Abstract
In this research project the operation of the Vaisala Carbocap GMP343 (Serial number D3520004) was studied to improve its functionality for atmospheric measurements of CO₂. Measurements of carbon dioxide are influenced by the pressure, temperature, oxygen content and humidity of the air. To get measurements independent of these four variables the measurements are translated into values corresponding to certain defined standard conditions by an internal correction function. These standard conditions are defined to be 1013 hPa, 25ºC, 0% oxygen and 0% relative humidity. Since the Carbocap GMP343 of the Finnish company Vaisala was designed to measure carbon dioxide concentrations in a very wide range the internal correction function for the four variables is not adapted very well to atmospheric conditions. This became clearly visible in measurements done in a small-scale network at schools, called the School – CO₂ – Web. To be able to use the atmospheric CO₂ measurements of the Vaisala Carbocap GMP343 for scientific purposes the device needs to be better adapted to these specific conditions.

A laboratory set-up has been built to study the influences of pressure, temperature and humidity on the CO₂ measurements. The correction for oxygen was removed since its concentration is very constant in ambient air and its influence is already captured in the calibration. The correction of Vaisala appeared to work reasonably well for pressure but it overcorrected significantly for temperature. For humidity no reliable correction could be found yet due to problems in the set-up and its complicated behavior. Some information was acquired about the influence of humidity on CO₂ measurements and the correction of Vaisala was shown to be wrong. Overall the correction of Vaisala was too complicated and inaccurate and could be simplified and improved considerably.

Together with a calibration the new correction was applied on the raw data coming from the Vaisala Carbocap GMP343 (serial number D3520004) that was installed on the roof of the Centre for Isotope Research building (University of Groningen, Zernike campus) for a verification test. The data were compared with data from the Oxzala system, a system that delivered CO₂ concentrations accurate to ≤ 0.3 ppm (van der Laan-Luijkx, 2010). It appeared that the new developed correction worked much better than the old correction of Vaisala. The new correction gave an average difference of only -0.62 ± 0.06 ppm with the Oxzala measurements, with a spread of single measurements of typically 2.46 ppm (1σ). The old Vaisala correction gave an average difference of -6.79 ± 0.06 ppm with the Oxzala record, with a scatter of 2.18 ppm (1σ).

The new corrected dataset appeared not to be dependent on the CO₂ concentration, but it showed residual dependences still on temperature, pressure and humidity. Since no correction was applied for humidity, a dependence on this was expected. Unfortunately it was still not possible to define a correction for this variable. The most important problem was the very low temperature during the verification test, resulting in very low partial pressures of water vapor in the atmosphere and therefore in a non-representative dataset. A second problem was the strong correlation between humidity and temperature during the verification test making it hard to indicate which variable had what influence on the dataset. Since a correction for temperature was already applied on the dataset one could however assume that the residual dependence was due to humidity only. The verification test also indicated that an adaptation of the pressure correction is probably needed but this could not be determined due to data problems caused by gaps in the humidity data.

Since all tests were done with the same device it is important to investigate the behavior of other devices from the Vaisala Carbocap GMP343 series, to see whether or not they respond in the same way to a changing pressure, temperature or humidity.

In spite of some unanswered questions this research can be seen as successful. The verification test clearly showed that it is possible to improve the measurements within the School CO₂ Web. It is very likely that measurements made with the Vaisala Carbocap GMP343 devices will be able to contribute to scientific research in the near future.
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1. Introduction
Since the beginning of the industrial revolution around 1850, humanity has burned a tremendous amount of fossil fuels in order to provide society with energy. Around 1959, Charles David Keeling discovered that carbon dioxide, a result of the burning of fossil fuels, was accumulating in the earth’s atmosphere. The longer he measured the carbon dioxide concentration in the air, the clearer it became that it was rising steadily.

Carbon dioxide is present naturally in the atmosphere of the earth. Together with other so-called greenhouse gasses like water vapor and methane it absorbs infrared radiation. As short wavelength solar radiation in the form of visible and UV light enters the earth, it is partly reflected back to space and partly absorbed by the earth’s surface. The earth is much colder than the sun and thus the energy it re-emits has a longer wavelength, mainly in the form of infrared radiation. The greenhouse gasses in the atmosphere absorb this radiation and afterwards re-emit it again in all directions. Because of this, part of the energy will not be able to escape to space and is trapped within the atmosphere of the earth. Due to this natural greenhouse effect, temperature on earth is on average 14°C instead of the -17°C that it would have been without any greenhouse gasses present (McKinney et al, 2007).

Increasing the carbon dioxide concentration in the atmosphere is probably not without consequences. After some time it became apparent that the average temperature on earth was rising. The presence of more greenhouse gasses was causing an enhanced greenhouse effect.

Of all the greenhouse gasses existing and emitted by humanity, carbon dioxide is considered to be the most important one since such immense volumes are involved. The behavior of carbon dioxide in our environment is not straightforward. Once released in the atmosphere, CO$_2$ can be absorbed by the oceans or taken 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 compartments of the earth is called the carbon cycle. Nowadays many aspects of the global carbon cycle are still unknown, like the exact sizes of the flows between the compartments or the exact locations of sources and sinks of carbon. Also related questions about the possible consequences are still waiting for an answer. Examples regard the earth’s temperature and the acidity of the oceans.

Although the exact consequences of the enhanced greenhouse effect are currently impossible to predict, there is little doubt that it will have consequences in the future. Since prevention is often better than cure it is best to reduce our emissions as soon as possible. Unfortunately changes are made at a very slow pace. The climate change conference that was held in Copenhagen last year was a big disappointment for many poor countries and environmental organizations since it did not result in a legally binding treaty. It made clear again that more willingness is needed. It would be of great help if the urgent questions considering the carbon cycle could be answered. Besides, a better-educated general public would also be more aware of the problem.

A project that will be of great help in both making society more aware as well as solving the urgent questions considering the carbon cycle is the so-called School – CO$_2$ – Web. In the year 2005 the Centre for Isotope Research of the University of Groningen started this project by installing CO$_2$ measurement devices on the roofs of schools. By installing devices on multiple locations close to each other small-scale measuring networks are established. The small differences in the CO$_2$ concentrations that will be measured at the different locations can be used to check and improve atmospheric models and identify sources and sinks of carbon. When models of the atmosphere become more accurate and reliable the carbon cycle of the earth will be better understood. By placing the equipment on schools and not at random locations the devices will not only benefit science but will also be of great use in educating pupils. Doing measurements is much more valuable and informative than learning facts from a book. The School – CO$_2$ – Web will therefore increase the knowledge and awareness of a new generation of people.
In the year 2005 three schools in and around the city of Groningen joined the project. They were situated close to the university to make sure scientists are nearby in order to help installing and maintaining the equipment. Now, five years later, the project is extended with more schools in the Netherlands but also schools in Germany, the United Kingdom, France, Spain and Italy. All schools are situated close to an institution or university that is able to install and maintain the measuring devices.

The device that is installed on the roofs of the schools is made by the Finnish company Vaisala and called Carbocap GMP343. For simplicity, the term Vaisala will be used mostly from now on to indicate the device. In order to get the proper carbon dioxide concentration the signal of the Vaisala needs to be corrected for pressure, temperature and humidity. To be able to do this, a small weather station is placed close to the Vaisala on the roof of each school. The required temperature, pressure and relative humidity values are sent to the Vaisala where an internal correction function translates the raw data into carbon dioxide values at a standard pressure, temperature and relative humidity. The next chapter deals in more detail with these operating principles of the Vaisala.

The schools already benefit from the School – CO$_2$ – Web project. Students are able to measure the carbon dioxide concentration continuously at their own school. They can discover seasonal and daily variations and the influence of traffic, the school heating system or wind direction. There are many possibilities for lessons and projects. Unfortunately, the schools cannot be compared very well to each other. Recordings in the past showed unexpected differences in the measurements, like is visible in Figure 1.

![Figure 1: The carbon dioxide concentration at three different locations in Groningen in June 2009](image)

During the night differences in carbon dioxide concentration can be expected since the cold earth prevents the atmosphere from mixing. Local sources and sinks then largely determine the concentration of CO$_2$. During the day however the atmosphere is supposed to be well mixed due to the rising of warm air coming from the surface. The graph above clearly shows that this is not the
case for the three locations in the city of Groningen. The records CIO (Centre for Isotope Research) and MAA (Maartenscollege) show some similarity during the day, but the record WLG (Willem Lodewijk Gymnasium) shows a much higher average CO₂ concentration with differences of sometimes more than 20 ppm during the day.

The poor accuracy of the measurements is not so much a problem for the students since they are still able to see trends and influences in the measurements. For science, however, much more accurate data are needed. It is clear that the relatively cheap Vaisala will never be able to compete with the very expensive equipment placed on the official measurement stations like the tower of the University of Groningen in Lutjewad. It is however also clear that the differences measured now are unacceptably large and the measurements need to and can be improved before data will be useful for scientific purposes.

In the beginning of the year 2009 a research project regarding this problem was carried out at the Centre for Isotope Research of the University of Groningen. It was suspected that the internal correction of Vaisala for pressure, temperature and humidity was wrong. Because of that, a device might give a systematic error in all its measurements after it is calibrated in extreme atmospheric conditions. The research revealed that there was indeed something wrong with the internal corrections for pressure, temperature and humidity carried out by Vaisala. More than a brief overview of the problem could however not be given (Meinema, 2009).

The aim of this research is to test and improve the internal correction of the Vaisala to improve the measurements made within the School – CO₂ – Web. A new correction formula should therefore be found and then implemented in the software.

In the next chapter of this report the operating principles of the Vaisala and its internal corrections for the atmospheric conditions are described. The next chapter then discusses the method that was used to find the deviations in the correction of Vaisala and to determine the right correction. After that the results of the research project are given for the three different atmospheric parameters pressure, temperature and humidity. A verification test that was carried out to check the new correction and compare it with the old correction is described in chapter 5. The report ends with a discussion and finally a conclusion.
2. Operation of the Vaisala carbocap GMP343

The Finnish company Vaisala produces various carbon dioxide measuring devices. On the roofs of the schools the Vaisala Carbocap GMP343 is placed. This relatively cheap carbon dioxide measuring device is coupled to a weather station to get the required atmospheric variables. This chapter describes the operating principles of the Vaisala Carbocap GMP343.

2.1 Principle of operation

The Vaisala Carbocap GMP343 sensor that is placed on the roofs of the schools is visible in Figure 2 below to the left. The air flows through the cap to the sensor where carbon dioxide is measured. A cable connects the device to the computer and provides it with power. When calibrations need to be done or testing takes place a special cap can be placed on the sensor, allowing a gas from a cylinder to go directly to the sensor. In Figure 2 this calibration cap is visible in the picture to the right. The gas enters through the hose (to the left in the picture) and leaves the sensor through very small gaps in the black cap (invisible in this picture).

![Figure 2: The Vaisala Carbocap GMP343 with diffusive cap (left) and calibration cap (right)](image)

The measurements made by the Vaisala Carbocap GMP343 are based on the characteristic of carbon dioxide to absorb infrared radiation. It is a so-called non-dispersive infrared (NDIR), single beam, dual wavelength sensor. Figure 3 below shows the operating principles of the device.

![Figure 3: Overview of the Vaisala Carbocap GMP343](image)
A pulse of light from a small filament lamp is reflected and re-focused back to an infrared detector. The infrared detector is placed behind a Fabry-Perot Interferometer (FPI), which is a filter that allows only certain wavelengths of light to pass through to the detector. It is tuned electrically in order to regularly change back and forth between two wavelengths: a wavelength in which CO$_2$ absorbs infrared radiation (4.26 µm) and a nearby non-absorbing wavelength (3.9 µm) (Kivelä, 2009). Because CO$_2$ absorbs infrared radiation in the first band, part of the initial emitted infrared light does not reach the infrared detector. In the reference band, where carbon dioxide does not absorb anything, the detector sees full light transmission (Vaisala, 2005) (Vaisala, 2010). The ratio of these two light transmissions indicate the degree of light absorption and this is related to the concentration of CO$_2$ according to Lambert-Beers law as is given in equation (1).

\[
\frac{I}{I_0} = e^{-A} = e^{-\varepsilon l C}
\]

(1)

With in this equation $I$ the intensity of the light transmission, $I_0$ the intensity of the full light transmission and $A$ the absorbance which is equal to $\varepsilon l C$. With in this, $\varepsilon$ the molar absorption coefficient (cm$^{-1}$ M$^{-1}$), $C$ the molar concentration (M) and $l$ the path length (cm). Equation (1) can be rewritten to find the expression for the molar concentration.

\[
C = -\frac{1}{\varepsilon l} \log \left( \frac{I}{I_0} \right)
\]

(1*)

The equation shows that the ratio of the two light transmission signals is related to the concentration of the gas in the volume of the Vaisala. The output of the Vaisala is thus exponentially proportional to the absolute number of CO$_2$ molecules in the volume of the device.

To avoid dew formation on the optics surface heating can be turned on. There are two heating elements as can be seen in Figure 3; one behind the mirror and one behind the window of the sensor. When the heating is on, the temperature of the optics is kept a few degrees above the ambient temperature (Vaisala, 2005).

The Vaisala Carbocap GMP343 gives three different outputs for the carbon dioxide concentration. The difference between the three values is determined by the revision of the measurement. The first output, called CO2RAWUC is based on Lambert-Beers law combined with a linearization function. This linearization is necessary since the absorption signal is not linear with the CO$_2$ concentration, as is obvious from formula (1). In this way, reasonable values for the carbon dioxide concentration are already acquired but the user has the possibility to apply a calibration on the measurements. This calibration, together with corrections for pressure, temperature, humidity and oxygen content, results into the second output of the Vaisala called CO2RAW. It is important to note here that Vaisala first applies a calibration on the data and afterwards corrects for the four atmospheric conditions. The acquired dataset CO2RAW can be adjusted again by filtering it, resulting in the third output called CO2. Three different filters can be used; the median filter, replacing all values by the median of a series of values previous to the one replaced, an average filter, operating in a similar way but by taking the average in stead of the median, and finally a smoothing filter, preventing fast concentration changes to be visible in the record. The user is able to switch the different filters on and off and adjust them. In this way, the required kind of data set can be acquired.
2.2 Correction for atmospheric conditions
As was explained in the previous section, the carbon dioxide concentration is measured by determining the absorption of infrared radiation in a certain volume of air. When more carbon dioxide molecules are present in this volume, more infrared radiation is absorbed and a higher concentration will be calculated. The amount of molecules in a certain volume of air is, however, not only determined by the absolute increase or decrease of the substance in our environment. According to the perfect gas law, the amount of gas molecules in a fixed volume of air is dependent on temperature and pressure. The perfect gas law is given in equation (2).

\[ pV = nRT \]  

With in this formula \( p \) the pressure (in Pa), \( V \) the volume (in m\(^3\)), \( n \) the amount of molecules (in mole), \( R \) the gas constant (8.314413 J/mole K) and \( T \) the temperature (in K).

From the formula it follows that a higher pressure results in more molecules in the same volume of air, assuming that the temperature remains constant. Likewise, a higher temperature means that fewer molecules will be present in the same volume of air (assuming constant pressure). Since not only the amount of CO\(_2\) molecules changes, but also the amount of other molecules, the net concentration in parts per million (ppm) remains the same. Inside the Vaisala however, more or less carbon dioxide molecules are present than before, so the measured absorption is different and thus the calculated concentration is different. It is important to correct for this effect. To do this, a standard pressure and temperature are chosen. In this way, measured values can be translated and become independent of the temperature and pressure. The choice for the standard is arbitrary as long as the calibration is valid at the defined standards. For the standard values Vaisala choose a pressure of 1 atm (or 1013 hPa) and a temperature of 25°C (or 298.15 K).

Besides changes of the gas itself according to the perfect gas law, other substances in the atmosphere can also have an influence on the measurements. Important contents of the atmosphere are oxygen and water vapor. Since water vapor is a greenhouse gas, it can also absorb infrared radiation. When water is present in the measured air, its absorption will interfere with that of carbon dioxide. Dependent on the amount of absorption by the water vapor and whether it is in the measurement or the reference band, the deduced carbon dioxide concentration can either be too large or too small. In principle, even both can happen as a function of the water vapor concentration. Besides this there is another effect of water vapor that should be accounted for. According to Dalton’s law of partial pressure, as is given in equation (3), the sum of the partial pressures of the components of a mixture is the total pressure of the gas mixture.

\[ p = p_{gas1} + p_{gas2} + p_{gas3} + ...p_{gasm} \]  

The law makes clear that if water vapor is added to a dry gas in constant \( p \), \( T \) and \( V \), water replaces some of the other gas molecules in the mixture. The water causes a dilution effect that should be taken into account too. Vaisala corrects the measured CO\(_2\) values in such a way that the value at a relative humidity of 0% is found.

The last effect that should be taken into account is the principle of spectrum changes. Due to a change in pressure, temperature or oxygen content the absorption spectrum of carbon dioxide can change. It is because of this spectrum broadening that the oxygen content is taken into account as well (Kivelä, 2009), and that the temperature and pressure corrections are not solely dependent on the perfect gas law. For oxygen, the standard content is taken to be 0% in the correction of Vaisala.
The formula Vaisala uses to correct for pressure, temperature, oxygen content and relative humidity is given in the iterative equation (4). In this equation G is the oxygen content in %, $c_i$ is the value CO2RAWUC (with or without calibration) and $c_{10}$ finally is the corrected value, given as the output CO2RAW.

\[
c_{i+1}(ppm) = c_i(ppm) \times \frac{1}{\frac{p(hPa)}{1013} \times \frac{298}{273 + T(°C)}} \times \frac{1}{k_p(c_i) \times \left(\frac{p(hPa) - 1013}{1013}\right)^2 + k_{p2}(c_i) \times \frac{p(hPa) - 1013}{1013} + 1} \times \frac{1}{K_4(c_i) \times \left(\frac{25 - T(°C)}{25}\right)^4 + K_3(c_i) \times \left(\frac{25 - T(°C)}{25}\right)^2 + K_2(c_i) \times \frac{25 - T(°C)}{25} + 1} \times \frac{1}{\frac{k_{RH1}(c_i)}{10000} \times \frac{RH(%)}{1013} \times \frac{p(hPa)}{1013}^2 + \frac{k_{RH2}(c_i)}{10000} \times \frac{RH(%)}{1013} \times \frac{p(hPa)}{1013} + 1} \times \frac{1}{\frac{k_{G1}(c_i)}{10000} \times G \times \frac{p(hPa)}{1013}^2 + \frac{k_{G2}(c_i)}{10000} \times G \times \frac{p(hPa)}{1013} + 1}
\]

The formula contains many formulas again:

\[
k_{p1}(c_i) = A_{p1} \times c_i(%)^4 + B_{p1} \times c_i(%)^3 + C_{p1} \times c_i(%)^2 + D_{p1} \times c_i(%) + E_{p1} \quad (4a)
\]

\[
k_{p2}(c_i) = A_{p2} \times c_i(%)^4 + B_{p2} \times c_i(%)^3 + C_{p2} \times c_i(%)^2 + D_{p2} \times c_i(%) + E_{p2} \quad (4b)
\]

\[
K_4(c_i) = A4 \times c_i(%)^2 + B4 \times c_i(%) + C4 \quad (4c)
\]

\[
K_3(c_i) = A3 \times c_i(%)^2 + B3 \times c_i(%) + C3 \quad (4d)
\]

\[
K_2(c_i) = A2 \times c_i(%)^2 + B2 \times c_i(%) + C2 \quad (4e)
\]

\[
k_{RH1}(c_i) = A_{RH1} \times c_i(%)^2 + B_{RH1} \times c_i(%) + C_{RH1} \quad (4f)
\]
\[ k_{RH2}(c_i) = A_{RH2} \times c_i(\%)^2 + B_{RH2} \times c_i(\%) + C_{RH2} \]  
\[ k_{G1}(c_i) = A_{G1} \times c_i(\%)^2 + B_{G1} \times c_i(\%) + C_{G1} \]  
\[ k_{G2}(c_i) = A_{G2} \times c_i(\%)^2 + B_{G2} \times c_i(\%) + C_{G2} \]  

\[ P_{ws}(hPa) = 1000 \times 10^{28.59051-8.2 \times \log(Ta(K)) + 0.0024804 \times Ta(K) - \frac{3142}{Ta(K)} \]  

In this, \( P_{ws} \) is at 1013 hPa and \( T_a(K) = 273.15 + T_a(\degree C) \).

The formulas above contain many constants again which are given in the next table. The first three columns contain parameters that are valid for every Vaisala Carbocap GMP343. The fourth column contains the specific parameters, which are different for every single Vaisala. The values given here belong to the Vaisala Carbocap GMP343 with the serial number D3520004.

**Table 1: General and specific constants of equation (4)**

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Relative humidity</th>
<th>Oxygen</th>
<th>Specific</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{p1} = 0 )</td>
<td>( A_{RH1} = 0.5981 )</td>
<td>( A_{G1} = 0 )</td>
<td>( A2 = -3.16447 )</td>
</tr>
<tr>
<td>( B_{p1} = 0 )</td>
<td>( B_{RH1} = -3.5555 )</td>
<td>( B_{G1} = 0 )</td>
<td>( B2 = 0.160891 )</td>
</tr>
<tr>
<td>( C_{p1} = 0 )</td>
<td>( C_{RH1} = 0.1837 )</td>
<td>( C_{G1} = 0 )</td>
<td>( C2 = -0.0189073 )</td>
</tr>
<tr>
<td>( D_{p1} = 0 )</td>
<td>( A_{RH2} = -17.803 )</td>
<td>( A_{G2} = 0 )</td>
<td>( A3 = 0 )</td>
</tr>
<tr>
<td>( E_{p1} = 0 )</td>
<td>( B_{RH2} = 102.39 )</td>
<td>( B_{G2} = 0 )</td>
<td>( B3 = -0.0065072 )</td>
</tr>
<tr>
<td>( A_{p2} = -155.36 )</td>
<td>( C_{RH2} = 14.603 )</td>
<td>( C_{G2} = -9.0 )</td>
<td>( C3 = -0.0155004 )</td>
</tr>
<tr>
<td>( B_{p2} = 209.51 )</td>
<td>( )</td>
<td>( )</td>
<td>( A4 = 0 )</td>
</tr>
<tr>
<td>( C_{p2} = -68.42 )</td>
<td>( )</td>
<td>( )</td>
<td>( B4 = -0.00977981 )</td>
</tr>
<tr>
<td>( D_{p2} = 9.2681 )</td>
<td>( )</td>
<td>( )</td>
<td>( C4 = 0.00672236 )</td>
</tr>
<tr>
<td>( E_{p2} = 0 )</td>
<td>( )</td>
<td>( )</td>
<td>( )</td>
</tr>
</tbody>
</table>

Since so many constants are equal to zero, equation (4) becomes somewhat simplified. When the atmospheric conditions are equal to the defined ideal circumstances the correction results into the simple formula \( c_{i+1} = c_1 \), which means that the raw value \( CO2RAWUC \) is equal to the corrected value \( CO2RAW \) (except for the possibly implemented calibration).

The value \( CO2RAW \) can only be calculated from formula (4) when the four atmospheric variables are known. Like is visible in Figure 3, the Vaisala has its own temperature sensor. The other three variables need to be given to the device by hand. The oxygen concentration in air is very close to 20.95% so for our purposes within the School – \( CO_2 \) – Web this value can be fixed. For other situations, for example when measuring combustion exhaust, this would of course be different. Within the School – \( CO_2 \) – Web, pressure and relative humidity are measured by an accompanying weather station, collected, and sent automatically to the Vaisala every 10 minutes.
Like was said before, the oxygen concentration in ambient air is very close to 20.95%. Although this is not the same as the by Vaisala defined ideal concentration of 0%, it is also not changing and thus the same correction always applies. When the other three variables are assumed to be at their ideal values for a moment, formula (4) can be simplified into the following:

\[
c_{i+1}(ppm) = c_i(ppm) \times \frac{1}{9.0 \times \frac{10.000}{20.95 + 1}}
\]

Which is again equal to:

\[
c_{i+1}(ppm) = c_i(ppm) \times 1.01922
\]

Since this formula does not contain \(c_i\) anymore, it is not iterative anymore. When oxygen is apparent in the air, the measured carbon dioxide concentration is too low and therefore the correction makes sure that it is increased a bit.

Instead of correcting for oxygen, one can make sure that the instruments are calibrated with whole air cylinders, containing the normal amount of oxygen. In this way, the effect of oxygen is incorporated in the calibration and a correction is not needed anymore.

The influences of the other three variables on the CO\(_2\) measurements were investigated more closely in a laboratory set-up that is described in the next chapter.
3. Method

To determine the right corrections for the three remaining atmospheric variables it is necessary to know exactly what happens with the measured carbon dioxide concentration when one of the circumstances changes. To this end, a set-up was designed in which both pressure and temperature could be independently varied (or kept constant). This set-up is visible in Figure 4. The carbon dioxide concentration could be kept constant by flushing whole air from a cylinder. This, originally dry, air could be moistured by leading it through a water reservoir at a certain temperature before entering the PVC pipe visible in the figure.

![Figure 4: The set-up built to keep temperature and pressure constant](image)

The six holes in the cap are used to connect the Vaisala to the computer, to let air going in and out of the pipe, to provide heat and to measure temperature and pressure. All holes are closed tightly to prevent leakage of air and to keep the pressure constant. The inlet, indicated by I in the figure, is connected to the gas cylinder. The tube of copper inside the PVC pipe makes sure the ingoing air has time to adapt to the temperature in the pipe. The outlet, indicated by J can be connected to a pump. By carefully adjusting the pump and the flow from the gas cylinder, the pressure can be maintained at a constant level. Placing the pipe into a fridge or freezer and heat inside the pipe at the same time controls the temperature. Both pressure and temperature are controlled by hand.

Since the small volume of the PVC pipe is filled with air from the gas cylinder, the normal diffusive cap can be used instead of the special calibration cap. In this way the set-up is more representative for the situation at the schools, where the diffusive cap is also used.
3.1 Determining the dependences on temperature and pressure

Figure 5 below shows the set-up that was used to find the dependence of the carbon dioxide concentration measured by the Vaisala on temperature and pressure.

In this figure, the PVC pipe indicated by D is the same PVC pipe that was given in more detail in Figure 4. It can be placed in a fridge or freezer, but of course also outside at room temperature. The dependence of the carbon dioxide concentration on temperature is investigated by creating a temperature gradient over the day. By slowly heating or cooling the PVC pipe and at the same time keeping the pressure constant at 1013 hPa the dependence of the carbon dioxide concentration on temperature can be determined. In a similar way, the dependence on pressure can be investigated. The carbon dioxide concentration is then measured at different pressures, keeping the temperature constant at 25°C. This can be done by cooling the pipe in the fridge and adjust the heating inside the pipe to keep it close to the desired 25°C.

3.2 Determining the dependence on humidity

Since the air in the cylinders does not contain any moisture, something needs to be done to add water vapor to the air in order to investigate the influence of humidity on the carbon dioxide measurements. The set-up of Figure 5 is therefore extended with a water vessel and a humidity sensor. The new set-up is visible in Figure 6 on the next page. The pump is removed since it is not necessary anymore to keep the pressure constant at 1013 hPa once the right correction for pressure is found. The same is true for the temperature and therefore the PVC pipe is placed outside the fridge. The raw carbon dioxide concentration is now first corrected for temperature and pressure. What remains is the dependence on humidity.

Like is visible in Figure 6, the dry air from the gas cylinder is first bubbled through the water in the vessel before it goes to the Vaisala in the PVC pipe. In this way the air becomes saturated with water vapor at the ambient temperature, which is assumed to be equal to the temperature of the water. Cooling the water in the fridge or heating it with a hair dryer, changes the temperature of the water and the air bubbling through it and, since warm air is able to contain more water vapor than cold air, thus the water vapor content of the air.

The humidity of the air that leaves the PVC pipe is measured by a humidity sensor, indicated with G in Figure 6. The sensor that was used here is a HygroPalm22 of Rotronic (serial number 60222939).
Relative humidity is defined as follows:

$$ RH(\%) = \frac{p_{H_2O}}{p^{*}_{H_2O}} \times 100\% \tag{7} $$

In this formula RH is the relative humidity of the mixture being considered, $p_{H_2O}$ is the partial pressure of water vapor in the mixture and $p^{*}_{H_2O}$ is the saturated vapor pressure of water at the specific temperature of the mixture. Relative humidity thus gives the amount of water vapor present as a percentage of the maximum amount of vapor that can be present at a specific temperature. Since warm air is able to contain more water vapor than cold air, relative humidity does not by itself produce the actual partial pressure of water vapor in a mixture. Since this would be a much more convenient unit to use to correct for humidity, it is necessary to convert relative humidity into $p_{H_2O}$. For this, the saturated vapor pressure, $p^{*}_{H_2O}$ is needed. There are several formulas capable of approaching these values. The formula that was used here is of Wagner and Pruss (1993):

$$ \ln\left(\frac{p}{p_C}\right) = \left(a_1 \tau + a_2 \tau^{1.5} + a_3 \tau^3 + a_4 \tau^{3.5} + a_5 \tau^4 + a_6 \tau^{7.5}\right) \frac{T_C}{T} \tag{8} $$

In this $p$ is the saturated vapor pressure of water in air (in kPa) at temperature $T$ (in K), and $\tau = 1 - \left(\frac{T}{T_C}\right)$, $T_C = 647.096$ K, $p_C = 22064$ kPa, $a_1 = -7.859$ 517 83, $a_2 = 1.844$ 082 59, $a_3 = -11.786$ 649 7, $a_4 = 22.680$ 741 1, $a_5 = -15.961$ 871 9 and $a_6 = 1.801$ 225 02

Combining formula (7) and (8) results in the partial pressure of water in the air in kPa. This can be used to find the influence of humidity on the carbon dioxide concentration measurements.
4. Results
This chapter gives the results of the experiments done to investigate the influence of pressure, temperature and humidity on CO\textsubscript{2} measurements. All tests were done with the Carbocap GMP343 with the serial number D3520004. In the first section of this chapter the influence of temperature and pressure are investigated. Section 4.2 then deals with the influence of humidity.

4.1 Influence of pressure and temperature on CO\textsubscript{2} measurements
To investigate the influence of pressure and temperature on CO\textsubscript{2} measurements, the set-up that was described in section 3.1 was used. For the dependence of the CO\textsubscript{2} concentration on temperature, the pressure is kept constant at 1013 hPa while the temperature is changed. For the dependence of the CO\textsubscript{2} concentration on pressure, the temperature is kept constant at 25\textdegree C while the pressure is changed. In this way both records will contain the CO\textsubscript{2} concentration at 1013 hPa and 25\textdegree C and the same CO\textsubscript{2} concentration should be found for this point. The two records need to be adjusted to each other before a correction can be applied. Because of that this section deals with both pressure and temperature.

4.1.1. Influence of pressure on CO\textsubscript{2} measurements
In the second chapter of this report it was already explained that pressure has an influence on carbon dioxide measurements in two ways. First, the perfect gas law indicates that the amount of molecules in a fixed volume of air changes when the pressure changes at constant temperature. A different amount of CO\textsubscript{2} molecules in the Vaisala means that a different absorption is measured and thus a different CO\textsubscript{2} concentration will be calculated from that. This is undesired, since not only the amount of CO\textsubscript{2} molecules in the volume is changed, but also the amount of the other molecules, leaving the concentration of CO\textsubscript{2} in parts per million unchanged. The second effect of pressure on the CO\textsubscript{2} measurements has to do with spectrum broadening. The absorption spectrum of CO\textsubscript{2} changes when the pressure changes and therefore also this effect should be taken into account. The two effects will be indicated further on as the “amount effect” and the “spectral effect”.

The figure on the next page shows the results of an experiment done at September 16\textsuperscript{th} 2009. In this experiment the CO\textsubscript{2} concentration from a gas cylinder (with a known CO\textsubscript{2} concentration of 396.22 ppm) was measured at 25\textdegree C at different pressures varying between 918 and 1063 hPa. Every point in the graph is the average of around 30 measurements at a certain pressure. The raw data are given by CO2RAWUC and the correction of Vaisala is given by CO2RAW. Although the temperature varied slightly around 25\textdegree C during the measurements, it was decided to disable the temperature correction of Vaisala. The corrections for humidity and oxygen were also disabled, leaving only the pressure correction visible in the signal CO2RAW. To separate the “amount effect” from the “spectral effect” the signal CO2RAWUC is also corrected taking only the perfect gas law into account. The next table gives the statistics of the fits of the three records.

Table 2: Statistics of the fits of the records of Figure 7 (16 Sept)

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2RAWUC</td>
<td>0.486 ( \pm ) 0.004</td>
<td>0.9985</td>
</tr>
<tr>
<td>CO2RAW</td>
<td>-0.004 ( \pm ) 0.003</td>
<td>0.0383</td>
</tr>
<tr>
<td>Perfect gas</td>
<td>0.102 ( \pm ) 0.003</td>
<td>0.9707</td>
</tr>
</tbody>
</table>

From the figure and the table it is clear that pressure has an important influence on the carbon dioxide measurements. The same gas cylinder is used all the time so a constant CO\textsubscript{2} concentra-
tion should be measured. The correction of Vaisala should make sure that the measured signal is translated into a constant, horizontal signal.

![Graph showing the influence of pressure on CO$_2$ concentration measured with the Vaisala at September 16$^{th}$, 2009.](image)

**Figure 7: Influence of pressure on the CO$_2$ concentration measured with the Vaisala at September 16$^{th}$, 2009**

Surprisingly, and different than expected from the previous research, the correction of Vaisala is working adequately. The slope of the signal CO2RAW is very small and has a large error and the $R^2$ value is close to zero indicating a poor correlation. This makes the slope insignificant. The amount effect explains ~ 79% of the total pressure dependence, leaving thus the remaining 21% attributed to the spectral effect.

The record visible in Figure 7 was made in a set-up that appeared to be unsuitable for temperature dependence measurements. The use of the calibration cap, the disconnection of the internal heating system of the Vaisala and the very low ingoing gas flow where circumstances that became a problem in the later measurements and where therefore changed. Because of that, the measurements of September 16$^{th}$ needed to be done again, with this time the diffusive cap, the internal heating switched on and a much higher gas flow of around 0.5 L/min. Two measurements were done in this new set-up. They are visible in Figure 8 and Figure 9 on the next pages.

Unfortunately the measurements were changed due to the change in the set-up. The slope of the raw measurements changed and thus the correction of Vaisala changed too, leading to a significant overcorrection. This is clearly illustrated in both figures.
Figure 8: Influence of pressure on the CO$_2$ concentration measured with the Vaisala at November 11$^{\text{th}}$ 2009

Figure 9: Influence of pressure on the CO$_2$ concentration measured with the Vaisala at November 23$^{\text{rd}}$ 2009
The statistics of the fits in Figure 8 and Figure 9 are given in the following tables.

### Table 3: Statistics of the fits of the records of Figure 8 (11 Nov)

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2RAWUC</td>
<td>0.424 ± 0.011</td>
<td>0.9883</td>
</tr>
<tr>
<td>CO2RAW</td>
<td>-0.076 ± 0.011</td>
<td>0.7167</td>
</tr>
<tr>
<td>Perfect gas</td>
<td>0.034 ± 0.011</td>
<td>0.3391</td>
</tr>
</tbody>
</table>

### Table 4: Statistics of the fits of the records of Figure 9 (23 Nov)

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2RAWUC</td>
<td>0.444 ± 0.012</td>
<td>0.9938</td>
</tr>
<tr>
<td>CO2RAW</td>
<td>-0.057 ± 0.012</td>
<td>0.7156</td>
</tr>
<tr>
<td>Perfect gas</td>
<td>0.052 ± 0.011</td>
<td>0.6957</td>
</tr>
</tbody>
</table>

The two records made with the new set-up are less precise than the old measurement done at September 16th 2009. The errors in the slope of the raw carbon dioxide measurements are much larger here. The slopes itself are smaller than the original one, leading to an overcorrection of Vaisala, indicated by the significant negative slopes of CO2RAW in both the November 11th and the November 23rd records.

The fact that the correction of Vaisala for pressure is right for the measurement with the calibration cap suggests that Vaisala determined the dependence of the carbon dioxide concentration on pressure with this cap installed on the device. The set-up used in the measurements of November 11th and November 23rd is however more reliable since this represents the circumstances in the School – CO2 – Web more closely.

The share of the amount effect is now larger than the 79% that was determined before. In the record of November 11th the amount effect explains 92% of the total pressure dependence. In the record of November 23rd this is 88%.

### 4.1.2. Influence of temperature on CO2 measurements

The temperature also has an influence on the carbon dioxide measurements. Just like pressure, the temperature can change the amount of molecules in a fixed volume of air, through the perfect gas law. Besides, temperature also influences the absorption spectrum of CO2. So, just like for pressure, the temperature is dependent on an amount effect and a spectral effect.

Unfortunately the first measurements made showed huge differences amongst each other. It appeared to be important if the device was cooled or warmed during recording. This effect needed to be eliminated before a new correction could be determined. Because of that the original set-up was changed. The diffusive cap replaced the calibration cap, the flow was increased to ca. 0.5 L/min and the heating of the device was switched on to prevent dew formation. These adaptations were the reason that the pressure dependence measurement of September 16th needed to be done again. With these adaptations the temperature dependence measurements showed more similar results for both cooling and warming of the device, as can be seen in Figure 10.
In this figure, the two records with “Cool” in the name were recorded during cooling of the device. The third record, named “29 Warm” was recorded during warming of the device. The temperature varied between -10°C and +35°C. Note that this is the temperature measured by the Vaisala itself, which is always some degrees above the temperature of the air outside the device.

The next table shows the statistics of the fits applied on the measurements.

Table 5: Statistics of the temperature dependence measurements as shown in Figure 10

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29 Cool</td>
<td>-0.636 ± 0.003</td>
<td>0.9436</td>
</tr>
<tr>
<td>29 Warm</td>
<td>-0.623 ± 0.003</td>
<td>0.9229</td>
</tr>
<tr>
<td>30 Cool</td>
<td>-0.631 ± 0.004</td>
<td>0.9393</td>
</tr>
</tbody>
</table>

Although the slopes of the fits are alike, their variability is larger than expected based on the slope error. The two recordings made during cooling of the Vaisala are within the margins of the errors. This suggests that there is still a difference between cooling and warming of the device.

The correction of Vaisala for temperature is indicated for the record “30 Cool” in Figure 11. In this figure, the raw carbon dioxide concentration record is also translated with the perfect gas law, to indicate the share of the amount effect in the correction.
Figure 11: The temperature correction of Vaisala and the share of the perfect gas law in the “30 Cool” record

In this figure, the raw data are given by CO2RAWUC and the by Vaisala corrected data are given by CO2RAW. The pink line gives the share of the perfect gas law. The statistics of the three fits in the figure are given in the next table.

Table 6: Statistics of the fits in Figure 11

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2RAWUC</td>
<td>-0.631 ± 0.004</td>
<td>0.9393</td>
</tr>
<tr>
<td>CO2RAW</td>
<td>0.373 ± 0.004</td>
<td>0.8376</td>
</tr>
<tr>
<td>Perfect gas</td>
<td>0.755 ± 0.004</td>
<td>0.9612</td>
</tr>
</tbody>
</table>

The figure makes clear that the amount effect needs to be counteracted by the spectral effect. In the correction of Vaisala, the spectral effect is not taken into account enough, leading to a significant overcorrection. Whereas the uncorrected data decrease by about 25.1 ppm over the shown temperature range, the Vaisala corrected data increase by about 15.6 ppm; an overcorrection of ca. 62%.

4.1.3. Establishing the relation of pressure and temperature with raw CO₂ concentration

The sections above made clear that the correction Vaisala applies to correct for temperature and pressure is not working adequately. Besides, the correction of Vaisala is unnecessarily complicated for our purpose of measuring ambient air. The oxygen concentration in ambient air is always close to 20.95%, the pressure varies between ~950 and ~1050 hPa, the temperature be-
tween ~ -20°C and ~40°C and the carbon dioxide concentration between ~380 and ~480 ppm. Because of this, our correction can be simpler.

A simple pressure and temperature correction can be determined when the relations of pressure and temperature with the raw carbon dioxide concentration are known. For both relations the same carbon dioxide concentration should be the result at 1013 hPa and 25°C.

For pressure two measurements were done in the right set-up. For temperature, three measurements are available for determining its relation with the raw CO₂ concentration. The next two tables show these five records and their raw carbon dioxide concentrations at 1013 hPa and 25°C.

### Table 7: Raw value for CO₂ at 1013 hPa and 25°C in pressure records

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Slope + error</th>
<th>R²</th>
<th>CO₂ + error (1013 hPa &amp; 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Nov</td>
<td>0.424 ± 0.011</td>
<td>0.9883</td>
<td>397.4 ± 0.5 ppm</td>
</tr>
<tr>
<td>23 Nov</td>
<td>0.444 ± 0.012</td>
<td>0.9938</td>
<td>398.4 ± 0.6 ppm</td>
</tr>
</tbody>
</table>

### Table 8: Raw value for CO₂ at 1013 hPa and 25°C in temperature records

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Slope + error</th>
<th>R²</th>
<th>CO₂ + error (1013 hPa &amp; 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29 Cool</td>
<td>-0.636 ± 0.003</td>
<td>0.9436</td>
<td>398.37 ± 0.07</td>
</tr>
<tr>
<td>29 Warm</td>
<td>-0.623 ± 0.003</td>
<td>0.9229</td>
<td>400.41 ± 0.08</td>
</tr>
<tr>
<td>30 Cool</td>
<td>-0.631 ± 0.004</td>
<td>0.9393</td>
<td>399.16 ± 0.07</td>
</tr>
</tbody>
</table>

Since the same air was measured in all five recordings the same raw carbon dioxide concentration should be measured at 1013 hPa and 25°C. The tables, however, make clear that these values differ outside their error margins. Some slight adaptations are preferable to make sure the same value is found in the relation of both dependences. Although it is possible to perform a statistical analysis on the records it was decided to use a more practical and quick method to adjust the temperature and pressure relations to each other.

The tables suggest that the records for temperature are more precise than the records for pressure. Unfortunately the values for the carbon dioxide concentration at 1013 hPa and 25°C of the temperature measurements differ outside their error margins, indicating measurement problems. The pressure measurements do vary within their error margins, but since the errors are big the measurements are still not very precise. Because the temperature measurements were based on many more data than the pressure records it was decided to choose one of the temperature records as the base and adapt the pressure records within their error margins to find the same raw carbon dioxide concentration at 1013 hPa and 25°C.

For temperature the record of “30 Cool” was chosen to represent the relation between temperature and raw CO₂ concentration since this one is in between the other two records. The error in the CO₂ concentration value at 1013 hPa and 25°C was determined based on the spread of the three measurements since this was considered to be more reliable than the internal errors given in Table 8. The average CO₂ concentration at 1013 hPa and 25°C of the three measurements given in Table 8 is then 399.3 ± 0.6 ppm. Although the number of the “30 Cool” measurement is not exactly the average, it is close and therefore the error is assumed to be the same. The value for the carbon dioxide concentration at 1013 hPa and 25°C is therefore 399.2 ± 0.6 ppm. The slope and the intercept of the pressure record of November 23rd were adapted slightly within its error margins to find the same value at 1013 hPa and 25°C. This is visible in Table 9.
Table 9: The established relations of pressure and temperature with raw CO₂ concentration

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>CO₂ + error (1013 hPa &amp; 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure “23 Nov”</td>
<td>0.4440 ± 0.012</td>
<td>398.4 ± 0.6</td>
</tr>
<tr>
<td>Pressure “23 Nov” adapted</td>
<td>0.4447 ± 0.012</td>
<td>399.2 ± 0.6</td>
</tr>
<tr>
<td>Temperature “30 Cool”</td>
<td>-0.631 ± 0.004</td>
<td>399.2 ± 0.6</td>
</tr>
</tbody>
</table>

In this table, the errors of the adapted pressure relation are assumed to be the same as they were in the original pressure relation.

4.1.4. Determination of the correction for pressure and temperature

In the previous section the dependence of the measured CO₂ concentration on pressure and temperature was established. The numbers of the two relations given in Table 9 can be used to find the corrections for pressure and temperature.

The dependence of the raw carbon dioxide concentration on temperature can be written in a general form as follows:

\[ CO2_{RAWUC} = a \times (T - 25) + CO2T \]  

(9)

In this formula CO2T is the raw carbon dioxide concentration at 25°C (and 1013 hPa) and “a” is the slope of the graph. Formula (9) can be rewritten again:

\[ CO2_{RAWUC} = CO2T \times \left[ 1 + \frac{a}{CO2T} (T - 25) \right] \]  

(9*)

The term \( a / CO2T \) can be indicated as a constant \( \alpha \). Since this alpha should be the same value no matter what the carbon dioxide concentration of the calibration gas is, the slope “a” must be linearly dependent on the carbon dioxide concentration. Formula (9*) can be rewritten to find the correction formula for temperature:

\[ CO2T = CO2_{RAWUC} \times \frac{1}{1 + \alpha(T - 25)} \]  

(10)

In this formula CO2T indicates the carbon dioxide concentration at 25°C, thus in other words the carbon dioxide concentration corrected for temperature. The value \( \alpha \) can be determined from the slope and intercept given in Table 9. The error in \( \alpha \) can be determined using the errors in the slope and intercept given in Table 9 and the following formula:

\[ \left( \frac{\Delta z}{z} \right)^2 = \left( \frac{\Delta a}{a} \right)^2 + \left( \frac{\Delta b}{b} \right)^2 \]  

(11)
The final correction formula for temperature is then given in equation (12).

\[ CO2T = CO2\text{RAWUC} \times \frac{1}{1 - (0.001581 \pm 0.000010) \times (T - 25)} \]  \hspace{1cm} (12)

Exactly the same procedure can be applied to find the correction formula for pressure. The differences are the use of \((p - 1013)\) instead of \((T - 25)\) and the term \(CO2P\) instead of \(CO2T\) to indicate the carbon dioxide concentration corrected for pressure. The result is given in equation (13).

\[ CO2P = CO2\text{RAWUC} \times \frac{1}{1 + (0.001114 \pm 0.000030) \times (p - 1013)} \]  \hspace{1cm} (13)

Just like Vaisala does with the corrections for the four atmospheric variables, the two equations (12) and (13) can be combined to find one correction for both variables:

\[ CO2TP = CO2\text{RAWUC} \times \frac{1}{1 - (0.001581 \times (T - 25))} \times \frac{1}{1 + (0.001114 \times (p - 1013))} \]  \hspace{1cm} (14)

4.2 Influence of humidity on CO₂ measurements

When water vapor is added to a dry gas in constant \(V\), \(p\) and \(T\), water replaces some of the other gas molecules in the mixture. This dilution effect causes a decrease in CO₂ molecules and thus influences the absorption of infrared light. The measured concentration will be too low compared to dry air. The characteristic of water vapor to absorb infrared light is however influencing this dilution effect. More infrared light will be absorbed than in dry air and the calculated CO₂ concentration will be too high. Another possibility is that the absorption of water vapor strengthens the dilution effect, when it absorbs in the reference band of the Vaisala. All the effects together make it complicated to determine the correction for humidity.

Vaisala itself corrects only very minimally for water vapor. The table below makes this clear. In this illustration, 400 ppm was assumed to be the real CO₂ concentration \(C_{10}\) in formula 4. The pressure was assumed to be 1013 hPa and the temperature 25°C. No oxygen correction was applied. The changes in the CO₂ concentration are therefore only caused by changes in humidity.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>(C_1) (ppm)</th>
<th>RH (%)</th>
<th>(C_1) (ppm)</th>
<th>RH (%)</th>
<th>(C_1) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>400.00</td>
<td>35</td>
<td>400.82</td>
<td>70</td>
<td>401.64</td>
</tr>
<tr>
<td>5</td>
<td>400.12</td>
<td>40</td>
<td>400.94</td>
<td>75</td>
<td>401.76</td>
</tr>
<tr>
<td>10</td>
<td>400.23</td>
<td>45</td>
<td>401.05</td>
<td>80</td>
<td>401.87</td>
</tr>
<tr>
<td>15</td>
<td>400.35</td>
<td>50</td>
<td>401.17</td>
<td>85</td>
<td>401.99</td>
</tr>
<tr>
<td>20</td>
<td>400.47</td>
<td>55</td>
<td>401.29</td>
<td>90</td>
<td>402.11</td>
</tr>
<tr>
<td>25</td>
<td>400.58</td>
<td>60</td>
<td>401.40</td>
<td>95</td>
<td>402.22</td>
</tr>
<tr>
<td>30</td>
<td>400.70</td>
<td>65</td>
<td>401.52</td>
<td>100</td>
<td>402.34</td>
</tr>
</tbody>
</table>
From the user’s guide of Vaisala it is not clear what the reasons of Vaisala are behind the humidity correction. The only thing that is mentioned is that “background gasses such as humidity have an effect on the absorption strength of CO₂” (Vaisala, 2005). It was first expected that Vaisala did not correct for the dilution effect, but only for the absorption of infrared radiation (Meinema, 2009).

Another document of Vaisala about CO₂ and carbon dioxide sensors does however mention the dilution effect of water (Vaisala, 2009). It seems therefore unlikely that this effect is not accounted for in the correction. Table 10 might suggest that, according to Vaisala, the absorption effect and the dilution effect almost cancel each other out. The absorption effect in the absorption band of CO₂ seems to be a little bit stronger and therefore a small downward correction is applied.

The behavior of the measured CO₂ concentration in the Vaisala as a function of humidity was investigated with the set-up described in section 3.2. The needed partial pressure of water vapor in the measured air was calculated in two different ways: one based on the temperature of the water in the water vessel, and the other based on the humidity sensor placed after the PVC pipe.

For the water vessel it is assumed that the air is saturated with water vapor at the temperature of the water. So, with the help of formula (8) and the recorded temperature of the water the p*H₂O can be calculated. It is assumed that the air is saturated, so RH = 100% and thus p*H₂O = pH₂O.

The humidity sensor records the relative humidity and the temperature. This is the same as in the actual set-up on the roofs of the schools. With these two values and equations (7) and (8) the pH₂O can be calculated again. The next figure shows the results of two experiments carried out at the 24th of November 2009 and the 4th of December 2009.

![Figure 12: The partial pressure of water in the air calculated in two different ways on the 24th of November 2009 (left) and on the 4th of December 2009 (right)](image_url)

The figure indicates that the pH₂O measured by the sensor does not coincide with the expected pH₂O based on the water temperature. The graphs even cross each other twice, presuming that during the way the air sometimes looses and sometimes acquires water vapor. Because the humidity of the air is not measured in the PVC pipe one can only assume the partial pressure of water vapor in the Vaisala. It was decided to trust the pH₂O that was calculated based on the sensor and use this value in further calculations.

During the experiments of November 24th and December the 4th, the temperature and pressure were not maintained at their standard values of 25°C and 1013 hPa. Instead pressure and temperature were recorded and the corrections determined in the previous section were used to translate the raw measured carbon dioxide concentrations into carbon dioxide concentrations at 25°C and 1013 hPa. The remaining dependences should be caused by humidity in this way.
The next figures show these two experiments. The gas cylinder with a carbon dioxide concentration of 396.22 ppm was used in both experiments so the raw measured concentration at 25°C and 1013 hPa in dry air should be around 399.2 ± 0.6 ppm (see Table 9).

![Figure 13: CO₂ concentration dependence on humidity investigation 24th of November 2009](image1)

![Figure 14: CO₂ concentration dependence on humidity investigation 4th of December 2009](image2)

The dependence of the CO₂ concentration on humidity based on the dilution effect can be estimated. For every 10 hPa water vapor pressure the measured carbon dioxide concentration will be ~ 4 ppm lower. Since in the graph the partial pressure of water vapor varies between 0 and 30
hPa the dilution effect would cause a change from \(~399\) to \(~387\) ppm. In the figures, this expected dilution effect is indicated with a pink line. A third order polynomial fit through the dataset is indicated with a black line in both graphs. For dry air this fit should be 399.2 ppm so this is implemented in the fit.

It seems that the dilution effect, eventually together with the absorption in the reference band, is most important during low partial pressures of water vapor, leaving the absorption effect in the CO\(_2\) absorption band unnoticed first. At increasing humidity, the dilution effect becomes less important, and in some range the measured CO\(_2\) concentration is hardly influenced by the changes in humidity. This is probably due to the fact that the two effects eliminate each other. At very high water vapor pressures the absorption effect in the CO\(_2\) absorption band takes over and an increase in measured CO\(_2\) concentration is noticed.

Unfortunately the two experiments only give a basic idea about the influence of humidity on the carbon dioxide concentration measurements of Vaisala. The two records show too many differences. Based on this no accurate correction can be developed. In case however it is indeed a third order polynomial fit the correction equation will look like equation (15):

\[
CO2H = \frac{CO2RAWUC}{(1 + \alpha H^3 + \beta H^2 + \gamma H)}
\]

(15)

With in this formula \(\alpha\), \(\beta\) and \(\gamma\) based on the polynomial constants divided by the carbon dioxide concentration of the dry calibration gas, CO2H.
5. Verification of the new correction
In the carbon dioxide concentration measuring system called the Oxzala, two Vaisala devices measure dried air under constant pressure and temperature. They alternate between outside air and a reference gas and in this way the carbon dioxide concentration is measured with an accuracy of ~0.3 ppm (van der Laan-Luijkx, 2010).

An experiment was performed in which the Oxzala and Vaisala measured the carbon dioxide concentration at the same time on the roof of the Centre for Isotope Research building (University of Groningen, Zernike campus). In this experiment, the Oxzala serves as the “truth” for the Vaisala. The Vaisala measurements can be compared with the Oxzala record to check the accuracy of the new correction.

The Vaisala Carbocap GMP343 (Serial number D3520004) that was used to study the influences of pressure, temperature and humidity in the laboratory set-up was used for this verification test. The air inlet of the Oxzala system was located near the weather station, on a small distance to the Vaisala.

5.1 Circumstances and settings of the test
The verification test was performed from the 19th of December 2009 till the 28th of December 2009. The variations in the atmospheric conditions during this period are visible in the next figures.

Figure 15 shows the variation in temperature during the experiment. Gaps in the dataset appeared when the equipment failed to work.

![Figure 15: The temperature of the Vaisala and the air during the verification test](image-url)
Although the experiment was carried out in the winter, in a period with heavy snowfall, the variation in temperature is pretty large, as is visible in Figure 15. The highest recorded temperature of the air was 7.8°C while the lowest temperature was -7.8°C. Since the air in the Vaisala is always slightly higher than the air outside the device, the maximum and minimum temperature of the measured air were 17.2°C and 0.0°C respectively. These low temperatures were very favorable for this experiment since the temperature correction becomes large in this way, and is thus scrutinized more effectively.

The pressure was predominantly low during the experiment; the highest recorded pressure was 1012.7 hPa, which is already below the average atmospheric pressure of 1 atmosphere or 1013 hPa. The variation was however sufficient. The pressure variation is visible in Figure 16.

![Figure 16: The pressure of the air during the verification test](image)

Where the cold atmospheric conditions were beneficial for the temperature correction, it was not very advantageous for the humidity testing. The relative humidity is very high during the whole period, varying between 72 and 94%. The high percentages are however misleading. Because the air is so cold, the actual partial pressure of water vapor in the air is low, varying between 2.8 and 8.0 hPa. Figure 17 on the next page shows both variables in one graph. Just like the temperature sensor, the humidity sensor did not work all the time resulting into gaps in the dataset.

The previous chapter showed that it was not possible to find a satisfying correction for humidity. It was therefore decided to use only the correction for pressure and temperature, together with a calibration. Figure 17 shows that the partial pressure of water vapor was very low during the whole experiment and therefore humidity was not expected to have a large influence on the measurements. Because of this, it is hardly possible to study the influence of humidity on the carbon dioxide concentration in this test.
The original School – CO₂ – Web settings of the Vaisala at the roof of the University were changed slightly in order to get the output CO2RAWUC instead of a calibrated, corrected and filtered signal. The program gave an output every minute. The record of this value CO2RAWUC was transferred to a computer and here calibrated and corrected.

Vaisala first applies a calibration on the raw data and afterwards corrects for the atmospheric conditions. In this verification test it was decided to do the same. The calibration was based on three different carbon dioxide concentrations. In the settings of the School – CO₂ – Web two different concentrations were mostly used and the calibrations were carried out at random atmospheric conditions. For this verification test, the Vaisala was calibrated in the laboratory set-up at 1013 hPa and 25°C. The average values read from the instrument and its reference concentrations are given in the next table. A fit through these three points will represent the relation between the measured raw carbon dioxide concentration (reading) and the real raw carbon dioxide concentration (reference) at 25°C and 1013 hPa.

Table 11: Calibration of Vaisala Carbocap GMP343 D3520004

<table>
<thead>
<tr>
<th>Reading</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>397.94</td>
<td>396.22</td>
</tr>
<tr>
<td>312.50</td>
<td>308.96</td>
</tr>
<tr>
<td>459.24</td>
<td>457.58</td>
</tr>
</tbody>
</table>

It is important to note that the reading of the cylinder with a reference CO₂ concentration of 396.22 ppm is different from what was expected from earlier experiments. In the pressure and temperature corrections it was assumed that this value was equal to 399.2 ± 0.6 ppm (see Table
9). The reading is now over 1 ppm lower which is thus outside the error margins of the estimated value. This indicates the difficultnes of measuring CO$_2$ in the laboratory set-up, or simply the limit of reachable accuracy (due to short-time drifts etc).

The signal that is acquired from calibrating the raw record CO2RAW is further transferred into a signal not only calibrated but also corrected for pressure and temperature. This is done with equation (14). To compare the acquired dataset of Vaisala with the Oxzala record the Vaisala record was averaged in 5-minute intervals.

5.2 First output and time shift

The result of the experiment is visible in Figure 18 below. The figure shows the Oxzala record that is supposed to be the real carbon dioxide concentration. The Vaisala record is given in two different outputs. The calibration determined from Table 11 was applied on both those records. The applied correction was however different. The pink output called CO2RAW is based on the old Vaisala correction, although without a correction for oxygen. The grey output called CO2CalTP is based on the new determined correction for pressure and temperature that was given in equation (14) in the previous chapter. Unfortunately, all three datasets contain gaps.

![Graph](image)

**Figure 18: The Oxzala and Vaisala records of the test between the 19th and 25th of December 2009**

The record visible in Figure 18 gives an overview only. Details are not visible here. It is, however, already clear that the record with the old correction of Vaisala sometimes strongly deviates from the Oxzala signal. The explanation is the fact that the temperature was very low during the experiment. The previous chapter showed that Vaisala is overcorrecting for the effect of temperature. For low temperatures, the raw signal for the CO$_2$ concentration is too high, and because of the extreme correction the corrected value becomes too low. This deviation is not fixed, since it depends on the temperature what the deviation actually becomes.
To investigate the record more closely, Figure 19 gives the record of only two days: from the 23rd till the 25th of December 2009.

**Figure 19: The Oxzala and Vaisala records from the 23rd till the 25th of December 2009**

The three records can be seen in much more detail in this figure. Two main conclusions can be drawn from this. First, the record CO2RAW that represents the correction of Vaisala itself is constantly too low. Second, the record of the Oxzala seems to lag in time compared to the two records of Vaisala. The reason for this is the long way the air has to travel before it reaches the Oxzala system. The flow rate in the tube towards the Oxzala is very low, and as a consequence the Oxzala measures "old" air. An estimate based on the flow, the length and the diameter of the tube indicates an average delay of about 80 minutes. Based on the measurements, we have determined the delay that let the two signals fit best in time. Appendix I describes the procedure of determining the exact time shift, which indeed appeared to be 80 minutes. The time of Vaisala is assumed to be the real time, so the dataset of Oxzala is shifted by 80 minutes.

Figure 20 on the next page shows Figure 19 with now consistent time axes. The figure illustrates the huge improvement that is achieved with the new correction. The graph in light pink (CO2RAW) shows the record that would have been recorded within the School CO₂ Web. It is clear that this strongly deviates from the Oxzala signal. In contrast, the new correction works very well, showing good overlap with the true signal measured by the Oxzala.

Appendix II shows the recordings of the other eight days of the verification test.
5.3 Detailed investigation of the new correction

A quick look already tells that the new correction works much better than the old correction Vaisala applies. More details are given in this section.

A way to investigate the difference between the measurements of Vaisala and the real carbon dioxide concentration measured by the Oxzala is simply subtracting the Oxzala dataset from the Vaisala dataset. When the result has a positive sign, the measured signal by the Vaisala is too high. A negative sign means that the measured Vaisala signal is too low. This can be used to investigate if there is still an influence of pressure or temperature on the carbon dioxide measurements visible. It can also be used to investigate the influence of humidity on the measurements or the influence of the carbon dioxide concentration itself. Plotting the difference signal against one of these variables and check for a correlation can do all this.

5.3.1 Influence of the CO$_2$ concentration

The corrections for the Vaisala were determined with a gas cylinder that contained air with a carbon dioxide concentration of 396.22 ppm. Since the atmospheric carbon dioxide concentration nowadays varies between ca. 380 and 480 ppm there is a possibility that the correction based on the 396.22 ppm cylinder does not work properly for all concentrations.

The graph on the next page shows the difference signal plotted against the real carbon dioxide concentration.
Figure 21: The difference of Vaisala with the Oxzala plotted against the real CO\textsubscript{2} concentration

The statistics of the fit are given in the next table.

Table 12: Statistics of the fit visible in Figure 21

<table>
<thead>
<tr>
<th>Slope + error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.005 ± 0.007</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

As is visible in the figure and table the slope of the fit is not significantly different from zero. The conclusion that can be drawn from this is that the correction made for the Vaisala is working properly for different carbon dioxide concentrations. It is not getting worse or better for lower or higher concentrations of CO\textsubscript{2} in the atmosphere.

5.3.2 Correlations between the three atmospheric variables

The new correction that was made for the Vaisala is expected to make sure that the carbon dioxide concentration is independent on temperature and pressure, just like it is independent on the CO\textsubscript{2} concentration as was showed in the previous section. It is, however, possible that there is still some effect visible in the measurements because the determination of the correction might not be perfect. The verification test that was carried out is extremely suitable for this investigation. Just like it was done for the CO\textsubscript{2} concentration in Figure 21, the difference of the Vaisala with the Oxzala record can be plotted against the temperature and pressure. The same can be done even for humidity. Although no correction was found for this effect in the set-up in the laboratory, the influence can be investigated now in the dataset of the verification test.

To interpret the results, however, it is important to know if there is any correlation between the three atmospheric conditions themselves. When the pressure for example rises when the tem-
perature rises too, as a coincidence or not, it is not possible anymore to subscribe a certain deviation in the dataset to one of the variables. Because of that the three variables are plotted against each other in the next three graphs to check if they correlate with each other.

**Figure 22:** The relation between temperature and pressure during the verification test

**Figure 23:** The relation between pressure and humidity during the verification test
Figure 24: The relation between temperature and humidity during the verification test

The next table gives the statistics of the three figures.

Table 13: Statistics of the fits visible in Figure 22, Figure 23 and Figure 24

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T – P</td>
<td>0.026 ± 0.008</td>
<td>0.0041</td>
</tr>
<tr>
<td>P – Hum</td>
<td>-0.79 ± 0.09</td>
<td>0.0281</td>
</tr>
<tr>
<td>T – Hum</td>
<td>1.78 ± 0.03</td>
<td>0.5983</td>
</tr>
</tbody>
</table>

From the figures and the table it is clear that pressure does not correlate with temperature or humidity. From the table both slopes look significant but the figures look like chaos and the $R^2$ value is very close to zero, indicating a poor or even absent correlation.

For temperature and humidity the situation is different, which is not a big surprise. The warmer the air is, the more moisture it is able to contain and thus the higher the partial pressure of water vapor in the atmosphere can be. This implies we cannot discriminate well between eventual Temperature and Humidity dependence of our data.

### 5.3.3 Influence of temperature and humidity

The previous section showed that there is an important correlation between temperature and humidity during the experiment. Because of this, it is not easy to subscribe probable deviations in the dataset to one of the two variables. For humidity no correction was applied at all so it would
be nice if this verification test could shed some light on the influence of this variable. Unfortunately it cannot really, due to the temperature – humidity correlation.

The next two figures show the difference between the Vaisala and the Oxzala plotted against the temperature and humidity.

![Figure 25: The difference of Vaisala with the Oxzala plotted against the temperature](image)

![Figure 26: The difference of Vaisala with the Oxzala plotted against the pH₂O](image)
The statistics of the fits in the two graphs are given in the next table.

Table 14: Statistics of the fit in Figure 25 and Figure 26

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td>-0.28 ± 0.03</td>
<td>0.0498</td>
</tr>
<tr>
<td>pH$_2$O</td>
<td>-0.59 ± 0.06</td>
<td>0.0608</td>
</tr>
</tbody>
</table>

As becomes clear from Table 14, the slopes of both graphs are significant, indicating a correlation between the error in the Vaisala measurements and the pH$_2$O and temperature. For low temperatures and moisture contents the Vaisala correction resulted in too high numbers. For higher temperatures and moisture contents the correction of Vaisala gave too low numbers. The slope of the pH$_2$O graph is bigger indicating that the influence of the partial pressure of water vapor is more important than the influence of temperature. Since temperature and humidity are correlated, it might well be that it is actually only the humidity dependence that we observe here.

The influence of humidity on the measurements visible in Figure 26 shows similarities with the earlier determined dependence visible in Figure 13 and Figure 14. Based on these figures it was expected that the dilution effect is most important at lower water vapor pressures, probably combined with an absorption effect in the reference band. The partial pressure of water vapor in the air was very low during the verification test and because of that a downward influence on the CO$_2$ concentration was expected. The slope of -0.59 ± 0.06 indicates that for every hPa water vapor pressure the measured CO$_2$ concentration is 0.59 ppm less. From the dilution effect alone this is expected to be close to 0.4 ppm (see page 30). The fact that the slope is even steeper can indicate the absorption effect of water vapor in the reference band but also the rest-effect of temperature. Because temperature and humidity are correlated it is not possible to say this.

A possible solution for the problem of the strong correlation between humidity and temperature is to take a part of the dataset where temperature and humidity do not show a strong correlation and use this part to do the same investigation again. When the difference plot of Vaisala and Oxzala against temperature or pH$_2$O show again a correlation, it is clear that the deviation is caused by that single atmospheric variable and not by the other, since they are uncorrelated.

This idea was tried for several parts of Figure 24. First a part of the dataset of this figure was selected and the correlation of it was determined. When it was clear that a correlation was absent, the dataset was further used to plot the difference of the Vaisala with the Oxzala against temperature and humidity. Unfortunately, exactly in the suitable uncorrelated parts of the humidity temperature graph, the data of the Oxzala were largely not available. This unfortunate coincidence ruled out the possibility of investigating the dependence of the CO$_2$ measurements on temperature and humidity in this way.

5.3.4 Influence of pressure

Section 5.3.2 showed that pressure is uncorrelated with both temperature and humidity. Because of that, a possible influence of pressure on the Vaisala CO$_2$ measurements can be unambiguously detected. The graph on the next page shows the difference of the Vaisala record with Oxzala record plotted against pressure.
Figure 27: The correlation of the difference between the Vaisala and Oxzala with the pressure

The next table shows the statistics of the fit in this graph.

**Table 15: Statistics of the fit in Figure 27**

<table>
<thead>
<tr>
<th>Slope + error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.208 \pm 0.011$</td>
<td>0.1520</td>
</tr>
</tbody>
</table>

The slope of the fit in Figure 27 is considerable and fully significant, which means that there is still an important influence of pressure on the measurements. At low pressures, the measured CO$_2$ concentration by the Vaisala is too low and for high pressures this measured value is too high. This was also originally the case (see for example Figure 7), which means that the applied correction for pressure is probably not enough.

From formula (13) or the slopes in Figure 9, we deduce that a change of 1 hPa leads to a correction of the carbon dioxide concentration of 0.45 ppm. The slope of the graph in Figure 27 indicates that for every hPa change in pressure, the CO$_2$ concentrations needs to be corrected by another 0.21 ppm, which is a large and unsatisfactory deviation from the correction terms derived in chapter 4.

### 5.4 Possible adaptations on the new correction

The previous section showed that the CO$_2$ measurements made with the Vaisala based on the new correction still show dependences; for certain on pressure but also on humidity and/or temperature. The original determined correction that was given in equation (14) can be adapted with the help of the residual dependences found.
Since no correction was applied for humidity yet it might be convenient to assume that the correlation of the difference of the Vaisala with the Oxzala and the humidity is due to humidity and not to temperature. The fact that the slope found in the test was also expected from the laboratory experiments justifies this assumption even more. For 0% humidity no correction should be applied. For every ppm water vapor an upward correction of 0.59 ppm is needed. One has to keep in mind that this correction is only valid for the humidity range in this verification test, so pH$_2$O $\leq$ 8 hPa. The formula derived here is therefore only chosen to improve the data of this verification test, and cannot be applied on other datasets. For that purpose, a formula of the form indicated in equation (15) is required. The correction that was used for this moment is given in equation (16):

$$CO2Hum = CO2NoHum + (0.5903 \times pH_2O)$$

(16)

When this formula is added to the old correction there will be no influence of pH$_2$O on the dataset anymore, as is visible in the next figure.

![Figure 28](image)

**Figure 28:** The correlation of the difference between the Vaisala record and the Oxzala record with humidity after a correction for humidity has been applied

The next page shows the difference between the Vaisala and the Oxzala against temperature and pressure respectively after this humidity correction. The influence of temperature on the measurements is changed. This is the logical result from the fact that temperature is strongly correlated with humidity and a correction for humidity has been applied. The influence of pressure on the difference between the Vaisala and the Oxzala should not have changed since pressure is not correlated with temperature and humidity as was clear from Figure 22 and Figure 23 in section 5.3.2. Unfortunately, the influence of pressure did change, as can be seen in Figure 30.
Figure 29: The correlation of the difference between the Vaisala record and the Oxzala record with temperature after a correction for humidity has been applied.

Figure 30: The correlation of the difference between the Vaisala record and the Oxzala record with pressure after a correction for humidity has been applied.
The next table shows the statistics of the fits in Figure 28, Figure 29 and Figure 30.

**Table 16: Statistics of the fits for dependences on humidity, temperature and pressure after humidity correction is applied**

<table>
<thead>
<tr>
<th></th>
<th>Slope + error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity</td>
<td>0.00 ± 0.06</td>
<td>$3 \times 10^{-10}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>-0.02 ± 0.02</td>
<td>0.0004</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.097 ± 0.012</td>
<td>0.0402</td>
</tr>
</tbody>
</table>

The reason for the pressure dependence to change is the unfortunate fact that the pH$_2$O could not be determined for the whole dataset. For some periods the humidity sensor broke down and for these periods the pH$_2$O could not be calculated and therefore the dataset could not be corrected for humidity. These parts were therefore removed from the record. As a coincidence these parts of the record were mostly during times of low pressure. As a result the residual pressure dependence graph changed strongly, resulting in a change of the slope from $0.21 \pm 0.01$ ppm/hPa to $0.097 \pm 0.012$ ppm/hPa.

Although the humidity correction turned out to have a bad influence on the residual pressure dependence because of data losses, it has a great influence on the residual temperature dependence. The rest effect of temperature on the measurements seems to be negligible now since the slope of the fit is only $-0.02$ with an error of 0.02, making it insignificant.

It is very important here to keep in mind that the correction for humidity is only suitable for this specific dataset. For other records, especially those with higher partial water vapor pressures, a totally different correction is probably needed. Because of this important fact and the problems with the pressure dependence due to data losses it was decided to keep the original correction, as determined in chapter 4, for this moment.

### 5.5 Accuracy of the new correction

To check the accuracy of the new correction the difference of the Vaisala record with the Oxzala record was studied more closely. It was assumed that differences between the Vaisala and Oxzala record of more than 10 ppm were not realistic and therefore all outliers below -10 (67 in total) as well as all outliers above 10 (10 in total) were removed. Exactly 1800 points were left after removing these outliers.

A histogram was made of the difference between the new corrected Vaisala measurements and the Oxzala measurements (without the outliers). This is shown in Figure 31 on the next page.

The figure shows a well-shaped, normal distribution with an average of $-0.62 \pm 0.06$ ppm and a scatter of typically 2.46 ppm ($1\sigma$). The significant negative average of the difference signal indicates that the Vaisala record is on average too low compared to the Oxzala record.

Different things can be the reason for this. First of all the Oxzala record itself is not the absolute truth, since it has an accuracy of 0.3 ppm (van der Laan-Luijkx, 2010). Secondly, the Vaisala record has a systematic error due to the absence of a correction for humidity, an error in the correction for pressure and an imprecise time shift. Last but not least the calibration could be wrong. In the settings of the School–CO$_2$–Web, however, the calibration will also be done in this way and therefore it will not be possible to avoid small errors.
The dataset of Vaisala with the old correction showed an average difference of $-6.79 \pm 0.06$ ppm with the Oxzala record, with a scatter of $2.18$ ppm (1σ). Also from this dataset the outliers were removed. Compared to the old correction, the new correction is thus much more accurate.
6. Discussion

Although this research project answered many questions considering the operation of the Vaisala Carbocap GMP343 and its deviations in atmospheric measurements, there are also still some questions left waiting for an answer.

The verification test was a powerful tool to check the corrections that were determined in the laboratory set-up. In this test the Vaisala Carbocap GMP343 operated in exactly the same way as it operates within the School – CO₂ – Web. There are however some very important things to keep in mind when drawing conclusions from the comparison between the Vaisala and the Oxzala measurements.

First of all a time delay was discovered between the Vaisala and the Oxzala records due to the traveling time the air needs to reach the Oxzala. The delay was determined to be 77.8 minutes (see Appendix I) but a shift of 80 minutes was applied because of the 5 – minute output format of the datasets. The time delay therefore already causes an error in the comparison of the Vaisala with the Oxzala. Even when a time shift of exactly 77.8 minutes could be applied there would be an error since there is also an uncertainty in this 77.8 minutes.

The time delay of the Oxzala record not only causes an uncertainty in the time scale but also creates the possibility of mixing of air. Where the Vaisala measures the air that is present at that time in the device, the Oxzala measures air that first traveled through a long tube. In this tube mixing of air resulting in the dampening of concentration variability is a possibility.

A third problem originates from settings of the output of the Vaisala during the test. One output was acquired every minute and this was summarized later to get an output for every 5 minutes. The Vaisala is however capable of giving an output every 2 seconds. When this was used the average for every 5 minutes could be based on 150 readings instead of only 5. For a possible second verification test on the roof this is strongly recommended. It should also be done for the continuous settings on the roofs of the schools. In the current system this summarizing is incorporated in the filter settings of Vaisala but since all the adaptations of Vaisala itself will be disabled in the new set-up this should be incorporated in another way. In our case, using such averaging would sharpen the distribution of Figure 31, and would show remaining dependences more clearly thanks to much lower scattering.

Other problems with the measurements are for example the location of the two devices. The Vaisala and the inlet of the Oxzala were not placed on exactly the same location but several meters away from each other, differing horizontally as well as vertically. Although the two locations are not very far away from each other it is possible that both systems do not measure exactly the same air. Another problem that was seen in this research project is the difficulty to acquire the same concentration when measuring in exactly the same circumstances on two different moments. Calibrations will therefore be dependent on the accidental circumstances. Because of this there will always be some errors in the measurements. It is however already much better to calibrate in the PVC pipe at 25°C and 1013 hPa than at random circumstances.

The main conclusion that can be drawn from the verification test is that the new correction for the atmospheric conditions works much better than the old correction. For all three variables there are however some remarks left.

The dependence on temperature seemed to be well estimated in the laboratory set-up. The verification test showed a residual dependence on temperature but since this was closely correlated with humidity it is also possible, in fact more likely, that the rest correlation was not due to temperature at all. Applying a correction for humidity showed that the correlation with temperature almost completely vanished as well.
For humidity no correction could be found in the laboratory set-up. The predictions made here did however correspond to the verification test although it could only be tested for very low partial pressures of water vapor. Humidity should therefore be the main focus of a follow-up research on the operating of the Vaisala Carbocap GMP343. The set-up in the laboratory needs some adaptations in order to be able to measure the humidity in the PVC pipe itself instead of outside the pipe. When this is not possible, measuring the humidity twice, after it leaves the pipe as well as before it enters it, can give a better estimation of the real humidity inside the pipe. In this way the dependence of the CO₂ concentration on humidity can be better determined. Next to this a second verification test should be carried out, this time during a warm period of the year with higher partial pressures of water vapor in the atmosphere.

The verification test showed a remarkable residual correlation for pressure. Compared to what was found in the laboratory setting it was a really big discrepancy. The data losses due to the application of the humidity correction showed however how vulnerable this residual correlation was for outliers. It is therefore hard to say what the real residual influence of pressure was on the corrected Vaisala dataset. The influence of pressure on the carbon dioxide concentration should be investigated more closely. This is also important for testing the humidity dependence in the laboratory set-up, since the raw signal here needs to be corrected for temperature and pressure first, before the dependence on humidity becomes visible. If the pressure correction is wrong, what seems to be the case, the dependence on humidity cannot be determined.

One of the problems in the verification test was the absence of data during some periods. The Oxxala and Vaisala both did not give an output during the whole period and also the humidity sensor in the weather station broke down several times. This was caused by the harsh weather conditions of snow and freezing during the test. A possibility to deal with this problem is to fill the gaps in the dataset by extrapolating trends. This would, however, not be possible for very big gaps since the uncertainties will be too large then.

Last but not least it is important to note that all tests in this research were done with the same device of the Vaisala Carbocap GMP343 series. For pressure, humidity and oxygen content all devices are supposed to operate in the same way. For temperature, however, Vaisala defines specific constants for every single device. It will be an important part of a new research project to investigate the behavior of different devices and to see whether or not the correction found in this research holds for every device.
7. Conclusions

In this research project the influences of pressure, temperature and humidity on carbon dioxide measurements made with the Vaisala Carbocap GMP343 (serial number D3520004) were studied in a laboratory set-up. The correction for oxygen was removed since this is already incorporated in the calibration when calibrated with whole air. The internal correction functions for temperature and pressure were proven to be wrong and new, simplified, corrections were determined. For humidity no correction could be found yet, although the form of the correction function was estimated.

A verification test on the roof of the Centre for Isotope Research building (University of Groningen, Zernike campus) showed that the new correction for the atmospheric conditions worked much better than the old correction of the Vaisala itself. In this verification test, measurements made with the Vaisala were compared with measurements made with the Oxzala system, a system that measures carbon dioxide in the atmosphere with an accuracy of 0.3 ppm (van der Laan-Luijkx, 2010). The dataset of the Vaisala with the new correction showed good overlap with the Oxzala record, whereas the Vaisala measurements with the old correction showed many discrepancies.

Within the new correction, the temperature correction is assumed to be quite accurate, while the correction for pressure needs some modifications. For humidity the predictions made for low water vapor pressures in the laboratory set-up showed similarities with the verification test. For high water vapor pressures the assumptions could unfortunately not be tested and therefore no correction for humidity could be determined.

Follow-up research is needed to determine a correction for humidity. Besides, the influence of pressure needs a closer look and the whole correction should be checked for devices other than the one with the serial number D3520004.

In spite of some unanswered questions this research project can be seen as successful. The verification test clearly showed that it is possible to improve the measurements within the School – CO₂ – Web. The average deviation of the Vaisala record with the new correction in the verification test was -0.62 ± 0.06 (with a scatter of 2.46 ppm (1σ)) instead of the -6.79 ± 0.06 ppm (with a scatter of 2.18 ppm (1σ)) that was found for the old correction of Vaisala. The new correction can be improved by merely averaging over more data points taken during the same period.

It is very likely that measurements made with the Vaisala Carbocap GMP343 devices will be able to contribute to scientific research in the near future.
8. Acknowledgements
During my research I had help from several people. I would like to thank:

- Prof. Dr. Harro Meijer for his supervision of this research
- Bert Kers for all his help with building the set-up, showing me around in the laboratory and facing the snowstorm together with me to change the Vaisala on the roof
- Henk Jansen for all his help with building the set-up, buying a freezer with me and answering all my questions about working with a Mac
- Jan Schut for adapting the software to be able to perform the verification test
- Hans Roeloffzen for helping me with my problems with the computer
- Corine Meinema for her help during the starting-up phase of my research
- Jelle Nauta for his first investigation of building a suitable set-up
- Eildert Slim for measuring with the Oxzala system
- Ingrid van der Laan-Luijkx for acquiring the data of the Oxzala system
- Rolf Neubert for his help with contacting Vaisala
- All the people working at the CIO for the great time
9. References


Meinema, Corine (2009), De werking van de Vaisala Carbocap GMP343 A1A1C0C0N0B – Centrum voor Isotopen Onderzoek – Rijksuniversiteit Groningen

Vaisala (2005) – Vaisala Carbocap® Carbon dioxide probe GMP343 User’s guide – Helsinki, Finland


Appendix I: Finding the optimal time shift of the dataset

The measurements done at the roof of the Centre for Isotope Research during the last days of December 2009 show a remarkable time shift between the two records. Events in the CO$_2$ concentration seem to be recorded more than an hour earlier by the Vaisala Carbocap GMP343 than by the Oxzala system. The time delay of the Oxzala is caused by the long travelling time of the air that is needed to reach the Oxzala. A rough estimate based on the flow rate, tube length and diameter directly shows a delay of about 80 minutes. For this research it is important to determine the exact time delay. This appendix makes clear how the size of the time shift was determined.

To determine the time delay in a more strict sense, the dataset of the Oxzala was plotted against the calibrated and for P & T corrected dataset of Vaisala shifted by 0, 75, 80, 85, 90 and 95 minutes. When the two datasets were exactly the same, a perfect correlation would be found in this way, with an $R^2$ value equal to one and an error equal to zero. So, the bigger the $R^2$ value and the smaller the error, the better the match is between the two datasets. The next table shows the results of this procedure.

Table 17: Estimating the time difference between the two datasets

<table>
<thead>
<tr>
<th>Shift</th>
<th>$R^2$ value</th>
<th>Average + error [CO$_2$CalTP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 minutes</td>
<td>0.6903</td>
<td>413.17 ± 0.16</td>
</tr>
<tr>
<td>75 minutes</td>
<td>0.9061</td>
<td>412.95 ± 0.09</td>
</tr>
<tr>
<td>80 minutes</td>
<td>0.9111</td>
<td>412.92 ± 0.09</td>
</tr>
<tr>
<td>85 minutes</td>
<td>0.9057</td>
<td>412.86 ± 0.09</td>
</tr>
<tr>
<td>90 minutes</td>
<td>0.8996</td>
<td>412.83 ± 0.09</td>
</tr>
<tr>
<td>95 minutes</td>
<td>0.8909</td>
<td>412.80 ± 0.10</td>
</tr>
</tbody>
</table>

The table shows that the $R^2$ value is the closest to one for the shift of 80 minutes, indicating that a shift of 80 minutes results in the best match between the Oxzala measurements and the Vaisala measurements. The next figure shows the plots of the Oxzala and Vaisala measurements without a shift, and with the 80-minutes shift.

Figure 32: The dataset of Oxzala plotted against the calibrated and for P and T corrected dataset of the Vaisala without a shift (left) and with an 80-minutes shift (right)
The figure clearly shows that the match between the two datasets is much better when a shift of 80 minutes has been applied.

The shift has now been determined for the whole dataset. It would however be nice to take a closer look at single events in the datasets because the time delay will be very well visible there. Looking at single peaks will also reveal a new opportunity to determine the shift more precise. So far, the shift is determined to be 80 minutes, but since the format of the dataset is one output every 5 minutes, it cannot be said if a shift of 79 or 81 minutes would be better. Three events in the data set were chosen to investigate more closely. The next figures show them.

Figure 33: The first peak used to investigate the time shift

Figure 34: The second peak used to investigate the time shift
Figure 35: The third peak used to investigate the time shift

The same process that was used to determine the match for the whole dataset can be used for the three single events. Now only the shifts of 75, 80 and 85 minutes were investigated. The results are given in the next tables.

Table 18: Estimating the time difference between the two datasets in peak 1

<table>
<thead>
<tr>
<th>Shift</th>
<th>$R^2$ value</th>
<th>Average $\text{[CO}_2\text{CalTP]}$ + error</th>
<th>Error in direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 minutes</td>
<td>0.9022</td>
<td>$407.2 \pm 0.3$</td>
<td>0.04</td>
</tr>
<tr>
<td>80 minutes</td>
<td>0.8925</td>
<td>$407.4 \pm 0.3$</td>
<td>0.04</td>
</tr>
<tr>
<td>85 minutes</td>
<td>0.8435</td>
<td>$407.7 \pm 0.4$</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 19: Estimating the time difference between the two datasets in peak 2

<table>
<thead>
<tr>
<th>Shift</th>
<th>$R^2$ value</th>
<th>Average $\text{[CO}_2\text{CalTP]}$ + error</th>
<th>Error in direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 minutes</td>
<td>0.9269</td>
<td>$420.71 \pm 0.11$</td>
<td>0.02</td>
</tr>
<tr>
<td>80 minutes</td>
<td>0.9128</td>
<td>$420.82 \pm 0.13$</td>
<td>0.03</td>
</tr>
<tr>
<td>85 minutes</td>
<td>0.9034</td>
<td>$420.91 \pm 0.13$</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 20: Estimating the time difference between the two datasets in peak 3

<table>
<thead>
<tr>
<th>Shift</th>
<th>$R^2$ value</th>
<th>Average $\text{[CO}_2\text{CalTP]}$ + error</th>
<th>Error in direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 minutes</td>
<td>0.8820</td>
<td>$433.1 \pm 0.3$</td>
<td>0.05</td>
</tr>
<tr>
<td>80 minutes</td>
<td>0.8843</td>
<td>$433.2 \pm 0.3$</td>
<td>0.05</td>
</tr>
<tr>
<td>85 minutes</td>
<td>0.8738</td>
<td>$433.3 \pm 0.3$</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The three tables show some remarkable results. For peak 1 and peak 2, the best fit is achieved with a time shift of 75 minutes, instead of the earlier determined 80 minutes. For peak 3, the best fit is still 80 minutes, although the differences are very small. A probable explanation for this is that the actual shift should be somewhere between 75 and 80 minutes. The peaks can be studied in a different way to investigate this.

The two datasets are supposed to have the same form, only shifted in time. Subtracting one dataset from the other can be a tool to find the best fit. This process is illustrated in the next figure.

![Graphs shifted (left) and their resulted difference-graphs (right)](image)

**Figure 36:** Graphs shifted (left) and their resulted difference-graphs (right)

The left graph in Figure 36 shows an example of how the datasets can look like. The thick pink graph represents the goal, or real value that should be achieved when the second graph, represented by the thick black line, is shifted in the right way. The two dashed lines in grey (shifts B and C) show two possible shifts, coming closer to the goal. The dashed pink line (shift C) shows a shift that is already too far. The three possible shifts and the original starting graph are subtracted from the goal to result in the graph on the right in Figure 36. The closer the shift approaches the goal graph, the closer the difference graph approaches zero. When the shift is too far, the graph turns upside down, as is indicated by shift C.

The three studied graphs in Figure 33, Figure 34 and Figure 35 are not exactly the same in form but the technique explained in Figure 36 can still be used. For every shift the average absolute difference can be determined, which is the average distance to zero. The closer to zero this average absolute difference is, the better the match is between the two datasets. When this average absolute difference is determined for all kinds of shifts between zero and 160 minutes (shifts of 0, 20, 40, 50, 60, 75, 80, 85, 100, 110, 120, 140 and 160 minutes were used), a certain minimum can be determined. Figure 37 shows the result of this procedure applied on peak 1.

The plot as represented in this figure shows that there is a minimum. The minimum can be chosen from the three differences calculated for 75, 80 and 85 minutes but it can also be estimated by fitting a fit through the whole dataset and estimate the minimum in this. Unfortunately the dataset does not seem to represent a parabolic function with a minimum very well. The minimum was therefore also estimated with the help of two linear trend lines. The adaptations on Figure 37 are visible in Figure 38.
The process indicated in Figure 38 was repeated for peak 2 and peak 3. The optimal shift or minimum of the graphs was now determined in three ways for the three different peaks. First of all, the three average absolute differences calculated for 75, 80 and 85 minutes are compared. The next table shows this process. For the 75, 80 and 85 minutes shifts the average absolute difference was determined and given in columns 2, 3 and 4 of the table. The last column shows the optimal shift, based on the lowest absolute average difference.

Table 21: Determination of optimal shift by comparing differences for 75, 80 and 85 minute shifts

<table>
<thead>
<tr>
<th></th>
<th>75</th>
<th>80</th>
<th>85</th>
<th>Optimal shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>2.955</td>
<td>2.899</td>
<td>3.132</td>
<td>80 min</td>
</tr>
<tr>
<td>Peak 2</td>
<td>1.187</td>
<td>1.211</td>
<td>1.195</td>
<td>75 min</td>
</tr>
<tr>
<td>Peak 3</td>
<td>1.787</td>
<td>1.723</td>
<td>1.908</td>
<td>80 min</td>
</tr>
</tbody>
</table>
Secondly, the minimum of the parabolic function is determined by calculating $x$ when $y'$ is equal to zero. This is visible in Table 22 below.

Table 22: Determination of optimal shift by fitting a parabolic fit through the differences

<table>
<thead>
<tr>
<th></th>
<th>$R^2$</th>
<th>Optimal shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.9116</td>
<td>80.4 min</td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.9457</td>
<td>68.1 min</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.9199</td>
<td>74.6 min</td>
</tr>
</tbody>
</table>

In the third method the minimum is determined by calculating $x$ when the two linear trend lines are set equal to each other. The next table shows all this for the three peaks. For all linear trend lines the errors were determined and given in the table.

Table 23: Determination of optimal shift by fitting two linear lines through the differences

<table>
<thead>
<tr>
<th></th>
<th>$R^2$ (1)</th>
<th>$R^2$ (2)</th>
<th>Direction error in (1)</th>
<th>Direction error in (2)</th>
<th>Error in 50</th>
<th>Error in 110</th>
<th>Optimal shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>0.9912</td>
<td>0.9777</td>
<td>0.004</td>
<td>0.007</td>
<td>0.11</td>
<td>0.18</td>
<td>82.3 min</td>
</tr>
<tr>
<td>Peak 2</td>
<td>0.9858</td>
<td>0.9772</td>
<td>0.0014</td>
<td>0.002</td>
<td>0.04</td>
<td>0.06</td>
<td>81.4 min</td>
</tr>
<tr>
<td>Peak 3</td>
<td>0.9930</td>
<td>0.9838</td>
<td>0.003</td>
<td>0.005</td>
<td>0.07</td>
<td>0.12</td>
<td>81.9 min</td>
</tr>
</tbody>
</table>

The next table summarizes the whole process of finding the optimal shift in three peaks.

Table 24: Summary of the determination of the optimal shift in three peaks

<table>
<thead>
<tr>
<th></th>
<th>Plot</th>
<th>3 points</th>
<th>Parabolic fit</th>
<th>Linear fit</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>75</td>
<td>80</td>
<td>80.4</td>
<td>82.3</td>
<td>79.4</td>
</tr>
<tr>
<td>Peak 2</td>
<td>75</td>
<td>75</td>
<td>68.1</td>
<td>81.4</td>
<td>74.9</td>
</tr>
<tr>
<td>Peak 3</td>
<td>80</td>
<td>80</td>
<td>74.6</td>
<td>81.9</td>
<td>79.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>77.8</td>
</tr>
</tbody>
</table>

The table shows that there is a large variation in the numbers found for the optimal shift. Especially for the parabolic fit the differences are huge. These fits were also very poor which indicates uncertainties in the fit and therefore in the minimum. Inserting more shifts in Figure 37 then only the 13 shifts used now might result into better estimations.

The total average found here for the optimal fit is 77.8 minutes. This is however only an estimation. Since the dataset is given in steps of 5 minutes, it is undoable to shift the data with 77.8 minutes. A choice should be made between 75 and 80 minutes. Because the old estimation based on the whole dataset was 80 minutes and 77.8 is closer to 80 than it is to 75, it was decided to keep this shift of 80 minutes.
Appendix II: Verification test in detail

This appendix shows the verification tests in graphs of two days.

Figure 39: The verification test from December 19th till December 21st 2009

Figure 40: The verification test from December 21st till December 23rd 2009
Figure 41: The verification test from December 25th till December 27th 2009

Figure 42: The verification test from December 27th till December 29th 2009