Detection of CO₂ leaks from Carbon Capture and Storage (CCS) sites with combined atmospheric CO₂ and O₂ measurements

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Use of CO₂ and O₂ measurements for leak detection
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Carbon Capture and Storage (CCS)

CO₂ is captured from (power) plants and stored underground in depleted oil and gas fields or deep saline aquifers.

Important concern is the possibility of leakage of stored CO₂ to the atmosphere.

Figure source: ZEP (Zero Emissions Platform)

Situation in the Netherlands

Partially empty gas fields present, ideal storage for CO₂
Densely populated region, multitude of (fossil) CO₂ sources present

complicated detection of possible leaks

Edgar CO₂ emissions (2010)
Detecting CCS leaks in the atmosphere is difficult

- Rapid mixing of emitted $\text{CO}_2$ with the surroundings
- High natural variability of the atmospheric $\text{CO}_2$ concentration

Is there a difference between these two nighttime events?

Possibilities for $\text{CO}_2$ leak detection: **Use of tracers**

- Add a tracer (e.g. $\text{SF}_6$, $\text{CH}_4$, perfluorocarbon)
  - Additional costs
  - Gases are strong greenhouse gases themselves
  - Migration of the tracers through the underground is not exactly the same as the migration of $\text{CO}_2$

- Use of natural tracers ($^{14}\text{CO}_2$, $^{13}\text{CO}_2$)
  - $^{14}\text{CO}_2$ measurements are very expensive and only possible by flask measurements
  - $^{13}\text{CO}_2$ only works when:
    - significant difference between the $\delta^{13}\text{C}$ of the biosphere and the source of $\text{CO}_2$
    - sufficient $\text{CO}_2$ perturbation caused by the leak
Measuring CO$_2$ at multiple locations

Both locations measure the same: natural variability

Two locations measure different signal.
Yellow = background. Black = leak detection.

Main drawback: not possible to discriminate between a random (biospheric or fossil fuel combustion) point source of CO$_2$ and a leak of CO$_2$.

This method was also applied on pipeline monitoring and published in: Van Leeuwen, C., Hensen, A. Meijer, H.A.J. (2013) Leak detection of CO$_2$ pipelines pipelines with simple atmospheric CO$_2$ sensors for carbon capture and storage. Int. j. greenhouse gas control 19, 420-431

Combined O$_2$ and CO$_2$ measurements

Most processes show an inverse relationship between O$_2$ and CO$_2$, but CO$_2$ leaks have no counterpart in O$_2$

O$_2$ and CO$_2$ together form the ideal leak detector
Disadvantage: precise and accurate O$_2$ measurements are complicated
O₂ for leak detection: design criteria

- precision down to the ppm level
- long term calibration is less of an issue
- sturdy design, needs to be “mobile”
- fully automated, remote control
- should be able to run for about a month between services (air dryer and reference gas cylinder should last that long)

Design of a transportable O₂ – CO₂ instrument

Our system would fit in any small building or van.

the equipment in three “flight cases” (or road cases)
the small air inlet mast (6 m)
the reference and calibration cylinders with protection cap

-60°C drying system, with Mg(ClO₄)₂ trap follow-up
The CO₂ / O₂ /(and δ¹³C) device: under the hood

CO₂ concentration (and δ¹³C) using the ABB NDIR device (URAS 26)

Differential oxygen: Oxzilla

Quality of the measurements

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (ppm) Target 1</th>
<th>CO₂ (ppm) Target 2</th>
<th>O₂ / N₂ (per meg) Target 1</th>
<th>O₂ / N₂ (per meg) Target 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average stdev within a target run (n = 48)</td>
<td>0.011</td>
<td>0.010</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Stdev of all target runs (n = 48)</td>
<td>0.021</td>
<td>0.018</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Stdev of pairs, averaged (n = 47)</td>
<td>0.011</td>
<td>0.009</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>
Demonstrations in the field, at our station Lutjewad

$\text{CO}_2$ release experiments: 3-5 g/s

station Lutjewad

the small mast

testing the wind

$\text{CO}_2$ cylinder pack

short term day-time $\text{CO}_2$ release experiments

Data during the $\text{CO}_2$ release tests are marked in red
24-hour CO$_2$ release experiments

Release particularly well visible at night

natural nocturnal peak

release (1) stable wind conditions

release (2) unstable wind conditions

“intermittant” CO$_2$ signal
**CO₂ release tests: analysis**

the three daytime releases: O₂/N₂ plotted against CO₂

![Graphs showing CO₂ release tests analysis](image)

slope in per meg/ppm -5.76, -5.46, -4.96

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**CO₂ release tests: analysis**

the two 24-hour releases: O₂/N₂ plotted against CO₂

(a) September 2014

(b) November 2014

leak detection qualitatively very clear. Quantitative analysis?
Strategies for analysis

I Compare time intervals (e.g. hours) with the general relationship

- determine, for a longer period, the $O_2$-$CO_2$ slope for all measurements (apply outlier filtering)
- calculate the standard deviation of the (horizontal) scattering around this slope (in ppm)

$$\mu_{\text{general}} = 0, \sigma_{\text{general}} = 3$$

$$\mu_{\text{general}} = 0, \sigma_{\text{general}} = 7$$

- now calculate the average value and scatter around the slope for every individual hour of the whole period

- Criterion for detection of a leak:

$$\left( \mu_{\text{hour}} + \sigma_{\text{hour}} \right) \geq \left( \mu_{\text{general}} + \alpha \times \sigma_{\text{general}} \right)$$

- the 16% highest points of the hour
- the 2.2% ($\alpha=2$) highest points of the total
- 0.1% ($\alpha=3$)

(in fact a modified $\chi^2$ test)
Strategies for analysis

- we can reformulate \((\mu_{\text{hour}} + \sigma_{\text{hour}}) \geq (\mu_{\text{general}} + \alpha \times \sigma_{\text{general}})\) into:

\[
\alpha = \frac{\left(\mu_{\text{hour}} + \sigma_{\text{hour}}\right)}{\sigma_{\text{general}}}
\]

- and then attribute an \(\alpha\) value to each individual hour

![Graphs showing CO2 levels over time with identified leaks and no-leak events]

With this strategy, persistent leaks can be identified automatically

detection level \(\approx 6\) ppm \((\alpha=2\) times observed variability of 3 ppm)
Two strategies for analysis

II) Calculate the slope of time intervals (e.g. 6 hours) throughout time (without outlier filtering)

- Most of the time the slope will be around -5 per meg / ppm
- In case the slope is significantly higher (with a small error) a leak is identified

Three categories:
(1) slope fit error < 0.7 per meg/ppm, and slope > -1.5 per meg/ppm: leak
(2) slope fit error > 0.7 per meg/ppm and variability of CO\textsubscript{2} > 2 ppm: inconclusive
(3) all others: no leaks
Two strategies for analysis

- Combined O\textsubscript{2} and CO\textsubscript{2} measurements are a strong tool in detecting CO\textsubscript{2} leaks from a CCS site and the only tool to discriminate between a leak and another CO\textsubscript{2} source
- Our transportable system can be moved easily from one site to another
- The two analysis methods demonstrated are easy to automate, and together have a high potential for leak detection
- Their set points have been optimised for our system during our release tests; for a system with different precision these set points might need to be adapted
- The precision for O\textsubscript{2} can still be improved. The detection limit might be lowered then from \( \approx 6 \) ppm to \( \approx 3 \) ppm in these surroundings (with both many biogenic and anthropogenic sources of CO\textsubscript{2})

Conclusions

- The best strategy for leak monitoring is:
  - Deploy a large number of cheap CO\textsubscript{2}-only sensors \hspace{1em} (\textit{van Leeuwen et al.}, 2013. Igggc. 19:420–431)
  - \textit{or alternatively one integrated large pathlength CO\textsubscript{2} sensor}
- When there is leak suspicion: bring in the CO\textsubscript{2}-O\textsubscript{2} system
Acknowledgements

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Alwin Stegeman for the slope idea

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