

UNIVERSITY OF GRONINGEN

BACHELOR RESEARCH PROJECT

Highly precise and continuous atmospheric O₂ measurements

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Abstract

A previously built system to measure atmospheric CO₂ and O₂ continuously has been tested on its new performance figures after recent updates. The most important updates were made to the switching time of two flow lines. The goal of these changes was to improve the $\delta(\text{O}_2/\text{N}_2)$ precision. The measurements were performed during springtime at the University of Groningen at the CIO labs. The system uses a fuel cell to measure O₂ and a compact infrared absorption instrument for CO₂ measurements. Data from twelve consecutive days is presented and the performance figures were determined from this period. Cylinder CO₂ precisions were found to be 0.08 ppm. The atmospheric CO₂ precisions (during stable hours) were found to be 0.13 - 0.32 ppm, which is at the limit of atmospheric variability. The CO₂ measurement results are also used to account for its diluting effect on oxygen measurements. For cylinder $\delta(\text{O}_2/\text{N}_2)$ measurements, precisions were found to be 8 per meg. While atmospheric $\delta(\text{O}_2/\text{N}_2)$ precisions (during stable hours) were found to be 4 - 8 per meg $\delta(\text{O}_2/\text{N}_2)$. However, there is a high uncertainty in the $\delta(\text{O}_2/\text{N}_2)$ precisions due to poor calibration. Only one calibration cylinder $\delta(\text{O}_2/\text{N}_2)$ value could be determined on a mass spectrometer and the others were instead estimated using the atmospheric potential oxygen (APO). This estimation increases the error in $\delta(\text{O}_2/\text{N}_2)$ massively. The measured exchange ratios for O₂:CO₂ events were compared with the expected ratios. From this comparison the accuracy of the estimated $\delta(\text{O}_2/\text{N}_2)$ value can be determined, and a better estimation can be made.

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1 Introduction

1.1 Why do we want to measure O₂?

Climate change is one of the most pressing problems of the 21st century. The warming of the earth is threatening many different ecosystems and its consequences will be devastating not only for humanity, but for all inhabitants of the earth (IPCC, 2014).

The temperature change is very likely to be caused by human emissions of greenhouse gasses like CO₂, CH₄ and N₂O. These gasses absorb in the spectrum of the outgoing radiation from earth, reducing the radiative energy going to space and thus acting as a blanket. A natural concentration of these gasses together with H₂O warm up the average temperature to 16°C instead of -17°C, which would be the earth's temperature without any greenhouse gasses present (Marshall & Plumb, 2008). An increase in these concentrations due to fossil fuel burning leads to an increase of absorbed outgoing radiation, which increases the temperature further. This is known as the enhanced greenhouse effect.

Although the radiative forcing of CO₂ on a per mole basis is much lower than than of CH₄ and N₂O, it is still the most important driver of this effect, because its absolute atmospheric concentration increase since the industrial revolution is by far the highest: 105 ppm versus 1050 ppb, or only 25 ppb for CH₄ and N₂O respectively (Marshall & Plumb, 2008). On top of this, CO₂ in the atmosphere has a high lifetime of 300-1000 years compared to just 12.4 years for CH₄ and 121 years for N₂O (IPCC, 2014)(Ciais et al., 2013). Besides emission reducing policies and measures there are also techniques available to capture and store CO₂ in order to help combat climate change. These carbon capture and storage (CCS) projects have started to grow in popularity again since 2017, after a few years of decline before that year (Page, Turan, & Zapantis, 2020). A risk of CCS, however, is the possibility of leakages of the stored of CO₂ into the atmosphere. For the public health, CO₂ is not harmful directly and the chances of suffocation are extremely low (Page et al., 2020). A leak is a bigger threat to the efficiency of CCS, as it would emit part of the captured carbon into the atmosphere again.

Detecting CO₂ leaks is a challenge, because the natural CO₂ concentration fluctuates significantly over time and location. Solutions like adding trace gasses as markers, or measuring the $\delta^{13}\text{C}$ between background and captured CO₂ content face problems of their own. A trace gas has different chemical properties and behaves differently to CO₂, so it does not necessarily occur at every leak and it is often a greenhouse gas itself. While the ¹³C signature of the stored CO₂ is often not different enough from the CO₂ in the atmosphere. CO₂ in combination with O₂ measurements do have the ability to detect such CO₂ leaks efficiently (van Leeuwen, 2015). CO₂ and O₂ are coupled for all their processes of combustion and photosynthesis on land and this shows an inverse behaviour in the atmosphere. For CO₂ leaks, O₂ clearly does not play a role and thus O₂

and CO_2 are not inversely correlated. Combustion of a fossil fuel for example would be a O_2 sink and a CO_2 source, or vice versa for photosynthesis, while a leak will only be a CO_2 source.

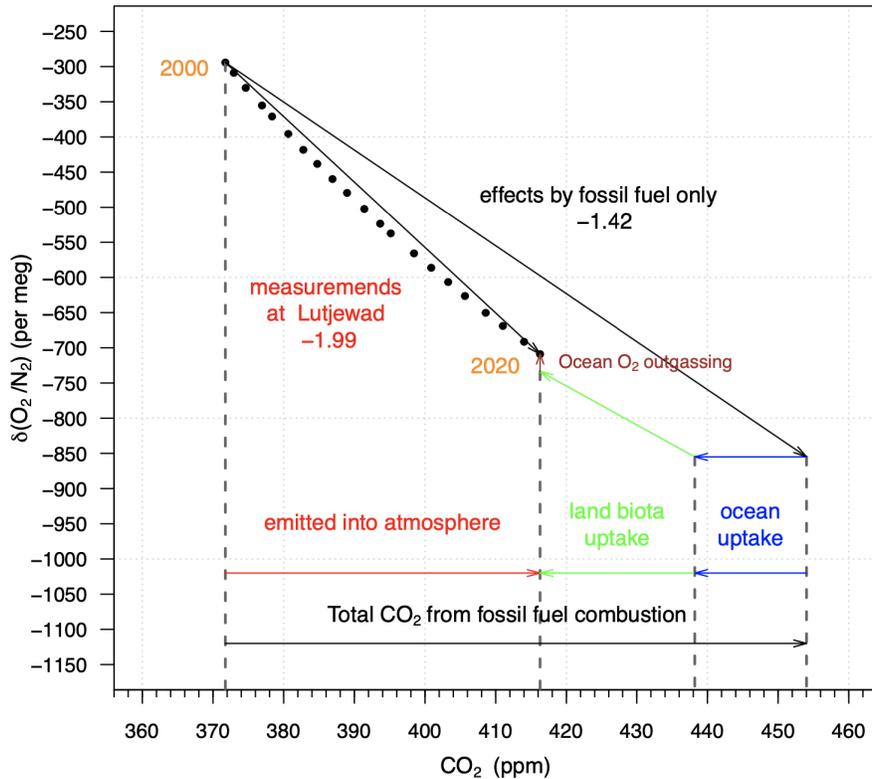


Figure 1: Oxygen versus CO_2 concentrations over the years. The effect of oceanic and land biotic carbon uptake on the increase of atmospheric CO_2 concentration from 2000 to 2020 are indicated. Image taken from (Nguyen et al., 2021)

Next to CCS there are also natural processes, which limit the atmospheric CO_2 increase significantly. Photosynthesis becomes more efficient under higher CO_2 concentrations, increasing the total carbon stored in biomass. Also part of the CO_2 emissions from combustion get dissolved in the oceans.

There are several techniques available to estimate the value of this global oceanic and land biotic uptake, each with their own challenges. For example, measurements of the oceanic partial CO_2 pressure would enable the calculation of oceanic CO_2 uptake. However, measurements are relatively sparse (in time and space), and the gas transfer velocity carries large uncertainties (Liss & Mer-

livat, 1986). The measurement of the rare ^{13}C isotope in CO_2 can, in principle, discriminate between land biotic uptake and oceanic uptake, because the lighter ^{12}C atom (in CO_2) is more likely to be taken up during photosynthesis compared to the ^{13}C (Ciais et al., 1995). For oceanic carbon this difference is much smaller, and opposite in sign. However, the atmospheric signals due to this difference are very small and require highly accurate and stable measurements over the years.

The technique, for which this thesis serves, uses the difference in behaviour of atmospheric O_2 and CO_2 concentrations. Land biotic uptake causes a decrease in CO_2 accompanied by an increase in O_2 , as it exchanges the two in its process. Oceanic uptake however, leads to a decrease in CO_2 but does not use O_2 in its process. Based on that difference CO_2 complemented with O_2 measurements can distinguish between oceanic and biotic uptake, and estimate their values. CO_2 and O_2 (which are more challenging) monitoring stations around the world can help provide more insight into the global carbon cycle. Figure 1 shows that oceanic and land biotic uptake are estimated to have halved the net atmospheric CO_2 increase. Therefore, they play a vital role in climate change mitigation.

1.2 Atmospheric O_2 measurements

Air consists of N_2 (78.1%), O_2 (20.9%), Ar (0.9%) and many more gasses, which are present in small amounts like CO_2 , CH_4 or Ne. Apart from water vapour, which can vary between 0-3% depending on conditions, the other constituents of the atmosphere stay rather constant. High background levels and relatively low variations of O_2 make precise and accurate measurements a challenge. Also variations in other constituents of the atmosphere have a relatively big impact on the concentration of O_2 compared to CO_2 (or other trace gasses) (van Leeuwen, 2015). To circumvent this problem the air is dried to <1 ppm water vapour and atmospheric oxygen measurements are expressed as the O_2/N_2 ratio relative to a reference gas (Keeling & Shertz, 1992).

$$\delta(\text{O}_2/\text{N}_2) = \frac{(\text{O}_2/\text{N}_2)_{\text{sample}}}{(\text{O}_2/\text{N}_2)_{\text{reference}}} - 1 \quad (1)$$

Where the O_2/N_2 ratio does not depend on other concentrations apart from oxygen and nitrogen, and $\delta(\text{O}_2/\text{N}_2)$ is usually given per meg (or 0.001‰). However, measuring the O_2/N_2 ratio directly is only possible using (isotope ratio) mass spectrometry. Many other systems measure the oxygen abundance, so a conversion to the internationally agreed $\delta(\text{O}_2/\text{N}_2)$ scale is necessary. And then, other trace gasses in the atmosphere, with varying abundances, still have a variable diluting effect on the oxygen measurement. Because CO_2 still forms 0.04% of the air compared to just 0.0018% for Ne (or even smaller for other trace gasses) and CO_2 variations are much higher compared to N_2 and Ar variations its diluting effect has to be taken into account here. A correction is given by (Kozlova,

Manning, Kisilyakhov, Seifert, & Heimann, 2008):

$$\delta(O_2/N_2)_{sample} = \frac{\delta X_{O_2} + (\Delta CO_2 \cdot S_{O_2})}{(1 - S_{O_2}) \cdot S_{O_2}} \quad (2)$$

Where $S_{O_2} = 0.20946$, which is the standard mole fraction of O_2 in air (Machta & Hughes, 1970). ΔCO_2 is the difference between the measured CO_2 and the (arbitrary, but consensus) standard CO_2 concentration, defined to be 363.29 ppm. And how the measured O_2 concentration (δX_{O_2}) is obtained will be covered in chapter 2.

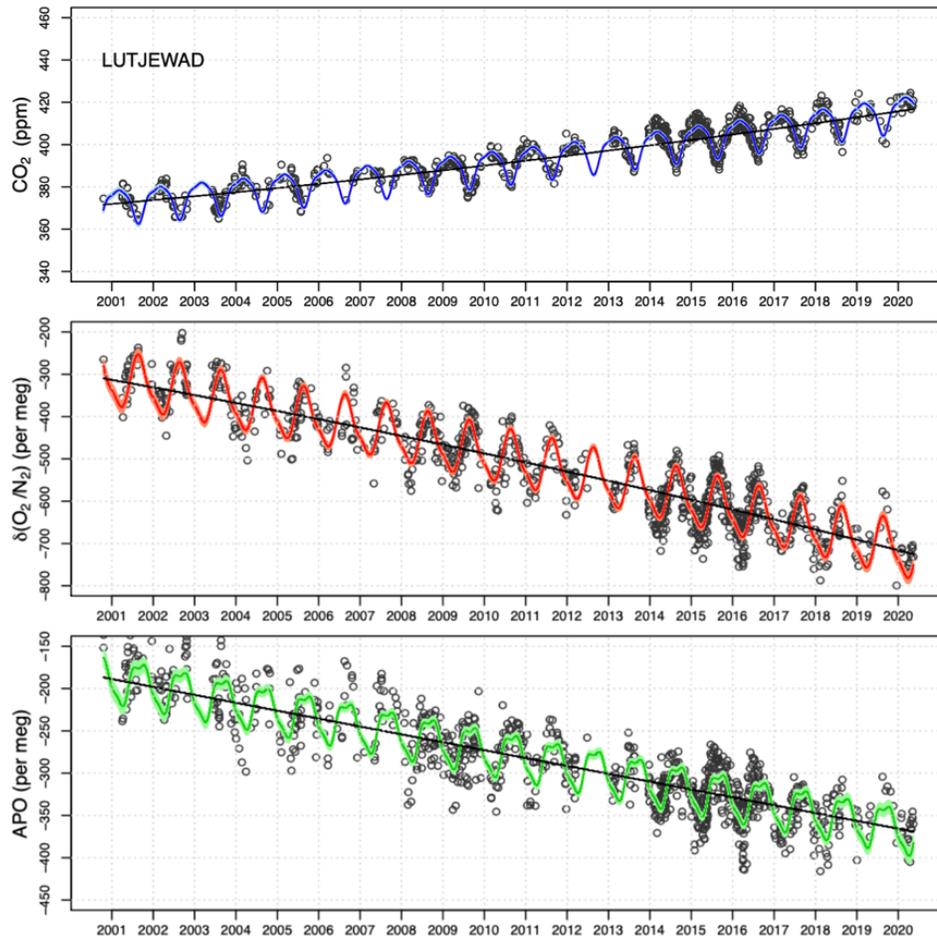


Figure 2: Atmospheric CO_2 , $\delta(O_2/N_2)$ and APO values from Lutjewad ($53^{\circ}24'N$ $6^{\circ}21'E$), the Netherlands taken from (Nguyen et al., 2021)

Figure 2 shows O_2 and CO_2 concentrations over the years. There is a general

increasing trend for CO₂ and a decreasing trend for O₂ due to large amounts of fossil fuel combustion. The increase in CO₂ is less compared to the decrease in O₂ and exactly this difference makes the partitioning between oceanic and land biotic carbon uptake possible (see fig 1 and ((Ciais et al., 2013))). The seasonal fluctuations can be assigned to biological processes in spring, plants take up carbon, and produce oxygen, while the opposite takes place in autumn. The measurements in this paper will be conducted in springtime, so a general increase in O₂ (and decrease in CO₂) is expected.

On a shorter timescale, the CO₂ and O₂ exchange ratio (also called oxidation ratio or stoichiometric ratio) can give information about the type of event happening. Biosphere activities for example have a ratio of 1.1 (Severinghaus, 1995) while different types of fossil fuel combustion have a higher ratio (the longer the carbon chain, the lower the ratio): natural gas 1.95, oil 1.4, coal 1.17 (Keeling, 1988). The exchange ratio for the biosphere (1.1) is also used to define the Atmospheric potential oxygen (APO). The APO is the weighted sum of O₂ and CO₂ adjusted such that it is independent of biological O₂ and CO₂ activities (Manning & Keeling, 2006). It is given by (Stephens et al., 1998):

$$\delta APO = \delta(O_2/N_2) + \frac{1.1 \cdot (CO_2 - 350)}{So_2} \quad (3)$$

Where So_2 is the standard mole fraction of O₂ again. 350 is a reference value defined by the Scripps Institution of Oceanography (SIO), which is subtracted from the measured CO₂ concentration. Using the average exchange ratio 1.1 makes sure that the effects of the terrestrial biosphere are removed. thus cancelled this way. The final δAPO is given per meg just like $\delta(O_2/N_2)$. It is clear that, if a system measures O₂, and not O₂ and N₂, that then also a CO₂ measurement is necessary. As such a measurement is usually necessary by itself, this is no problem.

2 The measurement system

The Centre for Isotope Research (CIO) at the University of Groningen has been measuring continuous O₂ concentrations since 2008 (van der Laan-Luijkx, Neubert, van der Laan, & Meijer, 2010). A transportable system was built for a project that demonstrated leak detection using O₂, but its compact design has been an improvement throughout, also for on-site atmospheric measurements (van Leeuwen, 2015). It currently uses a fuel cell (Oxzilla II) from Sable Systems for O₂ measurements and a compact infrared absorption instrument (the EL3020 NDIR) from ABB for CO₂. The complete system is schematically shown in figure 3.

The Oxzilla II consists of two fuel cells with a lead anode, a gold cathode and a weak acid electrolyte. Air is flowing onto the cathode where oxygen is

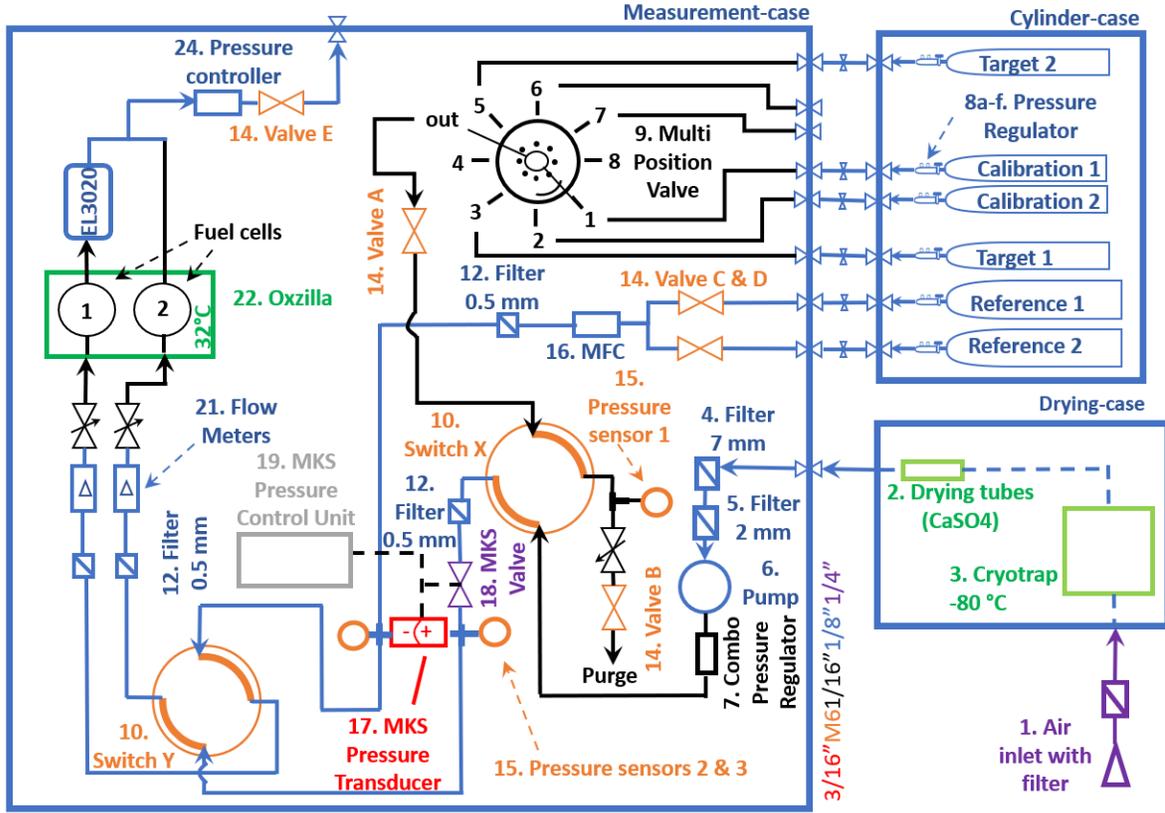
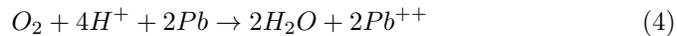


Figure 3: A schematic drawing of the transportable O_2 and CO_2 measuring system. The outside air is entering the system via the inlet (nr. 1), and dried in two steps, first a cryotrap of $-80^\circ C$ and secondly tubes filled with $CaSO_4$ (nr. 2, 3). A switching valve X switches every 23 hours to measure the calibration cylinders instead of the outside air, and a switching valve Y switches every 90 seconds between sample and reference air. The MKS control system (nr. 17-19) keeps the pressure equal in both lines - adapted from (van Leeuwen, 2015)

reduced, producing a current and at the anode the lead is oxidized. This leads to the following net reaction:



The current created by this chemical reaction is proportional to the O_2 amount in the cell. The two fuel cells alternate between sample and reference air to account for instrumental drift. The operation temperature is stabilized on $32^\circ C$. The Oxzilla II produces a data point for each cell every second. Every 90 seconds the air flows are switched. Of the total 90 data points, the first 75 are

disregarded and only the last 15 are used. The two fuel cells of the Oxzilla II each measure sample and reference air alternately, but they are never measuring the same air at the same time. The CO₂ measuring instrument is in phase with one of the oxygen fuel cells and is also producing a data point every second.

Using the switching between reference and sample air a double differential value for O₂ can be deduced (Thompson, Manning, Lowe, & Weatherburn, 2007):

$$\Delta(\Delta) = (S_1 - R_2) - (R_1 - S_2) \quad (5)$$

Where S and R refer to sample and reference air respectively and 1 and 2 to the fuel cells. The output of the Oxzilla II gives the partial oxygen pressure as %O₂, which is converted to XO₂ with the help of calibration gasses. Each 23 hours two calibration cylinders are measured for half an hour instead of the sample air (with respect to the same reference cylinder). Because it takes a while to flush the lines and regulators completely, only the data from the last 9 minutes of these measurements are used to obtain a value for $\Delta(\Delta)$. The final averages from both cylinders are then used to perform a linear calibration to convert $\Delta(\Delta)$ to XO₂. The calibration cylinders' values are determined using the Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) at the CIO, which measures O₂/N₂ ratios directly. This instrument is regularly calibrated and produces values according to the international "Scripps" scale. For the CO₂ measurements the calibration is also connected to the international (WMO) scale. Finally equation 2 is used together with the calibrated Δ CO₂ value from the EL3020 to calculate $\delta(\text{O}_2/\text{N}_2)$.

2.1 Gas handling

Apart from the cylinders and measuring devices, figure 3 shows many components which take care of the drying, switching and constant flow.

Drying the atmospheric sample air is necessary to remove the water content because it has a significant, and variable, diluting effect on the O₂ concentration, just like CO₂ does. A calcium sulphate (CaSO₄) drying tube in combination with a cryotap of -80 °C are used to cool the air and remove the water content effectively. The cold fingers have to be cleaned once a month to prevent them from being clogged with ice. Switch X together with the multi position valve in figure 3 are used to switch between measuring outside air or (calibration or target) cylinder air. Switch Y switches the reference and sample air flows every 90 seconds. The pressure in both flow lines is regulated by valves and kept equal by an MKS differential pressure control system. Constant and equal pressure in both flows is necessary because the O₂ signal is proportional to the amount of O₂ in the cell. Furthermore the flow is through stainless steel tubes to avoid any chemical reactions. The outside air is pumped in from the roof of the building.

2.2 Precision and accuracy

To determine the performance of the full system two target cylinders are measured every 24 hours as well. Just like with the calibration cylinders the average of the last 12 minutes is taken and their value is determined on the DI-IRMS. Precisions on cylinder measurement were found to be in the range of 0.009 - 0.021 ppm for CO₂ and 5 - 15 per meg for $\delta(\text{O}_2/\text{N}_2)$ (van Leeuwen, 2015).

Because atmospheric CO₂ and O₂ fluctuate significantly, the most stable moments in a measurement period have to be selected before determining its precision. By applying a running average the 20 most stable hours of data were selected, and the standard deviation of these hours was determined. In this way van Leeuwen (2015) found standard deviations of 0.13 - 0.29 ppm for CO₂ and 8 - 17 per meg for $\delta(\text{O}_2/\text{N}_2)$. The precision of CO₂ is about a factor of 10 lower for outside air measurements compared to cylinders therefore the CO₂ must be limited by atmospheric variability. On the other hand the $\delta(\text{O}_2/\text{N}_2)$ standard deviation stayed roughly the same, which means that the noise of the system itself is the limiting factor. Since van Leeuwen's work, the system has been improved slightly and in this paper we present new series of measurements from which we determine the updated precisions for the presented system.

The most important changes were made to the switching time, calibration measurements and drying system. The switching time was lowered from 3 minutes to just 90 seconds, this improves the temporal resolution but lowers the time available for a signal to stabilize. The calibration cylinders are measured for 30 minutes instead of 1h and 15 minutes, which also results in more data from atmospheric measurements. Finally the position of the chemical drying tubes filled with CaSO₄ was changed. The chemical tubes are placed directly after the cryotrap, they used to be after switch Y and in front of the oxygen fuel cells. There is also a different CO₂ analyser in this updated system, however it has the same working principle and was made by the same manufacturer.

3 Measurement conditions and data processing

The system was tested inside the CIO labs in Groningen, where the air is pumped in from the roof of the four-story high building. During the measurements we encountered several problems, some with cylinders but mostly with the drying of the air. In this section we discuss some of these problems, the conditions during the measurements and their effect on the final results.

The system measures not only CO₂ and O₂ but also keeps track of many other parameters such as: temperature, pressures, flow rates and pump speed. It produces a raw output for every parameter every second, creating a big data file, which was processed using Excel. Although Excel is clearly not the best

solution for processing of these data, it was nevertheless used for this investigation as it is easy and ready to use, contrary to the analysis programs that have been used in the past and that need an upgrade to make them work with the present set-up. However, for regular atmospheric monitoring this needs to be done.

3.1 Calibration cylinders

The measurement system's achievement crucially depends on the right values for the CO_2 and $\delta(\text{O}_2/\text{N}_2)$ of the calibration cylinders. At first the CO_2 and $\delta(\text{O}_2/\text{N}_2)$ concentrations of two out of four cylinders were wrong, because the cylinders had been refilled more recently. The CO_2 concentrations for the unknown cylinders were determined on a Cavity Ring-Down Spectrometer (CRDS) from Picarro, and also the known cylinders were checked. However, the $\delta(\text{O}_2/\text{N}_2)$ values for the unknown cylinders could not be determined, because the DI-IRMS at the CIO labs was defective. How this problem was circumvented regarding the calibration will be extensively discussed in section 5.2.

3.2 Drying

Drying the sample is crucial, not only to collect useful data but also to prevent damage to the system. The stainless steel tubes are too thin to accompany a water flow, and the pressure regulator can be damaged by the water. The sample air was not dried sufficiently enough at first, because the chemical trap was placed in front of the cryotrap in the line. The chemical trap is saturated quicker and more effective in removing small amounts of water vapour compared to the cryotrap. The cryotrap is also easier to replace, therefore the cryotrap should be first in line before the chemical trap.



After the traps were put in correct order the risk of clogging the cryotrap decreased. The water vapour content of the lower atmosphere can vary between 0-3% depending on weather conditions. Clogging of the cryotrap is a serious risk, not only will it impair proper measurements but it

Figure 4: Cryotrap cooling finger clogged with ice after it had been in use too long (photo taken on the 7th of June)

can also lead to damage to the whole system if not cleaned often enough. Our experiments indicated that cleaning is necessary after 3 to 4 days in the weather conditions of June 2021.

3.3 Weather conditions

Due to several problems as indicated above, and the time constraint of the research, the amount of useful data acquired, is somewhat limited, to the period from the 30th of May till the 10th of June. The weather conditions during this 12 day period were relatively stable, which was beneficial for the measurement quality. The period had sunny days with temperatures rising above 20°C regularly. This only got interrupted by some rainfall during the 5th and 6th of June. In general wind speeds were low especially during the evening and night, which led to a stable lower layer in the atmosphere, in which the emitted CO₂ could accumulate.

4 CO₂ measurements

In the first place, CO₂ is measured, because it is the most important signal to learn about CO₂ emission and uptake. While $\delta(\text{O}_2/\text{N}_2)$ is measured to partition the various sources and sinks for CO₂. As explained in the introduction, CO₂ measurements are also required to account for its diluting effect on $\delta(\text{O}_2/\text{N}_2)$. Combined CO₂ and $\delta(\text{O}_2/\text{N}_2)$ measurements also provide extra insights, because they are coupled for all processes of combustion and photosynthesis on land. The EL3020 sensors measure both ¹²CO₂ and ¹³CO₂ simultaneously, however the ¹³CO₂ data are accurate enough to be of practical use for atmospheric measurements. Therefore, we only use the ¹²CO₂ data in the results set out in this section.

Table 1: The CO₂ and $\delta(\text{O}_2/\text{N}_2)$ concentrations of the used cylinders as determined on the DI-IRMS and according to the international "Scripps" scale. *Note that the $\delta(\text{O}_2/\text{N}_2)$ values of cylinders 7213, 7201 & 1642 are determined differently as set out in section 5.2

	Cylinder number	CO ₂ concentration (ppm)	$\delta(\text{O}_2/\text{N}_2)$ concentration (per meg)
Calibration	7213	395.58 ± 0.05	-458 ± 83*
	6987	416.95 ± 0.04	-570.8 ± 2.2
Target	7201	394.99 ± 0.49	-455 ± 83*
Reference	1642	459.19 ± 0.33	-792 ± 83*

4.1 Calibration

To calibrate the raw data two calibration cylinders, one target cylinder and one reference cylinder were used, their values can be found in table 1. Cylinders 7213 and 6987 were used to construct a linear calibration line to convert the raw data to accurate CO₂ concentrations. Their values of 395.58 and 416.95 ppm are lower compared to the average of the atmospheric CO₂ concentrations, which is not ideal because it will lead to extrapolation of the calibration curve, which can decrease the accuracy and reliability of the calibration. Target cylinder 7201 was essentially measured to check the accuracy of the system, however its value is too close to calibration cylinder 7213 (394.99 and 395.58 ppm respectively) and they are measured close in time. Because the latter calibration cylinder is used to construct the linear relation, naturally a cylinder with almost identical CO₂ concentration would also be measuring very similar concentrations and thus be a poor check to the calibration process. Therefore, the reference cylinder was instead used to check the calibration process. Figure 5 shows the calibrated measured CO₂ concentrations of the reference cylinder for one day. The average for that day is 456.65 ppm which is 2.54 ppm off from the assigned value of 459.19 ± 0.33 ppm. The extrapolation of the calibration is the most likely cause of this deviation. The accuracy of the system is less important than its precision, and the CO₂ measurements are still valuable.

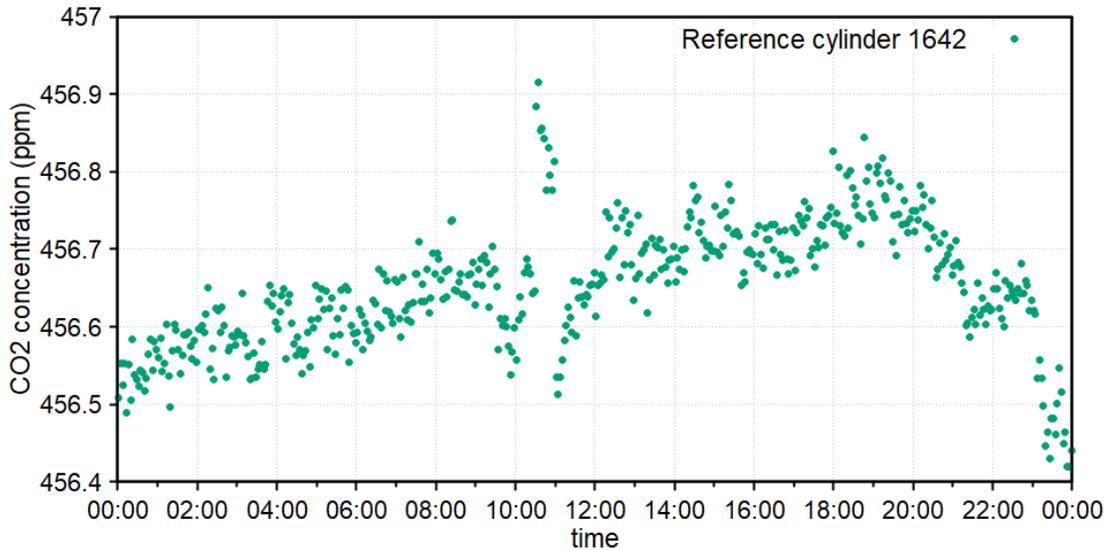


Figure 5: Measured and calibrated CO₂ concentration of reference cylinder 1642 from the 6th of June

4.2 Reference cylinder measurements

Next to this the reference cylinder is also continuously measured to account for instrument drift. As figure 5 also shows the measured value changes over the course of a single day. A line is fitted to this data and then used to correct the atmospheric CO₂ for instrumental drift as well. Although this effect is small it is still important to monitor. The instrument drift is not constant throughout the day, as figure 5 shows clearly at the end and for a short time during calibration measurements (at 11:00). However higher drifts only last for a short amount of time, they are likely related to conditions changes at the labs. Both the linear calibration and correction for instrumental drift are calculated for every day separately.

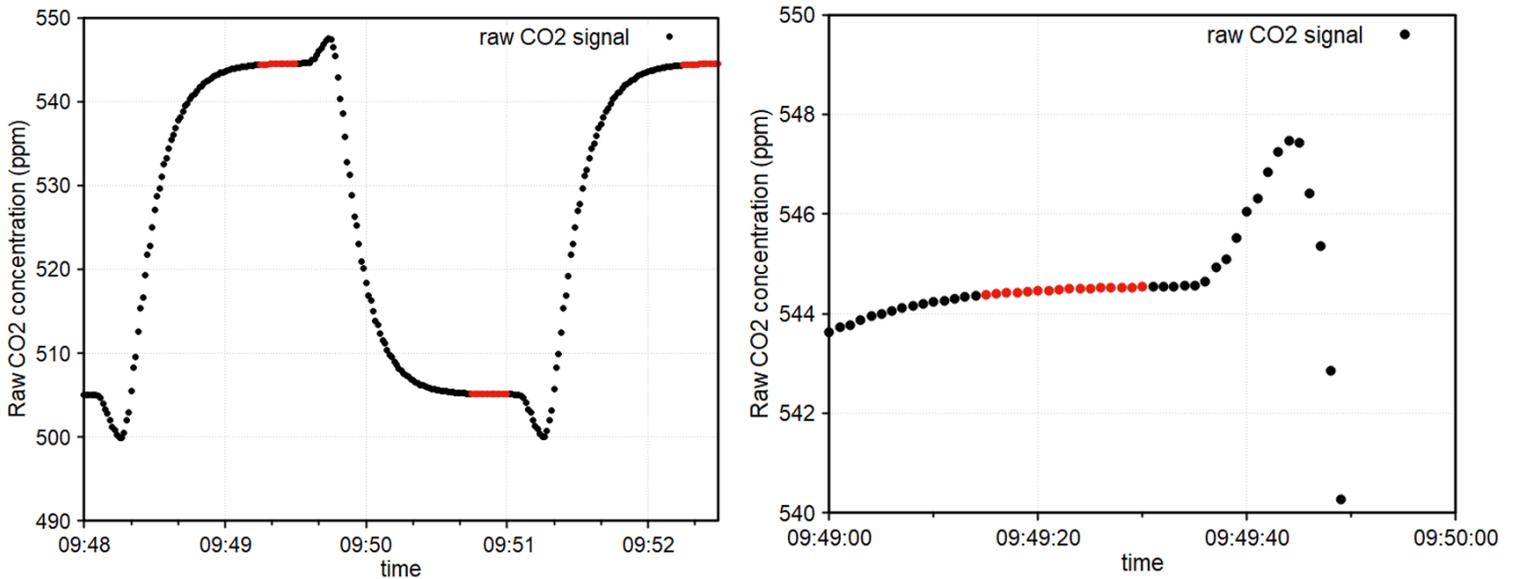


Figure 6: On the left: raw CO₂ data from three switching cycles during calibration measurement period. On the right: a more detailed plot of the first peak of the left plot. The red data are the last 15 seconds before a switch.

The precision for cylinder CO₂ measurements of the system can also be obtained from the reference cylinder data. From the reference measurements of a full day a standard deviation of 0.08 ppm CO₂ was found. The old system found significantly better precision for cylinder measurements of 0.009 - 0.021 ppm. A closer look at the raw CO₂ signal (figure 6) reveals the most likely cause for this deterioration. The lowered switching time (90 seconds) only leaves 75 seconds for the CO₂ signal to stabilize. The red data (last 15 seconds of each cycle) still show a slight upward drift. Using fewer data points to find the average of a switch does not improve precisions, because this increases the deviation between

the averages of each cycle. Three cycles during calibration cylinder measurement (09:48 till 09:52) were plotted in figure 6 to prevent unwanted variability resulting from the atmosphere itself.

Precisions determined from the calibration cylinders are worse, because these cylinders are only measured for 30 minutes each day. The first 18 minutes are already disregarded, because the line requires some time to be flushed. The calibration cylinder precision however, is crucial for the calibration process. Over 12 days of measuring each cylinder for 30 minutes a standard deviation of 0.22 ppm for CO₂ was found for cylinders 7213 & 6987 separately. Similarly for cylinder 7201 a standard deviation of 0.27 ppm CO₂ was found. This is compromised because cylinder 7201 was closed accidentally for a few days (only 8 measurement periods were taken).

4.3 Atmospheric measurements

Figure 7 shows the calibrated atmospheric CO₂ concentrations for twelve consecutive days. The calibration measurements (in green) are particularly stable as expected from cylinder CO₂ measurements. The standard deviation of the average values over these twelve days is 0.23 ppm CO₂. Note that calibration cylinder 7213 and target cylinder 7201 have similar values and their data points coincide in the plot. The atmospheric CO₂ measurements show a typical diurnal pattern caused by mixing and demixing of the lower atmospheric layer, leading to multiple significant peaks in CO₂ concentrations during the evening and night. During the last two days specifically the peaks are quite high.

Most of the high CO₂ concentrations are measured around nighttime. Soil and vegetation respiration together with the nocturnal boundary layer are the cause for this. During the night the CO₂ consuming process, photosynthesis, is not active. And plants do emit CO₂ by using the sugars produced during the day to get energy for growth. Together with the decomposition of soil organic matter, this emits significant amounts of CO₂. The conditions (wet ground from earlier rainfall and relatively high temperatures) were ideal for increased soil respiration as well (Froment, 1972). At night the cooling of earth's surface temperature also creates a nocturnal boundary layer. The air closest to the earth cools down first, and because colder air is denser it creates a stable atmospheric layer. This traps pollution (or CO₂ in this case) in a smaller part of the atmosphere.

The final CO₂ graph also reveals a few daytime peaks (on the 1st 7th & 8th of June), they might be caused by fossil fuel, and/or by a changing wind direction bringing a different air mass. This daytime variability is more clearly visible in figure 10, and in sections 5.4 & 5.5 we also discuss it in more detail together with its relation to the $\delta(\text{O}_2/\text{N}_2)$ concentration.

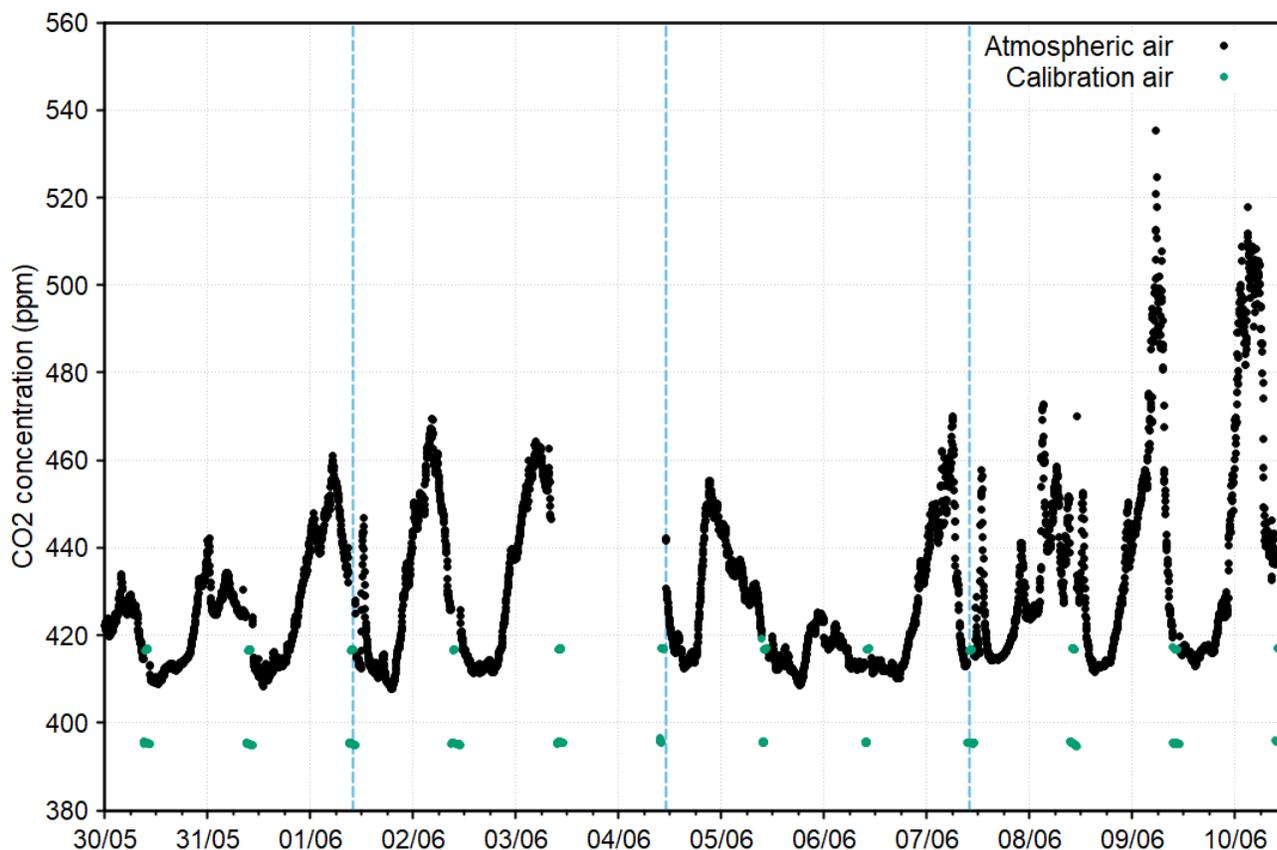


Figure 7: CO₂ concentration for atmospheric air (black), calibration and target cylinders (green). The x-axis shows the date in day/month format. The blue dotted lines represent a change of cooling trap and during the gap in the middle the chemical drying trap was saturated

To obtain the precision for atmospheric CO₂ measurements we first select the most stable hours by applying a running average with standard deviation ($n=20$). From these stable hours the standard deviation was calculated and found to be between 0.13 ppm and 0.32 ppm. In total 20 most stable hours were selected from twelve days of measurements.

Just like van Leeuwen (2015) stated for the older system, the CO₂ concentration is indeed determined very precise for cylinder air. The updated system however did show a deterioration of the precision to 0.08 ppm from the old performance of 0.009 - 0.021 ppm. This is just within the international compatibility goal of 0.1 ppm set by The United Nations World Meteorological

Organization (WMO) (WMO, 2012). Precision for atmospheric CO₂ measurements stayed very similar with new precision between 0.13 and 0.32 ppm. The older version of the system had precision for atmospheric measurement between 0.13 and 0.29 ppm. Outside air measurements are still considerably less precise compared to cylinder measurements, indicating that they are at the limit of atmospheric variability. The cylinder precisions are affected by the lower switching time, which does not leave enough time for the CO₂ signal to stabilize. The old system used the Uras26 NDIR CO₂ sensor from ABB, which was replaced with the EL2030 from ABB. The sensors are based on the same physical principles, but the EL2030 produces a data point every second instead of every 5 seconds for the Uras26 NDIR. These changes did not benefit the cylinder CO₂ precision, however the sample precision stayed similar as there are already compromised by the atmospheric variability. The CO₂ measurements are satisfactory as the primary goal of this system is to measure oxygen and APO. And CO₂ is still much more precise than $\delta(\text{O}_2/\text{N}_2)$.

5 $\delta(\text{O}_2/\text{N}_2)$ measurements

The $\delta(\text{O}_2/\text{N}_2)$ measurements, as explained in the introduction, are more elaborate compared to the CO₂ measurements. And it is challenging to achieve precisions in the range of the international goal of 2 per meg (WMO, 2012). In this section we first explain how the raw measured oxygen data was processed, before the final $\delta(\text{O}_2/\text{N}_2)$ results are presented.

5.1 The double differential ($\Delta\Delta$)

Rather than using the output of the Oxzilla II cells directly we make use of a $\Delta\Delta$ value (equation 5), because this increases precision and removes instrument drift. Figure 8 shows the calculation of a single $\Delta\Delta$ value graphically. The average of the red data points (last 15 seconds of each cycle) is first used to calculate the difference in O₂ concentration between sample and reference air. This step is automatically performed by the system and the measured difference can be found in the output file. Then the difference is taken between two switching cycles, as depicted in the lower plot of figure 8. The difference between the averages is calculated, this is one $\Delta\Delta$ value. The double differential thus originates from the differences between sample & reference and cell 1 & cell 2. This results in one $\Delta\Delta$ value per 3 minutes. Also note the difference in stabilization between the CO₂ & O₂ in figure 6 & figure 8.

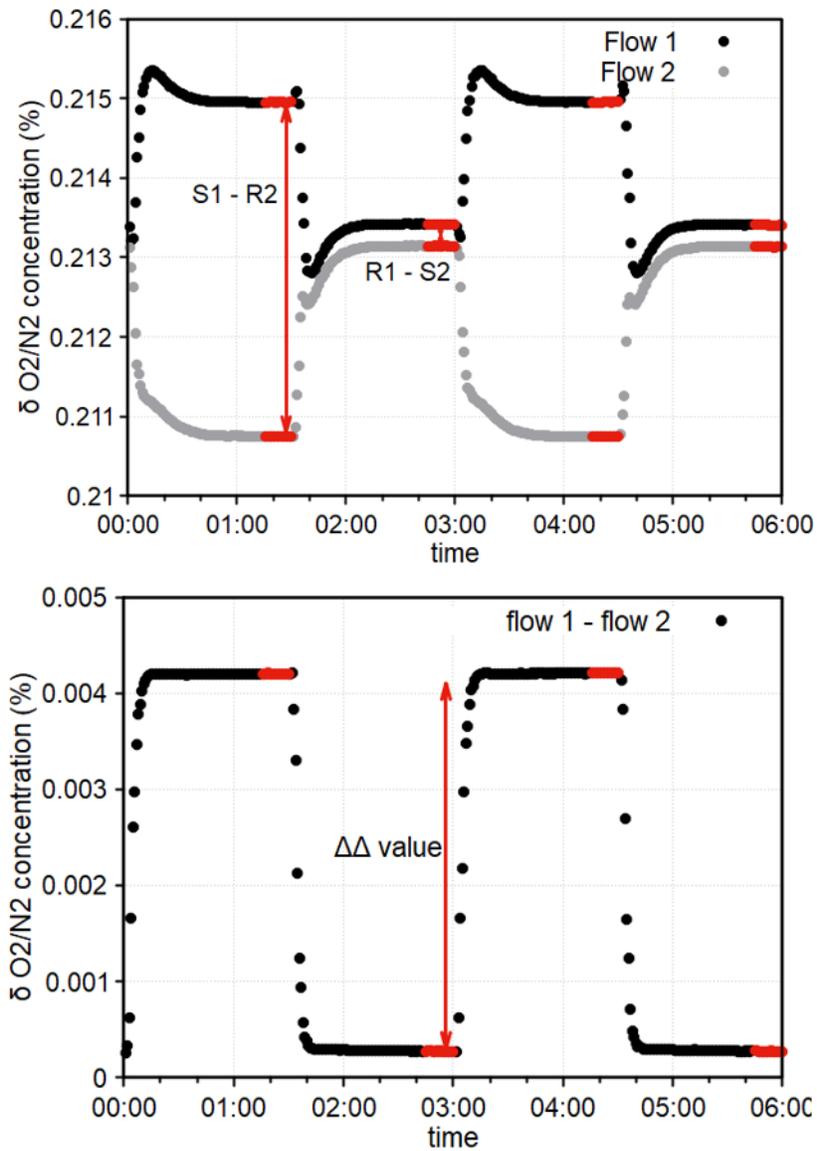


Figure 8: The calculation of a $\Delta\Delta$ value from raw data for outside air measurement. The upper plot shows the first step, taking the difference between reference and sample. The plot below shows this difference and a single $\Delta\Delta$ is represented by the red arrow. The red colored data are the last 15 seconds of data before a switch

5.2 Calibration

The calibration cylinders are needed to relate this $\Delta\Delta$ to a δXO_2 such that we can use equation 2. The same cylinders as for the CO_2 are used with their assigned or constructed $\delta(\text{O}_2/\text{N}_2)$ values in table 1. Only for calibration cylinder 6987 the $\delta(\text{O}_2/\text{N}_2)$ value is determined accurately on the DI-IRMS, for the other cylinders this was not possible because the DI-IRMS at the CIO labs was defect at the time of this research. The other $\delta(\text{O}_2/\text{N}_2)$ values in table 1 are determined by using their known CO_2 values and the atmospheric potential oxygen (APO). The cylinders are filled at the CIO labs with compressed outside air from a random day. This enables us to construct an estimated $\delta(\text{O}_2/\text{N}_2)$ value based on their CO_2 concentration, assuming only biological O_2 and CO_2 exchange. Under this assumption the APO (equation 3) is the same for all cylinders. Using the known concentrations from cylinder 6987 we found a corresponding APO of -219.22 per meg. To determine the estimated $\delta(\text{O}_2/\text{N}_2)$ concentrations of the other cylinder, the CO_2 concentrations as in table 1 with constant APO were used.

This solution however, does result in large uncertainties, as we know that the APO can change significantly between cylinders. Cylinder 7213 and 7201 also demonstrate this, they have similar CO_2 concentration and consequently we calculated very similar $\delta(\text{O}_2/\text{N}_2)$ concentrations as well. However the measured $\Delta\Delta$ values between these cylinders were much further apart from each other, on average 87 per meg difference was measured after calibration, while the difference in estimated value is just 3 per meg. For the eventual linear calibration cylinders 7213 and 6987 were chosen, because this resulted in the best linear calibration. Several days of data from cylinder 7201 are missing because it was left closed accidentally. Figure 9 shows all the calibration cylinder measurements in green.

The cylinders are measured for 30 minutes daily, of which only the last 12 minutes (4 data points) are used, because it takes time before the lines are flushed. The standard deviation of the average values over 12 days of measurements were taken for each cylinder. For cylinder 7213 and 6987 precisions of 8 per meg $\delta(\text{O}_2/\text{N}_2)$ were found. Cylinder 7201 however showed much higher standard deviations of 22 per meg for $\delta(\text{O}_2/\text{N}_2)$. This cylinder was closed for a while and also completely empty at the end of the measurements, which probably caused these higher variations.

5.3 Atmospheric $\delta(\text{O}_2/\text{N}_2)$ measurements

The measured CO_2 concentration from section 4.2 and equation 2 are used to obtain the O_2/N_2 concentrations shown in figure 9. The calibration cylinders again do not cover the complete range of measured $\delta(\text{O}_2/\text{N}_2)$ values. However, they are close to the average atmospheric $\delta(\text{O}_2/\text{N}_2)$ and the relation is linear,

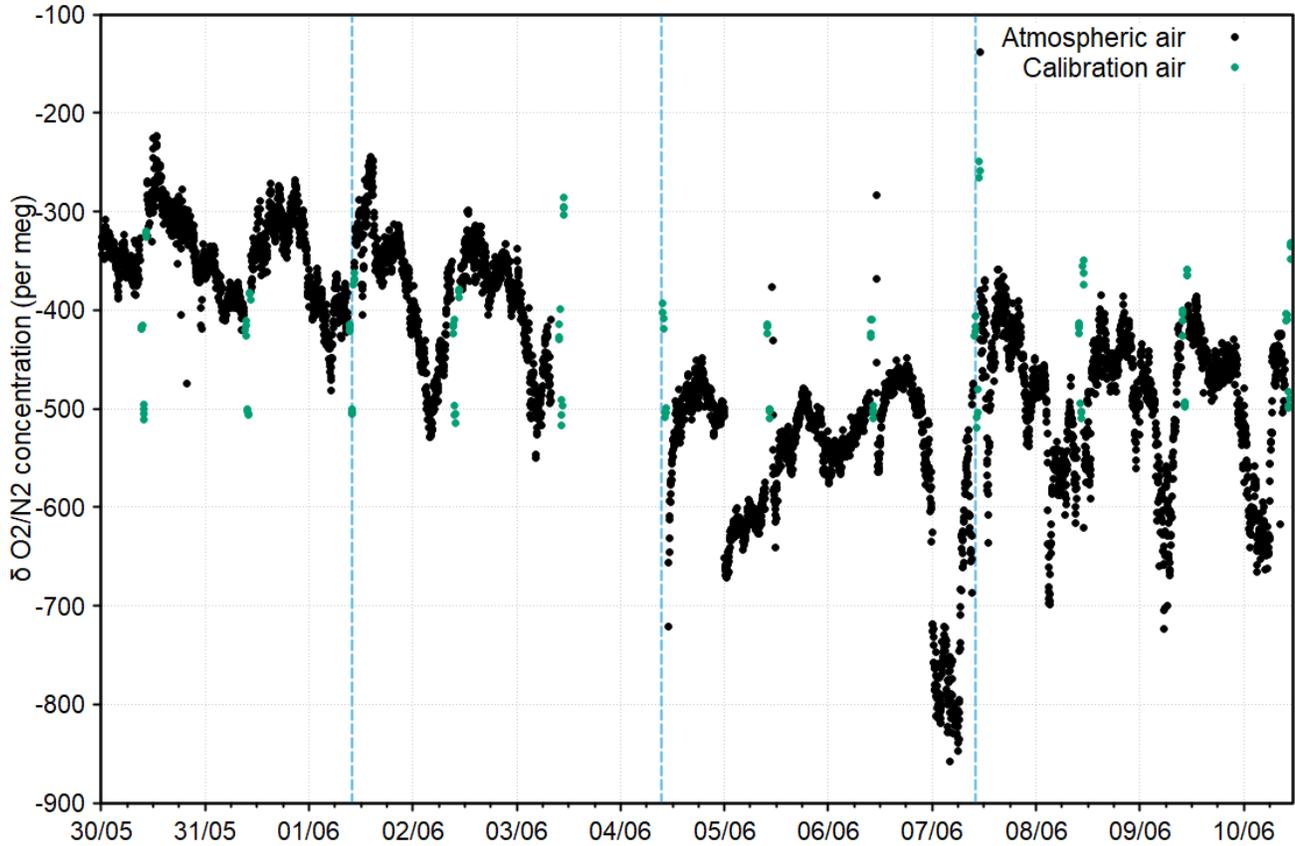


Figure 9: Final $\delta(\text{O}_2/\text{N}_2)$ concentration for atmospheric air (black), calibration and target cylinders (green). The x-axis shows the date in day/month format. The blue dotted lines represent a change of cooling trap and during the gap in the middle the chemical drying trap was saturated

so the necessary extrapolation will not affect the results.

Figure 9 shows the same gap of data related to the saturated chemical drying trap. The calibration measurements in green also fluctuate a lot more compared to cylinder CO_2 measurements. Single outliers shortly after calibration are related to the switch from cylinder to atmospheric measurements.

To determine the precision of atmospheric $\delta(\text{O}_2/\text{N}_2)$ measurement the most stable hours were selected, just like we did for CO_2 earlier. Again we take 1 hour of data ($n=20$) and calculated the standard deviation. Precisions between 4 and 8 per meg $\delta(\text{O}_2/\text{N}_2)$ were found, which is a significant improvement compared to

the old performances of 8 - 17 per meg $\delta(\text{O}_2/\text{N}_2)$. Lowering the switching time to 90 seconds, changing the position of the chemical trap and minimizing the time of calibration measurement have thus had a positive effect on the precision.

Although note that the uncertainty in the calibration method does not only affect the absolute measured values but can also affect the precision. The high error in assigning cylinder values could change the slope of the linear calibration. This could result in an over or underestimation of the variations in $\delta(\text{O}_2/\text{N}_2)$, and thus change the precision. The precisions of cylinder measurements and atmospheric measurements are similar, which indicates that the system itself can still be improved. van Leeuwen (2015) also reported similar precision for cylinder and atmospheric $\delta(\text{O}_2/\text{N}_2)$ measurements.

5.4 Combined CO_2 and $\delta(\text{O}_2/\text{N}_2)$

Comparing the CO_2 and $\delta(\text{O}_2/\text{N}_2)$ plots we see a clear correlation between an increase in CO_2 and a decrease in $\delta(\text{O}_2/\text{N}_2)$. A closer look at daily CO_2 and $\delta(\text{O}_2/\text{N}_2)$ variations in figure 10 illustrates this relation even better. An increase in CO_2 is at the exact same time accompanied by a decrease in $\delta(\text{O}_2/\text{N}_2)$. Figure 10 shows the CO_2 as well as the $\delta(\text{O}_2/\text{N}_2)$ results of 4 days. Apart from the top left one the other three are consecutive days as well. These specific days out of the total results were plotted because of their relatively high variability.

At several moments the $\delta(\text{O}_2/\text{N}_2)$ concentration does not mirror the changes in CO_2 very well. During the evening on 8th of June there is even a moment where both $\delta(\text{O}_2/\text{N}_2)$ and CO_2 are increasing. This could be related to a change in wind direct, and thus a different air mass passing by. Especially during the 7th of June around 09:00 the $\delta(\text{O}_2/\text{N}_2)$ show a drop unaccompanied by a CO_2 peak. The cryotrap replaced shortly later was clogged with ice and this likely caused this extreme deviation.

5.5 O_2 and CO_2 exchange ratio

Individual events with significant changes in both CO_2 and $\delta(\text{O}_2/\text{N}_2)$ can also be isolated to calculate the $\text{O}_2:\text{CO}_2$ exchange ratio of that specific event. Using equation 2 with $d\text{XO}_2$ and ΔCO_2 both equal to 1 we find a conversion factor of 4.77 per meg ppm^{-1} . Together with the found correlation between the changes in CO_2 and $\delta(\text{O}_2/\text{N}_2)$ the $\text{O}_2:\text{CO}_2$ exchange ratio of a specific event can be calculated. Table 2 shows these exchange ratios for the three daytime events encircled in figure 10 and for several nighttime fluctuations.

In total there are only 3 daytime events significant enough to calculate the exchange ratio. For the nighttime measurements, the 5 events which were most distinct were selected. Although there is high variability between the exchange

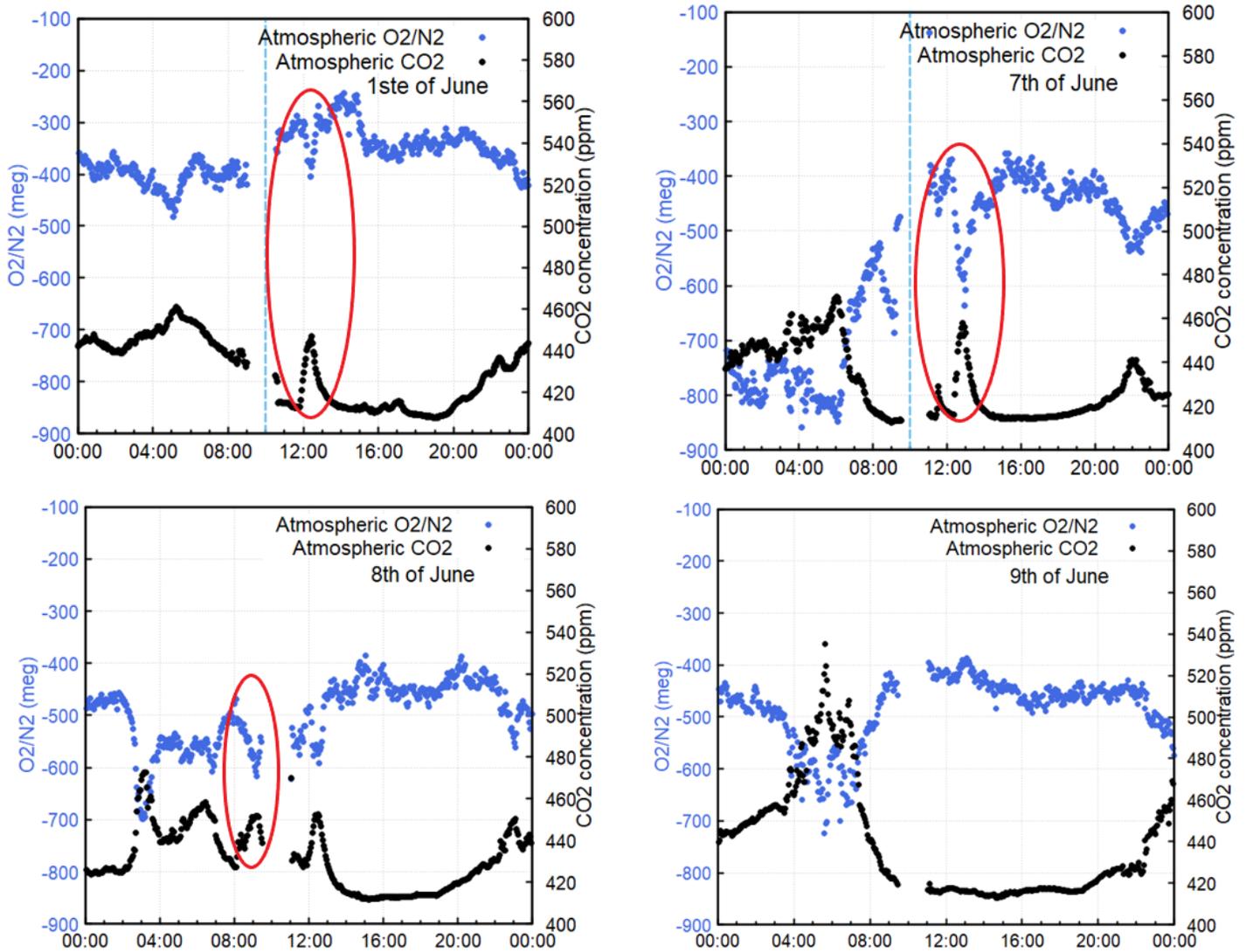


Figure 10: CO_2 and $\delta(\text{O}_2/\text{N}_2)$ concentrations of 4 individual days. The red circles point out daytime peaks. The small gaps around 10:00 are left out calibration measurements. The blue dotted lines represent a change of cryotrap.

ratios, the ratios during the day are systematically higher compared to nighttime ratios. Globally, the average exchange ratio for biological events is estimated to be 1.1, while fossil fuel combustion often leads to a higher ratio: natural gas 1.95, oil 1.4, coal 1.17 (Keeling, 1988) (Battle et al., 2019). Table 2 thus

Table 2: Date and O₂:CO₂ exchange ratios for several events, split up in daytime and nighttime events.

Nighttime event	O ₂ :CO ₂ ratio	Daytime event	O ₂ :CO ₂ ratio
01/06 - 02/06	0.85 ± 0.53	01/06	1.14 ± 0.51
06/06 - 07/06	0.94 ± 0.32	07/06	1.42 ± 0.42
07/06 - 08/06	0.97 ± 0.35	08/06	1.29 ± 0.47
08/06 - 09/06	0.71 ± 0.43		
09/06 - 10/06	0.74 ± 0.45		

supports the assumption that the daytime events are influenced by fossil fuel burning, while the nighttime activity is dominated by soil respiration accumulating the nocturnal boundary layer.

O₂:CO₂ exchange ratios on land below 1 are unrealistic, Battle et al. (2019) found ratios as low as 1.03 in a forest dominated by biological processes. The relatively large difference between the ratios in table 2 and literature values is likely caused by the poor calibration for $\delta(\text{O}_2/\text{N}_2)$. Because we expected generally higher ratios it could even be an indication that the current calibration is underexposing the $\delta(\text{O}_2/\text{N}_2)$ fluctuations. There were two cylinders used for the calibration (6987 & 7213) and for one of which the value was estimated using the APO equation. This poor calibration method is the biggest source of systematic uncertainty, and the values in table 2 can be used for a better estimated value of cylinder 7213. Leading to the conclusion that cylinder 7213 is likely to have a $\delta(\text{O}_2/\text{N}_2)$ less negative than the estimated -458 per meg. The absolute value of cylinder 7213 is estimate to be -389.1 per meg $\delta(\text{O}_2/\text{N}_2)$, because for this specific value the lowest exchange ratio in table 2 is 1.0.

6 Conclusion

Atmospheric oxygen measurement can provide information about climate change, more specifically, it can help us estimate the individual size of the oceanic and biotic carbon sinks. Precise oxygen measurements are challenging because of its high abundance in the atmosphere. The fuel cells, which measure O₂ concentrations, are not precise enough by themselves and we have to use a double differential technique. A series of other factors also affect the O₂ measurement results, which have to be monitored closely such as: flow rates, pressure, temperatures and CO₂ concentrations. CO₂ has a diluting effect on the O₂ concentration which has to be taken into account to achieve high precision. The CO₂ measurements themselves are indispensable for their own merit, as they also provide extra insights, since CO₂ and O₂ are coupled in almost all natural processes. All these factors result in a sophisticated system to measure $\delta(\text{O}_2/\text{N}_2)$ concentrations.

At the CIO labs in Groningen a system to measure atmospheric oxygen continuously was built some years ago and has been improved over time. The latest, most important changes were made to the switching time, which was halved to 90 seconds. This was made possible by the new CO₂ sensor, which produces a raw output every second instead of every 5 seconds like the previous sensor did. Furthermore the calibration cylinders are measured for a shorter period and the drying technique was changed slightly compared to the old system. This report focused on getting the new performance figures after these updates, with extra emphasis on the precision.

The measurements presented in this report got off to a slow start, because there were some problems with a pressure regulator, calibration cylinders and the drying system. Also, the data was analysed using Excel which is not ideal for quickly processing large amounts of data. It is recommended to use a programming language to process the data much quicker, for example Python or Matlab. The difficulties with drying the sample still remain after the measurements for this paper were finished. The traps need replacement often (3 to 4 days in June 2021), and when saturated the traps should not allow water to flow in the system. Eventually data were acquired during a consecutive 12 days period, and processed. This period is too short to draw conclusions about seasonal trends for O₂ and CO₂ concentration. However, there is enough data to determine the performance figures for the updated system.

The CO₂ precisions for cylinder measurements have deteriorated, while sample measurements have stayed the same. Cylinder precisions used to be in the range of 0.009 - 0.021 ppm and are measured to be 0.08 ppm after the updates. Atmospheric measurements precision have stayed very similar, from 0.13 - 0.29 ppm during stable hours to 0.13 - 0.32 ppm. Showing that atmospheric measurements are at the limit of the variability of the CO₂ concentrations in the air. These precisions are adequate to determine the dilution effect on O₂ concentration.

The precision for the oxygen measurements did improve. The two daily measured calibration cylinders both showed precisions of 8 per meg $\delta(\text{O}_2/\text{N}_2)$. The old precisions for cylinder measurements were in the range of 5 - 15 per meg $\delta(\text{O}_2/\text{N}_2)$, this thus stayed in the same range after the updates. The precisions for atmospheric $\delta(\text{O}_2/\text{N}_2)$ were found to be 4 - 8 per meg $\delta(\text{O}_2/\text{N}_2)$, which is a decent improvement compared to the old 8 - 17 per meg $\delta(\text{O}_2/\text{N}_2)$. Cylinder and atmospheric precisions for $\delta(\text{O}_2/\text{N}_2)$ are in the same range, indicating that they are limited by system noise. The oxygen measurements did face a calibration problem, because the $\delta(\text{O}_2/\text{N}_2)$ concentrations of the calibration cylinders were unknown. The APO equation was used to estimate the values, this caused a massive systematic uncertainty in the calibration. The O₂:CO₂ exchange ratios also indicated that the $\delta(\text{O}_2/\text{N}_2)$ measurements were indeed poorly calibrated.

Both the O₂ improvement and CO₂ deterioration were mainly consequences of the decreased switching time. This led to more data points, which helped the noise in the signal of the $\delta(\text{O}_2/\text{N}_2)$ measurements. At the same time the lower switching time did limit the stabilization of the CO₂ signal. Together with high atmospheric variability this decreased the CO₂ precision of the system. In the future the calibration cylinders have to be measured on the DI-IRMS to obtain more accurate values and improve the calibration for oxygen measurements. The drying process also has to be improved, or at least better monitored. This is not only important to obtain useful data but also to protect instruments used in the system from water.

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References

- Battle, M. O., Conley, M., Sofen, E., Perry, R., Hart, R., Davis, Z., . . . William, M. J. (2019). Atmospheric measurements of the terrestrial o_2 : co_2 exchange ratio of a midlatitude forest. *atmospheric. Chemistry and Physics*, *19(13)*, 8687–8701. doi: <https://doi.org/10.5194/acp-19-8687-2019>
- Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., . . . Thornton, P. (2013). Carbon and other biogeochemical cycles. in: *Climate change 2013: The physical science basis. contribution of working group i to the fifth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA*, 8-12.
- Ciais, P., Tans, P. P., White, J., Trolier, M., Francey, R., & co authors. (1995). Partitioning of ocean and land uptake of co_2 as inferred by $\delta^{13}\text{C}$ measurements from the noaa climate monitoring and diagnostics laboratory global air sampling network. *Geo-phys. Res.* *100*, 5051-5070.
- Froment, A. (1972). Soil respiration in a mixed oak forest. *Oikos* *23(2)*, 273-277.
- IPCC. (2014). *Climate change 2014: Synthesis report. contribution of working groups i, ii and iii to the fifth assessment report of the intergovernmental panel on climate change. , IPCC, Geneva, Switzerland, 151 pp.*
- Keeling, R. (1988). Development of an interferometric oxygen analyzer for precise measurement of the atmospheric o_2 mole fraction. *PhD thesis, Harvard University*.
- Keeling, R., & Shertz, S. (1992). Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, *358*, 723-727.
- Kozlova, E., Manning, A., Kisilyakhov, Y., Seifert, T., & Heimann, M. (2008). Seasonal, synoptic, and diurnal-scale variability of biogeochemical trace gases and o_2 from a 300-m tall tower in central siberia. *Global biogeochemical cycles*, *22*. doi: [doi:10.1029/2008GB003209](https://doi.org/10.1029/2008GB003209)
- Liss, P. S., & Merlivat, L. (1986). Air-sea gas exchange rates: Introduction and synthesis. in: *The role of air-sea exchange in geochemical cycling (ed. p. Buat-Menard). D Reidel, Norwell, Massachusetts*, 113-127.
- Machta, L., & Hughes, E. (1970). Atmospheric oxygen in 1967 to 1970. *Science*, *168*, 1582-1584. doi: [doi:10.1126/science.168.3939.1582](https://doi.org/10.1126/science.168.3939.1582)
- Manning, A. C., & Keeling, R. (2006). Global oceanic and land biotic carbon sinks from the scripps atmospheric oxygen flask sampling network. *Tellus B*.
- Marshall, J., & Plumb, R. A. (2008). *Atmosphere, ocean and climate dynamics: an introductory text. Elsevier, Cambridge, Massachusetts*, 33 ; 394-401.
- Nguyen, L. N. T., Meijer, H., van Leeuwen, C., Kers, B., Scheeren, H., Jones, A. E., . . . Luijkx, I. (2021). Two decades of flask observations of atmospheric $\delta\text{o}_2/\text{n}_2$, co_2 , and apo at stations lutjewad (the netherlands) and mace head (ireland) plus 3 years from halley station (antarctica), manuscript submitted to earth system science data.
- Page, B., Turan, G., & Zapantis, A. (2020). Global status of ccs 2020. *Global*

- CCS institute, Melbourne, Australia*, 11-16.
- Severinghaus, J. (1995). Studies of the terrestrial o₂ and carbon cycles in sand dune gases and in biosphere 2. doi: doi:10.2172/477735
- Stephens, B., Keeling, R., Heimann, M., Six, K., Murnane, R., & Caldeira, K. (1998). Testing global ocean carbon cycle models using measurements of atmospheric o₂ and co₂ concentration. *Global biogeochemical cycles*, 12, 213-230. doi: doi:10.1029/97GB03500
- Thompson, R., Manning, A., Lowe, D., & Weatherburn, D. (2007). A ship-based methodology for high precision atmospheric oxygen measurements and its application in the southern ocean region. *Tellus B*, 59, 643-653.
- van der Laan-Luijkx, I., Neubert, R., van der Laan, S., & Meijer, H. (2010). Continuous measurements of atmospheric oxygen and carbon dioxide on a north sea gas platform. *atmospheric measurement techniques*, , 113-125.
- van Leeuwen, C. (2015). Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from carbon capture and storage sites. *University of Groningen*.
- WMO. (2012). Gaw report no. 206, in: Brailsford, g. (ed.). presented at the 16th wmo/iaea meeting on carbon dioxide, other greenhouse gases, and related measurement techniques (ggmt-2011).