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QUANTIFICATION TECHNIQUES FOR CO_2 LEAKAGE

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QUANTIFICATION TECHNIQUES FOR CO_2 LEAKAGE

Background

On the whole, the primary focus of CO_2 storage monitoring techniques has been to monitor plume behaviour in storage formations, and to detect leakage to the biosphere. However, for emissions trading under the EU ETS and for national GHG inventory purposes it is necessary to quantify leaked emissions to the atmosphere should leakage occur, and there is a low level of understanding of the capabilities, accuracies and uncertainties of measurement techniques for this application. Quantification of leakage was identified as a significant gap in the knowledge base of the IEAGHG storage networks at the Joint Network Meeting in June 2008, and the IEAGHG Environmental Impacts of Leakage workshop held in September 2008 highlighted potential for quantitative measurements to a level of accuracy required although inconclusive. Both the EU ETS work on monitoring and reporting guidelines for CCS and the EU CCS Directive working group concluded there is insufficient knowledge in this area; hence, it is pivotal for policy, regulations and for the development of monitoring technologies to ascertain the current state of knowledge in this field and understand possible future developments to meet requirements.

Scope and Methodology

A contract for this study was awarded to CO_2GeoNet, with a project team led by Imperial College, London. The primary aim was to identify potential methods for quantifying CO_2 leakages from a geological storage site from the ground or seabed surface. The contractor was asked to review and identify techniques that have the potential to measure CO_2 leakage into the atmosphere and into the water column, for both point-source and dispersed leakage scenarios; once identified, provide a detailed review of quantification performance including sensitivity cost and future developments; suggest quantification improvements of a monitoring portfolio; review current requirements and, provide recommendations. The contractor was also asked to liaise with the British Geological Survey to ensure results are reflected in the updated IEAGHG Monitoring Selection Tool.

The contractor provides a description of the technologies that can measure CO_2 leakage from potential point and/or diffuse sources, reviewing the quantification performance of these methods, discussing potential improvements for quantifying CO_2 leakage through the implementation of a monitoring portfolio approach. The review focusses on methods relevant for monitoring the marine and terrestrial aquatic environments, the atmosphere, shallow subsurface and ecosystems for leaked emissions as defined for requirements in the EU ETS and GHG inventory guidelines; recognising the importance of deep subsurface monitoring techniques to identify potential pathways and migration in advance which are briefly discussed as part of monitoring portfolios.

Results and Discussion

Techniques to detect and quantify CO_2 leakage

Due to the nature of a CO_2 geological storage site, techniques to *detect* any potential leakage or likely pathway will be necessary prior to deployment of direct or indirect instrumentation for quantification. Deep subsurface methods will therefore be important to identify any potential leakage before it reaches the near subsurface, atmosphere or water column. Baseline monitoring is needed before any compartment is altered by the effect of CO_2 injection or exposure, especially as large spatial and temporal variation of background levels is likely to contribute the largest level of uncertainty. Modelling is also key to the planning of monitoring programmes; hence methods to help constrain model parameters and reduce

*Note all references are provided at the end of the full report reduce uncertainties will add value. Preference should be given to methods that are concurrently employed for performance monitoring, are favourable in terms of cost and benefit, are most reliable and accurate, can be deployed in conjunction with other techniques, can be operated with minimum human effort, are robust and have added benefit in improving calibration of models. Detectability and sensitivity of a monitoring method is not just dependant on the technology but also the implementation mode when used in a specified calibration range and of course, different technologies will be suitable for different conditions and environments.

Table 1 presents the suitability of available methods for CO_2 detection and quantification considering the rate of CO_2 that can be quantified using the proposed techniques.

Marine and terrestrial aquatic environment monitoring

CO_2 once in the water column will be rapidly dispersed by currents or dissolution and dilution. An understanding of baseline concentrations and variability as well as the local physical oceanography is crucial for interpretation of monitoring data. As there is likely to be a small signal in a large volume of water, methods with large spatial coverage provide the opportunity to detect but may be limited for quantification due to poor resolution; therefore monitoring strategies may be designed to focus on detection initially, and if a leak is suspected then techniques for flux quantification may be deployed.

Side scan sonar was initially deployed from ships, and later applied to towed vehicles and autonomous underwater vehicles (AUV). The bathymetric data is obtained by active sonar, generating high quality images which can resolve features as small as 1cm; hence can detect small changes in morphology should seabed surface topography be effected by any potential CO_2 leakage. Side scan sonar could also be used to detect CO_2 seeping into the water column: demonstrated in natural seepage of shallow methane gas. With high sensitivity they have been identified to have high potential for subsea hydrocarbon leakage detection systems (Carlsen and Mjaaland, 2006), with coverage in the range of some tens of metres for subsea oil and gas production systems (Hellevang et al., 2007), and such could be adapted for CO_2 leakage monitoring, as demonstrated in deep sea environments (e.g. Brewer et al, 2006).

Sonar system surveys, which are likely to be cost-effective, have the potential of covering a wide spatial area in a short period of time, and applying such to AUVs may be promising for monitoring, detecting and further quantification though multibeam systems may have limited resolution. High resolution (HR) reflection profiling methods are particularly sensitive to gas as source frequencies overlap resonance frequencies of naturally-occurring bubbles; hence with multifrequency surveys may have potential for gas flux estimates and quantification of gas content if combined with stream chemical analysis, though have limited penetration. Combining multibeam sonar with optical methods, acoustic tomography and flow sensors could assist in quantification of flux, and a swarm of AUVs equipped with multibeam sonar and sensors could survey a large area on a regular basis which though costly would be effective. Long-term in-situ monitoring however requires a stationary system such as GasQuant: a lander based hydroacoustic swath system developed to monitor temporal variability of bubble release at seep, recording bubbles crossing the horizontally orientated swath, capable of monitoring an area of $2km^2$. An energy supply is of course crucial for any long term system and a system such as GasQuant could be linked to storage technical installations. With areal coverage of thousands of square kilometres, the Long Range Ocean Acoustic Waveguide Remote Sensing (OAWRS) for bubble detection may be suitable for initial surveys though has low resolution therefore would be limited for detailed quantification.

Table 1. Suitability of available monitoring methods for detection and quantification of CO_2 leakage from a storage site.

AQUATIC MONITORING / **Leakage quantification**	**Monitoring method**	Sonar methods: Sidescan sonar bathymetry	Sonar methods: Seabed multibeam bathymetry	Sonar methods: Bubble stream detection	Surface water chemistry	Marine Bubble stream chemistry
Leakage rate	low (100 g/d)					
	intermediate (100 kg/d)				*case dependent*	
	high (100 t/d)					
Leakage type	diffuse	*case dependent*	*case dependent*		*case dependent*	
	disperse spots					
	single localised leak	*case dependent*	*case dependent*			

ATMOSPHERIC MONITORING / **Leakage quantification**	**Monitoring method**	Long open path (IP diode lasers)	Short open path (IR diode lasers)	Short closed path (NDIRs and IR)	Eddy covariance
Leakage rate	low (100 g/d)				
	intermediate (100 kg/d)	*case dependent*			
	high (100 t/d)				
Leakage type	diffuse	*case dependent*	*depends on contrast with background*	*case dependent*	
	disperse spots				
	single localised leak				

SHALLOW SUBSURFACE MONITORING / **Leakage quantification**	**Monitoring method**	Soil gas and flux	Downhole fluid chemistry	Hydrochemical methods	Tracers	Soil geochemistry
Leakage rate	low (100 g/d)	*dependant on size of mofette and back-ground level/fluctuations*		*localised discharge from fractured reservoirs only*		
	intermediate (100 kg/d)					
	high (100 t/d)					
Leakage type	diffuse	*dependant on contrast of leakage anomaly/background*		*low rates may not be detectable*		
	disperse spots					
	single localised leak		*require large fluxes and extensive geoch.anomalies*			

ECOSYSTEMS MONITORING / **Leakage quantification**	**Monitoring method**	Terrestrial ecosystems	Marine ecosystems
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)	*case dependent*	*case dependent*
	high (100 t/d)		
Leakage type	diffuse	*case dependent*	*case dependent*
	disperse spots		
	single localised leak	*case dependent*	*case dependent*

REMOTE SENSING / **Leakage quantification**	**Monitoring method**	Airborne and satellite spectral imaging	Airborne EM
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)		*case dependent*
	high (100 t/d)		
Leakage type	diffuse		*case dependent*
	disperse spots		
	single localised leak		*case dependent*

pink = method suitable; yellow = less suitable; white = not applicable

Geochemical methods are the only techniques that can directly quantify CO_2 seepage in the form of bubbles which dissolve as they rise or as dissolved CO_2 migrating with deep-origin waters. Composition of the leaking gas may elucidate its source and help determine the flux rate and, samples of the gas can be collected and analysed close to the potential leakage point before dissolution into the water column; either in-situ or in the laboratory with leakage rates estimated by conducting profiles and using associated current velocities to calculate mass flux. Laboratory analysis is useful for improved sensitivity or for analysing components in-situ, though in situ analysis reduces potential sampling artefacts and as a continuous method has the possibility of collecting large amounts of data. A CTD probe is commonly used for measurements such as these, however ROVs are more flexible, and equipped with sensors, an ROV can be deployed once sonar has identified a possible leakage site, measuring the size and shape of plume by manoeuvring the ROV in and out of the plume; or if also equipped with scanning sonar, can potential map the plume. Cost effective mini-ROVs are now available such as the Ocean Modules V8 Sii (€120k-€200k depending on the configuration). Alternatively, sensors could be mounted on AUVs offering good spatio-temporal resolution. Various types of sensors have been applied for commercial and research probes including non-dispersive infrared (NDIR), electrochemical, mass spectrometers, direct-absorption spectroscopy and calorimetric sensors. An example of such sensors is the SAMI^2; which uses a diffusion membrane and a wet chemical approach, as the dissolved CO_2 diffuses across the membrane onto a pH indicator where it transforms into carbonic acid, changing the solution pH; and can measure pCO_2 in the range of 150 to 750ppm, with a response time of 5 minutes, precision greater than 1ppm, accuracy of ±3ppm, long term drift of less than 1ppm in 6 months, and can be deployed up to 500m depth. There is extensive development of in-situ sensors and autonomous marine platforms that show promise for the future.

A technique lying between in-situ and remote analysis of dissolved gas is the equilibrator technique with good spatio-temporal coverage, involving the towing of a long hose behind a ship, with a ‘fish’ at the end of the hose which maintains a constant sampling depth and a pump which continuously transfers water to the ship, passing it through the equilibrator which strips dissolved gases from the water for analysis via either infrared or gas chromatography. This method has been used for the detection of pipeline leaks and seepages from oil and gas reservoirs (e.g. Logan et al., 2010; Figure 1).

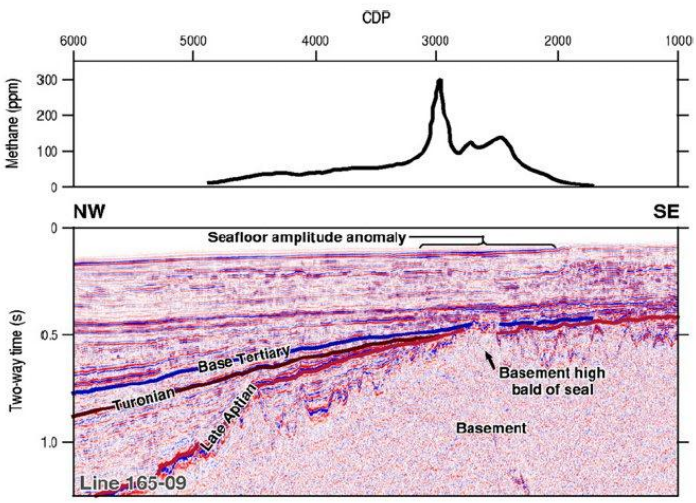

Figure 1. Dissolved CH_4 concentration profile conducted with an equilibrator system above a known gas field (Logan et al. 2010).

Benthic chambers also offer potential for direct quantification of flux rates from the sediment to the water, which consist of an enclosed volume with one end open for deployment on the sediment surface by divers in shallow water or ROVs or landers. However, these measurements are highly point specific and errors can occur due to spatial heterogeneity. As elevated CO_2 levels near the seabed and in ambient water will affect marine ecosystems, monitoring of seabed fauna could also be measured using AUVs or long-term time lapse video recording. Threshold values currently being researched in projects, such as the EU FR7 Research into Impacts and Safety of CO_2 Storage (RISCS) and ECO_2 (Sub-seabed CO_2 Storage: Impact on Marine Ecosystems), may represent a useful tool for the evaluation of biological impacts and in turn, quantification of potential CO_2 leakage.

Atmospheric monitoring

Similar to the marine environment, leaked emissions of CO_2 to atmosphere may be quickly dispersed, and may prove difficult to detect using techniques favouring wide areal coverage and low spatial resolution. Surface monitoring instrumentation is therefore best placed in areas where potential leakage pathways have been identified during risk assessments. There are a number of techniques tested and in development with potential for quantification of CO_2 flux, including the eddy covariance method (ECM) and long open path diode lasers.

The eddy covariance method offers relatively large spatial coverage, using statistics to compute turbulent fluxes of heat, water and gas exchange, and is one of the most effective methods to measure and determine gas fluxes in the atmospheric boundary layer; and has been proposed as a potential method for monitoring CO_2 storage sites (e.g. Oldenburg et al., 2003). ECM is an established technique with low to moderate costs largely associated with the requirement of significant specific knowledge regarding the application of mathematical corrections and processing workflows. ECM works by a gas flux determined as a number of molecules crossing a unit area per unit time, and the gas flux is based on the covariance between concentration and vertical air movement/speed. Measured flux rates lie within the typical range of natural CO_2 emissions from soils and land cover (tens of $g/m^2/d$) and higher emission rates can be easily determined, e.g. Werner et al. (2003) measured release rates between 950-4460 $g/d/m^2$ at the Solfatara volcano, Sicily. However, whether ECM can detect potential leakage from a storage site depends on the ratio between the integral CO_2 flux from the footprint area and the seepage rate from the point source, for example seepage rate of 0.1 t/d from a Zero Emission Research and Technology Center (ZERT) release experiment wasn't distinguishable from background CO_2 emissions, whereas a release of 0.3 t/d significantly increased the flux compared to the baseline (Lewicki et al., 2009).

With a finer spatial resolution than ECM, various open-path sensing techniques have been developed, measuring path-integrated concentration of a target gas between two points near the ground surface, with a measurement interval ranging from tens to hundreds of metres. These methods have been used to locate gas emission and estimate leakage rates to atmosphere from point or non-point sources such as landfills and coal mines (e.g. Piccot et al., 1996; EPA, 2006); and more recently have been applied to monitoring of CO_2 geological storage sites (e.g. Trottier et a., 2009). There are a number of different systems, including Open Path Tuneable Laser (TDL) and Open Path Fourier Transform Infrared (FTIR) which to date have been applied to CO_2 monitoring. As the location and quantification of various gaseous pollutants is an issue, not only for CO_2 monitoring, the US EPA has published a protocol for the use of open path optical techniques applied to emission monitoring (EPA, 2006). Longer path lengths ensure larger areas are monitored; however also result in loss of resolution and greater dilution of the leakage signal, therefore shorter path lengths are beneficial highlighting this method requires identification of a defined location. The method is well adapted for long-term unattended monitoring, as the lasers can be mounted on automated rotating platforms and most have an internal reference cell for self-calibration.

Leakage quantification can be performed on the resultant data from open-path sensing measurements by applying models such as vertical radial plume mapping (VRPM) (EPA, 2006); which employs multiple non-intersecting beam paths in a vertical plane down-wind from a leak to define a plume map, and the flux through the vertical plume is calculated by combining the plume map with the wind speed and direction. Another approach using a background Lagrangian stochastic (bLS) model (particle tracking) appears the most promising; assuming all required wind statistics can be determined from a few key surface parameters; and is valid when source and measurement point lie within a horizontal homogenous surface layer and, distance between these two points is sufficiently short that the particles remain in this surface layer. Controlled methane release experiments have yielded estimates within 5% of the true value at flux rates of 16-48 t/day (Flesch et al., 2004) and 3-6 t/day (Loh et al., 2009), in agreement with modelled minimum detectable rates of 1.7-7 t/day (Trottier et al., 2009; compared with modelled minimum detectable flux rates of 950 – 3800 t CO_2/day (Trottier et al., 2009) and an over estimation by 87% during controlled leakage of 43-100 t CO_2/day (Loh et al., 2009); hence similar results with CO_2 have produced larger errors due to more background variability and lower sensor sensitivity.

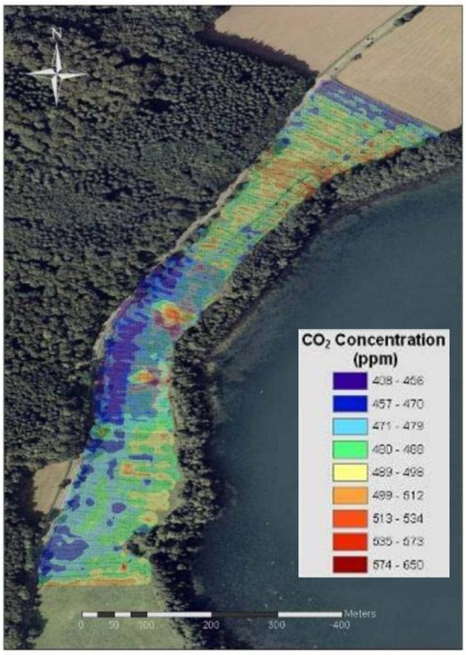

Figure 2. CO_2 concentrations in the air measured at about 30 cm height using a mobile, short open path infrared laser system, Laacher See, Germany (Jones et al. 2009).

Short open-path lasers are very similar to long open-path, with the difference of the equipment being mounted on ground or airborne vehicles for mapping of point sources compared to fixed installations; with TDL the most commonly applied method for CO_2 monitoring. Response times are rapid with little memory effects hence can be conducted at high speeds. Although the CO_2 unit is less sensitive than for CH_4 the sensor has undergone recent technological advances, improving performance, and the tuneable diode laser can now measure up to an IR absorption band of 2000 nm, enabling 5 ppm CO_2 sensitivity and a range of 10,000 ppm. The ground based CO_2 unit measures once every second at recommended speeds of 20 to 100 km/h. Such has been tested at natural seepage sites such as Latera, Italy and Laacher See, Germany: Figure 2 (Jones et al., 2009; Kruger et al., 2009); as well as during surface gas monitoring at the In Salah Gas project in 2009 using a Boreal Laser open path CO_2 detector linked to a GasFinder FC, mounted at 38cm above the ground on a Toyota Landcruiser, which used a detector wavelength of 2 µm with a 5-10ppm CO_2 sensitivity (Jones et al., 2011). Airborne methods for CO_2 detection and quantification may prove difficult due to low sensitivity, the influence of wind conditions and the tendency for CO_2 to remain closer to ground level.

Short closed-path detectors involve the introduction of a gas sample into a chamber via a pump or diffusion and the quantification of a specific gas component by passing light across the chamber and through the sample. This is similar to long and short open path laser due to the use of optical sources and detectors, but differs due to the measurement chamber, allowing for greater portability and reduced interference though can have lower sensitivity and a slower response time. As they are of relatively low cost, are flexible, robust and could be deployed in large numbers, they show promise for use in a monitoring network. It consists of an infrared source and an infrared detector separated by a measurement cell, with recent advances including an internal reference cell for calibration. There are two types of infrared detectors: non-dispersive (NDIR) and dispersive. In NDIR, all the light from the source passes through the sample, after which it is filtered prior to detection; however in a dispersive system a grating or prism is used prior to the sample to select a specific wavelength. NDIR are the most commonly used detectors for field application and are often used in soil gas and CO_2 gas flux surveys which is discussed in *Shallow Subsurface monitoring*.

In terms of atmospheric monitoring, Lewicki et al. (2010) concluded NDIR sensors showed great promise if deployed around areas of higher potential for leakage, and Loh et al. (2009) showed an enrichment of greater than 4 ppm above background levels for CO_2 was needed for detection and quantification of CO_2 flux, in comparison with CH_4 which only required an enrichment of 0.02 ppm. Additionally, Wimmer et al. (2011) noted elevated concentrations were not observed at heights greater than 2.5 cm except directly above the leakage point when deploying NDIR; highlighting detecting and quantifying CO_2 flux may be challenging. Short closed path tuneable diode lasers (TDL) can have better sensitivities and faster response times, with the added benefit of the potential for real-time isotopic analysis; however these tend to be more expensive.

Shallow subsurface monitoring

Near surface gas chemistry offers two relatively low cost methods of monitoring and quantifying CO_2 leaked emissions: gas flux measurements at the ground surface and gas concentrations or isotopes in the shallow sub-surface (typically from a depth between 0.5 and 1m), and are commonly deployed together. Gas flux measurements are generally conducted using either the closed chamber (CC) or dynamic closed chamber (DCC) techniques, involving monitoring of gas changes over time within an accumulation chamber placed on the soil surface, with samples collected manually in the CC method or continuously (commonly every second) via an in-line detector in the DCC method and such autonomous monitoring can be very valuable for collecting baseline data.

Soil gas samples are typically collected using small lightweight soil probes, involving driving a hollow steel tube into the ground and drawing soil air to the surface for analysis, or alternatively, sampling methods involve direct push, power hammered, augured or drilled systems but these are more costly, less portable and slower. In dry permeable ground such as in arid environments, deeper sampling at several metres depth may be essential to avoid atmospheric contamination (Gole & Butt, 1985). The samples can be analysed in the field, using portable equipment or stored in airtight containers for laboratory analysis, examining CO_2 plus other gases due to possible association with the reservoir (e.g. CH_4), as well as performing isotopic analysis to determine the origin of the gas i.e. to distinguish between naturally occurring CO_2 and that which may be originating from storage the reservoir. However, CO_2 isotopes may be limited as delta 13 Carbon values of CO_2 from burning of fossil fuels are similar to those from plant or microbial respiration; hence tracers are being examined for monitoring and quantification purposes, for example at the West Pearl Queen depleted oil formation in SE New Mexico study site where a Perflourocarbon tracer (PFT) was added to injected 2,090 tonnes of CO_2 and was used to quantify a CO_2 leakage rate of 2.82×10^3 g CO_2/yr (Wells et al., 2007).

Two main factors influence the success of soil gas and gas flux surveys for quantification: the methods much locate the leak and define its physical extent which can be addressed statistically, and the methods must be able to separate baseline flux from leakage flux rates for which baseline subtraction approach can be used or analysis for tracer species in soil gas which can be associated with the injected CO_2 and relating their concentration to CO_2 at the surface. Timeliness is also key hence it is important soil gas and gas flux measurements are integrated into a wider monitoring program. Sampling on a grid, interpolating between points, conversion to total flux for the measurement area and subtracting near-surface contributions, would typically be the process for quantification, for example, controlled leaks of 0.1 and 0.3 t CO_2/d at the ZERT site were accurately quantified with the latter 0.3 t CO_2/d leak quantified at a mean ± 1 standard deviation of 0.31 ±0.05 t CO_2/d (Lewicki et al., 2010).

In the near surface environment, CO_2 flow is likely to occur as bubbles migrating vertically along a fault or borehole, and in such a case, gravimetric and Elecromagnetic (EM)/Electrical Resistivity Tomography (ERT) methods may be deployed whilst simultaneously monitoring the reservoir, and can potentially be used for detection in groundwater. Continuous or time-lapse gravimetric methods may theoretically be able to characterise volumes of gas in the order of a few hundreds of tonnes in the shallow subsurface depending on saturation, though it is not established for CO_2 monitoring and may be prohibitively expensive. Airborne EM is well established in groundwater exploration studies (e.g. Siemon et al., 2009) however applicability may be limited due to noise from a variable water table and high natural CO_2 flux. Ground-based sampling would be needed to establish the cause of any enhanced conductivity, and for quantification a numerical simulator could be used to predict the groundwater impact of an ingression of CO_2 in terms of a change in total dissolved solids (TDS), using an empirical relationship between TDS and EM to estimate the amount of CO_2 dissolved in the groundwater which is a subject of current research.

Hydrochemical factors may be useful for both detection and quantification, particularly in inhabited areas with springs or streams, for example waters with elevated CO_2 levels emerging at the surface may visibly show signs such as bubbles or rusty deposits through mobilisation of iron and oxidation at the surface. Depending on the water composition, CO_2 may form numerous dissolved complex species which can be sampled and analysed. The relative accuracy of hydrochemical analyses is in the order of 1-3%, with detection limits of CO_2 being 2 mg/l and 3 mg/l for HCO_3^-. However, quantification into shallow groundwater is subject to a number of uncertainties, requiring dense and repeated sampling to reduce such uncertainties, and the accuracy of quantification required is unlikely to be sufficient for emissions accounting.

Ecosystem and Remote sensing monitoring

Ecosystem-based monitoring can be used to quantify and detect potential leakage into near surface environments, particularly when undertaken in combination with soil gas surveys, though accuracy necessary to meet requirements may be difficult. Botanical, soil gas, microbiological and gas flux surveys at the natural CO_2 seepage site at Latera has observed significant impact in a zone a few metres wide centre of the vent, with acid tolerant grasses dominating near the vent core, microbial populations regulated by near anoxic conditions, and small changes in mineralogy and bulk chemistry (Beaubien et al., 2008). Such impacts on vegetation and soil geochemistry may possibly be detected using airborne spectral (or optical) remote sensing techniques (Chadwick et al., 2009). Thermal imaging may also potentially detect leakage if there is a measurable temperature anomaly. Higher spectral resolution is achieved with hyperspectral sensors which can be as precise as 1m. Bateson et al. (2008) used spectral datasets to assess several indices related to plant stress and estimated a threshold of around 60 g m^{-2} d^{-1} would be the minimum CO_2 flux rate that could be detected with spectral remote sensing methods (Figure 3). Such vegetation indices can however contribute to false positives and hence care should be taken on interpretation.

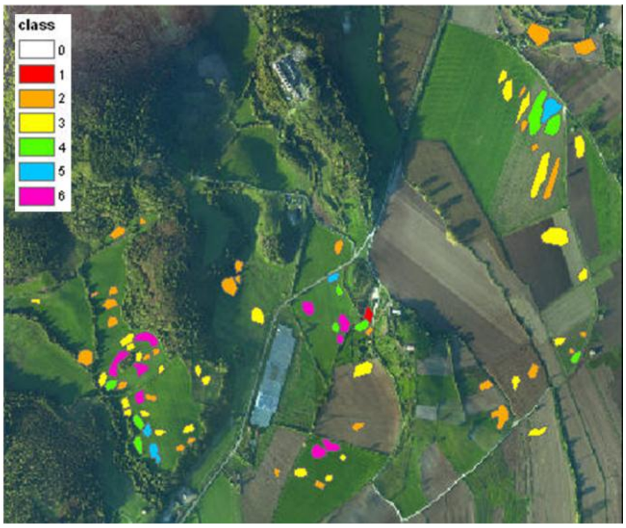

Figure 3. Map of possible CO_2 leakages in the Latera caldera (After Bateson *et al*., 2008). The polygon colours correspond to the number of datasets (methods) that showed an anomaly within that polygon.

CO_2 Leaked Emissions Requirements

Under EU regulations, requirements for leaked emissions falls under the EU Emissions Trading Scheme (EU ETS) (Directive 2003/87/EC); which, operating since 2005, builds upon mechanisms set up under the Kyoto Protocol, the Clean Development Mechanism (CDM) and Joint Implementation (JI) (EC, 2008); and for geological storage of CO_2 would now be triggered by the EU CCS Directive which entered into force in 2009. Article 16 of the EU CCS Directive 2009/31/EC lays out requirements in case of leakages or significant irregularities, ensuring should there be any leaked emissions there would be a surrender of allowances under the EU ETS. In June 2010, Decision 2007/589/EC (establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC) was amended to say leakage 'may be excluded as an emission source subject to the approval of the competent authority, when corrective measures pursuant to Article 16 of Directive 2009/31/EC have been taken and emissions or release into the water column from that leakage can no longer be detected.' A further amendment to Decision 2007/589/EC under Annex XVIII adds 'Monitoring shall start in the case that any leakage results in emissions or release to the water column. Emissions resulting from a release of CO_2 into the water column shall be deemed equal to the amount released to the water column' and defines an approach for quantification, stating 'The amount of emissions leaked from the storage complex shall be quantified for each of the leakage events with a maximum overall uncertainty over the reporting period of ± 7.5%. In case the overall uncertainty of the applied quantification approach exceeds ± 7.5%, an adjustment shall be applied'. The operator requirements for acknowledgement of uncertainties, using a cumulative approach as defined in the 1996 IPCC Guidelines indicates the greater the uncertainty the greater the penalty should CO_2 leakage occur.

Currently, there are no other national regulations requiring quantification of leaked emissions, despite some in place providing monitoring requirements; however, the US EPA has a proposed further rule, proposed in early 2010 (US EPA, 2010) which supplements the greenhouse gas reporting rule finalised in 2009, requiring carbon storage facilities to report their emissions by calculating the sequestered CO_2 by subtracting total CO_2 emissions from CO_2 injected in the reporting year. Such does not ask for specific procedures or methodologies to be implemented, but rather asks operators to develop and implement a site-specific approach to monitoring, detecting and quantifying CO_2 leakage. Additionally, the Australian Regulatory Guiding Principles for Carbon Dioxide Capture and Geological Storage, developed with the aim of establishing a national regulatory framework state: 'Regulation should provide a framework to establish, to an appropriate level of accuracy the quantity, composition and location of gas captured, transported, injected and stored and the net abatement of emissions. This should include identification and accounting of leakage.'

Technique Uncertainties

Given the specific requirement in the EU for defining level of uncertainty in quantification estimation, it is important to consider the current knowledge on measurement instrumentation/technique uncertainties. Level of uncertainty will decrease with further refinement through increased application; however the natural system will always impose some level of uncertainty. For example, in surface water chemistry techniques, Mau et al. (2006) estimated 10 to 20% of their uncertainty was due to variations in the local background with over 50% due to current velocity variations. From reported research there is evidence to suggest some technologies in their current level of development may have uncertainty ranges exceeding the required range of ±7.5%, i.e. Trotta et al. (2010) estimated the largest uncertainties can range from 10 to 40% for different set-ups of eddy-covariance-based estimates of net ecosystem exchange; and uncertainty of CO_2 flux increases with increasing absolute magnitude of the flux (Hollinger & Richardson, 2005). Research is required to improve current understanding of sensitivities and uncertainty ranges of both individual technologies and combined monitoring portfolios.

Expert Review Comments

Expert review comments on the draft report were received from five expert reviewers. The comments provided were detailed and constructive, enabling the study contractors to respond accordingly in preparation of the final report.

General suggestions from the reviews concentrated on the focus and structure of the report, recommending re-focussing towards the original aim of quantification of leaked CO_2 emissions and, the reports consistency and clarity. Specific technical comments included noted important information with regard to the ZERT, West Pearl Queen and Frio results such as the ZERT horizontal well was drilled without disturbing the surface and not 'buried' and the leakage mechanism at the West Pearl Queen site remains unclear. Comments also complimented the contractors on producing such a useful informative document.

The final report reflects the comments of IEAGHG and the expert reviewers. The final report has been re-focussed, summarising the detailed focus on subsurface monitoring techniques in Chapter 3 in reference to detecting potential leakage pathway, and the contractors have improved the text of individual methods and the report's consistency. The contractors have provided a detailed tabulated summary of the comments and their actions to address these comments which may be made available to interested parties.

Conclusions and Recommendations

The study results highlight that for potential leaked emissions in the shallow subsurface, atmosphere and marine environment, monitoring portfolios should be focussed on identified leakage pathways, making use of deep subsurface monitoring technologies to recognise potential pathways. Alternatively it will be necessary to deploy monitoring technologies with lower resolution and wide spatial coverage to detect any CO_2 seepage before deploying more sensitive measurement techniques for quantification. To quantify CO_2 flux, no one technology has been identified, and development of an efficient monitoring portfolio will depend on the specific environment.

The results show technologies suitable for quantification do exist, however these need further field testing and some proposed methods may prove unsuitable for quantification; for example ECM which though a powerful tool is expensive, complex and measurement errors and uncertainties are issues which remain to be solved. Additionally, the study highlights largest uncertainty ranges for some techniques may exceed that of current requirements, for example in surface water chemistry techniques and ECM, and it is recommended IEAGHG explore this further. For quantification purposes, further research should focus on defining sensitivities of instrumentation and uncertainty ranges, testing the technologies in a wide range of conditions for both controlled and natural releases of CO_2. Future research should also provide further insight into variability of baseline CO_2 flux which will be crucial for ascertaining suitability of techniques for specific environments; in addition to further understanding of CO_2 leakage mechanisms including conditions driving CO_2 release into the water column in a dissolved phase or as bubbles. On-going EU projects should help to build knowledge in this area. Some areas of the report are weaker than others due to data availability such as technologies in the marine environment; therefore such should be re-examined in future relevant studies. Therefore, it is recommended IEAGHG keep abreast of the latest developments in monitoring capabilities and uncertainties; with further future involvement in relevant collaborative research activities; and consider a re-evaluation of quantification techniques for CO_2 leakage once further research results become available.

The study also provides a number of technology specific recommendations, provided within the final chapter of the report. These specific recommendations include a need for further testing specific to CO_2 seeps for surface water chemistry techniques in order to assess method sensitivity, precision and costs for CO_2 monitoring. There is also a need for further development of long open path lasers with more stable baseline signals and that can measure more than one pathway and, further focus on deploying short open path lasers closer the ground surface to minimise potential anomalies and testing models to monitor tracer gases that have lower sensitivity. For shallow groundwater monitoring, further research should examine integration of indirect methods such as EM to enable wider spatial coverage and, for airborne EM further work should examine the discrimination of the effects of CO_2 leakage from alternative scenarios such as seawater intrusion.

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Quantification Techniques for CO_2 Leakage

IEA GHG R&D Programme

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Table of Contents

List of Figures

List of Tables

EXECUTIVE SUMMARY

Introduction

This study aimed at identifying and reviewing monitoring methods which have so far shown the potential to quantify CO_2 leakages from a geological storage site. The report primarily focuses on leaked CO_2 which may reach the ground or seabed surface, i.e. the atmosphere or the water column, as defined in the EU ETS. The main body of the report presents a detailed description of the technologies that can measure CO_2 leakage from potential point and/or diffuse sources, providing a detailed review of the quantification performance of these methods. Next, the improvements that can be achieved in quantifying leakage through the implementation of a monitoring portfolio approach are discussed. The CO_2 leakage quantification accuracy required for site permitting and accounting purposes by the current EU and international regulations is then reviewed and evaluated against the performance of individual leakage monitoring methods and monitoring portfolios considered. And finally, conclusions and recommendations for further research and development are provided.

The IEA GHG CO_2 Monitoring Decision Support Tool was developed to help identify appropriate techniques for monitoring CO_2 that has been injected into a geological storage reservoir. It also indicates the applicability of the various methods in detecting and quantifying CO_2 in the deep/shallow subsurface. Since the tool was designed there have been a number of new field test sites where different versions of these monitoring methods have been used and implemented as part of a monitoring portfolio. New technical advances have also assisted in improving the mentioned techniques in detecting CO_2 leakage and at improved levels of accuracy and precision.

CO_2 storage monitoring programmes aim to demonstrate the effectiveness of the project in controlling atmospheric CO_2 levels, by providing confidence in predictions of the long-term fate of stored CO_2 and identifying and measuring any potentially harmful leaks to the environment. In addition, the EU Emissions Trading Scheme (EU ETS) treats leakages of stored CO_2 from the geosphere in to the ocean or atmosphere as emissions, therefore, they need to be accounted for. This necessitates the availability of reliable methods for leakage quantification that cover a wide range of storage and leakage scenarios.

It is recognised that deep subsurface monitoring closer to the storage sites is essential in order to provide early detection of potential leakages to the water column or the atmosphere, so that appropriate monitoring systems can be deployed to facilitate quantification. Nevertheless, this report follows the EU ETS definition which only considers CO_2 emissions to the water column or the atmosphere as leakage. Therefore, the main focus is on methods that are relevant for monitoring the marine and terrestrial aquatic environments, the atmosphere, shallow subsurface and ecosystems, including remote sensing methods. These monitoring techniques are presented in detail in Section 2. Deep subsurface monitoring techniques targeting mainly the CO_2 storage formation and the overburden help identify potential leakage paths and migration of gas well in advance. Although not reviewed in detail in the main body of the report, the deep subsurface methods are briefly discussed as part of the CO_2 monitoring portfolios proposed in Section 3.

The first step in the monitoring sequence of any site would invariably involve the definition of the monitoring baseline. Since background levels of monitored parameters are likely to vary significantly in space as well as in time, repeated monitoring and wide spatial coverage may be essential to provide an adequate characterisation of the baseline variability at a given CO_2 storage site prior to the start of CO_2 injection. Next, wide area monitoring surveys, which may not necessarily have high quantification accuracy, may be used to support potential leak detection. Then, if leakage is detected, appropriate monitoring methods that allow for CO_2 quantification can be used to quantify the amount of leaked CO_2. The process that describes the steps involved in CO_2 leakage quantification are shown in Figure 1. It is recognised that detection, measurement and quantification steps introduce errors in the estimated CO_2 emissions, increasing the uncertainty around the quantification estimates. Considering the effects of natural variability together with these sources of errors, it is rather difficult, if not impossible, to specify the level of accuracy of monitoring methods without referring to the specific CO_2 storage site characteristics and its past operational history (e.g. for depleted oil and gas and EOR operations).

The most important question that needs to be answered when assigning a high or low value to the benefit of a particular monitoring method and for a given storage site setting is the amount of CO_2 over a given area and period of time that can be detected and possibly quantified. When referring to detection, this amount may be called detectability of the method, while when referring to quantification it would be better referred to as the sensitivity of the method. Figure 2 illustrates a typical example of the effects of natural variation on detectability and quantification sensitivity.

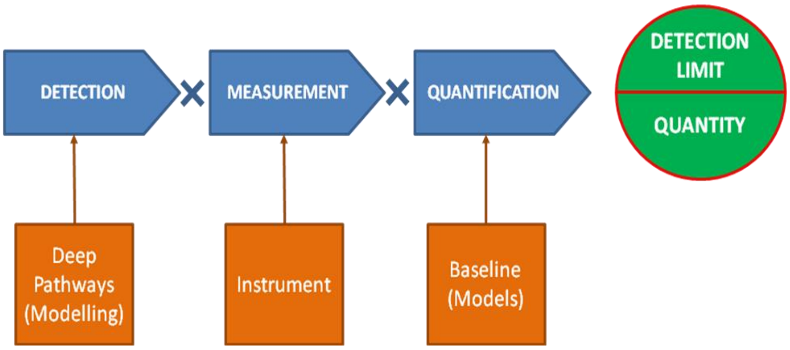


Figure 1. The CO_2 leakage quantification process.

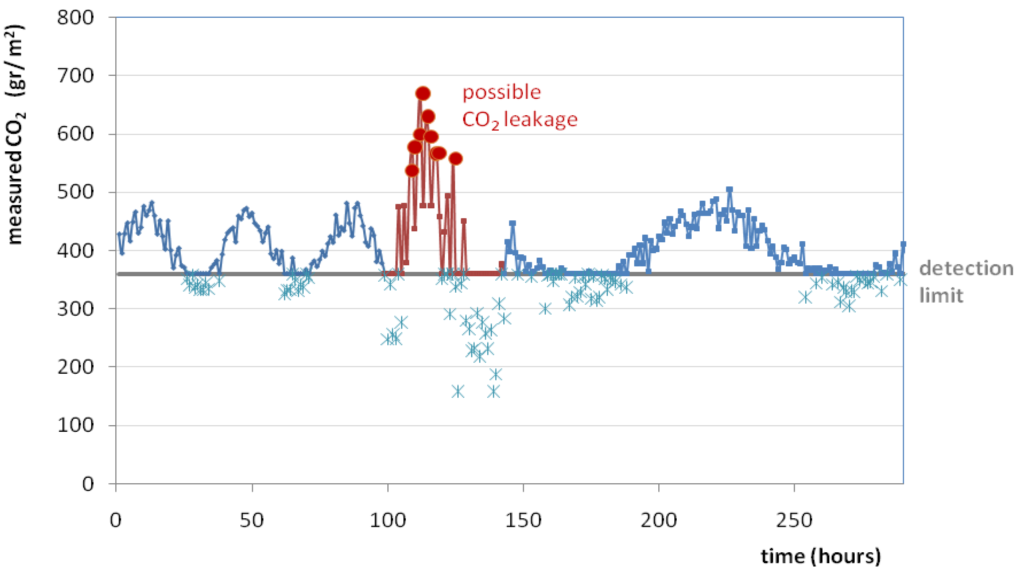


Figure 2. Example illustration indicating the natural variability in monitored CO_2 levels and the potential leakage levels in relation to an assumed constant detection limit (blue stars denote true values, not measured; red dots represent monitoring data that may be identified as potential leakage)..

Important issues that need to be considered when deciding on the methods to be used as part of the monitoring portfolio for a particular site are:

- the performance of the method, given the specific site characteristics
- the benefit expected in terms of value of information (accuracy, detection limit, validation of storage site model concepts and estimates)

- the cost of monitoring including the field implementation of the monitoring portfolio tools chosen (equipment, consumables, staff time) as well as the monitoring data interpretation cost and integration costs within the storage site models.

While data interpretation costs can be estimated with reasonable accuracy, monitoring tool deployment costs cannot easily be harmonised between different parts of the world. This is due to cost disparities between remote and more accessible sites, the importance of area coverage and temporal resolution and the labour and associated costs applicable. Naturally, the cost of CO_2 storage site monitoring portfolio is of particular importance for the site operators and also needs to be considered in the light of the storage site permit conditions as well as the CO_2 storage regulatory framework (e.g. EU Directive, ETS regulations).

This report presents a portfolio of monitoring methods that are appropriate for CO_2 leakage quantification, based on a review of the literature on current and upcoming applications of monitoring methods used in the CO_2 geological storage and other industries. The strengths and weaknesses of each method are considered, as well as their relative costs and general performance in terms of sensitivity, resolution and uncertainties.

Methods for detection and quantification of CO_2 leakage

Marine and terrestrial aquatic environment monitoring

Similar to surface/atmosphere monitoring, CO_2 escaping into the water column may be quickly dispersed by currents, or dissolution and dilution. Therefore, methods suitable for leakage detection with a large spatial coverage may be unsuitable for quantification due to poor spatial (and perhaps temporal) resolution. Monitoring strategies may be designed to prioritise leakage detection over quantification; if a leak is suspected then instrumentation suitable for CO_2 flux quantification may be deployed. Leaks may be found either directly, such as by acoustic reflection from bubble streams, or indirectly, through the observation of indicative pockmarks on the seabed.

Sidescan sonar systems are able to accurately image large areas of the ocean in a relatively short period of time, with a resolution fine enough to potentially detect small changes in the morphology of the seabed, due to seepage. It can operate on a passive basis, which would be of use in leakage detection. Costs are moderate and are mainly associated with equipment and its set-up. Seabed multibeam systems may also be used for leakage detection, by finding pockmarks on the seabed or streams of gas in the water column. *In situ* multibeam systems such as GasQuant have been used to quantify natural gas release (e.g. von Deimling *et al*., 2010). With a finer resolution, boomer/sparker profiling and high resolution acoustic imaging methods can detect and track free gas in marine sediments and the water column. High frequency echosounders can detect hydroacoustic plumes and trace them to vents on the seabed.

Geochemical analysis of the water column can provide direct measurements of leakage, either through the analysis of dissolved gases themselves, or of physical parameters or dissolved elements that may be associated with a co-migrating, deep-origin water. Measurements can be made *in situ*, or by taking water samples to a laboratory, with leakage rates being estimated by conducting profiles perpendicular through a dissolved plume and using associated current velocities to calculate total mass flux (e.g. Keir *et al*., 2008). Ideally, measurements could be taken using remotely operated vehicles (ROVs) in conjunction with acoustic or seismic surveys. Alternatively, sensors could be mounted on autonomous underwater vehicles (AUVs) for remote and autonomous deployment, offering good spatio-temporal resolution.

Equilibrators involve continuous pumping of water from a chosen depth while a ship steams and the stripping of dissolved gases for analysis, giving good spatial resolution close to the sea floor or at different depths through the water column. This method has been used for the detection of pipeline leaks and seepages from oil and gas reservoirs (Logan *et al*., 2010). This approach could conceivably also be applied for offshore CO_2 storage sites, with such measurements even being “piggy-backed” on 3D seismic surveys of the site.

Benthic chambers can also be used for the direct quantification of flux rates from the sediment floor to the water column. The change in composition of the water in the chamber over time is used to calculate the flux rate. However, these measurements are highly point specific, and errors due to spatial heterogeneity may be incurred.

Elevated CO_2 levels near the seabed and in ambient water will affect the physiology of fish and other marine biota, due in part to changes in pH and HCO_3^- and the sensitivity of the particular animal. Seabed fauna could be monitored using AUVs, which can operate on the seafloor for weeks or months, or by obtaining long-term time-lapse video recording to assess seasonal changes. Threshold values represent a useful tool for the evaluation of the biological impacts from a certain parameter on a certain species. With proper parameterisation, leakage quantification may be possible.

Atmospheric monitoring methods

CO_2 leakage at the surface may be quickly dispersed into the atmosphere, and therefore may prove difficult to detect using methods that favour a wide areal coverage over spatial resolution. Surface monitoring equipment would therefore preferably be positioned in the region of areas where possible leakage paths have been identified through studies of the reservoir and overburden.

Offering a relatively large spatial coverage, the eddy covariance method (ECM), which uses statistics to compute turbulent fluxes of heat, water and gas exchange, is one of the most effective methods to measure and determine gas fluxes in the atmospheric boundary layer. Able to average the integral flux of gases over several square kilometres and different temporal scales, it has been proposed as a potential method for monitoring geologic CO_2 storage sites (e.g. Leuning *et al*., 2008). It is an established technique with low to moderate costs, which are primarily associated with data processing and specialised equipment. Flux rates measured usually lie within the typical range of CO_2 emissions from soils and different land covers (10's of g/m²/d), while higher emission rates can easily be determined. However, whether the ECM could detect a release of CO_2 from a storage site strictly depends on the ratio between the integral CO_2 flux from the footprint area and the seepage rate from a point source. A seepage rate of 0.1 t/d from the ZERT release experiment (Lewicki *et al*., 2009) was not distinguishable from background CO_2 emissions, whereas the release of 0.3 t/d significantly increased the measured flux rates compared to the base line emission of the area.

With a finer spatial resolution than the ECM, long open path tuneable diode lasers can be used to measure the average concentration of a specific gas in the air between two points, with the measurement interval ranging from tens to hundreds of metres. Various experiments have been conducted to study the application of this method to geological CO_2 storage sites, due to its sensitivity, fast response time, and potential to intersect a temporally and spatially variable plume. Leakage quantification using these instruments can be done using such approaches as vertical radial plume mapping (VRPM) (US EPA, 2005) and backward Lagrangian Stochastics (bLS) (e.g. Loh *et al*., 2009). Controlled CH_4 release experiments using bLS have yielded estimates within 5% of the true value at leakage rates of 16-48 t /day (Flesch *et al*., 2004) and 3-6 t / day (Loh *et al*., 2009), in agreement with modelled minimum detectable CH_4 leakage rates of 1.7 to 7 t / day under different path lengths and wind conditions (Trottier *et al*., 2009). Similar experiments using CO_2 have produced much larger errors due to the lower sensitivity of the sensor and higher, more variable background levels of the gas species. For example leakage rates were over-estimated by 87% during a controlled leakage of 43-100 t CO_2 / day (Loh *et al*., 2009), whereas modelled minimum detectable CO_2 leakage rates have been estimated between 950 to 3,800 t / day (Trottier *et al*., 2009). The short distances between measurement paths and leakage location implies that successful application of the method requires a point source whose location is accurately defined.

Short closed path detectors involve the introduction of a gas sample into a chamber, prior to optical (typically infrared) analysis for quantification of specific gas components. Similar to the long open path systems, inverse dispersion modelling can be used with the short closed path detectors for leakage quantification. Since they are relatively cheap, flexible and robust with respect to interference from other gases, they can potentially be placed close to the ground, and deployed in large numbers to form a comprehensive monitoring network. An added potential for real-time isotopic analysis, which would help clarify the origin of the gas, is offered by short closed path diode lasers, although these are more cumbersome and expensive.

Shallow subsurface monitoring methods

Near surface gas chemistry offers two relatively low cost means of monitoring and quantifying CO_2 leakage: gas flux measurements at the ground surface and gas concentrations / isotopes in the shallow sub-surface (typically in the first metre). These two methods are often conducted together due to their complimentary nature, the former being used to define transfer rates out of the soil and the latter being used to constrain CO_2 origins and flux estimates. The success of soil gas and gas flux surveys to accurately quantify leakage will be a function of i) actually sampling within the anomalous zone, ii) recognising the anomaly as being the result of deep leakage, and then finally iii) quantifying the leakage flux rate in a manner that takes into consideration baseline biological contributions and spatial variability.

In regards to the first point, statistical analyses have shown that there is a close link between anomaly size and sampling density (Oldenburg *et al*., 2003), although recent sampling strategy developments have the potential to increase survey success (e.g. Cortis *et al*., 2008; Lewicki *et al*., 2006). Regarding the second point, leakage recognition requires analysis of multiple gas species (light hydrocarbons, helium, O_2/CO_2 and N_2/CO_2 ratios, man-made tracers, etc.) and isotopes (e.g. $\delta^{13}C_{CO2}$, $^{14}C_{CO2}$), as well as the use of deeper vertical profiles, to understand if a CO_2 anomaly originates from the storage reservoir or from near-surface biogenic production. Regarding the third point, quantification typically involves sampling on a grid, interpolating between points, conversion to total CO_2 flux for the measurement area, and subtracting near-surface contributions based on baseline studies or soil gas data. For example: controlled leaks of 0.1 and 0.3 t CO_2 /d at the ZERT site were accurately quantified using CO_2 flux measurements, with the latter leak rate being estimated at 0.31 ± 0.05 t CO_2 / day (mean ± 1 SD) (Lewicki *et al*., 2010); soil gas monitoring of perfluorocarbon tracers added to injected CO_2 at the West Pearl Queen depleted oil formation quantified a leakage rate of 2.82 kg CO_2 / year (Wells *et al*., 2007), which corresponded to 0.014% of the total injected CO_2; and flux and isotope results were modelled to estimate a total leakage rate from the Rangely CO_2-EOR project of less than 170 t / year CO_2, which converts to approximately 0.01% of the yearly injected CO_2 (Klusman, 2003). Autonomous monitoring stations can analyse gas concentrations and fluxes on a continual basis over extended periods of time, potentially providing valuable baseline data prior to calculating CO_2 leakage.

In the near-surface environment, CO_2 flow is likely to occur as bubbles migrating vertically along a fault or near a borehole. Gravimetric and EM/ERT methods may be deployed while simultaneously monitoring the reservoir, and can potentially be used for leakage detection in groundwater. The time series data collected can be used to assess and account for natural variations. Gravimetric methods operated in continuous or time-lapse mode may theoretically be able to characterise volumes of gas in the order of a few hundreds of tonnes in the shallow subsurface, depending on the saturation. At present the method is not established for use in CO_2 monitoring and may prove to be prohibitively expensive. The electrical and electromagnetic methods may also offer the potential to detect increased CO_2 presence in shallow groundwater. In particular, airborne EM techniques are well-established in groundwater exploration studies (e.g. Siemon *et al.,* 2009), having provided information on aquifer structure and water quality for over three decades. The applicability of the technique may be limited due to noise originating from a variable water table and high natural CO_2 flux. Therefore a long period of pre-injection baseline monitoring would be recommended. In addition, use of airborne EM may be limited in areas where significant clay contents, or naturally high background levels of dissolved solids are present. Since the method provides no geochemical discrimination, ground-based sampling techniques should be employed to establish the cause of any enhanced conductivity. In order to provide a quantitative estimate of CO_2 leakage, a potential method may be to use a numerical simulator to predict whether a measureable impact on the groundwater would occur given an ingression of leaked CO_2, in terms of a change in the total dissolved solids (TDS) content. An empirical relationship between TDS and electromagnetic recordings could theoretically then be used to estimate the amount of CO_2 that has dissolved in the groundwater. At present, these methods are not yet established, but are the subject of current research and may provide monitoring and quantification solutions in the future.

Hydrochemical factors may be useful for the detection and quantification of leakage, particularly in inhabited areas which contain springs or streams. For example, waters containing elevated CO_2 levels that emerge at the surface may visibly contain bubbles, and oxidation of dissolved iron may lead to the appearance of rusty deposits. Routine monitoring of pH and other indictors may also detect leakage, for example in more urban or agricultural areas served by a network of extraction or monitoring wells.

Once leakage of stored CO_2 into shallow groundwater has been detected, it may be possible to estimate quantities by combining measurements of groundwater flux with analysed concentrations of carbon species. The accuracy of the estimation would improve with repeated spatio-temporal sampling, particularly where the groundwater has significant natural variability. The flux of CO_2 bearing springs may be measured volumetrically using vessels, weirs or tracer dilution methods. Where the CO_2 can only be determined within the groundwater, the volume of water may be estimated using the porosity and size of the aquifer. The analysis of isotope or tracer concentrations may enable the differentiation between natural and anthropogenic sources.

Ecosystems monitoring and remote sensing methods

Ecosystem-based monitoring can be used to qualitatively detect and monitor leakage into near surface systems, particularly when undertaken in combination with soil gas surveys. Impacts on vegetation, and possibly soil geochemistry may be detected using airborne remote sensing techniques. Changes in vegetative cover between successive spectral images are usually assessed using the normalised difference vegetation index, among other methods (e.g. Govindan *et al*., 2010). However, leakage quantification based on vegetation may not be possible as above certain levels (or duration) of leakage, further damage will not occur. Thermal imaging may also potentially detect leakage indirectly given a measurable temperature anomaly, and it may be possible to estimate leakage rates by determining the heat energy required to produce it. High resolution airborne hyperspectral scanners may detect CO_2 (and CH_4) directly using absorption features within their wavelength range. Quantification of anomalous CO_2 flux may be attempted using an inversion technique which attempts to establish a relationship between CO_2 plume related radiance and CO_2 concentration, and the Continuum Interpolated Band ratio method (Spinetti *et al*., 2008). However, small scale surface emissions may be difficult to detect given the relatively coarse spatial resolution of satellite images.

Table 1 presents the suitability of available monitoring methods for CO_2 detection and quantification considering the rate of CO_2 that can be quantified using the proposed techniques. The choice of low, intermediate and high rates used (at 100g/d, 100 kg/d and 100 t/d respectively) is based on measured fluxes from natural analogue sites, where variation of leakage rate measurements has been found to span six orders of magnitude.

Table 1. Suitability of available monitoring methods for detection and quantification of CO_2 leakage from a storage site.

AQUATIC MONITORING	**Monitoring method**	Sonar methods			Surface water chemistry	Marine Bubble stream chemistry
Leakage quantification		Sidescan sonar bathymetry	Seabed multibeam bathymetry	Bubble stream detection		
Leakage rate	low (100 g/d)					
	intermediate (100 kg/d)				*case dependent*	
	high (100 t/d)					
Leakage type	diffuse	*case dependent*	*case dependent*		*case dependent*	
	disperse spots					
	single localised leak	*case dependent*	*case dependent*			

ATMOSPHERIC MONITORING	**Monitoring method**	Long open path (IP diode lasers)	Short open path (IR diode lasers)	Short closed path (NDIRs and IR)	Eddy covariance
Leakage quantification					
Leakage rate	low (100 g/d)				
	intermediate (100 kg/d)	*case dependent*			
	high (100 t/d)				
Leakage type	diffuse	*case dependent*	*depends on contrast with background*	*case dependent*	
	disperse spots				
	single localised leak				

SHALLOW SUBSURFACE MONITORING	**Monitoring method**	Soil gas and flux	Downhole fluid chemistry	Hydrochemical methods	Tracers	Soil geochemistry
Leakage quantification						
Leakage rate	low (100 g/d)	*dependant on size of mofette and back-ground level/fluctuations*		*localised discharge from fractured reservoirs only*		
	intermediate (100 kg/d)					
	high (100 t/d)					
Leakage type	diffuse	*dependant on contrast of leakage anomaly/background*		*low rates may not be detectable*		
	disperse spots					
	single localised leak		*require large fluxes and extensive geoch.anomalies*			

ECOSYSTEMS MONITORING	**Monitoring method**	Terrestrial ecosystems	Marine ecosystems
Leakage quantification			
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)	*case dependent*	*case dependent*
	high (100 t/d)		
Leakage type	diffuse	*case dependent*	*case dependent*
	disperse spots		
	single localised leak	*case dependent*	*case dependent*

REMOTE SENSING	**Monitoring method**	Airborne and satellite spectral imaging	Airborne EM
Leakage quantification			
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)		*case dependent*
	high (100 t/d)		
Leakage type	diffuse		*case dependent*
	disperse spots		
	single localised leak		*case dependent*

pink = method suitable; yellow = less suitable; white = not applicable

1 INTRODUCTION

The main objective of this study was to identify and review the potential methods for quantifying CO_2 leakages from a geological storage site from the ground or seabed surface and discuss the level of accuracy that is currently required for site permitting and accounting purposes. The report primarily focuses on leaked CO_2 which may reach the ground or seabed surface, i.e. the atmosphere or the water column, as defined in the EU ETS. The specific tasks that were carried out in order to meet this objective are as follows:

- Identify current and emerging techniques that can measure CO_2 leakage on shore and off-shore from potential point as well as diffuse sources
- Provide a detailed review of the quantification performance of each method individually including operational/technical details as wells as cost implications
- Evaluate the improvements in quantifying CO_2 leakage through the implementation of a monitoring portfolio tailored for on-shore and off-shore environments
- Review current and proposed regulations and evaluate the required CO_2 leakage quantification accuracy against the performance of individual leakage monitoring methods and monitoring portfolios
- Provide recommendations for best practice in using existing CO_2 leakage monitoring techniques for quantification purposes and provide recommendations for future research and development to address stakeholder and regulatory requirements

Monitoring is an essential element in the design, operation, decommissioning and post-closure of a CO_2 storage site on-shore or off-shore. The monitoring techniques that may form part of the monitoring programme at a CO_2 storage site very much depend on the particular site characteristics and the applicability of each method for a defined storage scenario may vary significantly. The monitoring methods aim at a number of different objectives, firstly to verify the plume location and migration of the CO_2 in the sub-surface; secondly to detect potential CO_2 leakage and to quantify the amount of CO_2 that may migrate outside the storage complex; and thirdly to detect and quantify the CO_2 leakages which may reach the ground or seabed surface. Monitoring and quantification techniques referred to in this report mainly address this third objective.

The leakage rate, variations in rate, and the pattern of escape from the leakage pathways, all depend on the geological characteristics of the leakage pathway. The processes involved can in principle range from natural phenomena as existing permeable faults, re-opened faults and fractures, breaching of sealing rock layers either by fracturing or by exceeding the threshold pressure, to artificial pathways created by drilling of wells or technical penetration of seals. The characteristics of the pathway will partly determine the possible maximum rate, and can shape the effects from any self-limiting or self-enhancing processes. The interaction can under some circumstances create pulsating rates that might be more complex to quantify with the monitoring tools. The positioning of monitoring tools and the expectations of rates and fluctuations can be supported by a characterisation of the geological structure and properties of the pathway system.

Table 2 presents the IEA GHG CO_2 Monitoring Selection Tool, which has been developed to help identify appropriate techniques for monitoring CO_2 that has been injected into a geological storage reservoir. This table also indicates the applicability of the various methods in detecting and quantifying CO_2 in the deep/shallow subsurface, the plume location and migration, fine scale processes as well as identifying leakage and quantifying some characteristics of the leakage. Since this tool was designed there have been a number of new field test sites where different versions of these monitoring methods have been used and implemented as part of a monitoring portfolio. New technical advances have also assisted in improving the mentioned techniques in detecting CO_2 leakage with improved levels of accuracy and precision. The objective of this study was to review the published materials and monitoring applications in the field and pilot CO_2 storage sites worldwide and compile this information in a succinct document that will facilitate the dialogue amongst the regulators, researchers, developers of monitoring tools and technologies and

Table 2. IEA GHG CO_2 Monitoring Selection Tool (IEA GHG, 2010).

				deep	shallow	Plume location / migration	Fine scale processes	Leakage	Quantification
Seismic			3D/4D surface seismic						
			Time lapse 2D surface seismic						
			Multi-component surface seismic						
	Acoustic imaging		Boomer/sparker profiling						
			High resolution acoustic imaging						
			Micro-seismic monitoring						
	Well based		4D cross-hole seismic						
			4D vertical seismic profiling						
Sonar bathymetry			Sidescan sonar						
			Multi beam echo sounding						
Gravimetry			Time lapse surface gravimetry						
			Time lapse well gravimetry						
Electric/electromagnetic			Surface EM						
			Seabottom EM						
			Crosshole EM						
			Permanent borehole EM						
			Crosshole ERT						
			Electric spontaneous potential						
Geochemical	Fluids	Downhole /Springs	Downhole fluid chemistry						
			pH measurements						
			Tracers						
		Marine	Sea water chemistry						
	Gases		Bubble stream chemistry						
		Atmosphere	Short closed path (NDIRs & IR)						
			Short open path (IR diode lasers)						
			Long open path (IR diode lasers)						
			Eddy covariance						
		Soil gas	Gas flux						
			Gas concentrations						
Ecosystems			Ecosystems studies						
Remote sensing			Airborne hyperspectral imaging						
			Satellite interferometry						
			Airborne EM						
Others			Geophysical logs						
			Downhole Pressure / temperature						
			Tiltmeters						

Dark pink = method suitable; pink = less suitable; white = not applicable

operators at an international level. The study aimed to provide a sound basis for interaction between these groups in order to ensure that:

- a realistic framework is set up for emissions trading purposes (EU ETS, EU CCS directive, and international dimension) national GHG inventory purposes,
- the stakeholders are informed about the leading edge technology, knowledge and methodologies that are being developed, as well as recognising the limitations currently perceived,

- a practical inventory of capabilities, sensitivity, accuracy, uncertainties of different methods and example applications are provided,
- future research needs to improve potential and existing CO_2 leakage monitoring techniques are targeted.

With these requirements in mind, the project focused on various methods for leaked CO_2 emissions monitoring and quantification. The following sections describe the various methodologies that are currently employed for ground and seabed surface CO_2 leakage monitoring, and those which have been identified as having potential for deployment. Where available, examples of their use have been given. The review covers techniques measuring CO_2 leakage into the atmosphere as well as the water column either from individual point sources or as dispersed CO_2 leakage. The potential of each methodology for use in quantifying CO_2 leakage is assessed. Care has been taken to include newly available methods and those that are currently breaking into the market or from different disciplines which have the potential to be applied in CO_2 leakage quantification.

2 IDENTIFICATION AND REVIEW OF TECHNIQUES THAT CAN MEASURE AND QUANTIFY CO_2 LEAKAGE

2.1 Marine and terrestrial aquatic environment monitoring methods

The use of geological formations in an offshore environment for CO_2 storage holds considerable promise, although costs of offshore operations are significantly higher than corresponding onshore operations. All equipment has to withstand a hostile environment, which especially for long-term monitoring systems multiplies the costs compared to onshore systems. This also applies to the costs for installation and maintenance of the monitoring equipment. For most work, highly qualified divers or remotely operated vehicles (ROV) are necessary, which again require support vessels and crew for operation.

On the other hand, CO_2 storage projects in an offshore environment come with a few advantages. Firstly, storage locations are more remote and thus less likely to cause as much direct public concern. Secondly, unlike an onshore storage site, access to the seafloor above a storage site is easier, because there are no buildings, roads, vegetation, etc. Thus, the possibilities of monitoring by automated autonomous vehicles are much better. Thirdly, the physical properties of water as the surrounding medium provide advantageous monitoring conditions, because the physical difference between CO_2 and water is greater than that of CO_2 and air.

2.1.1 Sidescan sonar bathymetry

Development of sonar bathymetry by monosource echosounders started in the early part of the 20th century and evolved rapidly after WW2, totally replacing the old sounding line method to measure ocean depths. Using the new method it was possible to conduct fairly detailed mapping of the seabed along transects. Merging data from many surveys allowed large-scale maps of the seabed to be created. One example is the set of seafloor maps drawn by Heezen and Tharp and published in the 1960's, which portrays the mid-ocean ridges as well as smaller scale features like rifts and fracture zones (Kunzig, 2000). Such detailed maps helped to formulate the theories of seafloor spreading and plate tectonics. Still, the sampling method had its shortcomings in terms of areal coverage and resolution of details on the seabed.

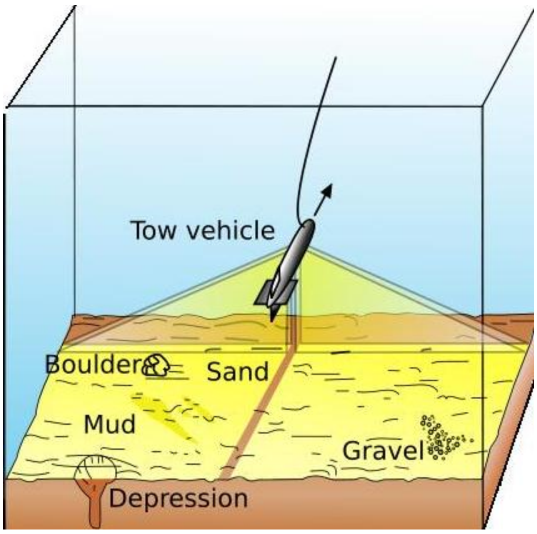


Figure 3. Sidescan survey by a towed vehicle (courtesy of the U.S. Geological Survey).

The sidescan sonar was developed by the Institute of Oceanographic Sciences (IOS) in the UK, with the additional capability of mapping the texture of the seabed, and cutting wider swaths than the Sea Beam. Sidescan sonar is currently used to accurately image large areas of the ocean with the acoustic beam being very wide in the sideways direction and very narrow in the forward direction (Figure 3).

Field examples
The initial deployment of this technology was from ships; later it was applied to underwater vehicles like towed vehicles and autonomous underwater vehicles (AUV) that can operate very close to the seabed, thus enabling more detailed mapping than what is achievable from the surface. It was the towed side scan that enabled the detection of pockmarks on the seabed. Untethered AUVs like the Hugin from Kongsberg (Figure 4) can operate to ocean depths of 3,000 m, i.e. far beyond the ocean depths presently suggested for offshore CO_2 storage sites (typically a few hundred metres). AUVs can carry a combination of sidescan sonar and multibeam echosounders to enhance mapping capabilities and resolution.

The bathymetric data is obtained by active sonar, where the seafloor topography is mapped by the received reflections. High quality photograph-like images can be generated from the survey and very small features in the scale of 1 cm can be resolved (Hellevang *et al*. 2007). This could render possible the opportunity of detecting even very small changes in morphology caused by a potential CO_2 seepage into the water column. Sidescan sonar could also be used to directly detect CO_2 seeping into the water column as such systems have demonstrated the ability of detecting natural seepage of shallow methane gas.

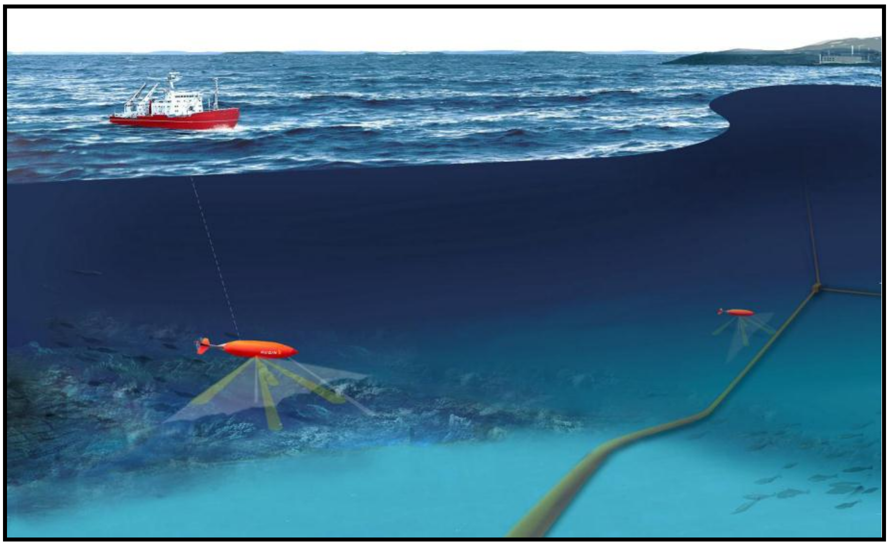


Figure 4. An illustration of AUVs in operation (courtesy of Kongsberg Maritime).

Sonar systems have high sensitivity, especially for gas, and have been regarded to have a high potential for subsea hydrocarbon leakage detection (Carlsen and Mjaaland, 2006). It should be possible to adapt existing hydrocarbon leakage detection systems based on active sonar principles into CO_2 leakage monitoring on the seabed and in the water column, as has been demonstrated in deep sea experiments with CO_2 by Brewer *et al*. (2006). Acoustic hydrocarbon leakage detection systems can be used to cover areas in the range of some tens of metres for subsea oil and gas production systems (Hellevang *et al*., 2007).

Passive acoustic systems are dependent on advanced signal processing to distinguish various sounds and sources from one. In subsea oil and gas production systems, noise can be generated from various sources. These sounds vary with flow conditions and settings in the system. Passive sonar systems have been suggested as a technique for condition performance monitoring in addition to leakage detection. Identification of the location of a leakage point could be a potential use for such a monitoring system.

Strengths and weaknesses
Surveys with sonar systems represent an effective method of covering wide areas in a relatively short time. It is likely to be a cost-effective method compared with other methods. Applying it to AUVs may represent

a promising means of monitoring and detecting leaks, for further quantification. However, multibeam systems may have limited resolution, so that small pockmarks may be undetected.

2.1.2 Seabed multibeam bathymetry

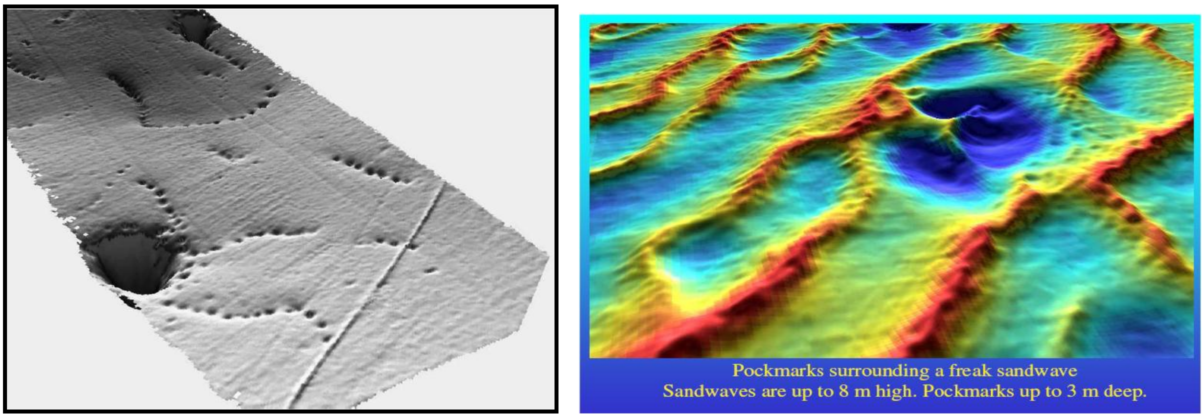
The simple seabed multibeam configuration may consist of two echosounder transceivers, one with high frequency and one with lower frequency, the latter giving information about the shallow sediments as well as depth. Advanced multibeam sonar was invented around 1960, and was kept as a military secret for a couple of decades. The transmitters were first arrayed along the ship's keel, and the fan of beams hit a stripe of seafloor extending sideways for hundreds of metres or longer. Later, when receivers were mounted in a line across the keel, depth information from the whole stripe could be obtained. This system was called multibeam sonar or swath-mapping sonar. By 1980, declassified multibeam systems were available for non-military use, and later the commercial Sea Beam appeared as an improved version of this system. High-frequency systems with high resolution are now commonly used in coastal waters for seabed surveying, and other versions are used in deep water by the oil and gas industry and others.

Multibeam echosounders consist of an array of narrow single beam echosounders. This gives the advantage of wide area coverage in a short period of time. The frequency region used in these systems is in the range of ten to a few hundred kHz. Higher frequencies will most often provide better resolution and accuracy compared to lower frequencies for the same water depth (distance to the seafloor). The optimal frequency will depend on the application and in some cases it will be valuable to perform a survey with more than one frequency. The systems can be located on an AUV or a boat. The frequency of the system mounted on a boat will typically need to be lower (below 100 kHz) if the water depth is larger than a few hundred metres due to increased attenuation in water with higher frequencies.

Field examples

Figure 5a shows an image made from a digital terrain model acquired by high-resolution multibeam bathymetry (Hovland *et al*., 2002). The pockmarks are occurring adjacent to a 20 inch gas pipeline located on a soft seabed at 300 metres water depth in the North Sea. Figure 5b shows a pockmark embedded within a pattern of sand-waves.

Regular sonar systems may also be used for leak detection and possibly quantification. Active sonar consists of both transmitter(s) and receiver(s). The transmitter(s) generate an acoustic sound pulse and the receiver(s) listen for any reflections/echoes. Reflections will occur where the transmitted sound pulse encounters a change in acoustic impedance.



a) b)

Figure 5. a) High-resolution multibeam echo sounder bathymetry from a ca 300 m deep location off Mid-Norway. The large, normal pockmark has a diameter of ca 30 m (depth ca 4 m), the smaller 'Unit-pockmarks' are ca 5 m wide, 1 m deep. The line to the right is the 20" 'Haltenpipe'; b) 2-3 m deep pockmarks embedded within sandwaves up to 8 m high in the North Sea observed by multibeam echosounder (Courtesy of M. Hovland, Statoil).

Strengths and weaknesses
With multibeam sonar one can cover wide areas in a relatively short time. As for the sidescan systems, it is likely to be a cost-effective method compared to other methods, if detailed mapping is required. It may also detect leaking gas, in the form of bubbles or even liquid gas, above the seabed. Using AUVs as the instrument platform represents a promising means of monitoring and detecting leaks, and for further quantification. However, there are limits in resolution so that small pockmarks and minor leaks could go undetected.

Quantification
By detecting escaping gas from the seabed, it could be possible to make some rough quantification of the leak. By combining with optical methods, acoustic tomography and flow sensors, more precise flux calculations could be obtained.

2.1.3 Bubble stream detection

Small gas leakages will dissolve in the water, but at significant leakage rates gas bubbles will form and rise from the seafloor. These rising bubbles show as characteristic flare signatures on ship-mounted sonar systems. Significant gas leakages are also often associated with structural features like pockmarks on the seafloor, which can be detected by sonar as discussed in the preceding sections. With modern sonar systems it is therefore possible to survey large areas of seafloor for signs of leakage.

Various aspects of the detection of bubble streams as hydroacoustic flares using high resolution methods (such as echosounders) are described in Section 2.1.5

Periodic monitoring of large areas
To reliably monitor a storage site it is necessary to scan the seafloor above the site regularly for signs of gas leakage. Realistically, such an area is too large for continuous monitoring, so a periodically repeated survey of the seafloor and the water column for unusual signals by ship-mounted systems is necessary to locate possible leakages.

These suspicious signs may include flare signatures from rising gas bubbles, sediment structures like pockmarks or seepage-related biology. In the last few years, the sonar technique has rapidly evolved due to the increase in on-site computing power from the 'traditional' single-beam sonar to multibeam systems and sidescan sonar, which allow the digitalisation and real-time 3D-visualisation of the water column.

Figure 6 shows an example of acoustically localised and imaged methane plumes near Spitzbergen (Westbrook *et al*., 2009). The use of single and multibeam sonar systems results in a detailed 3D bathymetry model of the survey area (Figure 6b) and the acoustic anomalies Figure 6c) caused by the rising bubbles. Further processing of the data gives estimates for the rates of the bubbles' upwards movement. Measurements from a stationary ship above a plume can give data about pulsating or continuous behaviour.

Figure 7 illustrates the capabilities of modern multibeam sonar imaging (here using a Kongsberg EM 302 system) and data visualisation (here using IVS 3D Fledermaus), taken from a cruise report of the NOAA ship *Okeanos Explorer*. The surveys revealed detailed information about the topography of the seafloor, also showing sediment structures that could indicate leakages. The data also give exact information about location, size and shape of the plumes.

However, even with modern visualisation software, data interpretation is not trivial and the typical flare signatures can easily be confused with fish swarms or be masked by background noise. Therefore, a thorough site specific survey of the seafloor prior to CO_2 storage is mandatory. Surveys repeated at regular intervals should provide a way to identify stationary features like a gas plume from 'non-durable' features such as fish.

A relatively complete and reliable coverage of a large area could be achieved by using a swarm of AUVs (e.g. Kongsberg's Hugin and Remus AUVs) equipped with multibeam sonar and optional additional sensors for T, pH, conductivity and dissolved gas (e.g. Contros HydroC). An AUV is basically an autonomous, usually torpedo-shaped robot that follows a pre-programmed course. Thus, it would be perfect for regular surveys. A swarm of AUVs could for example survey a relatively large area with a weekly interval, following a pre-programmed grid and providing very good data for leakage monitoring. The investments and maintenance costs for such a swarm would of course be significant (>10 M. Euro), because besides the AUVs a medium-sized dedicated support vessel and specialized crew are required.

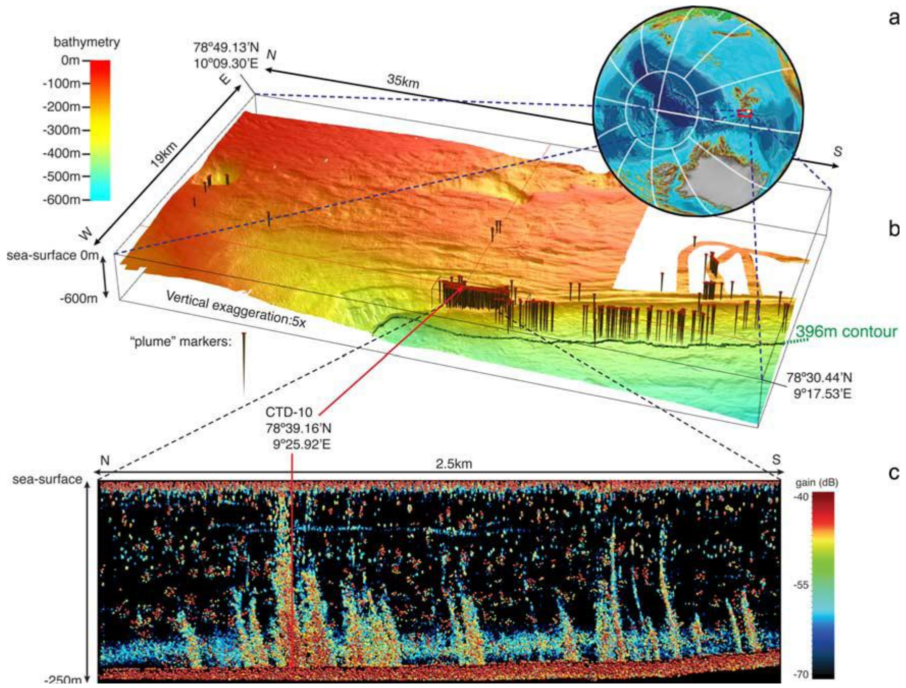


Figure 6. Example of plumes acoustically imaged with a ship-mounted Simrad EK60 sonar, showing the flare signatures of several methane plumes near Spitzbergen, in a water depth of 240 m (after Westbrook *et al*. 2009).

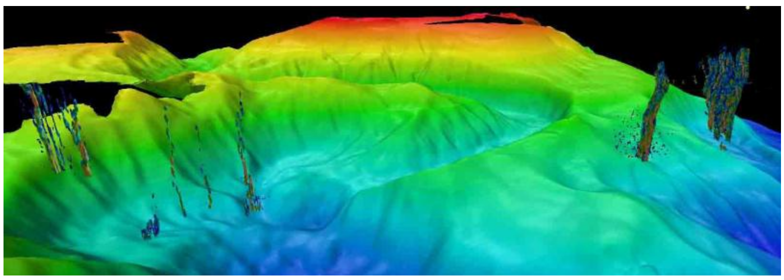


Figure 7. 3D visualisation of methane plumes in 1,200 – 1,900 m water depths off the USA's west coast, acoustically imaged with a Kongsberg EM 302 multibeam sonar (NOAA report 2009/07/16; Gardner *et al*., 2009).

Long-term leakage monitoring

Once a leakage is located by sonar and verified and analysed by a remotely operated vehicle (ROV), it is important to monitor the flow rate and the development of the leakage. Both sonar and ROV-based measurements only provide periodic short-term observations. For continuous long-term monitoring of the leakage, a stationary system is required.

GasQuant, a lander-based hydroacoustic swath system (Figure 8, after Greinert, 2008) was developed to monitor the temporal variability of bubble release at seeps. It is basically a sonar-like system with a horizontally oriented swath (63° swath angle), which records bubbles crossing the swath. Figure 8 illustrates the design of the system and the size of the area covered by the swath. It is capable of monitoring an area of about 2000 m². However, it was not designed for long-term monitoring over months, so energy supply is critical over a long time. Assuming that a CO_2 storage operation in progress requires technical installations on the seafloor anyway, GasQuant could be linked to these installations. This link could also be used for real-time data transmission.

A further option offering a large areal coverage, in the order of thousands of square kilometres, is the OAWRS (Long Range Ocean Acoustic Waveguide Remote Sensing) (Makris *et al*. 2006). This operates at a much lower frequency, and has relatively low resolution. Nonetheless, OAWRS may be suitable for first pass surveying of a storage site, potentially able to detect major leaks of significant spatial extent.

To summarise, although this is an established technique, it has yet to be demonstrated for the detection of bubble streams related to CO_2 leakage. However, in conjunction with methodologies able to measure flow rates and gas chemical composition, it may be possible to obtain estimates of leakage flux.

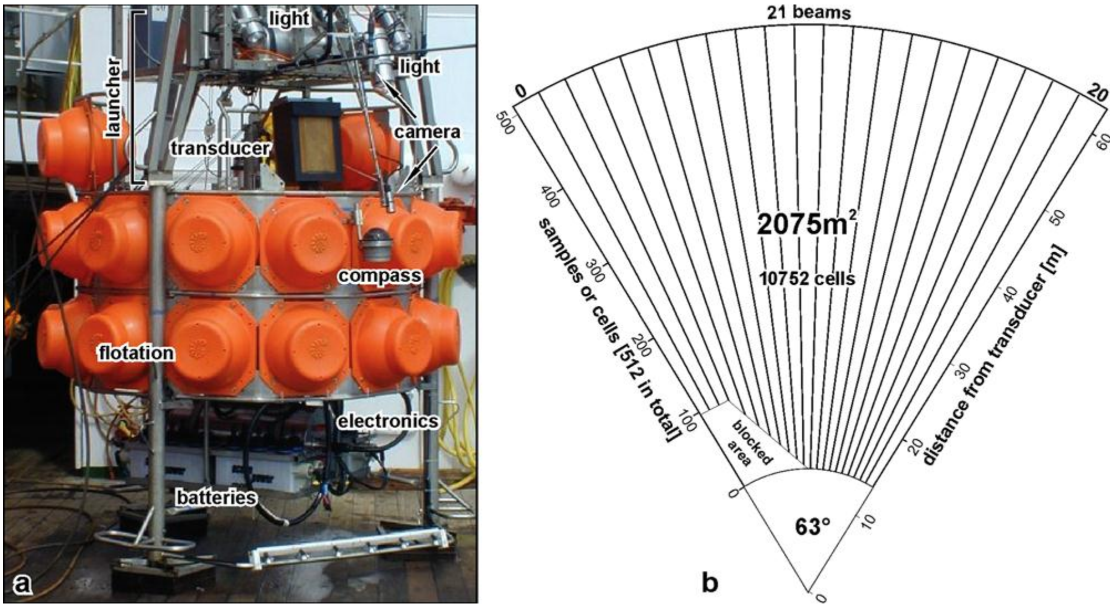


Figure 8. a) GasQuant Lander with launcher system; b) Dimensions of the hydroacoustic swath (Greinert, 2008).

2.1.4 Bubble stream chemistry

While small leakages of gas from the seabed may quickly dissolve into the water column, more significant releases can form plumes of rising bubbles that can be detected by sonar (see Section 2.1.3). Samples of the gas can be collected by funnels and analysed using routine techniques in a laboratory. The composition of the gas may elucidate its source, and help determine the flux rate of CO_2.

Monitoring methods

The study of natural gas analogue sites has demonstrated that bubbles dissolve as they rise. Furthermore, rising plumes are contorted by currents. Therefore, samples and measurements need to be collected close to the leakage point. Traditionally, a CTD probe is used for these measurements. The probe is lowered from a boat and can be equipped with additional sensors for e.g. pH and dissolved gas, as well as an acoustic positioning system to verify its exact position (the probe will drift off from its position directly under the boat due to currents). The position of a wire-mounted probe is difficult to control, because the whole boat has to be moved.

A much more flexible platform for sensor deployment is provided by ROVs. They are comparable to AUVs, but have much better manoeuvrability and remain tethered to a support boat. Thus, they can transmit data and optical images in real-time and be controlled by a pilot. With technical evolution, smaller versions of the formerly huge and expensive ROVs for the oil industry were developed. In the last 10 years, relatively affordable Mini-ROVs like the Ocean Modules V8 Sii (€120k – €200k, depending on configuration; Figure 9) are available. They do not require a dedicated support vessel and highly trained operators, which lowers upkeep costs significantly. Equipped with sensors for C, T, D, pH, dissolved gas etc., an ROV can be deployed on a possible leakage site that is identified from the sonar data. Micro-Sonars like the Tritech Micron Sonar and acoustic positioning like the Tritech Micron Nav USBL tracking system allow exact location of the anomaly and tracking of the ROV's path for later data analysis.

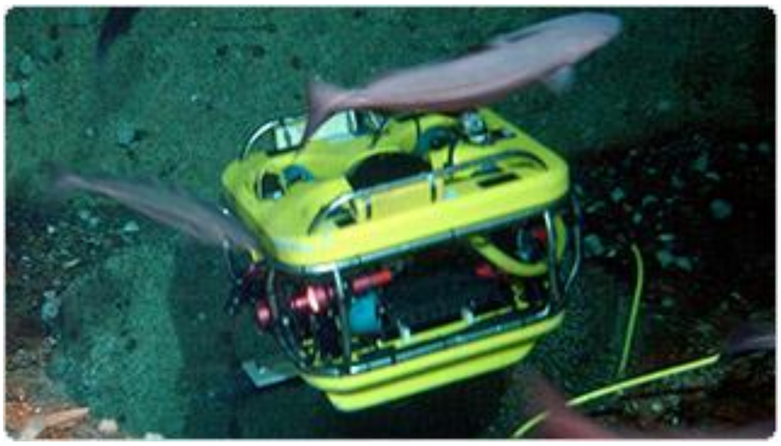


Figure 9. Remotely operated vehicle (ROV) Ocean Modules V8 Sii (www.ocean-modules.com).

With camera and lights a first optical examination of the anomaly can be conducted. In low visibility environments, recently developed acoustic cameras like the Coda Octopus Echoscope 3D real time sonar or the Soundmetrics DIDSON HD sonar imaging system can be used. These systems utilise a grid of sonar beams to obtain an image of the surroundings in real time. Impressive example movies of gas leakage can be found on the websites of both companies.

If the anomaly is identified as a gas leakage, estimations of the leakage rate can be made by optical and/or acoustic images. The gas and surrounding water can be sampled for later analysis, e.g. to identify the origin of the gas by isotope geochemistry. The exact size and shape of the plume can be determined by measuring the changing chemical parameters while manoeuvring the ROV in and out of the plume at several depths. Or, if the ROV is equipped with a suitable scanning sonar system, the plume can be mapped by measuring 'cross sections' through the plume at several depths by the sonar (Yapa *et al*., 2001). This data can be used for a 3D model of the plume.

A different approach for a direct measurement of the gas flow rate was developed over several EU-funded projects (e.g. CO_2GeoNet, CO_2ReMoVe). The first systems were derived from a prototype that was originally designed for monitoring of methane emissions in a mud volcano in Azerbaijan (Delisle *et al*., 2006). This prototype (Figure 10) used a raft with integrated funnel to collect the gas. Sensors, batteries and electronics were mounted on the raft, allowing the use of standard equipment and radio data transmission. The system was modified for installation in open sea by using a buoy instead of a raft and a funnel on the seafloor to collect the gas, connected to the buoy through a flexible tube (Figure 11). This setup still has the benefits of using standard electronics above water, but is more suitable to withstand waves and tides than the raft setup (Spickenbom *et al*., 2009a). It provides a cost-effective solution for shallow waters (< 20 m).

However, a buoy interferes with ship traffic, and it is also difficult to adapt this design to deeper waters. Therefore, a completely submersed autonomous system was designed (Spickenbom *et al*., 2009b). The focus was on keeping maintenance intervals as long as possible to reduce costs, so a 'low-tech' approach was chosen to keep the system as simple as possible, thus reducing sources of error.

The general setup and a small-scale prototype are shown in Figure 12. It consists of a gas collector, a sensor head and a pressure housing for electronics and power supply. This system is very robust and easily adjustable to specific site characteristics. In particular, the funnel size has to be chosen carefully because the collected data are only reliable for the area covered by the funnel. Since this setup is inexpensive, it can be distributed to cover larger areas. Leifer and Boles (2005) suggested an alternative design with tents instead of funnels for gas collection. Complex sensor networks can be set up by adding multi-channel data loggers, deep sea power supplies and, if real time monitoring is required, data transfer by cable or acoustic wireless modem to a relay station on a buoy or existing seafloor installations.

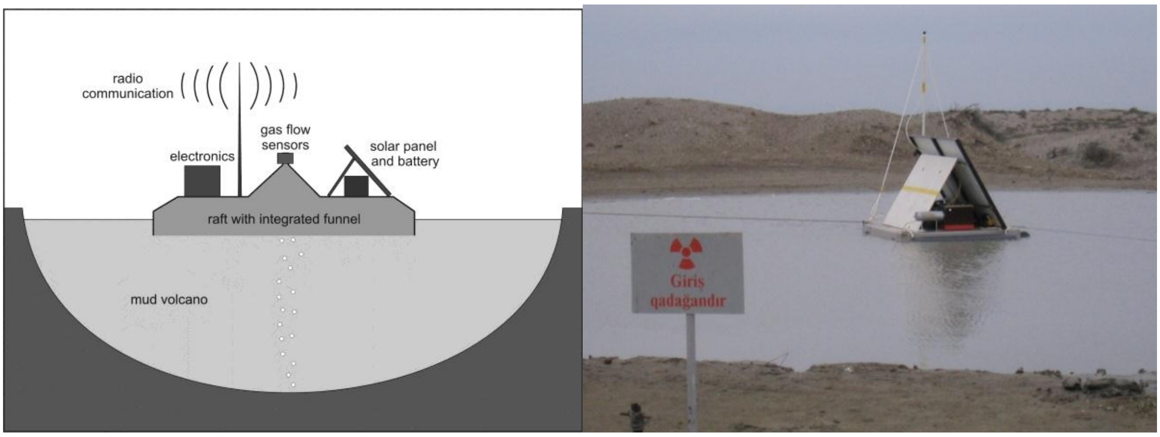


Figure 10. Prototype of a raft-mounted monitoring system on a mud volcano in Azerbaijan (illustration and photo by BGR).

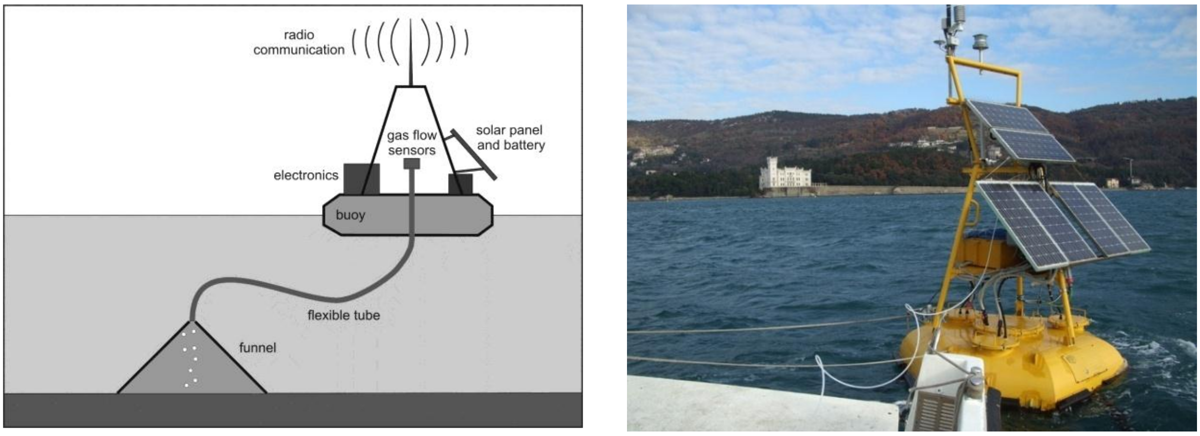


Figure 11. The MAMBO buoy, a buoy-mounted monitoring system with a funnel for gas collection on the seafloor, connected to the buoy by a flexible tube (illustration and photo by BGR).

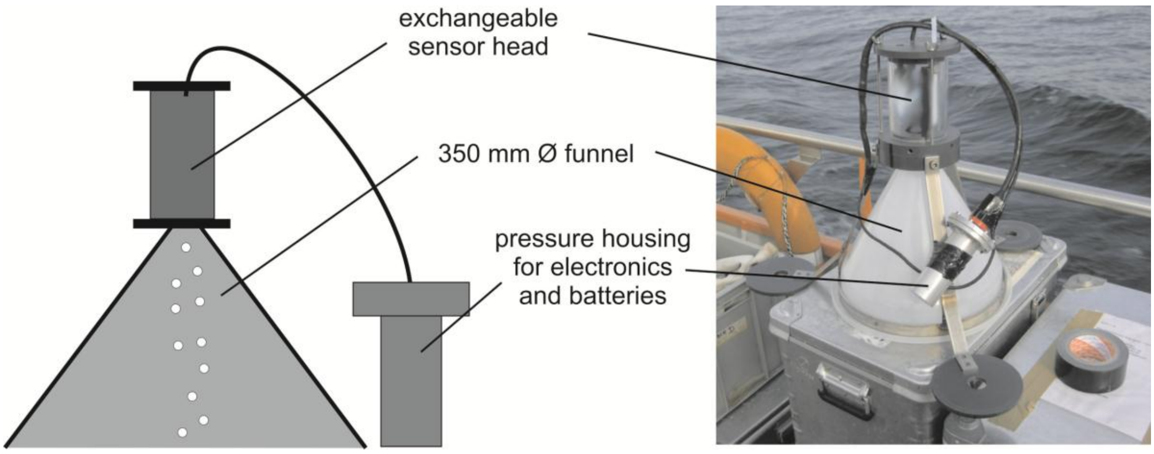


Figure 12. Prototype of a submarine autonomous gas flow monitoring system (illustration and photo by BGR).

A combination of GasQuant and funnel systems seems a reliable approach for long-term monitoring. Leakage rates can be recorded with the funnels, while GasQuant provides information for data verification, e.g. to ascertain if the funnels still cover the gas vents or if a vent has changed position outside of a funnel, which is then no longer collecting all the emanated gas.

Field examples

Examples of the study of bubble stream chemistry in the literature are scarce, with no direct applications to CO_2 leakage reported. However, Linke *et al*. (2009; 2010) assessed the spatial and temporal variability of seabed methane emission from natural cold seeps in the Hikurangi Margin, New Zealand. Benthic landers were equipped to measure several physical, chemical and biological parameters across the sediment/water interface. The Biogeochemical Observatory and the Fluid Flux Observatory were used for *in situ* flux measurements of CH_4 and O_2. As noted above, methane emissions from a mud volcano in Azerbaijan were also monitored by Delisle *et al*. (2006).

As part of a set of experiments to test a proposed method of CO_2 storage in the deep ocean, White *et al*. (2006) employed a deep-sea Raman spectrometer (DORISS: Deep Ocean Raman In Situ Spectrometer) to analyse preferential CO_2 dissolution from a 50%-50% CO_2 – N_2 mixture. Assuming a S/N ratio of 3, DORISS was able to detect CO_2 concentrations as low as 2.4 mol%. The authors concluded that the spectroscopic techniques developed could enhance future CO_2 studies in the deep ocean environment.

Caramanna *et al*. (2011) sampled both free and dissolved gas from a shallow natural analogue site close to Panarea in the Southern Tyrrhenian Sea. The free gas samples were collected using plastic funnels connected to Pyrex glass flasks with twin valves. The samples were subsequently analysed for O_2, H_2S, CH_4, N_2 and CO_2 using Carlo Erba 8000 Series gas chromatographs. The gas flow rate was measured by connecting the funnel to a tank of known volume and recording the time taken to fill it. A multiparametric probe (Sea-bird SBE 19 – Seacat profiler) was deployed by divers to obtain vertical logs of pH and redox potential. Reducing conditions and a low pH profile were clearly identified in the region of the gas emissions. The authors propose to use the site for the future development and testing of monitoring techniques for short and long term CO_2 seepage monitoring.

A combination of techniques to determine gas flux and composition may potentially be used to quantify CO_2 leakage. However, costs may become prohibitive in deeper waters.

2.1.5 High resolution (HR) reflection profiling

Seismic reflection methods that use acoustic sources of high frequency content (e.g. airguns, sparkers, boomers, echosounders) can provide information on the venting of free gas into the water column from seabed (or lakebed) structures. High resolution (HR) profiles can identify hydroacoustic flares within the water column corresponding to rising streams of gas bubbles, and examine their relationship to subbottom gas distribution around venting sites. HR methods provide a cost-effective means of surveying large areas and can also be used to construct pseudo-3D seismic or acoustic volumes across venting structures. Frequency-dependent resonance of bubble populations means that multi-frequency surveys may allow estimates of gas flux and raises the (as yet unrealised) potential of quantifying gas content.

HR acquisition systems

In marine or lacustrine settings, high resolution reflection methods refer to the use of relatively low energy sources of high peak frequency content (10^2-10^5 Hz), reflections from which are recorded at short offsets, typically via single-channel receivers, to acquire near-vertical incidence profiles that can be interpreted with minimal processing. HR methods yield data of limited penetration but high vertical and lateral resolution (Figure 13), at least one order of magnitude higher than more complex ‘commercial’ seismic reflection data.

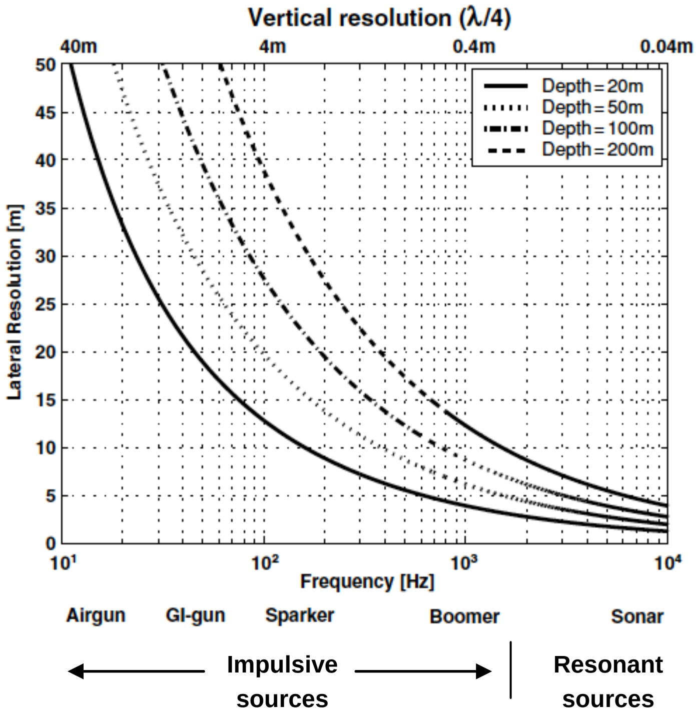


Figure 13. Theoretical vertical and lateral resolution over a range of frequencies corresponding to high-resolution (HR) sources and target depths (GI-gun = a tuned pair of airguns; sonar = echosounder) (after Müller *et al*. 2002).

A variety of systems are available to acquire HR marine reflection data: it is conventional to distinguish *impulsive* sources (airguns, sparkers, boomers), said to result in seismic wavelets, from higher resolution *resonant* sources (echosounders, Chirp profilers), said to result in acoustic or sonar pulses (Verbeek and McGee 1995). The theoretical vertical and lateral resolution of these systems varies with their peak frequencies, and with water depth, across several orders of magnitude (see Figure 13). Distinctions are often made between high-resolution (HR), very high-resolution (VHR) and ultra-high resolution (UHR) systems and/or data (e.g. articles in Missiaen *et al*. 2005), but there are no accepted definitions of these terms.

Impulsive sources use pneumatic or electric-discharge devices to generate pressure pulses in the water column, corresponding to seismic wavelets of short duration, broad frequency bandwidth and well-defined polarity; reflections are recorded through a separate hydrophone at short offset (Verbeek and McGee 1995; Mosher and Simpkin 1999). The most common HR impulsive sources are airguns (explosive release of compressed air), sparkers (explosive discharge from electrode arrays) and boomers (electro-dynamically accelerated pistons). Peak frequencies in the range 10^2-10^3 Hz yield vertical resolution from meters to decimetres, in general higher for sparkers and boomers as shown in Figure 13.

Resonant sources use piezo-electric transducers that act as both source and receiver, transforming electrical current into vibrations and vice versa (Verbeek and McGee 1995; Mosher and Simpkin 1999). Such transducers generate pressure pulses that approximate sine waves, resulting in high-frequency acoustic signals of narrow bandwidth (see Figure 14). The most common are echosounders (or pingers), typically hull-mounted, with frequencies in the range of 10^3-10^5 Hz. The modern standard is provided by Chirp profilers, which transmit a defined ‘sweep’ of amplitude-varying frequencies, of long duration and wide bandwidth, that can be digitally auto-correlated with the recorded signal to recover high-resolution data, including information on polarity (Quinn *et al*. 1998; Mosher & Simpkin 1999).

Short-offset profiles acquired using both impulsive and resonant sources can be used to construct *3D seismic (or acoustic) volumes* across shallow targets (typically gas venting sites). The basic approach is to acquire a series of closely-spaced HR profiles, which are reassigned to a matrix of bins to obtain single azimuth data volumes, described as pseudo-3D, quasi-3D or 2.5D. Such single azimuth volumes have been acquired using airgun, sparker, boomer and even Chirp sources, recorded through single-channel or short multichannel streamers (e.g. Newman 1990; Riedel *et al*. 2002; Müller 2005; Hornbach *et al*. 2007; Wagner-Friedrichs *et al*. 2008).

Indications of gas seepage

Even small quantities of gas may generate a strong acoustic response in the water column or in subbottom sediments, due to frequency-dependent effects on the velocities and attenuation of P-waves (Anderson and Hampton 1980; Wilkens and Richardson 1998). HR reflection data are particularly sensitive to the presence of gas, because the source frequencies used (Figure 13) overlap with the resonance frequencies of naturally occurring bubbles (Figure 14). Bubble streams in the water column may be observed on HR data as hydroacoustic flares, rising from venting sites that may also contain evidence of gas at or near seabed (Fig. 3a; Fleischer *et al*. 2001; Judd and Hovland 2007).

Populations of gas bubbles have been shown to have a typical resonance frequency (Figure 14a) that depends primarily on their size, shape and number (Anderson and Hampton, 1980; Wilkens and Richardson, 1998). The interactions of different source frequencies with a given bubble population result in changes in both the velocities and attenuation of P-waves, for which three main cases are recognized (Figure 14b): below, at and above resonance (e.g. Mathys *et al*. 2005). Below resonance, overall sound velocity is reduced by the presence of gas; at or near resonance, most energy is attenuated (by reverberation and scattering); above resonance, sound speed is unaffected but attenuation (by scattering) remains important (see Figure 14b). Thus the expression of free gas on a given reflection data type is strongly dependent on its frequency content relative to that of bubble resonance (cf. Figure 13 and Figure 14).

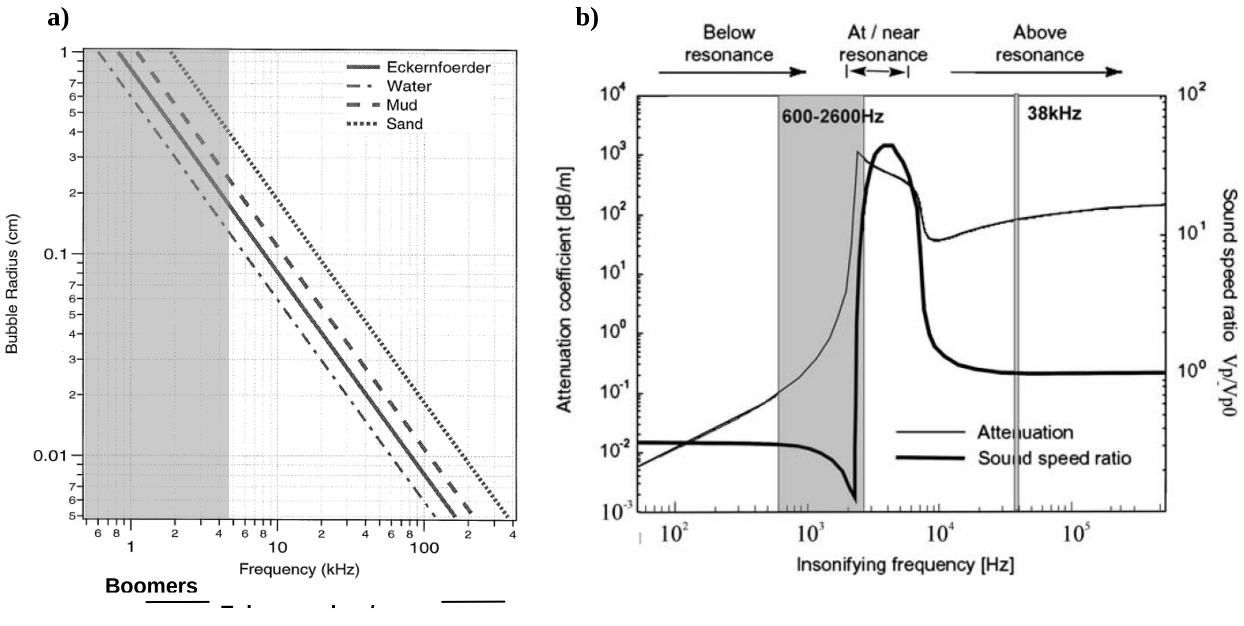


Figure 14. Modelled responses of gas bubble populations: a) resonance frequencies of gas bubbles as a function of representative radii in different materials; operating frequencies of boomers (shaded) and echosounders indicated (cf. Figure 13) (after Wilkens & Richardson, 1998); b) changes in P-wave velocity and attenuation below, at and above resonance, for bubbles with a resonance frequency of 2-5 kHz, shading shows operating frequencies of a boomer (0.6-2.6 kHz) and an echosounder (38 kHz) (after Mathys *et al*., 2005).

In the water column, gas escape from seabed may be observed as sub-vertical features, some over 1 km high, referred to as hydroacoustic flares (Figure 15a; Greinert *et al*. 2006; Judd and Hovland 2007). The term refers to the fact that flares are best detected using higher frequency echosounders (>25 kHz), which provide strong backscatter from naturally occurring bubble sizes in water (0.5-10 mm), above their resonance frequencies (Figure 14a; Greinert & Nützel 2004). Reduced ship speeds and a quiet water column help in imaging hydroacoustic flares, and in distinguishing them from other water column reflectors (such as fish; Judd *et al*. 1997). Hydroacoustic flares have been shown to record backscatter from single or multiple streams of bubbles (e.g. Naudts *et al*. 2006, 2009; Nikolovska *et al*. 2008), in some cases rising from areas where a subsurface gas front is observed at or near seabed (Figure 15a).

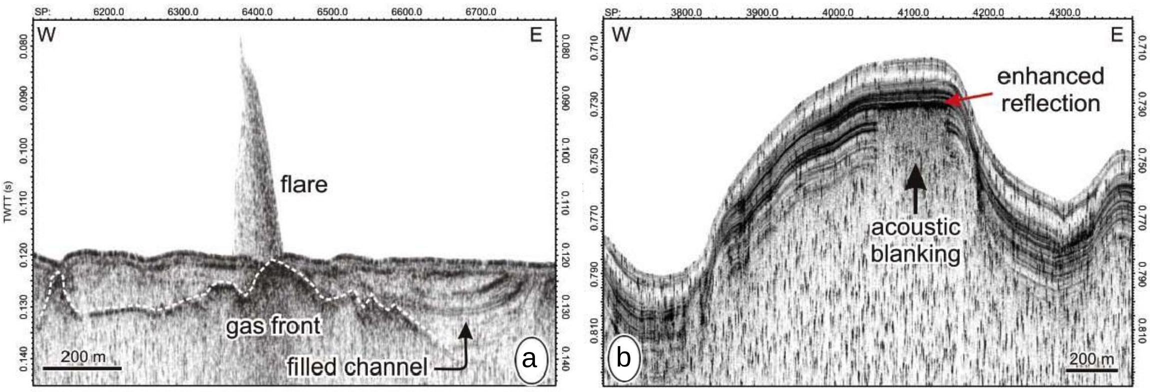


Figure 15. Examples of acoustic evidence of free gas in sediments and the water column (5 kHz pinger data, Black Sea), (after Naudts *et al*., 2009): a) hydroacoustic flare in the water column above a rising gas front; b) acoustic blanking (turbidity) and enhanced reflections.

In the subsurface, zones of acoustic turbidity - also referred to as masking or blanking or wipe-out – are the most commonly cited subbottom indication of shallow gas on HR profiles (Fig. 3; Fleischer *et al*. 2001; Judd and Hovland 2007). The top of such a zone may form a reflective 'gas front' that locally rises to seabed (Figure 15b). Acoustic turbidity is caused by frequency-dependent P-wave attenuation (scattering, reverberation) by gas bubbles (Schubel 1974; Anderson & Hampton 1980), which from core data may occur at concentrations as low as 0.5 % (Abegg & Anderson 1997). Acoustic turbidity is commonly associated with other features attributable to a change in P-wave velocities, such as reflections of enhanced amplitude (Figure 15), or reflection pull-downs (Fleischer *et al*. 2001; Judd and Hovland 2007).

Field examples

HR reflection methods have been used to identify and investigate occurrences of shallow gas and gas venting into the water column in marine and lacustrine settings around the world (see Fleischer *et al*. 2001; Judd and Hovland 2007). In general, HR methods have been used for two scales of study: to efficiently survey large areas; and as part of more detailed 2D or 3D investigations of gas structures.

HR short-offset reflection profiles have long been recognised to provide a cost-effective means of rapidly surveying large areas to obtain evidence of the distribution of gassy sediments (see Fleischer *et al*. 2001; Judd and Hovland 2007) and are increasingly being applied to the investigation of hydroacoustic flares in the water column (Figure 15a). Regional studies may be based on the re-examination of archived regional datasets (e.g. UK continental shelf - Judd *et al*. 1997) or the acquisition of data from known areas of venting (e.g. identification of 2,778 new hydroacoustic flares over an area of 1,540 km^2, in water depths of 66-825 m in the Black Sea - Naudts *et al*. 2006). The Black Sea has provided a useful natural laboratory for studies of hydroacoustic flares: studies have shown that echosounders of higher frequency content (>25 kHz) may allow individual bubble streams to be imaged and traced to seabed venting sites (e.g. Greinert *et* *al*. 2006; Nikolovska *et al*. 2008), while investigations using multiple frequencies may allow estimates of gas flux (see below).

HR reflection methods also allow analyses of individual gas venting structures, including via 3D approaches. HR single-azimuth pseudo-3D seismic volumes have been constructed across gas seeps (e.g. Riedel *et al*. 2002; Hornbach *et al*. 2007) and mud volcanoes (e.g. Wagner-Friedrichs *et al*. 2008) to study gas migration pathways at metric or even decimetric vertical resolution. The same methods can be applied to time-lapse acquisition of HR 4D seismic data from venting structures (Riedel 2007). HR short-offset 3D methods can represent a cost-effective scaling down of 'true' 3D marine seismic methods, avoiding their cost and complexity (Müller 2005; see Missiaen *et al*. 2005). However, they remain more costly than HR reflection profiling, with resource demands on acquisition (ship-time, source/receiver positioning) and data processing (volumes, manipulation) growing at higher frequencies.

Quantification of gas properties

Frequency-dependent changes in P-wave velocity and attenuation due to gas bubbles (Anderson and Hampton 1980; Wilkens & Richardson 1998) offer the theoretical potential of inverting HR reflection data to estimate gas properties. This potential has yet to be fully realized, mainly due to the lack of well-constrained experimental data to validate and improve theoretical models of P-wave velocity and attenuation across a full range of frequencies (Mathys *et al*. 2005; Best *et al*. 2006).

In gassy sediments, attention has focused on using P-wave properties to estimate two main gas properties, the void fraction (VF) and the bubble size distribution (BSD). The state of the art was reviewed by Robb *et al*. (2006), who noted that most results remain dependent on theoretical models of bubbles in water, rather than sediment; moreover, they require measurements across a range of frequencies which are not based solely on, or directly applicable to, HR reflection profiles. One exception is a simple technique proposed by Leighton & Robb (2008) to infer spatial variations in VF on single channel HR data, by relating observed or extrapolated changes in the separation of reflections (assumed to be parallel) to bubble-mediated changes in sound velocity.

In the water column, the use of echosounders employing multiple high frequencies has been shown to allow investigations of bubble size distribution, rates of rise and gas fluxes, assuming digital storage of the data (Greinert *et al*. 2006). Again, however, successful hydroacoustic techniques do not rely on HR profiles alone, but make use of horizontally looking swath sonar systems (e.g. Greinert and Nützel 2004; Nikolovska *et al*. 2008).

2.1.6 Surface water chemistry

Methods of monitoring surface water chemistry for quantifying CO_2 leakage from sediments into the overlying water column can be divided into two main groups: those that measure dissolved gases (from dissolution of ascending gas bubbles or from the expulsion of water with high levels of dissolved gas); and those that focus on dissolved elements and compounds that may be associated with deep-origin waters (e.g. brines) that could migrate together with the leaking gas. In this respect the first techniques can be considered as direct measurements, whereas the second are indirect, surrogate measurements.

Both *in situ* (continuous) and laboratory (discontinuous grab sampling) techniques exist for the analysis of dissolved gases, with *in situ* methods becoming more common due to technological advances, decreasing costs, the potential to reduce sampling artefacts, and the possibility to collect large amounts of data for either mapping or time-series analysis purposes. Problems still exist with these sensors, however, in terms of sensitivity and slow response times. Sampling for laboratory analysis is still useful in many cases for improved sensitivity or when analysing components for which *in situ* techniques do not exist. Most *in situ* methods have a gas permeable membrane which allows for the transfer of dissolved gas from the water into a headspace containing a detector. Various types of detectors have been applied both for commercial and research probes, including non-dispersive infrared (NDIR), electrochemical, mass spectrometers, direct-absorption spectroscopy, and colorimetric sensors. Various review papers on dissolved gas sensor types for CO_2 and or CH_4 have recently been published (Boulart et al. 2010; Prien 2007; Schuster et al. 2009). A brief description of some of the available *in situ* sensors is provided as follows.

The METS sensor (produced by Franatech, GmbH) uses a SnO_2 semiconductor to analyse methane concentrations in the quoted range of 50 nM to 10 µM up to a maximum deployment depth of 3,500 m. The METS has been limited by its typically slow response times (Newman et al. 2008), which according to the manufacturer range from 1 to 30 minutes, its inability to function in low O_2 environments, and by the fact that the sensing principle consumes analyte. In addition, because the semiconductor measures all gases that can be oxidised, it is necessary to heat the detector to 400°C for it to be selective for CH_4 (Boulart et al. 2010); clearly this necessitates a significant power supply and probably precludes long-term deployment.

The HydroC (produced by Contros, GmbH) has sensors for either dissolved CO_2 or CH_4 analysis, with both using non-dispersive infrared (NDIR) sensors for gas analysis (see Section 3.5.8). The dissolved CO_2 unit has a quoted response time of <10 seconds, accuracy of <10 ppm, and operational depths of up to 6,000 m. To date there are no peer-reviewed articles assessing the response, speed, or accuracy of the HydroC (Boulart et al. 2010) and thus it is difficult to determine its practicality for CO_2 leakage quantification problems. A similar instrument developed for research purposes has also been proposed by Annunziatellis *et al*. (2008).

The Deep-Sea Gas Analyzer (produced by Los Gatos. Inc.) uses high-resolution direct-absorption spectroscopy and is capable of simultaneous analysis of a wide range of gas types (including CH_4, CO_2 and carbon isotopes), however sensitivity and concentration ranges are not reported. According to the vendor the unit is self-calibrating, has a response time of <1 minute, and maximum depth deployment of 2,000 m. The probe can be cabled or installed remotely, however the stated battery life of 3 hours will limit deployment times unless linked with an external power supply.

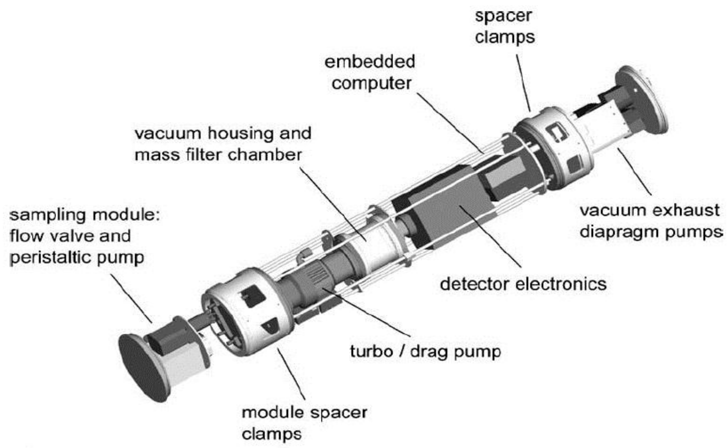


Figure 16. Example of a quadrupole Membrane inlet Mass Spectrometer (MIMS), (Kibelka et al. 2004).

A relatively new approach, which is still in the development phase, is membrane introduction mass spectrometer (MIMS) (e.g. Camilli and Duryea 2009; Kibelka et al. 2004; Short et al. 2006). Similar to those instruments described above, a gas permeable membrane is used to extract dissolved gas, but with analysis performed via an ion trap or quadrupole mass spectrometer (Figure 16). Clearly, the advantage of such a system is that it is capable of scanning through a wide range of mass/charge ratios. This does, however, create difficulties in interpretation and quantification, as different molecules can have the same mass. Various research models have been created, with deployment tests via cabled profiles, AUVs, ROVs, and on ocean floor landers. Being in the development phase, the individual units have different sensitivities, mass-ranges, response times and depth deployments.

The SAMI[2] (produced by Sunburst Sensors, LLC) also uses a diffusion membrane, however a "wet chemical" method is employed for the dissolved CO_2 analysis rather than a direct gas phase measurement. Dissolved CO_2 diffuses across the membrane into a pH indicator solution, where it transforms into carbonic acid thus changing the solution pH and the indicator form (DeGrandpre et al. 1995). According to the manufacturer response time is around 5 minutes, measured pCO_2 range is about 150 to 700 ppm, precision > 1 ppm, accuracy is ± 3 ppm, long term drift is < 1 ppm over 6 months, and the unit can be deployed up to 500 metres depth. Because of the long response times, the SAMI[2] is typically deployed for point monitoring.

In contrast with the methods described above, Raman spectrometry does not employ a membrane to measure a separate gas phase, but rather is able to measure concentrations directly. For this reason the technique could theoretically have much faster response times than membrane-based techniques, although in general the technique is not very sensitive. Unfortunately, experiments have been unsuccessful thus far for dissolved CO_2 analysis (Brewer et al. 2004), while detection of dissolved CH_4 has potential but is still in the development phase (Boulart et al. 2010).

A technique that lies between *in situ* and remote analysis of dissolved gases is the equilibrator technique. This method typically involves towing a long hose behind a ship, with a "fish" at the end of the hose which maintains a constant sampling depth and a pump which continuously transfers water to the ship for analysis (multiple hoses can be deployed to monitor at different depths). This water passes through an equilibrator, which strips the dissolved gases from the water for analysis via either infrared or gas chromatography instruments. By collecting the gases at regular intervals, representative of a fixed sampling distance, they can be analysed for a wide range of gas types or isotopes. Having the option to analyse for multiple gases can also give important information on the origin of a given anomaly. The advantage of this approach is that it combines the continuous sampling approach of *in situ* techniques with the greater sensitivity and simplicity of an analytical instrument onboard a ship. Although the tow configuration is most commonly used, the method can also be used for vertical profiling or temporal monitoring of a single point.

Discontinuous dissolved gas analysis typically involves sampling a finite number of points along a vertical profile through the water column using a cabled rosette of 6 to 36 remotely-triggered Niskin sampling bottles that are lowered via a winch onboard a ship. Analysis can then be conducted using the gas extraction line (typically used for dissolved CH_4) or headspace analysis that involve equilibrating the water sample with a known volume of pure gas, analysing the latter for the gas species of interest, and calculating dissolved concentrations based on its Henry's constant (applicable for all gas species). Gas extraction is a standard and well tested technique for CH_4 studies at mud volcanoes and ocean ridges (e.g. Lammers and Suess 1994), while head-space analysis is a very common technique which is applied to a wide range of environmental and geological research.

Similar to dissolved gases, there are *in situ* and laboratory techniques for the analysis of dissolved elements and compounds that might be associated with a CO_2 leakage, although the number of *in situ* methods is more limited with respect to the extensive range of options for laboratory analyses. The principle, and most widely used, tool for *in situ* measurements of chemical parameters in surface water studies is the CTD (conductivity, temperature, depth) sensor that is also often deployed together with a dissolved oxygen sensor (Figure 17). CTDs are standard oceanographic tools that are lowered through the water column via a winch on board a ship to give real-time data to help define hydrodynamic structure and to determine the distribution of water masses of different origins. In the case of deep-origin water migrating together with leaking CO_2 into surface water, a CTD/oxygen sensor may be capable of delineating the size and level-of-dilution of the resulting plume based on, for example, increased salinity or decreased oxygen content, information which could in turn be used for quantification purposes. In a similar manner, grab samples can be collected, using Niskin bottles mounted on a rosette together with the CTD (or using AUVs/ROVs), for organic or inorganic chemical analyses via an extremely wide range of ship- or land-based analytical techniques. The analysed species could include those elements associated with deep brines such as I, Br, SO_4, etc. (Griffis et al. 2004; Méndez-Ortiz et al. 2006) or elements that may be released due to water-rock-gas reactions mediated by the acid gas CO_2 (Ardelan and Steinnes 2010; Ardelan et al. 2009; Zheng et al. 2009). The resulting data could then be used, via various modelling approaches, to estimate the flux of the measured compounds and then, by association, the flux of leaking CO_2.

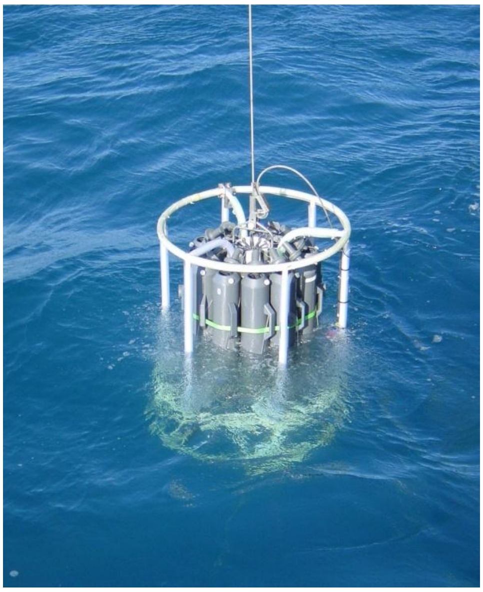


Figure 17. Deployment of a CTD and water sampling rosette (courtesy of URS).

Quantification Applications

From a chemical point of view, the issues and concepts that must be addressed for surface water monitoring are, in many ways, similar to those encountered in atmospheric monitoring (see Section 2.2). In both cases the gas leaks from the geological surface and is transported and diluted by a constantly flowing medium (wind or currents), with vertical and lateral distributions controlled by various parameters such as the density contrast between the leaking and "host" fluids, surface topography, flow rates, etc. In this regard quantification approaches could, in theory, be similar (e.g. plume cross-section measurements, line-averaged modelling, and possibly eddy covariance given proper conditions).

The main difference is related to the movement of the two migrating fluids (gas ± water) as a function of the medium into which they are leaking, as this will control their eventual lateral and, especially, vertical distribution. For example, in the case of leakage at the ground surface the gas phase will mix with the atmosphere while any co-migrating water will dissipate in near surface porous rocks or on the ground surface. In contrast, in the case of leakage from a sea- or lake-bed, the gas will ascend in the water column as bubbles, with the dissolution rate and the eventual vertical distribution of dissolved CO_2 (and associated gases) being controlled by such parameters as bubble size, solubility, and pressure/temperature conditions (McGinnis et al. 2006). Any water associated with the leaking gas will instead be controlled by the force of the leak, the potential for entrainment in the gas bubble plume, and the density contrast between the leaking and surrounding waters. As the force of any potential leak is expected to be small and entrainment will only occur with large gas volume leaks, it is most likely that the density contrast will primarily control the vertical distribution of co-migrating waters. In a salinity stratified system, a water plume may rise to the height where it becomes "density neutral". If these waters are brines they will be denser than fresh water and, possibly, bottom seawater, and thus one would expect them to remain in the bottom water environment closer to the sediments. As a result, the signal from the two fluids may be located at different depths, a fact that must be taken into consideration for monitoring and quantification purposes.

Compared to work on shore, geochemical monitoring of surface water systems is much more costly and logistically difficult, as well as being a more corrosive environment in the case of seawater. In addition, or perhaps as a result of these difficulties, there exists only one significant off-shore facility, Statoil's Sleipner in the North Sea, and no pilot research projects. This has meant that there are no examples in the peer-reviewed literature that specifically test methods for the quantification of leakage from an off-shore CO_2 storage facility, while articles for geochemical monitoring in these environments tend to be very general without field experimental data. To compensate for this lack of information, one can look at other research and industrial fields that may, in some manner, be analogous. These fields can include any in which gas and/or water migrate into a surface water body and produce a vertical or horizontal plume that has a different chemical composition from the surrounding water mass, such as: water and gas leakage from mud volcanoes and cold seeps; water and gas leakage from hydrothermal vents; gas leakage from sea-floor gas pipelines or from natural gas seeps; and effluent pollution plumes emanating from coastal rivers. In addition, the literature also describes the development and testing of various innovative tools. A few examples from these other fields are described below to indicate what could potentially be undertaken using surface-water geochemical techniques at CO_2 storage facilities. Although some describe actual leakage quantification, many of these examples involve innovative techniques for plume or anomaly delineation that may in the future be adapted for quantification purposes.

Probably the most standard and well-established techniques for plume delineation and quantification involve vertical profiling of the water column, collecting detailed *in situ* data with a CTD/dissolved oxygen sensor while at the same time collecting discrete water samples for chemical and dissolved gas analysis. In one such study on the Drachenschlund hydrothermal vent in the Mid Atlantic Ridge, Keir *et al*. (2008) performed a series of CTD/rosette hydrocasts along three transects perpendicular to the main current flow direction in the area and analysed the resultant water samples for dissolved CH_4 on board ship and isotopic analysis on shore. CH_4 flux rates of the dissolved gas plume emanating from the vent were calculated as follows. First the two-dimensional CH_4 inventory was calculated along the individual transects, with each transect having 4 to 7 stations consisting of an undisclosed number of samples collected with depth (Figure 18). For each sampling station the dissolved CH_4 values were first adjusted by subtracting the background concentration, and the resultant "excess" CH_4 over the depth interval 2,000 m to bottom was integrated using the trapezoidal method. The vertical inventories were then integrated along each transect to yield a 2D, cross-sectional inventory of excess methane in the plume, with each line yielding a similar result (14, 15, and 12 to 14 mol m^{-1}). Finally, the total plume flux of 0.5 mol s^{-1} (or 16 x 10^6 mol yr^{-1}) was calculated by multiplying the average value of 14 mol m^{-1} by the average current velocity (3.7 cm s^{-1}) passing through the cross-sections. This value was found to be 9 times higher than that calculated via direct vent sampling (plus a volume flow estimate based on the maximum height of the neutrally buoyant plume). The authors state that these two extremes probably represent upper and lower limits of actual source of methane, with the direct measurement possibly underestimating flux due to sample degassing and the plume measurement overestimating due to tidal smearing or averaging of multiple sources. Such a large difference between the two estimates clearly shows that other similar studies on natural leaking analogues (or controlled leaks) are needed to reduce uncertainty in the methods and to understand which of the two approaches is more accurate. This is especially needed on sites where CO_2 (not CH_4) is the main component to eliminate the added complication of the different chemical and biological reactivities of the two gases.

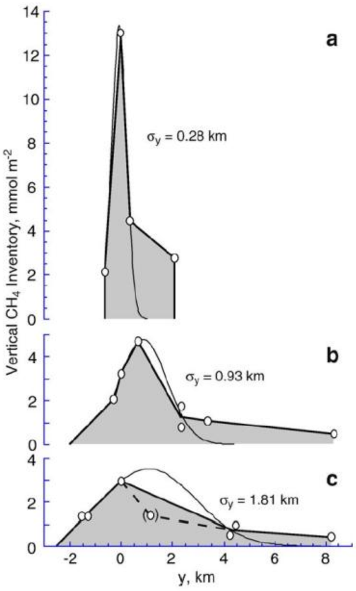


Figure 18. Vertical dissolved CH_4 inventory along three transects conducted down-gradient from the active Drachenschlund hydrothermal vent (Keir et al. 2008).

Additional studies on hydrothermal vents have also endeavoured to quantify gas fluxes using direct sampling techniques, although many of these exploit the fact that the resultant plumes also contain elevated quantities of suspended particles that can be mapped with backscatter techniques and correlated with dissolved constituents (e.g. German et al. 2010). These same authors also describe the potential for using tracers such as helium or radon to determine the conservative nature of plume chemical constituents. Although such particle plumes would not be expected from a cold CO_2 leak, these articles do raise some interesting points regarding plume behaviour. One of these is the concept of the buoyancy neutral plume, which results in a plume of leaked water (with its dissolved gases and elements) migrating upwards and entraining surrounding seawater until it has the same density as the surrounding water mass, after which the plume will spread laterally. Plumes have also been found "stacked" at different depths (Bennett et al. 2008; Marbler et al. 2010), possibly caused by temporal variations in one source or multiple sources with different physical/chemical characteristics, while the role of sea-floor topography and tidal cycling in plume migration has also been documented (German et al. 1998). Depending on site characteristics, these processes could potentially influence plume distribution from a CO_2 (±pore water) leak, affecting sampling strategies for plume delineation and eventual quantification estimates.

Perhaps a closer analogue to a CO_2 leakage can be found in cold methane seeps that exist throughout the world's oceans, often emanating from either pock-marks or mud volcanoes. Mau *et al.* (2006) used similar transect CTD/rosette sampling methods as those detailed in Keir *et al.* (2008) to determine the dissolved CH_4 flux from mud extrusions off the coast of Costa Rica, although a slightly different calculation approach was applied. First the methane inventory was calculated for a box defined by two CTD-transects perpendicular to the main current flow, with the upper and lower bounds of the box being defined by the limit of anomalous plume-related values. Methane concentrations were averaged in 10 m thick layers in the box, from which background values were subtracted. These "excess" CH_4 concentrations were multiplied by the volumes of the layers, which in turn were summed to give the inventory of the entire box. The flushing time (i.e. the time needed to remove all CH_4 from the box) was calculated by dividing the length of the box by the current velocity, then the total output flux of the plume was determined by dividing the inventory by the residence time. The authors state that 10-20% of the uncertainty in the final calculated values was due to variations in local background CH_4 concentrations and more than 50% were due to variations in current velocities. Calculated output rates ranged from 10^4 to 10^5 mol yr^{-1} for each of the 3 mud volcanoes measured with this technique. The source of the observed methane plume is believed to be gas dissolved in leaking porewaters, as bubbles were not observed via acoustic or video-guided surveys; these results show how chemical monitoring of the water column may be critical for marine CCS site monitoring as other techniques, such as echosounders, would not observe this type of leak.

In addition to vertical deployment of the CTD system, it can also be towed behind a ship to give lateral data, or even 3D monitoring by winching the unit up and down while towing along parallel transects (German et al. 1998) to produce a series of "saw-tooth" patterns through a plume. This approach, known as "tow-yo", has also been used for sensors other than CTDs, such as fluorometers used to monitor effluent plumes from sewage treatment plants (Hunt et al. 2010). In this latter study, Rhodamine WT dye was added to the effluent at the plant and the outfall was monitored offshore for two days to study mixing processes and dilution (Figure 19). In theory, if the source of a leak is known it may be possible to add similar sorts of fluorescent dyes to help monitor dispersion and quantify the dissolved fraction of a CO_2 related leak.

The equilibrator method is another towed technique which combines the advantages of manual analysis on board a ship or on land with almost continuous sampling This method is most commonly used to study exchanges between near-surface waters and the atmosphere for various greenhouse gases like CO_2 (Krasakopoulou et al. 2009) and CH_4 (Schmale et al. 2005), however deeper applications have included searching for pipeline leaks (Alderidge and Jones 1987) and seeping oil and gas reservoirs (Logan et al. 2010; and references therein), or for ecosystem studies (Abril et al. 2006). For example, studies have found spatial anomalies of dissolved C_1-C_8 hydrocarbons above known oil and gas fields (Figure 20) that are as much as 2 orders of magnitude above background levels (Logan et al. 2010; and references therein). Conceivably this approach could also be applied for marine CCS sites, with such measurements even being "piggy-backed" on 3D seismic surveys of the site. The resultant data could then be processed using the same quantification approach described above for the CTD transects, but with a greater spatial resolution which may reduce estimate errors caused by heterogeneities.

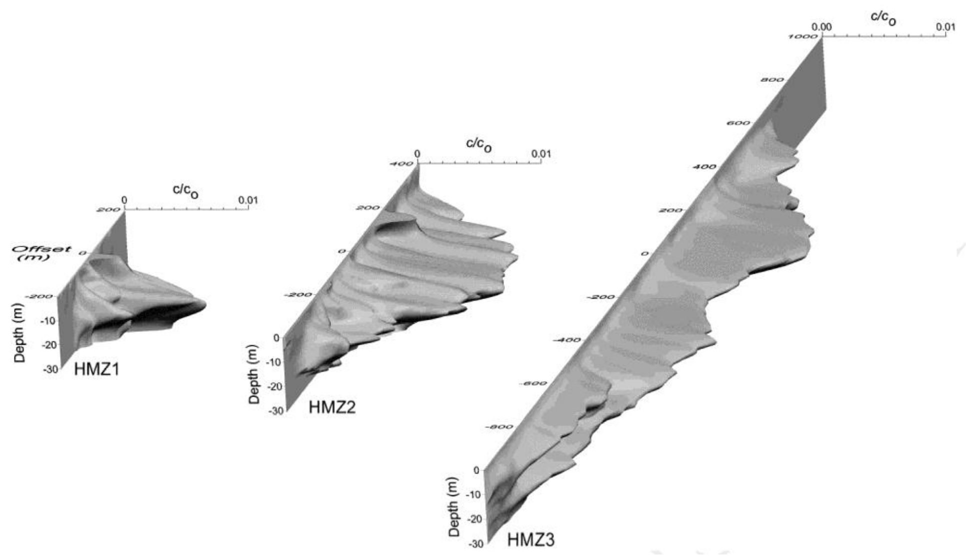


Figure 19. Concentration profiles of Rhodamine WT dye used to measure effluent plumes (Hunt et al. 2010).

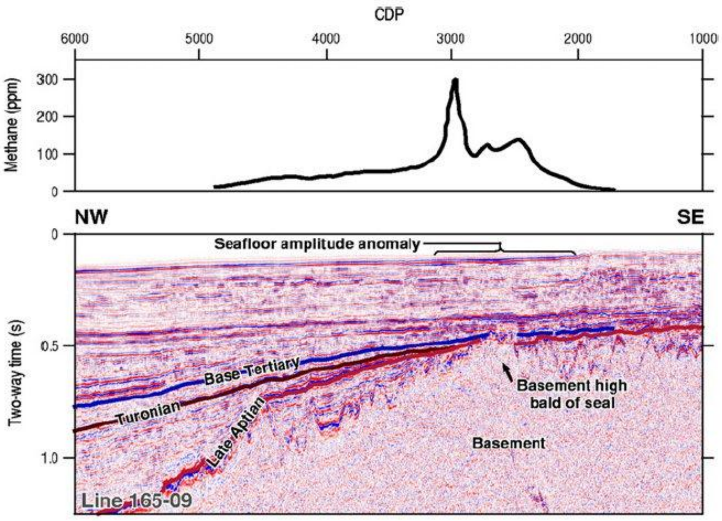


Figure 20. Dissolved CH_4 concentration profile conducted with an equilibrator system above a known gas field (Logan et al. 2010).

With recent technological advances there is now the potential for the deployment of sensors on Remotely Operated Vehicles (ROVs) and Autonomous Underwater Vehicles (AUVs) for spatial, *in situ* mapping of various parameters. In particular, deployment via AUVs has many advantages, including ease of field use, reduced costs, increased spatial resolution, reduced spatial aliasing, and adaptive sampling capabilities (Ramos et al. 2007). To date a number of different types of sensors have been mounted on AUVs for plume studies, including CTDs, fluorometers, and selective probes for dissolved CH_4 (METS). For example, Ramos *et alet al*. (2007) used an AUV-mounted CTD to monitor a sewage outfall plume over a rectangular area of 200 x 100 m, programming the unit to perform 6 parallel lines (200 m long and 20 m spaced) at 6 different depths to provide a 3D block image of the plume (Figure 21). At a velocity of 1 m/s and a sampling frequency of 2.4 Hz, measurements were made approximately once every 0.4 m. The conductivity, temperature and pressure data from the CTD were used to compute salinity, which was found to be the most useful parameter for delineating and observing the plume structure. In this case, the plume was visible as a low salinity region.

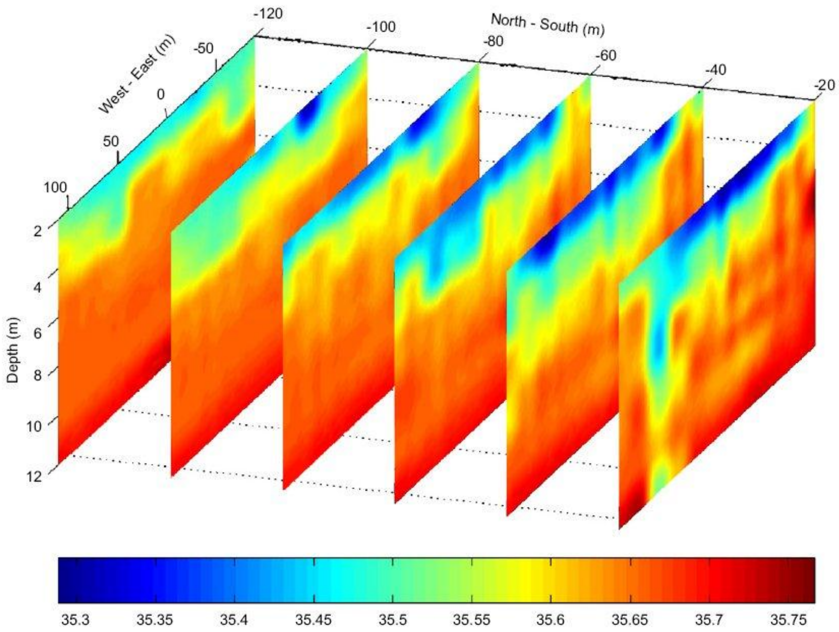


Figure 21. Contoured profiles of salinity (practical salinity units, psu) through the S. Jacinto effluent plume, located off the Portuguese west coast near the Aveiro estuary. Values were measured using a CTD mounted on an Autonomous Underwater Vehicle (AUV) (Ramos et al. 2007).

Hibler *et al*. (2008) used a fluorometer on an AUV to trace rhodamine WT dye added to a coastal current. In this study the AUV was deployed over a 400 x 100 m grid, consisting of 40 transects spaced 10 m apart and sample measurements about once every 1.75 m. While the previous two studies were near shore and conducted just below the water surface, a study of methane seepage from a km-scale pock-mark in the mid-Atlantic continental shelf in waters 100 to 150 m deep was reported by Newman *et al*. (2008). In this work dissolved CH_4 measurements were performed using a METS sensor mounted on an AUV, highlighting anomalies up to 100 nM in a background of 1-4 nM and locating CH_4 seepage areas on the edge of the pock-marks. Due to the slow response time (up to 15 minutes) of the METS sensor due to diffusion across the probe's gas-permeable membrane, the authors developed an algorithm to correct for and remove the time lag and give more accurate concentration values. After correction a direct negative correlation occurs between CH_4 and salinity, indicating that the vented methane rich fluid is less saline and cooler than the bottom water. As the AUV technology (and associated sensor packages) mature there is the potential in the future for these tools to be used for autonomous monitoring and possible leakage quantification purposes using some of the approaches described above for CTD surveys.

Camilli *et al*. (2009) mounted a MIMS on an ROV and conducted a field test in 200 m deep water in the Gulf of Mexico to try and locate hydrocarbon contamination on the seafloor caused by the failure of an oil production infrastructure. The authors surveyed a 0.5 km^2 area with 5 m spaced lines at a constant height of 1 m above the sediment surface. The spectrometer-monitored indicator peaks at m/z 15, 27, 41, and 43 showed a spatial correlation of hydrocarbon anomalies with local depressions, implying pooling of crude oil elements in low-lying areas on sea floor. MIMS has also been used to monitor CO_2 concentrations, both in the near-surface waters of a eutrophic lake (Wenner et al. 2004) and during a 300 hour fixed deployment in a marine embayment (Camilli and Duryea 2009). In this latter study the data was sensitive enough to observe temporal changes in CO_2 and O_2 concentrations, as well as CO_2 stable isotope ratios, caused by diurnal biogenic processes. Other examples of the testing of this method include qualitative mapping of dissolved CH_4 in surface waters (Mau et al. 2007) and the mapping of a controlled dimethyl sulphide plume (Short et al. 2006).

Aside from spatial measurements in the water column, the potential also exists for long-term temporal monitoring at fixed positions, both for leakage detection and quantification purposes. This involves the deployment of one of the *in situ* techniques described above on the sea floor or suspended in the water column at a fixed site, either as autonomous detectors (given sufficient battery life and resistance to the harsh marine environment) or cabled to an external power supply such as a buoy with solar panels or electrical mains from a drilling platform. These autonomous monitoring stations are still in the development phase; however deployments and prototype systems do currently exist (e.g. Annunziatellis et al. 2008; Marinaro et al. 2004).

Finally, whereas up to now the discussion has centred on quantifying the plume of dissolved gas in the overlying water column, methods also exist for the direct quantification of flux rates from the sediment floor to the water. These are benthic chambers, which consist of an enclosed volume with one end open for deployment on the sediment surface by divers in shallow water or by ROVs or landers in deep water. The change in composition of the water in the benthic chamber over time is used to calculate the flux rate from the sediments to the water column at that point (e.g. Linke et al. 2010). Although these are direct measurements they are only valid for the measurement point; as gas release can be highly heterogeneous, the extrapolation of a limited number of points over a wide area could introduce significant errors in the calculation of an overall leakage rate. This is particularly true because, although analogous to flux measurements on the ground surface, benthic chamber measurements are logistically much more difficult to conduct and thus only a limited number of samples can be collected.

In summary, the development, testing, and deployment of geochemical methods for monitoring and leakage quantification applications at marine CO_2 storage sites has been very limited due to logistical difficulties, costs, and perhaps a lack of familiarity with the methods. That said, various methods have been used extensively in the past for research purposes in other marine applications (like mud volcanoes and hydrothermal vents) and there is extensive development of new *in situ* sensors and autonomous marine platforms (e.g. AUVs, gliders) that show promise for the future. Many of these methods and approaches are directly applicable to marine CO_2 storage operations, and thus experiments and trials are needed to understand their sensitivity and resolution.

Strengths and Weaknesses

One advantage of these methods hinges on the fact that they are direct CO_2 measurements in the hydrosphere. As leaking CO_2 can be in the form of bubbles that dissolve in the water column as they rise, or as dissolved CO_2 migrating with deep-origin waters, geochemical methods are the only techniques that can directly quantify both of these contributions. This point was clearly illustrated by Newman *et al*. (2008), where in their study they defined the flux of CH_4 from the sediments despite the lack of observed gas bubbles. Other advantages include the potential for: i) multiple analyses of different components (associated gases like CH_4, tracer gases like He, isotopes, etc.) to help define origin and improve the precision of any estimate; ii) *in situ* measurements to reduce errors; and iii) autonomous monitoring or the piggy-backing of geochemical surveys on surveys conducted with other techniques to reduce costs. Disadvantages, or at least difficulties, are principally related to the potentially small signal in a large volume of ocean water. These measurements will certainly have to be coordinated together with other survey methods, in particular those that may be able to define the location of a leak so that geochemical sampling can be focused for plume delineation and quantification. Regarding the questions of sensitivity and resolution, this is difficult to quantify considering that no controlled experiments appear to have been conducted. That said, it is expected that an accurate estimate of background concentrations and current directions and strengths will be the factors that have the greatest influence on the precision of any plume flux calculations. Timeliness, instead, will depend upon the type of technology chosen for deployment, with the use of *in situ* continuous monitoring stations, or autonomous *in situ* surveys, giving the highest possibility for a rapid recognition of a leak as well as definition of baseline values and variability.

2.2 Atmospheric monitoring methods

2.2.1 Long open path (IP diode lasers)

Various open-path sensing techniques have been developed that measure the path-integrated concentration of a target gas between two points near the ground surface. These methods have been used to locate gas emission points from various point or non-point sources (e.g. landfills, coal mines, wastewater treatment plants) and estimate their leakage rates to the atmosphere (EPA 2006; Hashmonay et al. 2001; Piccot et al. 1996). Recently these methods have also been applied to the monitoring of CO_2 geological storage sites (Annunziatellis et al. 2007; Humphries et al. 2008; Loh et al. 2009; Trottier et al. 2009). At present there are a number of different systems which have been proposed for this type of monitoring (EPA 2006), including: Open-Path Fourier Transform Infrared (FTIR) Spectroscopy; Ultra-Violet Differential Optical Absorption Spectroscopy (UV-DOAS); Open-Path Tuneable Diode Laser (TDL) Absorption Spectroscopy; Differential Absorption LIDAR (DIAL). Of these technologies, the FTIR and UV-DOAS technologies have the advantage that they can simultaneously detect a large number of different gas species. To date, the TDL and, to a much lesser extent, the FTIR have been applied more in the field of CO_2 monitoring. Only the workings of the TDL will be discussed here due to its more common usage.

Open-Path Tuneable Diode Lasers, which consist of an integrated transmitter/receiver unit and a reflector, measure the distance-averaged concentration of a specific gas in the air. A signal emitted from the transmitter propagates through the air to the reflector (positioned metres to hundreds of metres away) and returns to the instrument where it is focused onto a detector. Because of absorption of the signal by the gas of interest, the decrease in the signal returned to the detector is directly proportional to the total amount of that gas over the entire path length.

Models exist for a number of gas species, but the ones of most interest for storage site monitoring are CO_2 and CH_4. The CH_4 detector has been recommended for monitoring at sites where it may be associated with CO_2 (e.g. CO_2-EOR) due to its greater sensitivity, although it should be remembered that: i) if CO_2 is the bulk gas then the mass of leaked CH_4 will be much lower and ii) although CH_4 is more mobile than CO_2 it can also be rapidly oxidised in the unsaturated soil horizon, thus further decreasing the amount of leaked CH_4. As such, if the mass ratio of *surface leaked* CH_4 to CO_2 is less than 0.2% then the above mentioned advantage in sensitivity will be lost.

The transmitter consists of a tuneable diode laser that emits light at a wavelength that is absorbed by the gas of interest. Each gas typically absorbs at more than one wavelength, with the absorption strength being different for each band. Using CO_2 as an example, the level of light absorption varies markedly between the 5 main absorbing wavelengths for this gas (Table 3). This variability can be exploited based on the sensitivity and interference requirements of the application. For example, portable CO_2 infrared detectors equipped with an internal, short-path cell usually use high absorption bands (e.g. 4.255 µm) to increase sensitivity. Such highly absorbing bands, however, are not appropriate where large amounts of CO_2 result in significant signal loss, such as in high concentration conditions or over long path lengths. As such long open path systems often employ the 1.58 mm wavelength (Flesch et al. 2004; Trottier et al. 2009), which has a much lower absorption strength and very little interference, although the band near 2.004 has also been applied (Humphries et al. 2008).

Table 3. Wavelengths for CO_2 absorption (from Shuler and Tang 2005).

Wavelength (µm)	*Relative absorption strength*
1.432	1
1.580	3.7
2.004	243
2.779	6,800
4.255	69,000

The choice of the reflector is important in order to balance the amount of light returned to the detector – enough to obtain a good sensitivity but not too much to avoid detector saturation. The type and size of the reflector should be chosen based on the optical path length and on the expected amount of monitored gas. As short path lengths and/or very low concentrations will return more light to the detector a low reflecting material is typically used. For long path lengths so-called retro-reflectors are applied, which consist of a series of aligned, gold-plated mirrors that maximise light reflection.

The light returning from the reflector is focused on a photodiode detector. At the same time, a portion of the IR laser beam is split off prior to leaving the transceiver, passing through a reference cell containing a stable CO_2 reference concentration of known value and then onto the detector. Comparison of the two waveforms allows for continuous calibration update, although deployment for extended periods of time may require periodic controls due to instrument drift. The accuracy of the measurement is evaluated by the coefficient of determination (R^2) which is a measure of the similarity between the waveform of the signal passed through the calibrating sample and that of the measurement. At least one manufacturer states that an R^2 above 0.95 ensures an accuracy of ± 2%. Optimal instrument sensitivity will depend on the individual unit and, in particular, on the gas type being measured. For example the relative sensitivity for CH_4 can be

10 times that for CO_2, which will also have an impact on the maximum path length for each gas type measurement. Measurements can be performed at different frequencies, the minimum typically being once every second.

Because the measurements are related to the linear distance of the total path covered by the laser (i.e. twice the distance between the transceiver and reflector), the resultant units are in parts per million metres (ppmm). These values can be divided by the total path length to give a "path-averaged" concentration in ppm. The concept of "linear concentrations" is important, as different gas distributions can yield the same path-averaged concentration. For example, a 50 m path length in which there is a homogeneous distribution of 400 ppm CO_2 will give the same response as 10 m with 480 ppm CO_2 plus 40 m with 380 ppm CO_2 (i.e. 20,000 ppmm, or a path-averaged value of 400 ppm). Therefore, although longer path lengths ensure that larger areas are monitored (thus increasing the possibility that a plume might be captured), these also result in a loss of resolution and greater dilution of a leakage signal.

Leakage quantification using these instruments requires modelling of the open path results combined with detailed wind measurements. As such, meteorological stations are usually deployed together with the laser units. Although originally designed for the monitoring of industrial installations, such as gas pipelines or factory emissions, long open path infrared laser systems have also recently been applied to the monitoring of geological systems.

Quantification Applications

The first geological applications of this technology focussed on the monitoring of natural CO_2 emissions, such as: tomographic mapping of CO_2 from a gas fumarole in the Solfatara Caldera near Naples, Italy (Belotti et al. 2003); fixed-monitoring of a geothermal degassing point near Sienna, Italy (Cuccoli et al. 2007); and risk assessment of natural CO_2 emission points in southern Tuscany, Italy (Tassi et al. 2009). These studies highlight the impact of wind on measured concentrations; the importance of defining background concentrations and variability; and how topography can control migration of the released CO_2 in the near-surface atmosphere due to density effects.

Annunziatellis *et al*. (2007) and Jones *et al*. (2009) also report results from tests conducted above natural CO_2 leaks, but with a focus on geological storage applications. Experiments were conducted which looked at the effect of both measurement height and total path length on sensitivity. In the first experiment a number of different 13 m-long pathways were measured across a 30 m wide gas vent with a published leakage rate of approximately 220 kg d^{-1} (Beaubien et al. 2008), first at 61 cm above ground surface and then at 143 cm. As expected, the average concentrations and standard deviations (σ) of the measurements increased closer to the ground, with a higher σ indicating mixing between background atmospheric air and the leaking CO_2 plume caused by variable wind. Under the atmospheric conditions during the measurements, which are not reported, path-averaged concentrations directly above the emission point ranged from 510 to 605 ppm with an average of 540 ± 15 ppm (1 σ). This compares with "background" measurements, conducted just to the side of the vent, which averaged 507 ± 2 ppm. The second experiment, conducted at different path lengths across a creek hosting a CO_2 emission point of a similar flux rate, shows how a leakage signal is progressively diluted as the path length is increased from 16 up to 100 m. At 100 m path length the average and standard deviation values were very similar to that measured at a background site. The authors state that this shows that this technique may be best adapted to the monitoring of small, high-risk targets (like well sites) rather than long distances.

Cuccoli and Facheris (2008) conducted modelling to better understand the optimal laser configuration needed for quantifying the emission flux from a soil surface. Here the authors used a Gaussian Slender Plume model, due to the need for a model that complies with the mass conservation principle but is simple enough to allow for extensive simulations within the adopted Monte Carlo approach. Three different configurations were modelled, each using multiple optical measurement paths to define five faces of a cubic form (the sixth being the ground surface). While the study yielded interesting results that gave accurate leakage estimates, the small size of the simulated area (500 m^2) and the large number of lasers and reflectors needed means that this approach may not be practical for a CO_2 quantification application.

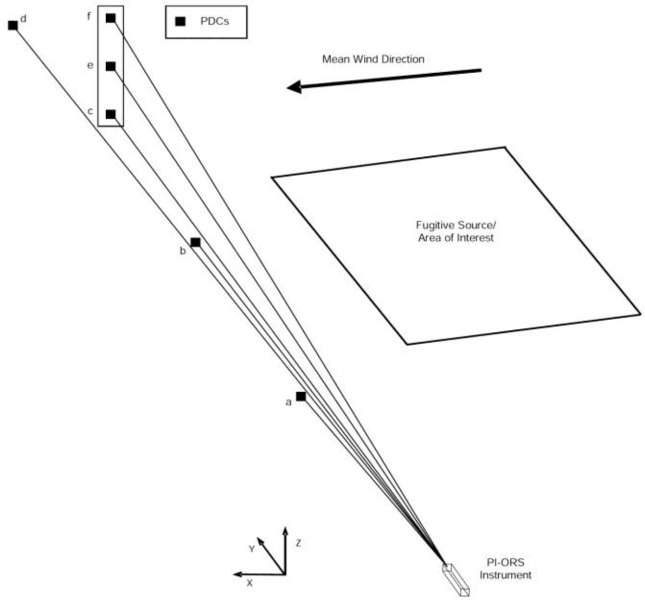


Figure 22. Example showing the setup of a Vertical Radial Plume Mapping (VRPM) Configuration (EPA 2006). PDC – Path Defining Component. IP-ORS - Path-Integrated Optical Remote Sensing System.

As the location and quantification of various types of gaseous pollutants is an issue not only for CO_2 monitoring, the US Environmental Protection Agency has recently published a protocol for the use of open path optical techniques (e.g. TDL, FTIR, UV-DOAS, etc.) as applied to emission monitoring (EPA 2006). This protocol is based on the radial plume mapping (RPM) approach developed by Hashmonay and co-workers (Hashmonay et al. 2001; Hashmonay and Yost 1999; Varma et al. 2003). This document details the procedure that should be followed for the Horizontal RPM (hot-spot location), the Vertical RPM (emission quantification), and the 1D-RPM (leakage location). Only the VRPM method, due to its use for leakage quantification, will be briefly described here. The VRPM technique employs multiple non-intersecting beam paths in a vertical plane down-wind from a leak to define a plume map, assuming a bivariate Gaussian function. The flux of the monitored gas through the vertical plane is calculated by combining the plume map with wind speed and direction data, and then this value is used to estimate the leakage rate of the upwind source. The setup for the VRPM requires a vertical structure, such as a building or scaffolding, for deployment of reflectors/detectors above the ground surface. The recommended layout requires that a measurement plane (rectangle) is defined downwind from the source, with the transmitter located at one bottom corner of the rectangle and at least 3 reflectors/detectors positioned at the far side of the rectangle at ground level, half way up, and at the top corner of the support structure (Figure 22). The plane should be large enough to capture as much of the plume as possible. The transmitter measures each path for between 10 to 60 seconds before moving to the next path, with a total of 12 cycles of all three pathways recommended for best results.

One of the approaches most commonly applied to CO_2 leakage quantificaiton was first described by Flesch *et al*. (2004), who conducted inverse dispersion modelling of data from single laser optical paths to estimate methane flux from a 6 x 6 m experimental gas release area located in a flat agricultural field. The work presented in this study, conducted for agricultural and pollution source-estimation problems, involved the release of essentially pure CH_4 at a rate of between 15 and 50 L/minute for periods of 1 to 3 hours under a wide range of meteorological conditions. Atmospheric monitoring was performed using a CH_4 long open path laser mounted at various orientations and distances from the source (up to 100 m) and at a height of 0.8 to 1 m above the ground surface. A 3D sonic anemometer was used to monitor wind conditions. The various results were modelled using a backward Lagrangian stochastic (bLS) model (i.e. particle tracking) in which they assumed an “ideal surface-layer” based on the Monin–Obukhov similarity theory (MOST).

The MOST approach assumes that all required wind statistics can be determined from a few key surface parameters and is valid when the source and the measurement point lie within a horizontally homogeneous surface layer (i.e. wind statistics do not deviate by more than 20% from their spatial average) and the distance between these two points is sufficiently short such that the individual particles remain in this approximately 50 m thick surface layer. The line-averaged laser results (C_L) were simulated as the average of a series of point concentrations equi-spaced along the laser path. The authors report the average model-estimated flux versus the known release rate (Q_{bLS}/Q) as well as the standard deviation ($\sigma_{Q/Q}$) as a measure of the model's accuracy and precision for leakage quantification. Using all data $Q_{bLS}/Q = 1.27 \pm 2.07$; however, the results improved markedly to $Q_{bLS}/Q = 1.02 \pm 0.2$ when the authors removed experiments conducted during periods in which the MOST assumptions are invalid (rapid atmospheric change or extreme stability) and experiments conducted with a short distance between source and laser path (in which the plume edge is encountered and thus errors are larger). With regard to this second point the study shows that although a greater source-laser path distance can improve plume intersection, the resultant decrease in the relative anomaly means that the modelling results become more sensitive to the background value used. The high sensitivity of the CH_4 TDL clearly has a significant impact on the quality of the results and pathlengths that can be used.

Both CO_2- and CH_4-sensing lasers were tested in a recent study (Trottier et al. 2009) conducted at the Pembina CO_2-EOR project, located about 2 hours west of Edmonton, Canada. At this site between 50 and 100 tonnes of CO_2 had been injected every day (between Spring 2005 and the study period) into the 1,650 m deep Cardium Formation. The laser – detector assembly was mounted on various well-head sites located in 150 x 150 m clearings in a forested area, with path lengths ranging from 30 to 150 m and path heights of about 1 m. The laser cycled through multiple optical pathways via a scanning platform which allowed for automatic targeting of fixed retro-reflectors for pre-determined time periods. Monitoring was conducted during the month of February for three successive years; the chosen period minimised variability caused by biological activity but caused logistical problems because of snow cover and freezing temperatures. Work in this study can be divided into three parts: equipment performance assessment; controlled leakage testing; and modelling for sensitivity analysis and quantification.

In the first phase, the standard deviations of background concentration measurements varied from 0.0 to 0.1 ppm for CH_4 and 3 to 6 ppm for CO_2. The automatic alignment system worked well for CH_4 (thus maintaining an R^2 value > 95% and an accuracy of ± 2%), but the CO_2 system suffered from alignment variations and low light levels. During the second phase a controlled CO_2 leak of 39 tonnes/year (40 standard litres per minute, SLPM) and a CH_4 leak of between 2-3 tonnes/year (6-9 SLPM) was monitored along an optical path located about 20 m away from the leakage point. Due to the higher sensitivity of the CH_4 unit and the lower background concentrations (2 ppm vs 380 ppm), the CH_4 leak was defined much more clearly than the CO_2 one, despite the fact that the CH_4 leakage rate was <1/10 that for CO_2 (Figure 23). That said, the CO_2 plume was identified, with the plume to background difference similar to that observed by Jones *et al*. (2009) for measurements on a vent having a similar total flux rate (220 kg/day versus 100 kg/day in this study).

In the third phase modelling of some of the results were obtained using the same backward Lagrangian Stochastic - MOST model employed by Flesch *et al*. (2004). Here, Trottier *et al*. (2009)modelled various environmental conditions (wind stability) and instrument parameters (path length, distance from source to path) to determine the leakage rate that would result in a 2% concentration increase above background values measured by the laser system (2% being chosen as the maximum standard deviation observed for the background CO_2 measurements). These simulations, which the authors consider as conservative, indicate that a leak of at least 350 t CO_2 / year and 0.6 t CH_4 / year are needed to meet this criterion. Backward leakage-quantification modelling of some of the controlled CH_4 leakage tests were much poorer than those reported by Flesch *et al*. (2004), with estimated values within 50% of the known flux rate; this large discrepancy was attributed to the complex wind patterns of the site.

Further testing of the bLS - MOST approach has been presented by Loh *et al*. (2009), based on the stated potential for this method to quantify leaks occurring on a scale of 0-500 m (Leuning et al. 2008). In the work by Loh *et al*. (2009), tubing was laid out around the perimeter of a 30 m long and 0.5 m wide rectangular area, with release points located every 30 cm along the entire tubing length. Pure CO_2 was released from the tubing at a rate of 0.5 and 1.2 g s^{-1}, while CH_4 (as 88.8% of natural gas) was released

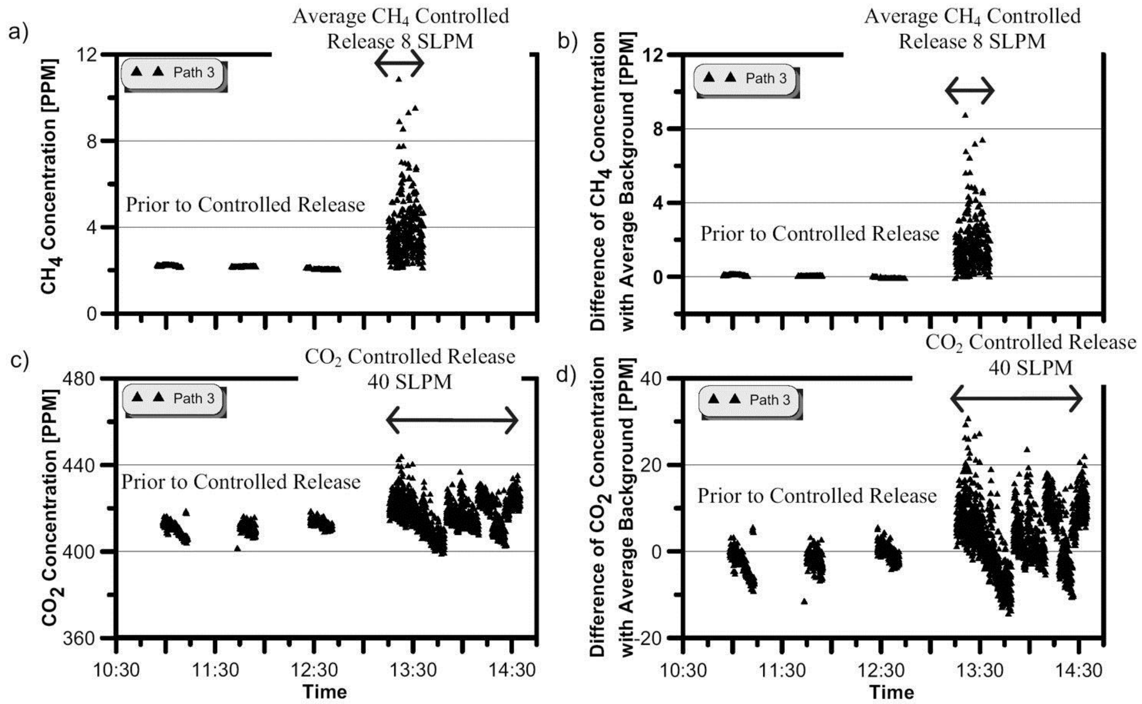


Figure 23. CH_4 and CO_2 concentrations before and during controlled release experiments conducted at a well site above the Pembina oil field, located about 200 km west of Edmonton, Canada. The plots show raw data (a and c) and background-subtracted results (b and d) for different release rates reported in Standard Litres Per Minute (SLPM) (Trottier et al. 2009).

during separate experiments at 34 and 69 mg s^{-1}. The concentrations in these tests were monitored in three different ways, using open-path tunable diode lasers (TDL), an open-path Fourier Transform Infrared spectrometer (FTIR), and line-averaged measurements conducted using closed path instruments. The results of the first two instruments are discussed here, whereas the third is presented under the section on closed path instruments. Two TDL were deployed 11 m either side of the source (path height = 1.5 m, path length = 50 m) for the distance-averaged measurement of CH_4, whereas a single FTIR was placed 20 m to one side of the source (path height = 1.55 m, path length = 69 m) for the distance averaged monitoring of both CH_4 and CO_2.

In contrast to previously described works, two sets of measurements were used for the quantification calculations, one upwind from the simulated leak to estimate background concentrations and a second downwind to quantify the leak itself. In this regard, the two available instruments were used for the TDL measurements, whereas the single FTIR was used for down-wind monitoring and background values were fixed at 1.7 ppm for CH_4 while data from one of the closed path lines was used for CO_2. CH_4 was monitored in addition to CO_2 due to its association with CO_2 at CO_2-EOR sites and the instrument's higher sensitivity. Again data needed to be filtered to attain valid MOST conditions (wind speed > 1.5 m/s) and to ensure sufficient intersection with the monitoring line (± 45°off normal from the line source). The ratio of predicted to actual emission rate, Q_{bLS}/Q, and the standard error of the mean, σ_X, were used to assess the performance of the techniques. Leakage rate estimates were made for both gases using data across all wind stability classes. For CH_4 the two TDL instruments underestimated the true value by about 5% (Q_{bLS}/Q = 0.95; σ_X = 0.09), whereas the FTIR data overestimated it by about 2% (Q_{bLS}/Q = 1.02; σ_X = 0.03). The larger error in the TDL results is believed to be due to differential drift between the two instruments used for upwind and downwind measurements. Estimates for the CO_2 flux results were much poorer, with the FTIR results overestimating the leakage rate by 87% (Q_{bLS}/Q = 1.87), due, probably, to poor measurement precision in the variable background concentration field. These results highlight the potential for more precise leakage estimates using CH_4 as a proxy for CO_2.

A new laser design has recently been tested at a controlled CO_2 release facility established at a relatively flat agricultural field at Montana State University (Humphries et al. 2008). In this study a controlled underground release of 0.3 t CO_2 / day was monitored both above and below ground using a distributed feedback diode laser that scans the 2.0027-2.0042 μm spectral region. For above ground measurements the laser and reflector were positioned at a height of 15 cm, 43 m apart directly along the 100 m long, horizontally-drilled pipe (ca. 1.8 m depth) that is the source of the leak. Every day for 8 days this optical path was monitored from 7-9 a.m., with each measurement taking about 3 minutes. The average and standard deviation of the results for each day are presented, along with those collected from 9:15-11 a.m. at a background site 120 m away along a similar path length but at a height of 75 cm. During the CO_2 release, the average atmospheric CO_2 concentration over the injection well was 618 ppm whereas that at the background site was 448 ppm. The larger difference observed between background and anomaly values is probably due to the fact that here the optical path is very near the ground (15 cm), is oriented along a linear source, and because the release rate is higher. Wind conditions during the experiment are not discussed.

Strengths and Weaknesses

As can be seen by the review above, the long open path technique has been studied due to a number of advantages that it has with respect to monitoring and leakage quantification. First, the large atmospheric volume that it can cross gives this method the potential to intersect a temporally and spatially variable plume. Second, because the lasers can be mounted on automated rotating platforms controlled by aligning software, and most units have an internal reference cell for self-calibration, the unit is well adapted for long-term, unattended monitoring of a site. Combined, these two advantages mean that it may be possible to monitor a large area with a single laser unit and a number of fixed reflectors (i.e. optical pathways). The deployment of multiple open path units has also been proposed (Loh et al. 2009) although issues related to differential instrument drift must be addressed. Authors using inverse modelling to quantify leakage rates state that a line-averaged concentration enhances flux-quantification accuracy due to the fact that the laser signal is indifferent to lateral displacement. Depending on the model used, other potential advantages could include: long path lengths up to 1 km, rapid response times on the order of 1 second, a wide measurement range that can span 4 orders of magnitude, and limited or no interference from other gas species. To improve the potential for quantitative results, it is considered essential to characterise the local meteorology and geography at each site so that instrumentation positioning is optimised for height, distance and frequency of wind direction relative to the most likely areas of leakage.

Despite these advantages there are certain limitations that will affect the eventual deployment of this technique. To begin with, although it may be physically possible to measure across great distances with the laser, the fact that the method yields a distance-averaged concentration means that with increasing path length there is a corresponding reduction in resolution and sensitivity due to dilution of the plume signature by background atmospheric air. The distance between the leakage point and the optical path is also critical, as long distances will decrease plume concentrations and reduce the potential wind directions that would result in plume intersection. As such, most authors recommend the use of these instruments at smaller, high-risk sites like well heads, as well head pressure monitoring may not be capable of sensing small volume leaks. Because the open path technique measures along a line there are also a number of deployment issues that must be considered. For example the pathway between transmitter and reflector could be completely blocked by accumulating snow or growing vegetation, meaning that the optical pathway cannot be placed too close to the ground surface otherwise pathway maintenance would have to be continual. The signal will also be attenuated by falling snow, rain, fog and dust (all of which may also coat the optical windows of both the transceiver and retro-reflector) and completely blocked by passing cars and people will also block the light path

Questions regarding the ability of the method to observe and quantify a CO_2 leakage area are complicated by various parameters related to deployment (height and length of the optical path and its orientation and distance away from any eventual leak), environmental conditions (wind stability, line of sight, existence of obstacles, topography), and leakage characteristics (total flux rate, number of leakage points, spatial size and distribution). Although various authors have conducted experiments looking at some of these issues (e.g. Beaubien et al. 2008; Flesch et al. 2004; Humphries et al. 2008; Jones et al. 2009), the preliminary dispersion modelling efforts of Trottier *et al*. (2009), using the bLS-MOST approach, give "order of magnitude" estimates of how some of these parameters may affect the minimum quantity of leaking gas that may be detected using this method (Table 4). Based on the presented modelling assumptions and a path height of 1 m, the minimum CO_2 leakage that would be observable with the long open path laser system ranges from 350 to 1,400 t CO_2 / year. These values were considered as conservative by the authors due to the fact that the modelling does not account for discrete variations in wind conditions. For example, the same authors reported a test with 90 m path length, 20 m distance between source and path, and a leakage rate of 39 t CO_2 / year (wind conditions not described), in which the system still showed a leakage-related anomaly despite the lower leakage rate. To put a leak of this size in context the 220 kg/day (80 t CO_2 / year) natural leak reported in Beaubien *et al*. (2008) has a 6 m wide area where no vegetation can grow and a total 40 m wide area where vegetation is stressed; as such, a leak of this size may be directly visible without the need for elaborate monitoring equipment.

Table 4. Dispersion modelling results, obtained with the bLS-MOST approach, that show the CH_4 and CO_2 emission rates needed in order to obtain a line-averaged concentration that is greater than 2% above background (from Trottier et al. 2009).

Distance from source to path (m)	Pasquill stability class	Path length (m)	CH_4 emission rate (g/sec)	CO_2 emission rate (g/sec)
25	C (slightly unstable)	100	0.02	13
50	B (moderately unstable)	100	0.05	26
50	C (slightly unstable)	50	0.02	11
50	C (slightly unstable)	100	0.04	23
50	C (slightly unstable)	200	0.08	42
50	D (neutral)	100	0.04	19
100	C (slightly unstable)	100	0.08	43

Although the laser may be capable, under certain conditions, of distinguishing a leak above background values, it cannot directly give a quantification of that leak. Instead, modelling of the resultant data must be used to make this estimate. Whereas some approaches appear to be unrealistic (Cuccoli and Facheris 2008) and others too qualitative (Shuler and Tang 2005), the backward Lagrangian Stochastic (bLS) approach using the Monin-Obuhkov Similarity Theory appears to hold the most promise (Flesch et al. 2004; Loh et al. 2009; Trottier et al. 2009). Using a single optical path and data filtering has resulted in leakage quantification within 20% of the actual value, although a more recent application using two optical paths (up- and down-wind measurements) appears to improve this precision to within 5-10% (Loh et al. 2009). These authors state, however, that enrichments in tracer gas concentration as air passes across a source must be greater than 1% above ambient concentration to obtain accurate results (Figure 24). Finally it should be noted that most experiments to date using open path instruments for leakage quantification have been deployed within 10 to 20 m of the leakage source, to limit dilution, to increase the changes of plume intersection, and to fulfil the MOST requirement that the distance is sufficiently short such that individual particles remain in the monitored surface layer. This implies that the leak must be a point source and that its location must be well defined to obtain accurate quantification estimates using this technique.

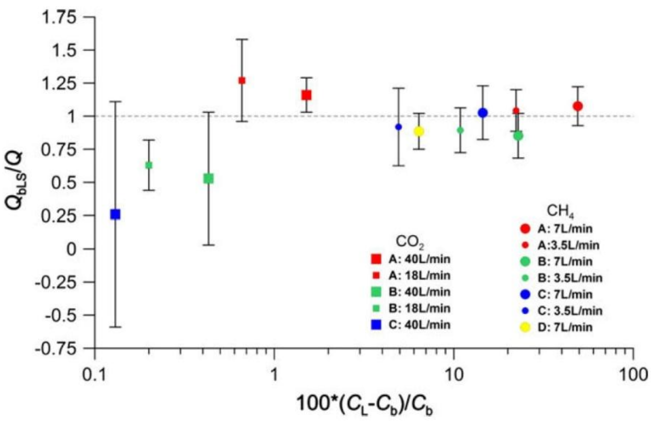


Figure 24. Average fractional flux recovery versus the percentage enrichment in the downwind concentration, CL, relative to its upwind pair, Cb, for different release rates. Experiments, performed at the CSIRO farm near Canberra, Australia, involved controlled CO_2 and CH_4 release and gas monitoring using line-averaged closed and open path instruments (Loh et al. 2009).

The time between when a leak starts on the surface and when it is recognised as such by a laser system could potentially be quite short if it is mounted for continuous monitoring, if it is (preferably) capable of monitoring multiple optical pathways, and if it is managed by a software package capable of determining a leakage-related anomaly and relaying this information to personnel in charge. However the actual time will depend on other factors, such as the behaviour of the leak, wind conditions, and environmental parameters. To begin with, most authors speak of leakage as a percentage of total injected volume, however, the total number and size of leakage locations will control local flux rates (i.e. for a given total flow rate in the sub-surface, fewer smaller leakage points will result in more concentrated anomalies). Then there is the issue of how the leak evolves. For example, does the leak start slowly and eventually grow to the point where it overcomes the monitoring system's sensitivity threshold, or does it immediately start above this value? Clearly in the first case the time needed for discovery will depend on leakage evolution, whereas in the second case time will depend on site conditions. With regard to this latter point, factors such as unfavourable wind conditions, elevated snow or rainfall, or more variable baseline concentrations of the monitored gas (e.g. during the plant growing season) may lengthen the discovery of the leak.

2.2.2 Short open path (IR diode) lasers

As with long open path instruments, various analytical instruments have been applied to the class of techniques defined as "short open path" sensors, including tuneable diode lasers (TDL) and Fourier Transform Infrared (FTIR) detectors. The basic principle of the short open path technique is that transmitter and receiver are separated by a fixed distance (typically on the order of 1-2 m), between which there is a free exchange of atmospheric air. Compared to long open path instruments, which are usually fixed installations at ground surface that provide distance-averaged concentrations, short open path equipment is mounted on ground or airborne vehicles for mapping of point concentrations. Due to the fact that the sensor measures concentrations directly in the air (as opposed to within a cell as occurs in a short closed path instrument) response times are very rapid with very little memory effects, and thus surveys can be conducted at high speeds. Also by reflecting the sensing beam multiple times across the unit casing, sensitivity can be increased while maintaining a small physical dimension (necessary both for logistical reasons and to provide a "point" measurement). Again the TDL is the most commonly deployed method for CO_2 monitoring applications, and thus it will be described in more detail below.

Short open path lasers were first developed as a tool for locating natural gas leaks along pipelines. Given the great distances through often highly vegetated and uninhabited areas, an airborne technique with rapid response times was required to efficiently and cost-effectively monitor this infrastructure. Methane sensors were the first units tested, with these instruments now in operation for over 10 years. A CO_2 detecting unit was subsequently developed, with recent advances in laser technology resulting in significant improvements in sensitivity. Despite this long period of use, there is unfortunately relatively little in the peer-reviewed literature detailing the method application and sensitivity. As a common, representative unit that has been applied in the CO_2 monitoring field, the GasFinder from Boreal Laser Inc. is described here based on web pages (Adam et al. 2008) and commercial brochures (Boreal Laser Inc. 2010).

The system consists of two main units. A control box (housing a laser diode, drive electronics, and microcomputer controller) is linked via a fibre optic cable to the external probe (consisting of reflectors and a photo-detector). As with the open path TDLs, laser light of a given wavelength is beamed across a distance and the amount of light absorbed by the gas of interest is proportional to its concentration. In this case the laser makes four passes across the fixed-length probe prior to quantification by the photo-detector. As stated, the laser pathway is open to the atmosphere and thus measured values are essentially instantaneous.

For CO_2 monitoring applications the more sensitive CH_4 unit can be used at sites where this gas may be associated with the storage reservoir (e.g. CO_2-EOR) or CO_2 sensing units can be used directly. Both airborne and mobile ground based units have been proposed for this type of work, with sample locations being located via an integrated GPS. The airborne methane unit has a quoted detection limit and accuracy of < 1 ppm, a full range of 100 ppm, collects samples 3 times every second, and surveys can be conducted at speeds ranging from 60 to 100 knots at recommended heights between 50 to 75 m. The ground based methane unit has a quoted detection limit and accuracy of 0.2 ppm, a full range of 500 ppm, collects samples once every second, and surveys can be conducted at speeds ranging from 20 to 100 km/h.

Although the CO_2 unit is less sensitive than that for CH_4, this sensor has recently undergone significant technological advances that have greatly improved its performance. Until recently room temperature tuneable diode lasers were only commercially available to about 1,800 nm, meaning that earlier units had to use a relatively weak IR absorption band near 1,580 nm. This resulted in a resolution of no greater than 500 ppm-m. Instead, the development of such lasers that measure up to 2,000 nm has enabled the use of adsorption lines in this spectral region that are 10 to 50 times stronger. As such, new-generation CO_2 lasers have a 5 ppm sensitivity and a range of 10,000 ppm. As for the CH_4 laser, the ground based CO_2 unit measures once every second at recommended speeds of 20 to 100 km/h.

According to the manufacturer the Boreal TDL does not suffer interference from other gases and does not need calibration due to the built-in reference cell. In addition, because it is housed within the protective casing, response is not affected by light, temperature, ground conditions, or weather problems that can interfere with other laser, ultraviolet or infrared systems.

Quantification Applications

Given the relatively new development of the short open path instruments the number of applications of this technique is quite limited, although recent technological advances may increase its use in the future. To date only the tuneable diode laser systems have been tested in the field of CO_2 monitoring, with research conducted into the use of the ground based CO_2 configuration at natural leaking test sites for monitoring and leak-location purposes only (Jones et al. 2009; Kruger et al. 2009). In these studies, a Boreal Laser GasFinderAB was mounted on an all terrain vehicle (ATV) and surveys were conducted first at the test site of Latera (Italy), and then subsequently two times at the Laacher See site (Germany). For all surveys the newly developed CO_2 sensing system was used, with a quoted sensitivity of about 5-10 ppm.

At the Latera site the instrument was mounted on an ATV at a height of about 60 cm above the ground and the instrument was driven along a series of parallel profiles on a flat field that hosts a number of natural CO_2 emanation points of different flux rates. These surveys located the two main leaks in the field, and showed small, irregular anomalies in the area of other vents. Due to wind conditions and the necessary deployment height of the probe, however, anomalies were shifted from their true positions, results were not always reproducible, and some false positives occurred. At the Laacher See site an initial survey was conducted in September 2007 using the same system, although the probe was deployed closer to the ground (30 cm) due to the type of ATV used (Jones et al. 2009). A second set of measurements were then conducted in July of 2008 after some modifications to the system. These surveys, conducted along the shore of a caldera lake where known and inferred natural CO_2 leaks occur, consisted of a series of parallel survey lines over an area of about 100,000 m^2. Preliminary data suggest very similar patterns for the surveys conducted during the two years, with atmospheric gas anomalies over the 2 known vents and further weaker features in the northernmost field closest to the lake (Figure 25).

Surface gas monitoring was carried out at the In Salah Gas project in 2009 using a Boreal Laser open path laser CO_2 detector, linked to a gasFinder FC analyser and mounted at a height of 38 cm above ground on a Toyota Landcruiser (Jones *et al*., 2011). The detector used a wavelength of 2 μm and had a sensitivity of around 5-10 ppm for CO_2. Data were collected at a rate of 1 measurement per second. The first traverses were made around the injection well KB-502, and subsequent measurements were collected within the uplifted area between KB-502 and KB-5, where breakthrough had earlier occurred. The majority of the measurements were close to a typical atmospheric level of around 380 ppm CO_2. The highest values were observed around KB-502, but were attributed to vehicle exhaust. Although vehicle exhaust continued to affect the measurements, subtle variations were also observed in two locations, although these were considered to fall within the bounds of natural diurnal variation. Traverses around KB-4 gave measurements that were elevated due to rainfall, both directly and indirectly through contamination of the laser optics by dirt. Measurements collected during a subsequent visit to the site were found to be affected by dry, dusty and breezy conditions. The authors reported that it was hard to distinguish the effect of dust from real variations in the atmospheric CO_2. It was suggested that a dust cover for the probe might help, although this would reduce response time. The impact of exhaust gases could potentially be reduced in a number of ways: by running lines perpendicular to the wind direction and travelling upwind; to use an electric vehicle, where possible; or to extend the tail pipe of the vehicle exhaust.

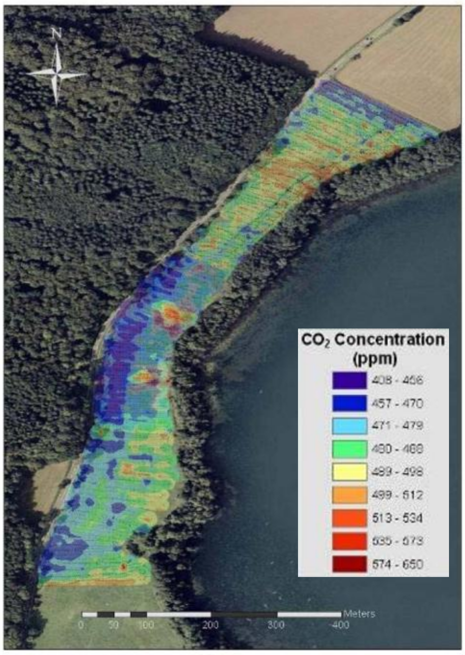


Figure 25. CO_2 concentrations in the air measured at about 30 cm height using a mobile, short open path infrared laser system, Laacher See, Germany (Jones et al. 2009).

As mentioned there have been few publications on the sensitivity of these methods for locating leaks. One exception is a report written for the US Department of Energy in which results are detailed of blind tests of an airborne CH_4-detecting system used to find leaks of different sizes along a simulated pipeline (Johnson et al. 2007). The simulated pipeline was 7.5 miles long and had 15 predetermined leak points that ranged between 1.8 and 5,000 standard cubic feet per hour (scfh) (c. 0.6 to 1,700 g/min); these points were changed twice a day for the three days of testing. The tester flew a helicopter with the mounted TDL probe at a height of 50 feet (15 m) and at a speed of 50 mph (80 km/h) along a pre-loaded pipeline route, with all testing conducted shortly after sunrise to minimise wind effects. The results of these tests were encouraging, with leaks, including the 1.8 scfh leak, being detected an average of 75% of the time and the detection of 90% of all emitted gas volume. Few false positive and false negative leaks were identified. Although promising, the direct extrapolation of these results to a CO_2 storage application are difficult for the following reasons: i) to use the same detector system, methane would have to be associated with the leaking CO_2 (e.g. CO_2-EOR); ii) if it is a CO_2-EOR site, tall infrastructure may limit flying elevation while hydrocarbons associated with wells may result in significant false positives; iii) a CO_2 storage site will be a large area (and not a well defined linear feature like a pipeline) and thus wind conditions will play an important role; iv) at present, sensitivity of the CO_2 detecting system is too low for such applications; and v) the denser CO_2 will tend to remain closer to ground level, thus airborne detection of a CO_2 leak will be inherently more difficult.

Airborne methods have also been used for leakage quantification, although to date using instruments other than TDLs. In principle, TDLs could also be deployed using the same surveying and data processing approach. The most common example of leakage quantification has been the attempt to measure gas flux rates being emitted by a volcano. In this technique an aircraft makes multiple passes through a plume, making continual gas measurements to define the cross-sectional concentration distribution normal to the wind direction (e.g. Casadevall et al. 1994). These results are then processed to calculate the total emission rate of the volcano taking into account the cross-sectional area of the plume, the wind speed, and its CO_2 content (Gerlach et al. 1997).

An alternative approach proposed for volcanoes that have multiple, diffuse release points that produce a wide plume that cannot be visibly defined (as occurs at the Mammoth Mountain site in California, USA), consists of multiple flight paths at different elevations that circle the mountain. The resultant “lampshade” distribution of CO_2 data (measured using a NDIR analyser) is then processed in a similar manner, but considering the curved plume cross-sections non-orthogonal to wind direction, to estimate the overall leakage rate of the volcano (Gerlach et al. 1999). Although these airborne quantification methods could, in theory, be applied to CO_2 storage sites using TDLs, the expected lower flux rates and the accumulation of the dense leaking CO_2 near ground surface greatly limits the potential for plume intersection with these instruments. This effect is even observed at volcanic sites, as it is believed that the total Mammoth Mountain degassing rate was underestimated due to high CO_2 concentrations at elevations below the lowest flight path (Gerlach et al. 1999).

Strengths and Weaknesses

Advantages of the airborne and ground-based short open path TDL systems include: temperature changes, ground, and cloud conditions do not affect the performance of the TDL; the direct measurement of concentrations in the air (i.e. open path) results in very rapid response times and little memory effects, thereby permitting fast surveying of large areas; for ground based systems, apparent anomalies can be followed up with static laser measurements (using the same mobile system) to help eliminate false positives; detectors are very sensitive for CH_4 (< 1 ppm) and moderately sensitive for CO_2 (5-10 ppm); internal calibration and lack of moving parts should result in good instrument stability and low maintenance costs; and the relatively small size and weight facilitates the mounting of this instrument on ground or airborne vehicles.

Disadvantages of the system include: because the technique is a series of point measurements in the atmosphere, changes in wind speed and direction will greatly affect absolute and relative measured values during the period of the survey; the influence of background variations in CO_2 concentrations on leak detection capability has not been quantified (i.e. false positives due to natural variability); for quantification purposes it appears difficult to use airborne instruments due to flight elevation restrictions and the dense nature of a CO_2 leak, whereas the use of ground-based vehicles will be limited by road access and the fact that any intersected plume will only be sampled at the height of the sensor. Although these techniques may develop to be highly useful monitoring tools for CO_2 storage sites, the basic physical restrictions listed above probably mean that the method is not particularly well adapted for leakage quantification.

2.2.3 Short closed path (NDIRs and IR)

Short closed path detectors involve the introduction of a gas sample into a chamber (i.e. “closed”) via a pump or by diffusion, and the quantification of a specific gas component by passing light across the chamber (i.e. “short path”) and through the sample. Thus these methods are similar to long open path and short open path due to the use of optical sources and detectors, but differ due to the use of the measurement chamber. This chamber allows for greater portability, reduces interferences like dust, and can also reduce costs. However, it can have a lower sensitivity due to the shorter path length and has a slower response time/greater sample memory due to mixing and dilution in the flow-through cell volume. Systems that use infrared light are an example of this type of detector.

In its simplest form, an infrared analyser consists of an infrared source and an infrared detector separated by a measurement cell. Recent advances have involved the addition of internal reference cells for internal calibration or drift correction. An air sample is passed through the measurement cell (or diffused into it), and the gas species of interest absorbs some of the radiation coming from the source. As the amount of absorption is proportional to concentration, according to the Lambert-Beer law, the decrease in signal arriving at the detector can be converted into a concentration value. Each gas species absorbs light at a series of different wavelengths as a function of its interatomic bond types and strengths, resulting in a spectrum of absorption peaks that is unique for each gas (Chou 1999). Infrared sensors measure one of the absorption wavelengths for the gas of interest, with the choice of wavelength depending on technical considerations, costs, sensitivity requirements (from ppm to percentage levels), and interferences from other gases (i.e. absorption peak overlap). There are various options for CO_2 infrared analysis, however care must be taken due to coincidence with some peaks related to water vapour.

There are two types of infrared detectors, non-dispersive (NDIR) and dispersive. In a non-dispersive infrared detector all the light from the source passes through the sample, after which it is filtered to the desired wavelength just prior to impinging on the detector. In a dispersive system a grating or prism is used prior to the sample to select a specific wavelength, and thus only this wavelength passes through the sample on its way to the detector. Dispersive IR detectors are typically used in laboratory instruments because they can scan a wide range of wavelengths, however they tend to be more costly and less suitable for portable instruments. Instead NDIR units are the most commonly used short closed path detectors for field applications, due to their robust nature, portability, low cost, stability and selectivity. In addition, a well-designed NDIR unit should have a life expectancy of more than 10 years. The NDIR are often used in soil gas and CO_2 gas flux surveys, as is discussed in greater detail below under the section on near-surface gas geochemistry. Instead these instruments are discussed here in terms of atmospheric monitoring applications, both for leakage monitoring and quantification.

Short closed path tuneable diode lasers (TDL) are also a possibility for CO_2 monitoring applications, as illustrated by work conducted to monitor volcanic gases (e.g. Gagliardi et al. 2002; Richter et al. 2002), however, their large size and greater expense makes widespread deployment more difficult. They do offer, however, the potential for real-time isotopic analysis ($\delta^{13}C$) which could provide important data for separating near-surface biological CO_2 from leaking CO_2 (Fessenden et al. 2010). The TDL short closed path instruments are most commonly used in the eddy covariance technique (e.g. Griffis et al. 2004), and thus they will not be treated here.

Quantification Applications

As first introduced above, Loh *et al*. (2009) created a test site where tubing with gas release points every 30 cm was laid out around the perimeter of a 30 m long and 0.5 m wide rectangular area. Release experiments were conducted with both pure CO_2 (0.5 and 1.2 g s^{-1}) and 88.8% CH_4 in natural gas (34 and 69 mg s^{-1}), and the surrounding area was monitored with various line-averaging techniques. The optical methods of TDL and Fourier Transform Infrared (FTIR) were described above under the topic of long open path methods. Instead a third method, described here, consisted of line averaged measurements conducted by drawing air from 50 m long sampling lines (with holes every 30 cm) and analysing it using closed path techniques (a tuneable diode laser for CH_4 and an infrared gas analyser for CO_2). Four pairs of sampling lines were deployed for these instruments: lines A and A1 at 10 m either side of the source at 0.8 m height; lines B and B1 at 10 m either side of the source at 1.5 m height; lines C and C1 at 30 m either side of the source at 1.5 m height; and lines D and D1 at 30 m from the source at 3 m height. The tubes were each sampled for 45 seconds using a diaphragm pump, resulting in a total sampling cycle for all 8 tubes of 6 minutes; the resultant data were averaged to give 30 minute means. By using paired lines and judicious data filtering based on wind direction the authors were able to use one line for background values and the second, down-wind line for leakage quantification.

As the backward Lagrangian Stochastic (bLS) method, the MOST assumptions, and the data filtering procedures employed by Loh *et al*. (2009) have already been described above, only the results of these experiments are presented here. The accuracy of the experiments was evaluated based on the ratio between the bLS-estimated and true leakage rates (Q_{bLS}/Q). For the CH_4 release experiments, line pairs A, B and D all gave Q_{bLS}/Q values close to 1 for various wind stabilities, while those from line pair C were more variable (Figure 26). Standard errors were less for line pairs A and B due to their closer proximity to the source (10 m), as the signal to noise ratio decreases at greater distances due to increased plume dilution.

By applying more stringent filtering criteria to these data the results for line pairs A and B changed very little, whereas the standard deviation, $\sigma_{Q/Q}$, for C improved markedly from 1.63 to 0.28 (Figure 26). This showed the importance of wind direction filtering, due, again, to greater plume spreading with increased fetch. Final results ranged from Q_{bLS}/Q = 0.87 to 1.06 and $\sigma_{Q/Q}$ = 0.17 to 0.28; on average the closed path measurements for all wind stability conditions underestimated the true CH_4 flux by 4% with a standard deviation of 23%. Closed path measurements with zero CH_4 flux yielded estimates of 0.1 to 0.2 mg/s, indicating limited false positives.

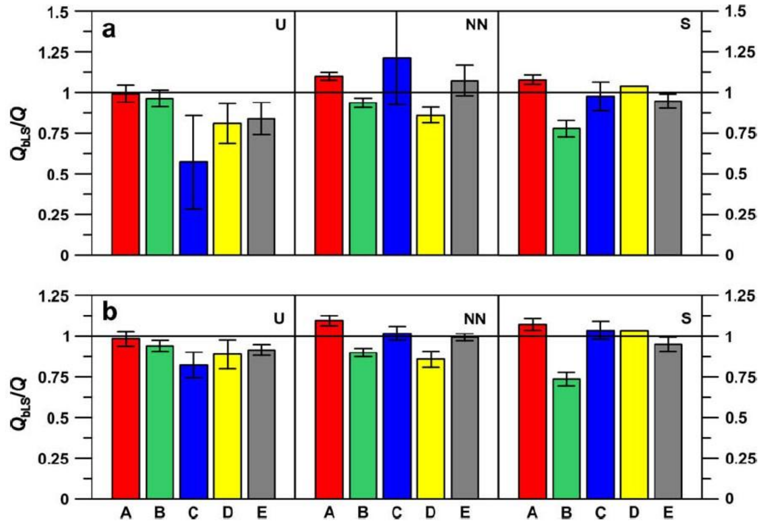


Figure 26. Comparison of bLS modelling estimates of flux versus true flux for CH_4 measured in line pairs A–D plus the ensemble (E) average of all four pairs; a) all processed data; b) filtered data (after Loh *et al*., 2009).

Q_{bLS}/Q values for the CO_2 experiments were much poorer, with line A yielding $Q_{bLS}/Q = 1.19$ but with B = 0.55, C = -0.30, and D = -2.02, meaning that *negative* flux rates were often calculated for the measurement lines located only 30 m from the source. These errors were the result of intermittent mixing, variable background concentrations, the relatively small perturbation caused by the imposed leakage rate, non-contemporaneous sampling due to the use of a single analytical instrument, and difficulty in measuring small δ concentration values of gas that has flowed over the source (i.e. $C_L - C_b$). This last parameter was found to be particularly important, with results showing that the percentage enrichment caused by the leak must be greater than 1% to provide accurate quantification estimates.

Comparing the results for the two gases, the authors found that detection and quantification of a CH_4 leak is easier than for CO_2 due to its more stable, lower background values. In fact an enrichment of only 0.02 ppm is needed for CH_4, whereas > 4 ppm is needed for CO_2. Finally, the authors also found that line-averaged measurements may not be optimal for monitoring purposes due to distance averaged values resulting in low signal/noise ratios; instead they suggest that continuous monitoring with a set of point concentration sensors around the source may be more precise.

Another application of NDIR CO_2 sensors is given by Lewicki *et al*. (2010), in which a number of units were deployed both in the shallow soil and 4 cm above ground surface to continuously monitor CO_2 concentrations over time during a long-term, shallow CO_2 injection test. Sensor data gave detailed results, with measurements being recorded once every second and data averaged over 30 minute periods. The results were used to discern background levels and related diurnal fluctuations, determine leakage breakthrough, and to correlate concentration trends with various atmospheric parameters. Although leakage quantification was performed using CO_2 flux accumulation chambers (see section on gas geochemistry methods below), the authors state that the NDIR sensors showed great promise for atmospheric monitoring of leaks if deployed around areas of higher potential for leakage. The combination of these instruments with the methods suggested above by Loh *et al*. (2009) may then be used for leakage quantification.

Finally, leakage from a CO_2-EOR pipeline operated by the Midwest Geologic Sequestration Consortium in Kentucky was used to assess the use of a number of surface monitoring technologies for leakage detection (Wimmer *et al*., 2011). An NDIR was deployed to measure atmospheric CO_2 and CH_4 concentrations across a grid centred on the leakage location, at heights of 2.5, 25, 50, 75 and 165 cm above the ground surface. Elevated concentrations were not observed at heights greater than 2.5 cm except directly above the leakage point. The authors concluded that although the technique proved to be relatively inexpensive and rapidly deployable, trying to detect and quantify an unknown leakage would be very challenging.

Strengths and Weaknesses

Advantages of the NDIR instruments are their low cost, their flexibility both in terms of concentration range and individual deployment configurations, and the limited interferences from other gases (depending on the wavelength of the chosen detector). In particular, the low cost per NDIR sensor means that a relatively large number could be deployed, while their small size and point measurement nature can allow for deployment also close to the ground (i.e. no line-of-sight or vegetation problems). As stated by Loh *et al*. (2009), multiple point measurements along a line may give better quantification results using the bLS method. Short closed path diode laser detectors, instead, can have better sensitivities and faster response times for a different gas types (e.g. CH_4), however these units tend to be more expensive and thus an individual instrument may need to be connected to multiple sampling ports to reduce costs. Disadvantages are centred, like most of the atmospheric methods influenced by wind dilution and dispersion, on sensitivity.

To date all reported experiments have been conducted at very short distances from the actual emission point, ranging from 0 to a maximum of 30 m. For example the tests conducted by Loh *et al*. (2009) with the CO_2 detector yielded a 20% overestimation and a 45% underestimation of total leakage from sampling lines located only 10 m away from the source, whereas the results from lines located 30 m away actually resulted in negative flux rate estimates. In contrast the estimates conducted using the CH_4 detector were much more accurate, on average underestimating total flux by 4% (± 23%), although again errors were larger for the greater source to measurement point distances. According to Loh *et al*. (2009) the sensitivity of the described line measurement technique, using line averaged measurements with short closed path detectors, will require that the leak must result in an increase of CO_2 concentration in air passing over the source of > 1%. As this will depend on such local parameters as wind conditions and leakage distribution a specific leakage detection limit is not reported. It can be said, however, that the CH_4 measurements were conducted at leakage rates of 0.003 and 0.006 t/day CH_4, while the CO_2 experiments were at rates of 0.04 and 0.1 t/day CO_2.

2.2.4 Eddy covariance

One of the most useful methods to measure and determine gas fluxes in the atmospheric boundary layer (surface layer or constant flux layer) is the Eddy Covariance Method (ECM). The ECM uses statistics to compute turbulent fluxes of heat, water and gas exchange (e.g. CO_2, CH_4 and trace gases). It has the ability to average the integral flux of gases over larger areas (fetch, m^2-km^2 areas) and different temporal scales (Baldocchi *et al*., 2001; Lewicki *et al*., 2009). Although the method is very complex in terms of hardware design and processing the large amounts of data, it has been proposed as a potential methodology for monitoring geologic carbon dioxide storage sites (Miles *et al*., 2005; Oldenburg *et al*., 2003; Leuning *et al*., 2008).

The ECM requires a great deal of specific knowledge, in particular regarding the application of mathematical corrections and processing workflows for the specific purpose of measurement. Unfortunately no uniform methodology and standard methodology for the ECM can be recommended. The generalised technique described here is to a large degree adopted from the excellent introduction to the method by Burba and Anderson (2007).

The ECM relies on the assumption that transport between the surface and the atmosphere is occurring by turbulent movement. These small confined turbulences are called eddies and the air flow can be imagined as a horizontal flow of numerous rotating three dimensional eddies with different sizes distributed over the measurement height (Figure 27; Kaimal and Finnigan, 1994).

In simple terms, gas flux can be described as the number of molecules crossing a unit area per unit time. By means of EC measurements the numbers of molecules (or any other entity like temperature or humidity) is determined and the gas flux is based on the covariance between concentration and vertical air movement/speed. This means that at a certain time step eddy 1 moves an air volume with a number of molecules downward with velocity V_1. At the same location at a later time, eddy 2 moves air upwards with velocity V_2. The net flux over this time and direction (upward/downward, source or sink) can then be determined by the different numbers of molecules (i.e. concentration in the air volume) moving with the different velocity through the area of interest at the tower (Figure 28).

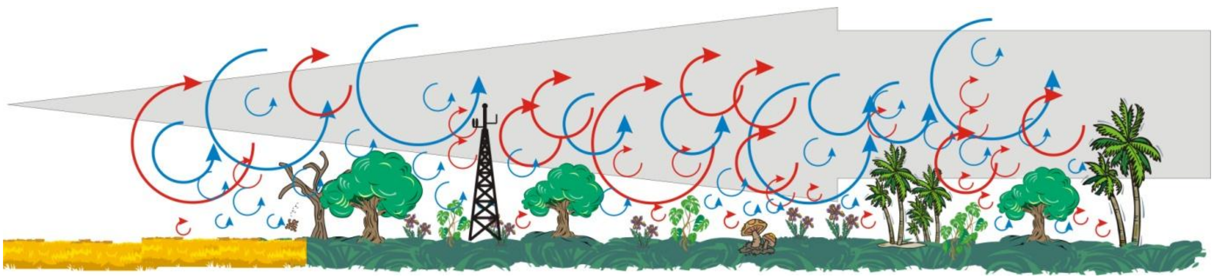


Figure 27. Air flow (grey arrow) consists of different sizes of eddies (after Burba and Anderson, 2007).

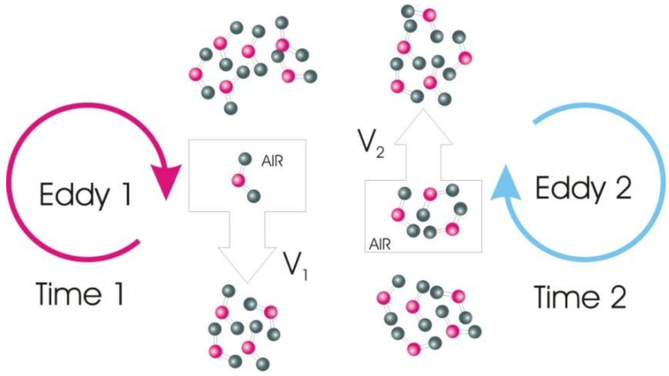


Figure 28. Vertical transport of gas molecules by single eddies at different time steps (after Burba and Anderson, 2007).

The vertical and turbulent flux occurs very fast, hence the requirements for technical instrumentation, survey design and data processing as well as the necessity to avoid deviations from the basic assumptions is exceptionally high compared to other flux measurements (e.g. chamber measurements). Some of the underlying assumptions rely on correct site selection and measurement set-up; others depend on atmospheric and weather conditions. Only under the condition that these preconditions are met, the derivation of the final Eddy Covariance flux equation based on general formulas is valid. The boundary conditions and basic assumptions for the ECM are:

- terrain is horizontal and uniform
- total vertical flow is negligible for horizontal homogenous terrains
- no convergence or divergence of flow
- point of measurement (location of tower) represents an upwind area and lies within the constant flux area of the boundary layer
- flux is fully turbulent
- density fluctuations are assumed to be negligible or can be corrected
- instruments are designed to detect very slight changes combined with high frequency of measurement

Site requirements/tower placement

As the EC-tower can only measure flux contribution from the upwind area, the tower should be located using the following criteria:

- tower location should represent the area of interest for most wind directions
- if this is not possible the tower be located downwind of the area of interest taking into account the prevailing wind directions
- if possible the selected site should be homogenous and flat
- if the terrain is complex or advection is possible, placement of the tower should be on a relatively flat part of the fetch to minimise convergence/divergence of flow

The height of the tower, or rather the height of the sensors, is subject to the following constraints:

- the tower should be high enough to attain the maximum upwind fetch available, but not above the boundary layer because contributions from outside the area of interest might influence the results;
- sensors need to be higher than the surrounding canopy (rule of thumb is 2-5 times the canopy height);
- sensors should be low enough so that the footprint during stable night-time conditions does not extend beyond the area of interest;
- lowest placement of instruments is restricted to the height of the roughness sub-layer;
- in terms of applied instruments the height should be at least five times the instrument path length.

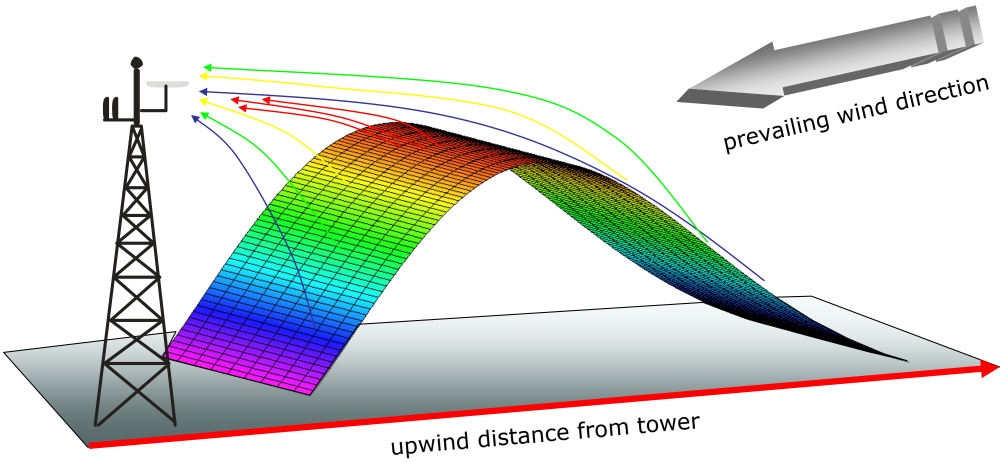


Figure 29. Flux footprint depending on tower height and upwind distance (after Burba and Anderson, 2007).

Flux Footprint

The flux footprint is the contribution, per unit emission, of each element of a surface area source upwind of the tower to vertical scalar flux (Horst and Weil, 1991). The flux footprint depends on the height of the instruments, the surface roughness and thermal stability. Figure 29 illustrates the contribution of flux depending on the upwind distance from the tower. The area with red colours contributes more to the measured flux than areas with green, blue and violet colours.

The contribution to measured flux rates under near neutral conditions as a function of distance depends on instrument and canopy height, wind speed, the friction velocity (a reference wind velocity depending on density and Reynolds stress) and zero-plane displacement (height scale in turbulent flows over rough areas). An estimate of friction velocity and roughness length can usually be extrapolated from the standard deviation of the vertical and mean horizontal wind speed under neutral conditions ($dT/dz = 0$). The peak contribution (as a function of distance) is highly variable as well as the area around the tower which does not contribute to measured flux rates.

With increasing height of the tower, the upwind distance to the flux is dramatically increased as well as the blind zone of no contribution around the tower. With increased surface roughness, the upwind distance to the peak contribution decreases considerably but the magnitude of peak contribution increases. Compared to smooth surfaces both the upwind distance covered by the instrumentation as well as the area of no contribution around the tower will decrease. Measurement height has a more powerful influence on the footprint area when the surface is rough as compared to a smooth surface. However, for a rough surface a low measurement height has a more profound effect on the footprint than a higher instrument installation.

Changes in atmospheric stability can significantly increase/decrease the footprint area. Under stable conditions ($dT/dz > 0$) the footprint as well as the zone of no contribution increases considerably. In case of unstable conditions ($dT/dz < 0$) most of the contribution to measured flux will be resulting from the area very close to the tower (no “blind” zone).

Instrumental setup

The distribution of eddies over the measurement height has implications for the instrument selection and tower setup. Lower to the ground surface small fast rotating eddies prevail (high frequency) whereas higher above the ground larger slower rotating eddies (low frequency) are dominating. Consequently, all instruments should:

- be fast enough to cover all expected frequency ranges;
- be very sensitive to small changes in quantities;
- be small enough to do not break large eddies at great heights;
- have aerodynamic shape to minimise creation of small eddies;
- have small sensing volumes to avoid averaging of small eddies.

The tower for the instrumentation should be constructed in a way to reduce flow obstructing and/or shadowing as far as possible. A basic EC system consists at least of a 3D sonic anemometer, a temperature and humidity probe, a high-speed non-dispersive infrared gas analyser (IRGA) and a data logger including A/D converter with sufficiently high resolution (minimum 12 bit, but depending on sensor span range). The orientation of the anemometer should be true north (apply site-specific correction for magnetic declination), fitted to a firm and steady support and facing the mean wind direction (avoiding flow distortions by the tower itself).

Closed path IR gas analysers have the advantages of potentially higher sensitivity and that automatic calibration procedures can be performed at regular intervals on site. Temperature and pressure within the cell are usually different from ambient conditions but must be controlled to avoid zero drift. Open path systems measure directly *in situ*, resulting in an excellent high frequency response. However, their performance may be adversely affected by rain or low temperatures (icing).

The necessary sampling rate strongly depends on the site characteristics. A minimum sampling frequency of 10 Hz might be acceptable over tall rough canopies, but it is recommended that EC signals are measured at a frequency of 20 Hz (Black *et al*., 2003). Additional variables used in data interpretation (Black *et al*., 2003) include atmospheric pressure, precipitation, radiation, soil temperature/moisture as well as soil and canopy properties (e.g. soil respiration, root dynamics and litter fall).

Raw data processing

Processing raw data usually involves the following most important steps:

- converting signals (volt, amperes, etc) to physical parameters using appropriate and quality controlled calibration functions;
- de-spiking the data by removing occasional spikes (due to electronic and physical noise) and outliers should be replaced with running means;
- missing values (e.g. due to instrument malfunction or errors in data collection system) should be interpolated, as no data gaps are allowed for spectral analysis of data;
- unlevelled instrumentation, with particular respect to the sonic anemometer, must be corrected by means of coordinate rotation;
- compensating for sensor time delay in signal acquisition (in particular for closed path sensors) since fluctuations in wind velocity will then fail to correlate with fluctuations in gas concentrations;
- by detrending values (block averaging, linear or non-linear), mean values are subtracted from the instantaneous values to compute the flux rates (Falge *et al*., 2003);
- averaging the high frequency data over longer periods (0.5 - 4 hours).

Corrections of frequency response errors

An important aspect of measuring flux is the assessment and correction for attenuation of the measured covariance caused by the inadequate frequency response of the sensors and the data acquisition system. The most important frequency response errors are related to:

- sensors which are not fast enough to measure all rapid changes caused by turbulent eddy transport (time response error);

- a mismatch of the gas and/or temperature sensors compared to faster sensors like anemometers (sensor response mismatch error);
- an inability to place sensors at the same location (sensor separation error);
- the fact that sensors do not represent point measurements but integrate over some distance/volume, such as the open IR sensor path (scalar path averaging error);
- turbulent flow in the gas analyser tube, which leads to an attenuation or dampening of the instantaneous concentration fluctuation (tube attenuation error);
- flux averaging periods in data processing which account for an under- or overestimation of flux (high pass and/or low pass filtering errors);
- analogue-to-digital sampling producing an aliasing of spectral contributions, exceeding the Nyquist frequency (digital sampling error).

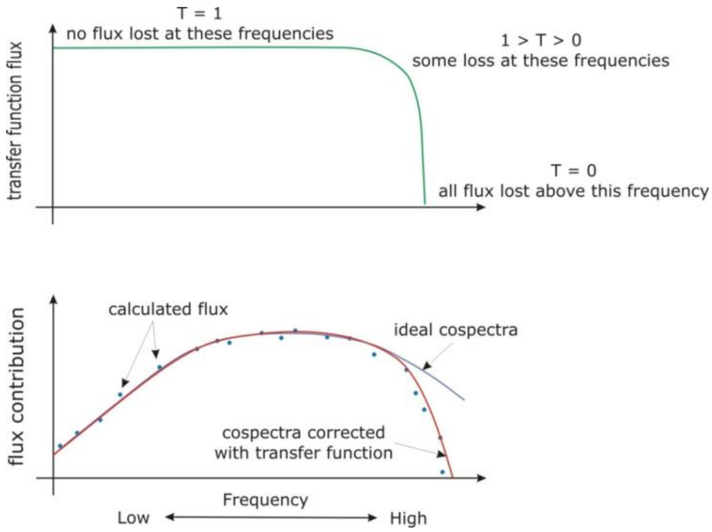


Figure 30. Co-spectra and transfer function (see text for explanation, after Burba and Anderson, 2007).

The fraction by which the flux is underestimated with a slow response scalar sensor is a function of both the response characteristics of the sensor and the frequency distribution of the eddies contributing to the total flux. The frequency response corrections are calculated from the difference between instantaneous data and the co-spectra of the raw data, which describe the frequency-dependant contribution of the flux to the overall flow rate. The ideal co-spectra can either be modelled (e.g. Kaimal *et al*., 1972; Horst, 1997) or can be derived from the sensible heat flux co-spectra. Modern anemometers measure with high frequency and almost no sensor separation between the wind velocity and corresponding temperature measurement occur. Hence, the heat flux co-spectra are mostly close to the ideal co-spectra and need no correction (Figure 30).

The actual co-spectra are located below the ideal co-spectra, in particular at higher frequencies. At those frequencies the calculated flux underestimates the true flux due to inadequate frequency response of the system. A transfer function describes how a system responds to input signals with varying frequencies. For each frequency response error listed above empirical or analytical transfer functions exist (e.g. Massmann, 2000) which describe the effect on the ideal co-spectra. Applying these corrections to the ideal co-spectra will bring the co-spectra curve down at each frequency (e.g. Wolf and Laca, 2007). The other way round, by applying the corrections (sum of transfer functions) to the measured co-spectra, it would be possible to calculate the ideal co-spectra from the actual co-spectra and hence determine the correct flux. A detailed description of all transfer functions would go beyond the scope of this comprehensive description of the ECM.

Other corrections which must be considered are related to density fluctuations when using open path sensors (Webb-Pearman-Leuning correction, after Webb *et al*., 1980), cross wind correction of sonic temperatures (e.g. Laubach and McNaughton, 1988) and eventually adjustment for band broadening effects on IR-sensors. A comprehensive review of available eddy covariance software is given by Mauder *et al.* (2007).

Quality control and calibration

Proper installation, maintenance, data assurance and sensor calibration is of highest importance when using the eddy covariance method. All acquired data must be screened regularly for validity and removed if (Munger and Loescher, 2004):

- instrument malfunctions occur;
- the sensors are out of range;
- a rainfall event occurred;
- 30-min data collection periods are incomplete;
- the data are outside a physically meaningful variance threshold;
- the stability parameters are outside the acceptable range;
- indications for non-stationary conditions occur;
- periods with wind directions other than from the footprint of interest are prevailing.

The data processing workflow can be controlled by analysing standard sets of raw data ("gold files") which are available from different networks (e.g. Euroflux or Ameriflux).

Ultimately, all measured data are only as good as the respective sensor calibrations. The ECM requires the highest level of precision and accuracy that is practical. General procedures for calibration of IRGA are published in Ocheltree and Loescher (2003a), and temperature sensors in Ocheltree and Loescher (2003b).

Range of application

Though more expensive and technically more complex, the eddy covariance method provides a powerful tool that allows for spatial integration and near-continuous, long-term monitoring of the soil-atmosphere flux. This holds for CO_2 but also for other greenhouse gases (e.g. methane, Smeets *et al*., 2009), but the method is restricted to onshore sites. Flux rates measured, i.e. the conventional application range, usually lie within the typical range of CO_2 emissions from soils and different land covers (10th's of g/m²/d). Higher emission rates can easily be determined. Werner *et al*. (2003) measured release rates between 950-4,460 g/d/m² at the Solfatara volcano, Sicily.

However, whether the ECM can detect a release of carbon dioxide from a storage site strictly depends on the ratio between the integral CO_2 flux from the footprint area and the seepage rate from the point source (e.g. an abandoned well). A seepage rate of 0.1 t/d from a release experiment (Lewicki *et al*., 2009) was not distinguishable from the background CO_2 emissions, whereas the release of 0.3 t/d significantly increased the measured flux rates compared to the base line emission of the area.

The ECM was employed at the CO2CRC Otway Project in SE Australia to monitor atmospheric CO_2 and test the possibility of detecting leakage (Etheridge *et al*., 2011). A scheduled venting of gas from the observation well showed that it would be unlikely that elevated CO_2 emissions from a leakage would be detected given the high natural background and its variability. However, levels of CH_4 and the tracer sulphur hexachloride (SF_6) were found to be significantly enhanced, and CO and $\delta^{13}CO_2$ provided additional information that elucidated the source of the gases.

2.3 Shallow subsurface monitoring methods

2.3.1 Near surface gas geochemistry

Near surface gas geochemistry can be divided into two general areas of study, gas flux measurements at the ground surface and the analysis of soil gas collected from a depth of 0.5 to 1 m. A short overview of these two techniques is given below.

Gas flux measurements are typically conducted using either the closed chamber (CC) or the dynamic closed chamber (DCC) techniques, due to their speed and portability. These methods involve the monitoring of gas concentration changes over time within an accumulation chamber placed on the soil surface, with samples collected manually at pre-determined times in the CC method and continuously (typically every second) via an in-line detector in the DCC method. The first linear segment of the growth curve is used to calculate the slope (dC/dT) and is combined with the surface area and volume of the accumulation chamber to calculate the flux (Lewicki et al. 2005a):

$$F_{CO_2} = k\left(\frac{V}{A}\right)\left(\frac{T_0}{T}\right)\left(\frac{P}{P_0}\right)\left(\frac{d[CO_2]}{dt}\right)$$

where F_{CO2} is flux in g m^{-2} d^{-1}; d[CO_2]/dt is the initial rate of change in CO_2 concentration in the chamber (vol% s^{-1}); V and A are the accumulation chamber volume (m^3) and surface area (m^2), T and T_0 are measured and standard temperature (K), P and P_0 are measured and standard pressure (kPa), and k is a conversion constant (1,558,656 g s m^{-3} d^{-1}). Where portable, inexpensive, non-destructive, rapid-response, sensitive instruments exist for a given gas species, such as infrared detectors for CO_2, the DCC method can be used. Instead when this type of instrument is not available, for example for helium or methane, the CC approach is usually applied. One significant difference between these two approaches is that a number of gas samples must be removed from the chamber using the CC method, whereas the DCC technique is a closed loop; this means that the CC chamber volume must be large or sample volume small to minimise any pressure drops during sample extraction. The light weight, rapid response (usually 1-2 minutes), and good precision of IR DCC (typically +/- 10%) has made it the most widespread technique for measuring CO_2 flux rates in various applications, including CCS monitoring. Gas flux measurements with the dynamic closed chamber technique are usually conducted manually via gridded surveys, although automated systems do exist for continual monitoring of a small site (e.g. a well head). Quantification of CO_2 leakage rates using gas flux measurements usually consists of sampling on a grid, interpolating between points, conversion to total CO_2 flux for the measurement area, and subtracting near-surface contributions based on baseline studies or soil gas data.

Soil gas samples are most typically collected using small, lightweight soil probes. The method involves driving a hollow steel tube into the ground, typically to a depth of 0-5-1.0 m, and drawing soil air to the surface for analysis. Alternative sampling methods involve direct push, power hammered, augered, or drilled systems. These are slower, less portable, and more costly than the simple probes but may allow sampling in difficult ground, or at greater depths where atmospheric effects are less significant (assuming a deep water table). In very dry permeable ground, such as in arid environments, deeper sampling at several metres depth may be essential to avoid atmospheric contamination (Gole and Butt 1985). The measurement of depth profiles, using either extended soil probes or shallow boreholes with nested sampling depths, can be used to distinguish between a shallow or deep origin of the measured gases. A balance is needed, however, between quick and inexpensive shallow techniques, which allow large areas to be covered relatively quickly, and the slower, more costly deeper investigations. In many cases a combination of the two approaches may be the best solution, with the more detailed deeper investigations being sited based on the results of initial shallow surveys.

The collected soil gas samples can be analysed in the field using portable equipment or stored in pre-evacuated airtight containers for eventual laboratory analysis. In addition to CO_2, various other gas species are also studied due to their association with the reservoir (e.g. CH_4 or H_2S in CO_2-EOR projects), man-made tracers that are added to the injected stream (e.g. fluorocarbons), or natural tracer gases (e.g. helium or radon). Isotopic analyses are also conducted; the most common are those of carbon in CO_2 ($\delta^{13}C$ to determine origin and ^{14}C to determine age), although the isotopes of various noble gases like xenon have also been proposed. The primary motivation for analysing various gas species is to help distinguish CO_2 which might be leaking from a geological storage reservoir from that which is produced naturally in the shallow subsurface via biological (e.g. plant or microbial respiration) or inorganic (e.g. groundwater degassing) processes. Therefore, soil gas measurements are typically not used to directly quantify CO_2 leakage rates, but rather to constrain and interpret calculations made with the direct flux measurements.

Field-based measurements are possible for a range of gases. Infra-red analysers exist for both CO_2 and CH_4. Units for CO_2 have been used extensively in soil gas studies, with detectors available that can measure the complete range of concentrations encountered in natural (0.5-10%) or leaking (3-100%) systems. Field based infrared instruments for CH_4 typically measure in the percentage range, and thus are not appropriate in most natural soil gas settings where concentrations are typically less than 2 ppm. In a CCS monitoring or leakage quantification application these instruments would only be able to detect a very significant CH_4 leak. Electrochemical sensors are common for a number of different gases, including O_2, CO_2, and H_2S, whereas radon is measured by alpha scintillation counting (Lucas cells) or by ionisation chambers. The most commonly used laboratory analytical method is gas chromatography equipped with columns and detectors specific for the analyte. Sensitivity and precision is typically high, with measurable concentrations ranging from the ppb level up to percent (depending on the configuration). Detectors could include flame ionisation detectors (FID) for hydrocarbon gases, flame photometric detectors (FPD) for sulphur gases, thermal conductivity detectors (TCD) for permanent gases (i.e. CO_2, N_2, and O_2), as well as many other more specialised units. Helium is usually analysed by mass spectrometry. Isotopic analysis of various gases can be performed, typically consisting of either wet-chemistry methods or gas chromatograph – mass spectrometry (GC/MS).

In addition to manual grab samples of the soil air, autonomous monitoring stations have been created that are able to sample and analyse the concentration of specific gas species on a continual basis for extended periods of time (e.g. Annunziatellis et al. 2004). Although these units have different designs and configurations, they all tend to consist of a power supply (batteries and solar panels or connected to the grid), data storage and/or transmission capability (internal memory or dedicated computer, wireless or land-line data transfer), system management software, and either buried sensors for direct *in situ* analysis or analytical equipment on the surface with gas being pumped from underground. The data acquisition time step is chosen based on the system's configuration, but can range from seconds to days. These units, because of their unattended and continual collection of data can give critical information on the natural diurnal and seasonal variability of the site, which is essential when subtracting natural biological flux during the calculation of CO_2 leakage rates.

The measurement of soil gas concentrations in the shallow subsurface and gas flux across the ground surface are often conducted together due to their complimentary nature, with soil gas values being less impacted by surface or atmospheric effects and flux measurements defining actual transfer rates out of the soil. In addition, both methods are point measurements and thus many of the issues related to resolution, sensitivity, and costs are similar for the two techniques. For these reasons soil gas and gas flux surveys have been grouped together for the following discussion.

Two main factors will influence the success of soil gas and gas flux surveys for accurately quantifying leakage from a geological storage site. First these methods must locate the leak and define its physical extent. This will be a function of the size, style (i.e. point vs diffuse), and magnitude (subtle or obvious anomalies) of the leak and the chosen sampling density. As described below the potential for locating a leak can be addressed statistically, with the focussing of sampling on higher-risk areas increasing the potential for success. Second these methods must be able to accurately separate baseline from leakage flux rates. As natural, near-surface, biologicall-produced CO_2 flux can be both significant and highly variable (both spatially, as a function of soil type and underlying geology, topography, land-use, etc., and temporally, based on diurnal and seasonal effects on rainfall, temperature, etc.), great care must be taken to correctly subtract baseline fluxes so as to ensure that calculated leakage rates are not grossly over- or under-estimated.

Because both soil gas and gas flux surveys are point measurements the issue has been raised regarding the number of samples required to locate, and eventually quantify, a leak of a given dimension above a storage site that could potentially be on the order of 1 to 100 km^2. To illustrate this Oldenburg *et al*. (2003) present a statistical analysis that relates the confidence level of finding a leak based on the size of the leak (x), the size of the total area (A), the number of samples (n), and the capability of the method to detect a gas leak anomaly. For example, if a technique has 100% capability to recognise a leak anomaly, the number of samples that will be needed to locate at least one gas leak at the 95% confidence level will be 30 at x/A = 0.1, 300 at x/A = 0.01, and 3000 at x/A = 0.001. Another approach calculates the number of samples (n) required to attain a required confidence level. For example, a low confidence level (e.g. 0.1) would be set in the case where there is a low possibility of a leak, resulting in n = 7, 70, 700, and 7000 for x/A = 0.1, 0.01, 0.001, and 0.0001. In contrast a high confidence level (e.g. 0.9) would be required in the case where other information indicated that a leak likely exists (e.g. reservoir pressure data), resulting in n = 50, 500, 5000, and 50,000 for the same the same range of x/A values.

These calculations assume that the method is 100% capable of detecting a gas leak anomaly. In reality, however, both false positives and negatives will likely occur due to the statistical distribution of both the background and anomaly populations. Parameters can be included in the calculations that estimate probability distributions (based on baseline studies and leakage modelling), and a threshold can be set above which a value is considered anomalous. Monte Carlo simulations that take into account these parameters, as well as x/A, can be used to estimate the number of measurements that will be required to determine with a desired confidence level whether a gas anomaly exists in the sampling area. The authors state that these examples highlight the importance of collecting site specific geological information to delineate the most probable gas leakage locations to minimise A, which will maximise the potential for successful location and quantification of a leak while at the same time minimising the number of samples and specialised analyses (i.e. costs).

A number of researchers have proposed different sampling strategies and approaches to improve leak detection success rates and thus leak quantification resolution. For example, Cortis *et al*. (2008) describe a dynamic sampling campaign of soil gas or gas flux measurements directed via an artificial neural network (ANN) model coupled with particle swarm optimisation (PSO). The ANN defines a regression correlation between the baseline CO_2 point measurements conducted prior to injection and various easily measured system properties (e.g. topography or vegetation), with points lying outside this regression being defined as anomalous. The PSO is then used to dynamically manage a sampling campaign, with subsequent sampling points (direction and distance) for multiple technicians in the field being directed by their current direction and by minimisation of the regression coefficient between their previous measured values and the ANN model at both the local (individual) and global (group or "swarm") level. Computer testing of this approach was conducted on simulated data for a hypothetical field site having variable topography, vegetation, and an average background CO_2 flux of about 10 g m^{-2} d^{-1}. On this baseline distribution a 20 times CO_2 flux anomaly was superimposed in one area within the grid. Multiple PSO simulations were conducted with different random initialisations, with the majority being capable of finding the anomaly (e.g. Figure 31). Unfortunately, however, the authors do not state the average number of iterations (i.e. sampling points) that were required for the various simulations. According to the authors, this approach will minimise the number of measurements and the total distance that a field technician will need to travel during a sampling campaign, thus reducing costs. Once a leakage point is defined, a regular, higher density grid of CO_2 flux measurements could then be conducted to precisely quantify the leak.

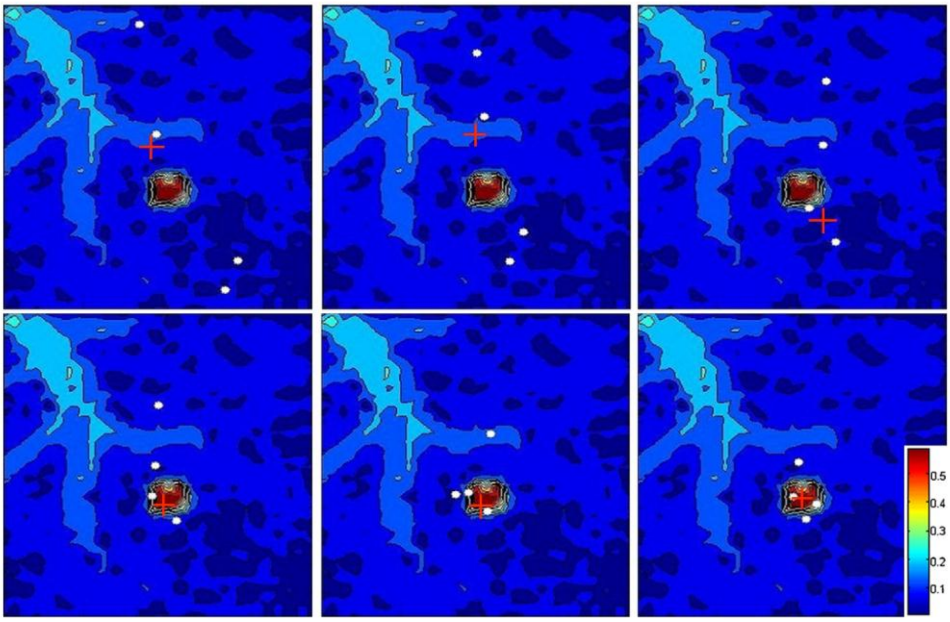


Figure 31. Simulation using the Particle Swarm Optimisation (PSO) algorithm to locate a gas leak (Cortis et al. 2008). The contoured colours represent the soil gas CO_2 distribution at 10 cm depth, the white dots represent particles which are randomly initiated and used to explore the search space according to the PSO rules, and the red crosses show the global minimum of the particle swarm. As the algorithm progresses, the red cross moves towards the red seepage anomaly.

Another approach (Lewicki et al. 2005b; Lewicki et al. 2006) proposes multiple measurement campaigns combined with spatial and temporal filters to both locate and subsequently quantify a leakage. This approach is based on the assumption that: i) shallow background processes like soil respiration are generally spatially heterogeneous and controlled by meteorological and biological processes that operate on diurnal or seasonal time scales; ii) leakage anomalies are relatively coherent in space and constant in time; and iii) both baseline and leakage signals are modified by near-surface processes on predictable time scales. The authors believe that by conducting multiple surveys and applying both temporal and spatial filters to the various datasets, it should be possible to exploit these differences to locate and quantify a leak. To test this, simulations were conducted on synthetic data consisting of a log-normal background CO_2 flux distribution and local leakage values created as a scaled Gaussian distribution. Strategy success was evaluated based on the fraction misestimation of the calculated leakage rate, comparing the rate obtained using the filtered sampled data with that for the total synthetic data source.

Initial tests showed that random sampling for all multiple campaigns yielded the best leakage detection results and thus this approach was applied for subsequent modelling of two different leakage scenarios: diffuse well leakage and concentrated leakage along a fault. These simulations showed that for a fixed A_S/A_T (leak versus total surface area) and F_S/F_B (leak versus baseline CO_2 flux), the error of the leakage rate estimate decreases non-linearly with increasing number of sampling campaigns, becoming relatively insensitive after a certain number depending on the used parameters. It was also found that the potential for a successful location and quantification of a leak improves with a large leakage area relative to the total area or a high flux rate compared to background, but not necessarily both together. This means that a small, high-flux leak associated with a well, and a large, low-flux diffuse leak along a fault may both be quantified to a reasonable level by conducting, in the words of the authors, an “acceptable” number of sampling campaigns. It is emphasised that due to the relatively high A_S/A_T ratios used for simulated fault leakage, relatively low leakage flux rates can be delineated with a reasonable number of samples. This implies that judicious selection of sampling areas based on known geology and structure will decrease the total measurement area (i.e. A_T), thus increasing the potential for leak detection and quantification. The authors state that 100 CO_2 flux measurements can be made in a day, therefore the number of repeat sampling campaigns would be equal to the number of days required to devote to storage verification. They state that in most cases 10-50 repeat sampling campaigns (i.e. days) should be reasonable within a year and should be sufficient to locate and quantify a certain range of leaks.

Quantification Applications

The simulated, multiple-sampling-campaign approach, described above, automatically filters out the spatial and temporal variability of the baseline CO_2 flux field, thereby separating out and directly quantifying the leakage flux. However, this approach is unique, as most researchers prefer to collect a larger number of samples during a more limited number of surveys in an effort to immediately locate and quantify a potential leak. In these studies, many involving surveys of leaking natural sites or controlled release experiments, a number of different approaches have been applied to remove the natural background contribution so that the leakage flux can be quantified. In general these approaches can be divided into two broad groups: i) subtract baseline flux survey results from the total monitoring flux survey data; and ii) use tracers (e.g. carbon isotopes, man-made gases added to the injected CO_2, etc.) analysed in soil gas samples to define the percentage of total flux that is due to leakage from a deep source.

The baseline subtraction approach has been used during shallow injection and surface monitoring experiments conducted by the Zero Emissions Research and Technology Project (ZERT) (Lewicki et al. 2007). This test site consists of a slotted pipe that was horizontally drilled in place at a depth of approximately 2 m below ground surface. The 73 m long pipe, which is divided into six 12 m-long zones separated by 0.4 m wide inflatable packers, was used to inject CO_2 below the water table. Preferential gas release at the pipe-packer junctions resulted in a series of relatively high-magnitude leakage points at the surface, mimicking localised gas migration along more permeable intervals of a fault. Two experiments were conducted using injection rates of 0.1 and 0.3 t CO_2 d^{-1}. Surface CO_2 flux was monitored for leakage detection and quantification purposes using a dynamic closed chamber (DCC), with samples being collected along a grid (100 - 150 points spaced from 1 to 10 m apart) that straddles the horizontal well. Leakage flux was quantified in the following manner: i) total CO_2 discharge (D_{tot}) of the measured area was estimated by calculating the declustered mean CO_2 flux and multiplying it by the total measurement area (7700 m^2); ii) background CO_2 discharge (D_{back}) was determined for the same period by calculating the mean CO_2 flux for distances 10–30 m from the well trace (as there was no evidence of leakage beyond 7.5m from the well) and multiplying it by 7,700 m^2; and iii) the CO_2 discharge associated with leakage from along the well (D_{leak}) was then estimated as D_{tot} - D_{back}.

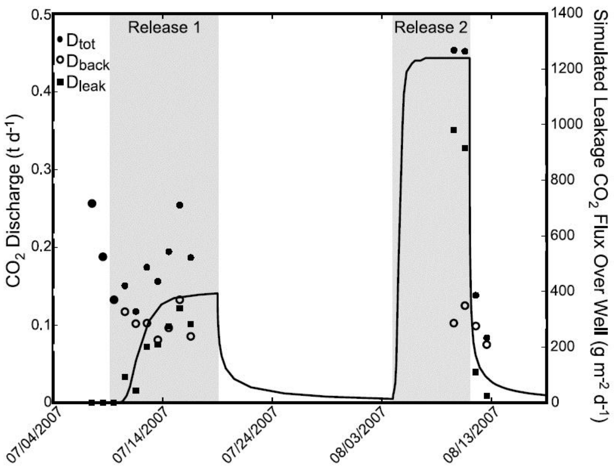


Figure 32. Plot of CO_2 discharge versus time showing total, background, and calculated leakage rates. The black line shows simulated time evolution of leakage CO_2 flux directly over the well (after Lewicki *et al*., 2010.

The results for both experiments closely followed the model predictions of CO_2 flux development (Figure 32), with an apparent steady state total flux rate quite similar to the injected rates of 0.1 and 0.3 t d^{-1}. These results illustrate how direct CO_2 flux measurements yield the most accurate estimate of surface leakage rate when the leakage location is well-constrained. Regarding a wider application at a CO_2 storage site, the authors stress the importance of careful characterisation of background CO_2 variability prior to CO_2 injection into the storage reservoir. This is because of the primary challenge of differentiating a leakage signal within background biological variability, which is especially challenging when background fluxes are high (such as during the growing season or after rain events). To capture the statistical distribution of the baseline concentrations and fluxes, surveys should be conducted at widely spaced sampling intervals along a large grid and at a greater density over smaller grids during different times of the year and encompassing all areas representative of the various topography, land-use and soil types found in the area.

In a subsequent experiment conducted a year later at the same site by the same group of researchers (Lewicki et al. 2010), gas flux measurements were able again to accurately quantify the amount of injected CO_2. In this case the injection rate of 0.3 t CO_2 / day was closely matched by calculated mean leakage rate (± 1 standard deviation) of 0.31 ± 0.05 t CO_2 / day.

The results of a different experiment at the ZERT site are reported in Strazisar *et al*. (2009). This work involved injection of CO_2 into a vertical, 2.5 m deep well and subsequent monitoring of CO_2 flux and soil gas CO_2 concentrations. Upward migration from the vertical well resulted in a semi-circular CO_2 flux anomaly centred on the well itself that extended no more than 3.5 m in any direction. Interpolation and integration of the flux grid results gave an estimated total CO_2 flux rate of 723 mL/min, which is reasonably similar to the actual injection rate of 800 mL/min.

As mentioned earlier, the alternative approach to separate leakage from baseline flux is to analyse for certain tracer species in soil gas that can be associated with the injected CO_2 (either naturally occurring or added) and to relate their concentration to CO_2 leakage rates at the surface. One technique is to use the CO_2 itself, as the injected CO_2 may have an isotopic signature that is different from that found in the shallow soil horizon. The primary advantages of this approach are that no additional tracer has to be added to the injection stream and that migration of the isotopic tracer should be essentially the same as the bulk CO_2 (i.e. fractionation will likely be limited, caused only by CO_2 reactions along the flow path).. The potential success of using the stable isotopic signature of CO_2 rests on whether the value of the injected gas is significantly different to that found naturally in the soil gas. The atmospheric $\delta^{13}C$ of CO_2 is around –7 ‰ and that of inorganically produced geological CO_2 is typically around 0‰, whereas CO_2 respired by plants using the C3 pathway has a range between –24‰ to -38‰ and that respired by plants using the C4 pathway is between –6‰ to –19‰. As the average $\delta^{13}C$ value of CO_2 derived from the burning of fossil fuels is in the order of –27‰, injected man-made CO_2 may potentially be distinguished from atmospheric and C4-derived CO_2 if leakage results in high enough concentrations, but not from C3 respired soil gas CO_2 (Oldenburg et al. 2003). An example of the potential application of this analysis was given by Krevor *et al*. (2010), in which a portable, real-time, stable carbon isotope ratio analyser was used to detect and characterise the intentional leakage event at the ZERT facility. The resulting concentration and $\delta^{13}C$ maps helped define specific leakage locations and discriminated petrogenic from biogenic sources of CO_2.

In contrast, the amount of the unstable carbon isotope, ^{14}C, is a measure of age, with higher values indicating a more modern carbon source. For example $\Delta^{14}C_{CO2}$ of atmospheric air is around 70‰ and soil gas CO_2 of a typical forest is about 128‰, whereas fossil-fuel-derived CO_2 is basically free of ^{14}C. Oldenburg *et al*. (2003) give a mass balance example which shows that leaks of 0.92, 9.2 and 92 µmol CO_2 m^{-2} s^{-1} in a background soil CO_2 respiration rate of 1.9 µmol m^{-2} s^{-1} would yield soil gas CO_2 samples with $\Delta^{14}C$ values of –240, -807, and –977 ‰. These values would easily be distinguished from the background levels (in the absence of oxidation of ancient organic matter in soil parent material) and could be used to back-calculate and make an estimate of the quantity of leaking CO_2.

Klusman (2003) used both stable and unstable carbon isotopic data, combined with CO_2 flux and other measurements, to estimate the amount of CO_2 leaking at surface from the Rangely CO_2-EOR project in Colorado, USA. The Rangely oil field has been in operation since the 1940s, with conversion to water flood in 1958 and to CO_2 flood in 1986. Approximately 23 million metric tonnes of inorganic geological CO_2 have been injected above hydrostatic pressure into the Weber Unit up until 2003 over the 78 km^2 area of the field. The fact that geological CO_2 was used means that it has a unique isotopic signature, with $\delta^{13}C$ values near –4‰ and ^{14}C (expressed as Percent Modern Carbon, PMC) near zero. Rangely has a semiarid climate and a deep water table located at approximately 60 m depth. Near-surface gas geochemistry research consisted of a limited number of initial measurement points (41 above the oil field and 16 in the control area) being sampled for soil gas along a shallow vertical profile at 30, 60, and 100 cm depths and triplicate CO_2 and CH_4 flux measurements. The results were then used to choose locations to install 5 multilevel boreholes: two indicating microseepage; one not indicating microseepage; one on a fault; and one in a control area. These boreholes consisted of sampling intervals at 1, 2, 3, 5 m and end-of-hole depths (typically 7-8 m); clearly a deep water table is needed for this approach. Soil gas samples were analysed for some or all of the following: concentration of CO_2, CH_4 and other alkanes, $\delta^{13}C$ in CO_2 and CH_4, and ^{14}C in CO_2.

Computer modelling of CH_4 in the unsaturated zone was conducted to define methanotrophic rate constants of CH_4 consumption and its eventual control on CH_4 and CO_2 concentrations. Quantification estimates of CO_2 for this site were conducted by first using the direct CO_2 flux measurements, and then subsequently reducing this amount based on a step-wise integration with soil gas and isotopic results. In the initial estimate the mean CO_2 flux value (based on the measurement of 41 points above the 78 km^2 Rangely oil field during the winter of 2001) of 0.302 g m^{-2} d^{-1} was extrapolated for the entire area to calculate a maximum potential leakage rate of 8,600 t CO_2 yr^{-1}. This calculation was based on the assumption that shallow biological production is at its minimum during the winter sampling season, however $\delta^{13}C_{CO2}$ values from these flux chamber measurements indicated that even during this dry and cold period the majority of the CO_2 released at surface was of biological origin, thus resulting in a reduction of the leakage estimate to < 4,300 t CO_2 yr^{-1}. An unspecified statistical analysis of soil gas $\delta^{13}C_{CO2}$ values at 30 cm depth then reduced this value to 3,800 t CO_2 yr^{-1}. A comparison of all 41 measurement points showed a proportion of 10% that were anomalous and an examination of $^{14}C_{CO2}$ from the deep multilevel boreholes indicated the proportion of radiocarbon dead CO_2 in the anomalous area compared to background was 90%. These two observations decreased the leakage estimate to a minimum value of 170 t yr^{-1}. Finally, the extremely high CH_4 values (from 1-10%) measured in some multi-level boreholes and modelling results that define significant methane oxidation rates indicate that observed ancient carbon in CO_2 may not be the direct result of leakage of the injected CO_2, but rather ancient leaking CH_4 that has been oxidised to CO_2. This observation means that the stated minimum value of 170 t yr^{-1} may be substantially too high, and thus the final estimated leakage rate is given as less than 170 t yr^{-1}. This value is approximately 0.01% of the yearly amount of CO_2 being injected into the reservoir, showing the potential of the approach for locating and quantifying low levels of CO_2 leakage at surface.

Although CO_2 isotopes have numerous advantages, the fact that the $\delta^{13}C$ values of CO_2 produced by the burning of fossil fuels are quite similar to some values formed via plant and microbial respiration means that their application may be limited. To address this issue various researchers have proposed the addition of different tracer gases to the CO_2 stream for both monitoring and leakage quantification purposes, including man-made chemicals such as perfluorocarbons and sulphur hexafluoride or natural species such as noble gas isotopes.

Perfluorocarbon tracers (PFTs) have many advantages for CO_2 leakage monitoring, including being soluble in CO_2, non-reactive and mobile, having very low natural concentrations, and being detectable at very low concentrations. The detection limit of PFT is in the parts per quadrillion range, which means that much smaller amounts are needed to be added to the CO_2 when compared with other tracers like SF_6 for the same detection level. A great deal of analytical pre-treatment is needed to attain this detection limit, however, and thus the number of laboratories capable of preparing the adsorption tubes and subsequently doing the analyses are likely to be limited. That said, research and subsequent commercialisation of new techniques has the potential to increase availability and decrease costs.

To date PFTs have been tested at a number of study sites, including the West Pearl Queen depleted oil formation in south-eastern New Mexico (Wells et al. 2007). This study involved the injection of about 2,090 tonnes of CO_2 into the reservoir over a 53 day period, together with slugs of three different PFTs. A total of 500 mL of each liquid PFT was added individually as a 12 hour, constant-injection slug at an eventual concentration of about 4.0 x 10^7 g CO_2/L of tracer. In contrast to standard soil gas sampling, the PFTs were sampled using capillary adsorption tubes (CATs) that were deployed for extended time periods in the soil vadose zone surrounding the injection well. The CATs were suspended in a number of 0.6 to 1.5 m deep holes placed in a radial pattern up to a maximum of 300 m away from the well. After deployment, analysis of the CATs and an estimate of the volume of soil gas to which each unit was exposed permits calculation of the *in situ* PFT concentrations. During monitoring, successive CATs were deployed after each unit was removed for analysis, with background values defined as less than twice the previous measurement and anomalous values defined as more than twice the previous concentration. The monitoring of the first 4 sets of CATs showed NW and SW aligned "hot spot" anomalies within 100 m of the injection well Leakage was observed immediately following injection and continued at a uniform rate until the injected CO_2 was vented to the atmosphere. The fact that the anomalies were observed immediately after injection does raise the question of the actual source of the observed anomalies, either leakage from the deep injection reservoir (as implied by the authors) or an artefact caused by leakage from a surface / near-surface source related to test-site infrastructure. Follow-up tests and transport modelling would have to be conducted to address this issue.

The PFT data was used to quantify leakage from the site as follows. The monitoring matrix was divided into 9 equal sized areas. Within each section, background concentrations were subtracted from points with anomalous values, an average calculated, and this value was projected for the entire section. The values for all sections with observed anomalies were then summed and this PFT leakage rate was converted to a CO_2 leakage rate by multiplying by the injected CO_2/PFT ratio. With this procedure a total CO_2 leakage rate of 2.82 x 10^3 g CO_2/year was calculated for one of the three tracers, which corresponds to 0.014% of the total injected CO_2. The average for all three tracers was, instead, on the order of 0.008%, again showing the potential sensitivity of near-surface gas geochemistry methods. Possible errors in the quantification calculations, as discussed by the authors, include the use of the average tracer concentration rather than a spatially distributed one, enhanced dilution of the tracer in the CO_2 over time during migration in the reservoir compared to the original injected ratio, and the possibility that "chromatographic" separation could have occurred as the tracer is far less water-soluble and reactive than the CO_2.

A monitoring program similar to that used at the West Queen Pearl site was also applied to the Frio CO_2 Sequestration Test Site in Texas (Nance et al. 2005). Here the same three perfluorocarbon tracers were co-injected with CO_2 and a system of groundwater monitoring wells, soil gas monitoring wells, and capillary adsorption tubes were deployed in a radial pattern around the injection well. During this experiment venting of CO_2 during the purge cycle of the downhole sampler released the tracer gases to the atmosphere, which resulted in rapid CAT detection in the soils around the injection wells due to downward migration into the soil and the high sensitivity of these measurements (Hovorka 2006). This aerosol contamination obscured any leakage signal that might have formed subsequently. Efforts were also made to apply PFTs to the ZERT experimental site described above; however the likely saturation of the sorbents for the highest concentrations did not allow for a calculation of the leakage rate using the tracer data (Strazisar et al. 2009).

In addition to man-made tracers, some authors have recommended the use of natural tracers like the noble gases (Nimz and Hudson 2005). Although discussed in terms of monitoring applications, the same mass balance calculations applied to PFTs could be used for these gas species. The advantages of noble gases are that they are chemically inert, environmentally safe, and are persistent and stable in the environment. All noble gases are addressed in this study by comparing their cost, availability, baseline concentrations and analytical sensitivity levels with those of other proposed tracers like ^{14}C of CO_2 and SF_6. In this comparison many noble gases were limited by cost or availability issues; however, three xenon isotopes (^{124}Xe, ^{129}Xe, and ^{136}Xe) were found to be inexpensive and readily available. (Unfortunately, although up-front material costs were addressed in this study, the authors did not address the subsequent analytical costs for the different isotopes). Amongst other advantages, tracer mixtures with different xenon isotopic compositions could be used to label different injections by the same operator or injections made by different corporations working in the same area, with only a single xenon isotope analysis needed to distinguish origin if leakage was observed. As a test of using xenon isotopes for monitoring the authors studied the Mabee CO_2-EOR project in Texas, where natural CO_2 with a unique (although low) noble gas isotope composition has been injected into the oil field since the early 1970's. Analysis of the injected gas in addition to that coming from the production wells showed a clear isotope signature related to the injected CO_2, although mixing with an *in situ* source was also observed. As the concentration in the injected CO_2 was about 2 orders of magnitude lower than that required for ground surface monitoring these types of measurements were not conducted.

In another example of the application of noble gases, Rouchon *et al*. (2011) performed CO_2 flux measurements and analysed soil gas concentrations and isotope compositions on a 32 point grid above the CO_2-EOR reservoir at Buracica, Bahia The fluxes and concentrations were found to be consistent with natural background levels observed for a variety of environmental settings. The authors suggested that noble gas ratios, which are conservative in fluid transport processes and can clearly distinguish between gas sources, would be most effective for detecting any CO_2 leakage. Modelling results indicated that the Ar/Kr and He/Kr ratios would be most useful in discriminating injection-related leaks and reservoir leaks, respectively. The authors emphasised the need for more measurements at varying depths within the soil column to fully characterise the natural background variation.

Numerous additional near surface gas geochemistry surveys have been conducted at other industrial CO_2 storage or test sites, such as Weyburn (Jones and Beaubien 2006), In Salah (Jones et al. 2006) Recopol (van Eijndthoven 2005); Buracica, Bahia (Rouchon *et al*., 2011); and the CO2CRC Otway Project in SE Australia (Schacht *et al*., 2011). However, no evidence of leakage has been observed at these sites and thus no quantification estimates were undertaken.

Strengths and Weaknesses

As shown by the various studies described above, soil gas and gas flux surveys have been examined at great length and in their present form can precisely quantify CO_2 leakage at the ground surface. Advantages include ease of application, non-invasive nature, low costs, applicable in urban and rural areas, flexibility, and improved data interpretation via analysis of additional components (e.g. natural and man-made tracers, isotopes, etc.). Perhaps the greatest advantage of these techniques is the fact that they are able to make *direct* measurements of transfer rates, and thus with judicious selection and design of sampling grids they have the potential to provide the most accurate estimate of CO_2 leakage. Many of these articles describe specific case study examples where leakage rates in the order of 0.01% of yearly injected CO_2 have been recognised and quantified, thereby meeting the low-limit requirement needed for CO_2 storage as a global warming mitigation tool.

That said, these methods must contend with three major issues in order to improve the quality of that estimate and its timeliness. The first is related to the methods' ability to first locate and then subsequently clearly delineate the boundaries of any leakage feature. As described, this will depend on the ratio between leakage and total area, between anomalous versus baseline values, and on the capability of the method to correctly identify a leakage anomaly. Continued work on devising improved sampling strategies and better integration with other techniques (e.g. detailed geological site knowledge, eddy covariance towers, etc.) that may decrease the total survey area hold great promise for future applications. Secondly, the baseline contribution of shallow biological CO_2 flux must be accurately quantified so that it can be removed from the total flux rate measured for the leakage area. To accomplish this, representative baseline CO_2 flux and soil gas measurements must be conducted prior to injection using manual spatial sampling and/or automatic temporal sampling.

The third issue relates to timeliness. Like many methods covered in this report, discontinuous measurements by their very nature are limited to assessing the state of the site at the time of the actual surveys. As a result there is the potential that if a survey is conducted, for example, on a yearly basis and leakage occurs just after a survey, then it may (depending on the characteristics of the leak) not be recognised until the following year. For this reason it is important that soil gas and gas flux surveys be integrated within a wider monitoring program that includes techniques capable of continuous measurements. This could include a network of eddy covariance towers (described in Section 2.2.4 or autonomous soil gas or gas flux monitoring stations. These latter tools could be deployed at high risk sites (such as abandoned wells, or along mapped fault traces) and could be programmed for regular analyses (e.g. every hour) and to alert an office or laboratory of anomalous behaviour. This would thus allow for leakage quantification using soil gas or gas flux geochemistry to take place shortly after recognisable leakage had occurred.

Costs are difficult to quantify, as this will depend greatly on the sampling strategy and analytical approach taken. Regarding sampling, a single technician can make about 100 CO_2 flux measurements or about 50 plus soil gas flux measurements in a day, although these numbers will depend on terrain and the distance between the points. Field sampling costs will thus depend on the total number of samples that are needed to cover the area. Fixed equipment costs, on the other hand, will be in the order of 5,000 to 10,000 Euros for a CO_2 flux detector, 5,000 Euros for an infrared field analyser for soil gas CO_2, and less than 5,000 Euros for soil gas sampling equipment and sample containers.

Laboratory costs for the analysis of collected soil gas samples will depend greatly on the species being studied. For example one laboratory charges about 50 Euros per sample for the analysis of permanent gases (CO_2, N_2, O_2 and Ar) and C1 to C5 hydrocarbon gases. Regarding isotope analyses, a single $\delta^{13}C$ analysis can be on the order of 30 Euros whereas a ^{14}C analysis can range from 150 to 500 Euros.

Finally, more specialised analyses, such as those for perfluorocarbons, would also be expected to be relatively expensive due to the limited number of properly equipped laboratories and due to the high quality control needed in creation and analysis of the adsorption samplers. That said, new technologies developed to take advantage of commercial applications (e.g. Praxair Seeper Trace) has the potential to decrease these costs. Due to this very wide range of analytical costs, many authors collect a large number of samples for routine, low-cost analysis to minimise and focus the collection and analysis of more specialised analysers for tracer gases or isotopes.

2.3.2 Shallow groundwater

CO_2 is a natural constituent of groundwater. Depending on the pH and chemical composition of the groundwater, CO_2 will form various chemical species. The concentrations of these species can be measured with established hydrochemical methods reasonably accurately. The quantification of leakage requires the integration of groundwater volumes and fluxes multiplied by the concentrations of carbon species that originate from the CO_2 ascending from the storage reservoir.

When CO_2 escaping from a storage complex enters into a shallow (freshwater) aquifer, it will dissolve in the water. Depending on the gas to water ratio, it can dissolve either completely or partially. When the amount of CO_2 exceeds the amount that can dissolve in the surrounding water, a free, mobile gas phase may remain within the aquifer. The solubility of CO_2 in groundwater is proportional to pressure and inversely proportional to the ambient temperature. At typical pressure and temperature gradients in aquifers, the solubility will increase rapidly with depth (Figure 33). With time, the groundwater will release excess and dissolved CO_2 until it is in equilibrium with the CO_2 partial pressure of the unsaturated zone or the atmosphere when it discharges. Thus, much of the dissolved CO_2 in shallow unconfined aquifers could be considered as climate related leakage.

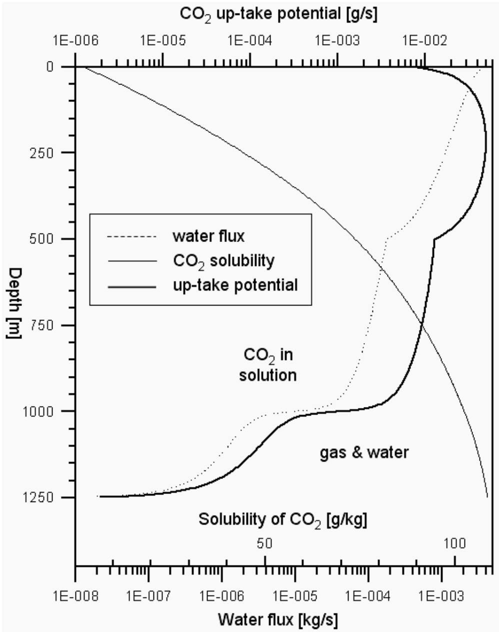


Figure 33. CO_2 up-take potential as a function of topography-driven groundwater flux in a three-layer homogeneous overburden of a CO_2 storage (after May, 2002).

Scenarios considered

The potential for quantifying leakage and the associated uncertainty depend very much on the local hydrogeological conditions. Two basic scenarios that are likely to be representative for many sites in humid climates are discussed:

A. Localised or dispersed leakage of CO_2 through a fractured hard rock overburden in hilly terrain.
B. Localised or dispersed ascent of CO_2 through caprocks in lowlands with alluvial aquifers at the surface.

In Scenario A, there usually are local, shallow groundwater flow systems discharging in valleys, often following faults in the bedrocks. CO_2 or CO_2-bearing waters are likely to ascend along faults and discharge in valleys (Tóth, 1962). Shallow flow systems, overlying deep regional flow systems with low groundwater velocities will 'sweep' fluids towards the discharge areas in the valleys (May *et al*., 1996; May, 2002; Figure 34). Thus, in such regions with natural CO_2 sources (e.g. Massif Central, Apennines or Rhenish Massif) the springs are usually rather confined spots.

Scenario B is frequently found in regions with glacial sediments, young sedimentary basins or meandering river beds. Sand and gravel aquifers contain plenty of groundwater that can take up ascending CO_2, mix with and dilute formation waters and transport it with the groundwater flow, following regional gradients. Groundwater/CO_2 phase ratios may be high. Thus, extensive plumes of CO_2-bearing species may develop downstream of a leak, without visible surface features. At low water to gas ratios, a free gas phase may decouple from the sub-horizontal groundwater flow and ascend sub-vertically to the surface.

Quantification of Leakage

Four steps are necessary to quantify leakage:

1. Detection of leakage
2. Sampling of phases and analysing concentrations of carbon species
3. Volume or flux measurements
4. Calculation of leakage mass or flux

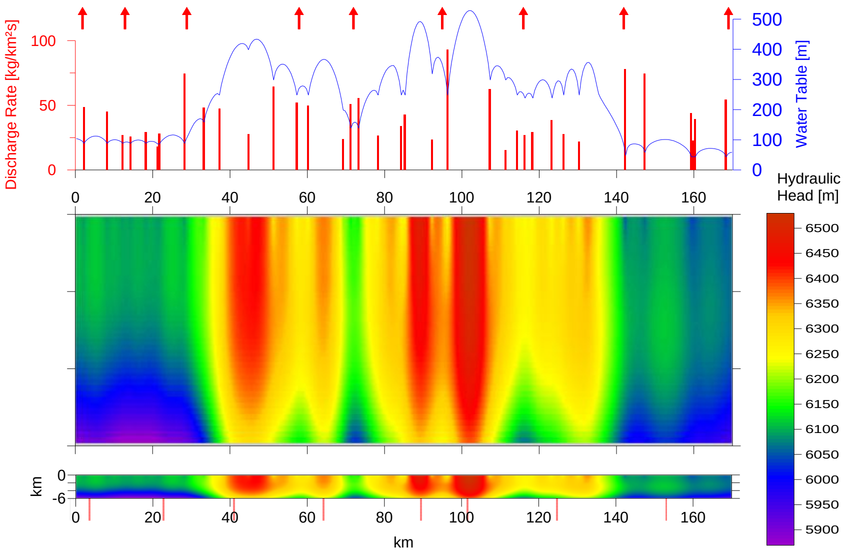


Figure 34. Numerical simulation of topography-driven groundwater flow in a hilly terrain. Superposition of shallow and deep regional flow systems. Top: groundwater table, discharge rates and discharge of deep flow systems (arrows). Middle: hydraulic head, vertical exaggeration 10 x. Bottom: Hydraulic heads and watersheds between deep regional flow systems (dashed lines), (modified after May *et al*., 1996).

Figure 35. Natural Seepage of 100 g of dissolved CO_2 per day (36.5 tons per millennium) at Wallenborn, Eifel, Germany (courtesy of F. May).

Each of these steps is associated with its own uncertainties, which will be discussed on the basis of the two scenarios defined above:

Detection of leakage

In Scenario A, the leakage of CO_2 or CO_2-bearing water is a conspicuous feature that should be discovered easily in inhabited areas. Depending on the water/CO_2 flow rates, the ascending gas may dissolve or exsolve repeatedly in a conduit along a fault. Generally the decreasing pressure will result in the formation of a free gas phase close to the Earth’s surface. The results are sparkling waters or gas bubbles in springs, streams, drainage ditches or on flooded ground.

Iron is a ubiquitous element in the subsurface that is likely to be mobilized and transported in CO_2-bearing water. The oxidation of dissolved iron at the surface results in visible rusty deposits of iron oxy-hydrates in and around seeps and springs (Figure 35). These deposits help identifying sites for sampling and further geochemical investigation of the origin of these deposits. However, such localised emissions may easily pass through a network of groundwater observation wells, as they only cause a small footprint (Figure 36).

CO_2 is likely to be transported in, or together with saline formation water. The electrical conductivity of water is a helpful parameter that can be measured rapidly and easily in groundwater discharges, which can indicate leakage of fluids from depth. Another indirect indicator for the presence of CO_2 is the pH of the groundwater.

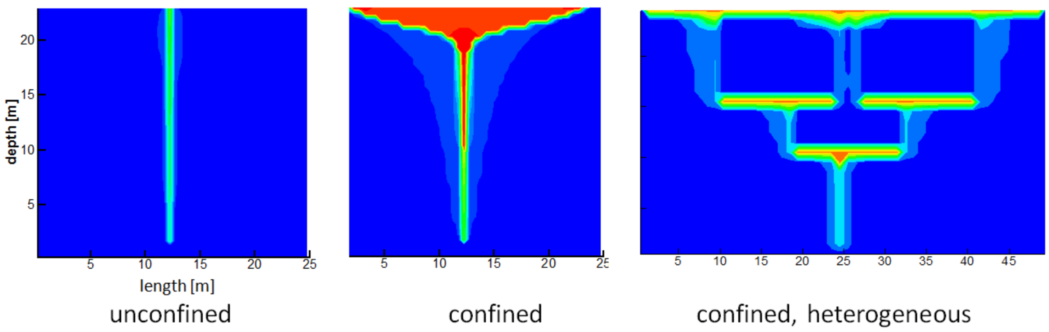


Figure 36. Computed footprint of CO_2 leakage into an unconfined and confined homogeneous aquifer and a confined, heterogeneous aquifer model (modified after Köber 2011).

In Scenario B, leakage is less obvious. Often such aquifers discharge along the beds into lowland rivers, so that natural springs are scarce. Geochemical anomalies may be detected in well bores. In order to map the concentrations and calculate leakage fluxes, many wells may be needed. The greater the heterogeneity of the aquifers are, the larger are the resulting footprints of the geochemical anomalies in confined aquifers can be. Less monitoring wells may be sufficient to detect CO_2 in heterogeneous aquifers. However the amplitude of the anomalies decreases. More wells are necessary to quantify fluxes, compared to more homogeneous aquifers (Figure 36). Anomalies are most likely to be detected in urban and industrial areas with groundwater monitoring networks, or in rural areas with groundwater extraction for agricultural irrigation. Alternatively, airborne electromagnetics can help to map the distribution of CO_2 or saline groundwater (Siemon *et al*., 2004). Transient electromagnetic surveys (TEM), can map electrical resistivity down to a few hundred meters of depth. The electrical conductivity of aquifers changes when CO_2 (decrease) or saline fluids (increase) replace fresh groundwater. Sky-TEM measurements have been used for baseline mapping at the pilot storage site in the Altmark (Köber *et al*. 2011).

With time, the footprint of a CO_2 leak increases in confined aquifers as well as in unconfined aquifers, when dissolved CO_2 is carried away with the groundwater flow. The enlargement of the geochemical footprint depends not only on the heterogeneity of the aquifer, but also on the groundwater flow and the CO_2 leakage rate. At low leakage rates, more time may pass before a CO_2 plume may be detected in a shallow aquifer. An indication of the order of magnitude of the number of wells that may be needed to identify an anomaly in a network of observation wells as a function of the duration of the leakage event can be obtained from simulations using simplified aquifer models. Figure x2 illustrates the results of a leakage simulations into a homogeneous confined aquifer without groundwater flow (Figure 37).

Sampling of phases and analyses

Some natural springs have considerable fluxes of a free CO_2-dominated gas phase. Avoiding dilution of the gas-phase by atmospheric air is sometimes difficult. Corrections for dilution may be applied later, based on the N_2, Ar or O_2 concentrations of the sampled gas.

Ascending waters often contain considerable quantities of excess CO_2, which has not yet degassed due to the pressure drop in the springs conduit. If pressurised sampling is possible, the waters may be degassed and analysed under controlled conditions in laboratories. The amount of excess CO_2 can also be determined volumetrically, albeit slightly less precisely, in the field. Groundwater sampling procedures are described in DIN 38402-13 (DIN, 1985), and other regulations (such as those of DVWK[1] or DVGW[2] in Germany), which should be followed in order to avoid degassing of water during sampling.

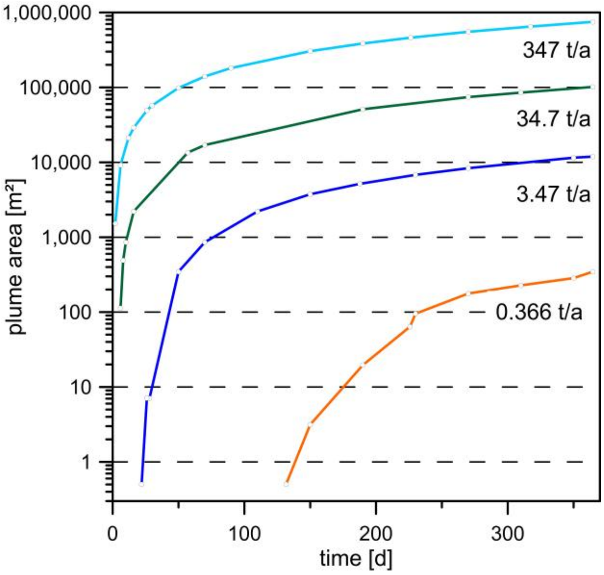


Figure 37. Calculated area covered by a gaseous CO2 Plume in a homogeneous shallow aquifer. Data kindly provided by Köber *et al*. (2011).

Depending on the water composition, CO_2 may form numerous dissolved complex species. As the equilibria between these species are quite sensitive to pressure and/or temperature changes, the concentrations of bicarbonate species are generally determined by titration immediately after sampling and filtration of the water. Samples can also be stabilised by the addition of nitric acid and analysed in laboratories. Standard hydrochemical procedures are defined in norms such as DIN 38404-5 for pH, DIN EN 27888 C8 for electrical conductivity, DIN EN ISO 9963-1 for alkalinity, DEV (Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung) D8 for CO_2 and HCO_3^-.

The relative accuracy of hydrochemical analyses is in the order of 1-3 %. Detection limits for CO_2 are 2 mg/l and 3 mg/l for HCO_3^-. This would mean that in an aquifer of 10 m thickness and 20 % porosity, 4 tonnes of CO_2 could be detected, even if they would (hypothetiocal assumed) dissolve homogeneously in an area of one square kilometre.

The accuracy of the analyses is less dependent on systematic errors related to laboratory methods than on the representativeness of the groundwater sample for the geochemical anomaly. The representativeness of a single sample, especially if taken from a natural source, for the surrounding groundwater volume or flow is generally unknown and should be constrained by obtaining several samples. Thus, sampling should be repeated both spatially and temporally. This can be done manually by taking grab samples or through automated groundwater observation wells.

While in case A sampling points can often be determined by obvious leakage spots or according to the topography and fault related drainage patterns, sampling of shallow aquifers and positioning of monitoring wells is less straightforward. The analogy of aquifer contamination from industrial point sources may provide an example of the number of wells that may be needed to map CO_2 concentrations in shallow aquifers. Within the framework of the KORA research programme (http://www.natural-attenuation.de/content.php), mapping of virtual contaminant plumes in aquifers has been undertaken through simulation (Figure 38).

[1] Deutscher Verband für Wasserwirtschaft und Kulturbau (DWWK) – incorporated in 2000 in the German Association for water management, wastewater and waste

[2] Deutsche Verein des Gas- und Wasserfaches (DVGW) - German Association for Gas and Water

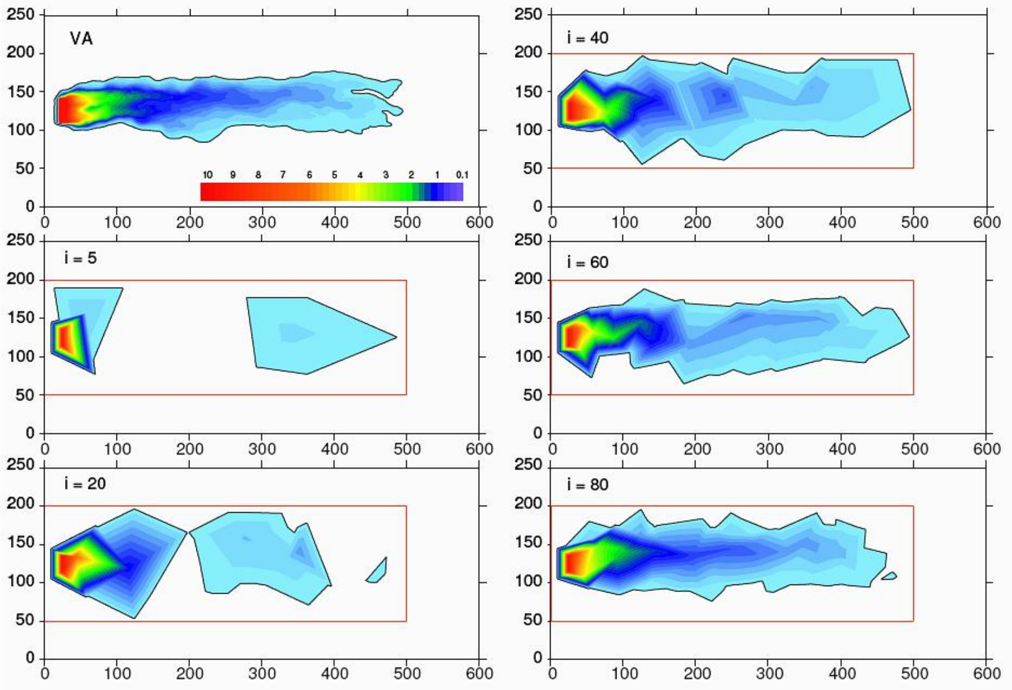


Figure 38. Mapping of a virtual hydrochemical anomaly (VA) in a contaminant plume extending downstream of a small linear source. The best fitting results of 50 well pattern realisations with 5 to 80 wells each are compared with the reference concentration distribution (VA) (Schäfer *et al*., 2008, Hornbruch *et al*., 2009).

Based on a modelled virtual concentration map (VA), the average error range obtained by 50 different well patterns has been shown to decrease exponentially with the number of wells in these patterns. The range of results obtained by different well patterns also decreases with greater numbers of wells. Even large numbers of wells will not significantly reduce the errors (Figure 39).

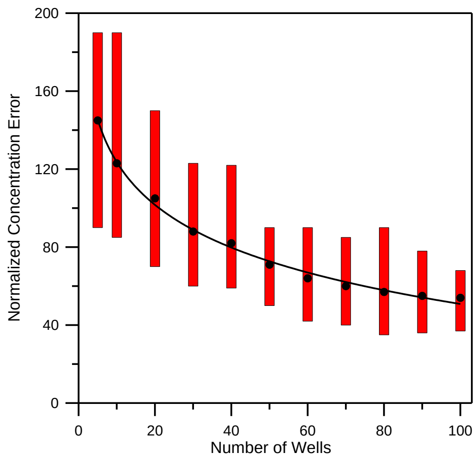


Figure 39. Results of the virtual contaminant plume mapping (after Schäfer *et al*., 2008).

The main uncertainties arise from the extrapolation of measurements near to the source, where concentration gradients are steep. The reasonable optimum number of wells has to be evaluated specifically for each site, on the basis of aquifer models and reactive groundwater flow simulations. The greater the heterogeneity of the aquifer, the more wells are required in order to reduce the uncertainty of the CO_2 quantification. Some real cases of groundwater contamination may provide examples of the number of wells that may be needed to map plumes of dissolved CO_2 or HCO_3^- in shallow aquifers (Table 5; Figure 40).

Table 5. Examples of contaminant plume mapping in alluvial aquifers at industrial sites. Data from Frey *et al*., 2005. Uncertainty estimates after Grandel and Dahmke (2006).

Site	*Aquifer Thickness [m]*	*Area of investigation [km³]*	*Numbers of wells*	*Wells per square kilometre*	*Estimated Uncertainty*
Hannover	10 – 20	1.5	60	40	middle
Perleberg	< 24	1	100	100	middle
Karlsruhe	15 – 20	3	40	13	middle-high
Düsseldorf	10 – 24	2.4	350	145	middle
Rosengarten	> 230	0.05	25	500	middle
Frankental	10 – 15	1.2	35	30	middle
Stuttgart	6	0.09	58	640	unknown
Leuna	4 – 10	2.5	104	42	unknown
Spandau	10 – 12	0.15	50	330	unknown
Schwedt	15 – 20	13.75	604	44	unknown
Castrop-Rauxel	7	0.75	96	130	unknown
Wülknitz	< 30	0.2	48	240	unknown

Figure 40. Soil gas concentrations measured in groundwater wells at the contaminated site of the former gas works in Stuttgart (after Eiswirth *et al*., 1998).

Volume or flux measurements

In Scenario A, the capacity of shallow, fractured reservoirs to take up CO_2 is limited and leakage pathways will probably soon facilitate a continuous flux of CO_2 into the atmosphere. In such situations it is reasonable to quantify leakage in terms of flux of dissolved carbon species and gas flux directly into the atmosphere.

At natural CO_2 seeps, the area of free gas is usually equivalent to the groundwater discharge area. Much of the gas flux is concentrated in the springs or wells, as gas and water that are transported partially in a single phase but also in two phase flow often follow common flow paths. The gas stream can be collected and measured using funnels, vessels or gas-meters. A number of examples are illustrated by Quattrochi *et al*., (2009). May (2002) measured CO_2 gas fluxes in wells and springs in the Westeifel volcanic field and calculated average relative errors of 6.2% for the CO_2 gas fluxes. Although most of the gas flux in springs can be captured and metered, some of the CO_2 may degas from ascending groundwater and escape as soil gas in the vicinity of springs.

The flux of CO_2-bearing springs can be measured volumetrically using vessels, weirs, or tracer dilution technologies. The average relative error for the determination of dissolved carbon species in the Westeifel springs is estimated to be 20%. These natural systems have probably established quasi-stationary conditions and the sources have been well captured since Roman times. In the case of a leaking CO_2 storage formation, the flow conditions may be more transient and sources have not been captured by wells, so that the uncertainty is probably larger. If CO_2-bearing groundwater discharges directly into rivers, the river/groundwater flux ratios can be too large to result in detectable and measurable changes of the river water composition, even if the CO_2 degasses from the river bed.

In Scenario B, shallow aquifers may take up large volumes of CO_2-bearing water by downstream transportation and accommodate excess CO_2 by mixing and dilution with under-saturated fresh groundwater. Thus, in this case, extensive geochemical anomalies, or CO_2 plumes within the aquifers may be observed. Hence, it may be appropriate to quantify leakage in terms of the absolute amounts of carbon species within the aquifer that have escaped from the deep reservoir.

The water volume can be calculated by multiplying aquifer porosity with the CO_2-bearing aquifer volume. The determination of the affected aquifer volume involves measurements at a sufficiently large number of wells. Porosity values are usually derived from grain size distributions of sediment samples or via pumping tests performed at groundwater observation wells. Hence, the representativeness of the measurements will be related to the number of wells used for sampling and testing. While concentrations vary over several orders of magnitude, the porosity of alluvial sediments and also of (clastic rocks) is less variable, usually within a range of between 10 to 30%. However the geometry of the associated pore network is more variable and results in permeability distributions which often span 3 orders of magnitude. This heterogeneity causes fingering of the CO_2 plume, so that the estimates of the CO_2-affected aquifer volumes become uncertain. This uncertainty is related to the sedimentary depositional environment, very much dependant on the heterogeneity, and is site specific. The use of efficiency factors, analogous to the factors used to estimate the CO_2 storage capacity of formations (Gorecki *et al*., 2009) is one approach to take into account this discontinuous distribution of the CO_2-charged aquifer volumes. Gorecki *et al*. (2009) calculated generic efficiency factors for fluvial sandstone scenarios in the order of 5%. As shallow flow systems are rather dynamic, sampling of concentrations needs to be done in a short time period (relative to groundwater velocities) and repeated as plume migrates, or changes in size.

Due to the shallow depth and accessibility of the aquifers considered, test sites with a reasonable number of closely spaced wells may also be installed in order to derive site specific, geostatistically derived aquifer parameters that would allow error calculations for real leakages.

1. Calculation of leakage mass or leakage flux

Besides the problems associated with detecting and measuring accurate concentrations, fluxes and volumes, additional uncertainties arise from the spatial integration of the point measurements. Baseline values are needed in order to define concentration anomalies.

Uniform baseline values or thresholds will not be sufficient. Due to natural variability and dilution effects, overlapping of concentration ranges between local unaffected waters and CO_2-bearing groundwater is likely. An example of overlapping concentration ranges may be found in the natural CO_2 springs in the Westeifel field (Figure 41). Additional information, such as isotope analyses or tracers may be needed to distinguish and quantify carbon species of natural and anthropogenic origin.

Fluxes are also subject to temporal variations of various frequencies, caused by various influencing factors. The example of two springs from the Westeifel field is illustrated in Figure 42. Although the concentrations of the springs did not significantly change, the discharge and thus the carbon fluxes varied considerably.

As a consequence of the seasonal variations, baseline monitoring of springs should cover at least one or two years.

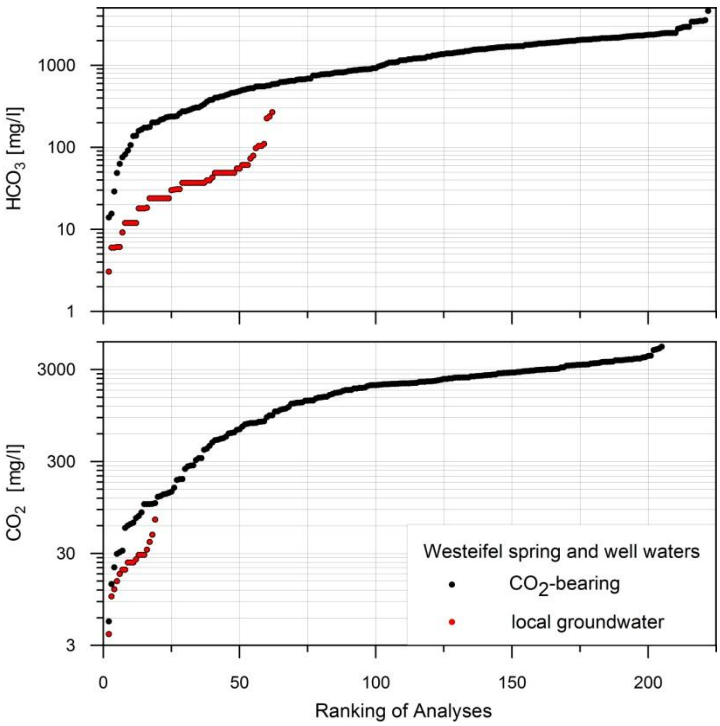


Figure 41. Overlapping concentration ranges of dissolved bicarbonate and CO_2 bicarbonate in spring and well waters that have interacted with ascending magmatic CO_2 and normal local groundwater (after May, 2002).

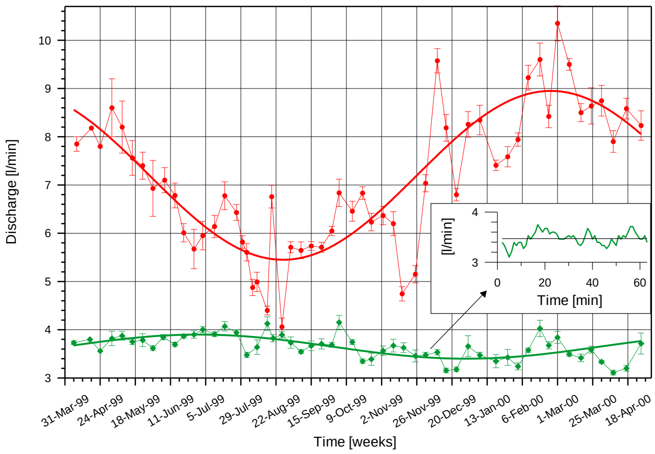


Figure 42. Seasonal trends, standard deviation, high frequency and weekly variation of two springs discharging CO_2 rich water from fractured aquifers in the Westeifel field (after May, 2002).

The interpolation and integration of geochemical point measurements, e.g. soil gas CO_2-fluxes in the vicinity of CO_2-sources, is usually carried out with various numerical tools and rarely based on geostatistical consideration of the spatial variability of the data. The choice of the integration algorithm is typically a default software setting or a selection made by the scientist, often chosen on the basis of aesthetic rather than technical considerations. However, due to orders of magnitude difference between flux or concentration values within an anomaly and the uncertain extent of the anomalies concerned, the choice of algorithm may result in considerable differences in CO_2 flux estimated from identical measurements. In particular, if surface conditions allow a few sampling points only, the errors may be large (Figure 43).

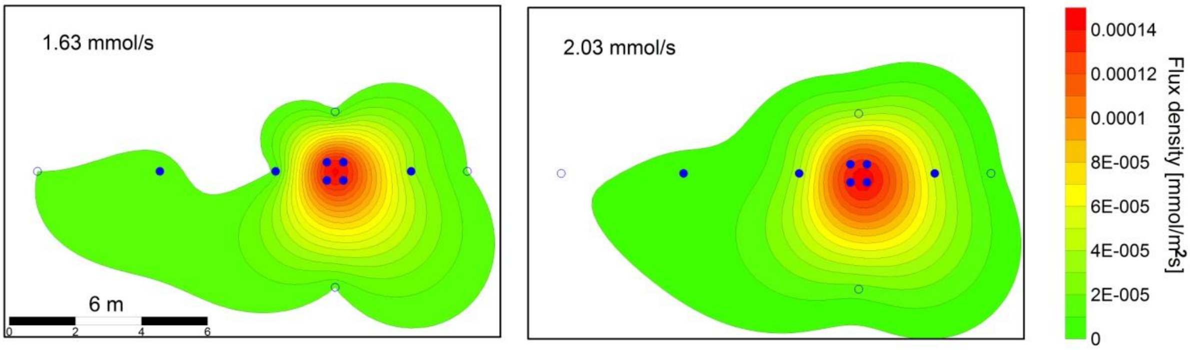


Figure 43. Total CO_2 flux estimation from point measurements of flux density at a Westeifel Spring. The calculated total flux values differ by 20% depending on the choice of integration algorithm (courtesy of BGR).

Field examples

Hydrogeological monitoring has been performed at the IEA-GHG Weyburn-Midale CO_2 storage project for a period of more than 10 years (Rostron and Whittaker, 2011). A shallow water-well monitoring and sampling program was initiated in 2000 to establish background water levels and groundwater chemistry.

The results from Weyburn illustrate some of the practical problems involved in conducting hydrogeological monitoring at a field in operation and subject to the limitations of research programmes:

- Monitoring wells have not been installed for purpose, at sites defined by a risk analysis. Instead, existing domestic wells in the area have been used.
- Groundwater samples of around 60, mostly domestic wells have been obtained. As the size of the field is about 180 km², the average number of about 0.33 wells per km² is much lower than in the examples shown above. As the background water chemistry in the area have proved to be highly variable, the selected wells may not represent the entire groundwater in an adequate manner (see Figure 39). A high level of uncertainty is likely and the chance of missing leakage is high.
- The use of wells has been changed, and sampling has been carried out by different teams and research institutions. Thus, multiple sampling has been possible at 20 sites only. Changes in water chemistry over time have been observed at 20% of the wells that have a time series of measurements. These have been attributed to near surface operations, such as agriculture, in the shallow wells. Thus, about 16 time series remain that can be used for the identification of possible groundwater impacts caused by the deep EOR operations.
- Seven sampling programs have been undertaken (twice in 2000; twice in 2001; once in 2002, 2006 and 2009). The sampling times reflect the challenges of co-ordination and integration of multiple hydrogeological research programs. It is difficult to take into account seasonal or inter-annual variations within a hydrological year from the irregular time series.

According to Rostron and Whittaker (2011), none of the wells has shown a significant long-term increase in CO_2. Even if there is no indication for leakage of CO_2, the hydrogeological monitoring results cannot be regarded as a proof that there is or was no leakage. The lesson to be learned from Weyburn is to carefully develop a comprehensive, site specific monitoring plan, including a thorough base-line definition, for the entire duration of the storage project.

Suitability of hydrochemical monitoring for quantifying CO2 leakage into shallow aquifers

Hydrochemical observation of shallow aquifers can be applied to any storage type, concept and structure. In rural areas there may be few groundwater observation wells unless shallow aquifers are used for irrigation. In urban and industrialised areas, natural groundwater discharge may be restricted due to sealed surfaces and channelised drainage. However, larger cities and industrial complexes often have networks of groundwater monitoring wells in operation. Full areal coverage of extensive storage sites is unlikely to be possible. Thus, monitoring wells should be concentrated in smaller areas, such as in the vicinity of pilot projects, or in the region of potential leakage pathways such as wells or faults. Baseline monitoring is essential for the detection or quantification of subsequent leakage. Leakage monitoring of shallow aquifers should be intensified. Post-closure monitoring, without prior indication of leakage, may be included with little additional effort into general groundwater observation schemes.

In summary, as CO_2 or brines should not affect shallow aquifers during normal operation, hydrochemical monitoring is not a suitable tool for storage site operation and reservoir management. Hydrochemical methods can detect small fluxes of CO_2 discharging at the surface. The quantification of CO_2 leakage into shallow groundwater is subject to a number of uncertainties. Dense sampling grids and repeated sampling are required in order to reduce the quantification uncertainties. The accuracy of quantification will probably be insufficient for emission certificate accounting. Groundwater monitoring is needed for health and environmental purposes in situations where CO_2 and/or brine migrate along wells or faults into shallow aquifers, resulting in dispersed or localised leakage. Fractured overburden and local topography related flow systems promote discharge from small local sites (metres to decametres). Higher flow rates can be detected more easily and facilitate more accurate determinations than diffuse leakage of small flow rates.

2.3.3 Soil geochemistry

Mineralogical studies of the clay-rich soils of the natural CO_2 leakage site at Latera, Italy, have indicated variations in soil geochemistry associated with increased acidity and anoxic conditions (Beaubien *et al.*, 2008; Pettinelli *et al.*, 2008). In particular, the results showed an increase in the concentration of K-feldspar with an associated decrease in albite, and a decline in the occurrence of oxides such as MgO, CaO, Fe_2O_3 and Mn_3O_4) in the region of the gas vent compared with the surrounding soils.

According to Stephens and Hering (2002; 2004), who reported differences in geochemical composition for volcanic soils with elevated CO_2 levels at Mammoth Mountain, California, the dissolution of minerals in soils is not directly affected by CO_2, but by the reduction in pH due to the increase in organic acids. It was noted that dissolution rates were more affected by pH for the spodosols (leached acidic soils) of Lead Mountain, as estimated by Asolekar *et al.* (1991), than for the volcanic soils of Mammoth Mountain. Golubev *et al.* (2005) concluded from laboratory experiments on a range of silicate minerals that the direct impact of CO_2 dissolved in soil solutions would be negligible. Therefore, any increase in CO_2 levels in soils would have to cause a decrease in pH before changes in the mineralogical composition could be observed. Changes in pH would result from degradation of organic matter.

In a study of the surface area over the enhanced oil recovery project at Rangely, Colorado, Pickles and Cover (2004) used hyperspectral remote sensing data (see Section 2.7.1) to identify and map soil minerals such as kaolinite and montmorillonite (clays), pyrite and haematite. The potential therefore exists to use remote sensing images to detect and monitor changes in soil mineralogy related to leakage of CO_2 from subsurface storage reservoirs by comparing successive images. Thermodynamic modelling of the changes in mineralogy would be required to derive a vague estimate of the amount of CO_2 that the soil was exposed to. The applicability of this method would depend on the minerals present in the soil and whether the reaction rates governing the changes in the soil geochemistry are fast enough. The studies undertaken at Latera and Mammoth Mountain were undertaken for gas seepage sites that have emitted CO_2 for at least 75 and 10 years respectively (Beaubien *et al.*, 2008; Stephens and Hering, 2002).

A mineralogical analysis of soils subjected to a controlled CO_2 release was undertaken as part of the ASGARD (Artificial Soil Gassing And Response Detection) project at the University of Nottingham (West *et al.*, 2009). Although pH was found to decrease in the A horizon (organic upper layer) of the gassed plots, no significant changes in the geochemical characteristics of the soil in comparison with control sites were observed after an exposure period of 19 weeks. This suggests that soil geochemistry analyses related to mineralogy may be unsuitable for CO_2 leakage monitoring due to the slow reaction rates involved. However, a number of researchers have used hyperspectral remote sensing data to estimate soil pH (e.g. Dermatte *et al.*, 2007; Qu *et al.*, 2009), which may offer an alternative solution.

2.4 Ecosystems monitoring methods

2.4.1 Marine ecosystems monitoring

The marine ecosystems may be divided roughly into pelagic and benthic ecosystems, which again may be subdivided into several vertical strata corresponding to the main water characteristics, and into water masses like brackish water, coastal water and oceanic water. Pelagic systems may be split into epipelagic (shallow) and mesopelagic (deeper) strata.

Deep water usually represents a relatively homogenous environment with respect to temperature and salinity. Pelagic ecosystems in deeper parts are usually reasonably rich in species and biomass, and typical numerical dominants among the larger zooplankton forms may be pelagic shrimps, euphausids, mysids and chaetognaths. Other important zooplankton organisms in the deep water during certain seasons include copepods. Several of the pelagic species perform substantial diurnal or seasonal vertical migration, even into the upper advective layers.

Near-seabed tools or features for detecting/monitoring leaks for subsequent quantification will concern impacts on microbiological communities, invertebrates, and marine vertebrates.

Seeps of CO_2 gas through the shallow sediments can dissolve both in pore water and in the overlying seawater. Dissolved CO_2 in seawater makes it denser, so it will tend to accumulate in layers or pools at the seabed (Figure 44). In this case, it is likely to cause some local environmental damage both in the sediments and in the water above, as exposure times will be significantly longer than the timescales of minutes related to the rising of gas bubbles to the surface. Such pools, and even the plumes, may be subjects both for detection and quantification of leaks, provided proper scaling and parameterisation.

For offshore operations risk analyses (oil/gas) the initial leak rate is often taken as 5 times the production rate, and such a factor may be used as a baseline for estimating leaks during CO_2 injection. After sealing of the reservoir, leaks in practice can take on any order of magnitude, depending on the cap rock geology, and flow path. Small seeps, which are most likely to take place, are difficult to model or quantify for taking into account in risk assessments.

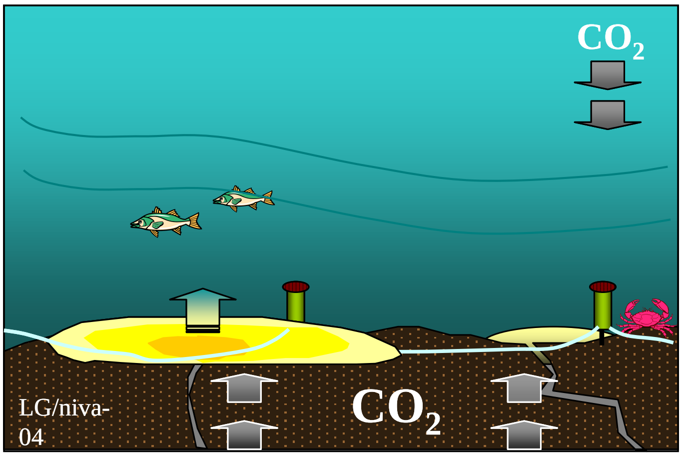


Figure 44. Schematic of how CO_2 from small leaks can accumulate as pools of CO_2-enriched seawater on the seabed (dissolved CO_2 increases the density of seawater). A monitoring network of sensors may possibly detect such accumulation, and data may be used for quantification. The ocean will also receive gradually more CO_2 from the atmosphere via natural influx.

The benthic boundary layer is the layer nearest to the seabed, including the upper parts of the sediments (Figure 45). This is a layer with significant vertical exchange of water and other matter, in both directions. The zone has high importance for the biology and chemistry of the local environment, and physical and chemical/biological processes in this layer will determine much of the behaviour and fate of CO_2 escaping from below. Physically, this layer is the primary location for dissipation of hydrodynamic energy and exchange of heat, solutes and particulates between the water and the sediments. Remineralisation of settled organic material, debris and shells is vigorous in this layer. A wide variety of benthic animals, plants and microorganisms live there, and intensive transport of solutes and (re)suspended particles takes place, causing high chemical and biological reactivity.

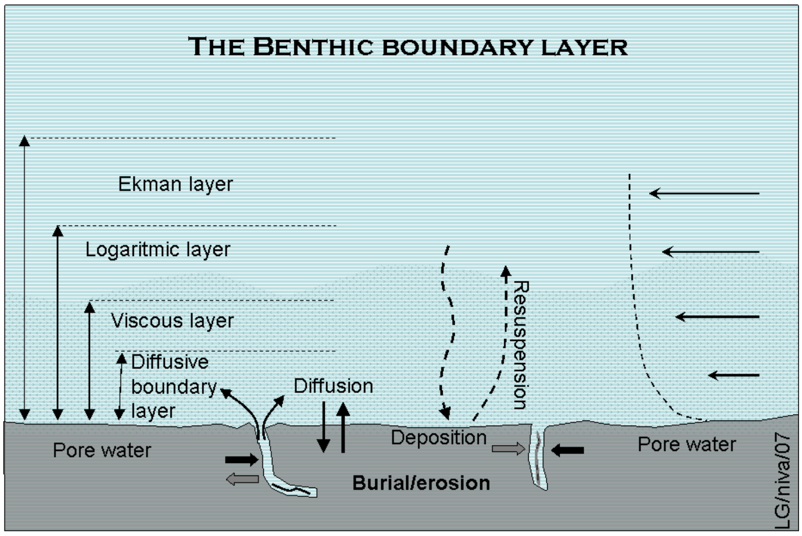


Figure 45. Physical sub-layers within the benthic boundary layer with some transfer paths of matter indicated. The Ekman layer is where the rotation of the earth and bottom friction affect the flow structure. The logarithmic layer represents a typical velocity profile, and the viscous sub-layer is where effects of molecular viscosity are important. In the diffusive boundary layer transfer of matter is controlled by molecular diffusion.

In the deep sea, the thickness of the benthic boundary layer is normally equivalent to the Ekman scale, which is the ratio (u_*/f) between the friction velocity, u_*, and the Coriolis parameter, f. It can reach several tens of metres or more. In shallow waters it may be better defined by the elevation at which the flow matches the potential flow, and may contain the whole water column if stratification is weak. For computational hydrodynamics the logarithmic layer is often referred to, where the flow velocity is assumed to follow a logarithmic decay towards the bottom, in agreement with what is often observed. This can be a few metres thick or more. Down in the centimetre-scale, friction dominates over eddy mixing and may create a viscous sub-layer over the sediment surface. Very close to the sediments a water film on the sub-millimetre scale exists where molecular diffusion exceeds eddy diffusion (Figure 45). This is of most relevance where there are dense, nearly non-penetrable sediments. Assessments and models for benthic layer processes may include some or all of these layers.

In porous sands the hydrodynamic forces may reach down into the sediment and define the Brinkman layer which also is of (sub)-millimetre scale in thickness. In porous sediments water flow and surface topography induces lateral pressure gradients that drive appreciable advective flows through the upper centimetres to decimetres. This has large importance for solute and particle fluxes across the bulk sediment-water interface.

Biological and physical activities promote mixing within the sediment and across the interface. Some bacteria, microalgae and invertebrates act contrarily by producing exopolymeric substances which tend to clog up the pore spaces and seal the sediment surface, thereby slowing the exchange across it.

The sediment macrofauna in a typical offshore location will contain all major benthic animal groups (e.g. polychaets, molluscs, crustaceans and echinoderms) with a high number of species and diversity of the major groups, as the offshore regions represent a diverse habitat in food resources and grain size composition which may support many species. Typical predatory fish near the bottom can be ling (*Molva molva*) and tusk (*Brosme brosme*), which are harvested commercially.

Elevated CO_2 levels near the seabed and in ambient water will affect the physiology of fish and other animals. Present knowledge ranges from effects on acid-base regulation to influence on respiration, excretion, energy turn over, and mode of metabolism. The main properties and biological impacts of CO_2 in water may be summarized in the following points:

- Compared to all other gases, CO_2 is very soluble in water (at 0^oC, CO_2 is 35 times more soluble than O_2, and is still 25 times more soluble at 30^oC).
- CO_2 affects pH, so that release of CO_2 into seawater results in increased concentrations of H^+ (lowered pH).
- The fact that most natural water has little CO_2 content makes CO_2 levels in fish blood low compared to air-breathers.
- A fish cannot regulate its respiratory system by changes in CO_2 level (as air-breathers do), but must sense O_2 changes instead.
- CO_2 may be excreted as HCO_3^- (from the kidney) as well as molecular CO_2 (from the gills), depending on the environmental pH and carbonate levels. This is a way of regulating blood pH (physiochemical buffering).

The effect on the physiology of marine fish species of increased concentrations of CO_2 in seawater, and the associated effects of increased HCO_3^- and pH, is dependent not only on the magnitude of those increased concentrations, but also on the tolerance of the particular marine animal.

Information is limited on the tolerance and physiological responses of most species. However, fish can be grouped in two broad categories, having different taxonomies and ecologies (Pörtner and Reipschläger, 1996):

- Pelagic fishes, which inhabit the water column. These can be further divided into species inhabiting inshore waters and off-shore oceanic waters. This group is adapted to constantly low CO_2 concentrations, and is expected to have a low tolerance to fluctuations in CO_2 and pH.
- Demersal (benthic) fish, which as adults spend their lives on, or close to, the sea bed, and can tolerate variations in CO_2 resulting from varying oxygen consumption and anaerobic metabolism of bacteria and fauna.

The fauna of open offshore waters will be adapted to a high-oxygen environment, except for in-fauna in the sediments. One may therefore expect fauna of rather limited CO_2 tolerance in these waters, compared to organisms living in low-oxygen water and near interfaces to anoxic layers. They may also be exposed to low water temperatures and thus have a reduced metabolic rate. However, long term exposure of high CO_2 concentrations may lead to sub-lethal or even lethal effects even on tolerant species, making such organisms suitable to act as possible indicators of CO_2 leaks.

Where CO_2 and other gases escape naturally through the seabed and into the seawater, the bottom fauna will over time adapt to the conditions of the source. This is observed at anomalous sites, such as black smokers and hot vents, where extreme forms of fauna may have formed. At other (shallower) locations, the fauna can remain more or less undisturbed outside a limited radius from the source. Closer to it, a change in characteristics occurs, with possibly bacteria alone existing near the centre of the emission. Such bacterial colonies are often clearly visible.

Field examples

There is only sparse information on the application of seabed CO_2 monitoring technologies on biota; most will be from experimental work on sensitivity and impacts and extrapolations from other cases. It is expected that even a moderate rise in seawater CO_2 may be critical for the most sensitive species, making those act as early warning “canaries” of CO_2 leaks. Although the number of species with acute sensitivity may be small, even tolerant species may react. Long term, sub-lethal effects at the ecosystem, population and individual levels are likely in the case of a long-lasting leak.

Several free vehicles have been constructed over the past decades, initially, mostly for short-term and stationary deployment. Mobile "rovers" have been developed that can operate on the seafloor for weeks or months, while repeatedly doing measurements and manipulations. These move from place to place in order to cover a variety of sediment surfaces and to escape the disturbance caused by their own presence and experiments. Furthermore, long-term time-lapse video recordings of the deep-sea floor over the seasons have provided new and stunning pictures of the highly dynamic environment of the sediment-water interface (Bourdeau and Jørgensen, 2000).

Threshold values represent a useful tool for the evaluation of the biological impacts from a certain ambient parameter on a certain species or test organism. The threshold value may be defined as mortality rate (response) related to a certain dose (concentration and exposure time), or to the appearance of specific physiological, behavioural or physical disorders that can be related to the impact parameter. Figure 46 shows an example of exposure data for marine organisms to reduced pH levels.

Similar experiments for the study and determination of tolerance levels of CO_2 exposure should be planned and designed to exclude disturbances from other ambient parameters like temperature, O_2 etc., which should be kept constant.

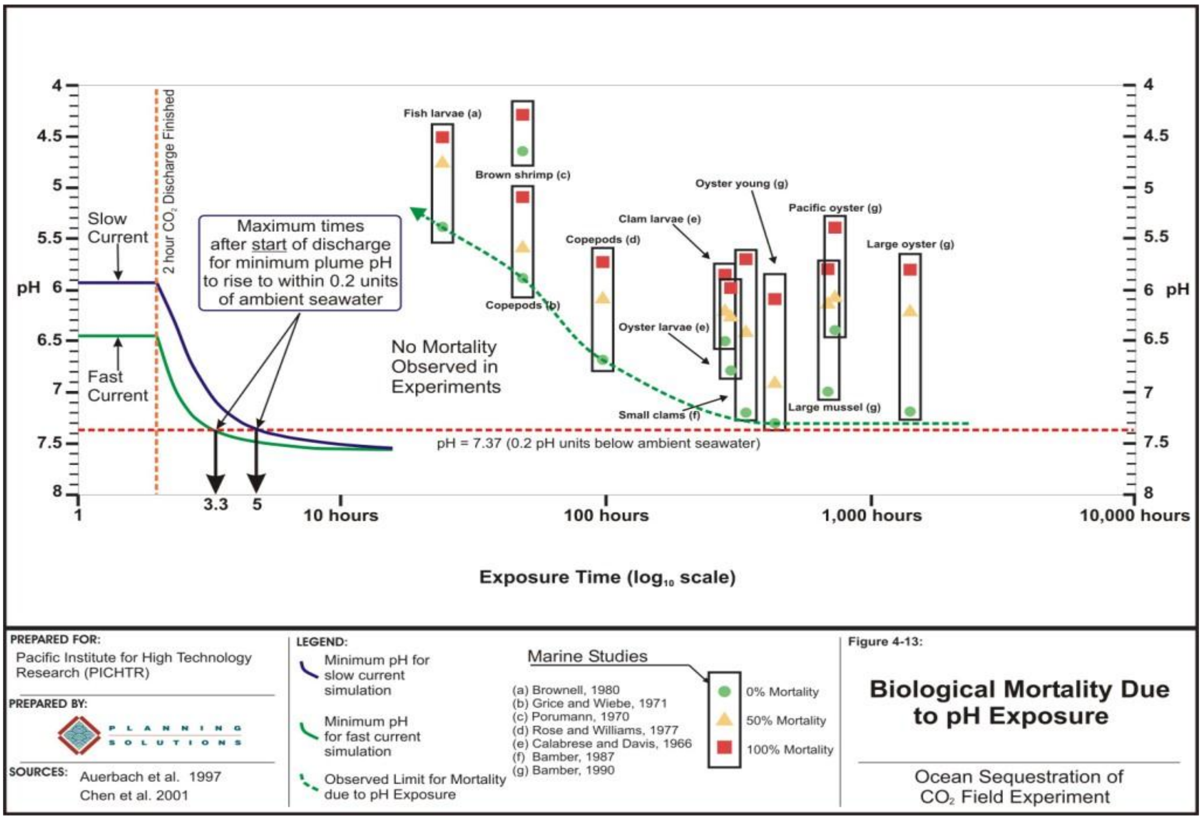


Figure 46. A compilation of results for exposure tests on marine organisms due to reduced pH (not necessarily due to added CO_2.) The figure was drafted in 2000 by PICHTR, Hawaii and MIT in connection with pre-studies for a CO_2 injection experiment.

Strengths and weaknesses

Effects of CO_2 on biota are mediated through lowering of pH (Magnesen and Wahl, 1993), which may have a toxic effect on the fauna or a hampering effect on the production of calcareous structures. The tolerance will vary from one species to another. If CO_2 that leaks causes effects on the benthic layer community level (e.g. changes in tropic dynamics, shift in relative abundance of feeding types, changes in diversity and dominance patterns), such results may be transferable to mesopelagic communities. Such disturbances may be quite easily detected, and with proper parameterisation leak quantification may be possible as well.

2.4.2 Terrestrial ecosystems monitoring

Ecosystem-based monitoring can be employed to qualitatively detect and monitor leakage into near surface systems. This technique can be used for terrestrial, freshwater as well as marine ecosystems. Ideally, ecosystem modelling is combined with a soil gas survey of the area assumed to be affected by leakage from deep reservoirs.

Generally, the monitoring of terrestrial ecosystems combines a detailed analysis of the non-mobile live form, i.e. plants, meiofauna and the microbial populations inhabiting the soil. This includes the identification of the (bio-) diversity of organisms present together with other parameters, including microbial activities and geochemical parameters as indicators for the health status of an ecosystem. The plant and microbial populations determined at a suspected leak are then compared with control sites representing the background to be expected without disturbances.

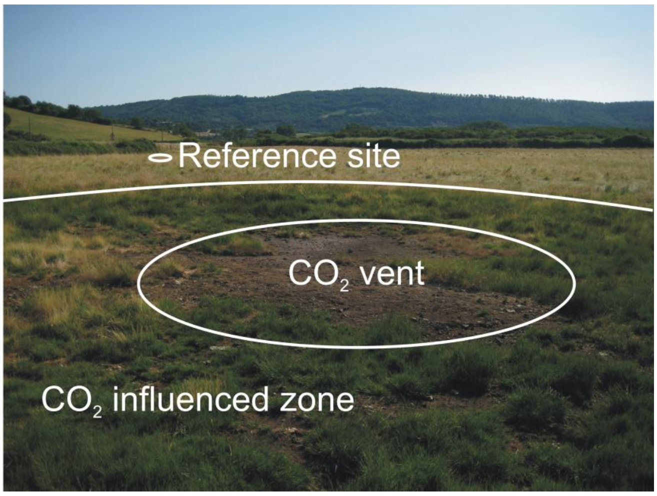


Figure 47. Study site at Latera. In the middle the area with highest CO_2 emissions is clearly visible as spot lacking all vegetation, towards the outside vegetation changes first to acid-tolerant species and then returns to normal agricultural plants (after Oppermann *et al*., 2010).

Field examples

Latera

To better understand the potential impact of a leakage event, a detailed geochemical and biological study was conducted during two different seasons on a naturally occurring gas vent located within a Mediterranean pasture ecosystem (Latera geothermal field, central Italy; Figure 47). Results from botanical, soil gas, microbiological and gas flux surveys show that a significant impact is only observed in a few metres wide centre of the vent, where CO_2 flux rates are extremely high. In this ‘‘vent core’’ there is no vegetation, pH is low, and small changes are observed in mineralogy and bulk chemistry (Beaubien *et al*., 2008). In addition, microbial activities and populations are regulated in this interval by near-anoxic conditions, and by elevated soil gas CO_2 and trace reduced gases (CH_4, H_2S, and H_2). An approximately 20 m wide area surrounding the core forms a transition zone, over which there is a gradual decrease in CO_2 concentrations, a rapid decrease in CO_2 fluxes, and the absence of reactive gas species. In this transition zone acid-tolerant grasses dominate near the vent core, but these are progressively replaced by clover and a greater plant diversity moving away from the vent centre. Physical parameters (e.g. pH, bulk chemistry, mineralogy) and microbial systems also gradually return to background values across this transition zone. Results indicate that, even at this anomalous high-flux site (2,000 – 3,000 g m^{-2} d^{-2}), the effects of the gas vent are spatially limited and that the ecosystem appears to have adapted to the different conditions through species substitution or adaptation (for further information see Beaubien *et al*., 2008; Oppermann *et al*., 2010).

In Salah CO_2 storage site
A botanical and microbiological survey was undertaken at the In Salah Gas project in 2009 (Jones *et al*., 2011). The survey area was focused on the three injection wells, with samples taken along transects at a spacing of 100 m to 200 m. Priority was given to vegetated sites. At each sample location a 0.5 x 0.5 m quadrate survey was performed on a 2.5 m cross, and the percentage area covered by vegetation within each quadrate was estimated. Soil samples were collected using an auger up to a depth of 50 cm and analysed on site to evaluate microbial mass by adenosine tri-phosphate assay using a Deltatox analyser, with subsequent laboratory analyses undertaken through epifluorescence microscopy.

The survey revealed flora typical of a desert environment, with vegetation generally sparse but more abundant in the dry wadi channels. A number of angiosperm plants were found, which gives rise to the potential for CO_2-sensitivity, as observed in similar communities in temperate climates (Beaubien *et al*., 2008; West *et al*., 2009). Several of the microbial samples were found be devoid of detectable life. The authors suggested that it would be informative to undertake a similar survey after a period of rain to ascertain the microbiological background and change in flora under these conditions.

Strengths and weaknesses

The monitoring of terrestrial and freshwater ecosystems can provide information to identify leaks from deep subsurface reservoirs into surface systems at a relatively low cost. The sites affected by high CO_2 concentrations are typically visible by bare eye and thus easy to detect, even from a distance or low-flying aircrafts.

However, to sufficiently describe the health status of an affected ecosystem a detailed and comprehensive assessment of its biodiversity, including plants, meio- and microfauna, has to be conducted. This is time consuming and requires substantial expertise by the investigators.

Quantification

Because relatively small amounts of leaking CO_2 can have visible effects, terrestrial ecosystem studies may offer a potential mechanism for the detection of leakage from a reservoir. Contaminants within the leaking gas may lead to distinct patterns of ecosystem effects. With regard to quantification, ecosystem monitoring is not applicable, since above certain levels further damage will not be observed. However, since these methods would support detection of leaking locations and constitute part of a monitoring portfolio, they are also briefly described here.

2.5 Remote sensing methods

2.5.1 Airborne and satellite spectral imaging

Spectral (or optical) remote sensing detection and monitoring methods for terrestrial CO_2 emissions can be classified as direct or indirect. Most current applications are indirect, and are largely based on changes in the vegetative cover (Chadwick *et al*., 2009). Thermal imaging may also potentially detect leakage if a measurable temperature anomaly is associated with the leakage. However, high resolution airborne hyperspectral scanners may detect CO_2 (and CH_4) directly using absorption features that lie within their wavelength range.

Airborne sensors can collect hyperspectral, multispectral, Light Detection and Ranging (LIDAR) data and digital photographic data (orthophotos). The spatial resolution of the images acquired depends on the height of the flight path, but may be as precise as 1 m for the hyperspectral and multispectral data and in the order of decimetres for the LIDAR and photographic data. Multispectral sensors sample the Electro Magnetic (EM) spectrum over a wide range of wavelengths in discrete regions (bands), and therefore have low spectral resolution. Higher spectral resolution is achieved with hyperspectral sensors, and this can allow more definitive information on the composition and physical properties of various targets. LIDAR uses the two-way travel time of an emitted near infrared pulse to measure distance.

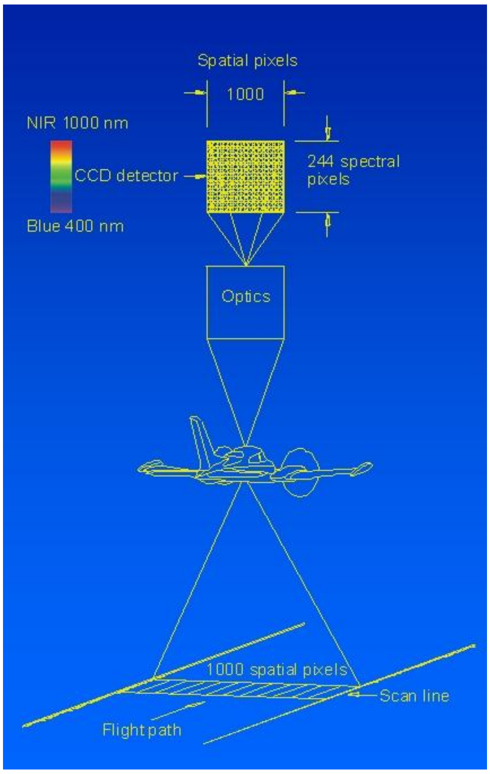


Figure 48. A hyperspectral system mounted on board of a plane during a survey.

A hyperspectral system is generally mounted on board helicopters or planes and scans the ground in the pushbroom mode (Figure 48). The light reflected by the targets on the ground is directed first to a lens, then to two prisms, where it is decomposed and redirected to a Charge Coupled Device (CCD) array; this array is bi-dimensional, so it is possible to read both the spatial and the spectral components of every pixel on the ground. Hyperspectral sensors are usually able to work in the Visible and Near Infrared (NIR) regions (from 400 to 1,000 nm). The spectrum acquired is divided into bands, which can be specified (in number and width) according to the project's goals. Some sensors can acquire up to 244 bands.

Spaceborne remote sensing varies in spatial, temporal and spectral resolution. Satellite remote sensing systems with a low spatial resolution (>15 m) could also potentially be useful for the detection and quantification of CO_2 leakage from subsurface storage reservoirs. Unfortunately, due to technical restraints associated with the sensor hardware, such as the number of array detectors for a given Full Width Half Maximum (FWHM) bandwidth, a fine spatial resolution is associated with a coarse spectral signature or vice versa. This means that hyperspectral data can only be obtained for relatively coarse spatial resolutions. Medium spatial resolution satellites collecting multispectral data include ASTER, LANDSAT 7 and CBERS-2. ASTER has a temporal resolution of 16 days and measures bands in the visible and NIR region with a spatial resolution of 15 m, Shortwave Infrared (SWIR) region with a spatial resolution of 30 m and Thermal Infrared (TIR) with a spatial resolution of 90 m. LANDSAT-7 carries the Enhanced Thematic Mapper Plus (ETM+), and collects multispectral images with a spatial, temporal and spectral resolution similar to those of ASTER. The CBERS-2 satellite, born from a partnership between China and Brazil, carries high resolution cameras, an infrared multispectral scanner and a wide field imager, and collects data with spatial resolutions varying between 20 and 260 m. The hyperspectral Hyperion scanner on board the EO-1 satellite has a spatial resolution of 30 m and a temporal resolution of 16 days.

A hyperspectral satellite system dedicated to atmospheric CO_2 retrievals (OCO-1) was launched by NASA in February 2009, but unfortunately it failed to reach orbit. However, there are plans to launch a replacement, OCO-2, in February 2013.

Detection of vegetation stress

Repeated remote sensing surveys over storage reservoirs could potentially detect CO_2 leakage through changes in vegetation cover due to the increased levels of polluting gases, either in the atmosphere or in the soil. Changes to the vegetation are usually assessed using the Normalised Difference Vegetation Index (NDVI). This essentially exploits the fact that live green plants absorb solar radiation in the photosynthetically active radiation region of the EM spectrum, i.e. the visible Red region between 550 and 750 nm (Figure 49), and also scatter solar radiation in the NIR region. It is calculated using:

$$NDVI = \frac{NIR - RED}{NIR + RED}$$

where *NIR* and *RED* are the spectral reflectance measurements acquired in the near infrared and red spectral regions respectively. The index varies between -1.0 and 1.0, with mid to high positive values for healthy vegetation, low positive values for sparsely vegetated soils and very low positive and negative values for water bodies. The use of the NDVI may be compromised by:

- Atmospheric effects, whereby moisture and aerosols can significantly affect the measurements.
- Clouds, which can contaminate the measurements if they are not large enough to be filtered out, or can create shadows which lead to misinterpretations of the NDVI values.
- Soil effects, whereby changes can be due to them becoming darker when wet.
- Anisotropic effects, whereby the value of the NDVI may be affected by the anisotropy of the target and the angle of illumination and observation at the time of measurement.
- Spectral effects, which may be important if different sensors with their own characteristics are used in successive surveys.

Alternative methods which aim to account for these limitations include the Perpendicular Vegetation Index (Richardson and Wiegand, 1977), the Soil-Adjusted Vegetation Index (Huete, 1988), and the Atmospherically Resistant Vegetation Index (Kaufman and Tanre, 1992). Inoue *et al*. (2008) found that Normalised Difference Spectral Indices were more effective than the NDVI in assessing plant productivity and ecosystem CO_2 exchange. Additional indices that may be sensitive to high CO_2 concentration in the soil include (Lakkaraju *et al*., 2010): the high carotenoid to chlorophyll ratio indicated by the Structural Independent Pigment Index (SIPI); the Chlorophyll Normalised Vegetation Index (Cl NVI); the Pigment Specific Simple Ratio (PSSR); and the Normalised difference First Derivative Index (NFDI).

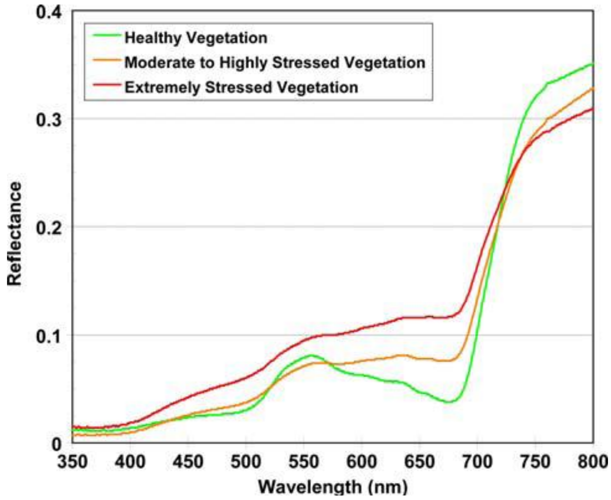


Figure 49. The general spectral response of vegetation under three different conditions (after Male *et al*., 2010).

Pickles and Cover (2004) conducted a study into hyperspectral geobotanical remote sensing for CO_2 storage monitoring over an enhanced oil recovery (EOR) field at Rangely, Colorado. The sensor used was a HYMAP™ hyperspectral scanner, which provided 126 bands contiguously from the reflective solar region of 450 to 2500 nm, with discrete FWHM bandwidths between 15-20 nm. The atmospheric water vapour regions were omitted. The spatial resolution of the acquired images was 3 m, and the Signal to Noise Ratio (SNR) was greater than 500:1. The survey was done across 18 flight lines, which were subsequently georectified and mosaicked together. ENVI software was used to process the images, in conjunction with photos, topographic maps, and Digital Elevation Models (DEM). The first step was to acquire a detailed map of the area to be used as a baseline against which to compare future images. A NDVI map covering the area was derived, whereby the values obtained for each pixel represented both the amount of vegetation in the pixel area and its healthiness. A subsequent flight was undertaken after rain, and the resulting images showed higher values of NDVI, although the general pattern of vegetation did not change. The authors concluded that the observing deviations from this distribution could potentially detect the effects of increased concentrations of CO_2 in the soil.

Keith *et al*. (2009), Rouse *et al*. (2010), and Male *et al*. (2010) used field-based hyperspectral spectrometric data that were collected over the Zero Emission Research Technology (ZERT) site located in Bozeman, Montana, U.S.A., where controlled shallow subsurface CO_2 releases are made. The ZERT is a partnership involving DOE laboratories (Los Alamos National Laboratory, Lawrence Berkeley National Laboratory, National Energy Technology Laboratory, Lawrence Livermore National Laboratory, and Pacific Northwest National Laboratory) as well as universities (Montana State and West Virginia University). One of the research goals is to assess near-surface detection techniques and models, including studying leakage effects on the local vegetation (Spangler *et al*., 2009).
Rather than employing the NDVI, one of the methods uses the Random Forest classifier (Breiman, 2001) to establish a positive correlation between the plant health index and the distance from the release site (Keith *et al*., 2009). The classifier finds the characteristics of the spectrum that give the best separation among the training data classes. It was indirectly used to provide a measure related to the changes in the reflectance spectra of alfalfa plants when exposed to elevated CO_2 levels. Furthermore, through regression analysis a relationship between this measure and the distance of the plant from the CO_2 emission source was established. However, it is unclear how the method would perform if the images were obtained from an airborne sensor.

Another study involved fitting a regression model between the reflectances in the Red, Green and NIR regions of the EM spectrum, and the NDVI (Rouse *et al*., 2010). This analysis showed that NDVI alone is best able to statistically separate stressed vegetation regions. The NDVI graphs revealed a decrease in overall plant health over the CO_2 hot spots, while it was also observed that the level of response to the injected CO_2 was dependent on plant species.

Male *et al*. (2010) applied the supervised Spectral Angle Mapping (SAM) technique using the hyperspectral plant signatures from the ZERT site. It was found that that the minimum amount of soil CO_2 concentration that induces vegetation stress within 4 days lies between 4% and 8% CO_2 by volume. A good correlation was also found between the stressed vegetation classification map and the logarithmic soil CO_2 flux map of the ZERT site (Lewicki *et al*., 2010). Most importantly, it was also suggested that relevant vegetation stresses could be distinguished from those caused by other possible factors, such as extreme heat or cold, insect infestation, water logging, bacterial diseases, soil oxygen depletion, nutrient deficiencies, or acidic soil (Lichtenthaler, 1998), by looking at their spatial distribution, namely circular or elliptical patterns.

Another airborne scanner that can be used to detect and monitor CO_2 leakage is the AISA Eagle 1K hyperspectral pushbroom scanner, manufactured by Specim. This operates in the NIR region, and can acquire up to 244 bands. Flight height has to be set in order to guarantee a pixel spacing of 1 to 2 m on the ground, enough to perform a detailed analysis. To monitor leakages in a CO_2 storage scenario, flights have to be performed before CO_2 injection and after, periodically (every 3 months should be enough); in this way it is possible to monitor CO_2 seepages, changes occurring in the whole area (morphological aspects, effects on vegetation), and eventually to plan technical activities. Hyperspectral data need to be subjected to radiometric correction, geocoded and then corrected for atmospheric effects, in order to obtain the reflectance value. The data are then classified, analysed and all the datasets are periodically compared. Supervised classification techniques can be used; training areas are chosen according to experimental data acquired on the ground (field campaigns – data coming from other methodologies, such as ground spectrometers or satellite data). Detailed analysis can be conducted on the spectral signature of vegetation, in order to locate potential CO_2 leakages and to indirectly quantify them (the more CO_2 escapes, the more stressed the vegetation is, or the larger the affected area). Some dedicated vegetation indexes can be calculated (e.g. NDVI) in order to widely monitor vegetation health during the injection and the storage phases. Bateson *et al*. (2008) and Govindan *et al*. (2011a) have developed and tested methodologies for detecting CO_2 leakage using data acquired by this sensor for a study site containing natural gas vents in Latera, Italy.

The Latera site contains high flux (~1,000 to 3,500 g m^{-2} d^{-1}) vents with visible impacts on the local vegetation (Beaubien *et al*., 2008), and lower flux vents which are less obvious. Two daytime airborne surveys were undertaken, with multispectral (ATM and CASI) and LIDAR data collected in May 2005, and the AISA Eagle 1K sensor, digital photography and LIDAR data collected in October 2005. The survey area is indicated by the yellow box in Figure 50(left). The multi- and hyperspectral images had spatial resolutions of 2.5 and 2 m respectively. The ATM (Airborne Thematic Mapper) data included 11 bands, covering the visible, NIR and TIR parts of the EM spectrum, while the CASI (Compact Airborne Spectrographic Imager) was configured to measure 15 bands from the visible to the infrared regions. The hyperspectral images contained 63 bands between the visible and NIR regions. Later, in July 2007, another survey was conducted using the hyperspectral sensor acquiring data at 1 m resolution. All the datasets were pre-processed to correct for atmospheric and geometric effects.

Bateson *et al*. (2008) used the spectral datasets to calculate several indices related to plants stress, of which the NDVI was found to distinguish best between healthy and stressed vegetation. Manmade objects and bare soil areas, which gave low NDVI values, were identified and eliminated using the aerial photographs. The ATM thermal image results picked out haloes corresponding to the largest vents, where either the emitted gas is warmer than its surroundings, or the sparsely vegetated or bare soil warms up more than the surrounding healthy vegetation. The LIDAR response, which is sensitive to surface roughness and moisture content, also showed anomalies related to reduced vegetative cover. After determining the locations of probable gas vents using ground based measurements (Figure 50), the detection ability of the different sensors and methods was compared. It was found that the October NDVI and the orthophoto results gave the highest success rates (around 47% and 42%) respectively, with the number of correct detections offset by false positives. Considering field measurement data, the authors estimated that a rough threshold of around 60 g m^{-2} d^{-1} would be the minimum CO_2 flux rate that could be detected using the spectral remote sensing methods.

A further drawback of vegetation indices, such as the NDVI, that further contributes to false positives is the requirement for the leakage to occur in a vegetated area, as opposed to a ploughed field (for example). Seasonal and diurnal variations, as well as agricultural practices, add further complications. It was recommended that thermal data should be acquired during winter and at night in order to avoid thermal anomalies being masked due to the sun's energy, while orthophoto and hyperspectral images should be obtained around noon to minimise the effect of shadows. False positives may also arise from factors which are unrelated to CO_2 seepage causing plant stress, as pointed out earlier. Moreover, Keith *et al*. (2009) note that any leaking CO_2 might initially cause fertilisation and stimulate growth. However, it has also been reported that tree kill can occur if the mole fraction of CO_2 gas in the soil exceeds 0.3 (Farrar *et al*., 1999). It was also acknowledged that the methodology of Bateson *et al*. (2008) involved a potentially prohibitive amount of manual interpretation.

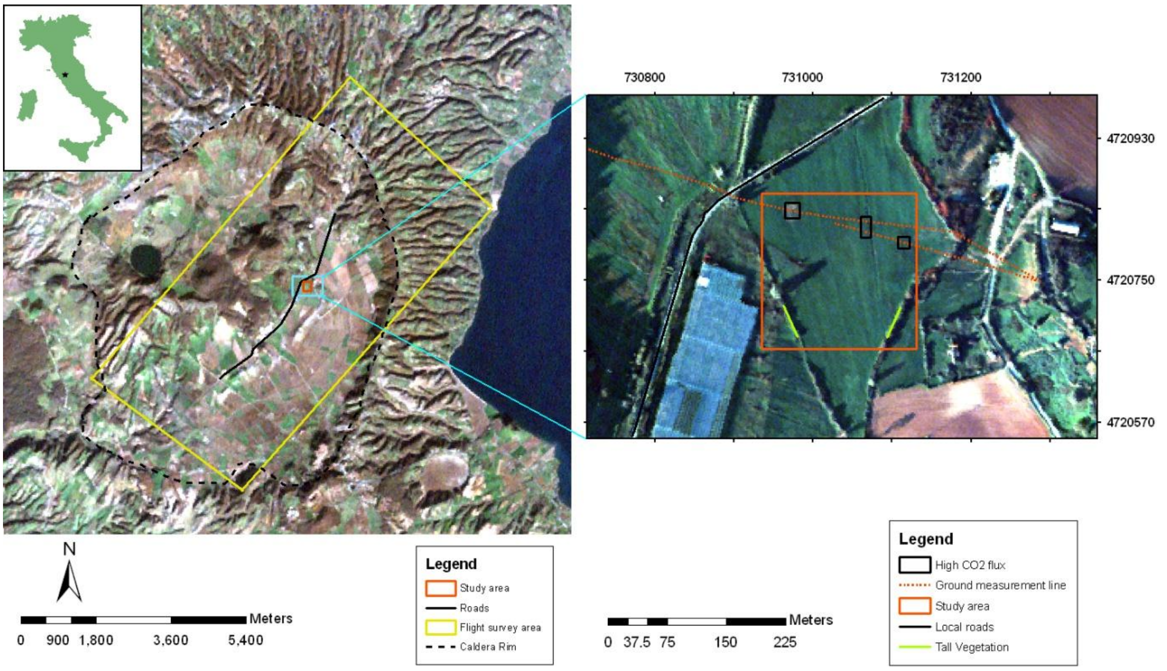


Figure 50. Left: the region of Later in Italy, shown with the flight survey area and the study region. Right: the study area containing the ground measurement line and gas vents, along with local features such as vegetation and road networks (after Govindan *et al.*, 2011a).

Research at Imperial College London is focused on developing an unsupervised technique for identifying CO_2 leakages using the hyperspectral and multispectral datasets acquired over Latera in 2005 and 2007 (Govindan *et al.*, 2011a). The methodology is based on using geostatistical techniques to filter out regional trends and spatially correlated variation in the area prior to anomaly detection. The dimensionality of the datasets is reduced using Independent Component Analysis |(ICA) (Jutten and Herault, 1991), and outlier detection is subsequently performed using parametric Reed-Xiaoli (RX) anomaly detection (Reed and Yu, 1990). Information fusion is then applied, exploiting the following features: stressed vegetation exhibits the phenomenon of red edge shift towards lower wavelengths (Horler *et al.*, 1983); and mineral alterations in the soil, such as red bleaching, occur due to low pH reducing Fe^{3+} to Fe^{2+} (van der Meer, 2002). These features have been confirmed by field data (Beaubien *et al.*, 2008).

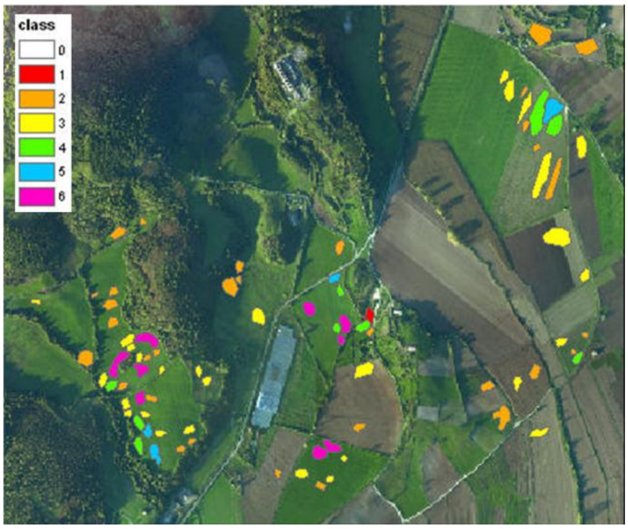


Figure 51. Map of possible CO_2 leakages in the Latera caldera (After Bateson *et al.*, 2008). The polygon colours correspond to the number of datasets (methods) that showed an anomaly within that polygon.

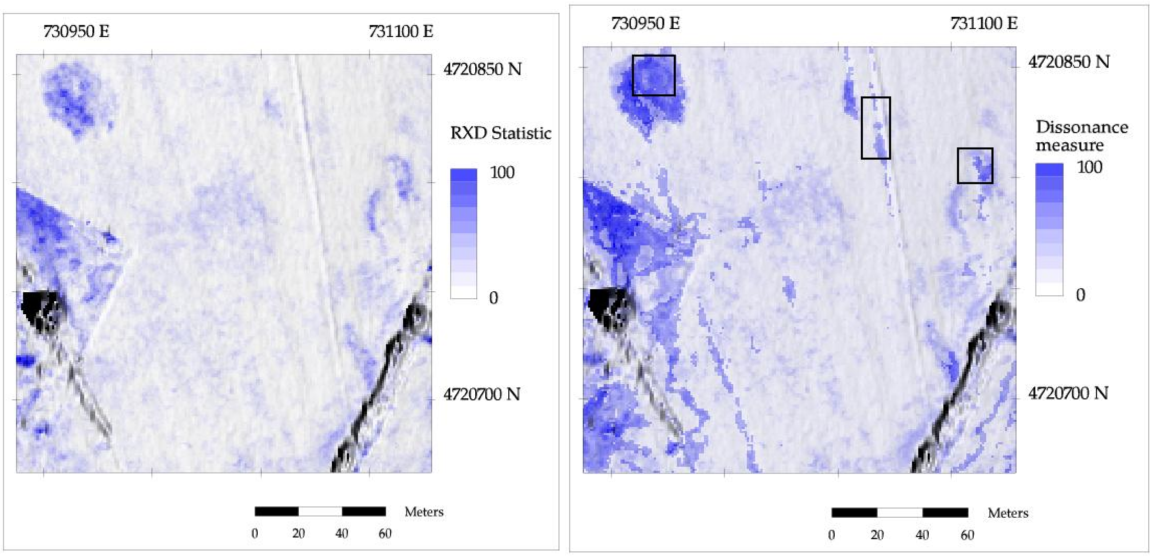


Figure 52. CO_2 leakage detection results obtained after (left): applying 1st order polynomial de-trend and kriging texture filter with terrain information as external drift, and (right): applying Dempster-Shafer theory of evidence combination (after Govindan *et al.*, 2011a).

After assuming that there exists a class of pixels in the red to near infrared regions that relate to CO_2 seepage, fuzzy c-means clustering analysis (Bezdek *et al.*, 1984) is applied to the 2005 and 2007 datasets. The results are combined and the joint fuzzy values for each pixel are used as evidence for the Dempster-Shafer (DS) theory of evidence combination (Dempster, 1967; Shafer, 1976) to enhance the geostatistical results (Figure 52left). A final measure of dissonance (entropy of plausibility) is then generated to provide a per-pixel measure of confidence for CO_2 seepage (Figure 52right). To date, the methodology has proved able to detect the main gas vents at Latera, although the problem of false positives needs to be given more attention. Current research at Imperial College is also aimed at assessing whether the methodology described above can be used for remote sensing images with coarser spatial resolutions, such as those acquired via satellite (Govindan *et al.*, 2011b). This would enable more frequent and regular monitoring without the need for specially designated airborne acquisitions.

The University of Nottingham's ongoing ASGARD (Artificial Soil Gassing And Response Detection) project (http://www.nottingham.ac.uk/geography/asgard) has also established a soil gassing facility, similar to the ZERT project, which simulates elevated soil CO_2 concentrations that could be caused by a leakage. Remote sensing techniques have been tested for their ability to detect signs of plants stress, using the ratio of the 725 nm and 702 nm absorption bands. Data were obtained from the IKONOS satellite, which has a high spatio-temporal resolution. The gassed plots were found to be more stressed than the controls, although seasonal differences have to be taken into consideration.

A leakage from a CO_2-EOR pipeline operated by the Midwest Geologic Sequestration Consortium in Kentucky provided the MVA team with an opportunity to assess the use of a number of surface monitoring technologies for leakage detection (Wimmer *et al.*, 2011). One of the methods tested was hyperspectral imagery. Aerial data were collected over the leak area from altitudes of 0.6, 1.1 and 2.1 km, and analysed for indications of plant stress. However, no changes were detected and it was concluded that the method was not well-suited for a leak of such a short duration and limited spatial influence.

LIDAR may also be of great benefit in monitoring vegetation stress related to CO_2 leakages. LIDAR data can be used as a support in the interpretation phase, since the backscatter intensity value helps to identify anomalies related to CO_2 leakages, both for vegetation and bare soil (Bateson *et al.*, 2008). Although vegetation stress identification is potentially a relatively straightforward and practicable technique for the detection of CO_2 leakage from subsurface storage sites, it is unclear how it may be used for the estimation of CO_2 flux rate. Nevertheless, by using signal reflection (or backscattering), airborne LIDAR sensors can also be used for direct detection of the CO_2 plume above vegetation surfaces (Benson and Myer, 2002), based on a technique known as the Differential Absorption Lidar (DIAL) (Browell *et al*., 1998). The suspended particles in the atmosphere, such as aerosols and dust, act as retroreflectors, relative to which the CO_2 plume absorption is measured. This principle is also used in field based instrumentation called the temperature tuneable feedback laser diode, which is capable of accessing the 2000–2005 nm region that contains CO_2 absorption lines (Repasky and Humphries, 2006; Humphries *et al*., 2008).

Thermal imagery

In order to improve the analysis, it is recommended that additional sensors should be used if possible. The use of a thermal camera, for example, is strongly advised. The thermal camera can be mounted on board an airplane, and it could be made to acquire data at the same time as a hyperspectral sensor does. Night time thermal camera acquisition is complementary to daytime hyperspectral sensor acquisitions over the same area. The images acquired contain important information (the thermal band is even more sensitive to CO_2 presence and its effects on vegetation), so hyperspectral and thermal images can be jointly interpreted. This is also a good option for those areas that lack vegetation. It is based on the assumption that a leaking CO_2 plume would have a different temperature to its surroundings. As noted earlier, Bateson *et al*. (2008) assessed the use of thermal imaging for detecting CO_2 seepage from an area with natural gas vents (Latera, Italy). The ATM thermal results picked out haloes corresponding to the largest vents, where either the emitted gas is warmer than its surroundings, or the bare soil warms up more than the surrounding vegetation. It was recommended that thermal data should be acquired during winter and at night in order to avoid thermal anomalies being masked due to the sun’s energy.

Tank *et al*. (2008) investigated new remote sensing techniques based on infrared imaging for the detection and quantification of earth surface CO_2 degassing. The methods were tested on the Bossoleto vent in Tuscany, Italy. The detection of degassing locations from infrared image time series was found to be reliable, particularly under dry, calm and cloudless weather between dusk and dawn. A method for quantifying the gas emitted was based on the determination of the heat energy required to generate the observed thermal anomaly. Further experimentation is required to validate the approach. While this research employed ground-based remote sensing technology, the authors suggest that they are applicable to airborne and spaceborne measurements, and that they may be useful for monitoring the storage safety of CO_2 storage sites.

Prata *et al*. (2004) demonstrated that suitably calibrated thermal cameras using 320 x 240 element arrays incorporating interference filters were capable of detecting gaseous plumes from volcanoes and industrial sources. However, it was unclear whether the cameras could maintain their calibration, and it was suggested that thermal imagers would be unlikely to monitor CO_2 leaks on their own. While these results were obtained from ground-based data, airborne versions are also feasible (Prata *et al*., 2005).

Gat *et al*. (1997) described a methodology for the detection and tracking of toxic gas plumes using the Airborne Thermal Infrared Imaging Spectrometer (TIRIS). The method depends on the temperature of the plume differing from that of the terrain, and the research was focused on the detection of organic gases.

As described above, leakage from a CO_2-EOR pipeline in Kentucky provided an opportunity to assess the use of a number of surface monitoring technologies for leakage detection (Wimmer *et al*., 2011). It was observed that the rapid release of pressurised CO_2 caused extensive freezing of the soil and subsurface water immediately above the leakage point. Thermal imagery was therefore obtained, with complimentary soil temperature measurements. The images successfully revealed a sharp contrast between the frozen and unaffected soil, and were consistent with the ground-based measurements.

In summary, thermal imagery may offer the potential to quantify CO_2 leakage, although a large number of potential drawbacks would need to be overcome. The method could possibly be used in combination with other techniques.

Spectral signature

Both CO_2 and CH_4 have absorption features in the SWIR region that lie within the wavelength range of high resolution hyperspectral scanners (1,400, 1,600 and 2,000 nm for CO_2) for direct detection. However, retrieval of CO_2 from typical hyperspectral sensors is difficult because most of the CO_2 absorption bands are relatively narrow and influenced by other atmospheric gases such as water vapour.

Gangopadhyay *et al*. (2008) attempted to identify the most CO_2 susceptible bands in the operating region of most present-day hyperspectral instruments with different atmospheric conditions and CO_2 concentrations. FASCOD (Clough *et al*., 1986), which calculates spectral transmittance, radiance or optical depth, was used to simulate atmospheric models accommodating atmosphere profiles, aerosol models and water and ice cloud models with variable CO_2 concentrations. Spectroscopic parameters were obtained from the HITRAN molecular spectroscopic database (Rothman *et al*., 2003). It was found that the 1,998-2,003 and 2,007-2,013 nm ranges are least influenced by other atmospheric gases.

Gangopadhyay *et al*. (2009) compared two techniques for detecting and measuring anomalous CO_2 flux due to coal fires using spaceborne spectroscopy. The data were obtained from the Hyperion pushbroom instrument mounted upon NASA's Earth Observing-1 satellite, with a spatial resolution of 30 m. The methods compared were the Continuum Interpolated Band Ratio (CIBR) (Green *et al*., 1989), which is an established method for atmospheric column average water vapour retrieval, and an inversion technique which attempts to establish a relation between CO_2 plume-related radiance and CO_2 concentration. The most suitable absorption bands were 2,001 nm and 2,010 nm, as these are not significantly influenced by other atmospheric constituents as noted above. Sources of error included sensor noise, surface properties (such as dust), terrain effects, model errors (in specifying FASCOD parameters such as the aerosol characteristics due to the terrain and climate, and stratospheric conditions), and interference from other atmospheric constituents. The authors concluded that the inversion method was more suitable for estimating CO_2 flux from particular events as it calculates only to a certain level of the atmosphere, and that the results could be improved by the use of sensors with higher spectral resolution.

Spinetti *et al*. (2008) used airborne hyperspectral images acquired over a vent of Kilauea Volcano, Hawaii, to estimate the CO_2 flux rate. The data were obtained using the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS), which is an optical hyperspectral sensor measuring radiance across 224 contiguous spectral channels between 400 and 2500 nm, in intervals of 10 nm. Obtained at an altitude of 19.4 km above sea level, the ground resolution was 18 m. Ground gas measurements were used to calculate a CO_2 emission rate of around 230 ± 90 t d^{-1}. The CIBR method was adapted to retrieve the volcanic CO_2 columnar abundance, and subsequently the CO_2 concentration was estimated using a new mapping technique based on the assumption that the depth of the CO_2 absorption lines varies with the concentration. It was necessary to apply corrections accounting for the water vapour in the plume and the background atmospheric CO_2 level. The estimated flux rate was 396 ± 138 t d^{-1}. For the mapped plume, the lowest volcanic CO_2 concentration detected was 40 ppmv above the ambient concentration of 372 ppmv, with the sensitivity influenced by noise and spatial resolution. Some saturated pixels were attributed to overbearing infrared emissions. It was suggested that Hyperion data could potentially be used, if the SNR is sufficient.

AVIRIS data were also employed to identify and map anomalous volcanic CO_2 concentrations in the atmospheric column above Mammoth Mountain (Martini and Silver, 2002). The 2,060 nm absorption band was selected, and subjected to continuum removal and minimum noise fraction analysis. While there was a degree of success in matching the detected CO_2 flux zones with ground observations, complications arose due to an unknown relationship between CO_2 absorptions and those absorptions due to plant biochemistry.

In June 2007 a joint test was carried out by ARSF (Airborne Research and Survey Facility) and the BGS to assess the use of hyperspectral data for direct detection of CO_2. A dry run was undertaken with large baths filled with CO_2 and lined with tarpaulins of known reflectance. The AISA Hawk was commissioned to obtain the images. The CIBR method has been tested, and has so far proved to be highly sensitive to noise derived from illumination effects, poorly known sensor calibration and poor weather conditions. Additional tests have been undertaken at Latera.

Pickles *et al*. (2009) also investigated the applicability of NASA's multispectral system, called the MODIS/ASTER Airborne simulator (MASTER), through data acquisitions carried out over the Naval Petroleum Reserve Site #3 (NPR3) which is operated by the US DOE's Rocky Mountain Oil Test Center (RMOTC) facility in Casper, Wyoming. The sensor was configured to have 50 bands in the wavelength range 400 - 13000 nm, taken at 2.5 m and 5 m resolutions. The objective was to map controlled leakage of CO_2 and CH_4 gas using the Moderate Spectral Resolution Atmospheric Transmittance (MODTRAN) algorithm (Berk *et al*., 1987) for atmospheric correction, at 4300 nm and 2400 nm respectively, followed by detailed neighbouring pixel comparisons through simple subtraction. The results obtained suggest that although it is unlikely that the MASTER instrument as currently configured (with broad spectral resolution) will be able to detect CO_2, it may be useful for large scale CH_4 leaks.

In summary, hyperspectral data may potentially be employed to detect and estimate CO_2 leakage from underground storage sites. However, if the plumes cannot be detected with a resolution of ~30 m as afforded by spaceborne sensors, dedicated airborne flights will be necessary.

2.5.2 Airborne EM

Electromagnetic (EM) techniques involve the use of time-varying source fields to induce secondary electrical and magnetic fields in the subsurface that relate to its conductivity (see Section 2.4). Their use could potentially detect changes in the resistivity of shallow groundwater associated with the dissolution of CO_2. Although they have yet to be applied to CO_2 storage, airborne EM techniques have been successfully used to detect pollution plumes in shallow aquifers.

Airborne EM systems have been used for groundwater exploration studies for three decades, providing information on both the aquifer structure and the water quality (Siemon *et al*., 2009). Helicopter surveys are more commonly undertaken than fixed-wing aircraft, and use a towed rigid boom for frequency domain EM systems and a large transmitter loop with a small receiver for time-domain systems. The depth of penetration depends on the frequency (or time channels) of the signal, and frequency domain EM surveys are appropriate for shallow to medium (1-100 m) depth analyses. Homogeneous or layered half-space models are typically used to invert secondary magnetic field values into resistivities and depths.

Lipinski *et al*. (2008) used helicopter-borne EM surveys to evaluate the disposal of wastewater into a shallow (2-3 m depth) alluvial aquifer from natural coalbed methane production in the Powder River Basin, Wyoming. The wastewater was characterised as moderately saline and sodic. The survey data were inverted using EM1DFM (UBC-GIF, 2000) in preference to the more traditional homogeneous half-space algorithms (Fraser, 1978), to provide more accurate electrical conductivity estimations in the phreatic zone. The model converged to a solution that represented a thin conductive layer, corresponding to observations from monitoring wells. The results were correlated with water quality measurements to define an empirical relationship between conductivity and pore water salinity.

Beamish and Klinck (2006) used a fixed-wing airborne EM survey to characterise the hydrochemistry of a coal mine plume in Nottinghamshire, UK. The results of the survey revealed extensive zones of elevated subsurface conductivity due to coal mine spoil heap leachate infiltrating the underlying sandstone aquifer.

For airborne EM to be a potential monitoring technique for CO_2 leakage into a shallow aquifer, the ingress must have a measureable impact on the salinity of the formation water. Various studies have been conducted on the effect of CO_2 migration into aquifers, focusing (for example) on the potential release of heavy metals such as Pb and As due to the reduction of pH and subsequent dissolution of minerals (e.g. Wang and Jeffe, 2004; Zheng *et al*., 2009). The dissolution of minerals such as feldspars and carbonates to buffer pH will result in an increase in total dissolved solids (TDS), and hence conductivity. The effects of the CO_2 influx will depend on the nature of the host rock, and the rate of groundwater flow may be important (Lu *et al*., 2009). It is expected that changes in TDS will be more detectable for carbonate aquifers than for sandstones due to the reaction rates involved.

The Frio Brine Pilot experiment in Texas was established to demonstrate the potential of the storage of CO_2 in saline aquifers without adverse health, safety or environmental effects (Hovorka *et al*., 2006). The subsurface CO_2 plume was monitored within the injection zone, the overlying formation and the near-surface environment. Monitoring of the groundwater below the surface was found to be ineffective due to noise, sources of which included a variable water table and high natural CO_2 flux. It was noted that a long period of pre-injection baseline measurements would be needed to separate any potential leakage signal from the natural background. This would be valid for airborne EM monitoring.

In order to employ airborne EM to detect, monitor and quantify CO_2 leakage into a shallow aquifer, the following procedure may be potentially applicable. Firstly, a pre-injection sampling campaign should define the geochemical and hydrological characteristics of the aquifer, and their natural variability. A numerical simulator such as TOUGHREACT (Xu *et al*., 2004) could then be used to predict whether a measureable impact on the groundwater would occur given an ingress of leaked CO_2, in terms of a change in the total dissolved solids content. An empirical relationship between TDS and electromagnetic recordings could then be used to estimate the amount of CO_2 that has dissolved in the groundwater.

The use of the airborne EM method may be limited in areas where significant clay contents, or naturally high background levels of TDS are present. Also, the method provides no geochemical discrimination and therefore ground-based sampling techniques must be employed to establish the cause of any enhanced conductivity (Beamish and Klinck, 2006).

3 QUANTIFICATION IMPROVEMENTS OF A MONITORING PORTFOLIO

In this section, methods and combinations of methods and their deployment for quantification of leakage are proposed, according to the monitoring compartment (marine and terrestrial aquatic environments, atmospheric/surface environment and shallow subsurface environment), whether the monitoring is being done during the operational period or post-closure, and whether the leakage is diffuse (such as through a semi-permeable caprock), dispersed (such as through a fault system) or localised (such as through an inadequately sealed well). This information is summarised in Tables 6 to 8 presented at the end of this Section.

In general, due to the horizontal extent of stored CO_2, it will be necessary to use one of a selection of techniques to first detect a leak, or a likely leakage pathway, prior to deploying instrumentation that can directly or indirectly estimate CO_2 flux in the surface or the water column.

Modelling will be key to the planning of monitoring programmes and the interpretation of data for the quantification of any leakage. An accurate Earth model may be able to identify possible leakage pathways so that surface monitoring systems can be optimally located. In addition, modelling should help to evaluate the period of risk, since leakage should decrease because of the trapping mechanisms in the reservoir and along the leakage pathway. Therefore, monitoring methods that can provide data that can be used to constrain model parameters and reduce uncertainties will provide added value.

Preference should be given to methods that:

- are concurrently employed for performance monitoring
- are favourable in terms of cost and benefit
- are most reliable and accurate
- can be deployed in conjunction with other monitoring techniques (e.g. piggy-backing on ship-based towed surveys)
- can be operated autonomously or involve minimum human effort
- are robust and low-maintenance
- have added benefit in improving the calibration of models

Since the deep subsurface is much closer to the CO_2 storage formation, it is essential to carry out monitoring in the deep subsurface in order to identify potential CO_2 leakages as early as possible. For this reason Section 3.1 briefly reviews the deep subsurface monitoring methods that have not been discussed in Section 2 and considers them as part of the CO_2 leakage quantification monitoring portfolio discussed in Section 3.2.

3.1 Deep subsurface monitoring methods

3.1.1 Seismic methods

The main objective of seismic methods is to deduce information about the geometry of the geological structures and about the physical properties of the rocks, using the observed arrival times together with variations in the waveform of the seismic signal. Recent studies have demonstrated the effectiveness of the seismic method in a time-lapse mode for CO_2 geological storage monitoring purposes (Arts *et al.*, 2004; Chadwick *et al.*, 2009).

3D seismic data can provide detailed information about fault distribution and subsurface structures. Computer-based interpretation and display of 3D seismic data often allows for more thorough analysis than when solely based on 2D seismic data. If 3D seismic is repeated over time it is referred to as 4D seismic. 4D seismic surveys are routinely run in oilfields to detect hydrocarbons. Gases and supercritical CO_2 appear as a 'bright spot' on seismic sections because the difference in acoustic impedance creates a strong reflection. This technique can image the evolution of the CO_2 plume in the reservoir over time, and may allow the detection and quantification of possible leakages.

Whereas conventional surface seismic surveys record only compressional, or P-waves, multi-component seismic surveys record both P-waves and shear, or S-waves. This is achieved by recording all components of the returning wavefield. Applications in the oil and gas industry for multi-component surface seismic range from imaging through and inside gas clouds, imaging of low impedance sands, lithology discrimination, increased shallow PS resolution, sub-seismic fracture characterisation, sub-salt imaging, density inversion and even pore pressure prediction (Thompson, 2005). Multi-component seismic can provide improved imaging and multiple attenuation over conventional P-Wave seismic.

Field examples

At *Sleipner*, CO_2 has been injected into a sandstone saline aquifer capped by mudstones at a depth of about 1,000 m in the North Sea. 4D seismic has successfully been used to image the CO_2 plume at Sleipner site (Arts *et al*., 2004; Chadwick *et al*., 2009). A baseline seismic survey was acquired in 1994 before injection and, since then, there have been seven surveys with the aim of imaging the plume to track the migration of CO_2. Observed effects of the CO_2 on the seismic data have been large (Eiken *et al*., 2000), both in terms of reflection amplitudes and also in the time delays observed (velocity pushdown effect). The time-lapse seismic data from Sleipner clearly shows the CO_2 plume development by the growth of high amplitude (bright) reflections.

A land-based time lapse 3D seismic monitoring programme has also been implemented at the *In Salah* storage site in Algeria (Mathieson *et al*., 2011). An initial survey was undertaken in 1997 to characterise the site prior to CO_2 injection. A high resolution repeat 3D survey was then acquired in 2009 for the purposes of monitoring plume migration. Initial interpretation of the data has indicated that the survey has provided excellent imaging of the overburden and the injection horizon, and a number of the features observed coincide with information gleaned from satellite data. However, compared to Sleipner (where extremely favourable reservoir conditions such as thick storage formation with large porosity/permeability exist), 4D seismic monitoring is believed to be much less effective in imaging the growth of CO_2 plumes at In Salah.

A time-lapse 3D seismic survey was implemented at the *CO2CRC Otway Pilot Project* in Australia, where over 65,000 tonnes of CO_2 have been injected into a depleted gas reservoir (Urosevic *et al*., 2011). The survey confirmed the outcome of modelling experiments and the expectation that the differences observed between successive surveys would not be sufficient for detecting anomalies due to the injection of CO_2 because of the residual CH_4 in the reservoir. However, it was noted that, in the event of a leakage, a 3D surface seismic survey should be able to detect the presence of CO_2 in the overlying strata.

At *Weyburn*, multi-component seismic has been used in time-lapse mode, to monitor the flooding of CO_2 in an EOR environment. Four surveys were acquired between 2000 and 2007, and have clearly identified the spread of CO_2 in the reservoir. Reductions of 12% in acoustic impedance around the horizontal injection wells have been attributed (through laboratory measurements) to a combination of increasing pore pressure and CO_2 saturation (White, 2010). While the primary objective of the seismic monitoring was to track the subsurface distribution of the CO_2 within the reservoir, the time-lapse interval travel times have also been used to monitor the overburden for leaked CO_2 or 'out-of-zone' injected gas. Using the cumulative travel time changes calculated between the 2000 and 2004 surveys and associated areal extent as a proxy for the volume of CO_2 present in the overburden, the observed anomalies were attributable to noise, or a maximum of 1.5% of the total injected CO_2.

Leakage Quantification

4D seismic surveying has been found to be a very suitable geophysical technique for monitoring CO_2 injection into the saline aquifers at Sleipner. With respect to quantification based on the change in seismic amplitudes, the largest change takes place at lower CO_2 saturation levels. Once the CO_2 saturation levels have increased the amplitude changes are less pronounced (Arts *et al*., 2008). Multi-component seismic represents an additional tool in order to better characterise the fluid content in the rocks, and therefore to better distinguish small variations in CO_2 state, through the analysis of the P-and S-waves. From the AVO analysis of both waves, it is possible to define the state of the CO_2 (gaseous, liquid or supercritical) better than with solely P-waves.

3.1.2 Time-lapse surface and well gravimetry

Gravimetry consists of studying the anomalies of the gravity field due to density variations underground. The amplitude of the variation of the gravity field due to fluid substitution is proportional to the difference in density of the fluids, to fluid volume (and then also to porosity), and more or less inversely proportional to the square of depth.

Application to monitoring geological storage of CO_2 by time-lapse or continuous measurements may contribute towards characterising displacements of large volumes either of brine or gas in the reservoir or possibly leakage at shallower depths. Its feasibility will depend upon the injected amount, the depth of the reservoir, CO_2 density and the precision of gravity measurements. The latter is not only a function of the instrument itself, but also of the proper correction of temporal variations of gravity, independent of the phenomenon studied, (e.g. variation of the water table). From a general perspective, the application of gravimetry is still at the feasibility stage; the more advanced works concern the Sleipner site (Alnes *et al*., 2011). Simulations and field experience from EOR case studies, seasonal gas (methane) storage and monitoring of geothermal fields or volcanoes may be exploited as well. In addition to surface gravity measurements, downhole gravity measurements obtained just above the reservoir could significantly constrain surface gravity measurements or detect variations not detectable from the surface. Gasperikova and Hoversten (2008) showed that inversion of measurements made in boreholes just above a reservoir where EOR was carried out over 20 years could map the area of net density changes caused by CO_2 injection and water within the reservoir.

In conclusion, surface gravimetry could be a useful method for monitoring large mass variations of supercritical CO_2, e.g. a few millions of tonnes, or, in the most favourable case, hundreds of Kt. As demonstrated at Sleipner, its added value is in constraining density and possibly the thermal gradient for thermo-hydrodynamic modelling. The main issue is that to obtain the accuracy of a few milligals needed to measure effectively such a small change of gravity, field operations are long and time-consuming. Downhole measurements could be an issue, but costs/benefits need to be compared to other methods. As aforementioned, seasonal surface variations need to be taken into account for surface measurements as well. Using airborne gradiometry, which measures all the components of the gravity tensor, could help in reducing this kind of error. However, this technique is in the development stage and very expensive.

Leakage detection and quantification
A leakage from a reservoir in the order of some tens of Kt could not be detected by gravimetry unless leaking CO_2 is trapped by a secondary caprock. Then, there are two possibilities:
1) The accumulated CO_2 remains in supercritical state, beneath 700-800 m. As noted before, only downhole measurements performed at distances of about 100-200 m of the trap would be able to detect this;
2) In the case of accumulation in the gaseous phase at shallower depths, surface microgravimetry could be able to detect some thousands of tonnes of CO_2, depending on the depth, porosity, partial saturation of CO_2, etc. Nevertheless, there are no examples of direct detection of this kind of accumulation to date. Application of microgravimetry to natural analogues where free CO_2 accumulation is known would provide invaluable information.

3.1.3 Electric/electromagnetic methods

The resistivity of a porous rock is highly sensitive to the pore fluid content. Since the introduction of supercritical CO_2 generates a strong increase of the resistivity, in particular in a saline aquifer, the variations of electrical resistivity could be used to image the CO_2 plume migration. DC electrical methods and low-frequency (diffusive) EM (Electromagnetic) methods can be envisaged to monitor the CO_2 injection by ERT (Electric resistivity tomography), as a low cost complement to 4D seismic methods. The value of coupling resistivity methods with seismics is already widely recognised in hydrocarbon exploration, where marine CSEM (Controlled Source EM) and land TEM have experienced a very rapid growth since 2002. Moreover, the repeated, time-lapse implementation used in monitoring should provide much greater sensitivity and resolution than the single-time implementation used in exploration. In order to increase the efficiency of electrical/EM methods, it has been proposed to bring the source closer to the CO_2 plume by using a pair of metal-cased boreholes, acting as long electrodes, to inject the electrical current at depth, and to measure the resulting EM field at the surface. A specific array configuration has been proposed by Bourgeois and Girard (2010), designated as LEMAM (for Long-Electrode Mise A la Masse). The casings used for injection must reach the reservoir, but there is no other requirement on the well completions. The boreholes can be pre-existing in the case of a depleted hydrocarbon reservoir or drilled especially for monitoring purposes in the case of a saline aquifer.

Cross well measurements
The usual depth of storage makes it difficult to detect and monitor resistivity changes in the reservoir using standard electrical/EM methods operated from the surface. Logging and cross-well electrical/EM methods overcome this limitation, but they need wells extending to or exceeding the reservoir depth, and which are appropriate for carrying out such measurements in terms of completion, inter-well distance, etc. This method requires deploying logging tools in wells located at distances of up to a few tens of metres. Another option is deploying permanent arrays of electrodes in the so-called "smart wells" Here, the electrodes of one well are used to inject a direct current; meanwhile voltage is measured by electrodes at the second well. On-going experiments at Cranfield and Ketzin show very promising results.

Shallow Electrical/EM measurements on natural analogues (Latera, Italy)
Electrical Resistivity Tomography (ERT) and shallow EM (EM31 and EM34) data showed a strong correlation of variations in conductivity with measured fluxes of CO_2. A significant amount of gas in the saturated sediments of the superficial aquifer would be expected to result in an increase in electrical resistivity. The low resistivity anomaly is therefore thought to be a secondary effect that is probably related to the CO_2 gas vent. The possible causes, ranked in order of likelihood are:

- mineralised local groundwater associated with the CO_2 gas vent;
- mineralised sediment in the local fault along which the CO_2 is leaking;
- deeper thermal conductive groundwater that finds its way up following the same route as the CO_2.

Strengths and weaknesses
The only real examples of direct detection of CO_2 migration by ERT come from downhole measurements, either by wireline logging or by cross-well experiments. In that case, the injected amounts are of the order of few thousands of tonnes. Although these results are very encouraging, it is important to note that:

1. They are limited to a very restricted zone with respect to the expected storage site extension covering several km²;
2. They require the deployment of specific downhole tools in a pair of nearby wells or the installation of expensive smart well equipment.

In the case of the CSEM method with injection of current through the metallic casing and measurements at the surface, as in the LEMAM configuration, simulations and initial field experiments indicate that they are promising methods for deep monitoring. Further simulations and field experiments at different scales are needed to elucidate the areas of applicability, limitations, sensitivity and effective resolution. Concerning offshore storage, CSEM is widely applied to oil and gas exploration, with a towed source at mid depth and ocean bottom sensors. A baseline was recently carried out at Sleipner, but no results have been published to date.

3.1.4 Downhole monitoring methods

Downhole fluid chemistry
Monitoring of the geochemical evolution of subsurface waters receiving injected CO_2 necessitates regular sampling, designed to conserve the *in situ* properties of the fluid (NETL, 2009). The analysis may include a wide range of parameters, such as pH, HCO_3^{2-}, alkalinity, dissolved gases, hydrocarbons,

major and minor elements, total organic and inorganic carbon, stable isotopes, redox potential, specific conductance, total dissolved solids, density, and natural and introduced tracers. Chemical analysis will provide the information required to validate model predictions, and determine the occurrence of processes such as dissolution and mineral trapping. Moreover, it may also alert operators to any geochemical interactions that may lead to an increased risk of leakage. Sampling of fluids from deep aquifers can be facilitated using different methods:

1. Pumping of large volumes of fluids until stagnant water has been removed from the well and the fluids' chemical composition stabilises.
2. Wireline sampling of fluids in pressurised sampling vessels, that maintain the reservoir pressure and avoid degassing of samples.
3. U-tubes, which facilitate repeated pressurised sampling of deep aquifers without involving heavy sampling equipment, as needed for the two methods described above.
4. Sensor based technologies.

Wireline sampling and U-tubes are currently the only ways to obtain fluid samples from deep aquifers for complete and reliable geochemical analyses for the monitoring of deep reservoir fluids. Sensors usually measure one or a few characteristic hydrochemical parameters that are good indicators for changes in the fluid composition surrounding the wells. Generally, useful parameters are electrical conductivity (for brine) and pH (for CO_2).

U-tubes facilitate the accurate determination of the arrival times of CO_2 or tracers at the monitoring wells, and thus provide valuable information for the calibration of geological models of the storage reservoirs. They allow repeated pressurised sampling of deep aquifers, without mobilising heavy sampling equipment, as is needed for wireline or wellhead sampling. Sampling is possible at high frequencies, in the order of one sample per hour. Samples have to be depressurised and analysed on site in specialised field labs. U-tube systems have been used in the CO_2 storage field sites at *Frio* in Texas, *Otway* in Australia and *Cranfield* in Mississippi as described by Freifeld *et al*. (2005), Freifeld and Trautz (2006) and Freifeld (2009). Due to the costs and complexity of U-tube monitoring, it is expected that it will probably be restricted to a few wells only (if at all) in full-scale storage projects.

As discussed for shallow groundwater monitoring in Section 2.3, many wells would be needed in order to quantify fluxes. Thus, detecting leakage require well-known pathways, large fluxes and permeable aquifers. If this happens to be the case, wells may be used to detect the downstream migration of CO_2 plumes. However, a limited number of wells is unlikely to enable accurate and precise quantification of migration or leakage in deep aquifers. The potential of geochemical analyses of deep fluids is a contribution to the detection, but not to the quantification of leakage.

Downhole pressure/temperature measurements

Downhole pressure/temperature sensors provide continuous measurements of the pressure and temperature of the CO_2 at the injection point. The measurements are generally either stored in a memory gauge for retrieval at certain intervals, or may be relayed to the operators at the surface through a fibre optic cable. These measurements can be used to detect casing failure which may lead to leakage of CO_2, accurate estimation of injection rates, viscosity and density of the injected CO_2, and calibration of reservoir models used (IPCC, 2005; Paterson *et al*., 2008).

The so-called 'smart' wells in the saline aquifer at *Ketzin* site in Germany contain a variety of permanent downhole sensing equipment, including a fibre-optic pressure/temperature gauge (Prevedel *et al*., 2009). The injection well and two observation wells are equipped with distributed temperature sensing technology, which allow quasi-continuous temperature profiles to be obtained from along the entire length of the wells. Analysis of the observed temperature anomalies led to an understanding of the flow processes within the wells and phenomena related to the spreading of CO_2. The downhole sensor system also provides real-time monitoring of the reservoir pressure during the injection process, while also allowing observation and control of the well.

High resolution pressure data from an observation well at the SECARB project at *Cranfield*, Mississippi, has been used to monitor reservoir response to an increased CO_2 injection rate (Hovorka *et* *al.*, 2011). Monitoring of the pressure above the injection zone is used to assess the integrity of the seal in a region of numerous well completions.

Downhole pressure/temperature data may potentially be used in combination with other CO_2 monitoring technologies, such as those which image the CO_2 plume in the reservoir, by providing information regarding flow rates and density of the fluid at the injection point. They may also be useful in alerting operators to leakages, whereupon more specialised CO_2 leakage quantification technologies may be deployed.

3.2 Monitoring portfolio performance for each monitored compartment

What is common between all monitored compartments is the monitoring sequence that should be followed and run in parallel with the storage site life time. The first step in this process involves the definition of the monitoring baseline, which requires sufficient spatial as well as temporal coverage in order to provide an adequate characterisation of the natural variability of the particular compartment considered.

Baseline monitoring needs to be carried out before the compartment to be monitored is altered by the effects of CO_2 injection, or is exposed to CO_2 itself in case of any leakage. This step is critical as both detectability and quantification of a potential CO_2 leak will vary due to the inherent natural variability of the marine, shallow subsurface and atmospheric environments. It is well known that such a baseline is neither homogenous (spatially invariable) nor constant (temporally invariable). Spatial heterogeneity depends on the scale (size of reference unit) considered and is generally a lot more difficult to characterise in the subsurface, than in the water column and the atmosphere since the data available for this compartment is much more sparse. In contrast, natural variations over time are much slower in the subsurface than that observed in the marine and fresh water column or the atmosphere, which would suggest that it can be characterised with lesser, yet more expensive monitoring efforts.

As the next step, the characterisation of the natural variability of the monitored compartments and knowledge of potential leakage pathways should be complemented with wide area monitoring surveys for leak detection. The monitoring tools that are currently available for wide area monitoring do not necessarily have, or are required to have, high CO_2 leakage quantification accuracy. In fact, the best tools available for this purpose may be better suited to deep subsurface monitoring. This is because the effects of the CO_2 storage and the volume of the CO_2 itself, if it has migrated outside the storage complex, are expected to be much larger closer to the storage complex and may indeed indicate vulnerable pathways for CO_2 leakage.

Then, if leakage is detected, appropriate monitoring methods that allow for CO_2 quantification can be used to quantify the amount of leaked CO_2. The process that describes the steps involved in CO_2 leakage quantification are shown in Figure 53. Inevitably, the detection, measurement and quantification steps introduce errors in the estimated CO_2 emissions, increasing the uncertainty around the quantification estimates.

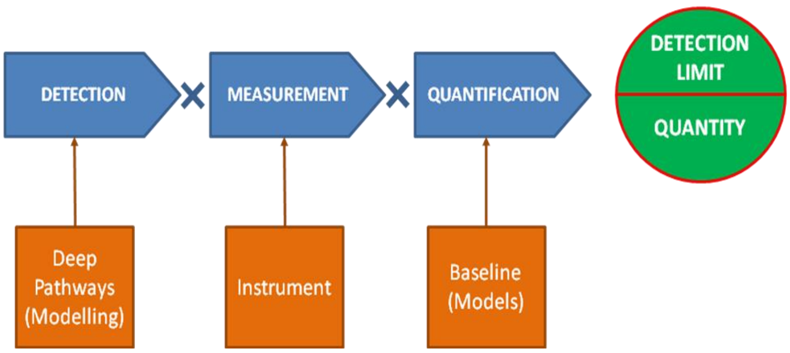


Figure 53. The CO_2 leakage quantification process.

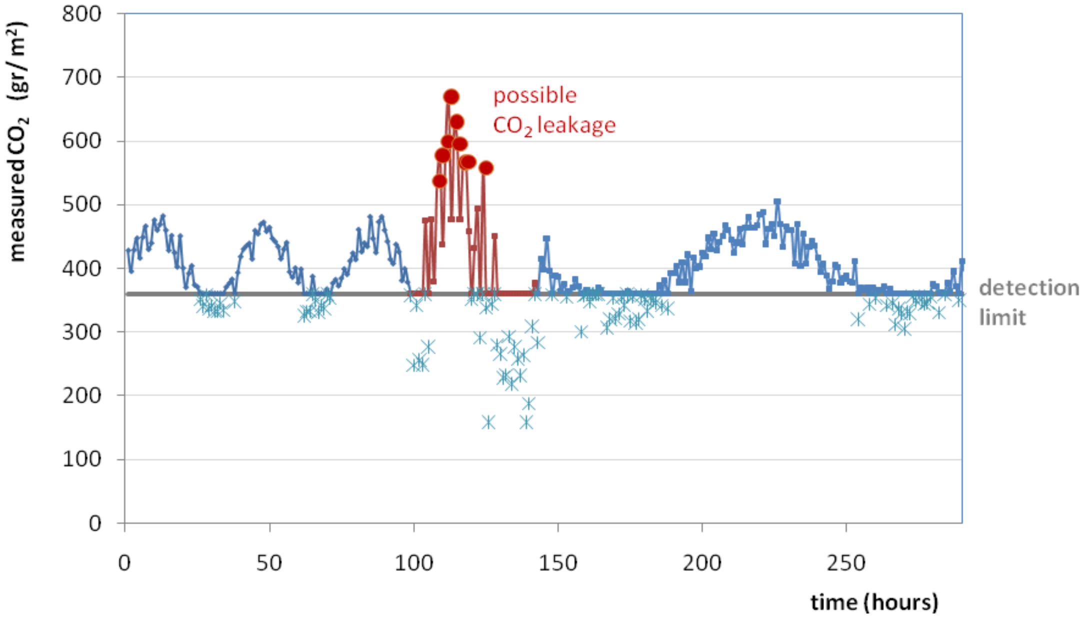


Figure 54. Example illustration indicating the natural variability in monitored CO_2 levels and the potential leakage levels in relation to an assumed constant detection limit (blue stars denote true values, not measured; red dots represent monitoring data that may be identified as potential leakage).

The large spatial and temporal variation of the background levels are likely to contribute the largest proportion of uncertainty in the estimation of leaked CO_2 as shown in Figure 54. As a result, the quantification of CO_2 leakage is a rather complex task that cannot be simply attributed to the monitoring methodology, as explained earlier.

Important issues that need to be considered when deciding on the methods to be used as part of the monitoring portfolio for a particular site are:

- the performance of the method, given the specific site characteristics
- the benefit expected in terms of value of information (accuracy, detection limit, validation of storage site model concepts and estimates)
- the cost of monitoring including the field implementation of the monitoring portfolio tools chosen (equipment, consumables, staff time) as well as the monitoring data interpretation cost and integration costs within the storage site models.

This last item is of particular importance for the storage site operators and also needs to be considered in the light of the storage site permit conditions as well as the CO_2 storage regulatory framework (e.g. EU Directive, ETS regulations).

An example site monitoring portfolio for a CO_2 storage site was published for the In Salah CO_2 storage project (Wright, 2007). Low cost monitoring methods that provide useful information are prioritised together with focused application of methods that are more costly but are recommended. This cost benefit prioritisation may indirectly consider the accuracy that may be achieved using each of the methods referred to. Inexpensive methods are considered as part of the site monitoring portfolio, although arguably they may be less valuable in terms of data quality, while some methods are thought to be too expensive to be worth the effort and cost.

One additional consideration is that different monitoring tools by nature measure different expressions of the CO_2 presence and effects. Combining all the information in a coherent way is not always easy and challenges our understanding of geological, environmental and ecosystems processes as well as the ability of the modelling tools available to the research community and industry.

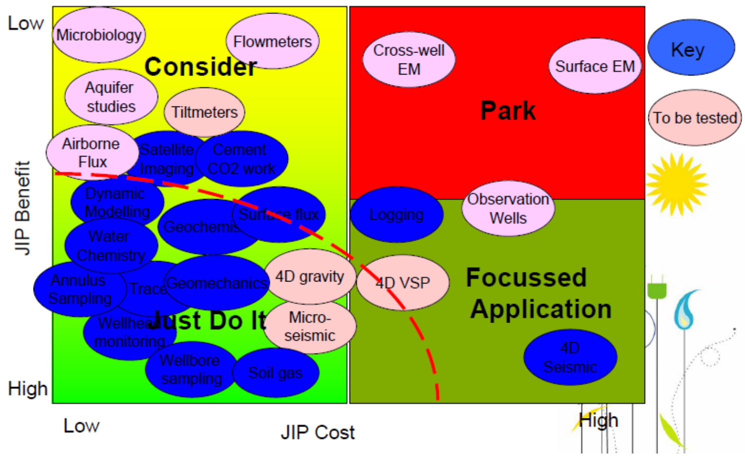


Figure 55. Cost-benefit assessment of monitoring technologies for the In Salah CO_2 storage project (after Wright, 2007).

The most important question that needs to be answered when assigning a high or low value to the benefit of a particular monitoring method and for a given storage site setting is the amount of CO_2 over a given area and period of time that can be detected and possibly quantified. When referring to detection, this amount may be called detectability of the method, while when referring to quantification it would be better referred to as the sensitivity of the method.

It must be stressed that both detectability and sensitivity of a monitoring method are not just dependant on the monitoring technology accuracy and precision for a given mode of implementation of the technology. Accuracy and precision are the qualities considered to specify the monitoring technology detection limit given the implementation mode and when used within the specified calibration range. In fact, the monitoring method accuracy and precision contribute the smallest amount of possible error to measurements when a monitoring method is implemented. A much larger proportion of error is introduced by the modelling that needs to be implemented in order to convert the monitoring measurements to estimates of CO_2 quantity present within the area monitored and over the time period the measurement is taken. To provide a practical example, the measurement of the quantity of CO_2 in the air above a CO_2 emission source using a short open path laser needs to be coupled with dispersion modelling in order to estimate the CO_2 emission rates. As a result, the detectability or sensitivity of the method used to measure CO_2 in the air would not only depend on the instrument concerned, but also on the modelling method and the atmospheric conditions on the day of monitoring. As this measure of CO_2 detectability or sensitivity is not specific to the monitoring method, and since the same principles apply to all monitoring methods discussed in this report, it is very difficult to specify the levels of detection that different monitoring methods can achieve and the uncertainty/errors expected in a uniform way.

The following Sections discuss the monitoring portfolios that may be implemented in the different environmental compartments where leakage quantification is necessary according to EU ETS and focuses on the marine environment, surface/atmosphere and the shallow subsurface.

3.2.1 Marine and terrestrial aquatic environment monitoring

CO_2 escaping into the water column may be quickly dispersed by currents, or dissolution and dilution. Therefore, methods suitable for leakage detection with a large spatial coverage may be unsuitable for quantification due to poor spatial (and perhaps temporal) resolution. Monitoring strategies may be designed to prioritise leakage detection over quantification; if a leak is suspected or identified then instrumentation suitable for CO_2 flux quantification may be deployed. Leaks may be identified either directly, such as by acoustic reflection from bubble streams, or indirectly, through the observation of seabed morphologies that may develop in response to gas escape (e.g. pockmarks).

Swath mapping systems (sidescan sonar, multibeam) are able to accurately image large areas of the ocean in a relatively short period of time, with a spatial resolution fine enough to potentially detect small changes in the morphology of the seabed, such as the development of pockmarks, due to seepage. It may also be possible to directly detect the migration of gas into the water column. Sidescan sonar systems can operate on a passive basis, which would be of use in leakage detection. Costs are moderate and are mainly associated with equipment and its set-up.

Multibeam systems may also be used for leakage quantification, in combination with optical methods, acoustic tomography and flow sensors to estimate flux, and bubble stream chemistry analysis to assess the concentrations of CO_2.

Complementary to the two swath methods described above, boomer/sparker profiling and high resolution acoustic imaging methods may be deployed to detect and track free gas occurring in marine sediments and escaping into the water column. High frequency echosounders can be used to identify hydroacoustic flares and trace these to venting sites on the sea floor. Multiple frequency surveys may allow estimates of gas flux (e.g. Geinert et al., 2006; Nikolovska *et al*., 2008), which can aid quantification of CO_2 leakage if combined with bubble stream chemistry analysis.

Deployment of a swarm of autonomous underwater vehicles (AUVs), equipped with multibeam sonar and ideally sensors for pH, temperature, conductivity and dissolved gas, could provide a complete and reliable coverage of a large area. However, this could be a prohibitively expensive undertaking. Costs could potentially be reduced by combining such surveys, for example deploying pH and dissolved CO_2 probes on remotely operated vehicles (ROVs) and conducting measurements during other surveys such as seismic or sonar.

Once a leakage site has been detected, continuous monitoring of the bubble stream can be performed by a stationary system, such as the lander-based hydroacoustic swath system GasQuant. Although this system can cover an area of around 2,000 m^2, it may need to be powered in conjunction with other equipment and therefore may only be suitable for use during the operational period and close to the injection well.

The dimensions of a detected bubble stream can be estimated in two ways: by mapping chemical determinants sampled using a ROV to determine the extent of the plume; or by measuring cross-sections of the plume at different depths by sonar. Funnels on the sea floor can collect gas for analysis and record leakage rates.

Geochemical analysis of the water column can provide direct measurements of leakage, either through the analysis of dissolved gases themselves, or of physical parameters (e.g. pH, T, salinity) or dissolved elements that may be associated with a co-migrating, deep-origin water. Measurements can be made using either *in situ* detectors, or by taking water samples to be analysed in a laboratory, with leakage rates being estimated by conducting profiles perpendicular through a dissolved plume and using associated current velocities to calculate total mass (e.g. Keir *et al*., 2008). Ideally, measurements could be taken in conjunction with acoustic or seismic surveys. Alternatively, sensors can be mounted on AUVs for remote and autonomous deployment, offering good spatio-temporal resolution.

Equilibrators involve continuous pumping of water from a chosen depth while a ship steams and the stripping of dissolved gases for analysis. This method has been used for the detection of pipeline leaks and seepages from oil and gas reservoirs (e.g. Logan *et al*., 2010). Conceivably, this approach could also be applied for marine CO_2 storage sites, with such measurements even being “piggy-backed” on 3D seismic surveys of the site.

Benthic chambers can also be used for the direct quantification of flux rates from the sediment floor to the water column. The change in composition of the water in the chamber over time is used to calculate the flux rate. However, these measurements are highly point specific, and errors due to significant spatial heterogeneity may be incurred.

Elevated CO_2 levels near the seabed and in ambient water will affect the physiology of fish and other marine biota, due in part to changes in pH and HCO_3^- and the sensitivity of the particular animal. Seabed fauna could be monitored using mobile rovers, which can operate on the seafloor for weeks or months, or by obtaining long-term time-lapse video recording at specific sites, which would enable seasonal changes to be accounted for. Threshold values represent a useful tool for the evaluation of the biological impacts from a certain ambient parameter on a certain species, and may be defined as the mortality rate related to a particular dose, or to the appearance of specific physiological, behavioural or physical disorders. With proper parameterisation, leakage quantification may be possible.

Table 6. Summary of methods suitable for various tasks in monitoring the marine and terrestrial aquatic environment.

Task	Method	Pre-injection	Operation	Post-injection	Comments
Leakage detection	Ecosystems				Samples or video recordings indicating changes; natural variation & source verification required
	Sidescan sonar				Detection of pockmarks indicating seepage; wide coverage in little time; can be passive; baseline required
	Seabed multibeam				Detection of pockmarks and maybe bubble streams; baseline required
	Boomer/sparker profiling/HR acoustic imaging				Finer resolution detection of subbottom gas accumulation and bubble streams; baseline required
	Equilibrators				Detection of gas anomalies ; could be piggy-backed on 3D seismic surveys; baseline and natural variation required
Leakage quantification	Chemistry combined with plume profiles for leakage rates				Quantification obtained from analysis of CO_2 concentrations and flux rate; baseline and natural variation required
	Benthic chambers				Highly point-specific but direct measurements; spatio-temporal variation may be important; baseline and natural variation
	Bubble stream analysis				High resolution acoustic imaging with multiple frequency for flux estimation combined with bubble stream chemistry
	Seabed multibeam system				Such as GasQuant, which is currently being used for assessing natural gas seepage sites
	CTD sensors and water chemistry analysis				CTD sensors lowered via a winch on a ship or using AUVs, to define extent of plume; water samples analysed
Reducing uncertainty	Isotopic analysis				Clarify origin of CO_2
	Tracers				Addition of e.g. perfluorocarbons to injected $CO_{2;}$
	Current meters				Enables currents to be taken into consideration in flux calculations

Colour coding represents suitability considerations: blue=good; yellow=medium; pink=poor.

Since leakages into the water column are likely to occur over a small area in comparison with the extent of the reservoir, monitoring strategies should be based either on the detection of pockmarks or bubble streams using acoustic methods that can offer a good spatio-temporal resolution, or involve monitoring focused on specific locations that lie over any identified potential leakage pathways. Geochemical methods are the only techniques that can directly quantify CO_2 in the form of gas or bubbles. Multiple analyses of different indicative components can help define origin and improve the precision of any estimate. *In situ* measurements will reduce errors, while autonomous monitoring may reduce costs, as will piggy-backing of geochemical surveys on surveys conducted with other techniques such as acoustic or seismic surveys. Sensitivity and resolution are difficult to quantify as no controlled experiments appear to have been conducted to date. However, precise estimates of background concentrations and current directions and strengths will have the greatest influence on the reduction of uncertainty related to plume flux calculations.

3.2.2 Atmospheric environment monitoring

CO_2 leakage at the surface may be quickly dispersed into the atmosphere, and therefore may prove difficult to detect using methods that favour a wide areal coverage over spatial resolution. Surface monitoring equipment would therefore preferably be positioned in areas where possible leakage paths have been identified through studies of the reservoir and overburden.

Offering a relatively large spatial coverage, the eddy covariance method (ECM), which uses statistics to compute turbulent fluxes of heat, water and gas exchange, is one of the most useful methods to measure and determine gas fluxes in the atmospheric boundary layer. Able to average the integral flux of gases over several square kilometres and different temporal scales, it has been proposed as a potential method for monitoring geologic CO_2 storage sites (e.g. Leuning *et al*., 2008). It is an established technique with low to moderate costs, which are primarily associated with data processing and specialised equipment. Flux rates measured usually lie within the typical range of CO_2 emissions from soils and different land covers (10's of g/m²/d), while higher emission rates can easily be determined. However, whether the ECM could detect a release of CO_2 from a storage site strictly depends on the ratio between the integral CO_2 flux from the footprint area and the seepage rate from the point source (e.g. an abandoned well). A seepage rate of 0.1 t/d from the ZERT release experiment (Lewicki *et al*., 2009) was not distinguishable from the background CO_2 emissions, whereas the release of 0.3 t/d significantly increased the measured flux rates compared to the base line emission of the area.

With a finer spatial resolution than the ECM, long open path tuneable diode lasers can be used to measure the distance-averaged concentration of a specific gas in the air, with the distance covered ranging from tens to hundreds of metres. Models exist for a number of gas species, including CO_2 and CH_4, and various experiments have been conducted to study their application to geological CO_2 storage sites. The long open path technique offers the potential to intersect a temporally and spatially variable plume, and can be adapted for long-term, unattended monitoring of a storage site. Since the relative sensitivity of the method to CH_4 can be ten times greater than CO_2, the method may be more suitable for monitoring sites where significant CH_4 is present (such as CO_2-EOR). Leakage quantification using these instruments can be done via modelling of the open path results in combination with detailed wind measurements. Vertical radial plume mapping (VRPM) has been recommended by the US EPA for quantifying gas-phase leakage (US EPA, 2005), while inverse dispersion modelling, involving the backward Lagrangian Stochastic approach with the Monin-Obuhkov Similarity Theory, has also been tested with some success (e.g. Loh *et al*., 2009).

Short closed path detectors involve the introduction of a gas sample into a chamber, prior to optical (typically infrared) analysis for quantification of specific gas components. Similar to the long open path systems, inverse dispersion modelling can be used with the short closed path detectors for leakage quantification. Since they are relatively cheap, flexible and robust with respect to interference from other gases, they can potentially be placed close to the ground, and deployed in large numbers to form a comprehensive monitoring network. An added potential for real-time isotopic analysis, which would help clarify the origin of the gas, is offered by short closed path diode lasers, although these are more cumbersome and expensive.

Near surface gas chemistry offers two relatively low cost means of monitoring and quantifying CO_2 leakage: gas flux measurements at the surface and analysis of soil gas sampled at a depth of 0.5 to 1 m. These two methods are often conducted together due to their complimentary nature: flux measurements defining actual transfer rates out of the soil and soil gas being used to constrain CO_2 origins and flux estimates. Both are point measurements that are affected by issues related to resolution, sensitivity, and costs. Flux measurements are typically made for CO_2 and sometimes associated CH_4, whereas soil gas samples can be analysed for any gas species that can give useful information (such as CO_2 and other major species, natural and man-made tracer gases, and various isotopes).

Typically, leakage quantification using gas flux measurements consists of sampling on a grid, interpolating between points, conversion to total CO_2 flux for the measurement area, and subtracting near-surface contributions based on baseline studies or soil gas data. Two main factors will influence the success of these methods for accurately quantifying leakage from a CO_2 storage site: their ability to locate the leak and define its physical extent, and their ability to accurately separate baseline from leakage flux rates. Based on the assumption that the location of a leak can be inferred to a reasonable level of accuracy, via regional gas measurements possibly combined with other techniques like eddy covariance, a number of studies have assessed the sensitivity of these methods. For example:

1. controlled leaks of 0.1 and 0.3 t/d CO_2 at the ZERT site were accurately quantified using CO_2 flux measurements, with the latter leak rate being estimated at 0.31 ± 0.05 t CO_2/day (mean ± 1 SD) (Lewicki *et al*., 2010);
2. soil gas monitoring of perfluorocarbon tracers added to injected CO_2 at the West Pearl Queen depleted oil formation quantified a leakage rate of 2.82 x 10^3 g CO_2/year (Wells *et al*., 2007), which corresponded to 0.014% of the total injected CO_2;
3. soil gas concentration and isotope measurements, CO_2 flux results and computer modelling were used to estimate a total leakage rate from the Rangely CO_2-EOR project of less than 170 t/year CO_2, which converts to approximately 0.01% of the yearly injected CO_2 (Klusman, 2003).

Autonomous monitoring stations have also been created that can analyse gas concentrations and fluxes on a continual basis over extended periods of time, potentially providing valuable baseline information prior to calculating CO_2 leakage (Annunziatellis *et al*., 2004).

Ecosystem-based monitoring can be used to qualitatively detect and monitor leakage into near surface systems, particularly when undertaken in combination with soil gas surveys. The health of plants and microbial populations inhabiting the soil at a suspected leak can be compared with control sites representing the background in a low cost way, perhaps by eye. However, ecosystem monitoring is unsuitable for leakage quantification since above certain levels, further damage will not be observed.

Impacts on vegetation, and possibly soil geochemistry, due to CO_2 leakage may also be detected using airborne remote sensing techniques. Changes in vegetative cover between successive spectral images are usually assessed using the normalised difference vegetation index, although other methods have been proposed to account for complicating factors such as atmospheric, soil moisture, anisotropic and spectral effects. However, leakage quantification may not be possible as above certain levels (or duration) of leakage, further damage will not occur. Thermal imaging may also potentially detect leakage indirectly if a measurable temperature anomaly is associated with the leakage, and it may be possible to estimate leakage rates based on determination of the heat energy required to produce it. High resolution airborne hyperspectral scanners may detect CO_2 (and CH_4) directly using absorption features that lie within their wavelength range. Quantification of anomalous CO2 flux may be estimated using methods including an inversion technique which attempts to establish a relationship between CO_2 plume related radiance and CO_2 concentration, and the Continuum Interpolated Band ratio method (Spinetti *et al*., 2008). However, at present it is not clear whether small scale surface emissions could be detected given the relatively coarse spatial resolution of satellite images.

Research is underway to develop a methodology for the unsupervised detection of CO_2 leakage using multispectral and hyperspectral images obtained from airborne and spaceborne sensors, which could prove an invaluable asset in terms of spatial and temporal coverage for long term storage monitoring (Govindan *et al*., 2011a). The methodology is based on finding anomalies in latent variables that may be related to changes in vegetation cover and soil geochemistry. Although false positives may arise from factors such as agricultural practices and other land use changes, the methodology could pinpoint areas worthy of further investigation with surface gas sampling or laser diode technologies for diagnosis and leakage quantification.

Since leakages into the soil or atmosphere are likely to occur over a small area in comparison with the extent of the reservoir, monitoring strategies should be based either on the detection of leakages using methods that can offer a good spatio-temporal resolution, or involve monitoring focused on specific locations that lie over identified potential leakage pathways. Multiple analyses of different indicative components including tracers can help clarify the origin of the gas and improve the precision of any estimate. *In situ* measurements will reduce errors, while autonomous monitoring may reduce costs, as will piggy-backing of geochemical surveys on surveys conducted with other techniques such as acoustic or seismic surveys. Sensitivity and resolution are difficult to quantify as no controlled experiments appear to have been conducted to date. However, accurate estimates of background concentrations and current directions and strengths will have the greatest influence on the reduction of uncertainty related to plume flux calculations.

Table 7. Summary of methods suitable for various tasks in monitoring the surface/atmosphere.

Task	Method	Pre-injection	Operation	Post-injection	Comments
Leakage detection	Ecosystems				Suitable in accessible and rural but populated areas; gas sampling required to verify cause of stress; baseline and natural variation required
	Long open path diode lasers				Can be left unattended for long-term monitoring; covers 10s to 100s of m so optimal siting required; baseline and natural variation required
	Eddy covariance method				Can cover a wide area (several km^2) but would probably require a high leakage rate; baseline and natural variation required
	Remote sensing				Based on vegetation stress, thermal variation or direct absorption; ground sampling to verify cause; baseline and natural variation required
Leakage quantification	Near surface gas chemistry				Analysis of soil gas combined with flux measurements; baseline and natural variation required
	Short closed path NDIR				Suitable for point monitoring (e.g. well head); baseline and natural variation required
	Short open path diode lasers				Can be deployed in large numbers to form a monitoring network; baseline and natural variation required
	Long open path diode lasers				More sensitive to CH_4, therefore may favour CO_2-EOR monitoring; baseline and natural variation required
	Eddy covariance method				Probably requires a significant leakage rate, but could cover a large area; baseline/natural variation required
	Remote sensing				Offers potential for post-closure monitoring but methods need to be developed; baseline and natural variation required
Reducing uncertainty	Isotopic analysis				Baseline and natural variation required
	Tracers				Addition of e.g. perfluorocarbons to injected CO_2 to clarify origin of CO_2;
	Meteorological monitoring				Enables winds and climatic effects to be taken into consideration

Colour coding represents suitability considerations: blue=good; yellow=medium; pink=poor.

Of the methods discussed above, soil gas and gas flux surveys show significant promise for quantifying CO_2 leakage at the ground surface, offering the potential to provide the most accurate estimates assuming appropriate sampling strategies. The extent of the leakage area must be established, and anthropogenic CO_2 must be distinguished from natural flux from, for example, biological activity in the soil. Temporal variations must also be considered. The deployment of soil gas and gas flux methods may be best undertaken in conjunction with a wider monitoring program, which may include, for example, a network of eddy covariance towers.

3.2.3 Shallow subsurface monitoring

Of the deep subsurface monitoring methods briefly referred to earlier in this Section, several are also suitable for shallow subsurface monitoring. In the near-surface environment, CO_2 flow is likely to occur as bubbles migrating vertically along a fault or near a borehole. Therefore, although 4D seismic methods with a short offset could detect shallow leakage, quantification may not be achievable. However, gravimetric and resistivity/conductivity-based methods may be deployed while simultaneously monitoring the reservoir, and can potentially be used for leakage detection in the shallow subsurface prior to the deployment of techniques able to quantify flux. The time series data collected can be used to assess and account for natural variations.

Gravimetric methods operated in continuous or time-lapse mode may theoretically be able to characterise volumes of gas in the order of a few hundreds of tonnes in the shallow subsurface, depending on the saturation. Surface variations would need to be taken into consideration. This could be accomplished with the aid of airborne gradiometry. At present the method is not established for use in CO_2 monitoring and may prove to be prohibitively expensive. Feasibility and calibration of such measurements should be undertaken on several natural analogues, where the geological models and CO_2 saturation are reasonably well characterised.

The electrical and electromagnetic methods discussed above may also offer the potential to detect increased CO_2 presence in shallow groundwater. In particular, airborne electromagnetic techniques are well-established in groundwater exploration studies (e.g. Siemon *et al*., 2009), having provided information on aquifer structure and water quality for over three decades. Helicopter or fixed wing aircraft surveys are carried out in the frequency domain or time domain, whereby the depth of penetration depends on the frequency (or time channel) of the signal. Homogeneous or layered half-space models are typically used to invert secondary magnetic field values into resistivities and depths. The applicability of the technique may be limited due to noise originating from a variable water table and high natural CO_2 flux. Therefore a long period of pre-injection baseline monitoring would be recommended. In addition, use of airborne EM may be limited in areas where significant clay contents, or naturally high background levels of dissolved solids are present. Since the method provides no geochemical discrimination, ground-based sampling techniques (see below) should be employed to establish the cause of any enhanced conductivity.

In order to provide a quantitative estimate of CO_2 leakage, a potential method may be to use a numerical simulator such as TOUGHREACT (Xu *et al*., 2004) to predict whether a measureable impact on the groundwater would occur given an ingression of leaked CO_2, in terms of a change in the total dissolved solids content. An empirical relationship between TDS and electromagnetic recordings could theoretically then be used to estimate the amount of CO_2 that has dissolved in the groundwater. At present, these methods are not yet established, but are the subject of current research and may provide monitoring and quantification solutions in the future.

Hydrochemical factors may be useful for the detection and quantification of leakage, particularly in inhabited areas which contain springs or streams. For example, waters containing elevated CO_2 levels that emerge at the surface may visibly contain bubbles, and oxidation of dissolved iron may lead to the appearance of rusty deposits. Routine monitoring of pH and other indictors may also detect leakage, for example in more urban or agricultural areas served by a network of extraction or monitoring wells.

Once leakage of stored CO_2 into shallow groundwater has been detected, it may be possible to estimate quantities by combining measurements of groundwater flux with analysed concentrations of carbon species. The accuracy of the estimation would improve with repeated spatio-temporal sampling, particularly where the groundwater has significant natural variability. The flux of CO_2 bearing springs may be measured volumetrically using vessels, weirs or tracer dilution methods. Where the CO_2 can only be determined within the groundwater, the volume of water may be estimated using the porosity and size of the aquifer.

Table 8. Summary of methods suitable for various tasks in monitoring the shallow subsurface.

Task	Method	Pre-injection	Operation	Post-injection	Comments
Leakage pathways	3D/4D seismic surveys				Imaging shallow subsurface structure; could be done at same time as reservoir/overburden monitoring with shorter offset
	4D multi-component seismic survey				More detailed shallow subsurface imaging
	Passive microseismic				Supplementary seismic data for subsurface imaging; usefulness may depend on seismic activity and noise
Leakage detection	Hydrochemical monitoring				Particularly suitable if a groundwater monitoring network already exists; baseline and natural variation required
	Visible surface effects				Indicators of possible leakage include bubbles and rusty deposits; baseline and natural variation
	Gravimetry				Detects changes in density; hydrochemical sampling required to verify CO_2 leakage; baseline and natural variation required
	Electrical/EM				Detects changes in conductivity or resistivity; hydrochemical sampling required to verify CO_2 leakage; baseline and natural variation required
	Airborne EM				Detects changes in resistivity; hydrochemical sampling required to verify CO_2 leakage; baseline and natural variation required
	4D seismic survey				Possibly not sensitive enough for detection of CO_2 bubbles in aquifer
	4D multi-component seismic survey				Possibly not sensitive enough for detection of CO_2 bubbles in aquifer
Leakage quantification	Hydrochemical monitoring combined with groundwater flux				Particularly suitable if a groundwater monitoring network already exists; baseline and natural variation required
	4D seismic survey				Probably not sensitive enough for detection of CO_2 bubbles in aquifer
	4D multi-component seismic survey				Probably not sensitive enough for detection of CO_2 bubbles in aquifer
	Gravimetry				Analysis of density changes; needs testing on analogues; hydrochemical sampling to verify CO_2 leakage; baseline and natural variation required
	Electrical/EM				Analysis of resistivity/conductivity changes; needs testing on analogues; hydrochemical sampling to verify CO_2 leakage; baseline and natural variation required
	Airborne EM				Analysis of resistivity changes; hydrochemical sampling to verify CO_2 leakage; baseline and natural variation required
Reducing uncertainty	Isotopic analysis				elucidates source of gases
	Tracers				Addition of e.g. perfluorocarbons to injected CO_2
	Gravimetry				Can help constrain density when used in conjunction with seismic quantification methods
	Electrical/EM and Airborne EM				Can help constrain saturation when used in conjunction with seismic quantification methods

Colour coding represents suitability considerations: blue=good; yellow=medium; pink=poor.

Due to natural variability and dilution effects, overlapping of the concentration ranges between adjacent unaffected waters and CO_2-bearing groundwater is likely. In this case, the analysis of isotope or tracer concentrations may enable the differentiation between natural and anthropogenic sources. In most CO_2 injection projects, perfluorocarbons are the preferred tracer chemical.

4 REVIEW OF REQUIRED CO_2 LEAKAGE QUANTIFICATION ACCURACY

This section reviews current and proposed regulations with respect to the required CO_2 leakage quantification accuracy

4.1 EU Regulations for CO_2 Geological Storage

The EU Emissions Trading Scheme (EU ETS) was launched at the beginning of 2005, and builds upon the mechanisms set up under the Kyoto Protocol: international emissions trading; the Clean Development Mechanism (CDM); and Joint Implementation (JI) (EC, 2008). The scheme relies on the fact that creating a price for carbon represents the most cost-effective way to achieve the target reductions in greenhouse gas emissions. In 2013 the scheme will be extended to include installations undertaking the capture, transport and geological storage of CO_2 emissions.

EU Directive 2009/31/EC, on the geological storage of CO_2, entered into force on the 25th June 2009. This lays down requirements covering the entire lifetime of a storage site, and specifies that the operation of a site must be closely monitored, with provisions on closure and post-closure obligations. The Directive states that:

"Monitoring is essential to assess whether injected CO_2 is behaving as expected, whether any migration or leakage occurs, and whether any identified leakage is damaging the environment or human health. To that end, Member States should ensure that during the operational phase, the operator monitors the storage complex and the injection facilities on the basis of a monitoring plan designed pursuant to specific monitoring requirements. The plan should be submitted to and approved by the competent authority. In the case of geological storage under the seabed, monitoring should further be adapted to the specific conditions for the management of CCS in the marine environment."

Article 16 of Directive 2009/31/EC lays out the required measures in case of leakages or significant irregularities. In the event of any leakage, inclusion in the EU ETS ensures that emissions would lead to the surrender of allowances. As stated in the Directive, "Liability for climate damage as a result of leakages is covered by the inclusion of storage sites in Directive 2003/87/EC, which requires surrender of emissions trading allowances for any leaked emissions." However, in June 2010, the Decision 2007/589/EC (establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC) was amended to state that the leakage "may be excluded as an emission source subject to the approval of the competent authority, when corrective measures pursuant to Article 16 of Directive 2009/31/EC have been taken and emissions or release into the water column from that leakage can no longer be detected."

A further amendment to Decision 2007/589/EC states that "where applicable, quantification approaches for emissions or CO_2 release to the water column from potential leakages as well as the applied and possibly adapted quantification approaches for actual emissions or CO_2 release to the water column from leakages, as specified in Annex XVIII." This Annex gives activity-specific guidelines for the geological storage of CO_2 in a storage site permitted under Directive 2009/31/EC. Part 3 concerns leakage from the storage complex. In particular:

"Monitoring shall start in the case that any leakage results in emissions or release to the water column. Emissions resulting from a release of CO_2 into the water column shall be deemed equal to the amount released to the water column."

Furthermore, with respect to quantification:

“Emissions and release to the water column shall be quantified as follows:

$$CO_{2\ emitted}\left[tCO_2\right] = \sum_{T_{start}}^{T_{end}} L\ CO_2\left[t\frac{CO_2}{d}\right]$$

“With

$L\ CO_2$ = mass of CO_2 emitted or released per calendar day due to the leakage. For each calendar day for which leakage is monitored it shall be calculated as the average of the mass leaked per hour [CO_2/h] multiplied by 24. The mass leaked per hour shall be determined according to the provisions in the approved monitoring plan for the storage site and the leakage. For each calendar day prior to commencement of monitoring, the mass leaked per day shall be taken to equal the mass leaked per day for the first day of monitoring.

T_{start} = the latest of:

(a) the last date when no emissions or release to the water column from the source under consideration were reported;
(b) the date the CO_2 injection started;
(c) another date such that there is evidence demonstrating to the satisfaction of the competent authority that the emission or release to the water column cannot have started before that date.

T_{end} = the date by which corrective measures pursuant to Article 16 of Directive 2009/31/EC have been taken and emissions or release to the water column can no longer be detected.

“Other methods for quantification of emissions or release into the water column from leakages can be applied if approved by the competent authority on the basis of providing a higher accuracy than the above approach.”

With regard to uncertainty related to the quantification to leakage, the amendment continues:

“The amount of emissions leaked from the storage complex shall be quantified for each of the leakage events with a maximum overall uncertainty over the reporting period of ± 7.5%. In case the overall uncertainty of the applied quantification approach exceeds ± 7.5%, an adjustment shall be applied, as follows:

$$CO_{2\ reported}[t\ CO_2] = CO_{2\ quantified}[t\ CO_2] \times \left(1 + \left(uncertainty_{system}[\%]/100\right) - 0.075\right)$$

“With

$CO_{2\ reported}$ = Amount of CO_2 to be included into the annual emission report with regards to the leakage event in question;

$CO_{2\ quantified}$ = Amount of CO_2 determined through the used quantification approach for the leakage event in question;

$Uncertainty_{system}$ = The level of uncertainty which is associated to the quantification approach used for the leakage event in question, determined according to section 7 of Annex I to these guidelines.”

Section 7 of Annex I requires that the operator has an understanding of the main sources of uncertainty when calculating emissions. Measurement-based calculations should be based on the specifications provided by the supplier of the instruments used, and if these are not available the operator should provide for an uncertainty assessment. In both cases, effects such as ageing, conditions of the physical environment, calibration and maintenance should be taken into account. The operator should consider the cumulative effect of all components of the measurement system on the uncertainty of the annual activity data using the error propagation law, which is provided in Annex I of the 2000 Good Practice Guidance and in Annex I of the revised 1996 IPCC Guidelines (Reporting Instructions). Finally, the operator is required, via the quality assurance and control process, to manage and reduce the remaining uncertainties of the emissions data in his emissions report.

From the information extracted from the guidelines and summarised in the preceding paragraphs, it is clear that the quantification and minimisation of uncertainties is a key requirement. Uncertainties must be fully accounted for, and the greater the uncertainty, the greater the penalty resulting from any CO_2 leakages.

4.2 Regulations for CO_2 Geological Storage in other regions

4.2.1 US

At present, there are no national regulations covering the geological storage of CO_2 in the US, although in 2008 the EPA proposed that the existing Underground Injection Control program of the Federal Safe Drinking Water Act be amended to regulate carbon injection facilities. This was primarily intended to prevent CO_2 from leaking into groundwater supplies, although protection of human health and ecosystems via surface emission is also likely (US EPA, 2008). The proposal requires that operators must monitor the injection activity using available technologies to verify the location of the injected fluid and the pressure front, and demonstrate that injected fluids are confined to intended storage zones. The addition of tracers to the injected fluid is recommended to help aid leak identification, although questions have been raised regarding their effectiveness, cost-effectiveness, possible environmental effects and the technical challenges posed in their analysis.

The EPA proposes that, along with their permit application, operators submit a testing and monitoring plan to verify that the project is operating as intended and not endangering drinking water resources. This plan would include: analysis of the chemical and physical characteristics of the CO_2 stream; monitoring of the injection pressure, rate and volume; monitoring of annular pressure and fluid volume; corrosion monitoring; determination of the position of the CO_2 plume and area of elevated pressure; monitoring of the geochemical changes in the subsurface; and, at the discretion of the Director, monitoring for CO_2 fluxes in surface air and soil gas. The program should be site-specific, based on the identification and assessment of potential CO_2 leakage paths complemented by computational modelling of the site.

The operators would be required to track the subsurface extent of the plume and pressure front using pressure gauges, indirect geophysical techniques or other down-hole CO_2 detection tools. Groundwater quality would be monitored and compared with baseline measurements. Pressure fall-off testing would be required at least once every 5 years in order to identify potential leakage. The EPA also proposes that the site is monitored over a 50-year post-injection timeframe, with this either being possibly reduced or extended according to the performance of the site. While the proposal does not specifically require quantification of any leakage of CO_2, the operator must take all steps reasonably necessary to identify and characterise any release.

A further rule, requiring carbon storage facilities to report their emissions, was proposed by the US EPA in early 2010 (US EPA, 2010). This supplements the greenhouse gas reporting rule that was finalised in 2009. Geologic storage facilities would be required to calculate CO_2 sequestered by subtracting total CO_2 emissions from the CO_2 injected in the reporting year, where the emitted quantity would include any injected CO_2 that leaked from the subsurface to the surface. The proposal notes that the Inland Revenue Service's Credit for Carbon Dioxide Sequestration notice does not outline procedures or provide a mechanism for quantifying and reporting any CO_2 leakage that may occur.

The EPA proposes that geologic storage facilities would be required to report the amount of leakage to the surface (if any), but refrains from proposing specific procedures or methodologies. Instead, operators would be required to develop and implement a site-specific approach to monitoring, detecting and quantifying CO_2 leakage. The Monitoring, Reporting and Verification (MRV) plan should describe the approaches that the operator will take to quantify CO_2 emissions if leakage is detected. The approach should be specific to the type of potential leak, and may involve estimation or direct measurement. In cases where a leak is not quantified by estimation, the reporter must assume that the duration of the leak is equal to the duration between null monitoring results unless supplementary data can provide a better indication of the timing of the leak. An approach for an uncertainty assessment of the leakage estimates and measurements derived from the proposed modelling and monitoring at the storage facility should also be included.

Although the national legislation has yet to be finalised, currently 21 US states have incentives or regulations in place for CCS.

4.2.2 Australia

On 25 November 2005, the Australian Ministerial Council on Mineral and Petroleum Resources (MCMPR) endorsed the Regulatory Guiding Principles for Carbon Dioxide Capture and Geological Storage, with the aim of achieving a nationally-consistent framework for CCS activities. Regarding monitoring and verification, the Principles state that (MCMPR, 2005):

1. Regulation should provide for appropriate monitoring and verification requirements enabling the generation of clear, comprehensive, timely, accurate and publicly accessible information that can be used to effectively and responsibly manage health, safety and economic risks.
2. Regulation should provide a framework to establish, to an appropriate level of accuracy the quantity, composition and location of gas captured, transported, injected and stored and the net abatement of emissions. This should include identification and accounting of leakage.

Subsequent amendments to the Commonwealth Offshore Petroleum Act 2006 (OPA) to provide access and property rights for CCS in Australian waters were developed in consistency with the Regulatory Guiding Principles for CCS. The legislation allows for the establishment of an effective regulatory framework to ensure that projects meet health, safety and environmental requirements, and incorporates a licensing framework broadly similar to the existing regime for petroleum activities. The regulatory framework, consisting of guidelines and regulations to underpin the legislation, is currently being developed.

The Proposed Greenhouse Gas Geological Sequestration Regulations 2009 are aimed at supporting the implementation and administration of the Greenhouse Gas Geological Sequestration Act 2008, and to address issues such as monitoring requirements. The 2008 Act requires that each site develop a monitoring and verification plan.

4.2.3 Canada

The Carbon Capture and Storage Statutes Amendment Act, 2010 (Legislative Assembly of Alberta, 2010), was passed in the Alberta legislature on December 1st, 2010. The legislation supports Alberta's four commercial-scale CCS projects by clarifying pore space ownership and ensuring that the Government of Alberta assumes long-term liability for the stored CO_2 after the operator has demonstrated that is has been successfully contained. The Act comprises amendments to the Energy Resources Conservation Act, the Mines and Minerals Act, the Oil and Gas Conservation Act, the Public Lands Act and the Surface Rights Act.

The legislation establishes a fund, to which the operators will contribute, that will be available to cover ongoing monitoring costs and any necessary remediation. The amended Oil and Gas Conservation Act allows the Board to takes action in the event of an escape of gas; however, at present there is no requirement to quantify any CO_2 leakage.

4.3 Uncertainty estimation and minimisation

As discussed above, the EU specifies that in the event of a leakage of stored CO_2, uncertainties must be fully accounted for, and the greater the uncertainty, the greater the penalty. International legislation may follow suite in the coming years. In general, the uncertainties associated with the estimation of CO_2 leakage are likely to be high for a number of reasons, including:

- Leakages may be too small to be quantified due to low sensitivity of the monitoring methods used.
- For leakages to the atmosphere or marine environment, wide areas above the injection zone will have to be monitored, and in general, the large the coverage, the lower the spatial resolution.

Uncertainties in leakage quantification estimates may be reduced through the integration of monitoring methods, as discussed in Section 3.

Whereas some methods have only been tested to date on natural analogues with high emission rates, others have been used on controlled release test sites (e.g. ZERT) and on analogues having lower flux rates. More such experiments are needed to improve our understanding of the capabilities, accuracies, and costs achievable using the various methods and their optimal combinations.

The following sections outline the current knowledge regarding uncertainties associated with the various methods identified for quantifying CO_2 leakage from a storage reservoir, and suggest how uncertainties may be accounted for and potentially reduced.

4.3.1 Marine and terrestrial aquatic environment monitoring methods

Hydroacoustic monitoring methods

Acoustic methods (sidescan sonar and multi-beam echo-sounding) applied in water/seawater hold a strong potential for efficient detection of leaks and seeps, both of dissolved CO_2 and in particular gas in the form of bubbles. However, there may be other major gases that will interfere and thus cause an unnecessary alarm. Methane is one such gas that may leak by itself, independent of any rising CO_2, or arrive with or before the CO_2. Therefore, gas testing should be performed after detection. The acoustic methods can be able to classify the size of a leak, as small, medium or large. For quantification, it may be necessary to undertake additional sampling, for example using the bubble stream chemistry analysis techniques described in Section 2.1.4. Then, acoustic methods can help to monitor and quantify with low uncertainty a leak with constant flux over time.

Acoustic impedance is dependent on difference, and in the dissolved gas case the uncertainty will therefore be large. On the other hand, such manifestations at depths of less than around 500 m will reflect a small leak, and bubbling with massive impedance difference will occur. Uncertainties might be reduced if the measurements are made close to the leak, and close to the seabed.

Bubble stream chemistry

Bubble streams detected by hydroacoustic monitoring methods can be sampled and analysed to determine the composition and source of the gas. A combination of techniques to determine gas flux and composition may potentially be used to quantify CO_2 leakage. Sources of error and uncertainty may include location measurements, sampling and analytical errors, variability in the gas composition and instrumental drift (in the case of, for example, CTD probes). The use of tracers in the injected CO_2 stream, and/or isotopic analysis, will help to confirm the source of the gas.

High Resolution Reflection Profiling

High resolution (HR) reflection profiling methods currently represent a cost-effective means for the qualitative detection of gas leakage in marine (or lacustrine) environments, as well as for the investigation of subsurface gas migration pathways within the shallow (102 m) subsurface. Rising streams of bubbles (of CO_2 or other gases) may be recognised as hydroacoustic plumes, while a variety of subbottom features may indicate gas at concentrations as low as 0.5%. The relatively high frequencies used (102-105 Hz) afford vertical resolution of metric to sub-metric scale, but the detection of individual leaks is ultimately limited by data densities, i.e. profile spacing. A practical means to reduce this uncertainty is to use HR methods in combination with sonar mapping systems (sidescan, multibeam), which allow the accurate detection of leaks within the water column (e.g. Naudts *et al.*, 2006).

Theoretical models of the frequency-dependent effects of gas bubbles on P-wave attenuation and velocity offer the potential of inverting multiple frequency HR data types to quantify gas properties (e.g. void fraction, bubble size distribution, gas flux over time). This is an area of active research, involving HR and other data types (e.g. sonar), the main uncertainty being the lack of experimental data to validate and improve theoretical models of P-wave attenuation across a full range of frequencies, including for bubbles in sediments (Mathys *et al.*, 2005; Best *et al.*, 2006).

Surface water chemistry

As described in Section 2.1.6, surface water chemistry methods can be subdivided into measurements of dissolved gas or dissolved elements, with the former being a direct estimate whereas the latter is a secondary or proxy estimate. Techniques for both exist which provide either continuous, *in situ* analysis of a monitored parameter using a wide variety of sensor types, or which involve discontinuous spatial sampling and eventual on-board or on-shore laboratory analysis. A hybrid method involves continual pumping of water from a fixed depth on board ship for continual dissolved gas analysis. Although there are a wide variety of sensors and analytical techniques available, their application to leakage quantification would likely involve variations on a single general approach in the water column. Typically this consists of measuring the dissolved CO_2 concentration (or proxy) along a cross-section perpendicular to the principle plume migration direction and combining these results with the measured current flow rates to estimate the total leakage rate (e.g. Keir *et al*., 2008; Mau *et al*., 2006).

Uncertainties associated with this approach are primarily linked with the complexities and unknowns of the natural system. For example, Mau *et al*. (2006) estimated that 10-20% of their uncertainty was due to variations in the local background, whereas over 50% was the result of current velocity variations. Other site specific uncertainties could include: variable current directions and tidal effects causing plume smearing; multiple leakage points that form overlapping and spatially incoherent plumes; temporal variations in gas flow rates causing a differential vertical distribution of dissolved plume constituents; the additional seepage of CO_2-saturated pore-water at the sediment-water interface that is not observed in measurements due to its different spatial distribution; and potential losses of dissolved CO_2 to the atmosphere at shallow release sites. Most of these uncertainties can be decreased by conducting long-term monitoring of currents and baseline concentrations prior to injection, by combining these measurements with other techniques that are able to define active leakage locations (such as hydroacoustic surveys for bubble release points and benthic chambers for CO_2-saturated water seepage), by combining other estimation techniques that account for different "compartments (such as equilibrator surveys for water-atmosphere losses or bottom water surveys for basal seepage), and by conducting multiple surveys at different times to assess site variability.

Uncertainties related to the actual measurement methods depend on whether they are discontinuous or continuous techniques. The discontinuous methods are typically well-developed and analytically sensitive; however only a limited number of samples can be collected due to time and cost limitations. A low sampling density can introduce uncertainties in the calculated leakage rates if the system is spatially heterogeneous. In contrast, the continuous methods can provide high density sampling (when towed or mounted on ROV's, AUV's, or gliders). However, they currently represent a new technology that is limited by lower sensitivities and slow response times (e.g. Neuman *et al.*, 2008). Uncertainties in the former could be reduced by reducing sample through-put times, whereas uncertainties in the latter will probably become smaller as these methods become more technologically mature.

Finally, considering that logistics are much more difficult and costs much higher for studies conducted in off-shore settings, there has been almost no systematic testing of leakage quantification methodologies.

Instead, the examples mentioned here and discussed in more detail in Section 2.1.6 were all taken from other disciplines that in some respects are similar, but which have different final scientific goals. As such, a principle need for reducing the uncertainties associated with surface water chemistry techniques will involve actual field trials on both natural leakage as well as controlled release sites.

4.3.2 Atmospheric monitoring methods

Long open path (IP diode lasers)
Long open path instruments measure the distance averaged concentration of a gas in the atmosphere between two points, typically a source/sensor at one end and a reflector at the other. The most common system used in CCS tests is the Tunable Diode Laser (TDL), although the FTIR (Fourier Transform InfraRed spectroscopy) has also been tested. For quantification purposes two different approaches have been proposed. The Vertical Radial Plume Mapping (VRPM) method involves creating multiple beam pathways in a vertical plane downwind from the leak and using the resultant two dimensional map of the plume, together with wind strength and direction data, to calculate the amount of leaking gas. In contrast, backward Lagrangian Stochastic modelling based on the Monin-Obukhov Similarity Theory (bLS-MOST) involves a single, horizontal beam pathway downwind of the leak and, preferably, continual monitoring of background concentrations of the gas of interest upwind. The VRPM method has been developed in collaboration with the US EPA for pollution monitoring, whereas bLS-MOST has been used to quantify known leakage rates of both CH_4 and CO_2. Because bLS-MOST has been tested more in the field of CCS we will concentrate more on it; however many of the uncertainties related to it also apply to VRPM.

As described in Section 2.2.1, the bLS-MOST has been applied with promising results. For example, Flesch *et al*. (2004) obtained an estimate/actual leakage ratio of 1.02 ± 0.2 for a controlled CH_4 leak using a TDL, Loh *et al*. (2009) obtained 0.95 ± 0.09 (TDL) and 1.02 ± 0.03 (FTIR) for a controlled CH_4 leak but only 1.87 using FTIR for a controlled CO_2 leak, while Trottier *et al*. (2009) report quantification “within 50%” of the released amount. These experiments have highlighted various uncertainties in the application of this technique.

According to the manufacturer of one TDL, an accuracy of ± 2% is attained when the R^2 parameter is greater than 95%. However the R^2 value will decrease (thus uncertainty / measurement error will increase) with poor source-reflector alignment, poor system maintenance, or difficult measurement conditions (e.g. dust, fog, etc.). It can be expected that instrument accuracy will improve with time (considering the relatively recent development of this technology), even if its contribution to the overall uncertainty of the quantification estimates is small compared to other uncertainties.

The choice of gas to be monitored can greatly influence uncertainty, as illustrated above by the great difference in accuracy obtained for CH_4 versus CO_2. This relates to the lower concentration and higher stability of the background values for the former compared to the latter. However considering that for CCS applications CO_2 is the principle gas, whereas CH_4 will likely be present in trace amounts and will be consumed to some extent by oxidative reactions in the soil, this advantage in sensitivity and precision may be lost. Related to this issue for the application of bLS-MOST is an accurate measurement of the upwind, background gas concentration. For example, Loh *et al*. (2009) attributed much of their error in the TDL experiment to the use of two different instruments (for upwind and downwind monitoring). These had differential drift, which resulted in an inaccurate background field measurement. In addition, the FTIR CO_2 experiment was able to obtain only poor precision on a variable background CO_2 system. As such the use of artificial tracers co-injected with the CO_2 may hold promise if open path systems can be developed for them with a sufficiently low detection limit and stable signal.

Particularly important for this method is that the basic assumptions within the MOST approach are respected, and thus data filtering to obtain appropriate wind conditions was found to be necessary to reduce quantification errors, including using only data whereby the plume was completely intersected by the open pathway. This observation is then, in turn, closely linked to the chosen distance between the leak and the pathway, as shorter distances allow for greater sensitivities while greater distances allow for better plume capture. Local site conditions are also critical, as variable winds, irregular terrain, the occurrence of barriers (like buildings or forested areas) can greatly complicate plume migration/distribution and thus data interpretation.

Other issues that have been raised regarding the accuracy of this method include the observations that: the enrichment in the monitored gas above ambient values must be >1% to obtain accurate results (Loh *et al.*, 2009); most experiments have been conducted with a source – beam pathway distance on the order of 10 to 50 m, meaning that the location of the leak must be very well defined; and all experiments have been performed on point sources, which implies (considering background and sensitivity issues) that this method could not be accurately applied to a diffuse leak.

Short open path (IR diode) lasers

Short open path instruments are similar to long open path instruments, with the primary difference being that the beam pathway is "folded" in on itself with mirrored systems such that a 10 or 20 m path length can be contained within a 1 – 2 m long interval. Typically these units are vehicle mounted (plane, truck, or ATV) due to their very rapid response times, minimal memory effects, and high sensitivity. However, as they conduct measurements in the air at specific locations at specific times, the complexity and rapidly changing nature of wind patterns means that it will be extremely difficult to obtain a static "snap-shot" of gas distribution in a plume which would allow for modelling and a subsequent leakage quantification. In fact, these tools are probably much more adapted to monitoring and leakage detection than to leakage quantification. Nonetheless, attempts have been made to use airborne instruments to estimate the leakage rates of gases from volcanoes (e.g. Casadevall *et al*., 1994) by making multiple orthogonal passes through a plume in the atmosphere and processing the results using the cross-sectional area of the plume, the wind speed, and its CO_2 content. Although theoretically applicable in a CCS context, the fact that any leakage plumes from a storage site would be closer to ground level and winds far less constant means that such surveys would be logistically difficult and unsafe, and probably not produce accurate results.

Short closed path (NDIRs and IR)

Short closed path detectors involve the introduction of a gas sample into a chamber via a pump or by diffusion, and the quantification of a specific gas component by passing light across the chamber and through the sample. Like some of the methods described above, these techniques use the absorption of a specific wavelength by the gas species of interest, but differ due to the use of the measurement chamber. Advantages include greater portability, reduced atmospheric interferences (such as dust), and lower costs, whereas disadvantages include a lower sensitivity, a slower response time, and greater required sample memory.

Short closed path detectors are used extensively in gas flux and soil gas measurements, and are thus also discussed below in the section on near-surface gas geochemistry. Instead examples here will be restricted to above ground leakage monitoring using these tools. Two CCS-related studies have been reported in the literature, although only one actually uses these instruments to quantify leakage (Loh *et al*., 2009). In the other study (Lewicki *et al*., 2010) the units are used strictly for monitoring purposes; however, the different approach described could be modified for quantification.

During the same set of experiments, mentioned above for long open path detectors (Loh *et al*., 2009), these authors also laid out parallel irrigation tubing (access point every 30 cm) both up- and downwind of the controlled source. They used a single closed path infrared instrument (CO_2) and TDL (CH_4) connected with a pump and a switching valve to sequentially sample the tubing lines (giving line-averaged values), and then applied the same bLS-MOST data processing techniques to estimate the leakage rate. The tubes were 50 m long and spaced both 10 m either side of the source at 0.8 and 1.5 m height and 30 m either side of the source at 1.5 and 3 m height. After extensive data filtering to obtain results coherent with the MOST assumptions and grouping all wind conditions, the estimated/actual CH_4 leakage ratio showed an underestimation of the true flux by about 4% with a standard deviation of 23%. Ratio values for the CO_2 experiments were much poorer, with line A = 1.19, B = 0.55, C = -0.30, and D = -2.02, meaning that negative flux rates were often calculated for the measurement lines located only 30 m from the source. The authors state that these errors were related to intermittent mixing, variable background concentrations, the relatively small perturbation caused by the imposed leakage rate, non-contemporaneous sampling, and difficulty in measuring small δ concentration values of gas that has flowed over the source.

For this type of application, Loh *et al*. (2009) stated that line-averaged measurements may not be optimal due to distance averaged values, which resulted in low signal/noise ratios. They therefore suggested that continuous monitoring with a set of point concentration sensors around the source may be more precise. Multiple NDIR CO_2 sensors were deployed above ground in another study (Lewicki *et al*., 2010); however these results were only used for monitoring purposes. Considering the fact that the costs of these "stand-alone" NDIR sensors are dropping, a relatively large number could be deployed, while their small size and point measurement nature can allow for deployment also close to the ground (i.e. no line-of-sight or vegetation problems).

Regarding issues that have a significant impact of the accuracy of these methods, many of those detailed above for long open path are the same for short closed path, including: the background stability and concentration of the monitored gas (e.g. CH_4 versus CO_2), accurate and stable measurement of those background values, the sensitivity of the measuring instrument, local wind variability, local topography and the existence of barriers affecting wind movement. In particular, the fact that experiments have been conducted at distances of only 10 to 30 m away from the source, due to dilution effects, plume capture, and MOST assumptions, and that these experiments already show significant errors in their estimates of gas leakage rates, means that the location of a leak must be very precisely defined and that it must be a point release (i.e. not diffuse degassing).

Eddy covariance

Although expensive and complex, the eddy covariance method (ECM) is a powerful technique for determining soil-atmosphere flux continuously. However, this method is restricted to onshore sites. Flux rates measured, i.e. the conventional application range, usually lie within the typical range of CO_2 emissions from soils and different land covers, but higher emission rates can easily be determined.

Whether the ECM can detect a leakage of CO_2 from a storage site depends on the ratio between the integral background CO_2 flux from the area and the additional CO_2 flux from a potential seepage area. A seepage rate of 0.1 t/d from a release experiment (Lewicki *et al*., 2009) was not distinguishable from the background CO_2 emissions, whereas the release of 0.3 t/d significantly increased the measured flux rates compared to the base line emission of the area. Similarly Etheridge *et al.* (2011) found that venting of gas from an observation well showed that it is unlikely that elevated CO_2 emissions from a leakage would be detected given the high natural background and its variability.

Eddy-covariance-based estimates of net ecosystem exchange are subject to various sources of systematic bias and random measurement uncertainty. For different set-ups (e.g. open path or closed path detectors; length of the flux averaging period; detrending method; etc.) the largest uncertainties can range from 10% to 40% (Trotta *et al*., 2010). Moreover, the uncertainty in flux data is not constant. The uncertainty increases with increasing absolute magnitude of the flux (Hollinger & Richardson, 2005). The knowledge of errors and uncertainties related to CO_2 and energy flux estimates by EC is still an outstanding issue remaining to be solved (e.g. Trotta *et al*., 2010).

4.3.3 Shallow subsurface monitoring methods

Near surface gas geochemistry

Near surface gas geochemistry techniques can be divided into two main groups, the measurement of the flux of gases from the ground surface to the atmosphere and the measurement of the concentration of gases in the shallow soil horizon. The former can be used to quantify the amount of CO_2 being transferred from the soil to the atmosphere whereas the latter can be used to help define how much of that CO_2 is from shallow biogenic sources and how much is from a deep leaking reservoir. These methods have the potential to be used for both spot and diffuse leakage, and have the advantage that they are direct measurements that have no dilution, are not affected by a rapidly changing system (like wind) and thus typically give relatively stable results, and do not require modelling with its inherent set of assumptions to calculate a leakage rate. These are point measurements, however, and thus are representative of the location sampled, meaning that numerous samples must be collected to characterise a site. Typically, a regular or irregular grid is sampled (detailed if spot leakage is occurring, regional if diffuse leakage is assumed), with obtained flux values being integrated across the grid to give an estimate of the total flux rate. From this value the background biologically produced flux of CO_2 must be subtracted to estimate the leakage rate, and it is this procedure that introduces the largest uncertainty in the calculation.

Various approaches have been applied in the literature to separate leakage from biogenic contributions. Lewicki *et al*. (2007; 2010) conducted shallow injection experiments at the ZERT site and used a grid of CO_2 flux measurements on surface to calculate the leakage rate, obtaining an estimate of 0.31 ± 0.05 t CO_2 / day for a known injection rate of 0.3 t CO_2 / day. Data from outside the leakage area was used to calculate the background biological CO_2 flux rate and this was subtracted from the total to determine the leakage rate. These authors stress the importance of accurately defining this background signal given its spatial and temporal variability. Also at the ZERT site Straziser *et al*. (2009) used flux measurements to calculate a leakage rate of 723 ml/min compared to an injected rate of 800 ml/min. This corresponds to 90% of the actual amount. It should be remembered, however, that underground injection may lead to migration and storage in the soil unsaturated zone, and thus the CO_2 injection rate may not be equivalent to the leakage rate at the soil surface.

Other approaches to subtract biogenic from deep leaking CO_2 include soil-gas measurements of tracers associated with the injected CO_2. Klusman (2003) used stable ($\delta^{13}C$) and radiogenic ($\delta^{14}C$) carbon isotopes of CO_2 to filter and recalculate flux data to estimate a total leakage rate of 170 t CO_2 / year above the Rangely EOR site. As this was not a controlled injection experiment it is not possible to assess the overall error or uncertainty of this approach, although it does demonstrate its potential for estimating low level diffuse leakage. Man-made chemicals have also been added to injected CO_2 and their concentrations used to calculate leakage rates. Wells *et al*. (2007) used perfluorocarbons to calculate a leakage rate of 3 kg CO_2 per year at West Pearl Queen, but acknowledged uncertainties related to: the sampling density; the definition criteria for anomalies; the use of point averages applied to large sectors; the ease of contamination of the monitoring probes by accidental atmospheric releases; and the potential that the CO_2 and the tracers do not migrate at the same rate given their highly different solubilities and reactivities.

Shallow groundwater

The main sources of uncertainty in the quantification of CO_2 leakage into shallow groundwater are the detection of leakage and the quantification of affected volumes or fluxes.

The detection of leakage into groundwater may be problematic in sparsely settled or difficult terrain. Chances for the detection of leakage could be enhanced when observation wells concentrate in areas where leakage risks are elevated, based on reservoir modelling or indications for leakage from deep monitoring (e.g. seismics). Additional techniques, such as remote sensing or ground surveys could help in early detection of discharge of affected groundwater.

Detection will require a reasonably dense network of observation points and continuous monitoring. The determination of dissolved carbon species in groundwater is a routine hydrochemical practice, subject to well established standards, which are sufficient for the given purpose. A thorough hydrochemical baseline assessment is essential for the detection of geochemical anomalies. If a well-established baseline is available, deviations can be detected at levels below the absolute range of the natural variability. Thus, baseline hydrological time series covering several years with preferably weekly or monthly measurements are recommended. The analyses should not only be restricted to alkalinity, pCO_2, ph, or conductivity, but also include other species that may be tracers of waters of different sources (e.g. Br/Cl ratios or stable isotopes).

The next source of uncertainty is the quantification of the groundwater volume affected or the discharge of carbon species from shallow aquifers. The quantification of volumes and fluxes bears a high degree of uncertainty, which can only be diminished by considerable efforts. Hundreds of observation wells may be needed (see examples in Section 2.3.2). Diffuse degassing from extensive aquifers will require additional soil-gas or atmospheric monitoring.

The detection limits of diffuse discharge of CO_2 bearing groundwater into rivers will depend on the contrast of the chemical composition of ground- and river water and the volume ratios of groundwater discharge to river flow.

Generally, uncertainties can be reduced by increasing the density of observation points in the areas of anticipated or detected leakage. This will reduce the uncertainties in the areal integration of concentrations over volumes or fluxes.

4.3.4 Ecosystems

Terrestrial ecosystems monitoring
The monitoring of terrestrial ecosystems involves an assessment of changes in the populations of non-mobile biota inhabiting the soil. This includes an assessment of the biodiversity of organisms present, together with other health indicators such as microbial activities and geochemical parameters. The plant and microbial populations determined at a suspected leak are then compared with control sites which represent the unaffected background.

Although ecosystem-based monitoring is unlikely to be suitable for leakage quantification, it can be employed to qualitatively detect and monitor leakage into near surface systems. However, experimentation at the natural analogue site at Latera, Italy, indicated that vegetation was significantly affected only within a few metres of a high CO_2 vent (emitting at 2,000 – 3,000 g m^{-2} d^{-2}), with a surrounding transition zone of around 10 m radius. It was noted that the effects of the gas vent were spatially limited and that the ecosystem appeared to have adapted to the different conditions (e.g. Beaubien *et al*., 2008; Oppermann *et al*., 2010). This suggests that uncertainties related to leakage detection will be high, and the main use of the method will be to provide a relatively inexpensive means of identifying potential leakages to be confirmed with soil gas analyses. A comprehensive characterisation of seasonal and spatial variation may help reduce the occurrence of false alarms.

Marine ecosystems monitoring
At present, there is limited information regarding the use of seabed CO_2 monitoring techniques on biota. However, it is expected that even a moderate rise in seawater CO_2 may be critical for the most sensitive species, allowing an early detection system for leakage. Long-term, sub-lethal effects at the ecosystem, population and individual scales are likely in the event of a long-lasting leak. Threshold values offer a potentially useful means of evaluating the biological impacts of certain parameters on certain species. The threshold value may be defined as mortality rate related to a certain dose (concentration and exposure time), or to the appearance of specific physiological, behavioural or physical disorders that can be attributed to the impact parameter. Figure 46 presented an example of exposure data for marine organisms to reduced pH levels.

Uncertainties related to detection and quantification of CO_2 leakage using marine ecosystem monitoring are likely to be very high, due to factors such as: no prior knowledge of the location of a leakage; interference from variation in other parameters (e.g. O_2, temperature, etc.); species tolerance and acclimatisation; and natural spatio-temporal variability. Increasing the spatial and temporal resolution of sampling campaigns will help to reduce some of this uncertainty. The source of the leakage should be confirmed using isotopic or tracer analysis of samples of the seeping CO_2.

4.3.5 Remote sensing methods

Airborne and satellite spectral imaging

To date, research on the use of remote sensing detection and monitoring methods for terrestrial CO_2 leakage have focused on detecting changes in plant health using indices such as the Normalised Difference Vegetation Index. Bateson *et al*. (2008) have estimated a minimum flux rate requirement for detection of around 60 g m^{-2} d^{-1}. However, this figure was estimated for clear sky conditions, and wind dispersion and atmospheric forcing was not taken into account. In addition, the night time flux rate requirement may be higher when using thermal cameras. Additional sources of uncertainty and error, potential leading to non-detection or false positives, include atmospheric effects, soil moisture, anisotropy of the target and the angle of illumination, seasonal and diurnal variability, land use changes, agricultural activities and spectral effects. Any suspected CO_2 leakage should be investigated using *in situ* gas sampling techniques.

A method for the quantification of earth surface CO_2 degassing was proposed by Tank *et al*. (2008), based on the determination of heat energy required to generate the observed thermal anomaly. Further research is required to validate the approach. In the case of detection and analysis of thermal anomalies, it is recommended that data should be acquired during winter and at night to avoid masking due to the sun's energy.

If a limitation exists in one remote sensing technology, it can generally be compensated by another. For example, optical remote sensing (using multispectral and hyperspectral sensors) cannot see though clouds and hence the datasets acquired under cloudy conditions are not useful for analysis. On the other hand, RADAR based technology, which operates on a single frequency and therefore has lower discriminatory power, works well under cloudy conditions. Both technologies can be used for the detection of thermal anomalies under low illumination conditions.

Research has indicated that one of the possible ways to reduce uncertainties and limitations in CO_2 leakage detection is by using information fusion techniques, which can combine information from various kinds of datasets (Govindan *et al*., 2011a).

Direct detection of CO_2 through absorption features using hyperspectral data may also provide a means of estimating CO_2 leakage flux. However, the CO_2 absorption bands are relatively narrow and this means that the method is subject to interference from other atmospheric gases such as water vapour. Additional sources of error included sensor noise, surface properties (such as dust), terrain effects and model errors (such as in the specifying of parameters such as the aerosol characteristics due to the terrain and climate, and stratospheric conditions.

Spinetti *et al*. (2008) used airborne hyperspectral images acquired with a ground resolution of 18 m over a vent of Kilauea Volcano, Hawaii, to estimate the CO_2 flux rate. Ground gas measurements were used to calculate a CO_2 emission rate of around 230 ± 90 t d^{-1}. Based on the assumption that the depth of the CO_2 absorption lines varies with the concentration, and after correcting for the water vapour in the plume and the background atmospheric CO_2 level, the estimated flux rate was 396 ± 138 t d^{-1}. For the mapped plume, the lowest volcanic CO_2 concentration detected was 40 ppmv above the ambient concentration of 372 ppmv, with the sensitivity influenced by noise and spatial resolution. Some saturated pixels were attributed to overbearing infrared emissions.

Airborne EM

Electromagnetic (EM) techniques involve the use of time-varying source fields to induce secondary electrical and magnetic fields in the subsurface that relate to its conductivity (see Section 2.5.2). Their use could potentially detect changes in the resistivity of shallow groundwater associated with the dissolution of CO_2. However, although airborne EM techniques have been successfully used to detect pollution plumes in shallow aquifers, they have yet to be applied to CO_2 storage.

The depth of penetration in an airborne survey depends on the frequency (or time channels) of the signal, and frequency domain EM surveys are appropriate for shallow to medium (1-100 m) depth analyses. Homogeneous or layered half-space models are typically used to invert secondary magnetic field values into resistivities and depths.

For airborne EM to be a potential monitoring technique for CO_2 leakage into a shallow aquifer, the ingress must have a measureable impact on the salinity of the formation water. CO_2 migration into aquifers may cause a release of heavy metals such as Pb and As due to the reduction of pH, and the dissolution of minerals such as feldspars and carbonates to buffer pH will result in an increase in total dissolved solids (TDS), and hence conductivity. The effects of the CO_2 influx will depend on the nature of the host rock and the rate of groundwater flow. It is expected that changes in TDS will be more detectable for carbonate aquifers than for sandstones due to the reaction rates involved. The use of the airborne EM method may be limited in areas where significant clay contents, or naturally high background levels of TDS are present. Also, the method provides no geochemical discrimination and therefore ground-based sampling techniques must be employed to establish the cause of any enhanced conductivity (Beamish and Klinck, 2006).

As with the ground-based and downhole EM monitoring methods (see above), the uncertainty will depend on the depth of the target, the geological setting, and the contrast between the injected CO_2 and the natural background. Knowledge of the spatio-temporal variability in the natural background levels must be fully established.

5 CONCLUSIONS AND RECOMMENDATIONS

For leakages occurring in the shallow subsurface, atmosphere and marine environments, unless clearly defined leakage pathways have been identified, a two-fold approach is recommended: to first use a monitoring methodology with a wide coverage and limited resolution to detect any leaking CO_2; then to deploy a more sensitive instrumentation to the leakage site to collect the necessary flux and concentration data for an estimation of the leakage quantity.

While certain methodologies have been proposed for quantifying CO_2 flux from, for example, remote sensing data and electromagnetic surveys, further work should be undertaken to determine the sensitivities of these methods to minor leakages. Future research efforts may also be focused on developing instrumentation that can operated remotely, such as on the sea bed, or be robust enough to be deployed for long time periods in hostile environments.

Tables 9 to 13 summarise the knowledge gained through the work carried out in this project. The following Sections provide conclusions and recommendations for further research and development for each of the CO_2 monitoring methods.

5.1 Marine and terrestrial aquatic environment monitoring methods

Hydroacoustic monitoring methods

Acoustic methods (sidescan sonar and multi-beam echo-sounding) applied in marine and terrestrial water systems are able to detect efficiently leaks and seeps of gas bubbles and dissolved CO_2. On this basis it may be possible to estimate the size of the leak, although this would be a rough estimate. When used together with optical data, such as acoustic tomography and flow sensors, it may be possible to obtain more precise and accurate flux estimates.

Acoustic surveys are suitable for covering wide areas in a relatively short period of time, and in comparison with other methods are likely to be cost-effective. Deploying the technology on AUVs may represent a promising means of detecting leaks and providing data for further quantification although limitations due to the resolution of the method may not detect small pockmarks and minor leaks.

Although the current available technology may possibly be adequate, there is a lack of experimental work and results to determine the uncertainty level. Experimental releases of CO_2 in the sea have been attempted several times before, but faced hard resistance from environmental groups. Unless attitudes change, it may be very difficult to conduct scientific experiments with CO_2 in the sea. Natural analogues are a possible source for information and calibration, but only for the actual flux and setting of that site.

Acoustic tomography and acoustic "cameras" may possibly enhance accuracy of the assessments. Also, the expected general technological improvements in the field of acoustic mapping in water/sea will help to reduce the uncertainty in the quantification of any CO_2 leaks.

Surface water chemistry

Surface water chemistry monitoring consists of either discontinuous sampling using mature and precise methods or *in situ* monitoring using probes and sensors that are in the early development stage. Quantification approaches for both the discontinuous and continuous methods typically involve measurements on a plane that is perpendicular to current direction and down-gradient from the source, subtraction of background values, and calculation of the amount of leaking CO_2 using these residual concentrations and the flow rate through the plane (assuming that all the CO_2 leaked is dissolved and is swept through the measured plane). Prior to applying this approach a detailed knowledge of current directions, site bathymetry, background concentrations, and seasonal variability are required. Sampling should be conducted along multiple, mutually-parallel planes, at a sampling density that permits defining plume heterogeneity, and if possible during different time periods to quantify variability and method precision. Various monitoring/analytical methods are available, but those chosen should allow for sufficient spatial resolution, relatively rapid response time, and should have sufficient sensitivity and precision. If CO_2 is monitored directly (as opposed to a proxy tracer), great care must be made to differentiate and subtract background CO_2 coming from biogenic reactions or from equilibration with the atmosphere.

The majority of the uncertainty in this method lies in site variability and background correction, and thus protocols should be developed for characterising important variables such as currents and background concentrations prior to injection. Future work should also include: increasing sample throughput for discontinuous methods and decreasing response times for continuous sensors to improve sampling density and thus plume resolution; decreasing costs and increasing autonomy for glider systems on which sensors can be mounted to improve temporal monitoring; and performing more tests using equilibrator systems. Finally, most of the methods described have been developed and applied for other applications (e.g. cold seeps, pollution, etc.), and thus tests of these instruments must be conducted on natural CO_2 seeps and controlled release sites in order to assess method sensitivity, precision, and costs for CO_2 monitoring and leakage quantification.

Bubble stream chemistry
Bubble streams detected by hydroacoustic monitoring methods can be sampled and analysed to determine the composition and source of the gas. A combination of techniques to determine gas flux and composition may potentially be used to quantify CO_2 leakage. The potential of the technique has been demonstrated at the natural analogue site near Panarea in the South Tyrrhenian Sea (Caramanna *et al*., 2011). Further work is aimed at developing reliable monitoring systems for CO_2 leakages, incorporating dissolved gas sensors in addition to pH probes, and active and passive acoustic instruments for bubble stream detection. The new systems should be tested on mobile devices (ROVs and AUVs), and verified for use at sites with lower emission rates.

5.2 Atmospheric monitoring methods

Long open path (IP diode) lasers
Monitoring using long open path lasers requires that: i) the leak is a well-defined, point source; ii) a clear line-of-sight exists between the laser source and remote reflector; iii) line-monitoring is conducted upwind and downwind of the source for the bLS-MOST approach and multiple line-monitoring is conducted on a plane downwind from the source for the VRPM method; and iv) wind direction and strength are monitored during the laser deployment period. The resultant data are then modelled, with an estimate given of the amount of CO_2 passing through the monitored line (or plane) over a given time period; if the entire plume is captured this represents the total CO_2 leakage rate. Distance from the source is a critical parameter for acceptable results, and site characteristics that affect wind complexity (topography, buildings, trees, etc.) can have a significant influence on method accuracy and precision. Measured path length is a compromise between being long enough to completely capture the plume but not too long to have excessive anomaly signal dilution, while the chosen path height will impact on the level of concentration dilution. Most controlled release studies have been conducted with CO_2 leakage rates of about 0.1 tonnes CO_2 / day; in one study the leakage calculated overestimated the true value by up to 87%. Much better results were obtained for CH_4 leakage rates, due to its lower background concentration and greater instrument sensitivity; for a leak of only 0.006 tonnes CH_4 / day leakage estimates were often within 5% of the true value.

Future improvements should focus on: developing instruments with more stable baseline signals and instruments that can measure more than one pathway (e.g. using fibre optic cables); expanding the study of the joint application of CH_4 and CO_2 sensing laser systems, in light of the different dispersion characteristics of the heavier CO_2 and more mobile CH_4; performing tests on sites with less than ideal conditions (e.g. complex topography) and during different periods to observe diurnal and seasonal effects;

developing units that measure man-made tracers with very low detection limits; conducting greater controlled release testing of the bLS-MOST method on CO_2 in an effort to find ways to adjust the experimental set-up to improve leakage estimate accuracy; and testing of the VRPM method on controlled releases of CO_2 and CH_4 to understand if this method has advantages over bLS-MOST. To date, one of the greatest limitations of this method for leakage quantification is that all experiments have been conducted within 10 to 50 m from a known, well-defined source, with precision decreasing significantly beyond 30 m. Work must therefore be conducted to improve results at greater distances.

Short open path (IR diode) lasers

Short open path lasers offer great potential for mapping large areas quickly for leakage detection. However, the method is greatly inhibited for leakage quantification due to the fact that it makes point measurements over time within a rapidly-changing concentration field. Instead it is seen more as a screening tool that can be used to define leakage locations and subsequently direct the focused application of other methods (such as gas flux measurements) for actual leakage quantification.

Future work should focus on: deploying the unit as close to the ground surface as possible to minimise dilution and the lateral translocation of potential anomaly signals; conducting tests using non-CO_2 emitting vehicles to improve sensitivity and eliminate spurious anomalies; and developing and testing models that monitor for other tracer gases (associated with the stored CO_2) that have a lower sensitivity.

Short closed path (NDIRs and IR)

Short closed path lasers have been used for monitoring in two main ways in the literature. The first involves pumping air from a long tube that has numerous sampling ports along its length and analysing the mixed air via a single closed chamber infrared detector. Results from these temporal, line-averaged measurements, conducted a few tens of metres both upwind and downwind from a known source, are then processed using the same bLS-MOST modelling approach applied to the line-averaged open path laser results described above. As this approach involves deployment and line-averaged measurements similar to those conducted using the open path laser technique described above, many of the issues are similar, such as distance from source, upwind and downwind concentration monitoring, precise wind monitoring, data filtering, and modelling of results, etc. Tests conducted with a leakage rate of 0.1 tonnes CO_2 produced results that ranged from underestimating by 50% at 10 m distance to estimating negative fluxes at 30 m. Again, CH_4 flux rates were significantly more accurate (on average underestimating by 4%) at lower leakage rates (0.006 tonnes/day). The second approach involves deploying a number of individual infrared detectors along a line or grid around a leak (near ground surface or potentially on a plane perpendicular to the ground surface), and then modelling the resultant data from these discrete measurement points using bLS-MOST to calculate the amount of leaking CO_2. Some studies have shown that point measurements may provide more sensitive and precise estimates of leakage compared to the line-averaged measurements as they do not suffer from concentration dilution. The recent decrease in costs and size of these NDIR sensors has made this approach feasible for the future.

The instruments used for short closed path laser (NDIR) measurements are mature, and thus higher end models have good sensitivity and rapid response times. Instrumental improvements could include decreases in the costs of these units, or the improvement of the specifications of smaller, more affordable NDIR models. Future work on the line-averaged approach will be similar to that described for the open path laser system, including improving quantification estimates at greater distances from a known source, resolving problems related to background values, and the testing of sensors for co-migrating tracer gases. Deployment of a large number of low-cost, small NDIR sensors has been proposed in the literature for leakage quantification; however, to date this approach has not been tested in the field with a controlled release. Work in this area should address optimal deployment configuration, determining minimum detectable leakage rates, and examining the effects of site characteristics (topography, wind conditions, etc.) on the eventual results. Effort should also be given to automating data processing, given the large amount of data produced by the gas sensors and meteorological stations.

Eddy covariance
The eddy covariance method (ECM) is a powerful technique for determining continuously soil-atmosphere flux. However, it is expensive and complex, and is restricted to onshore sites. Whether the ECM can detect a leakage of CO_2 from a storage site depends on the ratio between the integral background CO_2 flux from the area and the additional CO_2 flux from a potential seepage area. Various studies (e.g. Lewicki *et al*., 2009; Etheridge *et al*., 2011) have suggested that it is unlikely that CO_2 leakage from a subsurface storage site would be detected by the ECM given the high natural background and variability of CO_2 in the atmosphere.

Eddy-covariance-based estimates of net ecosystem exchange are subject to various sources of systematic bias and random measurement uncertainty. The knowledge of errors and uncertainties related to CO_2 and energy flux estimates is an issue that remains to be resolved (e.g. Trotta *et al*., 2010).

5.3 Shallow subsurface monitoring methods

Shallow groundwater
Depending on the pH and chemical composition of the receiving groundwater, leaking CO_2 will form various chemical species. The concentrations of these species can be measured with established hydrochemical methods with reasonable accuracy. The estimation of leakage can be done through multiplying groundwater volumes and fluxes with the concentrations of carbon species, after accounting for natural background levels.

While hydrochemical observation of shallow aquifers can be applied to any CO_2 storage type, concept and structure, full areal coverage of extensive storage sites is unlikely to be possible. In rural areas there may be few groundwater observation wells, unless shallow aquifers are used for irrigation. In urban and industrialised areas, natural groundwater discharge may be restricted due to sealed surfaces and channelised drainage. However, larger cities and industrial complexes often have networks of groundwater monitoring wells in operation. Thus, monitoring wells should be concentrated in smaller areas, such as in the vicinity of pilot projects, or in the region of potential leakage pathways such as wells or faults. Baseline monitoring is essential for the detection or quantification of subsequent leakage. Leakage monitoring of shallow aquifers should be intensified. Post-closure monitoring, without prior indication of leakage, may be included with little additional effort into general groundwater observation schemes.

As CO_2 leakage should not affect shallow aquifers during normal operation, hydrochemical monitoring is not a suitable tool for storage site operation and reservoir management. Although hydrochemical methods can detect small fluxes of CO_2 discharging at the surface, the quantification of CO_2 leakage into shallow groundwater will subject to a number of uncertainties. While increasing the density of the sampling grids and sampling frequency may reduce the quantification uncertainties, the accuracy of quantification is unlikely to be sufficient for emission certificate accounting.

Groundwater sampling methods are well established and there is little scope for further development of tools for groundwater monitoring of CO_2 leakage. However, future research could focus on integrating the results of sampling with other indirect monitoring methods such as electrical/electromagnetic surveys to enable wider spatial coverage in areas where access to wells or natural seepage is limited.

Near surface gas chemistry
Near surface gas chemistry monitoring involves making point measurements of i) the concentration of a gas within the unsaturated soil horizon and ii) the flux of a gas from the soil to the atmosphere. As they are complementary, these two tasks are often conducted together. Soil gas concentrations are particularly useful to determine the origin of an anomaly, whereas gas flux measurements can give a direct estimate of the CO_2 leakage rate. Measurements are conducted on a regular or irregular grid, with a low sampling density being used for regional studies (diffuse degassing leakage quantification, location of point leakage, definition of background concentrations/fluxes, etc.) and a high sampling density used when the general area of a leakage point is known or inferred (point-source leakage quantification). These methods have the potential to provide the most accurate estimate of CO_2 leakage to the atmosphere, as they involve a direct

analysis of the migrating gases and are conducted in an environment that is relatively stable with little dilution/variability caused by wind mixing. Moreover, CO_2 leakage estimates are calculated based on simple interpolation within the measurement grid (which has less inherent error compared to the assumptions involved in modelling). Detailed controlled release studies have quantified leaks at the 0.1 and 0.3 tonnes CO_2 / day level, with the latter estimated to be 0.31 ± 0.05 tonnes CO_2 / day using the gas flux measurement data.

The primary uncertainty in using near surface gas geochemistry techniques is subtracting the baseline CO_2 flux from that due to the leaking CO_2. More work is required using controlled release experiments involving shallow injection, so that there is a close relationship between the amount injected and the amount that leaks at the surface in order to assess the error of the applied approach. For example, to date the study of tracers has been applied only to deep injection where an unknown fraction of the injected gas may migrate to surface during the short term of the experiment. Work is also required to better understand the lower limit of quantification using this technique, especially that using baseline CO_2 flux values to calculate the biogenic contribution. Instead, analogue sites where natural CO_2 is leaking at surface could be used to better understand the variability of flux and how a seasonally-changing biogenic production can be accounted for.

5.4 Ecosystems monitoring

Terrestrial ecosystems monitoring
Terrestrial ecosystems monitoring involves detecting changes in the status of non-mobile biota inhabiting the soil due to increased exposure to CO_2. This includes an assessment of the biodiversity of the organisms present, together with other health indicators such as microbial activities and geochemical parameters. The plant and microbial populations determined at a suspected leak are then compared with control sites or earlier surveys which represent the unaffected background. Ideally, ecosystem modelling will be combined with a soil gas survey of the area to verify the cause of any change and elucidate the source of any detected gas emissions.

The monitoring of terrestrial and ecosystems can potentially lead to the identification of significant leaks from deep subsurface reservoirs at a relatively low cost. Sites affected by high CO_2 concentrations are typically visible by bare eye and thus easy to detect, even from a distance or low-flying aircrafts. However, with regard to quantification, ecosystem monitoring is unlikely to become applicable since above certain levels further change will not be observed.

Further research into the impact of CO_2 emissions on soil ecosystems may complement work undertaken on developing methods for automatic detection of leakage from remote sensing systems.

Marine ecosystems monitoring
Marine ecosystems monitoring involves the deployment of near-seabed technology for detecting and monitoring leaks by observing impacts on microbiological communities, invertebrates, and marine vertebrates. Seeps of CO_2 gas through the shallow sediments can dissolve in pore and sea water, with the resulting increase in density allowing it to accumulate in layers or pools at the seabed. In this case, the increased exposure times mean it is likely to cause some local environmental damage both in the sediments and in the water above.

The effects of elevated CO_2 levels on biota are mediated through the lowering of pH (Magnesen and Wahl, 1993), which may have a toxic effect on the fauna or a hampering effect on the production of calcareous structures. The tolerance will vary from one species to another. If CO_2 that leaks causes effects on the benthic layer community level (e.g. changes in tropic dynamics, shift in relative abundance of feeding types, changes in diversity and dominance patterns), such results may be transferable to mesopelagic communities. Such disturbances may be quite easily detected, and with proper parameterisation leak a vague quantification may be possible as well.

As discussed in Section 4.3.4, there is currently limited information regarding the use of seabed CO_2 monitoring techniques on biota. Experiments on the determination of tolerance levels of CO_2 exposure for a number of marine species should be undertaken in order to distinguish the effects of CO_2 from those of other variables such as temperature and O_2.

5.5 Remote sensing methods

Airborne and satellite spectral imaging

Spectral (or optical) remote sensing detection and monitoring methods for terrestrial CO_2 emissions can be classified as direct or indirect, as described in Section 2.7.1. Most of the reported applications on investigating the use of remote sensing methods for CO_2 storage monitoring are indirect, and are largely based on changes in the vegetative cover. Thermal imaging may also potentially detect leakage indirectly if a measurable temperature anomaly is associated with the leakage. High resolution airborne hyperspectral scanners may detect CO_2 (and CH_4) directly using absorption features that lie within their wavelength range. However, this suitability of this method is restricted due to the narrowness of the CO_2 absorption bands and interference from other atmospheric gases.

Work on the detection of CO_2 leakage sites through spectral analysis has demonstrated the potential of the technique for providing an unsupervised means of automatically detecting possible leakage sites, which may then be subject to ground-based investigation (e.g. Govindan *et al*., 2011b). The technique offers the ability to monitor large terrestrial areas with good spatio-temporal resolution, without the need for land access and instrumental instalment.

With regard to leakage quantification using remote sensing methods, a number of studies have aimed to estimate CO_2 flux from natural degassing sites (e.g. Martini and Silver, 2002; Tank *et al*., 2008) and from coal fires (Gangopadhyay *et al*., 2009). However, estimates of CO_2 leakage from subsurface storage sites are likely to be subject to considerable uncertainty.

In order to develop an unsupervised system for automatic detection of leakage, with extensive areal and coverage and good spatial resolution, further work may be undertaken on developing a new methodology that can be applied regardless of the light (day or night) and atmospheric conditions (i.e. clear or cloudy). Work should also be undertaken to assess the detection limits achievable for such a system. Furthermore, a system that could be used to detect leakage over marine bodies would be a valuable addition to the available monitoring tools. Further experimentation on the quantification of CO_2 emissions should be undertaken to assess whether leakage rates can be estimated with acceptable levels of confidence.

Airborne EM

Although airborne EM techniques have not yet been applied to monitoring CO_2 storage, they have been successfully used to detect pollution plumes in shallow aquifers, and offer the potential to monitor large areas without the installation of a large number of boreholes. The method detects changes in conductivity in the subsurface through the use of time-varying source fields to induce secondary electrical and magnetic fields (see Section 2.4). Such changes in the resistivity of shallow groundwater may be associated with the dissolution of leaking CO_2.

Depending on the frequency of the signal, the depth of penetration in an airborne EM survey may be between 1 and 100 m. Resistivities and depths are typically obtained through the inversion of secondary magnetic field values using homogeneous or layered half-space models. The effects of the CO_2 influx, and therefore the suitability of the monitoring method, will depend on the nature of the host rock and the rate of groundwater flow. The use of the airborne EM method may be limited in areas where significant clay contents, or naturally high background levels of total dissolved solids are present. Moreover, the method provides no geochemical discrimination and therefore ground-based sampling techniques must be employed to establish the cause of any enhanced conductivity (Beamish and Klinck, 2006).

Future research may involve assessing the use of a numerical simulator such as TOUGHREACT (Xu *et al*., 2004) to predict whether a measureable impact on the groundwater would occur given an introduction of leaked CO_2, in terms of a change in the total dissolved solids content. An empirical relationship between TDS and electromagnetic recordings could potentially be used to estimate the amount of CO_2 that has dissolved in the groundwater.

Further research is also required to assess the significance of factors such as the applied technology, calculation approach and geological settings (e.g. porosity, temperature, resistivity of solid phase and stratigraphy), and to discriminate the effects of CO_2 leakage from alternative scenarios such as seawater intrusion (Fahrner *et al*., 2011).

Table 9. Summary of aquatic monitoring methods suitable for various tasks in monitoring CO_2 leakage from a storage site.

AQUATIC MONITORING	**Monitoring method**	Sonar methods			Surface water chemistry	Marine Bubble stream chemistry
Storage and monitoring features		Sidescan sonar bathymetry	Seabed multibeam bathymetry	Bubble stream detection		
Storage option	saline aquifer					
	oil reservoir					
	gas reservoir					
	coal bed					
Environment	marine					
	rural				*lakes*	
	urban / industrial					
Structure	closed structure					
	open structure					
Storage project size	research and pilot					
	full scale industrial					
Potential pathways	faults					
	wells					
	permeable caprock					
Project phase	baseline					
	normal operation					
	unforeseen events					
	post closure					
Monitoring task	reservoir management					
	HSE, leak and migration detection					
	emission trading, flux quantification		*difficulty in assessing quantities*			
Substance	CO_2 rich gas phase					
	formation water					
Monitoring target	reservoir					
	overburden					
	shallow groundwater					
	Surface	*seabed*	*seabed*	*seabed*		
Leakage rate	low (100 g/d)					
	intermediate (100 kg/d)				*case dependent*	
	high (100 t/d)					
Leakage type	diffuse	*case dependent*	*case dependent*		*case dependent*	
	disperse spots					
	single localised leak	*case dependent*	*case dependent*			

pink = method suitable; yellow = less suitable; white = not applicable

Table 10. Summary of atmospheric methods suitable for various tasks in monitoring CO_2 leakage from a storage site.

ATMOSPHERIC MONITORING **Storage and monitoring features**	**Monitoring method**	Long open path (IP diode lasers)	Short open path (IR diode lasers)	Short closed path (NDIRs and IR)	Eddy covariance
Storage option	saline aquifer				
	oil reservoir				
	gas reservoir				
	coal bed				
Environment	marine				
	rural				
	urban / industrial		*limited coverage*		
Structure	closed structure				
	open structure				
Storage project size	research and pilot				
	full scale industrial				
Potential pathways	faults	*may depend on site knowledge*		*may depend on site knowledge*	
	wells				
	permeable caprock				
Project phase	baseline				
	normal operation				
	unforeseen events				
	post closure				
Monitoring task	reservoir management				
	HSE, leak and migration detection				
	emission trading, flux quantification				
Substance	CO_2 rich gas phase				
	formation water				
Monitoring target	reservoir				
	overburden				
	shallow groundwater				
	surface				
Leakage rate	low (100 g/d)				
	intermediate (100 kg/d)	*case dependent*			
	high (100 t/d)				
Leakage type	diffuse	*case dependent*	*depends on contrast with background*	*case dependent*	
	disperse spots				
	single localised leak				

pink = method suitable; yellow = less suitable; white = not applicable

Table 11. Summary of shallow subsurface methods suitable for monitoring CO_2 leakage from a storage site.

SHALLOW SUBSURFACE MONITORING / Storage and monitoring features	Monitoring method	Soil gas and flux	Soil geochemistry	Downhole fluid chemistry	Hydrochemical methods	Tracers
Storage option	saline aquifer					
	oil reservoir					
	gas reservoir	*requires additional monitoring if the residual gas contains CO_2*				
	coal bed					
Environment	marine					
	rural				*few wells, apart from irrigated agriculture*	
	urban / industrial	*sealed surfaces*			*use of existing monitoring networks*	
Structure	closed structure					
	open structure	*unknown leakage areas and pathways likely*				
Storage project size	research and pilot					
	full scale industrial			*calibration of reservoir models*	*may need extensive observation networks*	
Potential pathways	faults			*pathways should be known*		
	wells			*pathways should be known*		
	permeable caprock	*unknown leakage areas and pathways likely*		*pathways should be known*	*diffuse gas may be retained in deep aquifers*	
Project phase	baseline					
	normal operation					
	unforeseen events	*At leaking / suspect sites*		*pathways should be known*	*requires intensified monitoring*	
	post closure	*If leaking spots are known*				
Monitoring task	reservoir management					
	HSE, leak and migration detection					
	emission trading, flux quantification				*requires soil gas flux monitoring*	
Substance	CO_2 rich gas phase					
	formation water					
Monitoring target	reservoir					
	overburden					
	shallow groundwater	*diffuse degassing of supersaturated formation water in alluvial sediments*				
	surface					
Leakage rate	low (100 g/d)	*dependant on size of mofette and back-ground level/fluctuations*			*localised discharge from fractured reservoirs only*	
	intermediate (100 kg/d)					
	high (100 t/d)					
Leakage type	diffuse	*dependant on contrast of leakage anomaly / background*			*low rates may not be detectable*	
	disperse spots					
	single localised leak			*require large fluxes and extensive geoch.anomalies*		

Table 12. Summary of ecosystems methods suitable for various tasks in monitoring CO_2 leakage from a storage site.

ECOSYSTEMS MONITORING / Storage and monitoring features		Monitoring method: Terrestrial ecosystems	Marine ecosystems
Storage option	saline aquifer		
	oil reservoir		
	gas reservoir		
	coal bed		
Environment	marine		
	rural		
	urban / industrial	*coverage may be limited*	
Structure	closed structure		
	open structure		
Storage project size	research and pilot		
	full scale industrial		
Potential pathways	faults		
	wells	*depends on quantity and geometry*	
	permeable caprock		
Project phase	baseline		
	normal operation		
	unforeseen events		
	post closure		
Monitoring task	reservoir management		
	HSE, leak and migration detection		
	emission trading, flux quantification		*difficulty in assessing quantities*
Substance	CO_2 rich gas phase		
	formation water		
Monitoring target	reservoir		
	overburden		
	shallow groundwater		
	Surface		
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)	*case dependent*	*case dependent*
	high (100 t/d)		
Leakage type	diffuse	*case dependent*	*case dependent*
	disperse spots		
	single localised leak	*case dependent*	*case dependent*

pink = method suitable; yellow = less suitable; white = not applicable

Table 13. Summary of remote sensing methods suitable for various tasks in monitoring CO_2 leakage from a storage site.

REMOTE SENSING / **Storage and monitoring features**	**Monitoring method**	Airborne and satellite spectral imaging	Airborne EM
Storage option	saline aquifer		
	oil reservoir		
	gas reservoir		
	coal bed		
Environment	marine		
	rural		
	urban / industrial		
Structure	closed structure		
	open structure		
Storage project size	research and pilot		
	full scale industrial		
Potential pathways	faults		
	wells		
	permeable caprock		
Project phase	baseline		
	normal operation		
	unforeseen events		
	post closure		
Monitoring task	reservoir management		
	HSE, leak and migration detection		
	emission trading, flux quantification		
Substance	CO_2 rich gas phase		
	formation water		
Monitoring target	reservoir		
	overburden		
	shallow groundwater		
	Surface		
Leakage rate	low (100 g/d)		
	intermediate (100 kg/d)		*case dependent*
	high (100 t/d)		
Leakage type	diffuse		*case dependent*
	disperse spots		
	single localised leak		*case dependent*

pink = method suitable; yellow = less suitable; white = not applicable

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