Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites
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1.1. Global climate change

The climate of the earth is changing rapidly at the moment. Both the atmosphere and oceans have warmed, the sea level is rising and the amounts of snow and ice are diminishing. In recent years, evidence that human influence is the main cause of the current rapid climate change has grown (IPCC, 2013).

Humans are influencing the earth’s climate mainly by altering the composition of the atmosphere, through the emission of so-called greenhouse gases. Greenhouse gases are present naturally in our atmosphere and have the important characteristic that they can absorb thermal infrared radiation, thereby reducing the emission of radiative energy to outer space. This effect is called the greenhouse effect (although the analogy with a greenhouse is not entirely correct). Because of this greenhouse effect, the average temperature on earth is a benign 14°C instead of only -17°C that would have been the case if there were no greenhouse gases present in the atmosphere (McKinney et al., 2007). Nowadays we speak of the enhanced greenhouse effect, which refers to a shift in the energy balance of the earth caused by more absorption of infrared radiation by the additional greenhouse gases.

The main greenhouse gases emitted by humans are carbon dioxide (CO\(_2\)), methane (CH\(_4\)) and nitrous oxide (N\(_2\)O). The atmospheric concentrations of all three gases have increased since the start of the industrial revolution (defined as the year 1750) to levels that substantially exceed the highest concentrations recorded in ice cores that go back to 800,000 years ago (Ahn and Brook, 2008; Loulergue et al., 2008; Lüthi et al., 2008; Petit et al., 1999; Schilt et al., 2010; Siegenthaler, 2005). Also the recent rate of increase of all three gases is unprecedented in the last 22,000 years (Joos and Spahni, 2008).

CO\(_2\) is considered the most important greenhouse gas, and the emissions of other greenhouse gases are therefore often expressed in terms of CO\(_2\) equivalents. CO\(_2\) is emitted mainly through the burning of fossil fuels, but also by deforestation and other land use changes (IPCC, 2013). Figure 1.1 shows the atmospheric CO\(_2\) concentration over the last 800,000 years. The atmospheric CO\(_2\) concentration has increased by more than 40% from a background concentration of about 274 – 284 ppm around 1750 (Etheridge et al., 1996) to 395.2 ± 0.1 ppm in 2013 (Dlugokencky and Tans, 2015). Ice core records have shown that in the last 800,000 years before 1750 the concentration of CO\(_2\) in the atmosphere varied between 180 – 200 ppm during glacial periods and up to 300 ppm during interglacial periods (Ahn and Brook, 2008; Lüthi et al., 2008; Petit et al., 1999; Siegenthaler, 2005). The atmospheric CO\(_2\) concentration rose by 2.0 ± 0.1 ppm year\(^{-1}\) in the decade from 2002 – 2011, which is higher than all decades since atmospheric measurements of CO\(_2\) started in 1958 (Dlugokencky and Tans, 2015; IPCC, 2013).

The behavior of CO\(_2\) in the atmosphere is not straightforward. Once released in the atmosphere, it can be absorbed by the oceans or taken up by the biosphere through photosynthesis. Both the oceans and the biosphere are also able to release CO\(_2\). This
continuing exchange of carbon between the different reservoirs of the earth and its entire dynamic system is known as the global carbon cycle. The sizes of these reservoirs and fluxes between them are subject to many scientific studies. For the period 1750 – 2013 the total emission of carbon is estimated to be $580 \pm 70$ Gt, with $395 \pm 20$ GtC emitted by fossil fuel burning and $185 \pm 65$ GtC coming from land use changes. Less than half of the emitted carbon accumulated in the atmosphere ($250 \pm 5$ GtC), the rest was taken up by the ocean ($170 \pm 20$ GtC) and biosphere ($160 \pm 70$ GtC) (Le Quéré et al., 2015).

![Figure 1.1](image.png)

Figure 1.1 The atmospheric concentrations CO$_2$ over the last 800,000 years. The black lines show data from the Vostok and Dome Concordia ice cores in Antarctica (Lüthi et al., 2008; Monnin et al., 2001; Petit et al., 1999; Pépin et al., 2001; Raynaud et al., 2005; Siegenthaler, 2005). The orange lines represent data from the Law Dome ice core (Antarctica), revealing the atmospheric CO$_2$ concentration between 1006 and 1978 (Etheridge et al., 1996). The red lines show the atmospheric CO$_2$ measurements at Mauna Loa, starting in 1958 (Tans and Keeling, 2015).

While the emissions from land use changes remain roughly constant, the emissions from fossil fuel combustion have increased every decade since the 1960s. Currently fossil fuel combustion is by far the biggest contributor to the total CO$_2$ emissions, contributing 91% of the total emissions in the decade 2004 – 2013 (Le Quéré et al., 2015).

1.1.1. Combatting global climate change

In the year 1992 the risks of climate change were acknowledged in the United Nations Framework Convention on Climate Change in Rio de Janeiro. The objective of the treaty was to achieve stabilization of the concentration of greenhouse gases in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system.
In 1997, the Kyoto protocol was added to this treaty. The major aspect of this protocol was that it set binding targets for the industrialized countries for reducing their greenhouse gas emissions with an average of 5.2% from 1990 levels over the period 2008 – 2012 (United Nations, 1998). On 8 December 2012, the Doha amendment was added to the Kyoto protocol, determining a second commitment period from 2013 to 2020 for which parties committed to reduce their greenhouse gas emissions by at least 18 percent below the levels of 1990 (United Nations, 2012).

Looking at the European Union (including the Netherlands), targets for the first commitment period of 2008 – 2012 were overachieved. Although the goals were partly achieved by climate and energy policies, the economic crisis contributed to almost half of the observed reduction (European Commission, 2014). Although the emissions from the countries listed in Annex B of the Kyoto protocol have been stabilized, the worldwide CO$_2$ emissions are still increasing, due to rapid increases in the non-Annex B countries. Four regions dominate the global CO$_2$ emissions, together accounting for 58% of the emissions in 2013: China (28%), the USA (14%), the EU (10%) and India (7%). Out of these four regions, only the EU showed a negative CO$_2$ emission growth rate in 2012 – 2013 (Le Quéré et al., 2015).

There are several ways to reduce the anthropogenic emissions of CO$_2$. The most straightforward solution is to use less energy, which can be achieved by “simply” using less energy or improving the energy efficiency. A second solution is to change the source of energy, by using less carbon-intensive fossil fuels (e.g. natural gas instead of coal) or replacing fossil fuels by renewables such as solar and wind energy. A third solution is to capture CO$_2$ from (power) plants and store it somewhere underground instead of emitting it to the atmosphere; a process called Carbon Capture and Storage (CCS).

1.2. Carbon Capture and Storage (CCS)

Capture and geological storage of CO$_2$ is considered to be an important option in combating global climate change, especially in the coming decades when fossil fuels will still play an important role in our society. Instead of emitting CO$_2$ to the atmosphere, power plants and other large emitters can capture the CO$_2$ and transport it to a suitable location where it can be stored in a geological formation.

CO$_2$ accumulations exist naturally in the subsurface of the earth. They followed from biological activity and chemical reactions between rocks and fluids. Engineered storage of CO$_2$ was first carried out in the United States, Texas, in the early 1970s as part of Enhanced Oil Recovery (EOR). In Enhanced Oil Recovery, more oil is extracted from an oil field due to the injection of CO$_2$. Underground storage of CO$_2$ as a greenhouse gas mitigation method was first proposed in the 1970s but it took until 1996 before the world’s first large-scale storage project was initiated. This project of Statoil is at the Sleipner Gas Field in the North Sea (Metz et al., 2005).

CCS consists of three steps: the CO$_2$ needs to be captured, then transported and finally stored. There are several techniques for capturing the CO$_2$. In some industrial processes, CO$_2$ is an end product, which is ventilated to the atmosphere. In this case the process of
capturing is relatively easy and does not involve all the steps that are necessary for combustion processes (such as purifying the outgoing gases) in power plants. For these combustion processes, three main techniques exist to capture the CO\(_2\): post-combustion, pre-combustion and oxy-fuel (Metz et al., 2005).

There are two main ways to transport CO\(_2\) from an emitter to a geological storage location: through pipelines (both onshore and offshore) and by ships. Pipelines are the most common way to transport CO\(_2\). There are already several onshore pipelines for CO\(_2\) transport in place; most of them are in the United States; built for enhanced oil recovery in Texas and nearby states. Examples are the Canyon Reef pipeline that was built already in 1970 and the Cortex pipeline, which is the longest CO\(_2\) pipeline present with 808 km length (Metz et al., 2005). In the Netherlands, the company OCAP owns a network of pipelines for the transportation of CO\(_2\) to greenhouses (OCAP, 2012), where it is used to create an atmosphere with an artificially (up to threefold) increased CO\(_2\) concentration, in which plants grow faster.

Depleted oil and gas fields, saline water-saturated geological reservoirs and unminable coal beds can all be suitable geological formations for storage of CO\(_2\). Once stored in a reservoir, the CO\(_2\) undergoes several trapping mechanisms as a function of time. After physical trapping under a cap rock or in pores, geochemical reactions can further store the CO\(_2\), which includes dissolving in the formation water (solubility trapping) and conversion into stable carbonate minerals (mineral trapping) (Metz et al., 2005).

### 1.2.1. Status of CCS

CCS is starting to be widely adopted in the world. In the end of 2014, the global CCS institute has identified 55 large-scale CCS projects, with 13 of them already in operation, 9 in the construction phase and the remaining 33 in a stage of development. Most projects are in the United States (19 out of 55), followed by China (12 out of 55). Especially in the United States, most projects involve Enhanced Oil Recovery (17 out of 19). In Europe, only two projects are currently in operation and they are both in Norway (the Sleipner and Snøhvit projects). Furthermore there are 6 other projects in Europe, all in a development stage: five projects in the United Kingdom and one project in the Netherlands (ROAD – Rotterdam Opslag en Afvang Demonstratieproject) (Global CCS Institute, 2014).

In all large-scale European CCS projects CO\(_2\) is (planned to be) stored offshore, under the North Sea (Global CCS Institute, 2014). Originally there were multiple plans to store CO\(_2\) in empty gas fields under the Dutch surface, but in February 2011, after many protests in the Dutch society, the Dutch government decided to only store CO\(_2\) in empty gas fields under the sea (Verhagen, 2011).

### 1.3. Leaks and leak detection at CCS sites

One of the main concerns in CCS is the possibility of leakage of CO\(_2\) from the storage reservoir to the atmosphere, both from a public health and a climate change combat perspective. The public concerns for example lead to the cancelling of the onshore storage projects in the Netherlands. An important concern of most people is asphyxiation as a consequence of escaped gas in their neighborhood.
Leakage of CO\textsubscript{2} from a CCS site is considered to be unlikely. For large-scale CCS projects the available evidence suggests that it is likely that the fraction of CO\textsubscript{2} retained in the reservoir is more than 99% in the first 1000 years (Metz et al., 2005). In general, selected reservoirs in stable sedimentary basins will provide successful and secure storage of CO\textsubscript{2}. Abandoned gas fields for example contained natural gas for millions of years, which makes it likely that CO\textsubscript{2} can be stored safely for a very long time too – although CO\textsubscript{2}, unlike CH\textsubscript{4}, can become chemically active under storage conditions (Bolourinejad and Herber, 2015). The risks for leakage at a storage site are expected to be at the human-made parts: the injection wells and old abandoned wells used for gas production (Croezen et al., 2007).

Even if CO\textsubscript{2} would escape, the chance that people would suffocate due to extreme high levels of CO\textsubscript{2} is very unlikely. The Maximum Allowable Concentration (MAC), also known as the Threshold Limit Value (TLV), is 0.5 volume percent in both the European Union and the United States (8-hour time weighted average). The concentration of CO\textsubscript{2} can even be higher (1.5 – 3.0 %) without any consequences as long as the time exposure is short (15 minutes) (Croezen et al., 2007). These levels are almost two orders of magnitude higher than the normal background levels of CO\textsubscript{2}, which vary roughly between 390 and 500 ppm.

Even though leaks of CO\textsubscript{2} are unlikely and the risks for humans are very limited, leak detection of CCS sites is very important, both for the public as well as to evaluate the efficiency of the storage process. For CCS to be useful, leakage in the total chain must be kept to a very low level. Leakages in transport have to be incorporated into the total CO\textsubscript{2} capture efficiency at the source. As capture is costly, both in terms of energy and money, there is a clear incentive to keep leakages in transport and during injection as small as possible. Once stored, even small leakages on a yearly basis add up over the decades / centuries to unacceptable levels in climate change mitigation terms (also given the fact that capture leads to 14 – 30% more energy consumption, and thus more CO\textsubscript{2} production, in the first place (Hammond et al., 2011). Depending on the chosen time window and total amount of stored CO\textsubscript{2}, leakage rates of the injected CO\textsubscript{2} should be kept below 0.1% and preferably even below 0.01% per year to allow stabilization of the atmospheric CO\textsubscript{2} concentration (Enting et al., 2008; Haefeli et al., 2004).

Detecting leaks of CO\textsubscript{2} in the atmosphere and quantifying them is a difficult task due to the rapid mixing of the emitted CO\textsubscript{2} with the surrounding air masses in combination with the high natural variability of the CO\textsubscript{2} concentration in the atmosphere. Fossil fuel combustion, photosynthesis and biosphere respiration all locally influence the CO\textsubscript{2} concentration, especially during the night when the atmosphere is generally more stable and gases accumulate close to the ground. During the day, when the sun heats the earth’s surface, the atmosphere becomes well mixed and the CO\textsubscript{2} concentration close to the ground decreases (Stull, 1988). Because of this, during a day variations from below 400 ppm (daytime) to over 450 ppm (nighttime) are quite common and within one hour the natural concentration can change with several ppm.

Although the variability of the CO\textsubscript{2} concentration is high in time, it is low in terms of space, at least on small scales. In case several CO\textsubscript{2} sensors are located in close proximity of each other, they will measure the same concentration, unless there is a source of CO\textsubscript{2} in the area under investigation. Depending on the wind direction, wind speed and the locations of the
CO$_2$ source and sensors, the plume of CO$_2$ will reach only part of the sensors, while the others keep on measuring the background concentration. This principle can be used to monitor potential leaking locations of a storage site, such as wells, but also to monitor pipelines, as will be shown in chapter 2 of this thesis.

Another option is to co-inject a chemical tracer with the CO$_2$ that has a low background concentration and lower atmospheric variability, such as SF$_6$, CH$_4$ or a perfluorocarbon (Etheridge et al., 2011; Leuning et al., 2008; Luhar et al., 2014; Wells et al., 2007). This method has, however, several drawbacks, as these gases are strong greenhouse gases themselves (IPCC, 2013) and adding a tracer to the injected CO$_2$ is cumbersome and expensive. Besides, there is the principal problem that the migration of the tracer through the underground is not exactly the same as the migration of CO$_2$. For example, in dry reservoirs the movement of perfluorocarbon tracers was found to be slower than the movement of SF$_6$ and CO$_2$ whereas in wet reservoirs the transport of the CO$_2$ was retarded compared with the tracers as CO$_2$ partly dissolved in the water. The structure of the reservoir also determines (a difference in) the movement of the CO$_2$ and tracers (Zhong et al., 2014).

Using the isotopes $^{14}$CO$_2$ or $^{13}$CO$_2$ present in the injected CO$_2$ as natural tracers prevents these drawbacks. Unfortunately these methods have other problems. Although $^{14}$CO$_2$ could provide some insight in the leakage rate, its measurement is very expensive and can only be performed by taking flask samples (Keeling et al., 2011). Furthermore, $^{14}$CO$_2$ detection would not be able to discriminate (fossil) CO$_2$ leaks from the CCS site from actual combustion of fossil fuels, as both would cause increasing CO$_2$ concentrations accompanied by decreasing $^{14}$CO$_2$ levels (see for example Zondervan and Meijer (1996)). Using $^{13}$CO$_2$ is more promising, but the technique is very dependent on the specific $\delta^{13}$C of the injected (leaking) CO$_2$ and surroundings of the storage location. A significant difference between the $\delta^{13}$C of the biosphere and the source in combination with a sufficient CO$_2$ perturbation caused by the leak is required (McAlexander et al., 2011). For CO$_2$ captured from a coal-fired power plant in a surrounding with predominantly C3 vegetation – a very likely situation for CCS – the technique does not add anything to CO$_2$ concentration measurements alone as both have a $\delta^{13}$C of about -26‰ (Keeling et al., 2011; Leuning et al., 2008).

Measuring atmospheric oxygen (O$_2$) in addition to CO$_2$ to find leaks of a CCS location does not have any of the drawbacks outlined above and is therefore a strong tool (Keeling et al., 2011). CO$_2$ and O$_2$ are coupled in most processes on earth. In photosynthesis, plants take up CO$_2$ and release O$_2$ at the same time. In respiration and fossil fuel burning, O$_2$ is consumed while CO$_2$ is released. The O$_2$ – CO$_2$ exchange ratio for biosphere activities is about 1.1 (Severinghaus, 1995). For fossil fuel burning the exchange ratio is higher than for biosphere processes, and depends on the type of fossil fuel, varying from 1.95 for natural gas to 1.44 for crude oil and 1.17 for coal (Keeling, 1988). In case of a leak from a CCS site there is no relationship between CO$_2$ and O$_2$. Looking at the atmospheric O$_2$ – CO$_2$ ratio can therefore identify a leak from a CCS site. Plotting normal atmospheric O$_2$ and CO$_2$ measurements against each other reveals a linear relationship with a slope of about -1.1 on a mole-to-mole basis. The slope varies slightly throughout time, and gets more negative in case the share of fossil fuel combustion in the measured air mixture is higher. In case there
is a leak of CO₂ the slope is essentially zero in this plot: the CO₂ concentration is rising without any drop of O₂. Several CO₂ release experiments (which imitate leaks of CO₂ from a storage site) were performed to demonstrate the principle of using atmospheric O₂ measurements for CO₂ leak detection. This is all presented in chapter 4 of this thesis. The most difficult part of this technique is the measurement of atmospheric O₂, which is a delicate task.

1.4. Atmospheric O₂ measurements

While atmospheric CO₂ measurements have become increasingly straightforward in the past decades, atmospheric O₂ measurements are still considered a challenge. The variations in the atmospheric concentrations of CO₂ and O₂ are in the same range, but for O₂ the background concentration is orders of magnitude higher (21% or 210,000 ppm compared to 400 ppm for CO₂), making the relative variations smaller by the same orders of magnitude. Only about a dozen programs in the world are currently involved in atmospheric O₂ measurements (Keeling and Manning, 2014) – the Centre for Isotope Research (CIO) of the University of Groningen, the Netherlands, being one of them.

Figure 1.2 shows the time series of atmospheric O₂ and CO₂ at two stations from the Scripps atmospheric O₂ measurements network, as given in (Keeling and Manning, 2014). It clearly illustrates the different aspects of the CO₂ and O₂ concentration in the atmosphere. Both Alert station (Northern hemisphere) and Cape Grim (Tasmania, Southern hemisphere) show an upward trend in the CO₂ concentration and at the same time a downward trend in the O₂ concentration, both caused by the burning of fossil fuels. The CO₂ concentration is, however, not rising as fast as the O₂ concentration drops (axis in the figure have been scaled such that the two species can be compared on a mole to mole basis). The rise of the CO₂ concentration in the atmosphere is limited by the uptake of carbon by the oceans,
where it is buffered through chemical reactions, while the decline in the O$_2$ concentration is not buffered (Keeling and Shertz, 1992). With respect to the O$_2$ – CO$_2$ balance, CCS acts as a similar carbon sink, limiting the CO$_2$ increase but not the O$_2$ decrease (Keeling et al., 2011).

The seasonal variations visible in Figure 1.2 originate from photosynthesis and respiration in both the land biosphere and oceans. Plants take up CO$_2$ and release O$_2$ in summer, and vice versa in winter. Because the ocean is buffering the changes in the CO$_2$ concentration, the seasonal cycles visible for CO$_2$ are mainly reflecting the activities of the land biosphere, while the seasonal cycles visible for O$_2$ are reflecting activities of both the land biosphere and oceans. At Alert station, in the Northern hemisphere, the seasonal amplitude for O$_2$ is therefore nearly twice as large as for CO$_2$. Because the Southern hemisphere mainly consists of oceans, there is hardly a seasonal cycle visible in the CO$_2$ time series of Cape Grim station. The O$_2$ seasonal cycle at this station is almost entirely originating from oceanic processes (Keeling and Manning, 2014).

Due to the large differences between CO$_2$ and O$_2$ in land and ocean exchanges, combined measurements of the two species can be used to discriminate the uptake of carbon by the land biosphere and the oceans (e.g. Goto et al. (2013); Keeling and Manning (2014); van der Laan et al. (2014) and van der Laan-Luijkx et al. (2010a)).

The CIO currently performs atmospheric O$_2$ measurements from flask samples at two locations: 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. Previously, 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) and aircraft samples from Fyodorovskoye, Russia (van der Laan et al., 2014). 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. The measurements performed at Lutjewad (flasks and continuous) and Mace Head (flasks) are presented in chapter 5 of this thesis.

1.4.1. Calculating and expressing atmospheric O$_2$ measurements

O$_2$ measurements are usually expressed as the O$_2$/N$_2$ mole fraction ratio relative to a reference gas, according to (Keeling and Shertz, 1992).

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

Equation 1.1

Because the changes in $\delta$(O$_2$/N$_2$) are very small, they are expressed in per meg (0.0001% or 0.001‰). The O$_2$/N$_2$ ratio is not sensitive to changes in atmospheric gases other than O$_2$ and N$_2$, and expressing the atmospheric O$_2$ measurements in this way thus prevents the dependence on the concentration of other gases, as is the case with the O$_2$ mole fraction (Keeling et al., 1998). The atmospheric N$_2$ concentration is very stable, so changes in the ratio mainly represent changes in the O$_2$ content of the atmosphere. In detailed budgets, however, changes in N$_2$ caused by ocean warming and cooling are accounted for (Keeling
and Manning, 2014). As some techniques directly measure the O_2/N_2 ratio while others measure the O_2 mole fraction, expressing the O_2 variations in one conventional manner is necessary to compare the results by different techniques.

In case the O_2/N_2 ratio is not measured directly, a correction is required for the CO_2 concentration since this has a dilution effect on the O_2 measurements. (Furthermore, measurements have to be performed on dried air, see below). This is done according to (Kozlova et al., 2008):

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

Equation 1.2

In this formula \(S_{O_2}\) is the standard mole fraction of O_2 in air, which is defined to be 0.20946 (Machta and Hughes, 1970). \(\Delta CO_2\) is equal to the CO_2 concentration of the sample minus an arbitrary defined consensus standard atmospheric CO_2 concentration of 363.29 ppm.

The relationship between the O_2 and CO_2 mole fractions and O_2/N_2 ratio depends on the circumstances. Exchanging an O_2 molecule by a CO_2 molecule or vice versa leads to a conversion factor of 4.77 per meg ppm\(^{-1}\) (Keeling et al., 1998). Table 1.1 shows six examples that illustrate the confusion and difficulties when expressing changes of the O_2 content within an air parcel that originally contained 1 million molecules of which 209460 are O_2 and 780800 are N_2 (see also Stephens (1999) and van der Laan-Luijkx (2010)).

The scenarios illustrate that using the O_2/N_2 ratio instead of the O_2 mole fraction prevents confusion associated with changes in the concentrations of other gases in the atmosphere. In case the O_2/N_2 ratio is measured directly there is no confusion at all when concentrations of other gases are changing. This is different for instruments where the O_2 mole fraction is measured instead of the O_2/N_2 ratio. Because the CO_2 concentration is highly variable and also related to changes in the O_2 content of the air, the O_2 measurements should be corrected for changes in it. Therefore concurrent measurements of CO_2 are always required together with O_2 measurements.

Equation 1.2 only corrects for changes in the CO_2 content and not for changes in other atmospheric gases such as Argon (see scenarios 3 and 5 in Table 1.1). This is, however, not problematic in practice, as the variation of the concentration of these gases is usually very small. An exception is the water vapor content of the atmosphere, which is highly variable. Water vapor is causing a dilution effect for both CO_2 and O_2 measurements, but since the CO_2 concentration in the atmosphere is much smaller than the O_2 concentration, it is much more important for the O_2 measurements than it is for the CO_2 measurements, as is illustrated in Table 1.2.
Table 1.1 Six scenarios that illustrate the confusion and difficulties associated with expressing atmospheric O₂

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<tr>
<th>Scenario 1</th>
<th>Scenario 2</th>
<th>Scenario 3</th>
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<tr>
<td>O₂</td>
<td>CO₂</td>
<td>Ar</td>
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<tr>
<td>The O₂ mole fraction changes: $\frac{209461}{1000000} - \frac{209460}{1000000} = 0.79 \ \mu \text{mol/mol}$</td>
<td>The O₂ mole fraction changes: $\frac{209461}{1000000} - \frac{209460}{1000000} = -0.21 \ \mu \text{mol/mol}$</td>
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<tr>
<td>The O₂/N₂ ratio changes by: $\frac{209461/780800}{209460/780800} - 1 = 4.77$ per meg</td>
<td>The O₂/N₂ ratio changes by: $\frac{209461/780800}{209460/780800} - 1 = 0$ per meg</td>
<td>The O₂/N₂ ratio changes by: $\frac{209461/780800}{209460/780800} - 1 = 0$ per meg</td>
</tr>
<tr>
<td>Using equation 1.2: $0.79 + 0$</td>
<td>Using equation 1.2: $-0.21 + 1 \times 0.20946$</td>
<td>Using equation 1.2: $-0.21 + 0$</td>
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<tr>
<td>$(1 - 0.20946) \times 0.20946 = 4.77$ per meg</td>
<td>$(1 - 0.20946) \times 0.20946 = 0$ per meg</td>
<td>$(1 - 0.20946) \times 0.20946 = -1.26$ per meg</td>
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<td>per meg / ppm: $4.77 / 0.79 = 6.04$</td>
<td>per meg / ppm: $0$</td>
<td>per meg / ppm: $0$ or $6.04$</td>
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<tr>
<th>Scenario 4</th>
<th>Scenario 5</th>
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<td>The O₂/N₂ ratio changes by: $\frac{209461/780800}{209460/780800} - 1 = 6.05$ per meg</td>
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<tr>
<td>Using equation 1.2: $1 + 1 \times 0.20946$</td>
<td>Using equation 1.2: $1 + 0$</td>
<td>Using equation 1.2: $1 + 0$</td>
</tr>
<tr>
<td>$(1 - 0.20946) \times 0.20946 = 4.77$ per meg</td>
<td>$(1 - 0.20946) \times 0.20946 = 6.04$ per meg</td>
<td>$(1 - 0.20946) \times 0.20946 = 6.04$ per meg</td>
</tr>
<tr>
<td>per meg / ppm: $4.77 / 1 = 4.77$</td>
<td>per meg / ppm: $4.77$ or $6.04$</td>
<td>per meg / ppm: $6.04$ or $6.04$</td>
</tr>
</tbody>
</table>
**Table 1.2: The principle of the dilution effect on both O₂ and CO₂ measurements.**

<table>
<thead>
<tr>
<th></th>
<th>Start situation</th>
<th>New situation</th>
<th>Change in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total number of molecules</strong></td>
<td>1,000,000</td>
<td>1,000,001</td>
<td></td>
</tr>
<tr>
<td><strong>Number of O₂ molecules</strong></td>
<td>210,000</td>
<td>210,000</td>
<td>0.21</td>
</tr>
<tr>
<td><strong>Percentage O₂ molecules</strong></td>
<td>21</td>
<td>20.999979</td>
<td></td>
</tr>
<tr>
<td><strong>Number of CO₂ molecules</strong></td>
<td>400</td>
<td>400</td>
<td>0.0004</td>
</tr>
<tr>
<td><strong>Percentage CO₂ molecules</strong></td>
<td>0.04</td>
<td>0.0003999996</td>
<td></td>
</tr>
</tbody>
</table>

In the example in the table, one molecule (in this case water vapor) is added to an air parcel that originally contained one million particles. The percentage of O₂ or CO₂ particles is changed with this addition of a molecule. For O₂, the change is 0.21 ppm, which is significant, while for carbon dioxide the change is only 0.0004 ppm, which is (far) outside the detection limit. Drying the air before measuring it is necessary to prevent the influence of water vapor on the O₂ measurements.

### 1.5. Aims and structure of this thesis

This thesis presents the use of atmospheric O₂ measurements in CO₂ leak detection from Carbon Capture and Storage (CCS) sites.

Chapter 2 first demonstrates the use of multiple, relatively simple and cheap, CO₂ sensors for CO₂ leak detection of CCS sites. The strategy was applied to the monitoring of pipelines that transport CO₂, but could also serve to monitor a potential leakage point such as a well in a geological storage formation.

Chapter 3 gives an overview of the different instruments used by the Centre for Isotope Research (CIO) to measure atmospheric O₂. Flask samples are measured on a Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) to determine the O₂ concentration. An extensive overview of the calibration procedure of atmospheric O₂ measurements on the DI-IRMS is presented in the appendix of this thesis. For continuous measurements the Oxzilla II instrument from Sable Systems is used, which is combined with an instrument to concurrently measure the CO₂ concentration and an extensive gas-handling scheme. In this PhD project, a new, transportable, O₂ – CO₂ instrument was designed and built to aid in detecting leaks of CO₂ from CCS sites. The new instrument was based on the existing continuous O₂ – CO₂ instruments of the CIO, but has several important changes to make it transportable. This is all illustrated in the chapter.

In chapter 4 the use of the new, transportable, O₂ – CO₂ instrument in detecting CO₂ leaks from CCS sites is demonstrated by several CO₂ release experiments.

Chapter 5 presents the long-term data records of atmospheric O₂ measurements performed by the CIO from the stations Lutjewad (the Netherlands) and Mace Head (Ireland). It shows the flask sampling records from the two stations (both lasting for more than 15 years now) and the new continuous measurements from Lutjewad station that started in 2011.

The thesis ends with a concluding chapter.
Chapter 1

1.6. References


