# Continuous Greenhouse Gas and Isotopic $CO_2$ Measurements via WS-CRDS-based Analyzers:

## *Investigations in Real Time Monitoring at $CO_2$ Geological Storage Sites*

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## Introduction

The foremost risk associated with geologic sequestration of carbon dioxide is leakage of the $CO_2$ back to the atmosphere (Wilson and Gerard 2007). In some scenarios, because of the energy penalty associated with capture and storage, significant leakage can result in a worse climate outcome than if no sequestration had been attempted (see Figure 1, after Enting et al. 2008).

As we move toward a regulated carbon economy, it will become necessary to stipulate what are acceptable leak rates and to develop monitoring strategies that can demonstrate sufficient sensitivity to verify that leakage is below the agreed threshold.

In this work, we demonstrate how the sensitivity of leak detection will be greatly improved by adding continuous atmospheric measurements of tracers in the stored fluid body, such as $CH_4$ and isotopes of $CO_2$, to a monitoring scheme for geological $CO_2$ storage.

## The challenge of $CO_2$ leak detection

Carbon dioxide has a large and naturally varying concentration in the atmosphere: ecological respiration into a stable nighttime atmosphere often results in excursions of 100 – 200 ppm from clean air $CO_2$ concentrations. Although potentially climatically compromising leakage rates could result in large $CO_2$ concentration perturbations in the immediate vicinity of a point source leak, the perturbation will be rapidly diluted by atmospheric mixing and may become indistinguishable from the natural background variation, even within tens of meters of the leak. Consequently, atmospheric monitoring strategies at carbon storage sites that focus only on $CO_2$ will be weak, having relatively poor detection limits because the signal to noise ratio is highly unfavorable.

We conducted a controlled release experiment of both $CO_2$ and $CH_4$ (Loh et al. submitted) to gauge the sensitivity of atmospheric monitoring to detect and quantify leakage from geological $CO_2$ storage. Known amounts of $CO_2$ and $CH_4$ were released at two rates and paired (up and downwind) concentration measurements were made at increasing distances from the source area (pairs A-D).

A 3D sonic anemometer measured turbulence statistics.

**A: 10m up & downwind, 0.8m above ground**

**B: 10m up & downwind, 1.5m above ground**

**C: 30m up & downwind, 1.5m above ground**

**D: 30m up & downwind, 3.0m above ground**

A backward Lagrangian stochastic (bLS) dispersion analysis was used to calculate the fluxes ($Q_{bLS}$) of $CO_2$ and $CH_4$ based on our experimental data. We find, in addition to strict filtering of meteorological data (to ensure the validity of the Monin-Obukhov Similarity Theory on which the dispersion model is based) that detected enrichments in concentration must be at least 1% above the background concentration of that gas for the inverse modeling to recover leakage fluxes with acceptable accuracy and precision. Figure 2 shows the average flux recovery (ratio of calculated flux, $Q_{bLS}$, to known flux, Q) plotted against percentage enrichment in the downwind measurement, $C_L$, with respect to its upwind or background pair, $C_b$. Because the background concentration $CO_2$ is so large and variable, this enrichment criterion is much more onerous for $CO_2$ than for $CH_4$.

## CO2CRC Otway Project

Two analyzers, based on Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS), one for simultaneous $CH_4$ and $CO_2$ measurements and one for $^{12/13}CO_2$, are to be deployed by CSIRO at the CO2CRC Otway geological storage pilot project in Victoria, Australia. At this site, up to 100,000 tonnes of $CO_2$ of magmatic origin, discovered during natural gas exploration, is to be pumped into a commercially exhausted natural gas well nearby. The presence of residual natural gas at both source and sink results in a substantial mole fraction (approx 20%) of $CH_4$ in the stored fluid body, making methane an excellent natural tracer for any $CO_2$ that may leak, if it accompanies the $CO_2$ to the surface. As atmospheric $CH_4$ has both a lower background concentration and exhibits less diurnal variability than $CO_2$, simultaneous measurements of $CH_4$ with $CO_2$ should greatly enhance the sensitivity of $CO_2$ leak identification.

We define target detectable leak rates of 1000 t $CO_2$ p.a. based on global carbon cycle modeling (Enting et al. 2008), equivalent to 0.1% p.a. from a 10 Mt store of $CO_2$, and a commensurate 72 t $CH_4$ p.a. based on 20% mole fraction $CH_4$ as in the Otway storage reservoir. We use these targets to assess the sensitivity of our monitoring scheme. Forward atmospheric dispersion modeling is used to produce horizontal contour plots of concentration perturbations arising from point source leaks at our target rates. These plots are transformed to show what size leak (relative to the target) would be detectable as a function of atmospheric stability and position of monitoring equipment relative to the source. Figure 3 shows these data for a) $CH_4$, b) $CO_2$ under conditions of background $CO_2$ = 380 ppm (daytime) and c) $CO_2$ under conditions of background concentration = 500 ppm (nighttime).

Comparing Figure 3 panels a) & b) shows that under daytime conditions, $CH_4$ is at least ten times as sensitive for detecting leakage than are measurements of $CO_2$ at the Otway site. Future projects are unlikely to have such a high $CH_4$ component in the reservoir, but where $CH_4$ is present, it is likely to be a sensitive tracer, because its background concentration is so much lower than $CO_2$. Comparison of panels b) & c) illustrates that as the background concentration rises, sensitivity to detect leaks drops if monitoring is confined to $CO_2$.

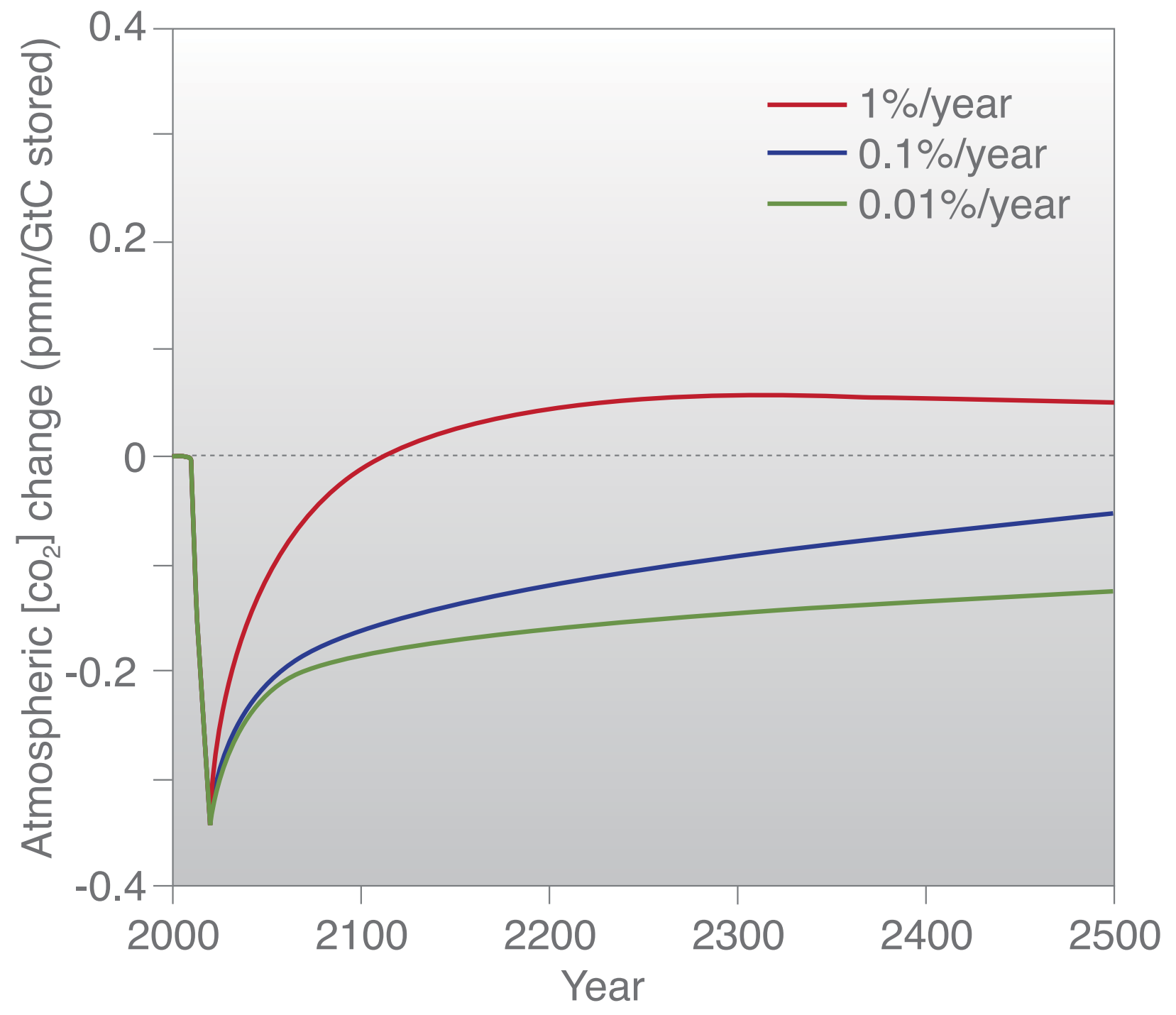


*Figure 1:* Simple carbon cycle modeling of the atmospheric response to geological storage of $CO_2$ with various leak rates. An energy (and therefore $CO_2$) penalty of 30% and a scenario of atmospheric $CO_2$ stabilization at 500ppm are assumed.

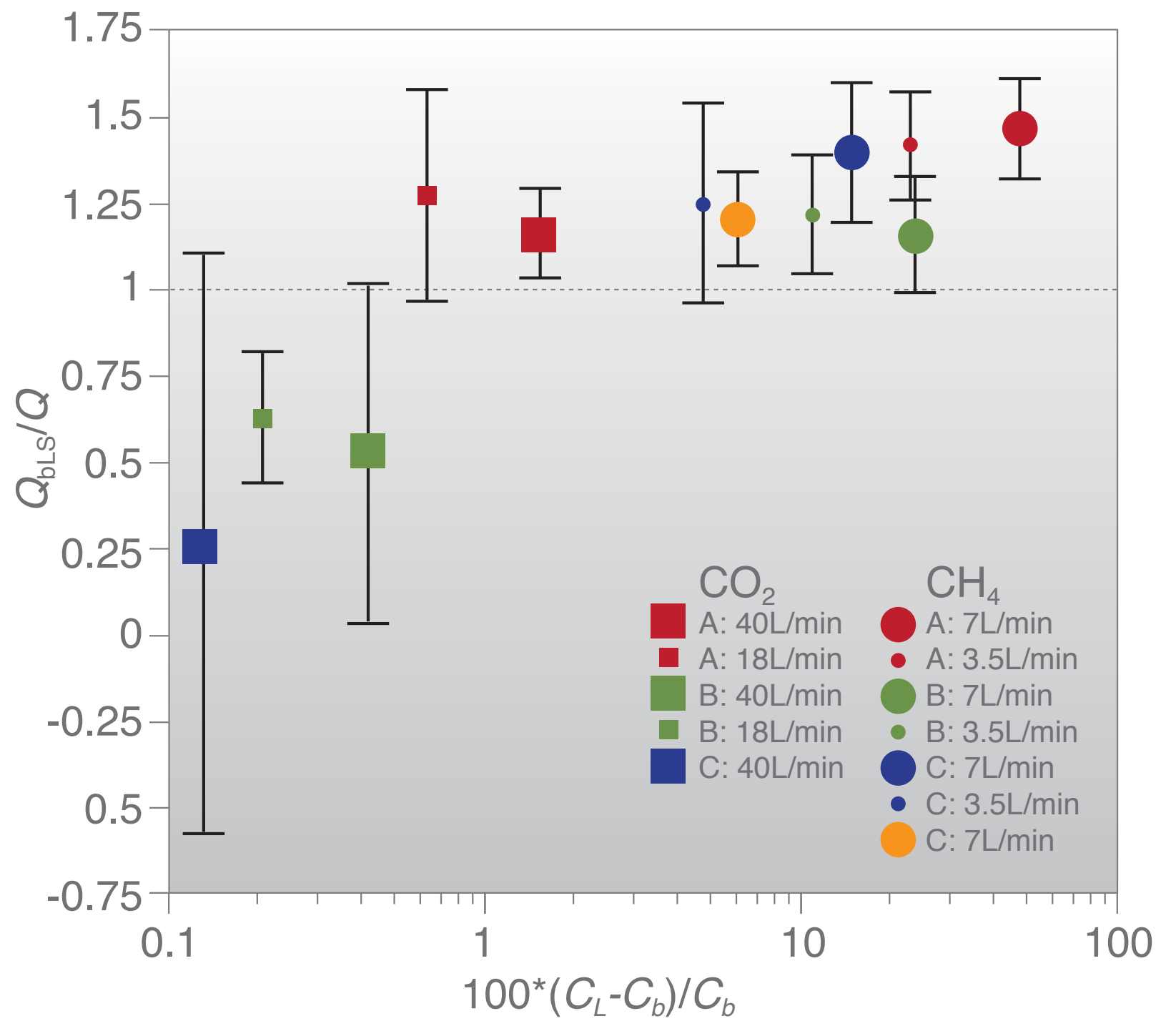


*Figure 2:* Average flux recovery plotted against concentration enrichment over background. Error bars are standard deviations.

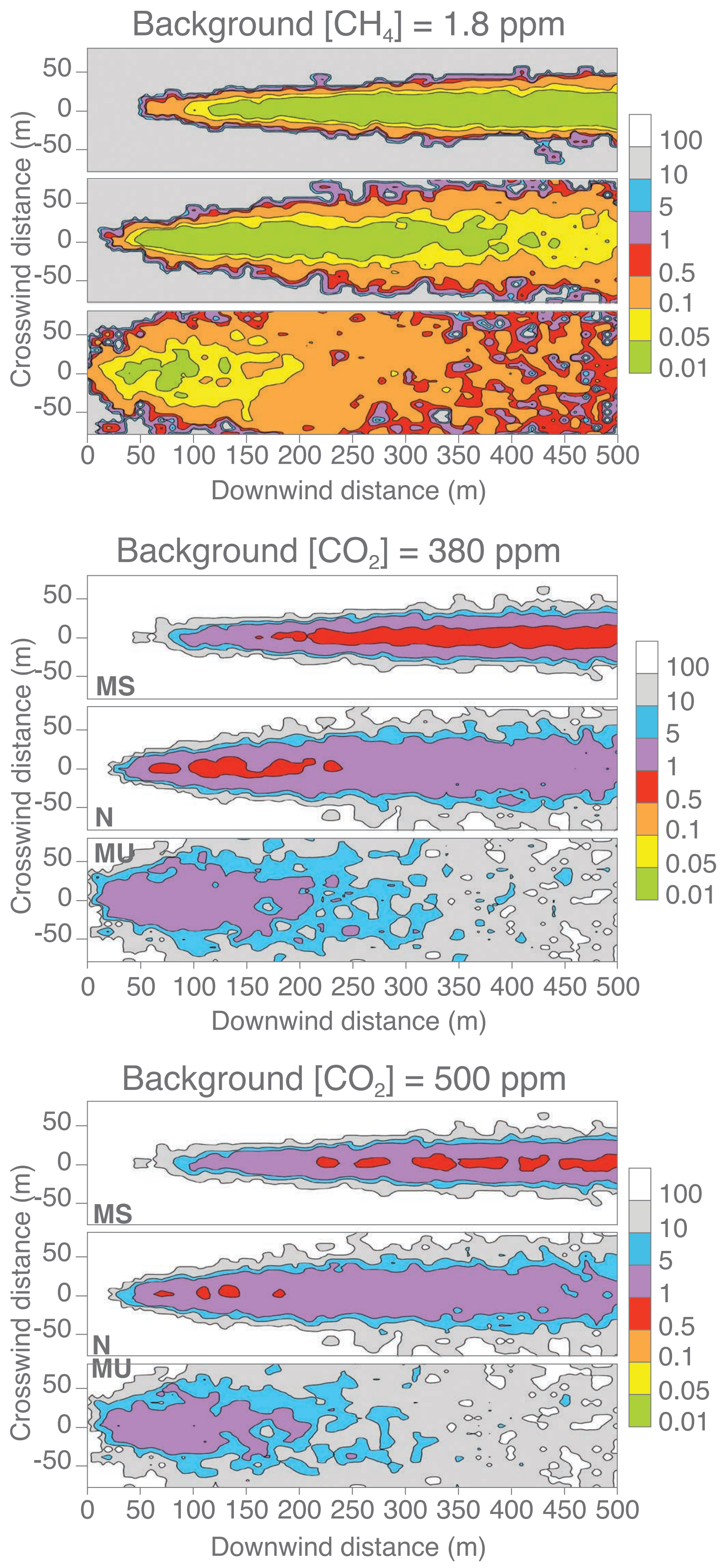
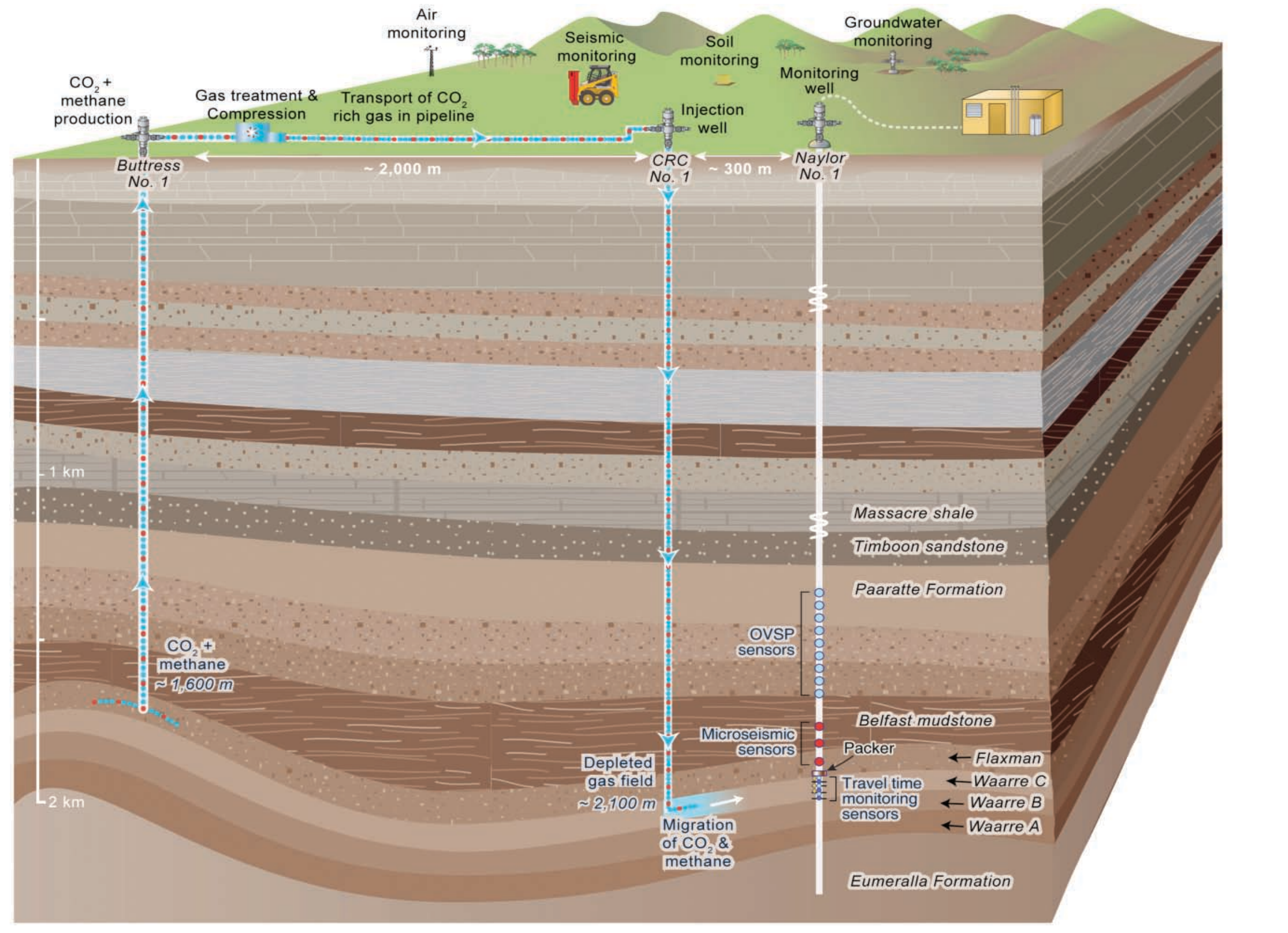


*Figure 3:* Horizontal contour plots of the strength of a point source, as a multiple of a target detectable leak rate, required to produce a 1% enrichment downwind of the source. Plots are shown for moderately stable (MS), neutral (N) and moderately unstable (MU) atmospheric conditions. Source is located at (0, 0, 0.1). Plots are in a plane 10 m above ground, with wind speed 5 m.s$^{-1}$. Panel a) is for $CH_4$ at a background concentration of 1.8 ppm, b) $CO_2$ at background concentration of 380 ppm and c) $CO_2$ at 500 ppm.



*Schematic diagram of the CO2CRC Otway Project site.* · http://www.co2crc.com.au/otway/index.html

## *Isotopic $CO_2$ measurements*

Figure 4 shows how a leak of isotopically distinct $CO_2$ generates potentially measureable perturbations in the atmosphere as the leak is dispersed. In the top panel, magmatic $CO_2$ ($\delta^{13}C$ = -6‰) leaks into an atmosphere at 380 ppm $CO_2$ and $\delta^{13}C$ = -8‰, typical of daytime conditions. In the lower panel, the same amount of magmatic $CO_2$ leaks into a well mixed atmosphere at 500 ppm $CO_2$ and $\delta^{13}C$ = -13‰, as might occur if the additional $CO_2$ mixing into the atmosphere was due to ecological respiration with constant $\delta^{13}C$ = -29‰.

It is clear from Figure 4 that whereas leak detection in the $CO_2$ concentration domain becomes less sensitive under elevated $CO_2$ conditions (Figure 3), for a scenario like that at Otway, detection sensitivity improves in the $\delta^{13}C$ domain under conditions of elevated $CO_2$. Consequently, continuous monitoring of $\delta^{13}C$ can be an informative addition to monitoring schemes.

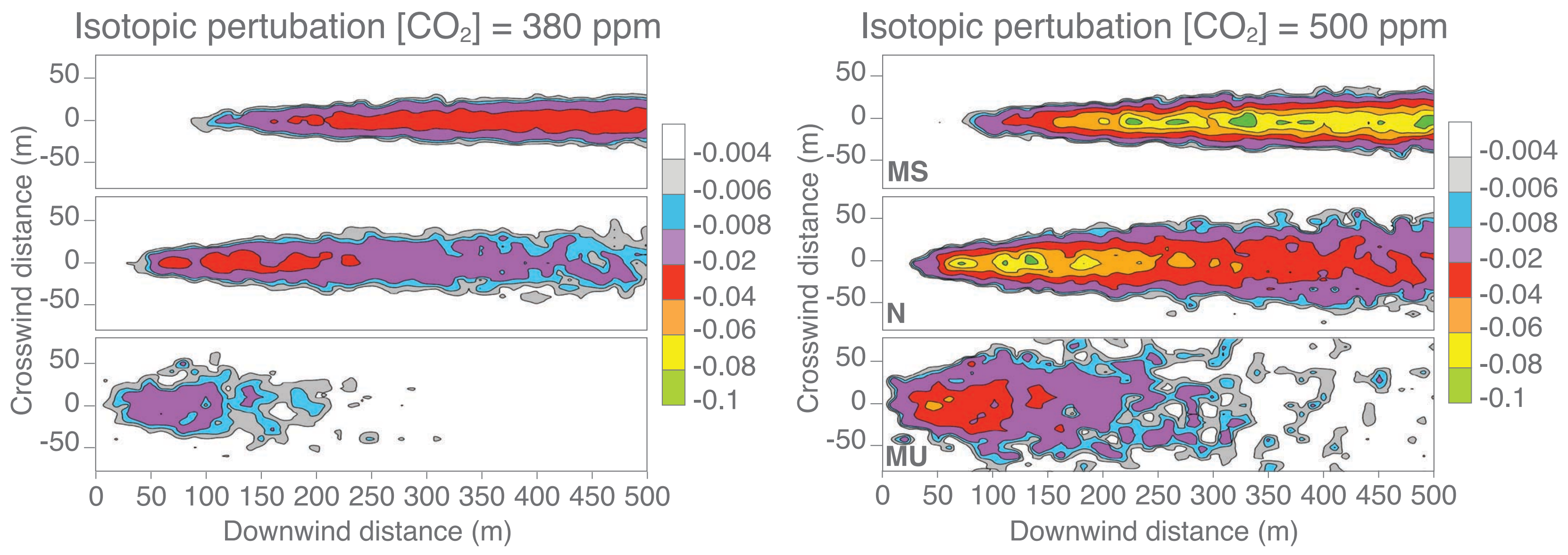


*Figure 4:* Horizontal contour plots of the perturbation in $\delta^{13}C$ (in per mille) resulting from a point source leak of 1000 t magmatic $CO_2$ p.a. ($\delta^{13}C$ = -6‰) into a) clean air day time atmosphere of 380 ppm and $\delta^{13}C$ = -8‰ and b) a night time atmosphere at 500 ppm $CO_2$ and $\delta^{13}C$ = -13‰, resulting from an ecological source of $\delta^{13}C$ = -29‰ elevating the $CO_2$ concentration at night. Plots are shown for moderately stable (MS), neutral (N) and moderately unstable atmospheric conditions.

## *Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) – How it Works*

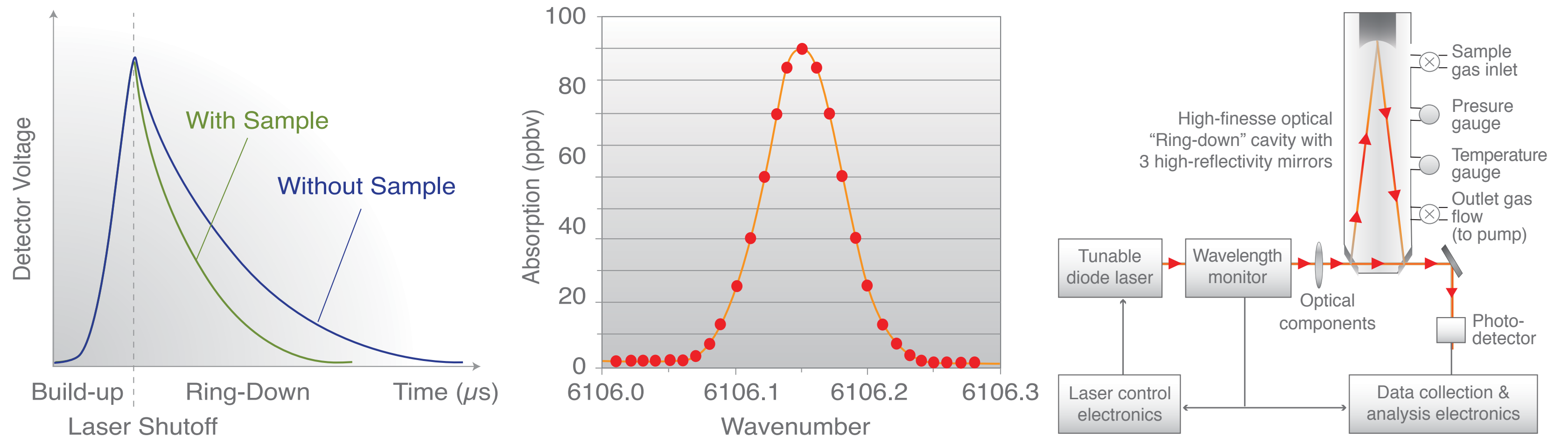
- Light from a tunable semiconductor diode laser is directed into an optical resonator cavity containing the analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- The energy decays from the cavity exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time is measured at several different wavelengths as the laser is tuned across the molecular signature of the analyte gas.
- WS-CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long.
- The concentration is proportional to the difference in these ring down times.

## *Conclusion*

Continuous data are crucial to a robust atmospheric monitoring strategy at geological $CO_2$ storage sites. Because the detection limits of atmospheric monitoring intrinsically depend on the atmospheric conditions (stability, wind speed, wind direction) data need to be filtered heavily. Without continuous measurements, good data are likely to be too sparse to be interpretable.

We have here illustrated that incorporating simultaneous measurement of natural tracers present in the stored fluid body ($CH_4$ and $\delta^{13}C$), can greatly improve the sensitivity of atmospheric leak detection.

Modeling of leakage detection sensitivity for synthetic tracers present in the atmosphere at ppt levels, such as $SF_6$, that might be introduced into the storage reservoir at ppm levels, indicates that they will also improve atmospheric monitoring sensitivity.



Light intensity as a function of time in a WS-CRDS system with and without a sample having resonant absorbance. Optical loss (absorption by the gas) is rendered into a time measurement (left). By using a patented wavelength monitor, this measurement is continuously repeated at a number of well-controlled points in wavelength (middle). The concentration is determined by a multi-parameter fit to this lineshape and is proportional to the gas concentration. Analyzer schematic (right).

**References**
Wilson and Gerard (2007) Risk Assessment and Management for Geologic Sequestration of Carbon Dioxide. Carbon Capture and Sequestration: integrating technology, monitoring and regulation. E. J. Wilson and D. Gerard, Blackwell Publishing: 101-125.
Enting et al. (2008) "A perturbation analysis of the climate benefit from geosequestration", *International Journal of Greenhouse Gas Control*, 2: 289-296
Loh et al, "Testing Lagrangian atmospheric dispersion modelling to monitor $CO_2$ and $CH_4$ leakage from geosequestration", submitted to *Atmospheric Environment*

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