasets. This is also in agreement with the recent observations at Weybourne (134 ± 8 per meg). Also Ochsenkopf (135 ± 7 per meg), Shetland Islands (134 per meg) and Fyodorovskoye (131 ± 13 per meg) show very similar seasonal amplitudes for δO$_2$/N$_2$. For the complete datasets of Lutjewad (130 ± 6 per meg) and Mace Head (142 ± 5 per meg) the amplitudes differ slightly from each other, but the difference is hardly significant. The flasks and continuous measurements at Sendai, Japan, show comparable, although slightly lower, amplitudes of 117 and 128 ± 22 per meg respectively (Goto et al., 2013; Ishidoya et al., 2012). At Cap Ochi-Ishi, Japan (43°N, 146°E) the amplitude found for flask measurements between 1999 – 2001 was 146 per meg, which is slightly higher but also in the same range (Tohjima et al., 2003).

The seasonal amplitudes of δO$_2$/N$_2$ are roughly twice as large on a molar basis as the seasonal amplitudes of CO$_2$ (using a conversion factor of 4.8 per meg ppm$^{-1}$). This is in agreement with other observations in the Northern hemisphere, such as at Alert Station, and reflects the additional O$_2$ exchange from the ocean (Keeling and Manning, 2014).
Table 5.3: Estimated seasonal cycles at different atmospheric measurement stations in the vicinity of Lutjewad and Mace Head atmospheric monitoring stations. The locations of these stations are shown in Figure 5.1. In this table, several flask measurements from stations other than Lutjewad and Mace Head were performed at the CIO as well (F3, Fyodorovskoye and one dataset from Jungfraujoch – all marked with “CIO” in the table).

<table>
<thead>
<tr>
<th>Location</th>
<th>Time period &amp; reference</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>Lutjewad (53.24°N 6.21°E)</td>
<td>2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)</td>
<td>12.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>2009 – 2015 [Flasks – CIO] (this work)</td>
<td>16.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>2000 – 2015 [Flasks – CIO] (this work)</td>
<td>14.5 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>2011 – 2014 [Continuous – CIO] (this work)</td>
<td>17.0 ± 0.2</td>
</tr>
<tr>
<td>Mace Head (53.20°N 9.54°W)</td>
<td>2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)</td>
<td>14.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>2009 – 2015 [Flasks – CIO] (this work)</td>
<td>14.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>2000 – 2015 [Flasks – CIO] (this work)</td>
<td>14.1 ± 0.3</td>
</tr>
<tr>
<td>Weybourne (52.95°N 1.12°E)</td>
<td>Jan 2009 – April 2012 [Continuous] (Wilson, 2012)</td>
<td>14.9 ± 0.8</td>
</tr>
<tr>
<td>F3 (54.51°N 4.44°E)</td>
<td>2006 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>Shetland Islands (60.28°N 1.28°W)</td>
<td>2004 – 2008 (Kozlova et al., 2008)</td>
<td>15.4</td>
</tr>
<tr>
<td>Ochsenkopf (50.01°N 11.48°E)</td>
<td>June 2006 – December 2008 (Thompson et al., 2009)</td>
<td>15.5 ± 1.0</td>
</tr>
<tr>
<td>Jungfraujoch (46.33°N 7.59°E)</td>
<td>2006 – 2008 [Flasks] (Uglietti, 2009)</td>
<td>8.6 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – CIO] (van der Laan-Luijkx et al., 2013)</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – MPI] (van der Laan-Luijkx et al., 2013)</td>
<td>10.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>2007 – 2011 [Flasks – Bern] (van der Laan-Luijkx et al., 2013)</td>
<td>10.3 ± 0.3</td>
</tr>
<tr>
<td>Puy de Dôme (45.46°N 2.58°E)</td>
<td>2004 – 2008 [Flasks] (Uglietti, 2009)</td>
<td>16.1 ± 1.2</td>
</tr>
<tr>
<td>Fyodorovskoye (56.27°N 32.55°E)</td>
<td>1998 – 2008 [Flasks 100 m– CIO] (van der Laan et al., 2014)</td>
<td>23.2 ± 1.0</td>
</tr>
<tr>
<td>Bialystok (53.13°N 23.01°E)</td>
<td>Aug 2005 – Jun 2008 [Continuous] (Popa et al., 2010)</td>
<td>25</td>
</tr>
</tbody>
</table>
For APO the seasonal amplitude at Lutjewad was found to be significantly lower for the most recent data and the complete dataset (both 49 ± 5 per meg) compared to the original value for the record from 2000 – 2009 (64 ± 6 per meg). They also correspond better to the value based on the continuous data (43.0 ± 0.8 per meg), although this dataset is less reliable, as was discussed before. The higher quality fit to the newest flask measurements (due to the earlier discussed increased sampling frequency in the narrow trough periods) apparently leads to a better removal of the biospheric signal from the resulting APO. Still, looking at Figure 5.3, the fit of the seasonal APO amplitude seems to be somewhat underestimated. For Mace Head the most recent data show a lower seasonal amplitude (66 ± 5 per meg) than the older data (74 ± 6 per meg), with the total dataset showing an average value of these two (71 ± 5 per meg). This seasonal amplitude is roughly half the δO2/N2 amplitude. The amplitude found at Weybourne is again in a similar range (59 ± 6 per meg), just as the amplitudes found at Sendai (52 per meg) and Cape Ochi-Ishi (65 per meg), Japan (Ishidoya et al., 2012; Tohjima et al., 2003). Stations that are relatively more influenced by the oceans than Lutjewad and Mace Head show an even higher seasonal amplitude of APO (e.g. Shetland Islands and F3), while more continentally based stations show much lower seasonal amplitudes.

Next to fitting the APO data calculated from the O2 and CO2 data records, the amplitude of APO could also be determined from the O2 and CO2 fits. The amplitudes found for the Lutjewad data records showed significant variation between the two methods. The reason is the influence of the biosphere, which is incorporated in the calculation of the separate O2 and CO2 fits and apparently is not cancelled out fully when combining the fits; it is, however, largely cancelled out when APO is calculated from the individual O2 and CO2 measurements. For Mace Head the amplitudes found with both methods are very similar. At this station, most of the sampled air comes from the ocean so the data record is barely influenced by the biosphere (or other local influences), as was already concluded before.

5.4. Discussion and conclusions

This chapter presents the updated flask observations of atmospheric δO2/N2 and CO2 at Lutjewad and Mace Head, and also shows the first results of the continuous O2 – CO2 instrument placed in Lutjewad in 2007. That measuring atmospheric O2 is challenging becomes clear again in the work presented in this chapter. The precision of the δO2/N2 measurements of the flasks is estimated to be about 4 per meg, which is very satisfactory. The accuracy on the internal scale is better than 2 per meg but the conversion to the international scale is not sufficiently accurate and reliable so far, due to problems in measuring high pressure gas cylinders. To deal with the high pressure in the cylinders, regulators are used, which are known to cause problems in δO2/N2 measurements (Keeling et al., 1998; 2007).

Sampling at Mace Head seems to be very efficient with almost no need to filter the data. At Lutjewad, a large part of the flasks needs to be removed from the dataset, as these flasks do not represent background conditions. For maintaining a “continental baseline” record, a more careful selection of sampling conditions is important. The large gap in the O2 data at Mace Head around 2009 has a large impact on the dataset, especially in determining the trends for δO2/N2 and APO.
The continuous O₂ – CO₂ system shows a relatively poor precision (see chapter 3) and the dataset also shows many gaps due to different reasons such as broken instrument parts and rebuilding of the laboratory with all kinds of start-up problems. The quality of the data is also deteriorated by local disturbances in the temperature of the laboratory. The temperature of the box that contains both the fuel cells and CO₂ sensors needs to be kept constant at 32°C. Before the moving to the new laboratory, the temperature was often too low in winter and too high in summer. In the new laboratory a climate control system was installed but this caused new problems, as now smaller, but fast temperature fluctuations in the lab occur, causing noise in the O₂ measurements. This is illustrated very well in chapter 4 of this thesis, and influenced the data of our fixed continuous system in a similar way. Apart from the direct influence of the temperature fluctuations in the instrument itself, also the calibration, target and reference cylinders are influenced by (long-term) temperature fluctuations. In that respect, the situation in the new laboratory has improved considerably.

The continuous data record at Lutjewad should become more robust to make it a more useful dataset. Gaps in the data should be prevented as much as possible and good quality climate control in the laboratory is essential. In addition, both the instrument and the cylinder box would benefit from better thermal insolation. The pressure control needs extra attention as well, as pressure fluctuations are another reason for noise in the O₂ measurements. Furthermore, an aspirated air inlet should be installed to prevent thermal fractionation due to solar radiation.

Besides these rather obvious – and in principle straightforward – improvements, the system could also be adapted to improve precision and accuracy. Although the Vaisala Carbocap GMP343 sensors were deliberately chosen, as they are cheap, and good enough as part of the APO record (that is, until the δO₂/N₂ precision gets below ≈ 4 per meg) replacement by a much more precise CO₂ sensor, such as the Uras26 NDIR used in the transportable system presented in chapter 3 has an additional advantage. This sensor can be adapted and installed in such a way that sample and reference air have their own path and do not need to be switched, similar to the setup described by (Wilson, 2012). In this way, the switching time of the fuel cells can be reduced to give a data output frequency of 1 point per minute, which is a factor 5 more than the current output. This will improve the precision and accuracy significantly.

The fitting procedure of trends and seasonal cycles on CO₂, δO₂/N₂ and APO is a delicate task, which is very sensitive to gaps in the data, irregular temporal sampling and obviously to errors in the measurements. Also the method used to fit the data has a significant influence on the final results, as was demonstrated by (Pickers and Manning, 2015) when comparing three different curve fitting programs often used in atmospheric sciences. Nevertheless, our flask sampling data records of Lutjewad and Mace Head have proven to be valuable, and the sampling and measurement, under improved conditions, will be continued in the future.

5.5. Acknowledgements

Part of this work is financially supported by the Dutch government (Ministry of Economic Affairs) and the CATO-2 consortium parties. CATO-2 is the Dutch national research program on CO₂ Capture and Storage technology (CCS).
We would like to thank our colleagues M. de Vries for his help with leak checking of the automated flask sampler and other assistance with the instrumentation in Lutjewad, J.J. Spriensma for her assistance with measuring flasks in the laboratory of the CIO and preparing them for reuse at the measurement stations and J.K. Schut for his help with electronics and programming for both the automated flask sampler and the Oxzala system at Lutjewad. We also thank T.G. Spain for filling the flasks at Mace Head.

5.6. References


