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Quantification techniques for potential CO_2 leakage from geological storage sites

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Abstract

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 (ETS) treats leakages of stored CO_2 from the geosphere in to the ocean or atmosphere as emissions, and as such they need to be accounted for. An escape of CO_2 from storage may be detected through losses from the reservoir, or migration through the overburden, into shallow groundwater systems, through topsoil and into the atmosphere, or through a seabed into the water column. Various monitoring techniques can be deployed to detect and in some cases quantify leakage in each of these compartments. This paper presents a portfolio of monitoring methods that are appropriate for CO_2 leakage quantification, with a view to minimising both uncertainties and costs.

1. Introduction

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, and as such 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, and can be implemented through pre-injection to post-closure.

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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.

In this paper we present 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 CO_2 geological storage and other industries. The strengths and weaknesses of each method are considered, as well as their relative costs and performance in terms of sensitivity, resolution and uncertainties. The paper focuses on four monitoring compartments: reservoir and overburden; shallow groundwater; surface; and the marine environment.

2. Methods for detection and quantification of CO_2 leakage

2.1. Reservoir and overburden

To focus on the storage reservoir and its caprock, deep monitoring techniques are used to monitor the quantity and migration of CO_2 within the reservoir and adjacent formations, and provide data to build and calibrate reservoir performance models. 3D seismic methods can provide detailed information regarding fault distribution and subsurface structures. In time-lapse mode (4D) they can track the migration of the CO_2 plume, and may be able to detect gas leaking into the overburden. Theoretically, under favourable conditions, less than 1000 tonnes of CO_2 should be detectable at depths of less than 1000 m [1]. Multi-component seismic methods can provide clearer imaging and enable mapping of horizons that may be obscured from 3D imaging due to unsuitable geology or overlying gas-filled layers. Improved characterisation of reservoir and overburden properties such as fracture intensity and orientation may aid the calibration of Earth models. From Amplitude Variation with Offset (AVO) analysis, the state of the gas can be determined better than with 3D seismic alone.

4D and multi-component seismic methods are well established and currently offer the best potential for quantifying leakage at depth from surface-based surveys. Time-lapse 2D seismic surveys may offer a relatively cheap means of detecting leakage if the subsurface is reasonably homogenous, and if they can be deployed over an area with a suspected possible leakage pathway. Surface-based seismic methods are likely to be more suitable for deployment in an offshore environment, as they are disruptive and access limitations may apply on land. The methods are likely to be less effective when imaging beneath horizons containing gas or salt, and due to insufficient impedance contrast it is not possible to detect dissolved CO_2.

Cross-well seismic technology, when deployed at depth in time-lapse mode, can enable a more detailed 2D image of CO_2 plume migration, and may allow the detection and quantification of possible leakages out of the reservoir at early stages. The method may be of more benefit in a hydrocarbon reservoir, where it may help distinguish between gases and where observation wells may already exist.

While the main reason to perform 3D vertical seismic profiling (VSP) is to help bind surface seismic to logs and stratigraphy information, when deployed in time-lapse mode it may offer the potential to give an early warning of well leakage. It may help to visualise the extension of a possible leakage previously detected by sonic logs, and if performed with a 3D walkaway geometry, it may reveal the migration path of CO_2.

Passive microseismic monitoring may facilitate 4D imaging of the subsurface structures and CO_2 plume migration, and track the development of fractures or loss of top-seal integrity during the injection period. It can help fill in the gaps between time-lapse seismic surveys through the use of seismic interferometry. In environmentally sensitive or built-up areas its benign environmental impact means that a survey that might otherwise never get permitted becomes possible. Once installed, it should require little maintenance, and data collection can largely be automated to provide continuous information. Various factors such as surface noise may limit the success of the technique, particularly if the reservoir is deep.

Ongoing research [e.g. 2] is investigating methods of quantifying the amount of CO_2 injected into a reservoir using seismic data, and it is possible that these could also be adapted for leakage. One method involves measurement and analysis of velocity pushdown combined with Gassmann modelling. This requires the density of the CO_2 under reservoir conditions to be known. The method was found to account for 85% of the injected CO_2 at Sleipner [1]. The discrepancies could be attributed to a number of factors; recent flow simulations have indicated that up to 10% of the free CO_2 would have dissolved into the aqueous phase, and become undetectable [2].

While bearing in mind this high level of uncertainty, the results could be compared with the quantity of injected CO_2 to assess possible losses from the storage horizon. Subsequent CO_2 volumes derived from structural analysis with calculated average saturations and an assumed mean porosity were higher than estimates derived from amplitude analysis, and are considered to be more reliable [2]. Alternative methods include post-stack stratigraphic inversion, which makes use of acoustic impedance logs [e.g. 3], and pre-stack stratigraphic inversion, which requires an *a priori* multi-parameter elastic model parameterised as P- and S-wave impedances. This seemed more able to characterise some parts of the reservoir at Sleipner than post-stack inversion [2]. Meadows [4] applied a simultaneous inversion of multiple time-lapse seismic attributes in an attempt to improve CO_2 volumetric estimates by constraining the solution in the process of minimising differences between the Sleipner datasets, and also estimate the uncertainty. Time-lapse changes in traveltime and amplitude were measured at the top of the reservoir and inverted to produce a CO_2 thickness map and its standard deviation. However, without quantifying the CO_2 in the deeper parts of the reservoir it was not possible to assess the accuracy of the estimation.

Major sources of uncertainty in the methods described for CO_2 quantification within the reservoir include density and saturation. A technique that may complement time-lapse seismic monitoring and quantification procedures and reduce uncertainty is gravimetry. This consists of studying anomalies in the gravity field due to subsurface density variations. The amplitude of the variation in gravity 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. Gravimetric methods operated in continuous or time-lapse mode may be able to characterise large volumes of gas in the reservoir or possibly leakage at shallower depths if the escaped gas is trapped by a secondary caprock. Gravimeters can be deployed downhole or placed on a grid on the surface, where onshore installations are relatively inexpensive. At present, the methodology is at the feasibility stage, although tests at Sleipner from seabed-based gravimeters have provided estimates of *in situ* CO_2 density [5], which can be used as a constraint for fluid flow modelling. Downhole deployment of gravimeters has been shown to enable mapping of density changes in a CO_2-EOR reservoir [6]. Although site-specific, the sensitivity of the method is likely to be relatively low, with large quantities of CO_2 (ca. 2 Mt for a typical reservoir) needed to provoke an observable response.

Electrical and electromagnetic (EM) methods are relatively inexpensive and may have potential for reducing uncertainties, particularly in a saline aquifer. These methods involve detecting changes in the electrical conductivity due to CO_2 displacement, and use expressions such as the Archie equation to estimate CO_2 saturation. Measurements can be obtained from the surface if wells are available at the level of the reservoir or a secondary storage formation above, downhole or through towed transmitters and seabed receivers in a marine environment. Electrical resistivity tomography (ERT) can be employed downhole if the casing is metal, or in a cross-well configuration if there are two wells closely spaced. Modelling constrained by the geological model and resistivity logs can predict changes in resistivity related either to the plume migration or saturation fluctuations. ERT methods could be used for permanent monitoring, either during operation or the post closure phase, using "Smart" wells fit-to-purpose and arrays of buried electrodes. A method for monitoring deep CO_2 storage from the surface has been proposed [7]. Initial experiments at Ketzin, where the formation water is highly saline, have proved promising, with downhole EM methods able to detect injected CO_2 in the region of tens of thousands of tonnes.

Well-characterised Earth models will help define structural boundaries and traps. Porosity and permeability data will aid the calibration of capillary pressure curves. Geophysical logs provide high resolution data on properties of the wellbore, near-well formation and its fluids. A CO_2 plume migrating near the well may be monitored using various geophysical methods, such as sonic, neutron, density, resistivity, nuclear magnetic resonance and pulsed neutron logging tools. These tools can detect initial CO_2 breakthrough and possibly saturation, via a distributed thermal perturbation sensor. Permanent installation of geophysical logging tools is also a possibility for semi-continuous downhole monitoring, to provide pre-injection baseline data followed by time-lapse logging during and after the operational period. A U-tube manometer can be used for measuring fluid densities. Geophysical tools are also used to monitor the integrity of the well casing, and can alert operators to corrosion that may lead to leakage, and in time-lapse mode provide corrosion rate estimates.

Downhole pressure/temperature sensors provide continuous measurements at the injection point. The data can alert operators to leakages, and facilitate the calibration of reservoir performance simulation models as they provide a more accurate representation of the conditions around the injection point than wellhead measurements.

Given specific geomechanical conditions in the overburden, deep injection of CO_2 and plume migration in the reservoir could induce ground deformations at the surface in the order of a few mm to cm per year, and this can be monitored using tiltmeters. In CCS projects, frequent real-time measurements from a surface array are processed through a geomechanical inversion model to determine what changes at reservoir level must have occurred in order

to cause the observed surface deformation. Tiltmeters can quickly identify out-of-zone fluid migration and cap rock integrity issues, and are very well suited to be used in conjunction with satellite interferometry (InSAR) and GPS data. Methods such as DInSAR, PSInSAR[TM] and CRInSAR use phase differences calculated from successive synthetic aperture radar images to detect and monitor millimetre-scale vertical land movement. InSAR offers the ability to provide frequent (such as monthly) observations of ground deformation over a wide area with a fine spatial resolution (a few metres), regardless of weather conditions. This can be used to track fluid pressure and may be able to detect a permeable leakage path through the overburden. DInSAR and PInSAR have been used to monitor surface deformation and estimate changes in reservoir pressure and permeability at the In Salah CO_2 storage site in Algeria [e.g. 8]. Various studies have indicated that it may be possible to infer quantities of leakage through consideration of reservoir volume changes [e.g. 9]. Surface deformation monitoring techniques such may prove to be significantly more cost effective than seismic-based methods for many land-based sequestration sites, while tiltmeters may offer a cost advantage over permanently installed seafloor seismic systems or repeat surveys.

2.2. Shallow groundwater

Of the deep monitoring methods discussed above for the reservoir and overburden, several are also suitable for simultaneous 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 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 discussed above 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. 10], having provided information on aquifer structure and water quality for over three decades. 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 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.

2.3. Surface/atmosphere

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 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. 11]. 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 [12] 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 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 [13], 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. 14].

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 issues will influence the success of these methods for accurately quantifying leakage from a CCS 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: 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 $\pm$ 1 SD) [15]; soil gas monitoring of perfluorocarbon tracers added to injected CO_2 at the West Pearl Queen depleted oil formation quantified a leakage rate of 2.82×10^3 g CO_2 / year [16], which corresponded to 0.014% of the total injected CO_2; 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 [17]. 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.

Dynamic closed chamber (DCC) techniques involve the monitoring of gas concentration changes over time within an accumulation chamber placed on the soil surface, with samples collected continuously via an in-line detector. Flux can be calculated using the slope of the growth curve and the volume of the accumulation chamber. Flux measurements can be automated for continual monitoring of a point site, such as a well head.

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. 18]. 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 [19]. However, small scale surface emissions may be difficult to detect given the relatively coarse spatial resolution of satellite images.

2.4. Marine environment

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. 20]. 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 [e.g. 21]. Ideally, measurements could be taken in conjunction with acoustic or seismic surveys. Alternatively, sensors can 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. This method has been used for the detection of pipeline leaks and seepages from oil and gas reservoirs [22]. This approach could conceivably also be applied for marine CCS 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.

3. Discussion

Monitoring programmes are required to commence pre-injection to establish baseline levels, and continue through the operational period for reasons of safety, public acceptance and the calibration of models. After CO_2 injection has ceased, leakage may occur even if the CO_2 pressure is declining in the reservoir if some diffuse/dispersed/point leakage existed prior to closure, since the buoyancy forces will continue to push CO_2 upward. 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. With respect to monitoring, the detection limit of post-closure leakage will depend on factors such as depth and saturation. The optimal deployment of monitoring techniques will be site specific, depending, for example, on the type of storage reservoir, its depth, the availability of monitoring wells and whether it is onshore or offshore.

With respect to the reservoir and overlying formations, 4D seismic methods currently offer the best potential for leakage quantification, albeit with sizeable uncertainties involved. These uncertainties can be reduced through the use of multicomponent and/or downhole seismic for clearer imaging and fracture characterisation. However, where the CO_2 is dissolved, or where salt or gas in overlying formations mask the plume, other methods may be required to reduce uncertainties, such as gravimetry, EM/ERT methods, surface deformation monitoring techniques and downhole geophysical/pressure/temperature sensors. Besides CO_2 monitoring, these methods can help identify potential leakage paths and improve the calibration of models, which will aid in planning post-closure monitoring.

While changes in density or conductivity in shallow groundwater detected in gravimetric or EM/ERT surveys may alert operators to CO_2 leakage, or provide an indication of the extent of the contamination, quantification methods require further research and at present sampling and hydrochemical analysis together with measurements of flux offer the most precise estimations. This may be relatively inexpensive in urban or agricultural areas served by a network of extraction or monitoring wells. Uncertainties may be reduced with a thorough understanding of natural variability and if the source of the CO_2 is identifiable through tracers and isotopic analyses.

Quantification of CO_2 leakage into the atmosphere (onshore) can be done using methods such as eddy covariance and long open path diode lasers, which range from wide area coverage/low resolution to relatively mobile small scale/high resolution monitoring. Short closed path detectors are relatively cheap and robust, and can be placed on a comprehensive monitoring grid. Near surface gas chemistry and flux methods focus on the soil, and offer the potential to provide the most accurate estimates, assuming the extent and spatial variability of the leakage can be established. The origin of the CO_2 should also be confirmed using tracers or isotopic analysis. Ecosystem studies or eddy covariance methods may be of use in locating potential leakages prior to deployment of instrumentation and manpower for quantification. In addition, recent research into remote sensing has indicated that it may be possible to detect leakage in an unsupervised manner using multi-or hyperspectral images routine obtained by satellite. Future research may reveal whether it can become possible to estimate flux from direct absorption of certain wavebands, which could offer a relatively inexpensive post-operational monitoring and quantification option with a good spatio-temporal coverage and resolution.

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.

Acknowledgements

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