Université of Groningen

Bachelor Thesis

The quality of $\delta^{13}CO_2$ measurements with the NDIR: ABB EL3020

Author:
Wietse Visser *(s2951029)*

first supervisor:
prof. dr. H.A.J. Meijer
second examiner:
prof. dr. U. Dusek

January 12, 2021

rijksuniversiteit
groningen

Abstract

In this article the quality of the NDIR: ABB EL3020 is tested. Between 20 October and 1 November 2020 the CO_2 and $^{13}CO_2$ levels were measured in Groningen, The Netherlands. When measured accurately $\delta^{13}CO_2$ can be useful for source attribution of CO_2 emissions. After calibration, the CO_2, $^{13}CO_2$ and, $\delta^{13}CO_2$ levels were calculated. The reliability and accuracy of the CO_2 and $^{13}CO_2$ levels were reasonable. The accuracy of the $\delta^{13}CO_2$ was also reasonable, with a standard deviation of $\pm0.26‰$, but the $\delta^{13}CO_2$ level was not reliable. The spread of the data was $\pm2‰$, while the differences between $\delta^{13}CO_2$ values should typically be within one per mille and should be able to follow with a precision of less than $0.1‰$ on an hourly basis. Even when the data was averaged out the spread stayed too high to be useful.

Contents

1 Introduction

1.1 Climate change

There is a strong scientific agreement that the massive emissions of greenhouse gasses like CO_2 by human activity leads to significant changes of climate [7] [22]. The main effect of these emissions is global warming. The worlds average temperature is now 1.15^oC higher than in the pre-industrial era [15], with a high likelihood largely because of human activities. In the Netherlands this is even 2.1^oC [4]. The global temperature rise can be 3.7^oC in 2100 if the emissions are not cut down [28]. This is the so-called RCP8.5 scenario: when the CO_2 emissions keep rising, and little is done to stop global warming. Emissions of greenhouse gasses also cause other changes in climate. The weather is becoming more extreme and unpredictable, for example there are more intense and quantitatively more droughts [28], storms [2] and heavy rain fall [28]. Sea level rise is also an issue, between 1901 and 2010 the global sea level rose by 0.19 meter [22]. It is expected that if the world does not lower their emissions of greenhouse gasses drastically the global sea level can rise by 0.74 meter in 2100 [5] in comparison with 1901. This is especially worrisome because 10% of the world's population lives not higher than ten meters above sea level [21].

That climate change causes problems for society is more and more becoming common knowledge with a median of 68% of people in the world see climate change as a major threat and another 20% as a minor threat to their country [25]. Also, governments acknowledge the problem with climate change. 197 countries in the world signed the Paris climate agreement, which means they are committed to "holding the increase in the global average temperature to well below 2^oC above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5^oC above pre-industrial levels" [24]. The seriousness of the situation is clear, but the world's CO_2 emission is becoming higher every year [10]. So, a global systematic change is needed to combat climate change.

1.2 CO_2 emission

The most important anthropogenically enhanced greenhouse gas is CO_2 which accounts for about 64% of the radiative forcing since the industrial era [22]. The rest are mostly from methane, nitrous oxide, and halocarbons. Around 87% of the deliberate (thus without land use change and deforestation) anthropogenic CO_2 emission in the world comes from burning coal, oil, and natural gas [11]. Other important deliberate anthropogenic sources of CO_2 are cement and steel production, the production of some chemicals, and the burning of biomass. The total amount of these CO_2 emission per year is around 36 Pg [10]. The current amount of CO_2 in the air is around 412 ppm [29], with the conversion factor of 7.82 [23] this is around 3,222 Pg of CO_2 in the atmosphere. The annual increase is around 2.5 ppm [29], which is equivalent to 19.55 Pg of CO_2, - less than humans emit. The deficit is because a part of the surplus CO_2 is dissolved in the oceans or is taken up by the terrestrial biosphere.
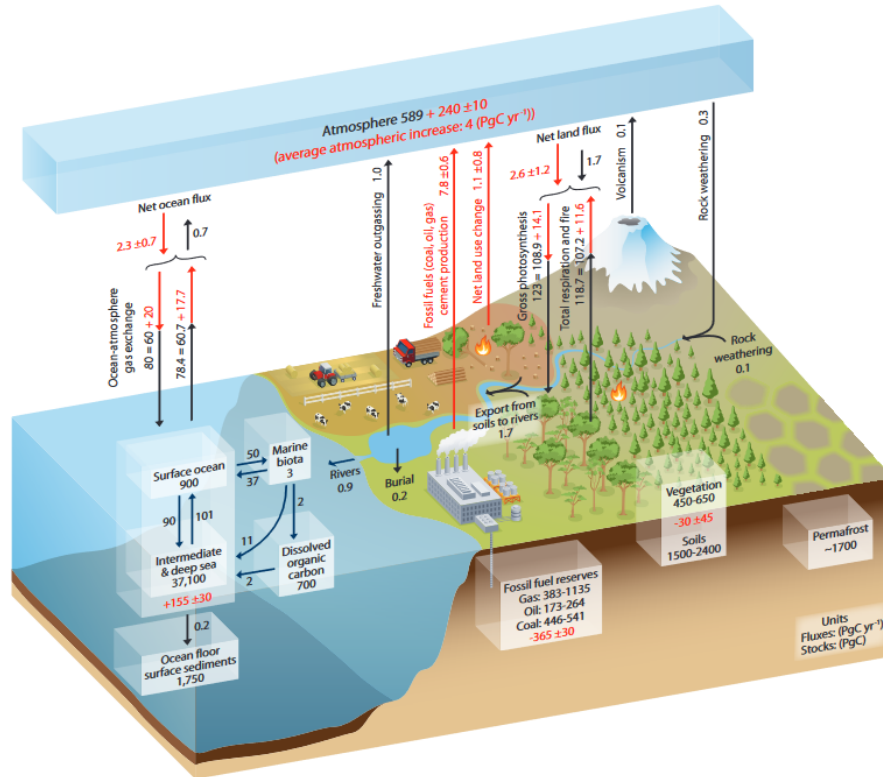
Figure 1: A schematic of the global carbon cycle. Black numbers and arrows indicate reservoir sizes and fluxes before the Industrial Era (1750). The red arrows and numbers represent anthropogenic changes on fluxes and reservoir sizes (averaged from 2000-2009). The blue numbers and arrows show the sizes of and interactions between different ocean carbon stocks. The fluxes are in Pg C (instead of Pg CO_2) [6].

The natural cycle of CO_2 is huge: the natural sources of CO_2 are: release from oceans, soil respiration, plant respiration, animal respiration and volcanic eruptions[14](see figure 1 for a schematic of the global carbon cycle). Oceans are the largest emitter of CO_2, every year they emit around 330 Pg of CO_2, but they take up more than they emit every year [26], this acidifies the oceans (that is, they become less basic), another consequence of CO_2 emissions. Plants and animals emit around 220 Pg of CO_2 every year [26], but plants also take up a large amount of CO_2. Soil respiration does also emit around 220 Pg of CO_2 every year. Soil respiration are all the processes that are below ground, such as plant roots, fungi, bacteria, and animals that live below ground. They use energy and create CO_2 within these processes [26]. Volcanoes emit a small part of the natural CO_2 emission with 0.15 to 0.26 Pg of CO_2 emission every year [12]. In total the natural sources emit around 770 Pg of CO_2 every year, which is around 21 times more than humans emit, but the natural sources are balanced. The CO_2 that humans emit disturbs this balance and creates a strong rise in CO_2 levels that never has been seen in at least the past 800,000 years (see figure [2]) [3].
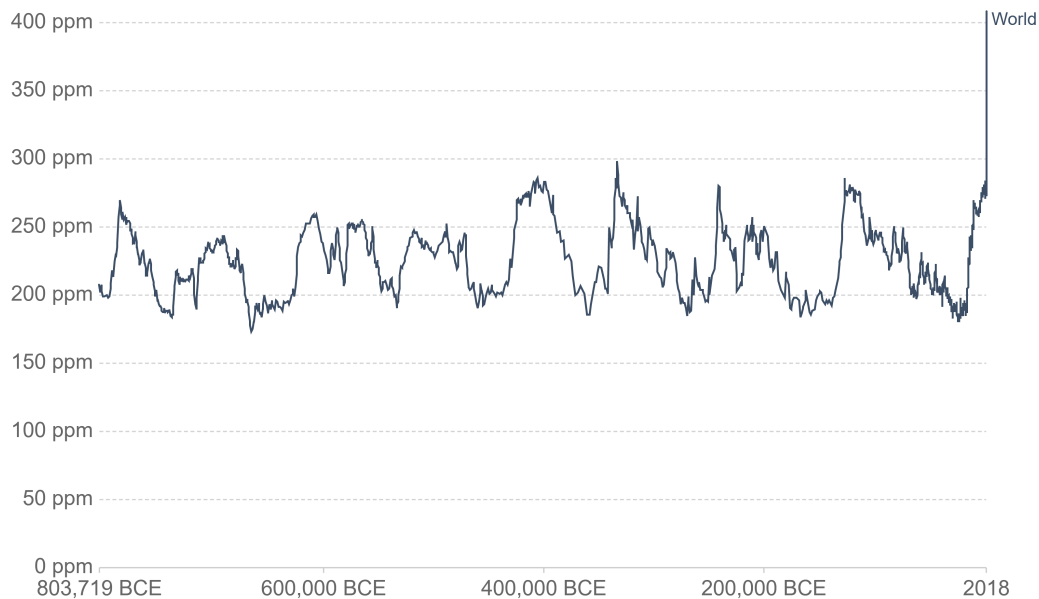
Figure 2: The CO_2 level in the atmosphere in the past 800,000 years[3].

1.3   Air measurements and source attribution

Because of the natural fluxes of CO_2 on the earth it is hard to measure the amount of CO_2 that is emitted by humans with air measurements. What the source of these emission is, is even harder. In a combination, measurements of CO_2, oxygen, $^{14}CO_2$, and $^{13}CO_2$ can give an image of the emissions of CO_2.

Oxygen is used to burn fossil fuels, thus the amount of oxygen in the air is an indicator how much CO_2 is created. Natural gas mostly exists of methane (CH_4), which produces one CO_2 molecule for every two oxygen molecules ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$). Ethane ($C_2H_6$) produces 4 CO_2 molecules for every seven oxygen molecules ($2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$). This is called the oxidative ratio, The longer the carbon chain the lower the oxidative ratio. For natural gas this is 1.95, for liquid fuels 1.44, and for coal 1.17 [18]. Precise measurement of oxygen can therefore help to attribute the CO_2 sources. In addition, those measurements can discriminate between CO_2 uptake by land processes (through photosynthesis, which produces O_2) and solution in the ocean (for which there is no counterpart in O_2).

Discrimination between fossil and "bio" CO_2 is also possible with $^{14}CO_2$, which is a radioactive isotope of carbon with a half-life of 5,730 years [13]. Fossil fuels are millions of years old and thus all the $^{14}CO_2$ is decayed. This lack of $^{14}CO_2$ can be measured for recently added CO_2 from fossil fuels.

A third way to do this is with $^{13}CO_2$. This study aims to measure the $^{13}CO_2$ levels to help attribute the source of recently added CO_2. A carbon atom normally has six neutrons and six protons, but around 1.1% of carbon atoms in the atmosphere have seven neutrons instead of six, this is a stable isotope called $^{13}CO_2$ [27]. Plants tend to take up slightly less $^{13}CO_2$ than $^{12}CO_2$ in photosynthesis, because the $^{13}CO_2$ molecule is heavier than $^{12}CO_2$ [9]. That is why fossil fuels have relatively less $^{13}CO_2$ in them, than the atmosphere. This

differences in $^{13}CO_2$ can be measured.

1.4 $\delta^{13}CO_2$

To measure the difference in $^{13}CO_2$ for different sources, $\delta^{13}CO_2$ has been defined. This is an isotopic signature which expresses the relative deviation of the ratio between $^{13}CO_2$ and $^{12}CO_2$ of a sample with respect to that same ratio for an international reference material. The formula for $\delta^{13}CO_2$ is:

$$\delta^{13}CO_2 = \left(\frac{(\frac{^{13}CO_2}{^{12}CO_2})_{sample}}{(\frac{^{13}CO_2}{^{12}CO_2})_{reference}} - 1 \right).$$ (1)

The outcome is most of the time a small number, that is why it is expressed in per mille. The VPDB (Vienna Pee Dee Belemnite) is the reference value accepted by the International Atomic Energy Agency. The value of the VPDB is 0.011117 [20]

The ratio of ^{13}C and ^{12}C is different for different sources of CO_2, even within different fossil fuels. Natural gas can have the least amount of ^{13}C, oil has more ^{13}C and coal has the most ^{13}C of these fossil fuels. Table 1 gives a description of CO_2 sources and their $\delta^{13}C$ values [8]. The first number is the lower bound of the values that are found, the second is the upper bound. The values can change for different extraction areas and can therefore not be generalised over the world. For very precise measurements, the $\delta^{13}C$ levels of local sources of CO_2 should first be determined, before starting the measurements of $\delta^{13}CO_2$. When the amount of $^{13}CO_2$ is measured very precisely in the air, it can help to trace the sources of the CO_2 emissions.

Table 1: The $\delta^{13}C$ of different sources of CO_2, from Coplen and Shrestha (2016)[8] (except for Groningen natural gas).

CO_2 source	Lower bound $\delta^{13}C$ (‰)	Upper Bound $\delta^{13}C$ (‰)
Sea Water	-0.8	+2.2
Land Plants (C3 metabolic process)	-35	-21
Land plants (C4 metabolic process)	-16	-9
Land Plants (CAM metabolic process)	-34	-10
Coal	-30	-19
Crude oil	-44	-16.8
Natural Gas	-51	-29
Groningen natural gas [17]	-29.11	-28.89

A possibility to perform continuous measurements of $^{13}CO_2$ in the air, is with a NonDispersive infraRed sensor (NDIR). This instrument measures the amount of infrared light that is absorbed by the $^{12}CO_2$ and the $^{13}CO_2$ in the air sample. The NDIR will be discussed in the method section in more detail.

1.5 This study

In this study the precision, accuracy, and reliability of $^{13}CO_2$ measurements is determined with the NDIR: ABB EL3020, as it is built in in a home-built air treatment rack designed

for atmospheric oxygen measurements [19]. Subsequently, continuous measurements of CO_2 and $^{13}CO_2$ levels of air from an inlet on the roof of the EAE building are shown, and first attempts for source attribution of CO_2 in Groningen are made.

This study is part of a bigger study to measure composition of the air in Rotterdam, focusing on oxygen, CO_2, $^{13}CO_2$, and $^{14}CO_2$.

In the methods it is explained how an NDIR works exactly and how this study is designed. In the results and discussion, the quality of the ABB EL3020 is investigated with twelve days of continuous measurements of the outside air in Zernike campus, Groningen. In the conclusion is concluded if the $^{13}CO_2$ capability of the analyser can help with source attribution of CO_2 emissions.

2 Methods

2.1 The NDIR

As mentioned in the introduction the NDIR: ABB EL3020 is used to measure the amount of CO_2 and $^{13}CO_2$ in the air. An NDIR is a device that has an infrared light source (a lamp, not a laser), an air chamber, and a light detector. The light shines through the air chamber onto the light detector. If the frequency of the light matches the frequency of a vibrational transition in $^{12}CO_2$ or $^{13}CO_2$ the light will be absorbed. For $^{12}CO_2$ the highest absorption is 2315.19 cm^{-1}, and for $^{13}CO_2$ this is at 2315.36 cm^{-1} [32]. The lack of light is measured at the detectors. The detectors consist of CO_2 and $^{13}CO_2$ which expand when the light is absorbed in the detector by the CO_2 and $^{13}CO_2$. Because when they absorb light, they get hotter, and therefor expand. This expansion is measured by the analyser. The less light shines on the detector, the less CO_2 and $^{13}CO_2$ expand, the more CO_2 and $^{13}CO_2$ is measured by the analyser. In figure 3 a schematic of the setup is shown.
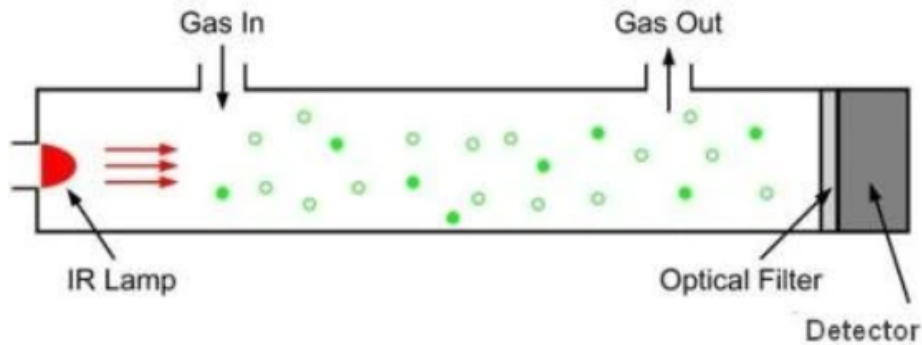

Figure 3: The setup of the NDIR [16].

To measure as precisely as possible the air chamber switches between the reference tank that has known values for CO_2 and $^{13}CO_2$ and the sample that is measured. If there are effects that influence the system, both the reference values and the sample values change and therefor the influence of such an effect largely cancels. The disadvantage of this system is that it takes time to switch between the reference and sample air. With the flow chosen in

our system this is typically 90 seconds. In figure 4 and 5 two cycles of switching are shown of CO_2 and $^{13}CO_2$, respectively.
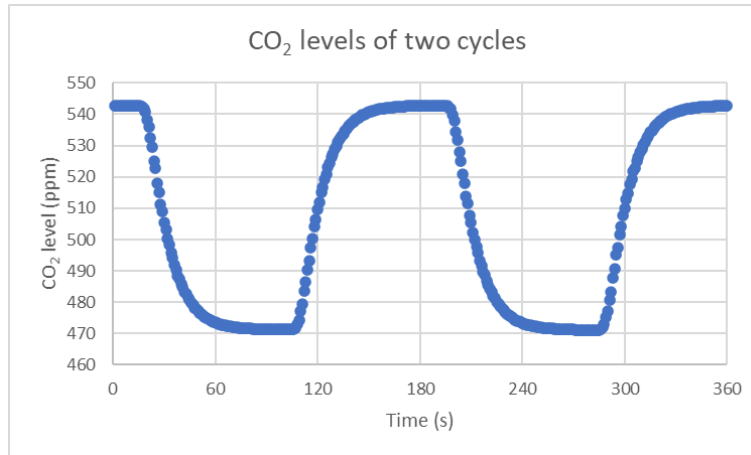

Figure 4: The CO_2 levels in two cycles of measurements.
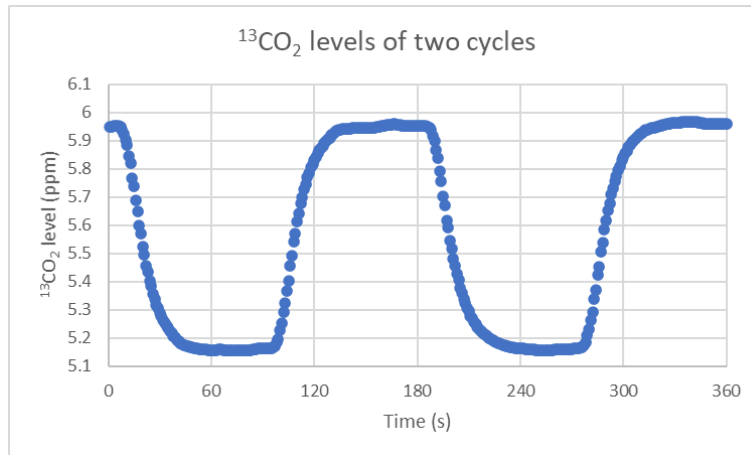

Figure 5: The $^{13}CO_2$ levels in two cycles of measurements.

2.2 Reliability of the NDIR

To test the reliability of the NDIR four different measures were used. One is the Allan variance, named after David Allan [1]. The Allan variance is a measure of instability of the data caused by noise, it will not detect environmental changes or systematic errors. The averages of the last 5, 10, 15, 30, 45, or, 60 seconds of every 120 second cycle is used. The difference between the first and the second cycle, the second and the third cycle etc. are calculated and squared. The average of this number is the Allan deviation, the square root of this is the Allan variance. The mathematical function is:

$$\sigma_y^2(\tau) = \frac{1}{2}\left\langle \left(\bar{y}_{n+1} - \bar{y}_n\right)^2 \right\rangle. \tag{2}$$

Next to the Allan variance the average standard deviation is used. The standard deviation of every cycle is calculated, the average of all these standard deviations is the average standard deviation. The same applies to the average standard error, the third measure. The fourth measure is the standard error of $\delta^{13}CO_2$. For this measure the $\delta^{13}CO_2$ of every cycle is calculated.

With the results of these parameters there is chosen to use the last 45 seconds of every 120 second cycle, and 15 seconds for a 90 second cycle, this choice will be elaborated later.

2.3   Calibration

After the test of reliability, the apparatus could be used to measure outside air, but before every measurement the analyser was first calibrated. Three air tanks with known values for CO_2 and $^{13}CO_2$ were measured and used to calibrate the analyser. The data of outside air was mainly measured from 20 October until 1 November 2020. The system was calibrated six times in this period. For every time the system was calibrated, the three calibration tanks were measured thirty minutes each. The last 15 seconds before switching were used and averaged out till one data point per 90 seconds remained. For the calibration of CO_2 and $^{13}CO_2$ the difference between the levels in the Calibration tank and the reference tank were used and plotted against the known values of the calibration tanks. The formula of the trendline is used to calculate the real values of outside air with the measured values (see figures 6 and 7). The analyser measures the CO_2 levels around 100 ppm higher than the real values, that is the reason why the slope is around 0.87 instead of the expected 1. After the main measurements from 20 October till 1 November with a switching time of 90 seconds, another day was measured with a switching time of 120 seconds.
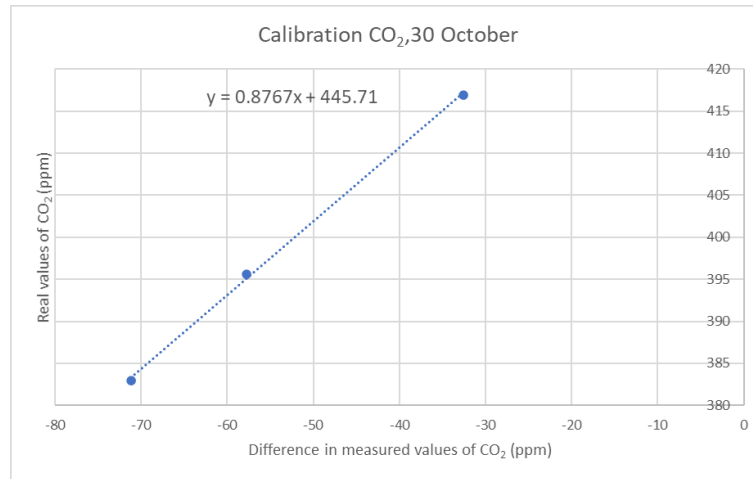

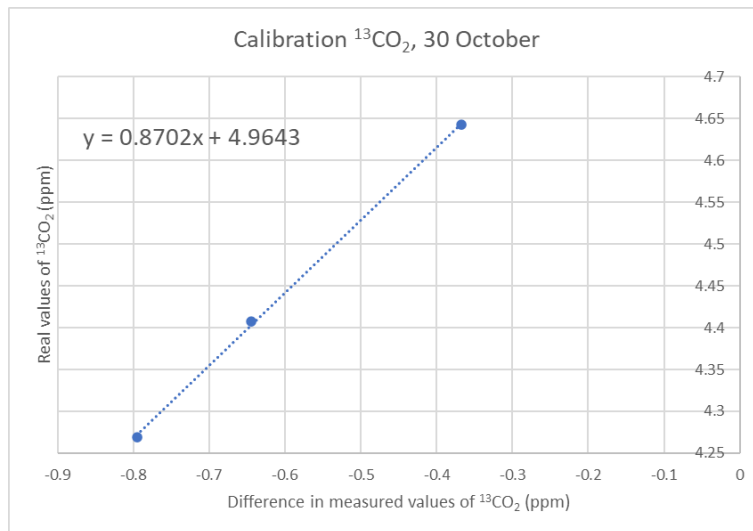Figure 6: The Calibration curve of CO_2 of 30 October.

Figure 7: The Calibration curve of $^{13}CO_2$ of 30 October.

The $\delta^{13}CO_2$ needed an extra calibration because the $\delta^{13}CO_2$ was dependant on the CO_2 concentration. This happens more often in optical instruments. When the CO_2 level is low the $^{13}CO_2$ levels are measured relatively high. This dependence follows from the differences in slope between CO_2 and $^{13}CO_2$ in the figures 6 and 7. The difference between the measured $\delta^{13}CO_2$ values and the real values of the calibration tanks were plotted against the real values of the CO_2 levels as seen in figure 8. The formula of the trendline is used to calibrate the $\delta^{13}CO_2$ values. For the x the CO_2 values were filled in, this number is added to the measured $\delta^{13}CO_2$ values, to get the calibrated $\delta^{13}CO_2$ values.

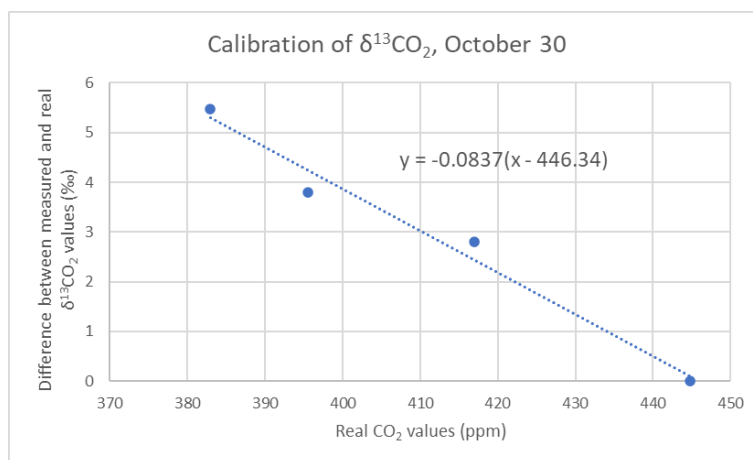Figure 8: The Calibration curve of $\delta^{13}CO_2$ of 30 October.

3 Results and Discussion

3.1 Reliability tests

In table 2 the average standard deviation, average standard error, the standard error of $\delta^{13}CO_2$, and the Allan variance of $^{13}CO_2$ are shown for 120 seconds switching time. The data is of 24 hours of data with two cylinders. The times on the left of the table are the last seconds before switching that are used for the average values of CO_2 and $^{13}CO_2$.

It seemed from the data that the analyser needed a bit more than 60 seconds to settle. Thus after 75 seconds most of the old air is out the system, and it measured the new air. To get as much data per switch there is chosen to use the last 45 seconds for a switching time of 120 seconds. For 90 seconds the last 15 seconds is used. Another reason to use these times, is because the standard error of the $\delta^{13}CO_2$ and the Allan variance went up the shorter the time used for the data.

Table 2: The average standard deviation and Average standard error of CO_2 and $^{13}CO_2$, the standard error of $\delta^{13}CO_2$ and the Allan variance of $^{13}CO_2$. The switching time was 120 seconds.

Time	Average standard deviation		Average standard error		Standard error	Allan variance
	CO_2	$^{13}CO_2$	CO_2	$^{13}CO_2$	$\delta^{13}CO_2$	$^{13}CO_2$
5 s	0.0056	0.0009	0.0025	0.00040	0.068	0.0072
10 s	0.0099	0.0015	0.0031	0.00049	0.064	0.0068
15 s	0.013	0.0020	0.0034	0.00052	0.060	0.0064
30 s	0.020	0.0029	0.0038	0.00053	0.053	0.0054
45 s	0.033	0.0034	0.0049	0.00051	0.049	0.0049
60 s	0.094	0.0037	0.012	0.00048	0.045	0.0044

For a switching time of 90 seconds the last 15 seconds are averaged and used as data point. In figure 9 the last 15 seconds before switching of CO_2 and $^{13}CO_2$ is shown. For CO_2 it could be better to use less than 15 seconds, but because the $^{13}CO_2$ levels are more unstable the last 15 seconds is chosen.
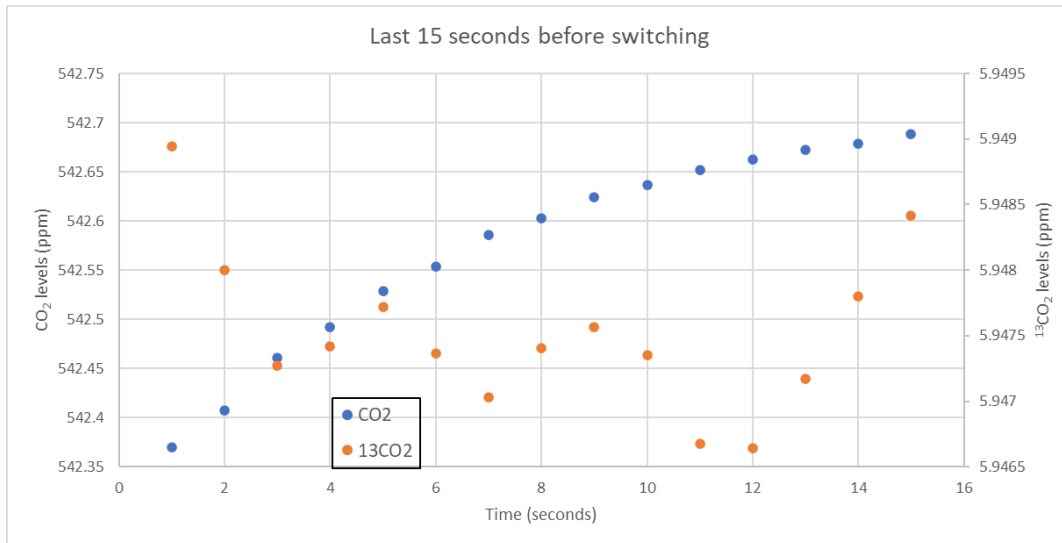
Figure 9: The last 15 seconds of data for the CO_2 and $^{13}CO_2$ before switching.

3.2 Outside air

In figure 10 and 11 the levels of CO_2 and $^{13}CO_2$ and $\delta^{13}CO_2$ are shown from 20 October until 1 November 2020. There is one data point for every three minutes. The switching time used is 90 seconds, and the last 15 seconds have been used.
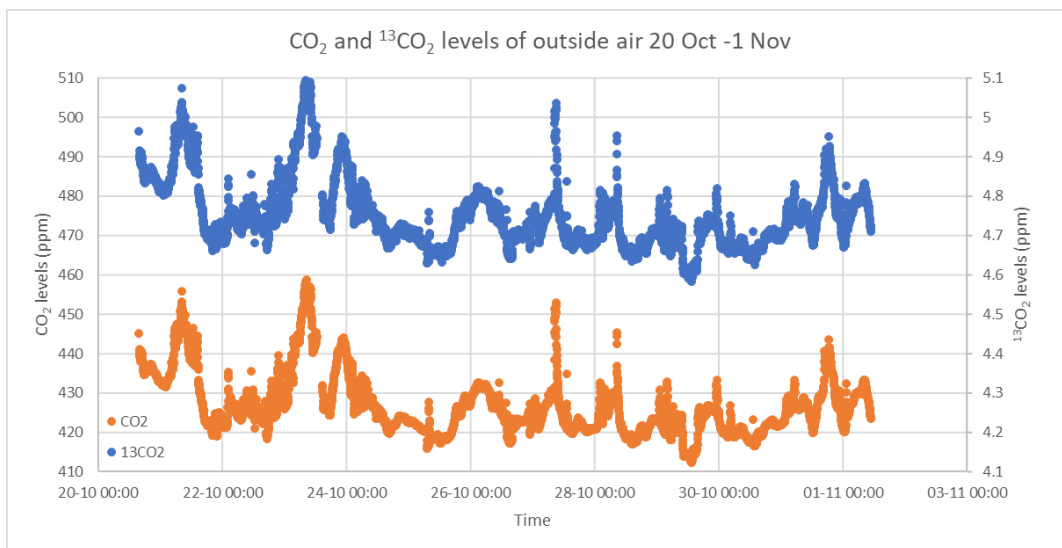

Figure 10: The CO_2 and $^{13}CO_2$ levels of the outside air from 20 October until 1 November 2020 in Groningen, The Netherlands.
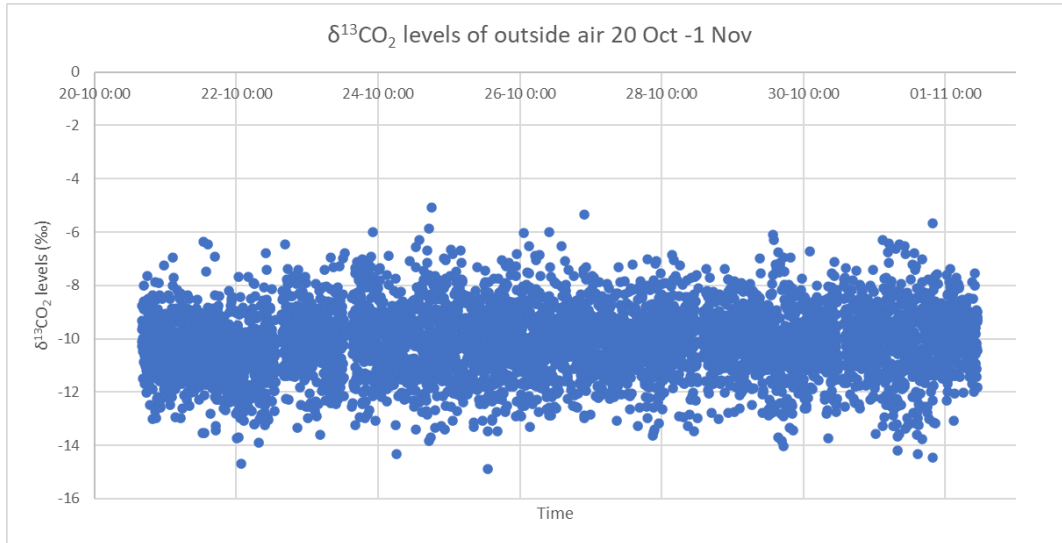
Figure 11: The $\delta^{13}CO_2$ levels of the outside air from 20 October until 1 November 2020 in Groningen, The Netherlands.

The results for the $\delta^{13}CO_2$ have a low reliability. The differences between $\delta^{13}CO_2$ values should typically be within one 1‰ and should be able to follow with a precision of less than 0.1‰ on an hourly basis. The data has a spread of about ±2‰ (see figure 11), This is not good enough to have any usefulness for source attribution of CO_2 emissions. To get more reliable results, the data is averaged out over 30 minutes as seen in figure 12. Although the spread is reduced from ±2‰ to ±0.5‰ it is still too wide to be useful for source attribution.
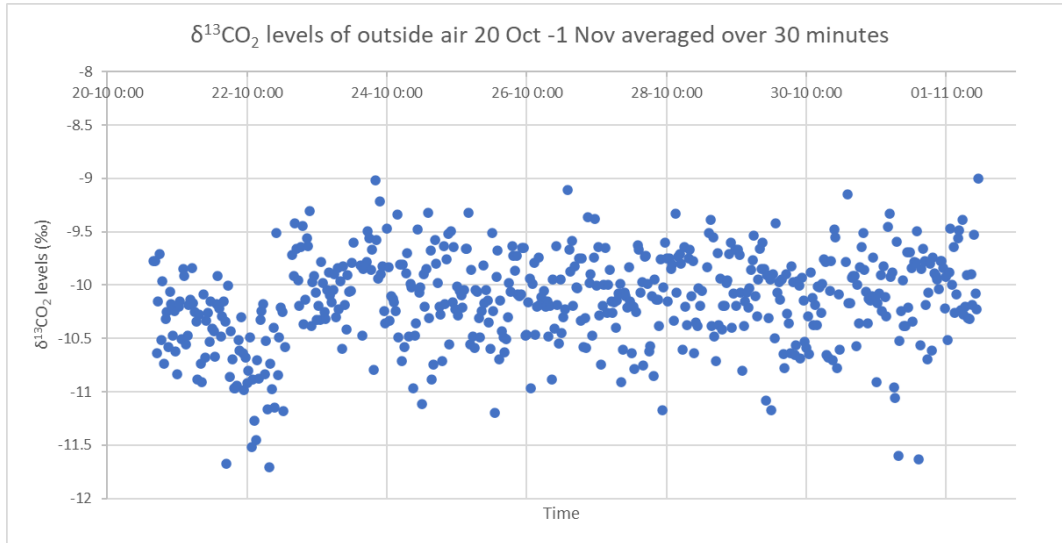
Figure 12: The $\delta^{13}CO_2$ levels of the outside air from 20 October until 1 November 2020 in Groningen The Netherlands averaged out over 30 minutes.

To investigate if a switching time of 120 seconds instead of 90 seconds would give better results an extra day of measurements was conducted. In figure 13, 24 hours of outside air measurements with 90 seconds switching time and 24 hours of data with 120 seconds switching time is combined. The spread of the data is less for the 120 second switching time than for the 90 seconds switching time. It is however still not good enough to be useful. In figure 14 the data with 120 seconds switching time is averaged out over 20 minutes. The spread shrinks again, this time from ±1‰ to ±0.4‰, but it is still not useful for source attribution. An important comment for this comparison is that the data is of two different days, so the input is different and therefore it is possible, however unlikely, that this is the reason for the difference in spread.
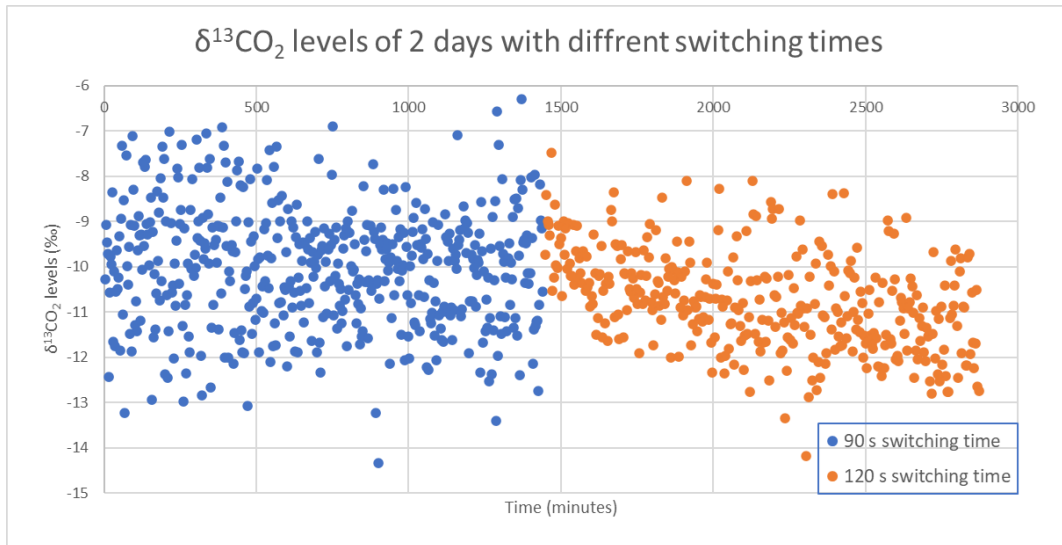
Figure 13: The $\delta^{13}CO_2$ levels of the outside air of two days, one with 90 second switching times and one with 120 second switching times (the X-axis is in minutes because the data is of two separate days)
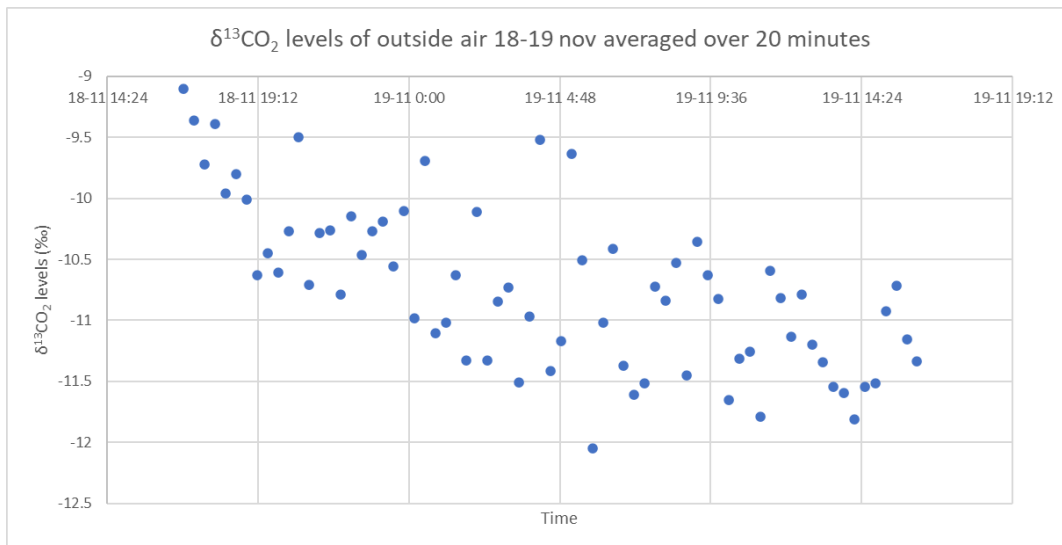

Figure 14: The $\delta^{13}CO_2$ levels of the outside air from 18 November 16:40 until 19 November 16:30 2020 in Groningen, The Netherlands averaged out over 20 minutes (120 seconds switching time).

3.3 Keeling plot

The Keeling plot is a method to analyse the source $\delta^{13}CO_2$ signature for a certain excursion in the CO2 mixing ratio. In our data, not many of such 'events' are visible, only the night of 23-10 is a candidate. For these data we plot the Keeling relation:

$$\delta^{13}CO_2(t) = <slope> *1000/CO_2(t) + \delta^{13}C_S \tag{3}$$

with $\delta^{13}C_s$ the $\delta^{13}C$ value for the source of the extra CO_2. Figure 15 shows the data plotted this way. The data shows a small positive trend, but it is very uncertain because of the low reliability of the data. In figure 15 there is also plotted an ideal line for a CO_2 source with a $\delta^{13}CO_2$ value of -25 ‰. Keeling plots of several peaks in the CO_2 level were made, but the data of 23 November gave the 'best' results. For most of the CO_2 peaks there was no correlation between CO_2 and $\delta^{13}CO_2$ values.
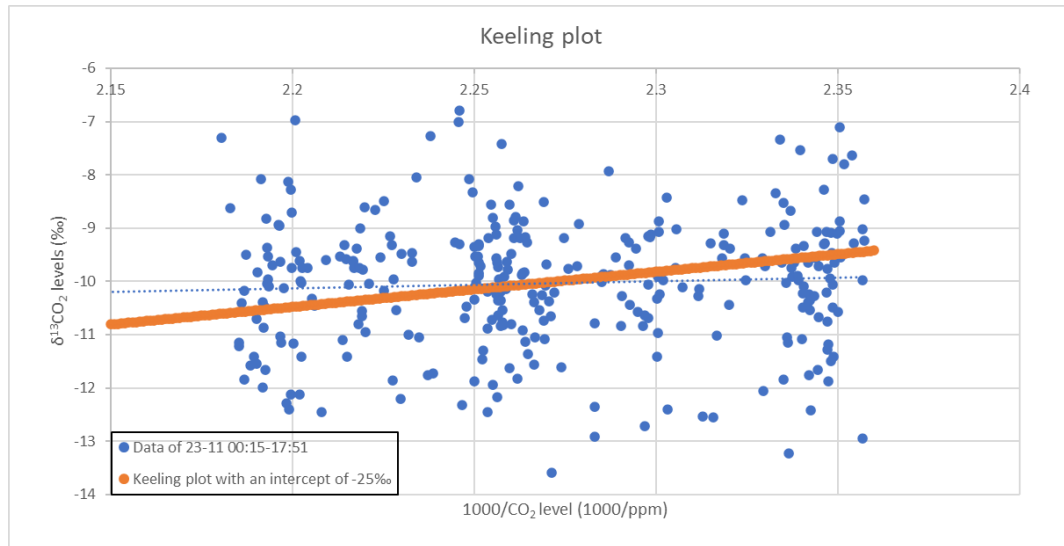

Figure 15: The keeling plot for the data of 23 November 00:15-17:51. With and ideal keeling plot For A CO_2 source with a $\delta^{13}CO_2$ level of -25‰.

To conceptualise what the reliability of the analyser should be, to become useful for source attribution of CO_2 emission, a calculation has been made. The biggest difference in CO_2 levels in the data from 18 October until 1 November was around 40 ppm (460 ppm till 420 ppm, see figure 10) If the $\delta^{13}CO_2$ of air is -9‰ at a CO_2 level of 420 ppm, and 40 ppm of fossil fuel CO_2 (or biogenic respiration CO_2) with a $\delta^{13}CO_2$ value of -25‰ is added. The expected $\delta^{13}CO_2$ value is -10.4‰. This change in data cannot be seen. If a research wants to distinguish between different sources of CO_2 that have a $\delta^{13}CO_2$ level that is close to each other, the data has to be even more precise. Local sources of CO_2 should have a known $\delta^{13}CO_2$ level to be this precise.

3.4 CO_2 levels

The CO_2 levels seemed reasonable reliable (see figure 10). There was not a clear day and night cycle in the CO_2 levels. Some days the CO_2 levels went up at night, but other days this was not the case. The mixing of air is different in daytime than in night-time. Normally it is expected that the CO_2 levels are higher at night than during the day [30]. On average the CO_2 levels was 3 ppm higher at night (20:00-7:00) than at daytime (10:00-17:00). There are some sharp peaks in the data, but this was probably the exhaust fumes close to the inlet of the pipe to the analyser. In total there are no clear patterns visible in the data of CO_2 levels. In the days of measuring the outside air the wind direction did not change much, it stayed between south and south-west wind (180°-225°) [31], so this should not have had an influence on the data. The wind speed was in the most days between 10 and 30 km/h, except for 21 November around 22:00 were it was at most 60 km/h [31]. There were no obvious trends visible that linked the CO_2 levels and the wind speeds.

3.5 Accuracy calibration

To test the accuracy of the data the standard deviations of the calibrations graphs were calculated. The calibration graphs of 30 October (see figure 6,7 and, 8) are comparable with the calibrations of other days. The Intercept and the slope of the graphs were used to calculate the calibrated levels of CO_2, $^{13}CO_2$ and, $\delta^{13}CO_2$. Both the intercept and the slope had a standard deviation. These standard deviations were added up with the formula $\Delta Y = \sqrt{(\Delta Ax)^2 + (\Delta B)^2}$. The ΔY is the standard deviation of the calibrated CO_2, $^{13}CO_2$ and, $\delta^{13}CO_2$ values. These standard deviations were reasonable for CO_2, $^{13}CO_2$ and, $\delta^{13}CO_2$ with a standard deviation of ±0.87 ppm, ±0.007 ppm and, ±0.26‰, respectively.

4 Conclusion

In conclusion, the quality of the NDIR: ABB EL3020 was not good enough to be useful for source attribution of CO_2 emissions. The $\delta^{13}CO_2$ levels were not reliable. The spread of the data for 90 seconds switching time was ±2‰ (see figure 11), while the differences between $\delta^{13}CO_2$ values should typically be within one per mille and should be able to follow with a precision of less than 0.1‰ on an hourly basis. With a 120 second switching time and averaging the data over twenty minutes, the spread shrank to ±0.4‰ (see figure 14), but this was still not good enough. The accuracy of the $\delta^{13}CO_2$ was reasonable. The intercept and slope of the calibration graphs had a standard deviation. When added up, the standard deviation of $\delta^{13}CO_2$ became ±0.26‰

The CO_2 and $13CO_2$ levels were reasonable reliable and accurate. Both values could be followed over the days that the outside air was measured. There were no obvious trends in the data. Some days there seemed to be a day and night cycle, but other days this was not the case.

References

[1] David W Allan. "Statistics of atomic frequency standards". In: *Proceedings of the IEEE* 54.2 (1966), pp. 221–230.

[2] HH Aumann and A Ruzmaikin. "Trends in severe storms from nine years of AIRS data". In: *AIP Conference Proceedings*. Vol. 1531. 1. American Institute of Physics. 2013, pp. 752–755.

[3] Bernhard Bereiter et al. "Revision of the EPICA Dome C CO2 record from 800 to 600 kyr before present". In: *Geophysical Research Letters* 42.2 (2015), pp. 542–549.

[4] CBS et al. *Temperatuur in Nederland en mondiaal, 1907 - 2019*. Apr. 2020. URL: https://www.clo.nl/indicatoren/nl0226-temperatuur-mondiaal-en-in-nederland.

[5] John A Church et al. *Sea level change*. Tech. rep. PM Cambridge University Press, 2013.

[6] Philippe Ciais et al. "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, 2014, pp. 465–570.

[7] John Cook et al. "Consensus on consensus: a synthesis of consensus estimates on human-caused global warming". In: *Environmental Research Letters* 11.4 (2016), p. 048002.

[8] Tyler B Coplen and Yesha Shrestha. "Isotope-abundance variations and atomic weights of selected elements: 2016 (IUPAC Technical Report)". In: *Pure and Applied Chemistry* 88.12 (2016), pp. 1203–1224.

[9] Graham D Farquhar, James R Ehleringer, and Kerry T Hubick. "Carbon isotope discrimination and photosynthesis". In: *Annual review of plant biology* 40.1 (1989), pp. 503–537.

[10] Pierre Friedlingstein et al. "Global carbon budget 2019". In: *Earth System Science Data* 11.4 (2019), pp. 1783–1838.

[11] John Gale et al. "Sources of CO2". In: *Carbon dioxide capture and storage, Cambridge University Press, UK* (2005), p. 94.

[12] Terry Gerlach. "Volcanic versus anthropogenic carbon dioxide". In: *Eos, Transactions American Geophysical Union* 92.24 (2011), pp. 201–202.

[13] Harry Godwin. "Half-life of radiocarbon". In: *Nature* 195.4845 (1962), pp. 984–984.

[14] J Graber et al. *Carbon Cycling and Biosequestration Integrating Biology and Climate Through Systems Science Report from the March 2008 Workshop*. Tech. rep. DOESC (USDOE Office of Science (SC)), 2008.

[15] K Haustein et al. "A real-time global warming index". In: *Scientific reports* 7.1 (2017), pp. 1–6.

[16] *How does an NDIR CO2 Sensor Work?* Jan. 2020. URL: https://www.co2meter.com/blogs/news/6010192-how-does-an-ndir-co2-sensor-work.

[17] G Hut, MJS Begemann, and HR Weerkamp. "Determination of isotope ratios in the natural gas components CH4 and N2 separated by gas chromatography". In: *Chemical geology* 46.1 (1984), pp. 75–83.

[18] Ralph Franklin Keeling. "Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O_2 mole fraction". In: *Ph. D. thesis, Harvard University* (1988).

[19] Charlotte van Leeuwen. "Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites". PhD thesis. University of Groningen, 2015.

[20] D Malinovsky et al. "Development and characterisation of new glycine certified reference materials for SI-traceable 13 C/12 C isotope amount ratio measurements". In: *Journal of Analytical Atomic Spectrometry* 34.1 (2019), pp. 147–159.

[21] Gordon McGranahan, Deborah Balk, and Bridget Anderson. "Risks of climate change for urban settlements in low elevation coastal zones". In: *The New Global Frontiers: Urbanization, Poverty and Environment in the 21st Century* (2008).

[22] Rajendra K Pachauri et al. *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, 2014.

[23] National Research Council (US). CO2/Climate Review Panel, National Research Council (US). Climate Research Committee, and National Research Council (US). Carbon Dioxide Assessment Committee. *Carbon dioxide and climate: A second assessment.* Natl Academy Pr, 1982.

[24] *Paris Agreement.* UNTC XXVII 7.d. Dec. 12, 2015.

[25] Jacob Poushter and Christine Huang. "Climate change still seen as the top global threat, but cyberattacks a rising concern". In: *Pew Research Center* 10 (2019), pp. 1–37.

[26] Susan Solomon et al. *Climate change 2007-the physical science basis: Working group I contribution to the fourth assessment report of the IPCC.* Vol. 4. Cambridge university press, 2007.

[27] W Stichler, R Gonfiantini, and K Rozanski. "Reference and intercomparison materials for stable isotopes of light elements". In: *IAEA TECDOC* 825.67-74 (1995), p. 5.

[28] Thomas F Stocker et al. "Climate change 2013: The physical science basis". In: *Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change* 1535 (2013).

[29] NOAA US Department of Commerce. *Global Monitoring Laboratory - Carbon Cycle Greenhouse Gases.* Oct. 2005. URL: https://www.esrl.noaa.gov/gmd/ccgg/.

[30] Shashi B Verma and Norman J Rosenberg. "Vertical profiles of carbon dioxide concentration in stable stratification". In: *Agricultural Meteorology* 16.3 (1976), pp. 359–369.

[31] *Weergrafieken.* URL: https://www.buienradar.nl/nederland/weerbericht/weergrafieken/6280.

[32] Hanquan Zhang et al. "High-Precision 13CO2/12CO2 Isotopic Ratio Measurement Using Tunable Diode Laser Absorption Spectroscopy at 4.3 μm for Deep-Sea Natural Gas Hydrate Exploration". In: *Applied Sciences* 9.17 (2019), p. 3444.