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## Highly precise atmospheric oxygen measurements as a tool to detect leaks of carbon dioxide from Carbon Capture and Storage sites

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Carbon Capture and Storage (CCS) is considered to be an important option in combatting global climate change, at least as long as fossil fuels still play an important role in our society. In this technique, carbon dioxide ( $\text{CO}_2$ ) is not emitted to the atmosphere but instead captured from the source (e.g. a power plant) and stored underground into a geological formation. Although geological storage of  $\text{CO}_2$  is considered to be very safe, leakage of the gas from the storage reservoir back to the atmosphere is an important concern, from a public health but even more from a climate change combat perspective. For CCS to be useful, leakage in the total chain must be kept to an absolute minimum.

Detecting and quantifying leaks of  $\text{CO}_2$  in the atmosphere is difficult due to the rapid mixing of the emitted  $\text{CO}_2$  with the surrounding air masses, in combination with the high natural variability of the  $\text{CO}_2$  concentration in the atmosphere. Sources of  $\text{CO}_2$  (both from biospheric origin and through fossil fuel burning) and sinks (photosynthesis) in combination with atmospheric mixing and demixing dynamics influence the  $\text{CO}_2$  concentration on a local scale. During a day variations from below 400 ppm (daytime) to over 450 ppm (night-time) are quite common. In this thesis two strategies are presented to nevertheless be able to detect leaks of  $\text{CO}_2$  by atmospheric measurements.

In the first technique, multiple  $\text{CO}_2$  sensors were placed in close proximity of each other. Although the variation of the  $\text{CO}_2$  concentration is high in time, it is low in terms of space, at least on small scales. When placed in a small area, all sensors should in principle measure the same  $\text{CO}_2$  concentration, unless there is a source of  $\text{CO}_2$  in the area under investigation. In that case, several sensors would still measure the same, background, concentration, while at least one sensor would measure an increased  $\text{CO}_2$  concentration, depending on the wind direction. This principle was demonstrated in a test field in Ten Post (Groningen, the Netherlands), where five relatively simple  $\text{CO}_2$  sensors (Vaisala Carbocap GMP343) were placed in a 70 m grid, imitating the monitoring of a  $\text{CO}_2$  pipeline (chapter 2). The sensors were deployed in the field for over one year and appeared to be robust enough to stand the year-round weather conditions. The sensors did, however, all react differently on temperature changes: a property that needed to be taken into account. Two different correction methods were developed to remove the influence of temperature on the  $\text{CO}_2$  measurements: a correction determined in the laboratory and a correction based on field data. Both methods had their own drawbacks: establishing a laboratory correction is labor-intensive and thus expensive, while using field data to determine a correction requires sufficient variability of the atmospheric circumstances and involves the risk of correcting for an actual leak. The principle of detecting  $\text{CO}_2$  leaks with this setup was demonstrated with a  $\text{CO}_2$  release experiment in which  $\text{CO}_2$  was released with a flow rate of  $10 \text{ g s}^{-1}$  for about 16 hours in the middle of the  $\text{CO}_2$  sensor configuration. It was shown that a leak of  $> 3 \text{ g s}^{-1}$  would be easily detectable with sensors placed in this 70 m grid.

The second technique presented in this thesis to detect a leak of  $\text{CO}_2$  from a CCS site is much more sophisticated: it combines highly precise atmospheric  $\text{CO}_2$  measurements with atmospheric oxygen ( $\text{O}_2$ ) measurements. Sources and sinks of  $\text{CO}_2$  and  $\text{O}_2$  are coupled in almost all processes on earth. In photosynthesis, plants take up  $\text{CO}_2$  and release  $\text{O}_2$  at the same time. In fossil fuel burning and biosphere respiration this is the other way around. The

$O_2 - CO_2$  exchange ratio depends on the process and is roughly -1.1 for biosphere activities and on average about -1.4 for fossil fuel burning. The  $CO_2$  and  $O_2$  concentrations show a roughly mirrored pattern in time, and when plotted against each other they show a linear relation, with a slope of -1.1 or slightly lower, depending on the share of fossil fuel combustion in the measured air mixture. In case of a leak of  $CO_2$  from a CCS site, there is no counterpart in  $O_2$ , which leads to a "slope" in an  $O_2 - CO_2$  plot of essentially zero. This principle was demonstrated by several  $CO_2$  release experiments (chapter 4), in which  $CO_2$  was released at a small distance from the air inlet of a new, transportable,  $O_2 - CO_2$  measurement system. Two (complementary) strategies were developed to analyze a combined  $O_2 - CO_2$  dataset to find a leak of  $CO_2$ . In the first technique, the  $O_2 - CO_2$  behavior in time intervals (e.g. hours) is compared to the general relationship between  $O_2$  and  $CO_2$  by quantifying the deviation from what is defined as normal (a slope of around -1.1). In the second strategy, the  $O_2 - CO_2$  slope is determined for certain time intervals and plotted over time. In case the slope is higher than a certain defined limit, the time interval is marked as suspicious (that is, a leak might be present).

The most difficult part of the leak detection strategy with combined  $O_2$  and  $CO_2$  measurements is measuring atmospheric  $O_2$ . Unlike atmospheric  $CO_2$  measurements, which have become increasingly straightforward in the past decades, measuring atmospheric  $O_2$  is still a challenging task that is currently only performed by about a dozen laboratories in the world. The reason for this is the high background concentration of  $O_2$  in the atmosphere (21% or 210000 ppm compared to 400 ppm for  $CO_2$ ), which makes it difficult to detect the relative variations of  $O_2$ . The Centre for Isotope Research (CIO) of the University of Groningen, the Netherlands, is one of the laboratories able to perform highly precise measurements of atmospheric  $O_2$ . Flask samples for  $O_2$  measurements are taken for already more than 15 years at the two measurement stations Lutjewad (the Netherlands) and Mace Head (Ireland). The flask samples are analyzed on a Micromass Optima Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) in a climate-controlled room at the laboratory of the CIO in Groningen, the Netherlands. Previously, the CIO also measured flask samples from other locations (the North Sea gas production platform F3, the Netherlands, Fyodorovskoye, Russia and Jungfrauoch, Switzerland). Very recently flask samples are also taken at Halley station, Antarctica. In addition to flask sample measurements, continuous atmospheric  $O_2$  measurements are performed at F3 since 2008 and at Lutjewad since 2011. All of these measurements can give valuable information about the global carbon cycle and specifically about the uptake of  $CO_2$  by the oceans, where  $O_2$  and  $CO_2$  are uncoupled, just as in CCS processes.

This thesis presents an update of the long-term flask sample data records of Lutjewad and Mace Head and in addition the first measurements of the continuous  $O_2 - CO_2$  measurements at Lutjewad (chapter 5). By using only samples collected at baseline conditions, trends and seasonal cycles could be fitted to the datasets. Due to its remote location and the wind coming mostly from the ocean, the dataset of Mace Head appeared to be very robust. A large gap in the  $O_2$  measurements around 2009 (caused by contamination issues in the flasks) did, however, cause problems in determining the trend. Lutjewad station included more locally influenced samples, with as a consequence a higher need for background condition filtering and more variation in the trends and seasonal cycles. The new continuous instrument running since 2011 suffered from many gaps in the dataset,

which caused problems in the trend and seasonal cycle determination. Trend and seasonal cycle determination is, just as measuring the O<sub>2</sub> concentration of the atmosphere, a delicate task.

For the purpose of leak detection at CCS sites, a new, transportable, instrument was designed for continuous O<sub>2</sub> – CO<sub>2</sub> measurements (chapter 3). The new instrument was based on the original continuous instruments of the CIO (placed at F3 and Lutjewad), but was made transportable by changing three main things: the packing of the core instruments, gas handling equipment and electronics, the packing of the high-pressure gas cylinders that are necessary for the measurements, and the air-drying of the system, a requirement for atmospheric O<sub>2</sub> measurements. Besides these three main changes to facilitate the transportability of the system, several things were improved compared to the original systems (amongst others the CO<sub>2</sub> sensor, the valves and switching time). The transportable system consists of three cases (for the instruments, gas cylinders and air drying respectively) that can be placed in any building, and a 6 meter tall mast containing the air inlet, that can be placed anywhere in the field. For the O<sub>2</sub> measurements, all three systems of the CIO use the fuel cell technique, with the commercially available Oxzilla II instrument from Sable Systems. Different from the two fixed systems of the CIO, the transportable system uses a high-quality CO<sub>2</sub> sensor (ABB's Uras26 NDIR) with an excellent precision for the CO<sub>2</sub> measurements ( $\pm 0.01 - 0.02$  ppm).

The quality of atmospheric O<sub>2</sub> measurements at the CIO (extensively discussed in the appendix of this thesis) is sufficient but not state-of-the-art compared to some other laboratories. For measurements on the DI-IRMS the precision depends on the type of measurement. The precision of a single measurement of a high-pressure gas cylinder was found to be 10 – 14 per meg, while the precision of a single flask measurement was found to be 6 per meg – a factor 2 better. The origin of this difference can be found in problems with the regulators that are necessary to deal with the high pressures in gas cylinders. These problems are also causing difficulties in establishing the international scale in the laboratory, as this is all based on gas cylinder measurements. Efforts to improve the gas cylinder measurements in the laboratory of the CIO are underway. For the two continuous instruments discussed in this thesis the precision of the O<sub>2</sub> measurements was found to be 11 – 15 per meg for (target) gas cylinder measurements. Similar values were found for outside air measurements of the new transportable system. For the fixed instrument at Lutjewad the outside air measurements appear to be significantly better (a precision of about 3 per meg was found), indicating that also here there are specific problems with measuring high-pressure gas cylinders.

The precision in both the CO<sub>2</sub> and O<sub>2</sub> measurements of the transportable system is very important as this determines the leak detection limit of the technique for leaks of CO<sub>2</sub>. The smaller the scatter about the linear relationship between O<sub>2</sub> and CO<sub>2</sub> in natural circumstances, the easier a leak will stand out. The leak detection limit of the new transportable instrument was estimated to be around 6 ppm. If a transportable design would not be necessary, the precision of the O<sub>2</sub> measurements could be improved such that the ultimate leak detection limit of this technique is estimated to be around 3 ppm. This would correspond to distances up to 500 meters for a leak of 1000 ton CO<sub>2</sub> year<sup>-1</sup> (32 g s<sup>-1</sup>) provided favorable atmospheric conditions (wind direction and atmospheric stability) exist.

The natural variability of the  $O_2 - CO_2$  exchange ratio is limiting a further reduction of the detection limit.

For a real CCS monitoring setup, a combination of the two techniques presented in this thesis is probably the ideal solution. Different combinations can be suggested. For  $CO_2$  measurements, one could use several simple and cheap sensors such as presented in this thesis, or use a smaller amount of more sophisticated sensors. Another alternative is to measure the  $CO_2$  concentration over a large area by using long-distance open path laser spectroscopy techniques. Atmospheric  $O_2$  measurements could be performed at only several of the measurement stations in the field that needs to be monitored, but one could also deploy a transportable instrument such as the one presented in this thesis and bring it to suspicious locations if necessary. One single atmospheric leak detection strategy cannot be given: the strategy should be adapted to the specific area that needs to be monitored. Using atmospheric  $O_2$  measurements for CCS leak detection does, however, always have the benefit that it can discriminate between random, fossil, sources of  $CO_2$  and a real leak.

Perhaps the most important conclusion of all is, however, that this thesis shows that the tools for reliable leak monitoring for sites on land exist, and that deploying them is a straightforward process, should the decision to store  $CO_2$  underground on land be taken.