



Final report of atmospheric monitoring of pipeline leakage

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1 Executive Summary (restricted)

This progress report presents the work that was done within project 3.6.4: atmospheric monitoring of pipeline leaks:

Within this part of the programme, we investigated the potential use of simple atmospheric CO_2 sensors for monitoring pipelines transporting CO_2 for CCS.

This work was done by the Energy Centre of the Netherlands (ECN) in close cooperation with the University of Groningen.

After initial modeling exercises that demonstrated the feasibility of a measurement setup a field test was performed with five relatively simple CO₂ sensors (Vaisala Carbocap GMP343) that were placed for more than one year in a field in Ten Post, Groningen, the Netherlands. Aim was to investigate their potential use in monitoring pipelines transporting CO₂ for CCS. The sensors showed different response to temperature changes which decreased signal to noise ratio for this application. Correction algorithms were developed that improved the detection limit for leak detection by a factor of 2.5 (the standard deviation of the average difference between two sensors decreased from 10 ppm to 4 ppm). Both laboratory or live field data correction method were used. When using lab calibration, sensor drift and temperature response calibrations have to be re-evaluated about every three months. In field data calibration can circumvent this but has some drawbacks too. Including a risk of "correcting" an actual leak during cross calibration. With a release test of CO₂ that a leak of >3 g/s would be easily detectable with sensors placed in a 70 m grid. The results of this work paper were submitted both to CATO2 and will be submitted a to a journal for peer reviewed publication.

The study shows that costs of a monitoring system, in the order of 30 keuro per km pipeline are small as compared to the pipeline cost. The detection limit of about 3 g/s is a factor 30 below the level of 100g/s that is reported as "significant leak" in the EZ-SODM annual reporting.

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2 Applicable/Reference documents and Abbreviations

2.1 Applicable Documents

(Applicable Documents, including their version, are the "legal" basis to the work performed)

Title	Doc nr	Version

2.2 Reference Documents

(Reference Documents are referred to in the document)

Title	Doc nr	Version

2.3 Abbreviations

(this refers to abbreviations used in this document)





3 Introduction

The CO₂ concentration in the atmosphere increases (Solomon et al., 2007) but reducing fossil fuel use is difficult. Carbon Capture and Storage (CCS) is considered an important option for the coming decades to reduce CO₂ emissions into the atmosphere and thus limit global climate change. In CCS, the CO₂ from fossil fuel burning is captured, transported and stored underground, for example in a depleted gas field. Doing so, CCS can buy time for the necessary energy transition. However CCS is controversial with the main public concern being potential risk on suffocation as a consequence of leaking gas. CO₂ leakage from a storage site is considered to be unlikely: chances that over 99% of the CO₂ remains in the reservoir during 100 years are in the range of 90 – 99% (Metz et al., 2005). Even if there is a leak, the change of people suffocating due to extreme high levels of carbon dioxide is even significantly more unlikely.

The maximum allowable concentration (8-hour time weighted average) is 0.5 volume percent in both the European Union and the United States. For short exposure times (15 minutes), the concentrations can be 1.5 to 3.0 percent without health danger (Croezen et al., 2007). These levels are almost two orders of magnitude above normal atmospheric concentrations that vary between 390 and 500 ppm. Concentration levels in the vicinity of a CO₂ source are set both by the source strength and by the level of mixing in the atmosphere (i.e.weather conditions).

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In spite of the low risk level it is foreseen that CCS sites will be monitored. In general, selected reservoirs in stable sedimentary basins will be safe. Abandoned gas fields contained natural gas for millions of years, which makes it likely that carbon dioxide can be stored safely for a very long time too. Wven if CO₂, unlike CH₄, can become chemically active under storage conditions (see Bolourinejad and Herber). The main risks at a storage

site are expected to be in the human-made parts: the injection wells and old abandoned wells once used for gas production (Croezen et al., 2007).

Transportation of the CO₂ to a storage location bares safety risks as well. Pipelines have an excellent safety record in general, but leakages can occur. Outside force such as damage by excavators is the most important cause of pipeline failure. Other reasons for damage are corrosion (CO₂ at high pressures is corrosive, especially in combination with water), welding and assembly faults and valve failure (Metz et al., 2005). CO2 is nonflammable

but since the gas is transported under high pressure it can explode. The induced pressure wave might injure or even kill people in the proximity of a ruptured pipe. Pipelines are equipped with emergency shutdown valves that will close to ensure that only one section of the pipe drains (OCAP, 2012). Sudden, big leaks like this will be easily noticed. It is more difficult to detect small leaks in an early stage before they gradually evolve into unacceptable situations. Monitoring leakages is not only motivated by safety considerations. For CCS to be useful in terms of mitigation of climate change, leakage in the total chain must be kept to a very low level. Leakages in transport have to be incorporated into the total CO₂ capture efficiency at the source. As capture is costly, both in terms of energy and money, there is a clear incentive to keep leakages in transport and during injection as small as possible.

Once stored, even small leakages on a yearly basis add up over the decades / centuries to unacceptable levels in climate change mitigation terms (also given the fact that capture leads to 20 - 30% more CO₂ production in the first place). Depending on the chosen time window and total amount of stored CO₂ leakage rates should be kept at least below 0.1 per cent and preferably even below 0.01 per cent per year to allow stabilization of the atmospheric CO₂ concentration (Enting et al, 2008; Haefeli et al, 2004). Atmospheric monitoring programs for CCS sites, or plans for such programs, usually consist of one

measurement location with high precision (and thus expensive and labor-intensive) measurements of CO_2 and all kinds of tracers (Etheridge et al. 2011; Fessenden et al. 2010; Jenkins et al. 2012; Spangler et al. 2009). This is not a viable option for pipeline monitoring. Leak detection of CO_2 in the free atmosphere is, however, not straightforward. The natural variability of the CO_2 concentration is considerable: day-night changes from below 380 to over 450 ppm and back are quite normal, as are changes of 10 ppm within an hour. Spatial

concentration gradients, however, tend to be small. Therefore, our leak detection strategy will have to make use of a network of detectors at relative short distance (50-100 m) from each other over the whole length of the pipeline. If there are no local CO₂ sources, such as a leak, the monitored concentration of all detectors within a certain distance varies in the same way. If there is a leak, however, the detector(s) closest to it will show a significantly higher CO₂ concentration than other detectors in their vicinity. The leak sensitivity of such a system now depends on several parameters: the geometry of the detector positions around the pipeline (most important feature is their mutual distance), and the detector characteristic short-term precision and especially long-term drift. Finally the design of such a system will always be a compromise between leak detection level and price, where the latter also includes the necessary number of maintenance and surveillance hours for the system.

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This paper evaluates the feasibility of such a leak detection system through a field test including a release of CO_2 . We have concentrated on the performance of a type of relatively cheap and simple atmospheric CO_2 sensors with which we had ample prior experience. We assessed if they are capable of operating for a long time without extensive calibration procedures or other maintenance and what their precision and long-term accuracy would be.

2. Materials and methods

3.1 Design

This project buids on the CATO 1 project in which the concept of a network was simulated. Using meteo data a from the Cabauw tall tower (KNMI, Lopik) in January, 1995, a simple Gaussian plume model was used to calculate the effect on the ambient CO2 concentration level that would emerge from a point source. These data wer added to CO_2 background concentrations that were also obtained from the Cabauw tall tower data set (Vermeulen, pers. Com.)



Figure 3.1 Spatial design of the simulation.

The simulation showed what concentration peaks can be expected at several receptors in s design illustrated by figure 3.1





Figure 3.22 Simulation series with a source of 100 g s-1in the centre of the grid(0,0) in figure 3.1. a noise level of 20 ppm was added to the background signal.

The result of these tests are documented in the Cato 1 report (Hensen & Lub, 2010) Figure 3.2 shows an example of the time series calculated for different receptor stations R1–R5. Clear deviations from the background data occur whenever the CO_2 plume "hits" one of the receptor stations.

In order to investigate the detection limit of such a design , random noise was added to the computed data series. Correlations were computed for various combinations of source strength, noise amplitude and distance of separation between the real source and the virtual source. And estimations were made of the time needed to detect a source, either by its direct effect on a downwind sensor or by the gradually increasing correlation between the real data and the virtual data on all adjacent sensors.

The main concept for the leak detection is to shift a virtual source along the pipeline transect and check for a sudden increase in the correlation between "measurement at the receptors and the and model occurs. The conclusions of the CATO-1 exercise was that a source strength of above 2 gram per seconds would be detectable when the sensor would add a noise amplitude of about 5 ppm. The calculation scheme would be able to pinpoint the leak position within a distance of about 10 m.

In this CATO-2 project actual in field measurements were carried out to further evaluate the options for a monitoring network. First a sensor was selected that is preferably robust maintenance free, stable, easy to use, accurate and not too expensive. There are many different sensors available on the market for CO₂, for various applications, varying in their

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precision, accuracy, robustness and price. Based on experiences in the EU-funded schoolCO₂web network (Carboschools), the Vaisala Carbocap GMP343 (0 – 1000 ppm) (Vaisala Finland) detector met the requirements, at a per sensor price level of about 2200 Euros (in 2012). According to specifications, the noise level should be of ± 1 ppm (30s averaging), which was confirmed already by the RUG team before this project started. This noise level should in principle allow for source detection below the 2 gram/second value obtained in the CATO-1 simulations mentioned above. The accuracy, influences of temperature and pressure on the reading of the instrument, and most importantly the long-term drift of the instruments were investigated in our field test project, which lasted over year.

3.2 Site description

The site we used for our field test is owned by the Dutch oil and gas company NAM and located close to the village of Ten Post, in the province of Groningen in the north of the Netherlands. The site is flat and the surroundings are mostly agricultural and grass lands. Since the site is a gas production site, there is a gas flare stack in the proximity of the sensors. During normal operation, the gas flare stack is not in use. There are no big towns or busy roads nearby. The field is shown in Figure 3.3 The red line in the middle of the field indicates our hypothetical pipeline.



Figure 3.3: The setup in Ten Post. Left: map of the setup. The five CO_2 sensors are number 0 to 4 in the figure. The red dotted line indicates a part of the service road around the site that was used for additional measurements with a mobile CO_2 analyzer during a release test. The black dot indicates the point of release during this test. Right: one of the sensors connected to a lamppost (no cables attached).

The setup scheme of our detectors was defined in the sensitivity mentioned above. In the simulation a 50 m grid with five CO_2 sensors was used. Because at the site lampposts were available in a grid of 70 meters, it was decided to use this configuration. The five sensors are numbered 0 to 4 in the figure. There is a service road around the gas production site (only for authorized vehicles). The dotted red line on the northeast part of this road indicates a track that was used for additional measurements with a mobile CO_2 analyzer in a truck during a CO_2 release test. The black dot in the figure indicates the point of release, our

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"leak", during this test (figure 3.4). The wind rose around it gives the orientation and distances (in 20 meter steps). The sensors were attached to the lampposts at a height of around 3 meters, as shown in the right picture in Figure 3. The lampposts are arranged in two rows, 70 meters apart from each other. Sensor 0 and 1 are 140 meters apart from each other, sensor 0 and 3 about 100 meters. At the position of sensor 0 a computer and a meteorological station (Vaisala WXT520) were installed. The meteorological station measured wind speed and direction, pressure, temperature, relative humidity and the amount of precipitation. All five carbon dioxide sensors also measured the temperature. Sensors 1 to 4 had a wireless connection with the base station while sensor 0 was directly connected to the pc at the base.

The sensors were first installed on June 16, 2011, connected on June 24, 2011 and removed again on September 19, 2011 for calibration in the laboratory. On November 4, 2011 they were back in place and they have been running more or less continuously until September 19, 2012.



Figure 3.4 : Artificial release experiment installation at the Ten Post site



3.3 Operating principle and characteristics of the CO₂ sensors

The Carbocap GMP343, like most carbon dioxide sensors, uses the infrared spectrum of carbon dioxide. The principle of the sensor is illustrated in Figure 3.5.



Fabry-Perot Interferometer

Figure 3.5: The layout and operating principle of the Vaisala Carbocap GMP343 (based on the manufacturer's manual). The miniature filament lamp gives a pulse of light that is reflected by the heated mirror on the right side of the figure. The detector is place behind a Fabry-Perot Interferometer, which is tuned to change between two wavelengths. The ratio of these two signals is used to calculate the CO₂ concentration.

The sensor is a non-dispersive infrared (NDIR) single beam, dual wavelength sensor. In the sensor, a pulse of light from a small filament lamp is reflected by a mirror and re-focused back to an infrared detector. The infrared detector is placed behind a Fabry-Perot Interferometer (FPI), which allows only certain wavelengths of light to pass to the detector. The Fabry-Perot Interferometer is tuned electrically to change back and forth between two wavelengths (4.26 and 3.9 µm). Carbon dioxide absorbs infrared radiation in the 4.26 µm band but not in the 3.9 µm region. The measurement at this wavelength thus serves as the 100% relative transmission reference signal. The ratio of the two signals is used to calculate the CO2 concentration. It takes two seconds to measure and calculate one reading (Vaisala, 2007). The Vaisala Carbocap GMP343 specifications indicate an accuracy of ±3 ppm + 1% of reading at 25°C and 1013 hPa. The noise level is determined to be ±1 ppm with 30 seconds output averaging at 370 ppm (Vaisala, 2007). Apart from random accuracy limitations, weather conditions also influence the reading of the instrument. To correct for their effect on the measurements, the manufacturer developed an algorithm to translate the CO_2 measurements to the CO_2 concentration at general atmospheric conditions, being 25°C, 1013 hPa, 0% relative humidity and 21% oxygen. Within this algorithm, the parameters for the temperature correction are sensor-specific whereas the parameters for the compensation for pressure, oxygen and humidity are supposed to be universal. The influences of pressure and relative humidity are in part easy to understand, since the measurement method is actually detecting the total number of CO2 molecules present (which

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again is a function of both relative humidity and pressure). Spectroscopic effects (like absorption line broadening as a function of pressure and water vapor absorption) are likely to be secondary effects only.

The temperature dependence, however, will be complicated, as this depends on the exact interplay between the FPI transmission pattern and the temperature dependence of the absorption of specific lines in the 4.26 μ m CO₂ absorption band. It is therefore not surprising that the temperature dependence will be instrument-specific. As the measured quantity by the detector is relative transmission, which is exponentially related to the number of CO₂ molecules present, the CO₂ concentration itself will influence the corrections as well.

3.4 Correction methods

The Centre for Isotope Research at the university of Groningen has ample experience (since 2005) with the Vaisala Carbocap GMP343 for atmospheric measurements from its deployment in the SchoolCO₂Web network (Carboschools, 2013) (van Leeuwen, 2010). The instrument has shown excellent robustness and durability in outside air, but also that the factory correction algorithm for temperature, pressure and humidity is not useful at all for ambient atmospheric conditions. Before starting the present field test, this was reexamined. An experiment was performed from January 21, 2011 to January 24, 2011 on the roof of the university. Two uncalibrated Carbocap GMP343 sensors were co-located to study their behavior in time. As expected, the raw, uncompensated, signals did not only differ by a constant value but also varied with temperature. The correction algorithm will not remove the absolute difference (which is caused by differences in calibration), but should remove, or at least considerably reduce the temperature dependence. Figure 3.6 shows the difference between the two sensors in time, both for the raw data (grey) as well as for the data that were corrected by the default correction of Vaisala (black). The correction algorithm changed the absolute signals of both sensors but not their difference. The temperature dependence was thus not removed.

The differences observed in this experiment were above the factory-specified level of ± 2 ppm. The observed behavior of the sensors in this experiment is typical for these sensors (we have tested many copies in the past years), and similar influences were thus expected for the five sensors in our field test.

The leak detection system might trigger an alarm when sensors show erroneous differences like in Figure 3.6. To implement a viable leak detection system, such effects must thus be avoided. The first option to achieve that is to calibrate all sensors and characterize them individually in terms of temperature, pressure and relative humidity dependence in a laboratory setup. Although drift of the sensors over time will still have an influence, at least the starting point will be the same, and a well-calibrated, "true" result will be delivered initially. This is a labor-intensive and expensive procedure.





Figure 3.6: Results of an experiment in January 2011. Grey: difference between the two sensors in the raw data. Black:difference after applying the default correction of Vaisala. Red: temperature registration of the sensors.

The second option is characterization and calibration while deployed with "live" data. This saves both time and money but there are several drawbacks. With this method, one of the sensors, or an ensemble average, should be chosen as the true value. The absolute level of this concentration will have an uncertainty and cross calibration of the sensors in a network assumes air concentration homogeneity. For a small area, such as our test field, and in the absence of significant sources this condition will be fulfilled. With larger areas cross calibration will have to be done in sub areas of the network. A source in the proximity of several sensors in combination with changing weather circumstances might then influence the calibration. Cross calibration should not somehow "correct" the effect of an actual leak.

Another important point is that one needs a certain level of variability of the atmospheric parameters (temperature, pressure and relative humidity) during the chosen calibration period, but at the same time has to avoid co-variation of several of them with the actual CO₂ concentration. When the calibration takes place during a few days in which the temperature and pressure are stable, it is unlikely that the correction algorithm found is also applicable in other atmospheric circumstances. For our field test, both methods were used. The influence of oxygen on the measurements has been ignored since its concentration in normal atmospheric conditions is virtually constant. The carbon dioxide concentration was also not compensated for changes in the relative humidity. Its effect was expected to be small and, more importantly, identical for all sensors, since most of the effect is due to the displacement effect described above.

3.4.1 Laboratory correction

For a laboratory calibration, a setup was developed at the Centre for Isotope Research in which the Carbocap GMP343 sensors could be calibrated and characterized for pressure and temperature. The setup consists first and foremost of a gas cylinder containing dry air with an in-house calibrated CO₂ concentration expressed on the international WMO scale. In

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the process of calibration of the sensors for this project, two cylinders have been in use: 431.6 ± 0.1 ppm for sensor 2 and 389.8 ± 0.1 ppm for the other sensors. A valve, a mass flow

controller, a leak-tight, heated, PVC tube placed in a freezer and a pump complete the system. The sensor is placed in the PVC tube. Air from the cylinder is flown through the pipe where a fan mixes the air. Pressure and temperature can be set. Changes in the sensor output are due to changes in either temperature or pressure. The pressure correction was determined and applied for all sensors. For temperature, an individual correction parameter was determined for each of the five sensors. The final correction formula is:

$$CO_2C = CO_2M * \left(\frac{1}{1 + A * (P - 1013)}\right) * \left(\frac{1}{1 + B * (T - 25)}\right) * C$$

In this equation, CO₂C is the calibrated carbon dioxide concentration, CO₂M is the measured concentration, A is the correction parameter for pressure which is the same for all sensors and equal to 0.001114, P is the pressure (in hPa), B is the correction parameter for temperature which is different per sensor, T is the measured temperature (in °C) and C is the calibration factor which is also different per sensor.

3.4.2 Live correction

For the live correction, a period was chosen for a multi linear regression. In the procedure, one sensor was chosen as a reference (another option would be to choose an ensemble average as the reference) and the measurements of the other sensors were cross-calibrated according to:

$$CO_2 R = A + (B * CO_2 M) + (C * T) + (D * P) + (E * CO_2 M * T) + (F * CO_2 M * P) + (G * T * P) + (H * CO_2 M * T * P)$$

In this formula, CO₂R is the reference carbon dioxide concentration (the concentration measured by the sensor chosen as the reference), CO₂M is the measured carbon dioxide concentration, T is the temperature (in °C) measured by the sensor itself and P is the pressure (in hPa) measured by the weather station. The parameters A till H are the results of the multi linear regression. The correction algorithm is over determined in the statistical

sense but appears to produce a proper and stable fit of good quality. In both correction methods, the raw data output from the sensor (so factory correction not applied) is taken as the measured concentration.



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4 Results

4.1 Robustness of the setup

The sensors in Ten Post have been running more or less continuously after their calibration and characterization in October 2011: from November 4, 2011 until September 19, 2012. The sensors themselves performed well over the whole period, and thus appeared to be robust enough to withstand the year-round weather conditions. Data from sensors 1 and 2 suffered from problems with the wireless data transmission, leading to considerable loss of data. These two sensors are at larger distance from the receiver. The transmission problems, although in a sense trivial, were annoying and unexpected, because initially all systems worked fine. After the calibration episode, the system in Ten Post shut down five times. Four times there was a power failure on the site, the fifth time a major system shut down was needed because of a flooding risk, the computer box had to be removed during site evacuation. No problems were encountered with the weather station.

4.2 Efficiency of the corrections and calibrations

Figure 4.1 provides an example of the signals of the five sensors with different correction methods in an arbitrary three-day period after the calibration, in December 2011. This means that at a pressure difference of 10 hPa from standard (1013 hPa) the correction in the CO₂ concentration is about 1.1%. The amount effect (perfect gas law) explains about 90% of the total pressure dependence, leaving the remaining 10% attributed to spectral effects (van Leeuwen, 2010). The laboratory correction and four different live corrections are visible in the figure and can be compared to the raw data. The manufacturer's correction algorithm is now shown here, as it did not significantly change the raw concentrations (as explained before). For the live corrections, data from the month November 2011 were used.

The full month correction uses all the data available from this month from November 4 onwards. The 15-Days calibration uses the data from November 7 till 21. Two different 3-Day periods were used: 10 - 12 and 22 - 24 November. This period from 22 to 25 December 2011 is representative for the first months after the calibration. The laboratory correction and the live correction with the full month November perform equally well. The Correction with 15 days is acceptable but gives slightly lower quality. The performance of the 3-Day corrections is more or less random, highly dependent on the atmospheric circumstances of those three days.



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Figure 4.1: A typical result of the CO₂ signals achieved with the different correction procedures available: the raw data, the laboratory correction and four different live data corrections. For these last methods data from November was used: the full month, 15 days and two times three days.

Using the period 10 - 12 November for the correction, sensor 1 becomes a significant outlier. When the data of 22 - 24 November are used, this is not the case for sensor 1 but instead for sensor 0. Because sensor 0 is regarded as the "true" sensor, all other sensors are thus collectively corrected in the wrong direction.

The fact that sensor 1 becomes an outlier in one case is not surprising. During the characterizations in the laboratory, sensor 1 appeared to be different in its behavior compared to the other sensors. In general a negative relation between the carbon dioxide concentration reading and the temperature was found. For sensor 1, however, this relation was positive. While for the laboratory correction algorithm this merely leads to a positive instead of a negative coefficient (B in equation 1), this deviant behavior apparently could not be determined well enough with a live correction using only 3 days.

Figure 4.1 gives an overview of the behavior of the different correction methods in time. They are compared to the raw data. The graph to the left gives the average of the difference



between all unique pairs of two sensors per month throughout the whole experiment. The graph to the right gives the accompanying standard deviations.



Figure 4.2: Left: the average of the difference between all unique pairs of two sensors per month, for five different methods and the raw data. Right: the accompanying standard deviations.

Figure 4.2 shows that the live correction we have performed is highly dependent on the specific sensors and the atmospheric conditions during the chosen period. Three days are not sufficient in any case, as was clear already from Figure 4.1. Live corrections with other three-day-periods showed similar results. The live correction with 15 days gave reasonable quality. For the average of the difference between all unique pairs of two sensors, this correction surprisingly worked out best in the end of the period that was studied. The standard deviation, however, is relatively high for this method, and above the standard deviation for the live correction of the full month and the laboratory correction.

The laboratory and full month live correction might be considered as equally well although in the long term the laboratory correction appears to work out better. The correction of the manufacturer did not significantly change the raw signals and its results are thus not displayed.

The standard deviation of the difference between two sensors is indicative for the noise in a difference signal. When looking for a leak, a sensor will be compared with the local background concentration, deduced from the other sensors nearby. The wider the noise band of this difference is, the more difficult it becomes to find a leak.

Because of this, the standard deviation of the difference between two sensors is more important than the absolute difference. With this in mind, the laboratory and full month live correction seem to be the best options for correcting the raw signals. We can conclude that at least in the first half year, the two correction methods improve the sensitivity for leaks considerably (on average around 45% in the first four months). After about eight months, however, these corrections are not beneficial anymore compared to the raw signal of the sensors. Figure 4.3 clearly shows that the sensors are significantly drifting over time, both in the absolute sense and in their temperature dependence, which is indicated by the growing

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standard deviation of the difference. The factory specifications report a long-term stability of less than 2% of reading per year in "easy" operating conditions. For "moderate" or even "harsh" operating conditions this is less than 2% of reading per six months or even three months respectively (Vaisala, 2007). For this application outside in a windy and rainy environment (see the right picture in Figure 3.3), the conditions can be considered harsh. In that case, at an average CO₂ concentration of around 400 ppm, the sensors are supposed to drift up to 8 ppm in half a year time. This implies a typical average difference of 11 ppm ($\sqrt{2}$ * 8) after half a year. Figure 9 illustrates the drift of the difference between the unique sensor sets in time (laboratory correction), based on an average difference for each month. The average in Figure 8 is based on this.



Figure 4.3: The drift between all unique pairs of sensors in Ten Post. For every month, the laboratory correction signals were subtracted from each other and averaged.

In this project the drift over time was above factory specifications. In November 2011, just after the calibration in the laboratory, an absolute average difference of 1.7 ppm was found. In June 2012 this difference for a pair of sensors had increased to 18.5 ppm. That level is above the expected value of 11 ppm mentioned above. In August 2012 the absolute average difference increased to 22.1 ppm for the other sensor combinations.

Based on our findings, a new calibration is needed every three months to maintain accurate performance. As the standard deviation will also increase after about 4 months (Figure 4.2), both a calibration and a new temperature characterization would be required.



4.3 Release test

On January 24, 2012 a release test was performed at the site in Ten Post. A total of sixteen cylinders with pure CO_2 gas (37.5 kg per cylinder) were placed on the site and the carbon dioxide was released with around 10 g/s (see photo in figure 3.4). The point of release is indicated with the black dot in Figure 1. Mobile measurements with the ECN truck (figure 4.4) were performed on the transect that is also shown in figure 3.3. These data were used to evaluate model settings.



Figure 4.4 mobile CO₂ and CH₄ plume measurements around the Ten Post site.

The release started at 11:00 hours and based on the content of the cylinders and the flow lasted for 16 hours. Unfortunately the wind speed dropped below 1 m/s from 17:00 onwards. At wind speeds lower than 1 m/s, the behavior of the plume of CO_2 is hard to predict. Because of that, only the time between 11:00 and 17:00 has been evaluated. Even during this time the wind speed was much lower than the Dutch average (2011) of 4.8 m/s (KNMI, 2012). Figure 4.5 shows the wind speed and wind direction over time (see Figure 3.3. for the wind rose) during the release test.



Figure 4.5: Left: the wind speed during the release test with wind speeds lower than 1 m/s indicated in grey. Right: the wind direction during the release test.

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During the release, the wind direction was such that one would expect to see the plume of CO₂ mainly on sensor 0 (at wind directions around 250/260° and also closest by) and partly on sensors 1 and 3 when the wind turned. Figure 4.6 shows the measurements (corrected with the laboratory correction) during the release test. It shows the expected increase at sensor 0 in the beginning of the test and again around 16:00. For sensor 3 there is also a small increase visible around 15:00 and around 16:45. For sensor 1 no clear increase is visible in this figure, which was unexpected. Sensor 3 gives a significantly lower concentration than the other sensors. As can be seen in Figure 4.1, it was already lower in December. Apparently this difference increased in the month that followed.



Figure 4.6: The measurements (laboratory calibrated) during the release test on January 24, 2012

A Gaussian plume model was used to predict the enhanced CO₂ concentration at the sensor positions. As expected, no increase was visible at sensors 2 and 4. They can be considered as background sensors during the test. The measured CO₂ increase of a sensor is now defined as the difference between this sensor output and the background level, the latter being the output of one of the background sensors. In our case sensor 4 was used as the background sensor. Figure 4.7 shows the modeled and measured CO₂ increase for sensor0.

The model corresponds reasonably well with the measurements, both in time scale and in the height of the CO_2 increase, the model overestimates the increase around 16:00. Part of this can be explained by the low wind speed during the test causing difficult determination of the wind direction and unpredictable behavior of the plume. A slight adaptation of the wind direction for example already makes the model more consistent with the measurements for this time.

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Figure 4.7: The output of the Gaussian plume model for the position of sensor 0 and the measured CO₂ increase of sensor 0 (the difference between sensor 0 and background sensor 4).

For sensor 1 and sensor 3, the model only shows an increase for the second half of the afternoon, and unfortunately this is exactly at the times around 15:00 and 16:45 when the wind speed was the low (Figure 4.5). Figure 4.8 shows the modeled and measured CO₂ increase of sensor 3 (corrected for the offset of sensor 3 with sensor 4). The measured increase in the CO₂ concentration at this sensor corresponds well with the modeled increase, at least in time. The model however predicts a concentration that is higher than the observed one, especially for the peak around 15:00.



Figure 4.8: The output of the Gaussian plume model for the position of sensor 3 and the measured CO₂ increase of sensor 3, slightly shifted to correct for the offset.

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Figure 4.9 shows the modeled and measured CO_2 increase of sensor 1. As was discussed before, sensor 1 has deviant temperature dependence. This is clearly visible in the figure. The measured CO_2 signal is not constant for most of the time, as was the case for both sensor 0 and 3. The temperature, plotted in the same figure, suggests that the temperature correction algorithm is not valid at the time of the experiment. This changed behavior of the sensor leads to extra noise that prohibits the detection of the peak from the released CO_2 .



Figure 4.9: The output of the Gaussian plume model for the position of sensor 1 and the difference between the measured concentration at sensor 1 and background sensor 4 (shifted a bit to correct for the offset).

A live correction with data from shortly before the release test might (at least partly) solve the problem but unfortunately only seven days of data were available due to the evacuation of the site in January. Using these data did not improve the signal. Also using sensor 2 as background instead of sensor 4 did not change the results significantly.

During the release test, mobile CO_2 measurements were done from a truck (figure 4.4) driving on the road indicated with a red dotted line in Figure 3.3 with its front pointed towards the southeast. The CO_2 concentration was measured with a LICOR 6262 non-dispersive infrared monitor, which is much more precise (0.1 ppm at 1 Hz) than the GMP343. The air intake was pumped with 7 L/min through a 5 meter ." tube (PTFE). The tube was attached to a boom that was held outside the truck to minimize the influence of the truck itself. Different inlet heights were used during the experiments.

Figure 4.10 shows the mobile measurements (left) and the corresponding model output (right). The measurements and model outputs are expressed on a relative scale since the GPS (Garmin 76 with 2 Hz output) could not determine the position of the truck precise enough.² When driving back and forth the truck was not turned, to keep the truck engine

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exhaust on the leeside of the vehicle. Still during these backward trips, a small CO₂ peak was visible every time in the beginning (not visible in the figure), caused by the exhaust of the truck itself, despite of the use of the boom for the air inlet.



Figure 4.10: Left: truck measurements with in grey-colors and indicated with an f: driving forward and in green-colors and indicated with a b: driving backwards. The height of the air inlet is indicated in cm. Right: the corresponding model outputs.

The measured peaks give an indication of the plume of CO_2 on the road. They corroborate the Gaussian shape of the plume. The width of the plume is hard to determine from the measurements as this is based on the GPS measurements, which were not very precise. The CO_2 peak height is more variable in the measurements as compared with the model output.

Measurements performed at different inlet heights (0.2-2m) did not show no clear differences. This is important because the idea that a CO₂ plume will stay close to the ground due to the CO₂ density is widespread. This however will only be the case at much higher mixing ratio's so for leaks that are high above the 10g/s used here.

It needs to be said that these mobile measurements were done in the middle of the afternoon when the atmosphere is well mixed.

Based on the measurements and the model the CO_2 source strength for the by leak at it's known position was between estimated to be 8 and 13 g/s. The average level agreed well with the known CO_2 source strength of 10 g/s. With the prevailing winddirection during the campaign Sensor 0 appeared provided most information: without this sensor the leak would have been estimated using the other sensors that were in the plume for during episodes with changing wind directions, using only these sensors the source estimate would have been underestimated, typically between 2 and 8 g/s.



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5 Conclusions

5.1 Technical and scientific issues

Aim of this work was to investigate the use of relatively simple atmospheric CO2 sensors for monitoring CO₂ pipelines (in connection with CCS). Five sensors were deployed in a field in Ten Post in the north of the Netherlands for more than one year. The sensors were robust enough to stand the year-round weather conditions but showed a drift above the manufacturer's specifications. After half a year, two sensors differed on average 18.5 ppm, which is above the expected 11 ppm. It was known that the sensors show an individual strong dependence on temperature, even with the factory correction algorithm switched on. Laboratory calibrations and characterization for temperature and pressure were performed and compared with corrections determined from field data. A correction algorithm based on field data of a full month appeared to be of equal quality as the laboratory correction. In both cases the average 1 standard deviation of the difference between two sensors decreased from around 10 to 4 ppm, which can be seen as an improvement of a factor 2.5 for the sensitivity for leaks. Unfortunately, this improvement gradually deteriorated and had disappeared after six months, meaning that frequent calibration and temperature characterization is required. There is a limited set of relatively low cost sensors available that can be used for leak detection monitoring along pipelines (or in a fence line application around CO₂ treatment facilities of whatever kind). It is very likely that other, often even simpler CO₂ sensors show similar or worse problems in calibration and temperature dependence.

A release test of several hours showed that a leak of 10 g/s is easily visible on sensors placed at a 70 m grid around a virtual pipeline. Even when the nearby sensor would have had a bandwidth of 10 ppm the leak would have been easily detected. For sensors further away (>80 m) detection of this leak appeared to be not only dependent on wind direction but also on the correction algorithm and quality of the sensor. The increase on one of the sensors was around 10 ppm, which was visible now because of the reduced bandwidth of the difference signal of this sensor with a background sensor. A Gaussian plume model predicted the rise of the CO₂ concentration on a third sensor but as this sensor was of poor quality no increase could be noticed on top of the wide noise-band. During the laboratory characterization it was discovered that this sensor had an opposite temperature dependence compared to the other sensors. It is very likely that the only indication one would have for a leak comes from sensors on a distance >80 m. To find small leaks (3 – 10 g/s) it is therefore necessary to calibrate and characterize the sensors for temperature dependence. Sensors of poor quality should be removed. Doing so, a system with sensors in a 70 m grid will be able to detect leaks > 3 g/s. We advise thorough calibration and characterization of the sensors in a lab situation before field operation To avoid deploying sensors with deviant behavior.

After installation, calibration and characterization can be maintained by a "moving average" approach, in which sensors are live calibrated on a daily basis using the last month of ensemble data of the subset of sensors close-by. In this way the average differences between sensors, and their standard deviation, can be kept minimal for an extended period of time. Nevertheless, in the course of time, the various subsets will inevitably collectively deviate from the true values. Also, since the readings of the different sensors will deviate

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more and more as time goes by, the live calibration will become less successful, leading to larger standard deviations and, thus, lower detection limits. Furthermore, the strategy as a whole bares a risk that a leak is mistreated as being a change in, for example, the temperature dependence of a sensor, or vice versa.

Leak detect does not only use the CO_2 measurement data. Continuous plume model calculations are needed assuming imaginary leaks that along the pipeline transect. Wind speed and wind direction data are used to calculate "expected" plumes for all relevant measurement stations. On-line correlation between the modeled data and sensor measurements will then reveal sources whenever they occur. In addition more accurate CO_2 sensors could be places along the transect in order to further improve absolute CO_2 concentration levels which might lower the detection limit. The collected data enable the further design of such a system.

Technical issues that have to be addressed are the wireless data transmission and the total shutdown of the system after a power failure. In this project this led to considerable data loss which is unacceptable for a real monitoring and surveillance system.

5.2 Cato project relevance

The Netherlands has a dense network with pipelines and extensive experience with pipeline management. Pipeline safety is high and monitoring of pipelines is done continuously. Significant releases can occur however when a pipeline is damaged at excavating work. The ministry (EZ-SODM) keeps track of release incidents. They define the source strength for a significant gas release as 100 gram/second or 1kg/second for 2-5 minutes. The aim of the measurement setup as described is to detect emissions that are at least a factor 10 below that level. The idea is that events with large emissions do not need an atmospheric tracer system because these leak are obvious. In fact the system as designed and tested in this project detects leaks above 3 gram CO_2 /second.

The tested configuration uses about 8 sensors per km pipeline, which will typically cost 15 keuros for the sensors. In addition, a weather station, computer, protective boxes and wireless data transmission system are required. Total costs for installation (including working hours) are estimated to be 30 keuros per km pipeline. The costs of a pipeline vary more than an order of magnitude, depending mainly on the trajectory and size of the pipe. Prices range from 232 to 1,730 keuro per km pipeline (price level third quarter of 2012) (DACE, 2012). The installation costs of a leak detection system like presented in this paper range thus from "affordable" to almost negligible. Maintenance costs are more difficult to estimate and compare. Nevertheless, we conclude that the price of such a monitoring system need not impair its implementation.

There are several reasons to deploy a system like this. It can provide an "operatorindependent" alarm system when run indeed by an independent organization or for example an environmental authority. Since there is much public controversy about CCS, an extra independent security system might help acceptance. Detecting small leaks of CO₂ is not important for human health, but a slightly increased level of CO₂ in the atmosphere

can indicate a bigger problem in the ground. As CO₂ is heavier than air, it can accumulate in the ground where high concentrations can arise. This can be a problem for the animals living

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there, for the groundwater and the plants (Croezen et al., 2007). It is also possible that high concentrations occur in basements or caves. The third reason for atmospheric emission monitoring, assessing the efficiency of the technique, is arguably the most important one. When a reservoir or pipeline is leaking, even when it is not much, the CO₂ emission reduction and thus climate change mitigation will be reduced.

Finally, the CO_2 sensor arrays along a pipeline can provide useful input for scientific evaluations of the CO_2 exchange between the atmosphere and biosphere. It can help to evaluate the spatial distribution of CO_2 source and sink areas. This might seem a side dish for the Cato menu, but it is not unlikely that, in the absence of leaks, this will turn out to be the main application of the data once a detection system is in operation.



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