FEASIBILITY OF MONITORING TECHNIQUES FOR SUBSTANCES MOBILISED BY CO_2 STORAGE IN GEOLOGICAL FORMATIONS

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This report describes research sponsored by IEAGHG. This report was prepared by:

CO2CRC

The principal researchers were:

- Linda Stalker
- Ryan Noble
- Bobby Pejcic
- Matt Leybourne
- Alison Hortle
- Karsten Michael

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The IEAGHG manager for this report was:

Ludmilla Basava-Reddi

The expert reviewers for this report were:

Hubert Fabriol	BRGM
Ziqiu Xue	RITE
Nikolaos Koukouzas	CERTH
Katherine Romanak	University of Texas

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Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

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Background to the Study

Monitoring programmes for geological storage of CO_2 have been focussed on techniques for detecting leakage of CO_2. However, it has been recognised that CO_2 may mobilise other substances and can cause displacement of saline water. All of which could have an environmental impact in the event of leakage from the geological storage formation to potable water, the water column, soil and the atmosphere.

Several regulatory regimes, including the guidelines for CO_2 storage in the London Protocol and OSPAR conventions, require that any effects of such substances mobilised by the CO_2 and any displaced saline water be included in the effects assessment and potentially monitored. Therefore it is necessary to review what the feasibilities and current capabilities are of techniques which can monitor movement of other substances in geological formations and in the event of leakage.

The injection of CO_2 may cause displacement of saline formation water, increasing pressure in the formation. This is particularly the case in deep saline formations. The extent of displacement is dependent on the geological setting and the injection scenario. A system may be considered to be ‘open’ or ‘closed’ depending on whether the target formation is compartmentalised by lateral flow boundaries (faults). In a ‘closed’ system, the boundaries limit fluid flow, whereas in an ‘open’ system there is a much greater pressure communication and hence fluid flow is more likely. It should be noted that many systems can be considered as ‘semi-closed’ with an intermediate pressure communication. Another factor is the number and location of injection wells, which may further complicate the resulting pressure fields within the formation.

The addition of CO_2 into a formation can cause changes in the pH and Eh (redox potential) in the formation water. This may, in turn, cause changes in the solubility of various trace metals, especially those of redox sensitive metals, causing them to mobilise. Which substances are mobilised will depend upon the lithology of the target formation and that of the caprock, as well and the pH and Eh. For example, in a poorly buffering (low $CaCO_3$) aquifer containing galena (PbS), it is likely that lead solubility, and possibly that of other toxic metals, will increase.

If leakage then occurs, the mobilised substances may enter the water column or soil and may affect bacterial production and cause a significant change in the microbial community structure. The mobilised substances along with the CO_2 may also enter into any overlying potable aquifers, making them unusable.

It may also occur that additional substances, remaining from the capture process, may be injected into the target formation along with the CO_2. It is important to be able to monitor these in conjunction with the CO_2.

CO2CRC, a consortium based in Australia and New Zealand, was commissioned by IEAGHG to undertake a study considering which substances that may be mobilised by CO_2 need to be considered in monitoring programmes and what technologies could be considered to detect them.

Scope of Work

The scope of this study was in two parts. The first part is, by using the existing literature to identify what substances should be addressed, i.e. which are those that could be mobilised by injected and stored $CO_{2,}$ as well as those contained in the CO_2 stream (incidental associated substances from the fuel, capture, transport and injection processes). For example, CO_2 can cause changes in pH in sediments which could mobilise trace metals and other compounds to a higher level of bioavailability. These substances should also include displaced saline water. Then the potential scale and effects of mobilisation of such substances be assessed, so as to identify those substances which are most likely to require monitoring.

Secondly, the main part of the study would review and assess potential technologies and techniques for their feasibility of detection of these substances, and for detection of any environmental impacts they might cause in the event of leakage. Potential technologies and techniques would include both direct sampling, including for downhole applications, and remote monitoring techniques, and shall be reviewed for both onshore and offshore applications. The study should look at each technique and discuss its current and possible applications, which substances it applies to, sensitivity and resolution, costs and future developments.

CO2CRC was asked to refer to the following recent or ongoing IEAGHG reports/studies relevant to this study, to avoid obvious duplication of effort and to ensure that the reports issued by the programme provide a reasonably coherent output:

- Development Issues for Saline Aquifer Storage, CO2CRC, Report 2008/12
- Assessment of Sub Sea Ecosystem Impacts, Report 2008/08
- Potential Impacts of Leaks from Onshore CO_2 Storage Projects on Terrestrial Ecosystems, Report 2007/3
- Environmental Impact Assessment for CO_2 Capture and Storage, Report 2007/1
- Pressurisation and Brine Displacement, Permedia, Report 2010/15
- Effects of Impurities in CO_2 on Geological Storage, Natural Resources Canada, Report 2011/04
- Potential Impacts on Groundwater Resources of CO2 Storage, CO_2GeoNet, Report 2011/11

Findings of the Study

Monitoring Opportunities

This section of the study looked at what effects could be monitored and is divided into physical and flow effects, effects on the near surface biosphere, geochemical effects, hydrocarbons and organics and captured gas compositions. Following this categorisation allowed identification of analytes that could be monitored and under what conditions (Table 1)

Table 1 (a) Analytes and detection levels of substances that could be mobilized by CO_2 and (b) the conditions, limitations and ranges of deployment of such tools

(a) Analytes	Levels
CO_2	ppb to percent
pH	Relative change
Hydrocarbons	ppb to percent
Anions and cations	mMol
Tracers or contaminants	ppb to percent
Pressure/temperature	kPa/°C
Geophysical properties	Varies with methods employed
Biological properties	Varies with methods employed

(b) Considerations	Approximate Ranges
Depth	Soil surface to +3km depth
Temperature	4°C to ~ 150°C
Aqueous environment	Yes
Power	240v maximum
Data transmission	Wire or wireless
Lifetime	Short to long-term
Self-calibration	Drift rates
Redundant/robust	Environmental challenges
Relative cost	Indicative costs

Injection of supercritical CO_2 into a deep, confined aquifer will cause mobilisation of the pre-existing fluids and depending on the injection scenario may include some migration of the supercritical CO_2 plume. In addition, there will be some degree of dissolution of the CO_2 front into the formation fluid and interaction between these fluids and the rock matrix. This will cause some physical changes in the pre-existing flow properties which may be detectable and therefore have application in monitoring and verification activities. Formation water properties that may change are pressure, density, viscosity, temperature, chemistry/redox potential of the original formation water and pH changes, due to the presence of the CO_2 and potential reactions with the rock matrix.

Effects of on the near surface biosphere may be monitored and potential changes can be identified by considering natural analogues. Mobilised minerals and compounds can act as an active nutrient supply or toxic substance, giving either positive or negative effects on plant and bacterial communities.

Geochemical effects that could be monitored include the oxidation and reduction states of fluids and minerals and monitoring of changes to metals, metalloids and anions.

The addition of CO_2 gas to a shallow aquifer would result in an increase in the partial pressure of CO_2. This increase in pCO_2 would in turn result in an increase in dissolved CO_2 and therefore a decrease in pH. There are likely significant consequences of large changes in aquifer pH including; 1) dissolution of carbonate and silicate minerals, releasing contained metals/metalloids 2) dissolution of oxide and hydroxide phases (i.e., primarily Fe-, Mn-, and Aloxyhydroxides), which will release adsorbed or co-precipitated metals/metalloids and 3) desorption of metals from mineral surfaces by lowering the pH below the characteristic adsorption edge of different aqueous species on different aquifer materials.

A review of published studies and consideration of natural analogues was carried out to identify the species of concern. These differ depending on the reservoir type and the extent of mobilisation may differ according to, amongst other factors, the pH level.

There is an opportunity to utilise tools and technologies for monitoring hydrocarbons for CO_2 storage in depleted oil and gas fields. Whether for EOR or using abandoned or uneconomic fields there may be significant quantities of hydrocarbons left as oil-in-place. As a consequence, there may be free gas, free oil and residual hydrocarbons that will mix with the added $CO_{2;}$ these hydrocarbons can be taken up by the supercritical CO_2 plume and easily mobilised during storage in these environments. In addition to this, hydrocarbons or functionalised organic compounds have been used as tracers.

Incidental substances can be present in CO_2 streams introduced from combustion fuels, capture, transport, industrial manufacturing and injection processes (e.g. as tracers). Depending on the processes involved, any additional substances and contaminants may be present in varying abundances and different chemical compositions. Important effects considered are pressure changes from the effect of limited or no compressibility of non-condensables; chemical reactions, which are scaling/fouling of the injector, changes in pH, mineral reactions beyond the injector and mobilisation of cations and anions; then there is transport of contaminants, movement of contaminants as pollutants or tracers.

Potential Technologies

The approach taken in the study was to consider anything from soil surface to deep subsurface and includes physical, chemical, biological and other approaches to identify tools. Potential technologies considered were divided into those that monitor flow or physical effects, biological technology, geochemical effects (mobilisation of anions and cations) and monitoring of hydrocarbons and organics.

The significant advantage in the types of tools and systems described in the physical monitoring tools section is their ability to detect changes due to the presence of CO_2 some distance away from the CO_2 itself. This increases the percentage of reservoir covered by the monitoring system, increasing confidence in the containment and allowing for the possibility of early detection and remediation.

The key parameter in this section is pressure. There are two reasons for this; 1) it is a mature technology with a range of options suitable for the types of monitoring environments required for CCS technology. It is off-the-shelf, cost effective, sensitive and robust for long term installations; 2) the movement of a plume of CO_2 will be accompanied by a propagating wave of pressure whose spatial footprint will far exceed the dimensions of the plume itself. A consideration in long-term pressure monitoring is the level of sophistication required for a specific site. The cost of installation, processing and interpreting increases with increasing complexity of the system and number of gauges installed. It is necessary to carefully consider what the monitoring objective is for each case.

Some geophysical methods can measure the CO_2 plume or the shift in salinity, density and pressure that can be detected. Although other associated compounds may be liberated, it is unlikely any of these are in large enough quantities to be seen through geophysical techniques. It is possible that shallow applications may have more flexibility in detecting other subtle parameters, but this is not certain.

Other systems, such as DTS (distributed temperature sensors) and ERT (electrical resistance tomography) have been demonstrated to have application to CO_2 monitoring, however, the longevity of these systems under reservoir conditions is also unclear and their cost may be prohibitive. For this reason, although they are potentially applicable to monitoring aquifers above the storage zone, it is unlikely they would be deployed here. The exception may be in specific, high risk locations. Fibre optic technologies have the potential for sensitive monitoring of acoustic, flow and temperature properties. This again produces large volumes of data which can be complex to handle, require sophisticated geological models to interpret, and considerable computing power to process. pH sensors are only beginning to be developed for deeper, hotter environments due to new applications in oilfield surveys but may not yet be deployable for longer term periods without some testing.

Biological monitoring for CCS presents challenges at depth, but is a relatively low cost and feasible option in the near surface environment. There is a gap in application of biological monitoring to CO_2 storage sites compared to chemical or geophysical methods, with only a few successful biological monitoring tests applied to natural analogues or shallow test injections. The most important finding in this section is the potential of newer monitoring tools for phylogenetic and functional gene characterisation of microbial communities that have not been tested in CO_2 storage. These tools offer rapid and more thorough microbial characterisation than older methods and have the potential to show changes in microbial communities due to CO_2 leakage and associated issues such as pH changes and mobilisation of potentially toxic metals and metalloids. Once a link can be established between species or functional genes that reflect changes due to leakage of CO_2 and associated substances, refining specific microbiological signals into simple-to-use, field portable, rapid biosensors may be possible.

For geochemical monitoring traditional ion selective electrodes (ISE) suffer from a number of drawbacks that make them largely unsuitable for long-term in situ monitoring of deep saline groundwater. These disadvantages include issues of matrix matching, sensor drift, need for calibration, need for variable storage solutions for different analytes, use of internal reference solutions, and in some cases, detection limits that are too high for trace metals. The new thin and thick film deposition of sensors means that many of these problems are in the process of being solved, in particular detection limits, miniaturisation and reduction in the need for repeated calibration. However, the most useful approach to long-term in situ monitoring for the alkalis, alkaline earths, transition metals and metalloids appears to lie in the area of ISE and ISE sensor arrays.

Key analytes could be identified that represent a larger group of elements that typically have similar behaviour in groundwater and in response to changes in pH and aquifer mineralogy through carbonation reactions. Pb and Zn could be monitored as proxies for many of the transition metals. A La, Ce or Nd electrode would be suitable to monitor changes in rare earth elements (REE) and actinide concentrations, as these are commonly the most abundant REE in groundwater. An ISE for Fe would permit monitoring of dissolution and precipitation of Fe and Mn oxyhydroxides, which are key mineral phases that control the mobility and attenuation of many metals and metalloids (especially Cu, Pb, Co, Ni, As, Se). Ca, Na, Mg and K ISE, in conjunction with pH and $CO_2(g)$, would permit monitoring of the extent of water-rock interaction and carbonation.

Changes in anion concentration as a result of CO_2 leakage could arise in a number of ways, including mixing with saline waters, which would increase Cl, Br, and I concentrations, lowering of pH resulting in enhanced water-rock interaction, which could release anions. Lowering of pH may result in increased adsorption of anions onto positively charged mineral surfaces and changes in redox conditions, resulting in changes in sulphide and sulfate values, reduction of nitrate or oxidation of ammonia.

There is much information published on the development of sensor technologies and tools for monitoring hydrocarbons, though very little has been applied to CCS monitoring applications. Many of the sensors are not particularly selective, though membrane based sensors are generally more selective compared to sensors that do not comprise a chemoselective material. However, those that employ an absorbing membrane are generally less stable at high temperatures and pressures and over long monitoring periods as the membrane material can degrade with time. Fluorescence based detection tends to be stable due to the robust nature of both the light source and photometer. Fluorescence and piezoelectric (surface acoustic wave) sensors appear most sensitive and can detect required levels (ppb). These sensors are relatively small and robust; however it is not known how they will perform in geological formations over long periods of time. The long-term drift of these sensors have not been properly evaluated will need to be addressed.

Application of Study

There is potential for an increasing number of tools to be used to develop integrated multi-analyte sensors for real time qualitative and quantitative analysis, along with data acquisition and transfer. Some of the electrochemical and optical detection platforms appear more suited to adaptation and deployment as they are already relatively inexpensive, rugged, easily miniaturised, low in power requirement and sensitive. Solid state devices, such as new generation pH probes are beginning to have specifications required for deployment in deeper and more aggressive environments.

Pressure measurement is a fundamental component of any CCS monitoring system. Pressure transients are likely to occur ahead of any CO_2 or brine plume potentially allowing the detection of changes some distance away from the source. It also needs to be considered that pressure can be affected by other factors including seasonal variations, unknown recharge rates and other uses of the subsurface, such as hydrocarbon extraction. Complexity of interpretation, for pressure and other tools, will also be increased by the large volumes of data produced. This may then require considerable understanding of the systems involved and extensive computing software, facilities and expertise. With most geophysical tools, depth to target may limit resolution with respect to leakage, however electromagnetic and gravity surveys appear to show some promise, as does magnetotellurics, though has yet to be tested in a CCS environment.

There is only limited information on biological monitoring for CCS and it is only likely to be useful in the shallow subsurface. Only a few tests have been conducted and mostly from natural analogues and slow release studies. Expected changes in vegetation and microbial communities need to be identified and understood. Following testing, they can be expected to be used as low cost assurance monitoring tools.

The geochemistry of subsurface fluids has traditionally been characterised by direct fluid sampling. Advances, such as the use of the U-tube or other sampling methods to obtain pristine samples at reservoir conditions have been complemented by analysis in field and laboratory environments. However, advances in ISEs, including lower detection limits, miniaturisation and increased robustness, make them potentially viable in-situ tools. Targeting the right group of species for a given site could allow for the building of a powerful array incorporating other monitoring tools looking specifically for changes in particular metal concentrations, pH and $CO_2(g)$. There are still drawbacks related to sensor drift and calibration requirements, necessitating further advancement and testing.

Hydrocarbons and organic sensors were included in the report due to their pervasive presence in the subsurface. In many situations, depleted oil and gas fields have and will continue to be targeted for CO_2 storage. Similarly EOR opportunities that aid in the economics of CO_2 storage will mean that monitoring will take place in locations with abundant hydrocarbon compounds present. Many of the sensors available for hydrocarbon detection are not particularly selective to specific compounds. This will not be a concern for monitoring of depleted hydrocarbon reservoirs where a range of compounds may be present, however, it will be an issue if the sensor is required to monitor for a specific organic tracer compound. There have been increased concerns about the mobilisation of volatile organic compounds into potable aquifers, related to gas extraction form shales and coal and could potentially become an issue for CCS. Tools may then need to be deployed in shallow aquifers for public assurance at new or existing CCS sites, especially if there are hydrocarbon recovery activities in the area.

While some small and relatively robust sensors for hydrocarbons are available, their long term drift and stability in aggressive environments may require further testing. It is anticipated that monitoring of overlying aquifers to show an absence of organics will be an increasing focus for assurance of potable water integrity.

The results from this study are also intended to be input into the IEAGHG monitoring selection webtool.

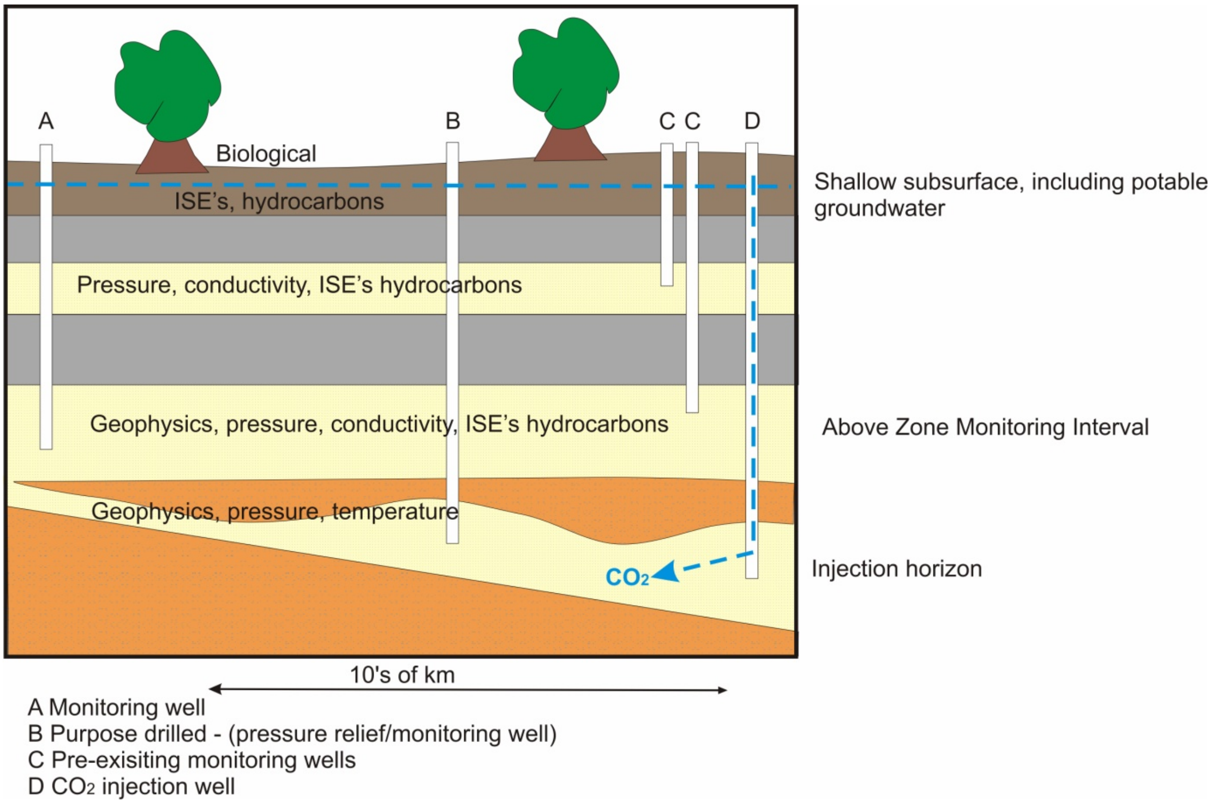
Expert Review Comments

Expert comments were received from 5 reviewers representing industry and academia. The overall response was positive and noted the need for work in this area. The main suggestion was to make sure the focus of the report was on the substances mobilised by CO_2 and not the CO_2 itself. This was addressed and a CO_2 section was included for completion. There were also comments on distinguishing between potable and saline aquifers. All comments were addressed in the final report.

Conclusions

The different methods described in the report are likely to be applicable at different depths and may therefore serve different purposes and can be summarised in figure 1. The key physical parameter measured in the subsurface is pressure as it covers an area much larger than that of the plume. Within the storage interval the main tools considered are geophysical, though some geochemical monitoring can happen at depth. Biological monitoring is currently restricted to the near surface.

Figure 1 Summary of likely tools that could be deployed at discrete locations during monitoring



Many tools and new technologies have been identified in the report, however a lot of these have not yet been tested in the field. Tools that have been deployed at previous and current sites have not been deployed across all sites. This may be due to costs and funding arrangements, or because they are not appropriate at some sites or there has been mixed experience with some tools or the datasets generated. Many of the current CCS sites have relied strongly on equipment from the oil and gas sector, where the tools are already appropriately rated for pressure and temperature, but may not always be tested in terms of longevity, ease of data retrieval or manipulating the extensive data generated.

In almost all cases, tools have been deployed to investigate the injection horizon, and some shallow aquifers, soil gas or atmosphere. Monitoring of the formation directly overlying the injection horizon has been limited to indirect measurements, except at the Cranfield test site in Mississippi. There is a specific monitoring zone above the first sealing unit where pre-existing wells could be equipped with monitoring tools relatively cost effectively More focus with selected tools sampling the zone directly overlying the injection horizon is needed, as this may provide detection of substances that might be mobilised by a leak.

There have been improvements in several tools regarding miniaturisation, ruggedisation, lower costs, lower detection levels and increasing electronic communications to report the data obtained.

This report demonstrates that the tools can be split into different technology readiness levels. Many seismic tools would be in the upper zone, where technology is mature, tested and deployed and only incremental improvements may be anticipated. By contrast, some tools, such as the biological tools would more likely fall in the lower to mid zone, where the tools may have been tried for other applications reasonably successfully, but would require further research to prove the feasibility of the tools in CCS M&V applications. Evaluating tools in terms of their technology readiness might be a good way to flag tools that could be trialled alongside proven technologies during future storage operations.

Future goals identified are field testing of identified tools, both at natural analogue sites and CO_2 storage sites if possible. The longevity, stability and operational costs (retrieval, replacement of power supplies, data processing and manipulation etc.) need to be identified in order to quantify the true cost of M&V and also assess the relevance of different tools in different settings. Tool can be evaluated for their readiness level.

Any mechanism that provides low cost, large spatial coverage of a CCS site and assures us that the CO_2 is safely stored is an important outcome for the CCS domain, however significant testing and augmentation of many tools may be required before we achieve a full toolbox of techniques that can fit any geological storage site.

Recommendations

Some technologies considered in this report are still in the early stages of development and it is unknown whether they will prove to be useful for monitoring of substances mobilised by CO_2. It is important that IEAGHG keep updated on the progress of testing, possibly through the IEAGHG web based monitoring tool. The monitoring tool will also need to be updated with the results from this report.

IEAGHG should ensure that adequate attention is paid to these topics through future storage network meetings and by the study programme.

Feasibility of monitoring techniques for substances mobilised by CO_2 storage in geological formations

Project for the IEA GHG ref IEA/CON/10/182

Stalker, L, Noble, R, Pejcic, B, Leybourne, M, Hortle, A and Michael, K.

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Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC)

GPO Box 463
Ground Floor NFF House, 14-16 Brisbane Avenue, Barton ACT 2600
CANBERRA ACT 2601
Phone: +61 2 6120 1600
Fax: +61 2 6273 7181
Email: info@co2crc.com.au
Web: www.co2crc.com.au

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Executive summary

This report sets out to identify and evaluate appropriate monitoring tools for substances mobilised by the actions/reactions caused by CO_2 injection during CCS operations and includes a brief description of the types of physical, chemical and biological parameters that might be affected. Monitoring these is important for verifying predicted migration pathways and characterising changes in the physical and chemical properties of associated sedimentary formations and groundwater. Understanding these processes and mapping their distribution aids in the identification of potential monitoring tools and facilitates an assessment of their utility in a particular monitoring domain. Matching the appropriate monitoring tool with the monitoring environment is therefore critical to designing an effective monitoring and verification program.

The tools assessed include those that can specifically look at substances such as changes in specific ion concentrations, or mobilisation of organics during enhanced oil (and gas) recovery (EOR or EGR). There are also physical effects, for example, changes in pH and pressure and temperature transients. Furthermore, in the shallow subsurface, changes in water chemistry could affect microbial communities in the vadose zone impacting local biogeochemical cycles, particularly those of major nutrients (C, N and P). For completeness, or where it was considered appropriate (for example, some geophysical methods), these have been included in a section that specifically looks at CO_2 monitoring.

A variety of literature sources were used to identify substances (including physical, chemical, geophysical and biological) that are likely to be mobilised or affected during the storage of CO_2 in the subsurface. Literature used included peer reviewed papers, conference proceedings and many recent, relevant reports from the IEA GHG.

The workflows used to identify tools with potential to monitor the various mobilised substances were based on an earlier report by Ross, Pejcic and Stalker (2007) on “Down-hole Monitoring of Chemical Changes Associated with CO_2 Storage – A Review of Chemical Sensor Technology” for the CO2CRC. This new report both updates and expands considerably on that work.

Methods and approaches for identifying substances that could be affected by CO_2 storage are partly evaluated by looking at a series of case studies where monitoring for changes in the subsurface following CO_2 storage have taken place. Monitoring set-ups from the following sites are briefly reviewed: Pembina (Enhanced Oil Recovery - EOR), Ketzin (Saline formation), Cranfield (EOR), Frio (Saline formation), and Otway (Depleted gas reservoir). Interestingly, in almost all cases sampling tools have been deployed to investigate the injection horizon and some aspect of the shallow subsurface (aquifers, soil gas) or surface (atmosphere, surface deformation). On the other hand, monitoring of the formation directly overlying the injection horizon is limited to indirect measurements (i.e., geophysics), with the exception of Cranfield where there are observation wells completed directly above the first sealing unit.

Areas of potential monitoring opportunities include:

- Physical effects
    - Including pressure, density, viscosity, temperature and associated geophysical measurements and displacement of fluids.
- Biological effects or changes

    - Including changes to plant species, bacteria and general ecology,.

- Geochemical effects

    - Including the oxidation/reduction state of fluids and minerals, and the monitoring of changes to the metals, metalloids and anions.

    - Contaminant species entrained in the capture gas are also considered.

- Hydrocarbons and Organics

    - Including compounds present in depleted oil and gas fields or in EOR environments.

    - Mobilisation of hydrocarbons removed by the solvent effects of supercritical CO_2 from organic matter (source rocks, coals or hydrocarbon reservoirs).

    - Organics entrained in the capture gases from fossil fuel processing or burning.

- Carbon dioxide (CO_2)

    - Where the review of CO_2 sensors in the Ross et al, (2007) report has been revisited to include some updates.

Figure A has been used to characterise the main zones or intervals of interest for the deployment of monitoring tools. The interval from soil surface to the injection horizon was considered, and some aspects of offshore/marine monitoring were also included. The injection horizon may be a saline aquifer/saline formation, or depleted hydrocarbon reservoir. The above zone monitoring interval covers the entire sedimentary section above the injection horizon and overlaps with the shallow groundwater aquifer commonly monitored for potable water supply. The monitoring environment of each of these zones is slightly different. The injection interval is likely to be at high pressure and temperature and there may be significant concentrations of hydrocarbons, either naturally occurring or from the injection stream. In general, a monitoring strategy would minimise the number of wells penetrating this horizon. Further, these conditions are often detrimental to the longevity and stability of many monitoring tools. The zone immediately above the injection horizon would likely have lower pressure and temperature relative to the injection horizon and retrievable monitoring tools are an option. It is also possible that the effects of any formation water or CO_2 leaving the storage container (such as pressure or geochemical changes) would be measureable in this interval. Those monitoring zones in the shallow sub-surface include monitoring groundwater in open bores and soil sampling. In these environments temperature and pressure are much less extreme and there are many more options for monitoring tools. However, the likelihood of detectable impacts of CO_2 storage reaching these environments is generally low and monitoring in these environments may be perceived to be primarily about assurance monitoring.

Not surprisingly, many of the tools able to withstand the higher temperatures and pressures in the injection horizon come from the petroleum exploration and production industries. Pressure gauges area a key example. These tools are often the mainstay of CCS sites as the propagation of the pressure pulse in advance of the CO_2 plume significantly increases the measurement footprint to many times the size of the CO_2 plume itself. In addition, these gauges are designed for the harsh environmental conditions within the injection horizon and can also be applied to zones above the injection horizon. Groundwater monitoring tools developed within the water resource industry are also suitable for application to monitoring zones above the injection horizon and can measure pressure, temperature and formation water conductivity. Oilfield and water resource industry tools are available off the shelf and are suitably sensitive and robust for deployment in a number of settings.

Nevertheless, there are distinct gaps in the availability of other deployable tools. There is the potential for the development of tools such as those measuring electrical conductivity, density or acoustic perturbations, with sufficient robustness and longevity to have the same utility for CCS operations. Previously, there has been no great interest in monitoring pH down-hole in an oilfield setting; however, this is an important geochemical parameter to indicate the presence of CO_2. Currently the tools available for pH monitoring are limited to short term shallow groundwater monitoring as the longevity and stability of the instruments are limited. However, new advances in measuring pH have been made in recent years and are discussed.

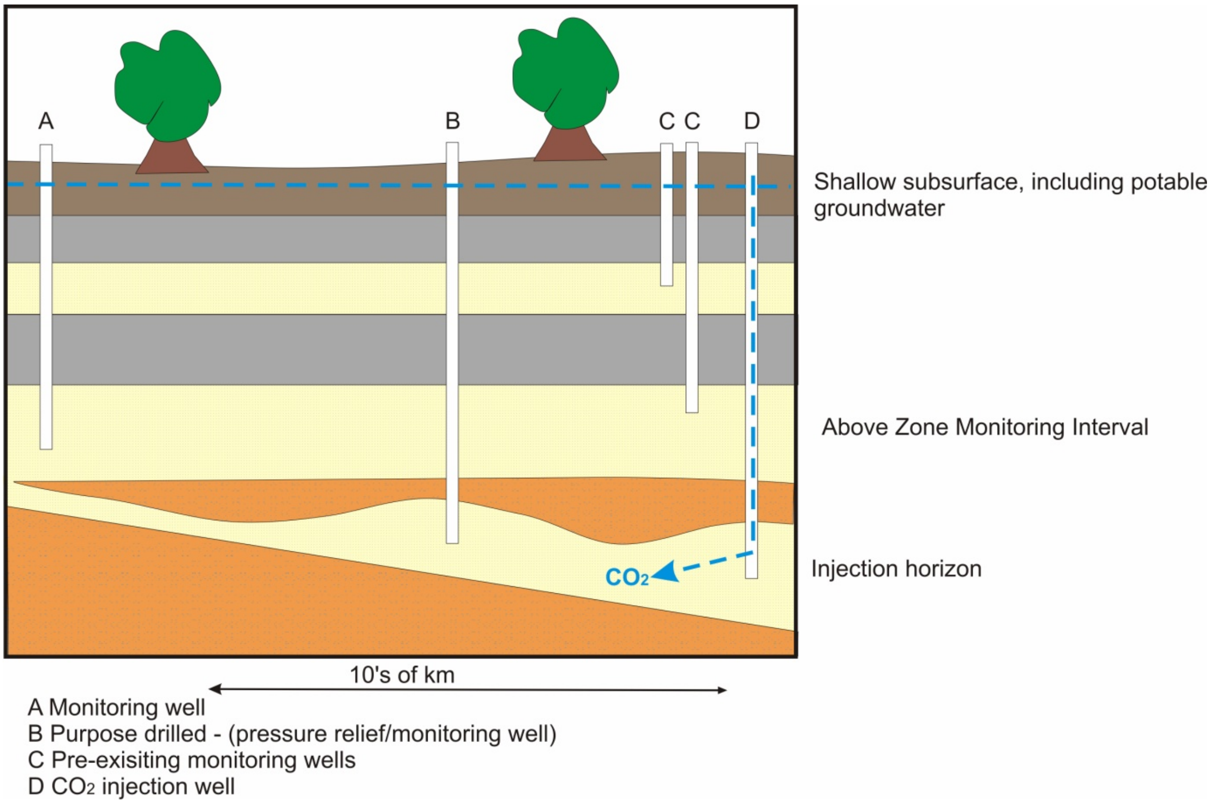

Figure A Schematic of the monitoring intervals considered for evaluation of suitable tools for monitoring substances mobilised by CO_2.

The inorganic geochemical changes associated with the presence of dissolved CO_2 are reasonably well understood and this knowledge can be applied to monitoring in both injection horizons and overlying aquifers/groundwater zones. In general, it is straightforward to identify potentially mobilised cations or anions that may increase or decrease over time during the passage of CO_2.

There have been a number of advances in solid state and ion selective electrodes (ISEs) that are increasingly being ruggedized for deployment in more extreme settings. Their stability and longevity need further testing, as well as a good program design to determine where and when to deploy such instrumentation for monitoring purposes.

The presence of contaminants from various flue gases (both organic and inorganic), their concentrations and impacts are still being understood, but can generally be identified for monitoring purposes prior to injection.

Hydrocarbons and organics are subject to mobilisation by the CO_2 plume, either due to extraction by supercritical CO_2 of compounds from organic carbon-rich shales and mudstones or due to their presence in depleted oil and gas fields. There are numerous tools that have varying degrees of compound specificity and robustness/sensitivity. Many of these tools are used in offshore settings in shallow and deep marine environments and have good robustness with respect to pressure, however they may not be quite so effective in hotter downhole settings. Fouling or degradation of some membranes may be an issue for deployment in certain settings, but these tools are also being improved and taken out of the laboratory for testing and deployment.

Some areas of research and tool development are more mature than others, such as CO_2 monitoring with geophysics, while geophysical monitoring of other substances is not as well developed and may have significant limitations. Further changes in how geophysical tools are developed or deployed or the limits of their resolution in the deep subsurface may produce incremental improvements. Alternatively, there are some geophysical tools that have only been tested to a limited degree in the CCS domain (for example magnetotellurics or CSMT, ground penetrating radar or magnetic resonance sounding) that may provide suitable shallow monitoring alternatives that could be used to observe changes in salinity, for example.

Other areas of research and application are less mature with significant potential for development, for example, in the case of biological monitoring with low cost arrays and other tools arriving on the market. Many of the approaches identified in this domain have been used successfully in ecological studies and bio-prospecting for mineral exploration. These tools could provide a non-invasive approach to monitoring that may prove effective for stakeholders and landowners that are often adversely affected by large grid testing during soil gas or geophysical surveys. Further testing is required to evaluate the effectiveness of some of these biological tools as well as the economic viability of such testing.

Many tools described within this report have not yet been tested in the carbon capture storage, monitoring and verification (CCS M&V) domains, and of greater concern is that some of these tools have not been tested outside of a laboratory. In spite of these caveats, it is still possible to identify the types of tools that could be deployed in the monitoring intervals as shown in Figure B. In this figure, we have identified likely technologies that may perform best at different depths, from soil surface to the injection horizon. Biological monitoring tools, such as the Phylochip® do appear test-worthy based on previous mineral exploration experiences. ISEs may be easily deployable in shallower groundwater bores as they currently need to be easily retrievable for testing and regular re-calibration. Some hydrocarbon sensors may be deployable to greater depths depending on their ability to withstand heat. At the injection horizon, existing geophysical, pressure and temperature tools remain the most robust. Adding to the package of tools in this interval would be those predominantly used for R&D purposes rather than for specific monitoring of the CO_2 plume or substances mobilised by CO_2. Therefore there is perhaps less need to be able to deploy ISEs or hydrocarbon sensors that might be unstable at say > 2km depths.

The tools and measurements must still be integrated with the models prepared for a CO_2 storage site in order to understand the meaning of the information acquired. Meaningful thresholds for measured parameters alerting a possible change in the physical, chemical or biological properties during the assurance M&V still have to be developed for each site in order for these tools to be of overarching benefit to CCS programs.

Many of the results presented and tools and technologies identified here can be integrated with the current IEA GHG Monitoring Selection Tool[1] having examples of usage and some key specifications presented either in this document or referred to in the source materials. It is hoped that some of the work presented in this report can update that package.

In conclusion, we have been able to complement some of the other reports recently commissioned by the IEA GHG to provide more potential alternatives to the standard monitoring tools used in CCS M&V to date. Our research indicates that there is indeed potential for some of these tools to be further developed such that they have sufficient robustness, longevity and sensitivity to detect the signatures of substances mobilised with respect to CO_2 leaks with sufficient timeliness for remedial actions to be taken.

We look forward to being able to test some of these tools in the future in order to evaluate their robustness, longevity, sensitivity and utility at both smaller scale tests and larger commercial scale sites in order to further low cost, appropriate M&V to assure that we can indeed find signatures for other substances mobilised with respect to CO_2 leaks with sufficient timeliness for remedial actions to be taken.

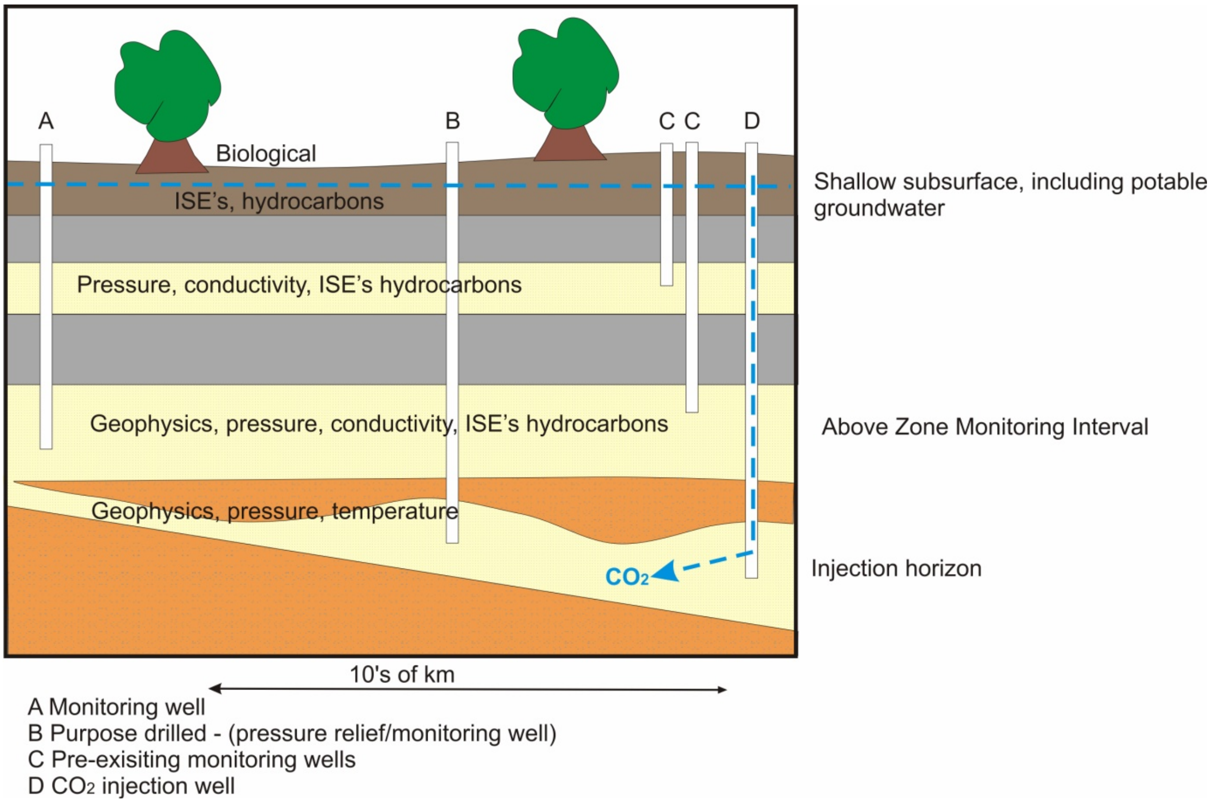

Figure B. Likely types of tools to be used during monitoring and verification on a commercial scale CCS site based on the work in this report.

[1] (http://www.ieaghg.org/co2tool_v2.2.2_product_joomla/co2tool_panel.php)

1. Introduction

This study has been conducted to identify suitable analytes and monitoring tools for substances mobilized by CO_2 as proxy indicators of CO_2 movement or release. These indicators were divided into four main categories; (1) physical effects (e.g. changes in pressure, temperature, density, flow); (2) geochemical effects (e.g. diagenetic or dissolution effects); (3) shallow/surface effects (e.g. changes to microbial or ecological communities), and (4) capture gas contaminants that would be entrained in the CO_2 plume but could act as chemical tracers.

While relatively broad, these categories allowed the identification of typical “analytes” that could be monitored, and necessarily included consideration of the anticipated concentration levels of each of these (Table 1a). The dynamic range of the analyte concentrations can limit the deployment of certain tools where ranges might exceed the measurement capacity of the tool, for example, CO_2 concentrations (Table 1a). Furthermore, the conditions of deployment, for example temperature, had to be defined in order for the tools to be suitably evaluated as fit for purpose in a range of likely monitoring and verification (M&V) settings (Table 1b).

The project builds on an earlier study carried out for the CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) by Ross et al., (2007) which reviewed the available sensor technologies for the detection and quantification of CO_2 and some proxy indicators. That report concluded that optical sensors were the most likely technology to be employed for direct measurement of CO_2. Included in the scope of that study were other substances mobilised by CO_2. At the time of writing, it was acknowledged that many of the sensors and monitoring tools that performed well in laboratory testing were likely to have limited capacity to cope with depth, temperature and the aggressive environments within which these tools would subsequently be deployed. It is possible that many tools could be modified (i.e. miniaturised, ruggedized) to become low cost, use low amounts of power and be sufficiently sensitive for carbon capture and storage (CCS) M&V. This project revisits many of these technologies in more detail to determine whether sufficient advances have been made to aid deployment of such tools to provide low cost, broad coverage monitoring in the future.

The scope of the previous study has now been expanded, but the approach remains similar. Substances likely to be mobilized have been identified, followed by an evaluation of the tools that might be used in monitoring them in a carbon capture and storage site. Literature reviews (ISI Web of Science, ISI Derwent Innovations Index [patent search] and other standard search engines) and case study evaluations were effective sources of information. The case studies used were; (1) Pembina, Canada, (2) Ketzin, Germany, (3) Cranfield, USA, (4) Frio, USA and (5) CO2CRC Otway Project, Australia. These case studies gave a good overview of the suite of typical M&V tools currently applied to monitoring CO_2.

One of the main difficulties with this project is the ability to define substances mobilised by CO_2 versus the impact of the CO_2 itself. Section 2 of this report attempts to review what we know from the literature regarding substances mobilised by CO_2. This is conducted in some detail and is used to develop appropriate literature searches for tools that may measure substances and analytes that could be monitored for as a proxy for the CO_2 plume itself. These substances include a range of “analytes” from pressure transients to changes in abundance of metal species such as calcium. Details of the potential tools identified are presented in Section 3. Behaviour of many geochemical substances in CO_2 and water are relatively well understood. Types of contaminants in flue gases are generally known, but not quantitatively well characterised at this stage. The effect of CO_2 on the soil surface and biological communitites is a relatively immature area of research, but there is growing activity in this area, and experience in particular from the mineral exploration industry suggests that more could be done in this area to expand research to look at relatively cheap and low invasivity studies in the future. And while geophysical monitoring has taken place at many CO_2 sites, this approach has often been used to visualise the CO_2 plume, rather than substances mobilised by that plume.

Table 1 (a) Analytes and detection levels of substances that could be mobilized by CO_2 and (b) the conditions, limitations and ranges of deployment of such tools.

(a) Analytes	Levels
CO_2	ppb to percent
pH	Relative change
Hydrocarbons	ppb to percent
Anions and cations	mMol
Tracers or contaminants	ppb to percent
Pressure/temperature	kPa/°C
Geophysical properties	Varies with methods employed
Biological properties	Varies with methods employed

(b) Considerations	Approximate Ranges
Depth	Soil surface to +3km depth
Temperature	4°C to ~ 150°C
Aqueous environment	Yes
Power	240v maximum
Data transmission	Wire or wireless
Lifetime	Short to long-term
Self-calibration	Drift rates
Redundant/robust	Environmental challenges
Relative cost	Indicative costs

1.1 Background and information on the Tender

The IEA GHG requested submissions on Tender IEA/CON/10/182 entitled “Feasibility of Monitoring Techniques for Substances Mobilised by CO_2 Storage in Geological Formations” (see Appendix 1). Hereafter, this report is referred to as the “Feasibility Study”.

This study consists of an assessment and review of the feasibility of current techniques that could be available to detect not only CO_2 migrating from a storage site, but the potential for monitoring other mobilised substances and effects. This includes physical changes (most notably changes in pressure) and changes to the chemistry of fluids and rocks that have been in contact with mobilised CO_2 (e.g. changes in pH, trace elements, heavy metals and so on). It is recognised that mobilising these substances could cause changes to baseline conditions and affect other resources, for example changes in groundwater quality and microbial communities. Compounds, in addition to CO_2, added as part of the combustion and capture process (i.e. power generation) which may be regarded as contaminants or potential tracers also need to be addressed in terms of their potential effects on re-mobilisation in the subsurface and their potential to represent monitored species. Thus, there is a need to identify and examine a variety of subsurface tools that may be used to monitor changes of a suite of different physical, chemical and biological parameters in response to the movement of CO_2 and other substances.

The team who conducted this study was assembled by CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) and include:

- Linda Stalker (CSIRO & CO2CRC) – organic/gas geochemistry (project leader)

- Allison Hortle (CSIRO & CO2CRC) – physical hydrogeology
- Karsten Michael (CSIRO & CO2CRC) – physical hydrogeology
- Andrew Ross (CSIRO) – sensor technology/oceanography
- Bobby Pejcic (CSIRO) – sensor technology/analytical chemistry
- Ryan Noble (CSIRO) – inorganic geochemistry
- Matthew Leybourne (GNS & CO2CRC) – inorganic geochemistry

Two reviewers were identified to assess our work for internal peer review:

- Jim Underschultz (CSIRO, CO2CRC & ANLEC) – hydrogeology
- Barry Freifeld (LBNL) – monitoring and CCS projects

1.2 Related projects

The IEA GHG indicated in the tender a series of recent reports that would be relevant to this study, including the following published reports:

- Development Issues for Saline Aquifer Storage, CO2CRC, Report 2008/12
- Assessment of Sub Sea Ecosystem Impacts, Report 2008/08
- Potential Impacts of Leaks from Onshore CO_2 Storage Projects on Terrestrial Ecosystems, Report 2007/3
- Environmental Impact Assessment for CO_2 Capture and Storage, Report 2007/1
- Pressurisation and Brine Displacement Issues for Deep Saline Formation CO_2 Storage, 2010/15, November, 2010

And work in progress:

- Effects of Impurities on Geological Storage of CO_2, 2011/04, June, 2011
- Potential Impacts on Groundwater Resources of CO_2 Storage, CO2GeoNet which commenced mid 2010. (received for review on 7th February, 2011)
- Quantification Techniques for CO_2 Leakage, CO2GeoNet, commenced mid 2010 (received for review 19th January, 2011)

The team was invited to review the “Effects of Impurities in CO_2 on Geological Storage” in September, 2010, which was of benefit to the section dealing with identifying likely materials that could be mobilised. The team members were introduced to the group from CO2GEONET Association and BRGM to obtain any information or prepared materials on their “Potential Impacts on Groundwater Resources of CO_2 Storage” project. However that project commenced only slightly before the “Feasibility” project reported here. The draft report was circulated in early February and was able to be referred to for confirmation and to avoid duplication of effort. Circulation of other reports during review (listed above) also aided this project.

Some members of the team were involved in the CO2CRC Otway Project Stage 1, conducted from 2005-2010 in Victoria, Australia. Significant learnings were made in that project and gave rise to certain expectations of the sorts of tools that could be available and their efficacy and robustness. The CO2CRC also previously commissioned a report by CSIRO and CO2CRC staff that evaluated the state of the art with respect to down-hole monitoring tools for CO_2 and proxy indicators. The report “Down-hole Monitoring of Chemical Changes Associated with CO_2 Storage: A Review of Chemical Sensor Technology” by Ross et al. (2007) was a valuable resource for the current project and many of its methods were utilised to provide a similar report but with a far wider remit. More detail of that report and the new work that has come from this report is discussed below.

1.3 Rate of development of new tools

An earlier report by Ross et al. (2007) was commissioned to specifically evaluate down-hole tools that could potentially be used in a CO_2 injection test of the Paaratte Formation in Otway, Victoria, at the CO2CRC site. A new well had been planned to reach depths of approximately 1500m in the form of a slim-hole or mineral well drilled bore. Drilling a slim-hole well had the advantages of reduced costs and rigs had shorter lead times for drilling the well.

Thus the 2007 study tended to focus on well-based monitoring options only, omitting the shallow subsurface (specifically shallow groundwater) or near surface (soils). The study also did not evaluate tools other than “sensors”. The scope of the earlier project was expanded for the current report. The physico-chemical properties that were identified in Ross et al. (2007) as being important to monitoring CO_2 movement in the subsurface are listed in Table 2. New additions to the list of analytes for this project have been added to the table in order to show the extent of the current report.

It was recognised that many of these tools could be complimentary to the analysis of samples acquired in the reservoir or storage interval via a fluid acquisition system. In the case of the work done at the CO2CRC Otway site, this meant comparison with the samples acquired via U-tubes (Freifeld et al., 2005; Freifeld, 2009). Fluid samples (both gases and liquids) collected at different depths could be returned to the surface at preserved pressures prior to analysis (particularly for all the analytical properties presented in the upper portion of Table 2). This method is ideal for obtaining detailed information during pilot and research scale field trials, and has been used to good effect in those situations (Freifeld, 2009). Less labour intensive however is the use of deployed tools that could report the relevant information back to a centralised area, and the Ross et al. (2007) report attempted to identify some tools that were at or near readiness for testing in the subsurface.

Table 2 Physico-chemical properties of monitoring interest identified by Ross et al. (2007) and new properties identified as being important for this Feasibility study.

Analyte	Detection Levels	Purpose (relative to U-tube)
Information from Ross et al., 2007		
CO_2	ppb to percent	Direct sampling of injected CO_2. CO_2 dissolution front ahead of main CO_2 plume.
pH	Relative change	Evidence of dissolution, mineral reactions ahead of main plume.
Hydrocarbons	ppb to percent	May include methane as well as higher hydrocarbons. Purpose is to monitor (a) residual hydrocarbons or gas, (b) sweeping of possible accumulations/migration pathways incorporated into the CO_2 plume.
Anions	mMol	Rather than TDS (total dissolved solids). Slightly more information about negative ions that may be added to the formation waters as a result of mineral dissolution (e.g. sulphate and chloride).
Cations	mMol	Rather than TDS. Slightly more information about positive ions that may be added to the formation waters as a result of mineral dissolution (e.g. calcium and iron).
Tracers	ppb to ppm	May find sensors that monitor for tracers (e.g.SF_6). May be important to monitor for subsequent tracers added.
New parameters identified in current work		
All of the above	Same ranges	Wider scope, to cover reservoir level, overlying aquifers, groundwater and soil gases.
Pressure	kPa	Changes in in situ pressure as a consequence of fluid movement, including brine, water saturated with CO_2 or CO_2. Has application in reservoir and groundwater, cost effective, sensitive and robust.
Geophysical properties	Varied and specific to methods employed	To track plume migration, rock deformation and potential leaks.
Temperature	°C	Correlation for pressure changes, DTS systems to measure changes in thermal conductivity as a consequence of the presence of CO_2. Has application in both reservoir and groundwater; however installation cost and data processing requirements may be prohibitive for monitoring.
Pulsed neutron capture	Unquantified as yet	Changes in residual saturation (RST) as a consequence of the presence of CO_2. Has application in both reservoir and groundwater; however, installation cost and data processing requirement may be prohibitive for monitoring.
Acoustic	Unquantified as yet	Changes in acoustic properties as a consequence of the presence of CO_2. Has application in both reservoir and groundwater; however installation cost and data processing requirement may be prohibitive for monitoring. Has application in correlation of seismic processing.
Biological changes	Varied and specific to methods employed	Changes in the biological community can be indicative of CO_2 leaks and other subsequent effects such as pH decrease, TDS increase, mineral dissolution and release of anions and cations.
Contaminants from flue gases	ppb to ppm	Includes reactive and non-reactive contaminants from coal fired power plants, LNG etc.

The Ross et al. (2007) project provided a number of interesting conclusions and recommendations. The study focussed mainly on sensing devices that were close to commercialisation or offered the most appropriate off-the-shelf solutions, of which a large number of component devices could, in theory, be readily adapted for the task of down-hole sensing in slim-hole environments at elevated temperatures and pressures. The report also concluded that there was significant opportunity for development of IP relating to down-hole monitoring. The reason for this statement came from the observation that, while there are a large number of analytical and chemical sensors, much of the important information on sensor sensitivity and selectivity was absent from the literature.

Very little has been published on the application and testing of such sensors in down-hole environments with most sensors being tested in the laboratory only. Other issues included the risk of chemical interferences and cross-sensitivity, suggesting the need for the development of tools that comprise a sampling and separation unit prior to analyte detection.

The authors proposed the development of an integrated multi-analyte sensor platform utilising various sensor technologies to provide real-time qualitative and quantitative information on several different analytes simultaneously as there were few suitable technologies available to fill the remit currently.

1.4 Literature search

Since carrying out the first searches for the Ross et al. (2007) review 3 years prior, it was decided to compare that study with the work being conducted now in order to highlight the hotspots of activity in different research domains in sensor technologies. In Ross et al. (2007), a series of literature searches was carried out to identify, in general terms, the relative research activity in the field of sensor technologies as well as identifying specific tools. The following databases were searched to identify the relevant technologies:

- ISI Web of Science (key journal publications only – no conference proceedings at that time)
- ISI Derwent Innovations Index (Patents)
- Google (for industry based activities)

Keywords for the searches from the Ross et al. (2007) report were built upon by the subsequent literature reviews (Section 2) that occurred for the key groups of mobilised substances, namely;

1. Flow effects
2. Geochemical effects
3. Shallow/surface effects
4. Capture gas compositions

The methods used to carry out the searches revolved mainly around the use of the ISI search products (Web of Science and Derwent Innovation Index), though other search engines/databases were also used where appropriate. Details of how the process was conducted are described in Appendix 2.

It was decided that there would be some value in quickly repeating the higher level part of the earlier searches on ISI Web of Science and ISI Derwent Innovations Index to see how the landscape with respect to publications and patents may have changed over the last 3 years. The work for Ross et al. (2007) was conducted in September of that year and was repeated in late August, 2010. Please note that while ISI Web of Science now includes Conference Proceedings, that option was turned off to allow for similar searches to be carried out as in 2007 (before the Conference Proceedings option was available).

No repetition of the Google survey was carried out as initial results quickly indicated that the Google search engine had changed their search algorithms substantially to be much more targeted; thus significantly reducing the number of hits for several searches. Where substantial increases in “hits” were noticed, they were most likely related to the recent events in the Gulf of Mexico and the oil spill. Searched results for “Oil and Sensor” had increased significantly (76%) whereas a search for “Oilfield and Monitoring and Hydrocarbon” had reduced results by over 400%.

The results of this comparison are presented in Appendix 2.

2. Monitoring opportunities

The following is a summary of the effects that could be monitored based on the impacts that CO_2 release might have on the subsurface. The summary is limited in depth as a number of very useful resources recently commissioned by IEA GHG perform far more detailed studies on these effects listed below. More time was spent on identifying and assessing monitoring tools as is detailed in the next chapter.

In this report we distinguish between monitoring of the injection horizon, which can be a saline aquifer (equivalent term: saline formation) or depleted petroleum reservoir, and above-zone or assurance monitoring. The latter covers the monitoring of processes in the entire sedimentary succession above the injection horizon, including shallow groundwater aquifers. With respect to CO2 geological storage, the term “saline aquifer” usually infers a depth below 800 m and formation water salinities of at least 10,000 mg/l. However, there are exceptions in which CO2 storage is considered in aquifers with lower salinities, if these are not used for other purposes.

The dissolution of CO2 into the in-situ formation water and geochemical interactions between the CO2 rich formation water and the rock matrix will result in, to various degrees, time dependant physical and chemical changes in the rock and fluids. This is also true for interaction between the free, supercritical CO2 phase and the rock matrix. Physical effects include changes in pressure, density, viscosity and temperature. Geochemical changes include chemical composition and redox potential of the original formation water and pH changes. Depending on the injection scenario, some of these may be detectable and therefore have application in monitoring and verification activities.

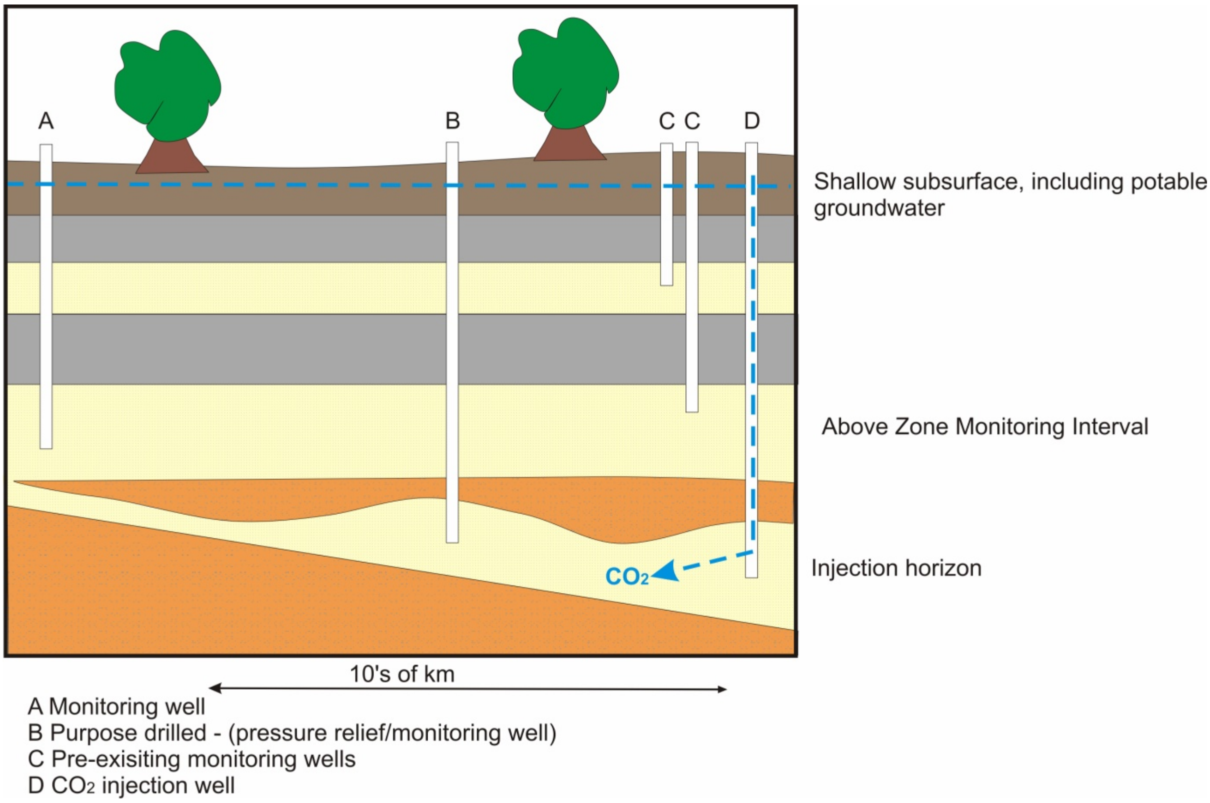

Figure 1 Schematic of the areas reviewed as potential monitoring areas

Geophysical monitoring measures either physical or chemical effects that changes in salinity, density, pressure and fluid type (e.g. gases) have on the rock properties at varying depths. The types of locations where geophysical monitoring takes place (shallow cover versus deep hydrocarbon reservoir characterisation) and the lateral and vertical extent of the CO_2 plume all impact on the preferences that may be considered for a geophysical survey. Geophysical tools are an established and mature area of research for monitoring CO_2, but have not been studied extensively in their ability to detect other effects and are limited in their application. They are designed to work both on land and offshore, and at both deeper and shallower levels in the subsurface. Depending on the actual scenario, geophysical monitoring tools may be employed to measure changes in salinity (solution conductance), density (rock conductivity/resistivity) or pressure and can be particularly useful in indirectly monitoring the presence of gases such as CH_4 or CO_2. The ability to interpret other mobilised substances such as metals or pH flux is limited, presently. Most geophysical methods monitor CO_2, and not the subsequent mobilised substances. Therefore geophysical methods are discussed briefly where appropriate, though some less common tools are mentioned in Section 3.1, but are generally regarded as being the focus of this report.

It is recognised that surface expressions of CO_2 release and related effects will have impacts on local biology and this is discussed in relation to microbial communities as well as some effects on plants. The detection of hydrocarbons and organic compounds are also discussed as they may be present in some formations including depleted oil and gas fields, areas of enhanced oil or coal seam gas recovery, or even as the result of CO_2 solubilising organics as they pass through organic carbon in source rocks or coals. Organic compounds and hydrocarbons can also be by-products of power production (from coal, oil or gas) or even from petrochemical processes or LNG production and are discussed as potential contaminants along with heavy metals and other materials that could be transported in flue gases.

2.1 Physical effects

Injection of supercritical CO_2 into a deep, confined saline aquifer or reservoir will cause displacement of the pre-existing fluids occupying the pore space, usually formation water, and an increase in pressure. Once injection has ceased the pressure will dissipate and any further migration will be driven by either buoyancy of the free, supercritical CO_2 phase or by dissolved CO_2 moving with the formation water. Concomitant with changes in pressure will be changes in density, viscosity, temperature, thermal and electrical conductivity related to the CO_2 plume directly and/or as a consequence of its interaction with the formation water.

The key monitoring points for detecting these changes are the storage reservoir itself, overlying permeable formations and non-saline (or potable), aquifers. Each of these domains has advantages and disadvantages for the installation of long-term robust and cost effective monitoring systems. In general, measurement of these properties requires the tool to be installed within a wellbore. Some, such as formation water sampling, require the wellbore to be open to the formation being monitored. Increasing the number of well penetrations into the storage reservoir represents a significant increase in the risks associated with storage. Monitoring the overlying permeable, but deep, formations is an option, and negates this risk, however, there is an associated loss of sensitivity, for example, with pressure. Nogues et al. (2011) point out, that leakage of CO_2 vertically through a seal into overlying formations might be detected through a combination of the use of pressure-monitoring wells, surface geophysical methods and geochemical sampling because each leakage point (e.g. an abandoned well) may have an associated pressure change and a CO_2 plume. There may be potential to detect leakage prior to CO_2 reaching the surface and while the CO_2 plume is small enough for remediation

(Nogues et al., 2011). One of the limiting factors identified is the accuracy threshold associated with the monitoring equipment (i.e. the pressure gauges), (Nogues et al., 2011). However, these studies have shown that pressure monitoring has potential, not only for "accounting and inventory purposes" but also for reducing the environmental risk. In some cases, such as at In Salah, Algeria, injection of CO_2 in conjunction with nearby hydrocarbon production from the same reservoir, has produced surface deformation detectable by radar (Ferretti et al., 2011; Onuma et al., 2011; Vasco et al., 2008; 2010).

Jordan and Doughty (2009) conducted numerical simulations for a range of pressure and temperatures from the oil field data at the WESTCARB Phase III injection test site and showed that, across the range of likely pressure and temperatures, variation in brine viscosity causes virtually no difference in plume evolution and final size, but variations in CO_2 density causes a large difference. According to reported experimental data the density of aqueous solutions of CO_2 can be up to 2-3 % higher than formation water density with no CO_2 saturation (Garcia, 2001). There are several tools available for down-hole density measurements (densitometers), but these are often deployed as part of permanent down-hole pressure monitoring arrays within a producing field – often known as "smart wells". These tools will have resolution and longevity limitations due to the deep environment (high termperature and pressure) and, as in the case of geochemical sampling, will be limited to modified fluid actually reaching the instrumented well.

Introduction of CO_2 into a well will cause changes in temperature; in addition, the substitution of formation water with CO_2 into the pore space will cause a potentially detectible change in thermal conductivity. Hurter et al. (2007), wrote an overview of the potential detectability of CO_2 using temperature logging. They evaluated and compared conventional logging and distributed temperature sensors (DTS) and the use of fibre optic cables. Their evaluation was carried out using the CO2SINK project at Ketzin as a case study to illustrate their points.

- They concluded that CO_2 was detectible by measuring changes in thermal conductivity.
- The change in thermal conductivity decreased with increasing porosity and increasing CO_2 saturation.
- Their modelling indicated that CO_2 would be detected as a temperature anomaly at a monitoring well 50m away from the injection well.
- They predict a Joule-Thompson effect will be present if CO_2 moves out of the primary container via faults or fractures or even behind the well-bore, but these effects would be subtle.
- In the absence of other sources and sinks and significant fluid flow, the presence of CO_2 in a previously fluid saturated rock has the potential to imprint a quantitative thermal signature related to the saturation and thickness of the CO_2 layer present.
- Current conventional logging and DTS systems have sufficient resolution to detect changes.

A further consequence of the injection of large volumes of CO_2 into a reservoir is the displacement of similarly large volumes of formation water. To date, brine displacement effects have been investigated only in the form of numerical simulations (e.g. Nicot, 2008; Birkholzer et al., 2009; Yamamoto et al., 2009). These processes and their impacts are discussed in detail in the IEAGHG Report on Potential Impacts on Groundwater Resources of CO_2 Storage (IEA/CON/09/177), however, it is clear the potential for changes in groundwater flux as a consequence of CO_2 injection exists. Monitoring changes in groundwater is a mature field and there are many off-the-shelf groundwater monitoring tools that may be applicable to the CCS industry.

2.2 Effects of CO_2 leaks on the near surface biosphere

Natural analogue studies have been a useful means of identifying changes in the biological structure of a location exposed to naturally occurring CO_2. Observations of changes in vegetation, or even dieback due to excessive $CO_{2,}$ change in pH or toxicity related to other mobilised compounds all show evidence of leaks. The mineral, aqueous and biological components of the ecosystem are inextricably linked therefore changes in the mineral and aqueous chemistry from CO_2 leakage (Section 2.3) will result in changes to the biosphere. Significant vegetation changes and more recently observed changes in microbial communities related to metal flux, coupled with advanced microbial community characterisation applied in microbial ecology has demonstrated the potential to apply biological tools and sensors to the CCS domain.

While the presence, absence or change of CO_2 in a location is a major variable and will partially control the vegetation or microbial communities in soils etc., the effects of remobilisation of minerals and compounds such as active nutrient supply or toxicity will have a pronounced effect as well. Monitoring for positive or negative effects on the plant or bacterial communities will give subtle early warning of changes of the subsequent mobilisation of compounds related to increased CO_2 presence.

As there has been little work done previously in the CCS field with sensors for the detection of biomolecules/biological-based organisms, relative to other areas, a review of potential tools and current applications has been conducted to illustrate the potential of this approach. Some work has been conducted through use of natural (CO_2) analogues while other researchers have used this approach at shallow release sites to gain an understanding of the potential of these tools. This has been addressed in Section 3.2.

2.3 Geochemical effects of CO_2 sequestration

In CO_2 geological storage applications, there is the potential that buoyant CO_2 could leak from a deep storage formation and migrate to shallower aquifers used as a groundwater resource (Kharaka et al., 2009; Zheng et al., 2009). The addition of CO_2 gas to a shallow aquifer would result in an increase in the partial pressure of CO_2. This increase in P_{CO2} would in turn result in an increase in dissolved CO_2 and therefore a decrease in pH. There are likely significant consequences of large changes in aquifer pH including; 1) dissolution of carbonate and silicate minerals, releasing contained metals/metalloids (Lu et al., 2010), 2) dissolution of oxide and hydroxide phases (i.e., primarily Fe-, Mn-, and Al-oxyhydroxides), which will release adsorbed or co-precipitated metals/metalloids (Balistrieri et al., 2008; Leybourne and Cameron, 2008), and 3) desorption of metals from mineral surfaces by lowering the pH below the characteristic adsorption edge of different aqueous species on different aquifer materials (Yang et al., 2005; Shaker, 2007; Tofighy and Mohammadi, 2011).In addition, the displacement of large volumes of brackish and saline waters may lead to cross-aquifer migration and mixing with shallower, fresh water systems.

Transport of gas-phase CO_2, CO_2-charged formation water or formation water itself, could occur along faults and fractures, poorly constructed well bores, for example CO_2-brine flow along the casing-cement microannulus (William Carey et al., 2010), or through leaky aquitards/caprocks (Siirila et al., 2011). Keating et al (2010) showed, in a CO_2 sequestration analogue study of a sandstone aquifer with high buffering capacity (high carbonate contents), that changes in pH owing to high concentrations of CO_2 derived from brackish underlying lithologies were not significant. Conversely, mixing of the fresh aquifer waters with CO_2-rich brackish waters resulted in elevated As, U and Pb concentrations. These authors concluded that monitoring of pH changes alone is insufficient to adequately track deleterious effects of CO_2 contamination in aquifers with high buffering capacities (Keating et al., 2010).

There are relatively few published studies on the effects of significant pH reduction in an aquifer and release of toxic metals and metalloids (Lu et al., 2010). Several recent studies have used reactive transport models to predict if certain toxic metals and metalloids are likely to be mobilised by the addition of CO_2 to an aquifer with concomitant changes in pH (e.g., Wang and Jaffe, 2004; Thibeau et al., 2007; Assayag et al., 2009; Zheng et al., 2009; Apps et al., 2010; Siirila et al., 2011). Studies where the monitoring of groundwater chemistry in response to deliberate addition of CO_2 are starting to appear in the literature (Kharaka et al., 2009; Kharaka et al., 2010) along with laboratory experiments testing different aquifer materials (Little and Jackson, 2010; Lu et al., 2010). Therefore, there is a need to be able to monitor changes in metal and metalloid concentrations in both the repository aquifer and overlying potable water aquifers during and following cessation of CO_2 sequestration. Modern analytical techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), ICP optical spectroscopy (ICP-ES), ion chromatography (among others), are readily able to measure essentially all metal and metalloid species of concern (e.g., As, Se, Pb, Cu, Co, Ni, Zn, Mn, Fe etc) to the required levels of detection. However, the limiting factor for this type of monitoring is that continuous sampling of groundwater, especially from deep repository aquifers, is complex and costly, through the use of U-tube samplers (Freifeld et al., 2005), straddle-packers (Leybourne and Goodfellow, 2003) or wireline sampling (Wakahama et al., 2009). Furthermore, sampling of repository formation waters at the well head, and subsequent reconstruction of the in situ aquifer geochemistry based on surface and laboratory measurement is problematic owing to difficulties in collecting key parameters (i.e., in situ P-T conditions) (Newell et al., 2008) as well as the impact on the fluids by the presence of drilling muds. The alternative then would be to monitor groundwater for changes in metal and metalloid concentrations in situ. In situ monitoring cannot simply consist of monitoring the changes in CO_2 concentration, as changes in metal concentrations may be more readily detectable and occur long before direct changes in CO_2 are observable (Little and Jackson, 2010).

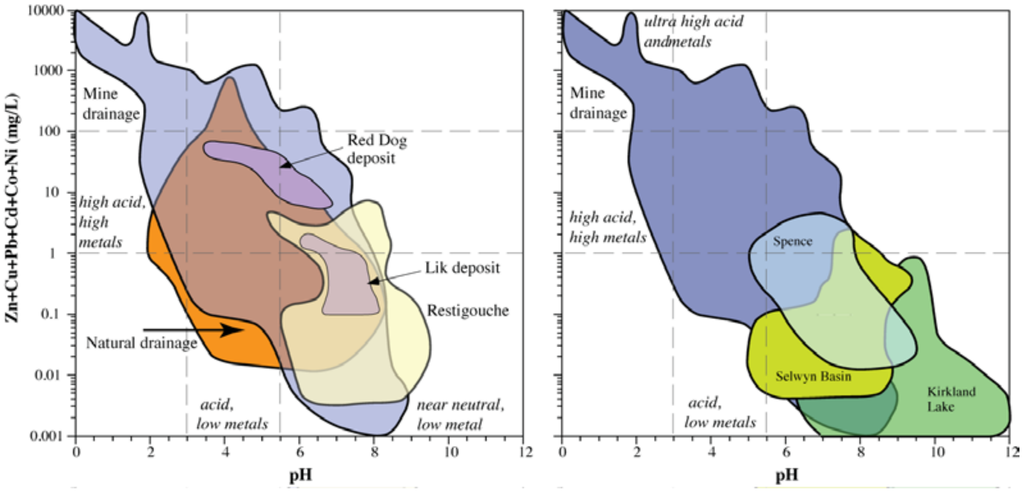

Figure 2 Ficklin-type diagram showing the influence of pH on mobility of transition metals associated with different styles (i.e. volcanogenic massive sulfide, sedimentary exhalative, porphyry copper, and kimberlite) of mineralisation under natural and acid-min

Although the number of studies focused specifically on the geochemical effects on aquifers from CO_2 sequestration are limited (as noted above), inferences can be drawn from the large literature on water-rock interaction in terms of understanding potential effects on reservoir and caprocks (e.g., Frape et al., 1984; Banner et al., 1988; Nordstrom et al., 1989; Banner and Hanson, 1990; Jacobson and Wasserburg, 2005; McIntosh and Walter, 2006; Leybourne and Goodfellow, 2007; Leybourne et al., 2009), and from the mineral exploration literature in terms of mobility of metals as a function of changes in pH and Eh conditions (Leybourne and Cameron, 2006; Leybourne, 2007; Leybourne and Cameron, 2008) (Figure 2). Studies of metal migration and subsequent attenuation at mine tailings sites are also useful in understanding the likely effects of aquifer acidification (Kossoff et al., 2011). There are many studies available on carbonate aquifers (Luquot and Gouze, 2009), sedimentary aquifers, basaltic rock aquifers (Matter et al., 2007; Schaef et al., 2009) and ultramafic rock aquifers (e.g., Sader et al., 2007; Boschi et al., 2008). Studies of natural CO_2 addition have also documented changes in ground and surface water chemistry, as for example, at Yellowstone National Park, USA (Hurwitz et al., 2010) and the Taupo Volcanic Zone, NZ (Giggenbach and Sheppard, 1989; Giggenbach and Glover, 1992; Stoffers et al., 1999; Giggenbach et al., 2003).

Recently, the Geological Survey of Queensland (Australia) has investigated the potential impacts of carbon dioxide injection into freshwater aquifers in the Great Artesian Basin because of the lack of sufficient storage capacity in saline aquifers in Queensland (Hodgkinson et al., 2009; 2010; Hodgkinson and Preda, 2010). They found that partial pressure changes in CO_2 will increase bicarbonate concentration and decrease pH, leading to other chemical changes in water composition. Due to carbonic acid generation, a number of potentially toxic metals and metalloids (e.g. Fe, Mn, Pb, As) may be released from sediments and directly impact on the potability of water supplies.

For most aquifer lithologies, introduction of CO_2 will most likely result in a decrease in groundwater pH (e.g., Wang and Jaffe, 2004; Thibeau et al., 2007; Assayag et al., 2009; Zheng et al., 2009; Siirila et al., 2011). Hence, many recent studies looking at the impacts of CO_2 sequestration on groundwater quality have focused on these kinds of aquifers, primarily because of the large potential for storage and proximity to major point sources of CO_2. Results of thermodynamic calculations performed by Apps et al. (2010) for mineral assemblages typical for sedimentary aquifers in the United States suggest that arsenic and lead are the trace elements of greatest concern, Their reactive transport simulations predict a significant, yet below respective maximum contaminant levels, aqueous As and Pb concentrations as a result of CO_2 injection. However, some potential storage sites are located in rocks in which addition of CO_2 will ultimately lead to increased groundwater pH i.e., those in mafic and ultramafic rocks (e.g., Sader et al., 2007; Flaathen et al., 2009). In addition to acidification, carbonation is one of the main consequences for aquifers from CO_2 sequestration (Noh et al., 2007). Carbonation reactions appear to be particularly enhanced in mafic and ultramafic aquifers with the formation of magnesite in addition to calcite.

Lu et al. (2010) recently performed a series of batch experiments on various aquifer sediments to investigate the behaviour of major and trace elements to the addition of CO_2. They found that the inorganic metal cations could be subdivided into two groups based on their response to acidification. Type I cations (i.e., Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, and Zn) showed rapid increases in aqueous concentration after CO_2 injection by the end of the experiment. Type I cations remained at these elevated concentrations. Type II cations (i.e., Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) also showed rapid increases in concentration after the influx of CO_2, but concentrations declined to levels at or below the initial concentrations as a result of pH increases due to buffering caused by carbonate mineral (calcite, dolomite) dissolution (Lu et al., 2010). Similar results were observed by Patterson et al. (2010) in a series of column experiments; increases in metal and metalloid concentrations occurred following pyrite oxidation, mineral dissolution or pH induced metal desorption, but the increases were transient, with metal re-adsorption down-gradient in the oxygen depleted zone. In siliciclastic aquifers, available carbonate minerals for buffering may be limited. In this case, silicate dissolution should also provide additional buffering capacity (Kharaka et al., 2009), albeit with considerably slower kinetics. Indeed, long term column experiments of silicate-carbonate aquifer material showed that silicate minerals were largely unaffected by CO_2-induced pH decrease (Bateman et al., 2005). Comparison of the experimental results with geochemical modelling showed that the latter commonly overestimate carbonation reactions. For example, Bateman et al. (2005) found that although many geochemical models predict formation of large amounts of dawsonite ($NaAl(CO_3)(OH)_2$), none was formed during the column experiments. Similar results based on hydrothermal experiments have been reported by Newell et al (2008). Silicate dissolution rates and carbonation capacity are generally much higher for mafic rocks than for sedimentary aquifers (Matter et al., 2007), and are further enhanced by addition of sulfate (Flaathen et al., 2010).

In some cases, and again with reference to the exploration literature, changes in aquifer composition might also be monitored using changes in surface water chemistry; even where mineralisation is deeply buried, subtle changes in surface water chemistry have been noted, including changes in major ion chemistry (Leybourne et al., 2003; Leybourne and Goodfellow, 2010).

An impact not widely discussed previously in relation to CO_2 storage, is the potential for intrusion of seawater into freshwater aquifers, a major concern in many coastal areas. The mixing between meteoric groundwater and seawater (~35 g/l salt) can prompt various water-rock interactions, possibly resulting in calcite dissolution/precipitation or dolomitization, thereby altering the hydraulic properties of the aquifer. Techniques employed for monitoring the location of the seawater-freshwater interface may be applicable for the detection of displaced brines from CO_2 storage sites. Parameters commonly measured in monitoring wells for the detection of saline intrusions include: total dissolved solids (TDS) as measured by electrical resistivity, pH, major ion chemistry, and density. Indirect methods are usually based on geophysical techniques such as ground penetrating radar, geoelectrics [i.e., direct current method (DC)], electromagnetics [i.e., frequency or time domain electromagnetics (FDEM or TDEM)], induced polarization (IP), and nuclear magnetic resonance (NMR) (Melloul and Goldenberg, 1997). Many of these methods can be set up in 2D, 3D or 4D studies with surface, down-hole, cross-well, permanent or temporary configurations dependant on monitoring objectives and budget.

2.4 Hydrocarbons and organics

There is an opportunity to utilise tools and technologies for monitoring hydrocarbons in CCS monitoring and verification programs where depleted oil and gas fields are used. Whether for EOR (e.g. Weyburn, Cranfield) or using abandoned or uneconomic fields (e.g. Otway) there tends to be significant quantities of hydrocarbons left as “oil-in-place”. As a consequence, there may be free gas, free oil and residual hydrocarbons that will mix with the added CO_2, and these hydrocarbons can be taken up by the supercritical CO_2 plume and easily mobilised during geosequestration.

In addition, hydrocarbons or functionalised organic compounds have been used as tracers, for example the application of perdeuterated methane (CD_4) at Otway Stage 1 (Stalker et al, 2009), or perfluorocarbon tracers (PFCs) at Frio (Freifeld et al., 2005) and K12-B (Vandeweijer et al., 2011). As these compounds can be dissolved in CO_2 or partition between CO_2 and formation waters, they can be monitored for as CO_2 or formation fluids are mobilised during the injection process.

Many tools and technologies have been developed for the environmental monitoring of hydrocarbons in rivers, coastal waters and oceans (Johnson et al., 2007; Prien 2007; Moore et al., 2009). Similarly, a number of them have been used to quantify volatile organic compound contaminants in both air and soil (Hoet al., 2005). However, the groundwater monitoring of aromatic compounds, particularly BTEX (benzene, toluene, ethylbenzene and xylene) and PAHs (polycyclic aromatic hydrocarbons) is a growing area of research predominantly for those associated with coal seam gas extraction (CSM), underground coal gasification (UCG) and shale gas production. As most of these compounds are also present in depleted oil and gas fields, the ability to monitor for the mobilisation of these compounds at the baseline stage and onwards is of great interest and importance to obtaining public acceptance of any new subsurface technology application where potable water may be affected in overlying aquifers. Therefore, not only conventional n-alkanes (most abundant individual compounds in a hydrocarbon reservoir) but BTEX and other hydrocarbon sensors have been evaluated in Section 3.5. These substances may be mobilised by supercritical CO_2 as it passes through organic-rich rock matrices (coals, source rocks, shales, muds etc.). Supercritical CO_2 is used as a solvent to extract organic compounds, particularly polyaromatic hydrocarbons (PAHs) in the laboratory (Langenfeld et al., 1993; Librando et al, 2004) and this process may possibly occur in the subsurface.

Both the organic-rich rocks and fluids containing organics can also be attacked by microbes to break down macromolecules and produce other species such as hydrocarbons both in the shallow and deep subsurface (Aitken et al, 2004 and references therein). These processes may be aerobic or anaerobic and produce a suite of compounds from methane, n-alkanes to surfactants.

Other potential means of introducing hydrocarbons into the subsurface during carbon capture and storage is via the contaminants in the flue gas and this is discussed in the next section (Section 2.5).

Hydrocarbon sensors and monitoring tools can be deployed at shallow levels for monitoring pollution or deeper as part of a petroleum exploration program; so may be well suited to CCS deployment.

2.5 Capture gas compositions

Incidental substances can be present in CO_2 streams introduced from combustion fuels, capture, transport, industrial manufacturing and injection processes (e.g. as tracers). Depending on the processes involved, any additional substances, hereafter referred to as contaminants, may be present in varying abundances and with quite different chemical compositions.

The main capture gas types are summarised in Table 3 and are the basis for a literature review to identify the key potential contaminants in terms of their chemistry.

Table 3 Potential types of emissions to be sequestered.

Capture gas from power plants	
i	Post-combustion capture (PCC)
ii	Oxyfiring/oxyfuel
iii	Integrated gasification combined cycle (IGCC) or integrated drying and gasification combined cycle (IDGCC)
Capture gas from petroleum industry and other large point source emitters	
i	High CO2 petroleum/condensate/gas fields (e.g. Sleipner or Gorgon)
ii	Liquid natural gas (LNG) or gas-to-liquids (GTL) processing
iii	Chemicals/Processing industry (e.g. coal to urea; steel manufacturing etc.)

The draft report “Effects of Impurities on Geological Storage of Carbon Dioxide” by Wang et al. (2010) at CanmetENERGY written under contract IEA/CON/09/172 has been the main source of information on contaminants, and has been highly valued as a reference material for this section. This work tended to focus on capture gases from either pre- or post-combustion processes from power plants, but many of the observations about those flue gases also relate to other point source emissions.

Each of the effluent types have different ranges of concentrations of contaminants (Table 4), which may be classified in a number of ways; non-condensables versus condensables, or reactive versus conservative in chemical reactivity. The result of the presence of certain contaminants can mean physical or chemical changes in the behaviour of the CO_2 plume. For this work, the most important effects the contaminants have on substances mobilised by CO_2 storage are likely to be;

- Pressure changes
    - effect of limited/no compressibility of non-condensables
- Chemical reactions
    - Scaling/fouling of the injector
    - Changes in pH
    - Mineral reactions beyond the injector
    - Mobilisation of cations/anions
- Transport of contaminants
    - Movement of contaminants as pollutants or tracers

2.5.1 Capture gas from power plants

Wang et al. (2010) lists a series of effluent streams and likely compositions of contaminants in Table 4. Although the elements and compounds listed in Table 4 tend to make up the most quantitatively significant contaminants in the flue gas streams post-clean up, there are other potential contaminants that could be present, if not removed by filtration. A small scale literature search suggests the following potential contaminants (Table 5).

The most commonly recurring contaminants are those listed previously by Wang et al. (2010) in Table 4, however, there is potential for other species to be present in the sequestered gas stream that could be mobilised and monitored, including some metals or organic compounds. Some of these species may be present in concentrations that are unlike those of deliberately added tracer compounds. At the Otway Stage 1 site, Kr, SF_6, perdeuterated CH_4 and R-134a (CH_2FCF_3) were added to the injected gas and recovered in concentrations of ppb to ppm levels (Boreham et al., 2011). Wang et al. (2010) noted that Ar present in many of the gas streams (Table 4) was present in sufficiently high concentrations (well above air background levels of 0.934 vol %) and as it is conservative in its behaviour, it could be used as a potential tracer. Argon has been used previously during monitoring of volcanic emissions (Magro and Pennisi, 1991), while Kr (another noble gas) has been used to good effect in monitoring CO_2 at the Frio Brine 1 experiment (Freifeld et al., 2005) and at CO2CRC Otway Stage 1 (Stalker et al., 2009).

Table 4 Capture gas compositions. Table modified after Wang et al. (2010).

Stream	CO_2 Vol %	O_2 Vol %	N_2 Vol %	Ar Vol %	H_2O ppm	NO_x ppm	SO_2 ppm	SO_3 ppm	CO ppm	H_2S & COS	H_2	CH_4 ppm	NH_3 ppm	CH_3OH ppm
PCC Selexol[1]	97.95	-	0.9	0.03	600	-	-	-	400	100	1 vol%	100	-	-
PCC Rectisol[1]	99.7	-	0.21	0.15	10	-	-	-	400	100	20ppm	100	-	200
PCC 1[1]	99.93	0.015	0.045		100	20	10		10	-	-	-	-	-
PCC 2[1]	99.92	0.015	0.045		100	20	10		10	-	-	-	50	-
PCC 3[1]	99.81	0.03	0.09		600	20	20		20	-	-	-	-	-
PCC average	**99.89**	**0.02**	**0.06**		**266.67**	**20**	**13.33**		**13.33**				**50**	
Oxyf 1[1]	85.0	4.70	5.80	4.47	100	100	50	20	50	-	-	-	-	-
Oxyf 2[1]	98.0	0.67	0.71	0.59	100	100	50	20	50	-	-	-	-	-
Oxyf 3[1]	99.94	0.01	0.01	0.01	100	100	50	20	50	-	-	-	-	-
Oxyfiring/fuel average	**94.31**	**1.79**	**2.17**	**1.69**	**100**	**100**	**50**	**20**	**50**					

Footnote1 – from Wang et al., (2010) much of which has come from IEA (2004) PH4/32.

Table 5 List of additional potential contaminants.

Element or compound	Source	Reference
Mercury	Coal	Pavlish et al, (2010)
NO_x, SO_2, N_2	coal	Shuckerow et al, (1996)
Amines	CO_2 separation process	R. Sakurovs (Pers. Comm.) and Sakurovs et al, (2010)
SO_x, NO_x, particulates, ammonium salts, sulphur, COS, CO, SO_2, H_2S, Ar, CH_4, N_2, H_2, C_4+ compounds	Coal combustion	Zheng and Furinsky, (2005)
CO, NO_x, SO_2, UHC (unburnt hydrocarbons), H_2O, fly ash	Coal combustion	Blumrich and Engler, (1993)
S, Hg, particulates, H_2S, COS, halides, ammonia, HCN, alkali metals, metal carbonyls, As, Se, Cd	Coal combustion	Layne et al, (2007)
NO_x. SO_x, chlorine species, UHC or partly burned fuel components (aldehydes, CO, aromatic and polyaromatic hydrocarbons), aerosols (e.g., soot, alkali aerosols), N, S, Cl, K/Na species, HCl.	Coal combustion	Glareborg, (2007)
H_2S, CH_4, N_2, SO_2	Petroleum (heavy oils)	Bachu and Bennion, (2009)
Hg, As, Se, P, arsine, phosphine, hydrogen selenide		Rupp et al, (2010)
CO, H_2S, HCl, Be, Cr, K, Na, V, Zn, As, Cd, Hg, Pb, Se, Sb, Ni, CH_4, CO, H_2, H_2O, N_2, HCN, HCl, particulates, alkali species, B, Be, Co, Mn, Mo		Trembley et al, (2007)
H_2O, O_2, N_2, Ni, poly ethylenimine (PEI)	Combustion, catalysts	Song, (2006)
S, Pb		Thiruvenkatachari et al, (2009)

Other materials that may be present in quantities that could be applied to tracer monitoring include amines and other materials used in the capture process e.g., poly-ethelyenimine (PEI) (Song, 2006). The mobility of these chemicals is uncertain in some environments, though observations by Day et al. (2010) and Sakurovs et al. (2010) suggest that some of these contaminants are present in concentrations that could cause swelling in coals; hence reduce storage potential. Furthermore, as amine from the capture process could be present in similar (ppm) amounts, this could also be added to the list of contaminants, and affect coal swelling (Sakrurovs, pers. comm). This suggests some of these compounds may be progressively immobilised by organic-rich shales or clays if present in the storage reservoir. Otherwise, monitoring for these compounds could give indications of the presence of gas from particular gas streams as a source fingerprint (which may be useful in cases where large saline aquifers receive gas streams from multiple commercial scale operations in the future).

Unburned or partly burned fuel components such as aldehydes, aromatic or PAHs, aerosols (Glareborg, 2007), volatile organic compounds (VOCs) or essentially any organic compounds in coals or petroleum feedstocks and their combustion products, could potentially be entrained in the gas stream as well and could be monitored for as substances become mobilised within the storage reservoir or during leakage. Metals, for example, nickel and vanadium in porphyrins (Tissot and Welte, 1984; Sundararaman and Boreham, 1993) can be relatively abundant in preserved organic matter and can act as a contaminant. However, the most commonly recurring metals listed in the literature observed here were mercury (Hg) and arsenic (As), both of which are of major health concern. As mercury moves through the subsurface it may not be readily immobilised while arsenic may be taken up and immobilised by clays or organics such as humic substances in shallower aquifers (e.g. Simeoni and Hostetler, 2006). Many of the compounds listed in Table 5 may actually be filtered or scrubbed out of the different flue gases, but the efficiency of the scrubbers/filters/catalysts could vary over time as they degrade and change in performance.

Of the extensive list of potential contaminants, many will also appear in the lists for hydrocarbons or inorganic geochemical reactions and so the searches can be combined for some of these cases.

2.5.2 Capture gas from the petroleum industry and other large point source emitters

Aside from the direct generation of power (from coal, gas or oil) there are several other major point source emitters. These include oil and gas fields that are high in naturally co-occurring CO_2 concentrations, Liquid-Natural-Gas (LNG) plants, Gas-to-Liquid (GTL) conversion plants and other chemical or high energy usage plants (e.g., refineries or smelting plants).

High CO_2 petroleum/condensate/gas fields

The oil and gas industry are increasingly finding fields that contain high quantities of CO_2 or other contaminants (Chevron's Gorgon field or Statoil's Sleipner field being the best known examples in the CCS community). Aside from CO_2, another major contaminant in natural gas is H_2S, as sour gas (containing both CO_2 and H_2S) is produced in increasing quantities in many petroleum provinces such as some North American basins, i.e. the Smackover (Heydari, 1997), some basins in China (Zhu et al, 2009) and parts of the Middle East such as Abu Dhabi (Worden and Smalley, 1996). In Texas and Alberta, the acid gas (CO_2 & H_2S) is re-injected into saline aquifers or depleted hydrocarbon reservoirs (i.e., Bachu and Gunter, 2004; Bachu et al., 2005). At Zama, a PCOR pilot project in northern Alberta, acid gas is used for enhanced oil recovery (Smith et al., 2009). These contaminants are stripped out to meet sales and transport specifications, and use more energy (further emissions) in this clean-up process, in addition to the potential release of the stripped CO_2.

Liquified natural gas (LNG) or gas-to-liquids (GTL) processing

Associated with the processing of diluted gas or oil is the conversion of hydrocarbons to LNG (liquified natural gas) or GTL (gas to liquid) conversion. These processes use significant amounts of energy and are major point source emitters. Often these emission points are at or near the fields from which the hydrocarbons were recovered, and so are in an ideal location for new storage sites to be identified (based on the presence of good reservoir-seal pairs to contain the original hydrocarbons). One example is Snohvit managed by Statoil in northern Norway.

The process of LNG uses energy to treat hydrocarbons, mainly natural gas, in preparation for refrigeration and liquefaction. This reduces the volume of gas significantly making it cheaper to transport. Early or pre-treatments of the natural gas include the removal of CO_2, water, liquid hydrocarbons and the removal of inorganic species such as Hg and H_2S. There are a number of different processes designed by different oil and gas companies to achieve this. LNG conversion is carried out at Snohvit (Statoil) in northern Norway and the CO_2 from the gas field and is being captured and stored (Aspelund and Gundesen, 2009; Estublier and Lackner, 2009).

GTL processing uses air and natural gas as primary components (Figure 3). As well as using energy, CO_2 is also a by-product at an early stage of the process. Prior to processing, the natural gas has to be cleaned up and a number of contaminants are removed (including CO_2) to enable efficient manufacture of syngas. Contaminants removed include any CO_2, H_2S, H_2O, wetter hydrocarbons and liquid petroleum species. As the catalysts used in the Fischer-Tropsch process tend to be very highly sensitive to S poisoning, the gas at the start of the process has to be pre-cleaned to < 1ppm S. These contaminants, (including CO_2) may be treated further to utilise the C_{5+} hydrocarbons and any liquid petroleum products; however some may remain entrained in a separately captured stream of CO_2 with the other contaminants.

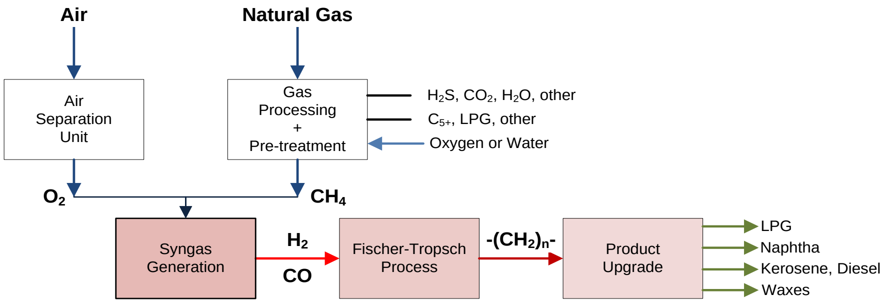

Figure 3 A schematic diagram of the GTL process based on general literature.

Based on the general processes involved, the risk of other hydrocarbons and some metal contaminants is possible in CO_2 streams from both GTL and LNG processing. However, the contaminants are expected to be very like those from power generation as discussed above.

Chemicals/processing industries

There are other industrial processes that can produce substantial CO_2 emissions and would be a significant point source ideal for geosequestration. Primary industries such as iron and steel manufacture, alumina processing, cement/ceramics production, other mineral processing as well as paper and pulp mills all use significant amounts of energy. Various chemical and petrochemical processes such as coal to urea/fertiliser processing, ammonia plants, plastics/synthetics, paints and so forth use large feedstocks and energy for production (IEA, 2007 – Tracking industrial energy efficiency and CO_2 emissions).

Irrespective of the processing methods employed, the basic feedstocks in most cases are coal, oil or gas, as is used in the energy generation industry. Thus many of the contaminants are similar. In the case of the removal of CO_2 from hydrocarbon reservoirs, the main potential contaminants are traces of the hydrocarbons themselves. This could range from CH_4 (methane) to higher n-alkanes, likely to be the most quantitatively significant. The amines used in the scrubbing process will again be somewhat entrained in the CO_2 effluent as discussed earlier. As coal fired power is covered in the section above, the likely contaminants in oil and gas are collated there.

2.6 Case studies

2.6.1 Monitoring at selected CO_2 pilot sites

For the monitoring of CO_2 storage, commercial sites like Sleipner and In Salah largely rely on a range of geophysical and remote sensing techniques employed at the ground surface. Pilot and research CO_2 storage sites, on the other hand, have comprehensive monitoring set-ups that include geochemical sampling and other subsurface measurements such as pressure and temperature using monitoring wells. See Table 6 and references therein for saline aquifer storage site examples.

Generally, standard petroleum industry monitoring equipment is used in existing projects for the injection interval (with the addition of a few novel tools such as the LBNL U-Tube system; Freifeld et al., 2005; Freifeld, 2009) and standard groundwater industry tools are employed for shallow aquifer monitoring. In most cases, direct monitoring of pressure, temperature and fluid chemistry occurs in the injection horizon and in shallow groundwater aquifers, with the exception of Cranfield (Hovorka et al., 2011) the unit directly overlying the reservoir seal is only monitored by indirect methods.

Aside from well schematics showing the conceptual monitoring design and placement of tools, technical specifications of the sensors used are generally not available in the published literature. The following pages summarise the monitoring efforts at selected pilot sites with emphasis on the direct measurement tools. Finding detailed and complete technical information about monitoring tools in the literature and on project websites is often very difficult, resulting in a lot of gaps when listing tool specifications for individual sites. For more information, the reader is referred to the cited references.

Table 6 Summary of monitoring technologies from injection operations in saline aquifers (Michael et al, 2010).

Site	Monitoring Methods	Selected References
Sleipner	1. Time – lapse seismic 2. Time – lapse gravity 3. Micro-seismic	Arts et al. (2004 a,b; 2008), Arts & Winthaegen (2005), Audigane et al. (2007), Chadwick et al. (2005), Ghaderi & Landro (2005), Nooner et al. (2007), Torp & Gale (2004), Zweigel et al. (1999, 2004)
Frio	1. Well logging 2. Geochemical samplings 3. Cross-well seismic 4. Vertical Seismic Profiling 5. Cross-well electro-magnetic surveys 6. Tracer injection 7. Pressure and temperature measurements 8. Soil-gas measurements	Daley et al. (2006, 2008), Doughty et al. (2008), Freifeld et al. (2005), Hovorka & Knox (2003), Hovorka et al. (2006a,b), Kharaka et al. (2006 a,b), Müller et al. (2007)
Nagaoka	1. Time-lapse crosswell seismic tomography 2. Well-logging 3. Pressure and temperature measurements 4. Geochemical monitoring - Fluid and core sampling 5. Micro-seismic 6. Observation of Mid-Niigata Chuetsu	Kikuta et al. (2005), Mito et al. (2006; 2008), Onishi et al. (2009), Saito et al. (2006), Xue et al. (2006; 2009), Zwingmann et al. (2005)

	earthquake	
Ketzin	1. Time – lapse seismic 2. Cross-hole electrical resistivity 3. Temperature and pressure profiling 4. Time – lapse vertical seismic profiling 5. Time – lapse moving-source seismic profiling 6. Microbiology	Förster et al. (2006), Giese et al. (2009), Juhlin et al. (2007), Kazemeini et al. (2008), Prevedel et al. (2009), Schilling et al. (2009), Yordkayhun et al. (2007)
In Salah	1. Time-lapse seismic surveys 2. Time-lapse gravity surveys 3. Time-lapse electrical / electromagnetic techniques 4. Tracers 5. Analysing formation fluids 6. Soil gas sampling and injection monitoring 7. Remote sensing (INSAR)	Mathieson et al. (2009; 2011), Onuma & Ohkawa (2009), Riddiford et al. (2003, 2005), Rutqvist et al. (2010)

2.6.2 Pembina

During 2004-2008, a CO_2 EOR monitoring pilot study was performed at Penn West Petroleum Ltd's Pembina-Cardium pool in Alberta Canada (Hitchon, 2009). The M&V program included environmental, seismic, and geochemical monitoring in addition to pressure/temperature monitoring in a deep observation well (Figure 4).

Injection horizon

- Well depth: 1650 m
- Bottomhole pressure: 18500 kPa; Bottomhole temperature: 50°C
- Pressure-Temperature sensors: Roctest Ltd. (vibrating wire piezometers)
- Max. pressure: 35 MPa absolute; Pressure accuracy: +/- 0.1%
- Temperature range: -40^{o}C to 65^{o}C; Temperature accuracy: +/- 0.5%
- Cabling: two twisted shielded pairs w/polyethylene jacket; P/T sensor are rigidly clamped to the tubing string and each has its own signal cable run to the surface
    - *Other: Geophones, U-tube*

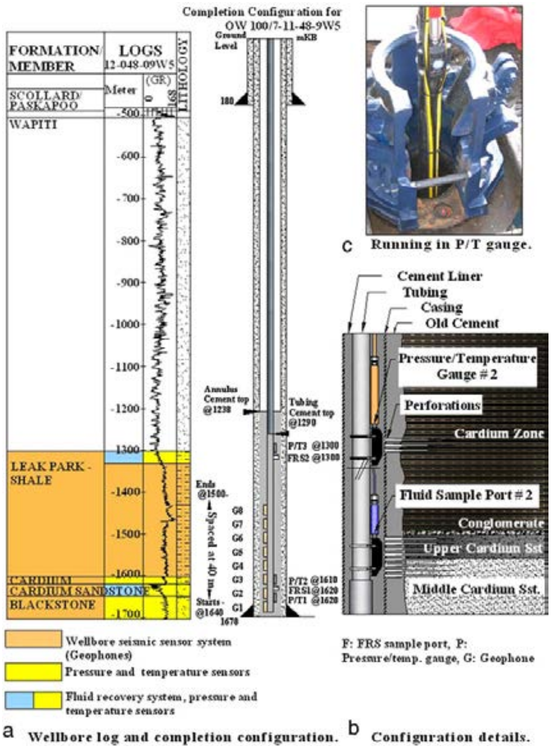

Figure 4 Installation schematic of sensors within the borehole (Zambrano-Narvaez and Chalaturnyk, 2011).

Environmental monitoring

- Atmospheric monitoring: tunable diode laser system for CO_2 and methane
- Gas monitoring: soil flux @ 1 m and 3 – 20 m below surface; 3 gas sampling wells (open hole) at location of groundwater monitoring wells.
- Groundwater: 3 monitoring wells (water quality and water level) down to 50 m below surface. Telemetry system was installed in one of the wells for remotely monitoring water quality.

2.6.3 Ketzin (CO2SINK)

The CO2SINK project officially started in April 2004 and is aimed at developing an in situ laboratory for the investigation of onshore CO_2 storage (Förster et al., 2006). The target for the storage of CO_2 is a sandstone aquifer in the Upper Triassic Stuttgart Formation in the Ketzin anticline in northern Germany. Approximately 30,000 tons per year are anticipated to be injected over 3 years and injection started in June 2008. All wells (Figure 5), one for injection and two for observation, are equipped with smart casings (sensors behind casing, facing the rocks) containing a Distributed Temperature Sensing (DTS) and electrodes for Electrical Resistivity Tomography (ERT).

Injection horizon

- Well depth: 630 - 800 m (1 injector, 2 observation wells)
- Bottomhole pressure: 6300 kPa
- Bottomhole temperature: 35°C
- Pressure (fibre optic)-Temperature (distributed temperature sensing) sensors
- Manufacturer: Weatherford International Ltd.
- Max. pressure: 135 MPa
- Max. temperature: 150°C;
    - *Other: vertical electrical resistivity array, gas membrane sensor*

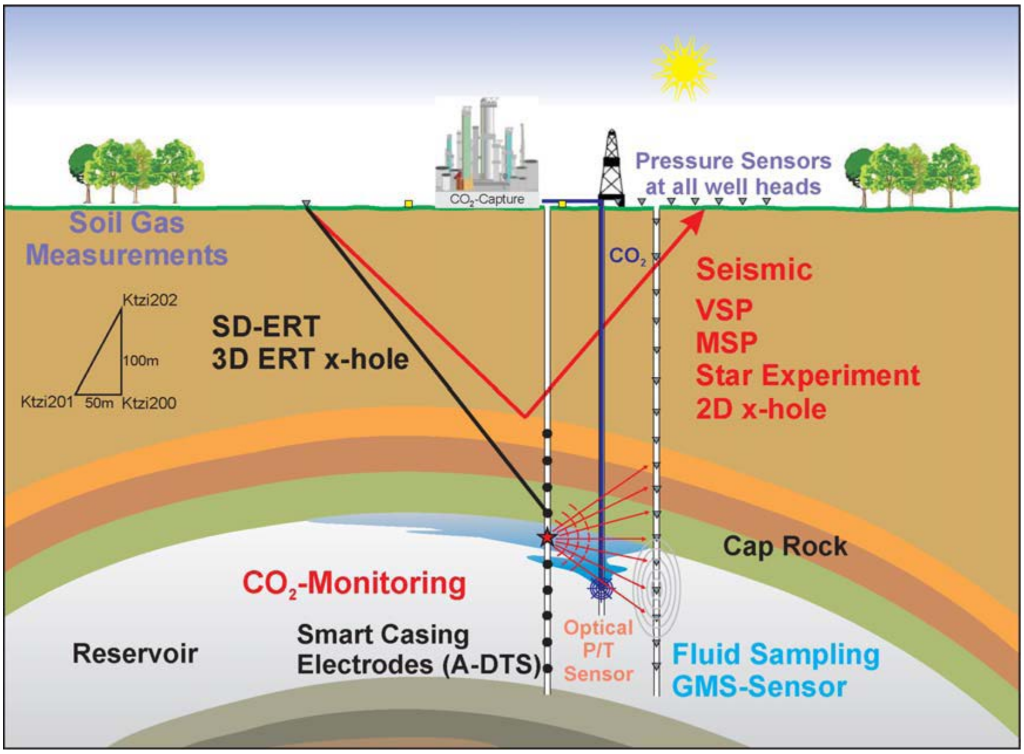

Figure 5 Monitoring set-up of the CO2SINK project at Ketzin (Würdemann et al., 2010).

Environmental monitoring

- Atmospheric monitoring: tuneable diode laser system for CO_2 and methane
- Gas monitoring: surface soil flux (20 stations), methane @ 2 m (10 wells)
- Groundwater: 2 multi-sensor monitoring wells

2.6.4 Cranfield

The Cranfield Field in southwest Mississippi is the location for a SECARB large-scale injection project conducted by the Gulf Coast Carbon Center (GCCC) with support from NETL and the US DOE. Injection started in July 2008, ramping up to rates greater than 1.2 Mt/year through 23 injectors (Hovorka et al., 2011). Continuous pressure and temperature measurements (Figure 6, Table 7) in the injection interval showed high sensitivity to distant changes in injection rate, confirming reservoir compartmentalisation. Pressure monitoring ~120 m above the injection interval is used to test the sensitivity of this approach for documentation of integrity of the confining system.

Injection horizon

- Well depth: 3300 m;
- Bottomhole pressure: 31,100 kPa (initial) increased to up to 41,000 kPa
- Bottomhole temperature:
- Pressure-Temperature sensors (observation well): Panex 6250 (digital)
- Pressure accuracy: 0.01 psi
- Temperature accuracy: 0.01 degree F
- Cabling: tubing-conveyed to surface via ¼” stainless steel encapsulated tubing.
    - *Other: U-tube (LBNL), Kuster (USGS), ERT, RST*

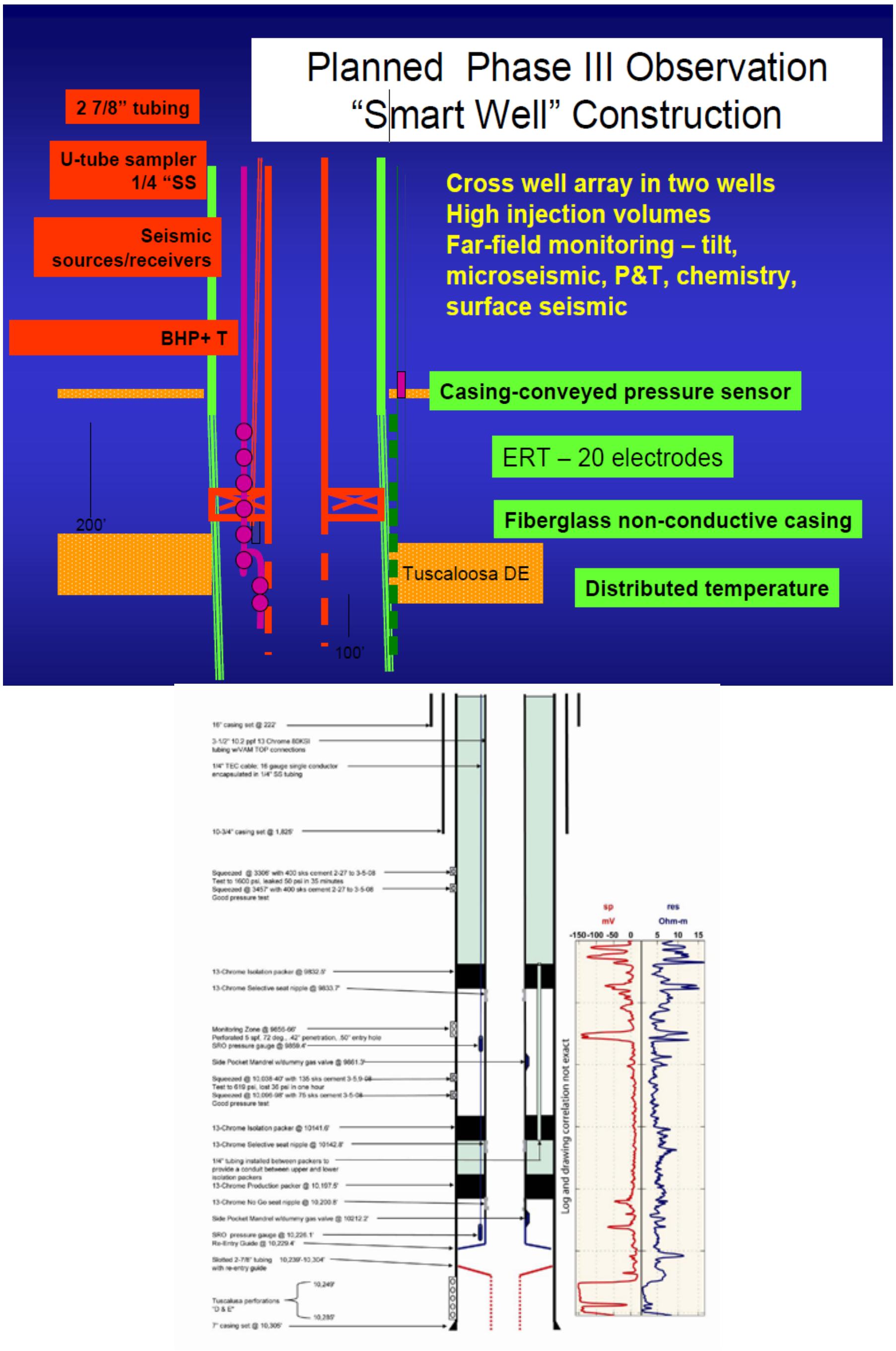

Figure 6 Observation well completion diagram indicating pressure and temperature gauge locations at Cranfield. Log image to right shows correlated approximately to well design (from Hovorka et al, 2009; Meckel et al, 2008).

Environmental monitoring

Groundwater: Geochemical monitoring of confined freshwater aquifers at 70-100 m depth. Four sampling trips since August 2008 measuring: Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Pb, Se, Zn (Cations), F^-, Cl^-, SO_4^{2-}, Br^-, NO_3^-, PO_4^{3-} (Anions), TOC, TIC, pH, Alkalinity, VOC, $\delta^{13}C$.

Table 7. Measurement technologies employed by SECARB projects. Adapted from http://www.secarbon.org/value/nonpublic/secarbfactsheetssebIII.pdf.

Measurement Technique	Measurement Parameters	Application
Introduced – noble gasses/partitioning tracers	Dissolution of CO_2 into brine	The SECARB Early Test will deploy the U-tube to reservoir depths to obtain tracer chromatography to assess dissolution via chromatography.
Produced fluid composition	CO_2 via mass, DIC, DOC; Selected major and minor cations, organics	Validation of well log and cross-well CO_2 detection, index of rock-water reaction.
Bottom-hole pressure	Pressure transducers on wireline with real-time readout	Key measurement assessing relationship between pressure field and multiphase field.
Distributed down hole temperature	Measure zones of fluid movement	Additional data to constrain flow units, especially to determine flow-unit thicknesses under relevant conditions. Also indicates well integrity.
Pulsed neutron reservoir saturation; Cased hole sonic if modelling predicts sensitive	CO_2 saturation	Distribution of CO_2 at measurements points, model match, validation and quantification of CASSM and cross-well ERT. Key input to capacity calculation term ”E.”
Time-lapse 3-D seismic imaging (surface deployed)	Change from baseline, only if baseline assessment shows reasonable sensitivity to the expected CO_2 saturation change	Extent of CO_2 plume, especially down-dip. May substitute VSP if sensitivity is higher.
Continuous Active Source Seismic Monitoring (CASSM); Cross-well seismic tomography	Detect timing of CO_2 movement cross the plane of measurement	History match model, with high frequency temporal records with pressure signal
Passive seismic monitoring	Assess stress distribution	Development of stress in formation
Above-zone pressure and fluid monitoring	Assess leakage signal (possible through well completions - poor cement bond)	Continuation from Phase II to obtain long record
Cross-well electrical resistance tomography (ERT)	Improve measurement of saturation; will be used if proves feasible and economic	Tool development will extend the range of cross-well measurement of saturation and improve the rigor of history match and seismic inversion.
Subsurface deformation	Tilt; Measurements at surface to assess depth effectiveness of tool under high injection rates	Quantify geomechanical effects on storage formation as part of pressure field assessment.
CO_2 land surface-soil gas assessment	Measure natural CO_2 fluxes – aquifer-vadose zone-soil and-surface and atmosphere in depth over time.	Determine sensitivity of these techniques under regional conditions. Possible follow-on-tracer test to validate hypothesis.
Aquifer monitoring	Alkalinity, DIC, DOC, isotopes, chloride selected cations and anions.	Assessment of method in compact possibly contaminated setting, directly regulated recourse. Possible follow-on-tracer test to validate hypothesis.

2.6.5 Frio

Planning for the Frio Brine Pilot Experiment began in 2002, funded by the U.S. DOE National Energy Technology Laboratory. The site for this experiment is in the South Liberty oilfield, northeast of Houston. Before injection, extensive monitoring, including baseline aqueous geochemistry, wireline logging and vertical seismic profiling, and modelling was conducted. Injection began on October 4, 2004, and over 10 days 1,600 tonnes of CO_2 was injected into the brine formation. Monitoring was carried out during injection to monitor the movement of the CO_2 (Figure 7), and is continuing to monitor the post-injection migration. In summer 2006, a deeper injection interval in the Frio Sand package was used to conduct a second CO_2 injection experiment.

Injection horizon

- Well depth: 1545 m
- Bottomhole pressure: 14,850 kPa
- Bottomhole temperature: 56°C
- Pressure-Temperature sensors (observation well): Panex sensors
- Pressure accuracy: 0.02% of full scale (at Frio was 5000 or 10 000 psi or 34.5 or 69 MPa)
- Temperature accuracy: ± 0.5°C with a resolution of 0.005°C.
- Cabling: TEC (Tubing Encapsulated Conductor) Baker Hughes Temperature rating to 177°C Collapse pressure rating 20,000psi.
- *Other: U-tube (LBNL)*
- *Frio II used the CASSM system for Frio II (see Daley et al, 2007)*

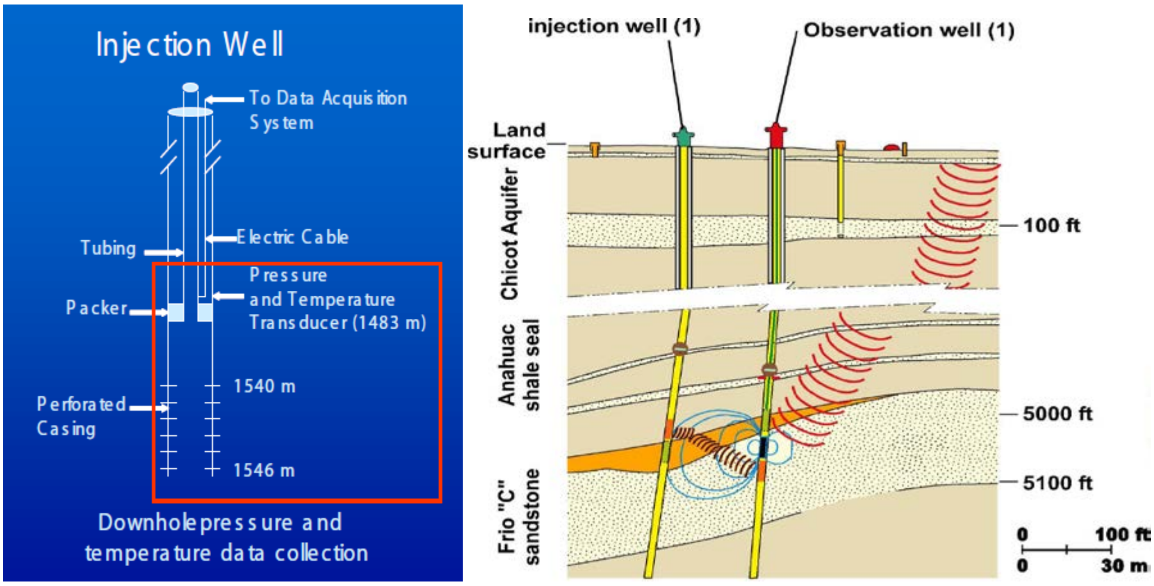

Figure 7 Monitoring set up at the Frio pilot project (Source: Www.beg.utexas.edu/environqlty/co2seq/fieldexperiment.htm).

2.6.6 CO2CRC Otway Project

The CO2CRC Otway Project is located near Nirranda, Victoria in Australia. During the first stage of the project both baseline monitoring and monitoring and verification programs were established prior to the injection of up to 100,000 tonnes of gas. By the end of this stage of the project 65,445 tonnes gas was injected in total. As at Frio, there was significant research using petroleum exploration tools and information to establish baseline information, including wireline logging, VSP and other seismic surveys prior to commencing the project. The monitoring well (Figures 7 and 8) is a former gas production well (Naylor-1). The gas injected is an approximate 80:20 mol % mix of CO_2 and CH_4 from a nearby gas field (Buttress). Baseline monitoring consisted of soil gas surveys, ground water surveys, seismic and atmospheric surveys. These are still ongoing post-injection as monitoring and verification surveys. A variety of difficulties were encountered during the deployment of the bottom hole assembly containing the reservoir level tools, due to the utilisation of a production well that was both narrow and contained a casing patch at a critical depth close to the injection formation (Figure 8 and 9).

Otway Stage 1 Project (from CRC-1 to Naylor-1) Injection horizon

- Monitoring well depth: 2028 - 2065 m
- Bottomhole pressure: 19,500 kPa
- Bottomhole temperature: 85°C
- Pressure-Temperature sensors (obs well): Panex sensors
- Pressure accuracy: 0.02% of full scale (at Naylor-1 was 5000 psi or 34.5 MPa)
- Temperature accuracy: ± 0.5°C with a resolution of 0.005°C.
- Cabling: TEC (Tubing Encapsulated Conductor) Baker Hughes Temperature rating to 177°C Collapse pressure rating 20,000psi.
- 3 single-component geophones for HRTT monitoring. 3 3-component geophones above reservoir for passive microseismics and 9 single-component gephones for reflection surveys.
- *Other: 3 U-tubes (LBNL)*

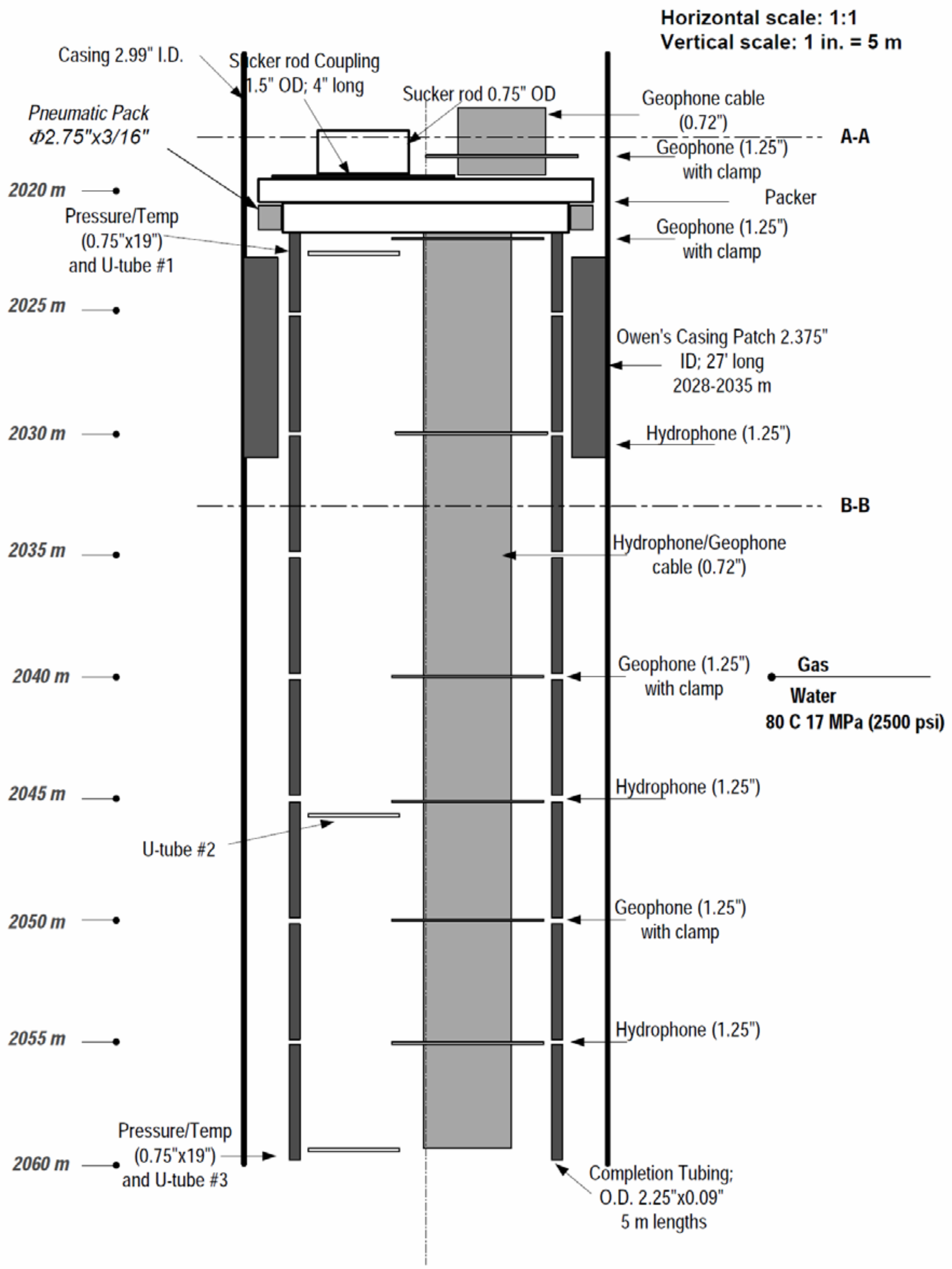

Figure 8 Schematic of the bottom-hole-assembly in the Naylor-1 observation well at the CO2CRC Otway Stage 1 site showing the distribution of equipment below the single packer in the Waarre C formation being tested.

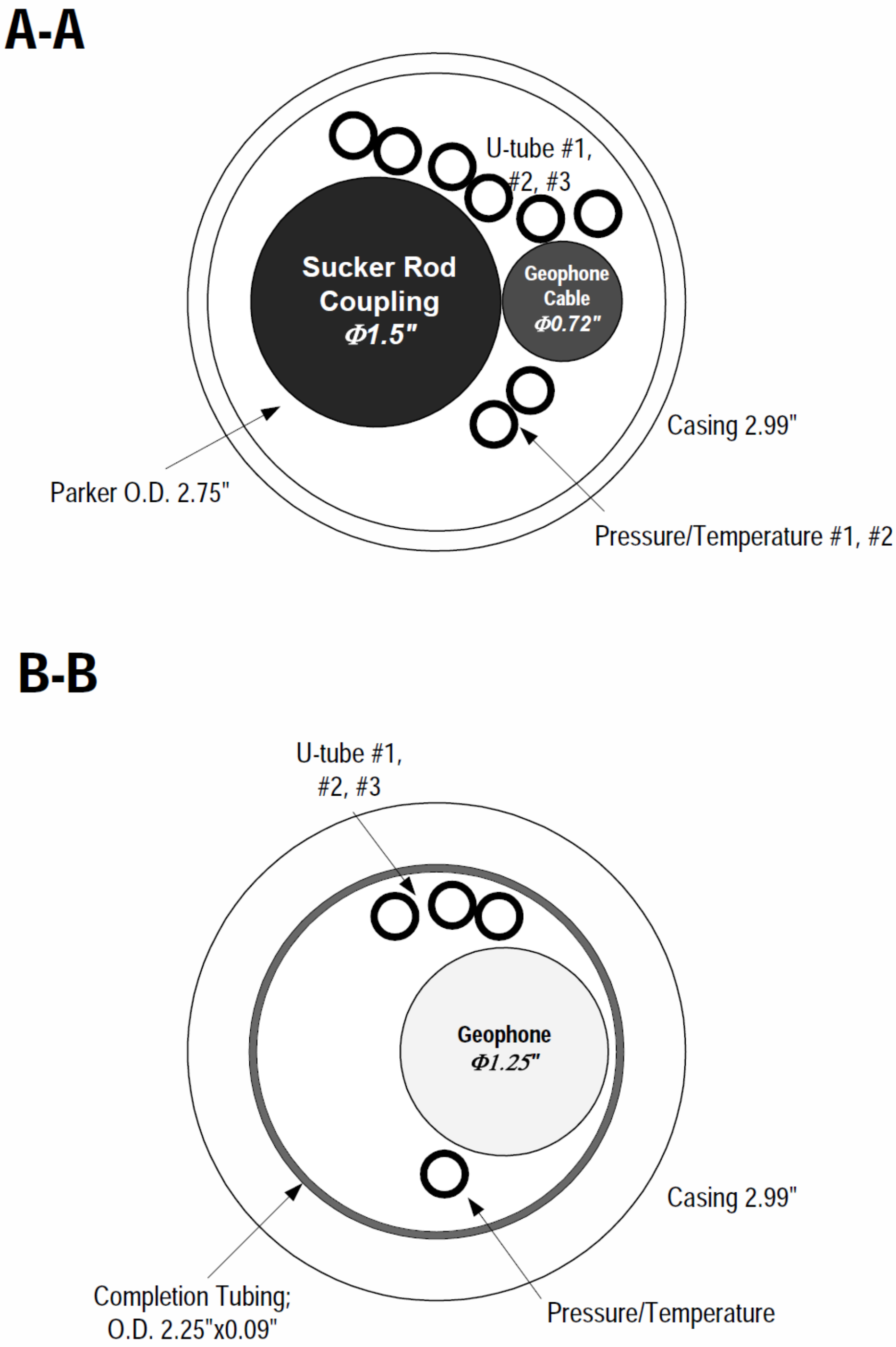

Figure 9 Cross section of tools and communications systems from injection interval to surface in the Naylor-1 monitoring well.

Otway Stage 2B Project (CRC-2 single well test) Injection horizon

- Monitoring well depth: 1440-1448m test interval
- Bottomhole pressure: 15 MPa
- Bottomhole temperature: 65°C
- Pressure-Temperature sensors: Down-hole Digital Quartz Pressure/Temperature Probe (Panex) Model 6250 Permanent Hybrid Digital Addressable Surface Read Out (DASRO)
- Pressure accuracy: ±0.02% of full scale including linearity, hysteresis and repeatability over calibrated temperature range from 200 psi to full scale
- Temperature accuracy: ±0.5°C (±0.9°F) within calibrated temperature range. Pressure accuracy is independent of indicated temperature accuracy.
- Cabling:
    - *Other: U-tube (LBNL)*

Environmental monitoring

Atmospheric monitoring: CSIRO LoFlo CO_2 analyser and CO_2 flux tower (Leuning et al., 2008).

Gas monitoring: annual soil gas sampling surveys using a post run tubing system (PRT) (Schacht et al., 2011) for gas composition and more recently SF_6 analysis in the field. Carbon isotopes of carbon dioxide and methane are measured in the laboratory. A subset of samples also undergoes helium composition characterisation and ^{14}C CO_2 in the laboratory.

Groundwater: biannual sampling of shallow unconfined Port Cambell Limestone (21 bores) and deeper, confined Dilwyn aquifer (3 bores) for water quality; 6 bores equipped with pressure and temperature (T) data loggers (de Caritat et al., 2009). The analysis of groundwater composition consisted of field determinations of pH, Eh, electrical conductivity (EC), dissolved oxygen (DO), T, Fe^{2+} and alkalinity (HCO_3^- or dissolved inorganic carbon, DIC). In the laboratory, concentrations of Ag, Al, As, Au, B, Ba, Be, Bi, Br^-, Ca, Cd, Ce, Cl^-, Co, Cr, Cs, Cu, Dy, Er, Eu, F^-, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I^-, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, NO_3^-, Pb, Pd, PO_4^{3-}, Pr, Rb, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, SO_4^{2-}, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, and Zr were determined on 0.45 µm filtered aliquots. In addition, the C and O isotopic compositions of DIC ($\delta^{13}C$ (DIC) and $\delta^{18}O$ (DIC)), S (and for selected samples also O) isotopic compositions of dissolved sulfate ($\delta^{34}S$ (SO_4^{2-}) and $\delta^{18}O$ (SO_4^{2-})), and the H and O isotopic compositions of water (δ^2H (H_2O) or δD (H_2O) and $\delta^{18}O$ (H_2O)) were determined. A comprehensive quality control/quality assessment program was deployed to monitor precision and bias.

3. Potential technologies evaluated

The following section is the main review of potential technologies that may be used in the monitoring of substances mobilised by CO_2 storage in geological formations. The searches used information from the previous section to identify processes that could be measured and monitored. The approach was to consider anything from soil surface to deep subsurface and includes physical, geophysical, chemical, biological and other approaches to identify tools. The efficacy and prior testing of these tools is also discussed. Finding information on the cost of purchasing individual tools or their deployment cost, analyses or other financial factors was difficult and it became clear that it would be exceedingly time consuming to complete accurately. Therefore the subject of cost was kept to a minimum, but concerns have been noted where experience has provided some estimate of financial or manpower costs.

Deeper geophysical methods measure the CO_2 plume or the shift in salinity/density/pressure that can be detected. Although other associated compounds may also be liberated, it is unlikely any of these are in large enough quantities to change the geophysical technique and its application. Shallow applications may have more flexibility in detecting other subtle parameters, but this is not certain. The following subsection briefly reviews the CO_2 leakage monitoring methods available from geophysics, with particular reference to the most recent literature. The recent IEA GHG report, Quantification Techniques for CO_2 leakage (2011), covers geophysical monitoring extensively, particularly seismic, gravity and remote sensing technologies. As geophysical monitoring is a minor component of this report, this document aims to discuss other areas of geophysical monitoring that were not covered as thoroughly, and will only report on land applications. Key considerations for monitoring according to Arts et al. (2011b) are: 1) spreading of the plume, 2) sealing behaviour of the caprock, 3) fault integrity, 4) spreading across spill points, 5) shallow variations in CO_2 content indicative of leakage, 6) groundwater quality, and 7) terrestrial and marine ecosystem quality. Geophysical technologies can aid in all of these areas, and many studies have tested and modelled these abilities, but the real-world ability of shallow monitoring to detect and quantify a CO_2 leak is unproven (Wimmer et al., 2011). Natural analogues (e.g. Latera, Italy) and shallow release studies (e.g. ZERT, Bozeman, U.S.A) present the best examples of detecting CO_2 leaks.

3.1 Tools that monitor for changes in flow or physical effects

3.1.1 Pressure

Understanding the in situ pressure has application to almost all aspects of CO_2 storage; from site characterisation to capacity estimates and monitoring and verification. The IEAGHG Monitoring Selection Tool strongly recommends monitoring pressure as part of any CCS project. All of the CCS projects referred to in this report monitor the pressure in the storage reservoir and some also monitor overlying permeable zones [i.e. Cranfield, USA (Meckel and Hovorka., 2010)] and Otway, Australia (de Caritat et al., 2009).

Monitoring pressure is standard practice and a mature technology in both the water resource and oilfield industries. Both industries have developed tools which can be purchased off-the-shelf, are sensitive and robust and can remain in situ for many years. These systems can be also very cost-effective, depending on the level of sophistication required.

The application of these tools is dependent on the monitoring environment they are required to operate in. Water resource tools monitor the pressure (or head), temperature and often conductivity, of borehole fluids from bores generally less than 1000 m. These tools are appropriate for monitoring bores that are screened (or open) in an aquifer or permeable unit above the storage reservoir. As such, they have lower pressure and temperature ratings relative to oilfield tools, but are consequently longer lived and less expensive. Oilfield tools are rated for higher pressures and temperatures and are applicable to deeper units, including the storage reservoir. Some examples of each type of tool and their key parameters are described in Table 10.

Permanent down-hole gauges (PDG)

Permanent down-hole gauges (PDG) are increasingly being used in the oil and gas industry for long term monitoring of pressure and flow properties. It is likely they will have application for long term CO_2 storage monitoring. These types of gauges are most suited for installation within the storage reservoir as they are rated to withstand the pressure and temperatures in these environments. More complex down-hole monitoring systems are being installed, known as intelligent or smart wells. These systems currently have a reputation for unreliability and a limited lifetime, which limits their application as a long term monitoring tool for CO_2. However, as their value becomes more apparent these issues are being addressed and the associated risks reduced.

Van Gisbergen and Vanderweijer (1999) evaluated the performance of 952 pressure and temperature monitoring systems installed since 1987. The majority of the installations they evaluated were pressure and temperature gauges, however, there were other systems available for permanent down-hole monitoring, including flowmeters (limited to liquid only), fibre optic well monitoring and systems for cableless communication. Van Gisbergen and Vanderweijer (1999) found that the 5-year survival probability of these systems improved from 40% for systems installed in 1987-88 to 75% for those installed in 1991-92. However, they noted no improvement in systems installed between 1993 and 98, which resulted in a 5-year survival probability of only 69% for this period. They also evaluated failure modes for PDG systems installed between 1995-8 and concluded that the majority of failures could be attributed to the down-hole gauge and to the cable. The failure rate of the electronic circuitry is temperature dependant, and as a rule of thumb the failure rate doubles for each 8°C increase in temperature (van Gisbergen and Vanderweijer, 1999).

Frota and Destro (2006) carried out a similar reliability and lifetime study on PDG systems installed since 1992 in 12 oilfields in the Campos Basin, (offshore) Brazil. The temperature in the reservoir ranges from 70 to 110°C and the PDG systems were installed, on average, at 2000m below the wellhead. The water depth ranges from 150-1912 m. The system, as described by Frota and Destro (2006), consists of a sensing element in an electronic gauge which continuously measures temperature and pressure at the bottom of the hole. The gauge is mounted on a mandrel which forms part of the tubing string. The gauge is connected to electrical cable and to the production platform via the Christmas tree. The technical specifications of the Campos Basin systems are:

- Capacity: 10,000 psi/150°C
- Resolution: 0.1 psi/0.05°C
- Sensor: Quartz crystal
- Transmission: digital and analogue

The cable is coaxial and consists of an insulated monoconductor encapsulated in a metal sheath, which is in turn encapsulated in thermoplastic to prevent it from damage (Frota and Destro, 2006 and references therein).

Frota and Destro (2006) found that for systems installed between 1995-2005 (three generations of systems) the failure rate was similar: 34% from gauge failure, 30% from connections/interfaces in the cable. As did van Gisbergen and Vanderweijer, Frota and Destro established that the longevity of each system was also dependant on the service company performing the installation. The best result they achieved for the most recent generation of PDG systems, installed between 2002 and 2005 resulted in a mean life of 11.86 years. They also noted a number of improvements relating to installation and maintenence procedures to further increase the life of these systems.

Meckel and Hovorka (2010) evaluated the use of PDG systems at the Cranfield site, Mississippi. At the Cranfield site, industrial scale CO_2 injection is occurring for EOR where down-hole pressure and temperature data have been collected since July, 2008. The gauges monitor both the injection wells and the monitoring well. The down-hole monitoring tools are located in the wellbore by the target reservoir and in an overlying aquifer, which is referred to as the above zone monitoring interval (AMZI). They noted three challenges in regard to the interpretation of the data obtained through these systems: 1) the data are high-resolution and highly sensitive, whereas the ability to history match reservoir data is imperfect, and may lead to ambiguous or non-unique solutions; 2) precise correlation with observed pressure transients requires accurate knowledge and temporal resolution of injection rates (and, in the case of EOR, production rates); 3) deployment of AMZI techniques increases the geologic domain over which simulations and predictions are required. They recommend that CO_2 fields investing in PDG systems include digital flowmeters and a detailed field log of all activities. The simulations required for dynamic and adaptive flow are computationally and labor intensive. This increases the cost of deploying these systems and any decision to include this type of monitoring requires careful evaluation of the increased value. Furthermore, Paterson et al. (2008) states that the application of these tools can exceed the interpretative ability of the current algorithms and is complicated by the volume of data produced.

Shallow groundwater monitoring

Potential impacts on shallow groundwater from leakage are discussed in other sections and include:

- Pressure changes
- Salinity increase
- pH reduction
- Metal mobilisation (Fe, Mn, Pb)
- Eh reduction
- Temperature reduction

These changes provide multiple opportunities for geophysical monitoring. Regardless of the technique employed, baseline characterisation is critical for geophysical (biological and chemical) monitoring. Shallow groundwater monitoring generally consists of a tool suspended in an open borehole which measures the overlying weight of water (hydraulic head), the temperature of the water and often the conductivity. More recently, this technology has advanced to enable monitoring of multiple zones within a single well. Both techniques have potential application to CCS projects in the vicinity of freshwater aquifers whose long term integrity must be monitored.

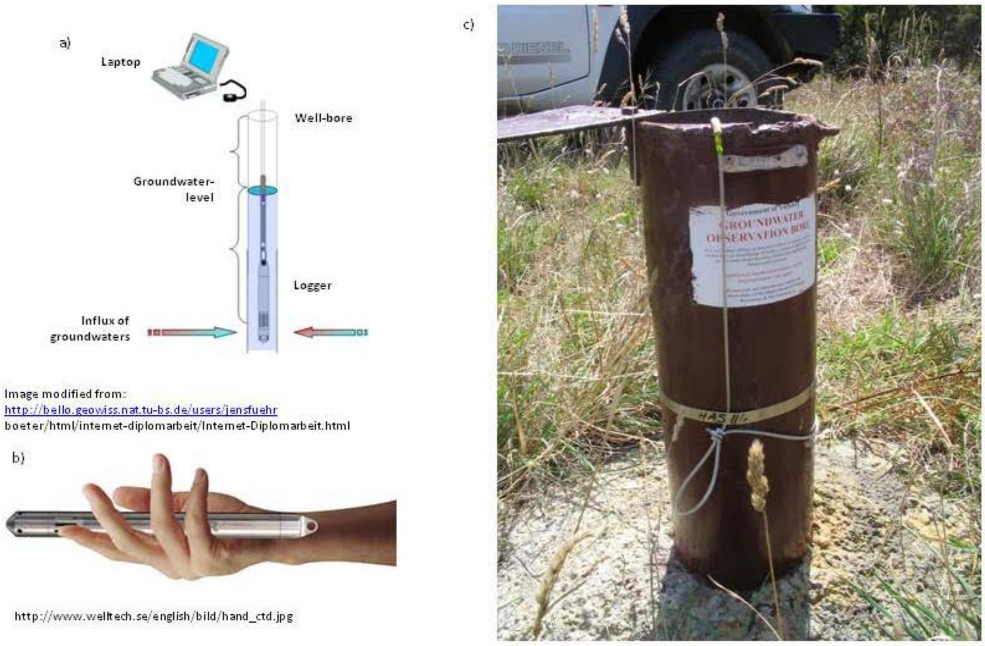

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Figure 10 a) Schematic of ground water monitoring installation; b) water level logger c) water level logging installation at CO2CRC Otway Project, Australia.

Water level loggers typically incorporate pressure and temperature sensors and battery power into a corrosion resistant casing designed for long-term underwater deployment. This type of monitoring is applied at the CO2CRC Otway project where the loggers have been installed since 2006. These units are manually downloaded at biannual intervals when direct readings of water level are taken for calibration purposes. No appreciable drift has been observed over this time. Cabled loggers that transmit data wirelessly are also available for installation, and although these increase the initial cost, the field time and personnel cost is reduced. Figure 10 shows a schematic of a typical logger set-up and the size and shape of a standard water level logger. Figure 10c) shows one of the installations using a pre-existing groundwater bore at the CO2CRC Otway Site. Setting these instruments to record only predefined "events" extends their recording life, for example a change in water level greater than "normal". The challenge is defining the boundaries for such an event appropriate for the specific CCS environment.

Multi-packer monitoring systems have been proven to effectively monitor groundwater. They consist of a series of 1) casing with a set of packers, which can be multiple sets per well; 2) ports through the casing to allow fluid to move from the formation into the sampling chamber and 3) wireline probes to allow in situ monitoring and sampling operations (including pumping, where necessary). The Schlumberger Westbay system is a frequently used system and has been used extensively at nuclear study sites (Delouvrier and Delay, 2004); however, there are others (Table 10). The advantage of these systems is that they can sample and monitor multiple levels in a single well, reducing the requirement for multiple wells monitoring specific horizons. Delouvrier and Delay (2004) describe multi-level pressure monitoring at the Meuse/Haute underground research laboratory in France at depths of up to 600m using the Westbay MP System® (Figure 11). The system consists of a series of packers (inflated with water), only metres apart, isolating specific sections of the borehole. Ports are installed through the casing, between packers at the depths of interest. The ports remain closed until opened by an instrument probe. The setting of the probe on a port is done with no volume exchange from the monitoring chamber and minimal pressure disturbances. For operations involving large flow rates, i.e. chemical sampling or hydraulic testing, the casing may be equipped with pumping ports that have larger flow capacities. The probes are run on a wireline cable to perform various functions in the ports, which include monitoring pressure and temperature as well as opening and closing the ports. The probes may be run either singly, in sequence or simultaneously. The monitoring system was installed and has been fully operational since 2000 and is connected to the facilities data processing centre to allow continuous collection of data from the pressure probes. The quality and stability of the information acquired enables the identification of pressure changes down to 1 kPa, once the barometric effect and the tidal effects have been removed (Delouvrier and Delay, 2004).

Delay and Cruchaudet (2004) have also developed an electromagnetic permanent gauge (EPG) for the long term monitoring of pressures at the above site. The EPG is permanently cemented into a borehole with no wire or tubing connections (Figure 12). The data is transmitted electromagnetically through the rock. Improvements in batteries have extended the life of the EPG to six years or more. The details of this installation can be found in Delay and Cruchaudet (2004).

Injecting CO_2 into deep strata can deform overlying lithology. This deformation can extend to and be observed at the surface. The best example of this is using Inferometric Syntheic Aperture Radar (InSAR) at In Salah, Algeria. Radar interferometry can be used to measure ground heave related to CCS with mm precision (Ferretti et al., 2011; Onuma et al., 2011; Vasco et al., 2008; 2010). The results of Onuma et al. (2011) show the surface deformation from CCS at In Salah was 15-20 mm over 8 years at sites near the injection wells. Other results indicate an average upheaval of 3mm (Mathieson et al., 2011) to 5 mm (Vasco et al., 2010) per year and presently, this monitoring method is considered the most valuable at this site.

Measurement results may vary depending on different satellite data and inversion techniques, and many of these are being tested and proving successful. The technique is able to show extent of the plume and possible fracture development. Different signal processing applications are available. Other techniques such as Differential InSAR (DInSAR) and the multi-interferogram Persistent Scatterer (PSInSAR^{TM}) have improved the monitoring capability further (Ferretti et al. 2011; Onuma et al. 2011).

Initial limitations of InSAR techniques were the long revisiting time of the satellites, but newer generations of satellites in operation since 2008 have improved the repeat cycle to within 8 days and soon to 4 days or less – resulting in near real-time monitoring of surface shifts related to CCS (Ferretti et al., 2011).

Optical levelling, differential GPS and tiltmeters could also be used, are potentially more economical, but would be more time consuming. These methods have been combined with InSAR for calibration purposes at In Salah (Mathieson et al., 2011). InSAR is subject to a subtle, but significant phase shift from atmospheric conditions particularly in tropical and temperate climates. This can be improved by using Permanent Scatterers (Ferretti et al., 2011). InSAR coupled with increased repeat times and ground resolution provides a viable monitoring technique for.

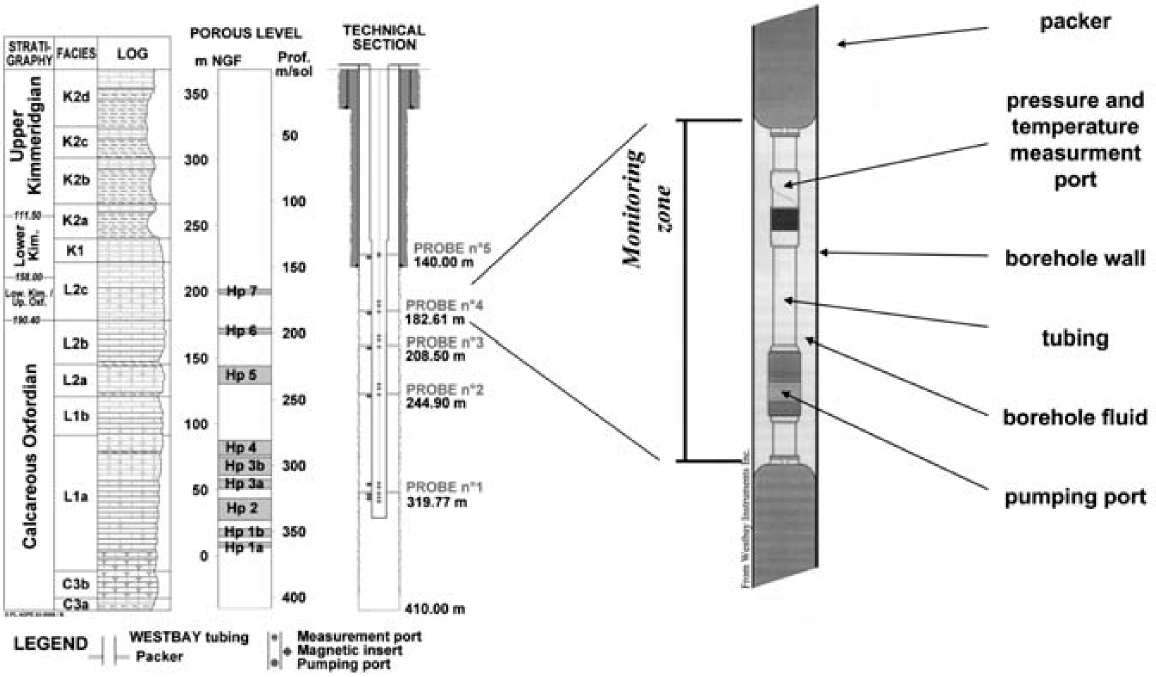


Figure 11 Westbay multi-packer borehole completion (from Delouvrier and Delay, 2004).

The multi-port system described above can also be used for in situ chemical monitoring, including conductivity, pH, redox potential and dissolved oxygen, depending on the requirement. The limitations of the Westbay system, specifically, are that it can only be deployed at depths down to 1220 m (www.slb.com).

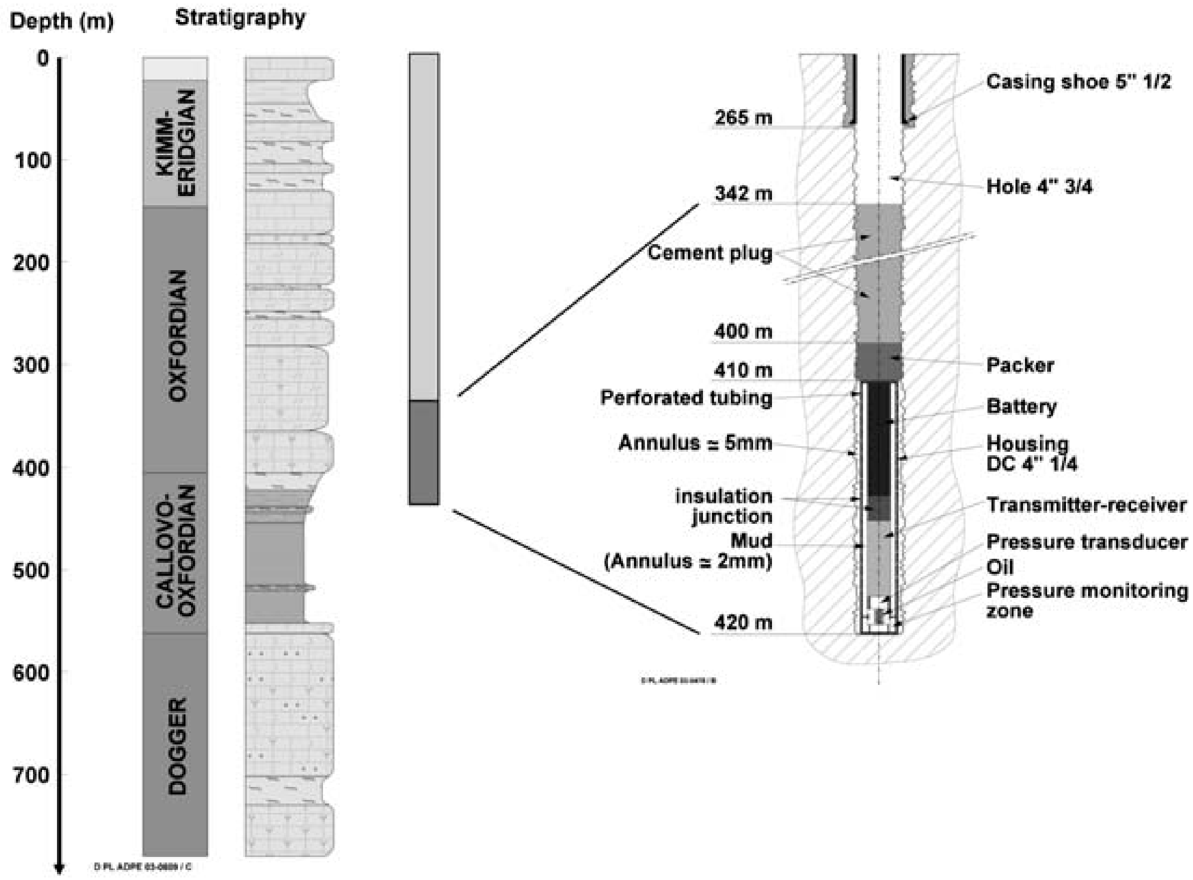


Figure 12 Schematic of the EPG installation (from Delay and Cruchaudet, 2004).

3.1.2 Conductivity

Conductivity is the measurement of the ability of an aqueous solution to transmit an electrical current. The addition of CO_2 to water changes the conductivity of the water in a measurable and predictable way. In addition to the water level loggers discussed previously, similar tools exist for monitoring conductivity and temperature in groundwater. Some tools include pressure, temperature and conductivity in a single unit. The advantages of these tools include their relatively low cost, ease of deployment and compatibility with pressure and temperature sensors. The disadvantage may be in their potential for drift, although newer tools utilise 4-pole electrode technology (as opposed to single or 2-pole electrodes) to minimise these effects.

Resistivity logs are a standard reservoir characterisation tool in the oilfield. More recent developments in this field include the use of electrical resistance tomography (ERT) where an array of electrodes are permanently installed, usually in a cross-well arrangement. This technique has been successfully demonstrated at the Mansfield sandstone reservoir in Indiana (Bryant et al., 2001). They used a 16-electrode resistivity array on the outside of insulated casing in the injector and a similar system in the annulus of the monitoring well. They used the arrangement to monitor water flooding in the reservoir and observed a high signal-to-noise ratio and were able to detect the movement of the oil-water front several meters away from the well bore. Their results in conjunction with forward modelling and inversion using 3D finite element code suggest the possibility of observing the movement of conductive or resistive fronts.

An ERT system was installed at the Cranfield Project, USA as part of the SECARB project where they were able to image the CO_2 plume as it moved out from the injection well. This project demonstrates the applicability of this system to monitor CO_2, however, the longevity or cost effectiveness of deploying such a system for long-term monitoring is not clear.

At Ketzin, cross-borehole ERT is presently being tested as part of the VERA experiment with an expected increase of 200% electrical resistivity caused by injection of CO_2 based on laboratory and modelling studies (Girard et al., 2011; Kieβling et al., 2010). This permanent monitoring array has been used for over two years at a depth of 590-735 m, 35°C, pH 5.5 and 75 bar pressure. Assessment of the degradation of the electrodes is presently being studied to determine the long term monitoring viability of this method (Schmidt-Hattenberger et al., 2011). The results of monitoring the volume of stored CO_2 appear promising, but it is limited by the modelled input data for geometry and petrophysical properties of the geology. A limitation of ERT is the spatial resolution as the lateral coverage is limited to 30 m around each well (Fabriol et al. 2011). The additional costs associated with making the wells non-conductive above and below the electrodes are also considerable (Fabriol et al., 2011)**.** ERT was effective in mapping a surface leak along a fault, showing deeper extension of a naturally occurring CO_2 seep (Pettinelli et al., 2010)

Long Electrode Electrical Resistance Tomography (LEERT) provides another monitoring capability where the use of metal case boreholes act as electrodes for resistivity imaging showing changes over time that could relate to CO_2 migration, but initial modelling suggests this approach will not be effective due to low signal-to-noise ratio, current density and sensitivity in between electrodes (White, 2011).

Another method termed LEMAM (Long Electrode Mise-A-la-Masse; Fabriol et al., 2011) designed to overcome this issue of EM resolution at depth, is to use existing deep metallic casings (old wells) as long electrodes to achieve a deeper EM current. The resolution is not as good as in seismic techniques, but resistive targets were modelled at depths greater than 1000 m. More research is recommended in this area before it can be used to monitor CO_2 leakage (Fabriol et al. 2011).

Cross-well methods and time-lapse measurements are major improvements for monitoring the CO_2 plume, but require multiple holes not more than 1000 m apart (Arts et al., 2011b) which can be a limitation in some sites.

Electromagnetics (EM) is less expensive than seismic, but lacks depth penetration. EM certainly has value in shallow monitoring, particularly if brine from a saline aquifer (CO_2 injection zone) is leaking into a fresh near-surface aquifer. We are currently unaware whether any CCS sites that have used EM for monitoring in the shallow environment, but Transient or Time-domain Electromagnetics (TEM) have been proposed for use of monitoring the groundwater (fresh/saline interface) at the Vedsted CCS site in Denmark. Uniform sedimentary units tend to provide the best environment for effective shallow monitoring of saline intrusions related to CO_2 leaks.

3.1.3 Thermal

The use of distributed thermal sensors (DTS) as a monitoring tool for CO_2 is a current topic of research. In oilfields, DTS is used as a production monitoring tool where it is considered to have long term stability and reliability. The application requires an understanding of a thermal model. Reservoir simulations use a thermal model and a transient, 3D, multiphase flow reservoir model to calculate the wellbore temperature distribution in horizontal wells. By comparing the simulated temperature and the observed data, the first outcomes are large-scale permeability trends in the reservoir. These permeability trends are then incorporated as ‘secondary’ information in the geologic model building and history matching. Finally, the updated permeability models from history matching are used to infer the down-hole flow conditions along horizontal wells. The final outcome is a geologic model that is consistent with reservoir static and dynamic information, and also the wellbore temperature measurements (Li et al., 2010). There are additional applications to detecting behind casing leaks.

Yamano and Goto (2005) describe the use of the distributed optical fibre temperature sensing technique for long term temperature monitoring in a deep borehole designed to monitor an active fault in SW Japan. This type of DTS is based on the temperature dependence of backscattering of laser light in an optical fibre. By measuring the backscattered light at the end of the optical fibre the temperature distribution all along the cable can be determined (e.g. Hurtig et al., 1994), though the temperature resolution is relatively low, 0.1–0.3 K. A fibre optic cable was installed down to a depth of 1460 m and the temperature monitored for 6 years, producing a continuous borehole profile. The results could clearly trace movement of the water in the borehole caused by water injection and natural groundwater discharge through observation of the temperature profile.

Hurter et al. (2007), wrote an overview of the potential detectability of CO_2 using temperature logging. They evaluated and compared conventional logging and DTS and the use of fibre optic cables. Their evaluation was carried out using the CO2SINK project at Ketzin as a case study to illustrate their points.

- They concluded that CO_2 was detectible by measuring changes in thermal conductivity.
- The change in thermal conductivity decreased with increasing porosity and increasing CO_2 saturation.
- Their modelling indicated that CO_2 would be detected as a temperature anomaly at a monitoring well 50m away from the injection well.
- They predict a Joule-Thompson effect will be present if CO_2 moves out of the primary container via faults or fractures or even behind the well-bore, but these effects would be subtle.
- In the absence of other sources and sinks and significant fluid flow, the presence of CO_2 in a previously fluid saturated rock has the potential to imprint a quantitative thermal signature related to the saturation and thickness of the CO_2 layer present.
- Current conventional logging and DTS systems have sufficient resolution to detect changes.

Freifeld et al. (2008) developed a borehole methodology to estimate in situ thermal conductivity. They state a spatial resolution of 1 m and describe the methodology as follows: "In parallel with a fibre-optic distributed temperature sensor (DTS), a resistance heater is deployed to create a controlled thermal perturbation. The transient thermal data is inverted to estimate the formation's thermal conductivity. We refer to this instrumentation as a Distributed Thermal Perturbation Sensor (DTPS), given the distributed nature of the DTS measurement technology". A DTPS is being applied at the CO2CRC Otway Project, Stage II as part of a suite of measurements to quantitatively determine residual saturation.

A study by Wimmer et al. (2011) on a CO_2 leak from a supply pipe showed airbourne hyperspectral was not effective in detecting the leak from plant stress, but thermal imagery did show the cooler temperatures in the soil at the leak point and could be a viable monitoring option that has not been widely tested. A number of other variables in heat sources may contribute to thermal fluxes over CCS sites making the application of this technology difficult for CCS M&V.

3.1.4 Density (RST)

The use of density tools and residual saturation tools is currently being investigated for research purposes. RST was used at Frio to determine residual saturation at both the injection and monitoring well. The high resolution results appeared to agree well with other methods used at the site (Hovorka, 2006a,b). The value of this measurement lies in the relationship between laboratory measured RS on cores and actual saturation achieved during CO_2 injection and storage. The Schlumberger wire-line reservoir saturation tool (RST) used pulsed neutron capture to determine changing brine saturation as brine was displaced by CO_2. Sigma (S), the parameter collected by the RST tool, is derived from the rate of capture of thermal neutrons (mainly chlorine) (Hovorka et al., 2006a). The high value of S for formation water derived from brine conductivity allows estimation of water saturation and the inverse, CO_2 saturation (Sakurai et al., 2005). Hovorka (2006b) reports that "saturation logs collected with the RST tool, cross-well seismic tomograms and VSP documents that the CO_2 developed similarly to that predicted by modelling." However, the authors also state that "the assumptions, simplifications and corrections used in the calculation of saturation from RST log response are significant." The RST tool has also been used successfully at the Nagaoka site (Xue et al., 2006).

3.1.5 Acoustic sensors

A DSI (dipole sonic imager) system was trialled at the Frio site where it was used to calculate shear and compressional wave velocities both pre- and post- injection. Hovorka et al. (2006a) state that "the DSI acoustic log collected during day 66 showed weak compressional velocity in the interval where the RST shows CO_2 saturation", as expected. This suggests that acoustic systems have some potential application for CO_2 monitoring. They also have application to correlating log response to seismic response. Sonic logging was also applied at the Nagaoko Site, Japan where they confirmed P-wave velocity reduction that agreed fairly well with a laboratory measurement on drilled core samples from the Nagaoka site (Xue et al, 2006).

Hull et al. (2010) have proposed the use of distributed acoustic sensors (DAS) as a potential tool for detecting the flow of fluids behind casing. As with the temperature sensors, the entire optical cable can be used to detect acoustic disturbances along its entire length. They designed processing algorithms that tuned the system to a specific leak signature which eliminates unwanted events and simplifies data processing. They consider this technique to be particularly applicable for low volume leaks. In addition, they propose a new method of data analysis specific to low volume, non linear leak events. They use wavelet transforms to analyse the data by using mathematical functions that cup up data into different frequency components and then studying each component with a resolution matched to its scale. Although this is an emerging technology, it does have the advantage of having a low cost, simple sensor of extremely high fidelity and, as with DTS, no need for down-hole circuitry as the fibre is the sensor. The prototype was developed for application at a leaking gas well and consists of three fibre optic hydrophones spaced 2 m apart. Each sensor comprises 100 m of fibre wrapped to a coiled physical length of 0.25 m. Each zone is separated by Fibre Brag Grating (FBG), which acts as a partial reflector of light. As a pressure wave hits the mandrel, the energy is transferred to the fibre and influences the light reflecting in between the FBGs. This influence is observed at surface, de-modulated off the fibre line, and translated to a high fidelity representation of the actual acoustic event down-hole.

Hull et al. (2010) note that the challenges with these types of techniques include the packaging of the fibre optic cable for deployment down-hole and the additional cost of fibre optic acquisition systems and the cable itself. The large amounts of data generated also require greater computing power which also adds to the cost. Further, it does not seem at this stage that these tools have been considered for permanent installations.

3.1.6 Electrokinetic potential

The self potential, or SP log, is a commonly used tool in the oil and gas industry. It has application to CO_2 monitoring, however, this requires knowledge of the SP response to changes in the saturation of CO_2 i.e., the coupling between the fluid pressure gradient and the electrical current density. Moore et al. (2004) carried out laboratory experiments on a core of water-saturated Berea sandstone and analysed the SP response resulting from pore water displacement by an advancing liquid CO_2 front. They concluded that trapped and bound water control the electrical conduction and electrokinetic response and that this method has potential application for subsurface CO_2 monitoring. Jackson et al. (2005) used the concept of electrokinetic potential to numerically simulate the use of permanently installed down-hole electrodes to detect the movement of water towards wells during hydrocarbon production. They concluded that in this circumstance the encroaching water produced resolvable changes in electrokinetic potential above background electrical noise and could detect water "several tens to hundreds of meters from the well". However, they also noted that there are "significant uncertainties in the technique which relate to the coupling between electrical and fluid-potential during multi-phase flow". The longevity and cost of these systems was not discussed.

3.1.7 Flow meters

Monitoring flow is standard procedure in groundwater monitoring and there are many tools available off-the-shelf at low cost. Flow rate is also routinely monitored at the wellhead in hydrocarbon producing wells. Meckel and Hovorka (2010) point out the importance of monitoring flow as part of understanding the source of pressure fluctuations in a multi-well field. Kragas et al. (2003) describe the installation of a fibre optic down-hole flowmeter. The flowmeter provided real-time measurement of the flow rate, phase fraction, pressure and temperature. The system they used is rated to 125°C and 15,000 psi and is electrically passive with no moving parts. They found they were able to measure flow rates and water fractions in oil/water systems to within 5% of the entire range of water cuts and validated their results from several field installations. The system consisted of two modules, the pressure and temperature assembly and the flowmeter assembly. The fibre optic flowmeter measures the bulk velocity and the speed of sound of the flowing fluid mixture. According to the authors, from these measurements and with knowledge of the density and sound speeds of mixed fluids, the individual phase flow rates in two phase systems may be determined. They state that a similar system was installed in a condensate well in Trinidad in 2002 and was operating within technical specifications when their paper was written in 2003.

3.1.8 pH

Sensors for pH were previously reviewed as part of the Ross et al. (2007) report. They found that while there were many publications and patents on the subject of pH, there seemed to be only a few sensors that showed any ability to deal with the depth requirements. There are a large variety of methods for measuring pH, which may have contributed to the large volume of references found (Figure 13a; Appendix 2). However, this work will focus on the main types of sensors and the attempts to improve their suitability for longer term deployment in deeper environments for CCS M&V.

Many pH meters or sensors contain glass electrodes and require standard buffer solutions for calibration. While quite sensitive and accurate, glass electrodes do require frequent calibration with these solutions to compensate for drift. The sensor consists of a glass electrode with a sodium silicate membrane which is fused to an oxide (SiO_2, Al_2O_3, Na_2O or similar; Figure 13b). As a consequence, the choice of oxide can cause significant variations in the hydronium ion selectivity.

Common laboratory-based glass pH electrodes are unsuitable for long term or deeper deployment. The glass bulb is prone to leakage (osmosis) and these sensors are generally restricted in their temperature range (10-60°C; Vonau and Guth, 2006). These glass sensors with their internal reference liquids were first proposed over 100 years ago (Vonau and Guth, 2006 and references therein). Extensive development is still ongoing to improve the working range of these sensors some of which can now operate in the range -25 to 130°C.

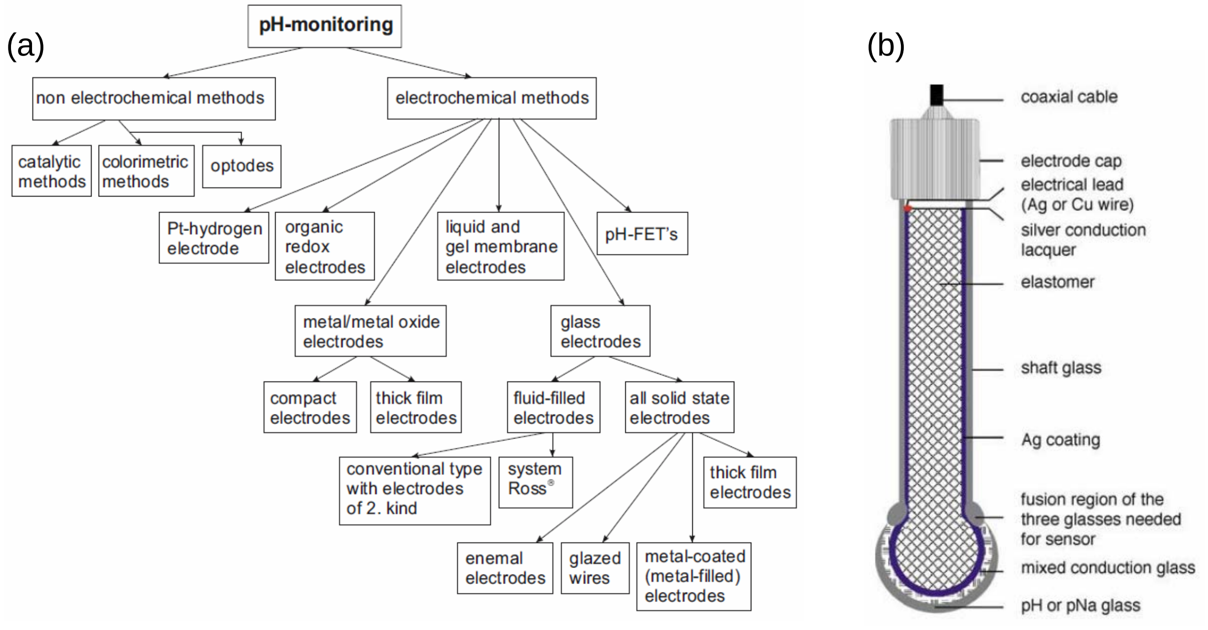
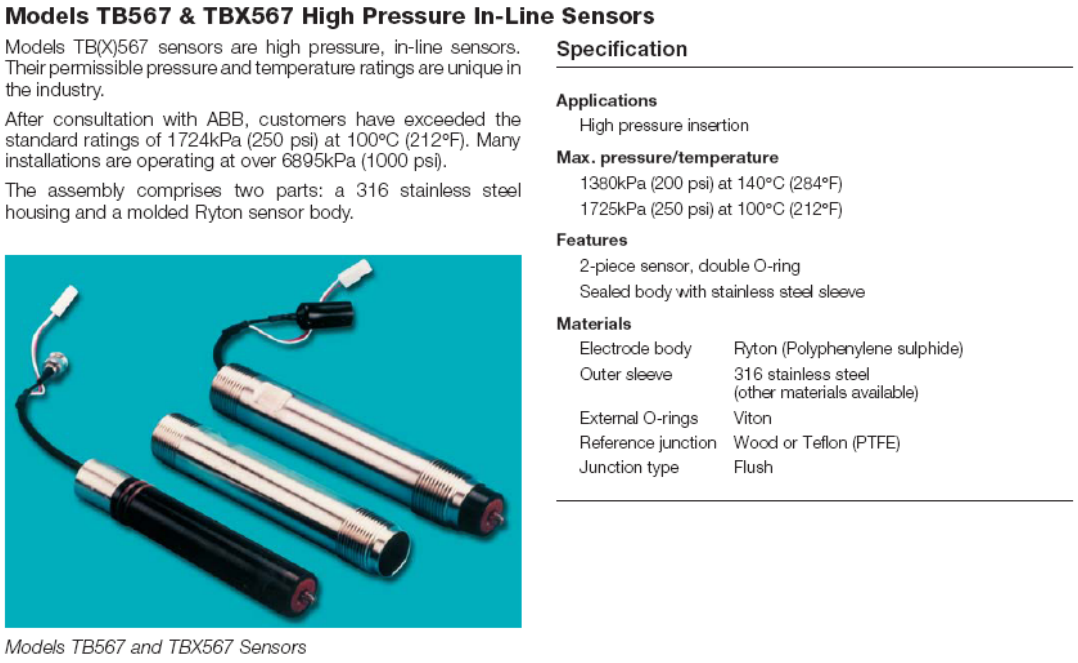


Figure 13 (a) varying methods for conducting pH measurements; (b) schematic diagram of a modified pH glass electrode (Vonau and Guth, 2009).

This type of glass pH sensor was used in-line in a moderately high pressure and temperature environment as part of the surface facility U-tube sample recovery system located at the Naylor-1 monitoring well at the CO2CRC Otway site (ABB High Pressure pH Sensor Model TB567J1A08T04). The instrument is ruggedized (Figure 14) but did appear to drift over time. It may have suffered from the drying process of gas-rich liquids passing over it during later sampling once the CO_2 plume arrived, as the instrument is supposed to remain moist at all times. Other factors, such as its positioning in the line may also have been a contributing factor to its less accurate longer term performance (Vonau and Guth, 2006).



Models TB567 & TBX567 High Pressure In-Line Sensors

Models TB(X)567 sensors are high pressure, in-line sensors. Their permissible pressure and temperature ratings are unique in the industry.

After consultation with ABB, customers have exceeded the standard ratings of 1724kPa (250 psi) at 100°C (212°F). Many installations are operating at over 6895kPa (1000 psi).

The assembly comprises two parts: a 316 stainless steel housing and a molded Ryton sensor body.

Models TB567 and TBX567 Sensors

Specification

Applications

High pressure insertion

Max. pressure/temperature

1380kPa (200 psi) at 140°C (284°F)

1725kPa (250 psi) at 100°C (212°F)

Features

2-piece sensor, double O-ring

Sealed body with stainless steel sleeve

Materials

Electrode body	Ryton (Polyphenylene sulphide)
Outer sleeve	316 stainless steel (other materials available)
External O-rings	Viton
Reference junction	Wood or Teflon (PTFE)
Junction type	Flush

Figure 14 Specifications for ABB sensor used in-line with U-tube sample recovery system at the Naylor-1 monitoring well at the CO2CRC Otway site.

As the lack of robustness of pH sensors does appear to be a significant concern, some researchers have developed alternative pH sensors that are based on a metal-metal oxide membrane. Several solid state sensors were reported in the earlier report (Ross et al., 2007) including one based on nanoporous platinum (Park et al., 2005) and one using titanium nitride as the sensitive film (Wang et al., 2006). These are designed to operate in the range 4-150°C and at depths of 800-1300 m.

Kurzweil (2009) in his review of metal oxides and ion-exchange surfaces as pH sensors in liquids acknowledges the same issues of poor performance at varied temperatures, and other noted issues of handling and long-term stability of conventional pH electrodes. One particular problem for glass electrodes and ion selective field effect transistors (ISFETs) is that they require regular calibration in standard solutions. Advancements in coulometric proton counting as a replacement technology was believed to be far from ready as a deployable technology for pH measurements (Kurzweil, 2009).

Table 8 Information on a range of pH sensors listing some of the conditions of use and ongoing challenges for these tools (Kurzweil, 2009).

	Range of application	Challenges
Glass electrode	Temperature: < 80…130°C Pressure: < 60 bar (with counter pressure) Stability: ± 1mV week-1	• Interaction of surfactants and film formation on the glass surface in reaction mixtures • Mechanical instability of the glass membrane • Individual calibration of each electrode • Destruction by fluoride and highly hydroscopic solutions • Sodium error in alkaline solutions • Expensive manufacture
ISFET	Temperature: < 85°C Pressure: < 2 bar (with counter pressure)	• Film formation on the surface • Bad long-term stability • Poor stability of the reference electrode
Antimony electrode	e.g. strong caustic solutions (no sodium erro0< fluoride containing waste water	• High degree of asymmetry (pH_{iso} approx. -3) • Chloride causes potential shift • Deleterious effect of sulfides, and citrates (which form complexes with Sb^{III})
Optical sensors	Transparent liquids Small and flexible (fibre sensors) No reference element required Signal transmittance over large distances	• Change of transparency of the solution • Photobleaching and washout of indicator phases • Non-linear calibration curve with immobilized indicators

Kurzweil (2009) went on to review a variety of pH sensors including ISFETs which were first developed in the 1970s. There are a variety of ISFETs with different coatings but which are limited to a pressure of about 2 bar (29 psi) and temperatures of not greater than 85°C. Alternatives such as probes containing enamel electrodes are particularly suited to obtaining pH measurements under high mechanical stress (Kurzweil, 2009). They have a working range of pH 0-10, but this window narrows significantly to pH 6-8 at temperatures >140°C.

Metal electrodes are being developed for pH measurements, for detection of acidic gases dissolved in liquids. These probes however, are not simple hydrogen electrodes but measure a number of processes that are a proxy used to calculate pH. Titanium (Zhao et al., 2010), platinum (Noh et al., 2011), ruthenium and iridium oxide probes (Kursweil, 2009 and references therein) have been developed which are more robust and stable during long term measurements. A solid state reference electrode combining nanoporous Pt has been developed (Noh et al., 2011). These authors utilised a system that had exhibited excellent performance (i.e. reproducibility of ± 4 mV [n=5], good long term stability of ± 1 mV [for 50 hr]) and appeared independent of the solution environment. From this basis, a miniaturised chip-type solid state sensor was developed which is believed to show reliable pH response following testing with buffers, beverages and biological samples. However, the duration of stability (~ 50 hr) and lack of temperature or pressure information suggests that this tool is untested for more extreme environments.

Similar sensors with TiO_2 nanotube arrays are under development and being tested in the food and beverage industry (Zhao et al., 2010) which suggests that modifying for temperature may be a consideration for the processing industries, but pressure may be less important. More detailed reviews can be found in Vonau and Guth (2006), Guth et al. (2009), Kurzweil (2009) and Vonau (2010).

A RuO_2 film pH sensor was able to perform well over 200 hrs at different pH values (Kurzweil, 2009 and references therein) however this time period does not aid in long term deployment situations on the scale of CCS monitoring and verification. IrO_2 sensors could be better suited to “technical” media (e.g., fuels, food and biological materials; Kurzweil, 2009 and references therein). These probes have wide linear ranges in pH response, are fast, and stable in aqueous, non-aqueous and potentially corrosive media. Other sensors using transition metal oxides, e.g., ZrO_2 and Y_2O_3 blends may have application under higher pressures (Kurzweil, 2009 and references therein).

An alternative approach to pH measurement that can be applied to deeper zones is the use of spectroscopic pH measurements (Raghuraman et al., 2006; 2007; Xian et al., 2008). Raghuraman and co-workers from Schlumberger have developed and tested a wireline tool that provides real-time pH measurement of water samples during production. Briefly, the method involves the injection of pH sensitive dyes into the flowline of a down-hole fluid analyser. Raghuraman et al. (2006) regard this method as extremely robust. The instrumentation has been calibrated for temperatures up to 373K (100°C), pressures to 65.5 MPa (9500 psi) and ionic strengths in the 0-3 mol/kg water range but could be extended higher (Raghuraman et al., 2006).

One drawback noted by Raghuraman et al. (2006) was that there were no available calibration standards for pH in the extended p/t ranges they required. This has been overcome by the use of chemical equilibrium modelling (Raghuraman et al., 2006) and more recently validated via fluid sampling and measurement of samples taken at surface with conventional pH tools (Xian et al., 2008). This equipment has been deployed in oilfields and data successfully compared with other tools to demonstrate its efficacy (Xian et al., 2008).

A brief summary of some pH measuring systems (Table 8) confirms a paucity of suitable pH tools that comfortably withstand sufficient pressure, temperature and robust enough for longer term deployment. Conventional glass pH probes containing liquid reference materials will always complicate miniaturisation and applications directed towards the deep subsurface environments. However, in terms of accuracy and stability, these glass probes remain superior to other forms, particularly ISFETs. Other tools, particularly those containing metal-metal oxide probes show promise, however they do not appear ready for deployment at the temperatures or pressures or duration required for CCS. One set of tools, using spectroscopic pH measurements does seem to fulfil the pressure and temperature requirements, however it is unknown whether this tool could be applied over long term monitoring, particularly if dyes are used consistently.

3.1.9 Summary of physical monitoring tools

The significant advantage in the types of tools and systems described in this section is their ability to detect changes due to the presence of CO_2 some distance away from the CO_2 itself. This increases the percentage of reservoir (or aquifer) "covered" by the monitoring system, increasing confidence in the containment and allowing for the possibility of early detection and remediation.

The key parameter in this section is pressure. There are two reasons for this; 1) it is a mature technology with a range of options suitable for the types of monitoring environments required for CCS technology. It is off-the-shelf, cost effective, sensitive and robust for long term installations; 2) the movement of a plume of CO_2 will be accompanied by a propagating transient wave of pressure increase whose spatial footprint will normally far exceed the dimensions of the plume itself. The key parameter to consider in long-term pressure monitoring is the level of sophistication required for a specific site. The cost of installation, processing and interpreting increases with increasing complexity of the system and number of gauges installed. It is necessary to carefully consider what the monitoring objective is for each case.

The other systems described here, such as DTS and ERT have been demonstrated to have application to CO_2 monitoring (Table 9), however, their longevity of these systems under reservoir conditions is also unclear and their cost may be prohibitive. For this reason, although they are potentially applicable to monitoring aquifers above the storage zone, it is unlikely they would be deployed here. The exception may be in specific, high risk locations. Fibre optic technologies have the potential for quite sensitive monitoring of acoustic, flow and temperature properties. This again produces large volumes of data which can be complex to handle, require sophisticated geological models to interpret, and considerable computing power to process. pH sensors are only beginning to be developed for deeper, hotter environments due to new applications in oilfield surveys but may not be deployable for longer term periods as yet without some testing.

Table 9 Potential monitoring tools for subsurface flow regimes.

	Cost	Suitability at reservoir conditions	Long-term Down-hole monitoring	Shallow CCS	Deep CCS
Permanent Down-hole Gauges (PDG)	H	Y	Y	Y	Y
Water Level Loggers	L	N	Y	Y	N
Multi-interval Logging	M	N	Y	Y	N
DTS	H	Y	Y	Y	Y
RST	H	Y	Y	Y	Y
DSI	H	Y	Y	Y	Y
SP	H	Y	Y	Y	Y
ERT	H	Y	Y	N	Y
Flowmeters	M	Y	Y	Y	Y

Green = Appropriate
Yellow = possible, requires more testing or development
Red = possible, but unlikely

Table 10 Technical specifications for a range of pressure and temperature gauges for application to groundwater and oil and gas industries.

Sensor Type	Sensor Type	Company	Designed for:	Pressure Range (psi)	Temp Range (ºC)	Pressure Resolution (psi)	Pressure Accuracy (psi)	Pressure Stability	Temp Resolution (ºC)	Temp Accuracy (ºC)	Battery Life Time	Corrosion Resistant	Wireless Comms
Oilfield	Optical Pressure transducer, distributed temperature	Weatherford (http://www.ep-solutions.com/PDF/Literature/wft010201_Optical_Pressure_Temperature_Gauge.pdf)	Integrated permanent P/T, mulitphase flow, distributed or multipoint temperature and multi station seismic	Atm – 10000 Max: 35000	25-150, Max: 175	≤0.03	±2	<0.5/y (Optical in well gauges demontrate zero or negligible drift over time)*	0.02	±0.1	4-5 years		Y
	Quartz (WCQR or CQG Quartz , WTQR)	SLB: UNIGAGE	Permanent down-hole P/T gauge; slickline	25000	177	0.01	±3.2	0.5/month @ 10k, 150ºC	0.001	±0.5	Tests up to 1 year	H_2S, CO_2, acid, TCP	Y
	Sapphire (WTSR or SLSR)	SLB: UNIGAGE	Permanent down-hole P/T gauge; slickline	20000	210	0.15	±10	1/week @ 10k, 150ºC	0.001	±1.8	Tests up to 1 year	H_2S, CO_2, acid, TCP	Y
	Shear Mode Quartz Resonator; Quartz resonator	PANEX (http://www.panex.com/DOWNHOLE/4275_DASRO_Data_Sheet.pdf)	Down-hole pressure and temperature	0-16000	-20-200	0.01	±0.02 % FS	repeatability ≤0.01% FS	0.005	±1.0	Microelectronic (no battery)'	INCONEL	Digital transmission surface readout (DASRO)
	Mechanical, Bourdon tube, temperature compensated	AMERADA and KUSTER (http://www.mcdonaldgauges.com/Gauges/gauges.html)	Down-hole pressure	500-25000	0-370	1 in 2000	±0.2 % FS		0.001	±2 deg F			N

Sensor Type	Sensor Type	Company	Designed for:	Pressure Range (psi)	Temp Range (ºC)	Pressure Resolution (psi)	Pressure Accuracy (psi)	Pressure Stability	Temp Resolution (ºC)	Temp Accuracy (ºC)	Battery Life Time	Corrosion Resistant	Wireless Comms
	Piezoresistive Sensor	METROLOG (http://www.metrolog.com/doc/PRM5.pdf)	Down-hole pressure and temperature	0-15000	-20-150	<0.05	±0.5 % FS		<0.005	±0.3	4.2 MM	INCONEL, 17-4 PH sour services (H_2S, CO_2, acid)	Memory Gauge
	Quartz	METROLOG (http://www.metrolog.com/doc/CGM5.pdf)	Down-hole pressure and temperature	0-30000	-20-150	<0.01	±0.02 % FS		<0.01	±0.3	4.2 MM	INCONEL, 17-4 PH sour services (H_2S, CO_2, acid)	Memory Gauge
Ground water	Quartz	MOSDAX, Westbay SLB	Multi-level, groundwater monitoring and fluid sampling, P/T										
	Quartz	CTD-DIVER, SLB (http://www.swstechnology.com/pdfs/technology_sheet/CTD-Diver_Tech_Sheet.pdf)	Pressure, temperature, conductivity Groundwater monitoring & quality	10m	0-50 Conductivity 10-120 µS/cm	0.02 m	±0.05 m		0.01 Conductivity ±0.1% of reading	±0.1 Conductivity ±1% of reading	2MM readings	Ceramic housing	Y
	Strain-gauged diaphram type transducer in 316L SS	Sigra Vented Pressure Transducers	Water level monitoring	Not available	Not available	Not available	Not available		Not available	Not available	Not available	Not available	N, cable

Sensor Type	Sensor Type	Company	Designed for:	Pressure Range (psi)	Temp Range (ºC)	Pressure Resolution (psi)	Pressure Accuracy (psi)	Pressure Stability	Temp Resolution (ºC)	Temp Accuracy (ºC)	Battery Life Time	Corrosion Resistant	Wireless Comms
	Peizoresistive, SS or titanium; Silicon Temperature Sensor	In-situ Inc. (http://www.in-situ.com/cp/uploads/SS_LevelTROLL.pdf)	Groundwater monitoring, P/T	351 m	-5-50	0.005 % FS	±0.1-0.2% FS		0.1	0.01 or better	5yrs, 2MM	Titanium	Y
	Piezoresistive Silicon in 316L Stainless steel; Platinum Resistance Temperature Detector	Solinst Levelogger Series (http://www.solinst.com/Prod/Data/3001Gold.pdf)	Groundwater monitoring and quality, P/T	1.5-100 (m)	-10-40	0.002 - 0.0006% FS	0.05 % net FS	Superior, low noise, automatic temperature compensation	0.003	±0.05	10 yrs @ 1 reading/ min	ZrN coating	Y, optical infrared

3.2 Biological methods to monitor changes related to CO_2 flux

Geophysical and chemical methods far outweigh any biological monitoring developments. Here we present a review of biological monitoring options for CCS M&V and, more importantly, present new tools and monitoring options based on other unrelated studies that could be applied to the detection of CO_2 leaks or compounds mobilised by CO_2, principally in the near surface environment. Along with the need to develop monitoring tools, there is the additional need to understand the effects of CO_2 injection indirectly on the biosphere for successful implementation of CCS and general public acceptance. Monitoring the biosphere is a critical step in achieving the successful implementation of CO_2 geological storage.

3.2.1 Ecosystem – botanical monitoring

Baseline surveys of flora and fauna, both in the terrestrial and marine settings could be used to monitor the environment both at and near CCS projects. Biological characterisation of major plant species was conducted at BP's In Salah CCS project in Algeria, but changes in macroflora were not apparent in relation to the location of the CO_2 injection wells (Jones et al., 2011). On the other hand, botanical surveys conducted along transects showed vegetation changes in two studies of natural analogues for CO_2 leakage. Krüger et al. (2009) showed total grasses (monocotyledons) decreased as CO_2 increased, whereas a dicotyledon grass (*Polygonatum arenastrum*) was <u>only</u> observed near the CO_2 vent in Germany. This research indicates a potential bioindicator plant species (Figure 15). Beaubien et al. (2008) found no vegetation occurred immediately over a CO_2 seep, but acid (soil pH) tolerant grasses (Agrostis capillaries) dominate nearby with a shift to clover distal to this zone Figure 16). The acid soil conditions are caused by the increase in CO_2 (See Section 2.2) and the biosphere is responding to the pH change. The dicotyledon species that was more tolerant of the high CO_2 soil concentrations in Germany seems to be less common compared to the grasses (monocotyledons) that were prevalent at the Italian study site and a controlled injection site near Nottingham in the UK under pasture (West et al., 2009).

These vegetation changes are local effects, but could be used pre- and post CO_2 injection as a surface biological monitoring tool particularly if soil-pH-specific species are identified. The benefit of plant species as bioindicators are that once determined these can easily be visually identified without the need for analysis. However, the time lag for niche vegetation development in a leak zone is probably too slow compared to other available techniques. Also, knowing which species will fill an acid pH change or related metal-rich (CO_2-rich) niche at a CCS site will not be known unless other experiments are conducted (microcosms) or natural analogues are also present in the area (unlikely).

Diversity counts and changes could also be adapted to spectral imaging. Shallow injection of CO_2 (300 kg day^{-1}) resulted in changes in the visible and near-infrared reflectance spectra from vegetation observed at the ZERT study site in Bozeman, Montana (Keith et al., 2009; Male et al., 2010; Rouse et al., 2010). The use of ground and airborne hyperspectral methods successfully observed the plant stress when CO_2 levels were 2-8% by volume and 4-5 days after injection (Keith et al., 2009; Male et al., 2010). This technique was able to detect the yellow and brown dying vegetation and bare earth of the controlled injection CO_2 site with 75% CO_2 at > 20 cm depth (West et al., 2009). Potentially this type of biological monitoring could be used in CCS M&V. As with plant species bioindicators, the lag time of influence to the soil, plants and subsequent detection could be great and other methods may detect CO_2 leaks first. This is evident in the study by Wimmer et al. (2011) where airborne hyperspectral imaging was not effective in detecting the leak via plant stress compared to thermal imagery soil surface CO_2 flux manual monitoring. These field examples use concentrated or point source CO_2 leaks, whereas a more broadly dispersed CO_2 signature may give a more subtle pattern. More diffuse leaks may be best observed in the subsurface by microbial changes as microbial populations can be quickly and significantly altered by external environmental conditions. It is important to recognise that although CO_2 flux was the monitored major variable, associated changes in the soils also occur. These studies did not focus on the changes in metal mobility or pH and the plant stress could be a response to metal toxicity (e.g. Fe, Al or Mn) brought on from the increase in CO_2.

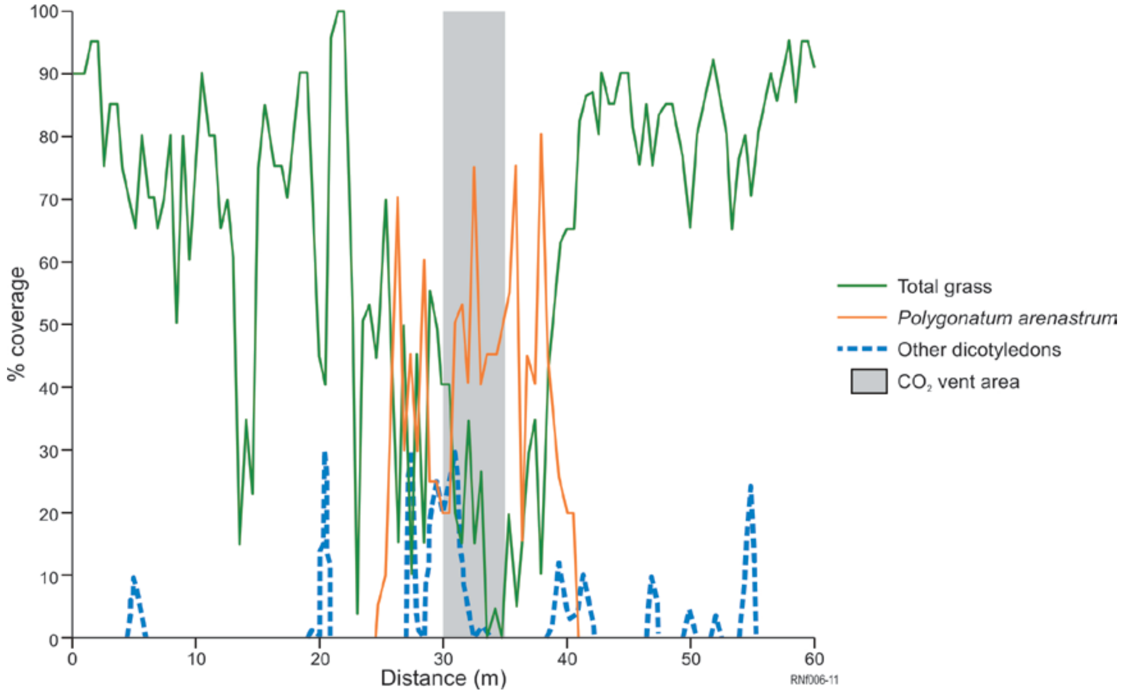


Figure 15 Plant distribution across a natural CO_2 seep in Germany (modified from Krüger et al., 2009).

Rhizosphere soil (that is in direct proximity and therefore influenced by plant roots) could also be a zone of biological monitoring. This would involve culture tests relating dominant plant species response to increased CO_2 and also by physicochemical changes as a result of root activity. This can incorporate rhizosphere sampling, visualization techniques, molecular and genetic methods and remote sensing tools (Neumann et al., 2009). The rhizosphere is a hot spot of microbial activity, and rhizosphere communities are greater in numbers than in the surrounding bulk soil. They also have a more active metabolism and are dynamic in terms of microbial species shifts related to external conditions. This habitat, therefore, has greater potential to rapidly respond to CO_2 leakage and subsequent effects such as pH change and mobilised, potentially toxic, compounds. Modelling of CO_2 flux related to vegetation biomass changes, and in turn leakage monitoring, could be adapted to CCS programs, but this approach is only in a preliminary development stage using natural analogues (e.g. Maul et al., 2009).

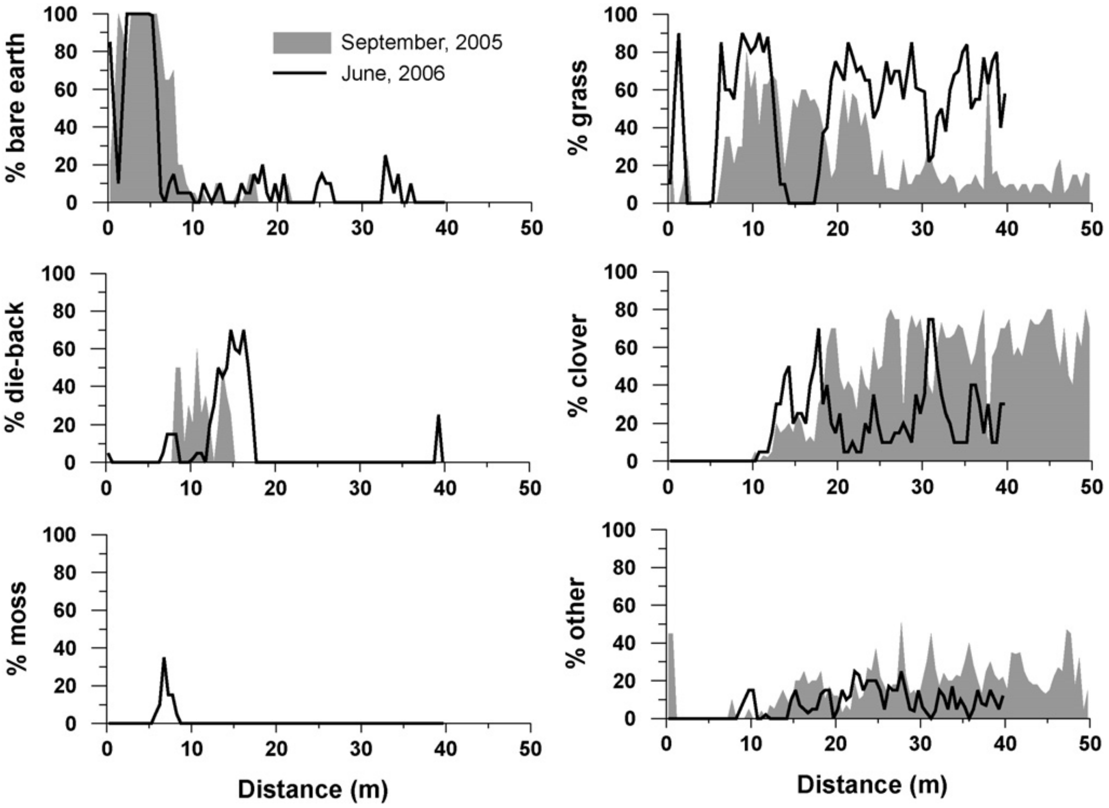


Figure 16 Percentage plant cover of different vegetation groups from a natural analogue study in Italy (from Beaubien et al. 2008).

The issues with the botanical modelling and monitoring approach is that there are a lot of additional variables and that the sample medium for monitoring (biomass/roots) is another step removed from the source. Also, there are significant interactions between plant and soil (unrelated to CO_2 leakage) that are not well understood and potentially slow response times from leakage then plant response to analysis of information. Most of the previous rhizosphere models and studies are on specific crop species and soil types in agricultural settings that will not be easily adapted to CCS projects without further study.

3.2.2 Microbiological monitoring

Soil is heterogeneous with very diverse microbial populations that are responsible for many critical processes in the biosphere such as nutrient cycling. Bacteria and archaea are the major group of organisms in subsurface soil and groundwater, however in topsoil, fungi and other Eukaryia are present in high numbers. The biogeochemical conditions of the subsurface influence the occurrences and activities of microorganisms. As a result, the structure of microbial communities, individual species, and specific functional genes are potentially valuable bioindicators which are reflective of the wider habitat (physicochemical conditions). Understanding the complex relationships and responses between potential contaminants from CCS, water quality and microbial communities is difficult (Pronk et al., 2009), but essential for biological monitoring.

For the majority of biological monitoring methods, soil or groundwater can be sampled and analysed. With soils a suspension is usually produced prior to analysis. Soil monitoring can be done at different depths, but consistency and quality background data are essential to understand other environmental effects such as seasonal temperature shifts and rainfall. Specific details for each method are not documented in this report, but are available in the references cited.

The purpose of microbial monitoring is to locate, identify and understand the composition and activity of the microbial community regardless of depth. By doing this, the origin and fate of many compounds (metabolites, substrates) can be better assessed for CCS (Giese et al., 2009). Different microbial species can influence and be influenced by the surrounding environment. Changes in pH, Eh, salinity, temperature, metal speciation, precipitation and complexation could be associated with CO_2 leakage into the near surface environment (Section 2.2). Microorganisms are the first to be exposed to toxic and/or beneficial chemicals entering the soil and groundwater as a result of CCS leakage and may display the first changes that can be detected by monitoring for effects other than CO_2. Furthermore, within the wider microbial community, highly-responsive *indicator* species for specific habitat types are likely to be present. Identification of these species would provide a valuable mechanism where ecosystem properties can be assessed against the occurrence of one or a few species.

Bacterial community structure has been shown to change along physico-chemical gradients. CO_2 increasing in (shallow) environments will cause shifts of the community structure to more anaerobic communities. Microbiological analytical methods used to investigate community types can be adapted to monitor for CO_2 and the related changes (pH, metal mobilisation) in the near surface environment. Although some methods can be laborious (Polymerase Chain Reaction Denaturing Gradient Gel Electrophoresis or PCR-DGGE), DNA fingerprinting methods exists for specific biosensors linked to shifts in enzyme use/metabolism/DNA sequences which could be developed and applied specifically for CCS M&V.

A number of methods with varying degrees of complexity are available for microbial monitoring, with variable advantages and disadvantages. A generalised list of methods include the following:

- Plating and counting methods
- Biomass/activity determinations (ATP)
- Metabolic profiles (Biolog, soil enzyme characterisation)
- Phospholipid fatty acid
- PCR (polymerase chain reaction) with –
    - DGGE (denaturing gradient gel electrophoresis)
    - TGGE (temperature gradient gel electrophoresis)
    - ARDRA (amplified ribosomal DNA restriction analysis)
    - T-RFLP (terminal restriction fragment length polymorphism)
- Microarrays
- Next Generation DNA Sequencing (Pyrosequencing)
- Ecological genomics

These various methods will be discussed below, but there are many references included that present specific examples and detail the techniques further, which should be consulted for more information.

3.2.3 Bacterial counts

One of the most simplistic tests for microbial monitoring is direct counts of bacteria present in the soil. This method has been tested at the In Salah CCS site in Algeria, on transects over the area of uplift caused from deep CO_2 injection and observed by radar, however the results were inconclusive. Bacterial numbers were between 10^4 and 10^5 g^{-1} soil at 30-50 cm depth (Jones et al., 2011) and not different in relation to the proximity to CO_2 injection. The bacterial numbers were within the range expected for arid environments. This study was also discussed by Mathieson et al. (2011) who indicate that the benefit of this method was low in this case, but the cost were also small. As a result, the methods are continuing to be employed as part of the monitoring program in the near surface environment at the In Salah site.

Bacterial counts were used successfully at the shallow artificial injection site (ASGARD) under pasture near Nottingham in the U.K. where bacterial numbers declined with increasing CO_2 and depth (West et al., 2009). In general, however, it is recognised that only a very small percentage (~5%) of the total bacterial community from any sample can be readily cultured using standard laboratory techniques. As such, bacterial counts give a highly conservative estimate of the biomass present, and a skewed perspective on species present or their response to environmental change. In particular, culture based methods are (generally) biased towards growth of heterotrophic, aerobic, mesophilic bacteria – these organisms may be considered atypical for subsurface conditions.

Using a natural CO_2 vent as an analogue, Oppermann et al. (2011) and Krüger et al. (2009) sampled the soils and found lower bacterial counts near the CO_2 leak compared to background in the shallow surface.

DAPI-staining of bacteria showed 10^6 cell mL^{-1} existed in solutions taken from 670 m depth at the Ketzin CCS site prior to CO_2 injection (Morozova et al., 2010; 2011a). Numbers were influenced by the pH drop following injection and then recovered. However, the structural make up of the community differed from the baseline sample. The use of staining techniques such as those by Morozova et al. (2010) provide more information than simple counts, classifying broad groups of bacteria. Most bacterial count studies related to CCS are in the near surface environment with this study from Morozova et al. (2010) being unusual (i.e. deep), but valuable for future monitoring options.

It important to recognise that the changes in bacterial mumbers may be indirectly caused by CO_2. The subsequent shift in pH and mobilisation of potentially toxic compounds could be the cause of the reduced sample numbers. These studies concentrated on CO_2 changes, but testing of other variables is required to better assess these microbiological changes.

3.2.4 Microbiological/metabolic activity

The use of adenosine tri-phosphate (ATP) concentration is used to measure microbiological activity as it is a recycled nucleotide used within cells for metabolism (photophosphorylation and cellular respiration). The more ATP in the soil environment, the more active or larger the microbial community is. ATP is relatively easily measured with devices such as a DeltaTox analyser. This is a field portable procedure. Testing of this technique at In Salah had no success (Jones et al., 2011), but it was valuable at the artificial shallow injection study (ASGARD) by West et al. (2009). In the artificial CO_2 injection site, microbial activity was below detection in the samples nearest the CO_2 injection point (87% CO_2; West et al., 2009). A study at a natural CO_2 seep in Germany also reported significant differences in the microbial activity, with activity being lower nearthe greatest CO_2 concentrations. The methods used to obtain this activity parameter are not clear (Krüger et al., 2009). A large number of gas fluxes (along with qPCR discussed later) were measured by Krüger et al. (2009) that may indicate the metabolic types of bacteria present in this study.

Table 11 Major nutritional groups of shallow surface bacteria (modified from Alexander, 1999)

Classification	Carbon source	Energy source	Example group
Chemoheterotrophs/ Organotrophs	Organic	Organic	Most common bacteria and fungi
Photoautotrophs	CO_2	Light	Cyanobacteria
Chemoautotrophs / Lithotrophs	CO_2	Inorganic	S-, H-, and Fe oxidising bacteria,

Methods of testing microbial functions are tied to the broad types of bacteria, particularly the major source of carbon and their energy sources. The broadest classifications are shown in Table 11.

The availability of CO_2 can directly influence metabolism of hetero- and autotrophs. A change in CO_2 will change the dynamic equilibrium of the environment, modifying the surrounding environment and water quality due to trace metal mobilisation, pH and salinity changes. Subsurface CO_2 could impact and change deep biological communities – perturbing the deeper geosphere (West et al. 2011). It is unlikely microbial populations could survive supercritical CO_2, however where leaks occur and the CO_2 gradually builds up biological shifts are possible. Methanogens and S-oxidising bacteria could build up and influence pH and trace metal mobility akin to acid mine drainage systems. It is important to consider also other impurities such as NOx, SOx and H_2S (West et al., 2011) that could be used as an energy source for deep microbes. Based on thermodynamic models of various impurities related to methanogens reducing CO_2 to form CH_4, the presence of NOx and many other compounds are not thermodynamically favourable oxidants, with some oxidation of S_2O_4 or S_3O_6 being viable reactions. This information provides compounds that could be indicators of reactions related to CO_2 leakage into groundwater (West et al., 2011), but observations need to be confirmed using natural analogues.

If carbonate is formed due to CO_2 leakage with a decrease in pCO_2 at the CCS site, methanogenic bacteria may become more abundant as they use carbonate as the terminal electron acceptor and produce CH_4 as waste (Alexander, 1999).

Deep biosphere studies (Ehinger et al., 2008) have also shown microbes are present and thus could be monitored. These species are usually lithoautotrophs (using CO_2 as a C source and electron acceptor) and may indicate a more direct influence on the rate of CO_2 plume migration at depth. However, lithoautotrophsare less abundant and therefore are of limited use as a monitoring tool compared to the monitoring of the shallow biosphere. A predominance of Methanolobus spp. and Methanocelleus spp. were identified in sulphate-rich saline formation fluids of a natural gas reservoir being assessed for use in CCS (Ehinger et al., 2008). The noted phylotypes could influence CO_2 fate and their presence and effects are more important for modelling than monitoring based on the results of Ehlinger et al. (2008).

Heavy metal release into the shallow subsurface is a potential effect of CO_2 leakage through carbonic acid attack on host sediments. Sulphate-reducing bacteria (SRB) are known for their ability to reduce and precipitate these elements as metal sulphides (Geets et al., 2005). Indirectly, monitoring the changes in the community structure such as the SRB population could be a potential method for biological monitoring of subsurface CO_2 leaks. SRB use SO_4 as the Terminal Electron Acceptor (TEA) and produce H_2S as a waste product (Alexander 1999). SRB were found to have the highest activity near a natural CO_2 analogue (Beaubien et al., 2008). Greater activity of autotrophic methanogenic Archaea, SRB and methanotrophic bacteria were observed at a natural CO_2 seep compared to background (Oppermann et al., 2011).

At Ketzin, after CO_2 injection, an preliminary increase in Archaea was observed, but over the longer term SRB were more dominant, becauseinitially the pH change is more influential than the thermodynamic energy yield (methanogenic Archaea are highly resistant organisms; Morozova et al. 2011a). Although the results of Beaubien et al. (2008), Morozova et al. (2010) and Opperman et al. (2011) are discussed here under the major metabolic functions, their methods for determining these results are based on PCR. Understanding the initial populations and the by-products of these dominant species may be a way to indirectly track CO_2 leakage in both deep and shallow settings. West et al. (2011) used thermodynamic calculations of potential CH_4 that could be produced from S-compound oxidation. Knowing the CH_4 input to the CCS system, in addition to estimates of S-oxidation rates and monitoring near surface CH_4 levels, could be an indirect measurement of microbial activity in these environments (West et al., 2011).

While metabolic information could be gleaned from measuring product gases of microbes, specific devices such as BioLog plates can be used (Figure 17). Biologs are essentially simplistic versions of some of the larger microarray technology discussed later. The BioLogs are assays of nutritional pathways for C, N, P, and S metabolism, along with sensitivity to osmotic, pH and various chemical gradients. Depending on the reaction of the individual sample to the various wells of solution provides general information about the microbial community metabolism.

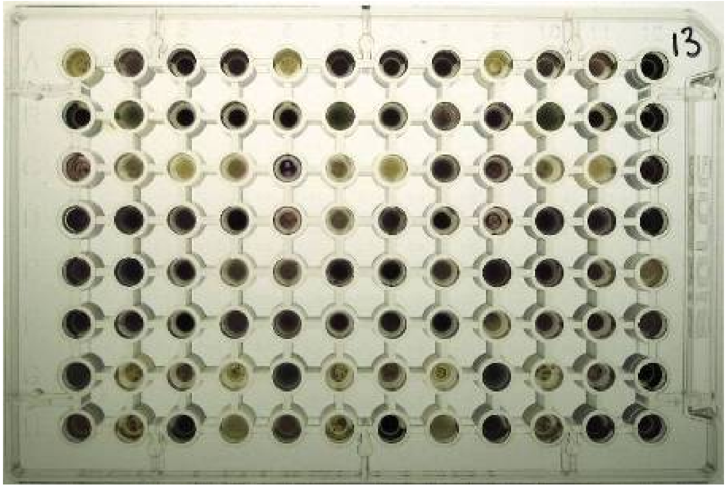


Figure 17 An example of a BioLog plate being used to evaluate metabolic information from a soil sample.

Of the limited biological monitoring studies linked to CCS only a recent paper by Dictor et al. (2011) has used BioLog plates for microbial monitoring of a natural analogue, indicating significant changes in the structure of nitrifying and denitrifying bacteria related to soil CO_2 concentration. Microbiological analyses of bacterial types and functions and Muszyna, Poland, and Ketzin, Germany, also showed species involved in nitrification in soil may be indicators of CO_2 in soil gas (Tarkowski et al., 2009). In an assessment of microbial communities influenced by increased transition metal concentration (Zn near a mine site), patterns of heterotrophic processes were clearly determined by BioLog analysis. Additional association with C and N cycling, showed a direct link between mineral weathering by both lithotrophic bacteria and abiotic processes, as well as secondary biogeochemical processes by associated heterotrophic communities (Wakelin et al. in press(a)).

3.2.5 Biosensors for selected enzymes/metabolic shifts

Linked to the release of toxic metals/metalloids associated with CO_2 leakage and acidification of the host-sediments, biosensors can be adapted to detect low concentrations of specific compounds. Online sensitive monitoring of gene expression can be done particularly with reference to stress-induced conditions like the encroachment of environmental pollutants into an ecosystem. For instance, Cd can be detected within minutes to nanomolar concentrations in groundwater, seawater and soil using online and continuous in situ monitoring. Biran et al. (2000) use a promoter-based (Cd) electrochemical biosensor from *E. coli* bacteria fused to another gene (promoter-less lacZ) and monitored using beta-galactosidase activity.

A variety of other biosensors have been developed. For example, biosensors are available to detect Hg in the soil (He et al., 2010a), traces of explosive compounds (Kusterbeck and Charles 1998), middle chain length alkanes (Sticher et al., 1997) and bioavailable As (Liao and Ou, 2005) in groundwater, bioavailable iron in seawater (Lam et al., 2006) to name just a few. Biosensors have also been developed to show changes in biochemical oxygen demand (BOD) that could also be adapted to CO_2 leakage situations (Chen et al., 2008; Sakaguchi et al., 2007). Tarkowski et al. (2009) have suggested that Thiobacillus may be adapted for a CCS biosensor in their assessment of microorganisms associated with CO_2 induced changes.

Depending on the CCS setting and on which metals and metalloids may potentially move in the subsurface, an appropriate biosensor can be developed. It is important to determine what to detect specifically in relation to CO_2 leakage for the appropriate development of biosensors. Biological monitoring of chemical leaks is more advanced than CCS biological monitoring. BTEX (benzene, toluene, ethylene and xylene) detection research is one example. Luminescent biosensors are able to detect BTEX toxicity and bioavailability during dispersion and breakdown in the environment (Dawson et al., 2008).

Many biosensors rely on some form of luminescence for detection. Bioluminescent bacterial strains can be produced that may be effective methods for monitoring bacterial mobility through the subsurface using specific fluorophores, in essence creating a biological tracer. Newer stains are being developed that do not affect stained cell mobility (Fuller et al., 2000). Although these could be effective in shallow test studies (e.g. Beaubien, 2008; Krüger et al., 2009; West et al., 2009), the bacteria tracers have little value in monitoring the injection horizon, as they would not survive the high P/T and CO_2 conditions.

It is important to note that the development of many of these biosensors is based on the genetic fingerprinting methods described in the following sections and should not be considered as a separate method; rather they are a specific application refined from other methods.

3.2.6 Community structure analysis

Community structure analysis can be used to provide detailed information for environmental monitoring. Numerous methods exist which can be employed to gain further understanding of the microbiology within different ecosystems.

3.2.7 Phospholipid fatty acids

Analysis and shifts within microbial communities of total phospholipid fatty acids has been used to study microbial ecological changes (van Elsas et al., 1998; Vestal and White, 1989) and has been useful to indicate broad microbial groups, but does not provide the detailed classification or resolution for CCS monitoring. This technique has not been tested at a CCS project, does not offer advantages over the others presented and it is not worth pursuing in the future.

3.2.8 Microcosms

While microcosm experiments may play an important role in developing biosensors and other biological monitoring methods adapted directly to CCS, there has been very limited study in this field. Beaubein et al. (2008) have focused on attempting to identify CH_4 and S fluxes related to bacterial communities in soils near a natural analogue for a CO_2 leak. Methane oxidising bacteria showed a negative trend relative to increasing CO_2 and subsequent effects, whereas SRB showed a positive trend. Future research with microcosm studies for CCS may occur as the community structure and function are better understood.

3.2.9 PCR-based DNA fingerprinting

For phylogenetic characterisation of samples, PCR of soil DNA followed by various separations has been the preferred method for generating microbial community fingerprints (van Elsas et al., 1998). This method is superior to other cultivation-based methods, and faster, but considered laborious relative to more recent developments discussed below. Biomonitoring using PCR is a valuable supplementary tool for groundwater quality, but is less quantitative than chemical analyses and does not have the required throughput (rapid sample processing) for monitoring (Pronk et al., 2009). For the study of structural diversity of bacterial communities, 16S ribosomal RNA genes are most commonly used due to the presence of alternating sequences of invariant and highly variable regions in the genetic code (van Elsas et al., 1998).

Other variations of DNA based fingerprinting include amplified ribosomal DNA restriction analysis and terminal restriction fragment length polymorphism. These variations in the techniques have different advantages, but the important information for CCS M&V is that the methods can produce community microbial fingerprint profiles of samples that can be compared in relation to baseline surveys. When changes are found and validated, the individual microbial components associated with change can be identified and highly sensitive tools developed to target this “informative” species. This development phase for the monitoring tools may take months to a few years for full development, but does not require a decade or more to become a reality.

As with the applications for biosensors, the PCR has primarily been used in other fields for monitoring chemical pollutants. Examples include the use of PCR to characterise the microbial community in groundwater and soil contaminated with phenol and tar acids (Pickup et al., 2001). BTEX specific PCR methods have been developed (Hendrickx et al., 2006). Some of these real-time (quantitative) PCR methods have also been developed for the detection of BTEX breakdown products by isolating genes from hydrocarbon consuming anaerobic bacteria (Baldwin et al., 2010; Beller et al., 2002; Junca and Pieper, 2004). For field and high through-put monitoring, CE-SSCP (capillary electrophoresis with single strand conformation polymorphism) has been used in profiling complex bioremediation communities and has been shown to offer some advantages over DGGE in characterising more diversity with less sample preparation and analysis time (Hong et al., 2007). For example, PCR SSCP has been valuable in characterising BTEX contaminated soil microbial communities in the Czech Republic (Junca and Pieper, 2004). BTEX along with other organics and inorganic compounds have been observed to be increased adjacent to shallow release CO_2 sites (ZERT; Kharaka et al., 2010) so these microbiological monitoring methods are pertinent to CCS M&V.

PCR primers for the detection of tetracycline efflux genes in bacteria have been developed to trace mobility from a surface source into the groundwater over 200m away (Aminov et al., 2002), giving a potential range that could be expected in terms of biological monitoring of CO_2 leakage in groundwater should appropriate biomarkers be discovered. Similar type monitoring capabilities are possible once the known “contaminants” associated with CO_2 seepage are determined. Gene biomarkers can then be used to create “fingerprints” of the contaminant that can be traced.

Microcosm experiments and PCR-based community characterisation has been used to study alkane breakdown in seawater (Sei et al., 2003). Although not directly applicable, the use of the methods to identify alkane hydroxylase genes in bacterial species that live in brines may be valuable for deep, saline aquifer, biological monitoring. Often CH_4 is abundant in CO_2 injection streams and the study of these genes in other microbes may provide a deep biomonitoring opportunity in the future, although as stated previously, the application of deep biological monitoring is limited and presents additional challenges in terms of sample collection or down-hole sensors.

DGGE is a viable method to monitor microbiological quality of groundwater (Dewettinick et al., 2001) and soils. Whilst DGGE provides a tool to monitor bacterial community shifts, a study by Bruce et al. (2000) showed that under elevated CO_2 concentrations in a controlled and replicated terrestrial ecosystem the bacteria became more diverse over time, but that there was no change in the study related to the CO_2 level. This change in CO_2 was a more subtle atmospheric change and not akin to those expected from a CCS leak in the near surface. More recently, similar low-level CO_2 atmospheric enrichment showed metabolic shifts increasing carbon input into the soil with molecular markers for degradation by plant-derived steroids and cutin-derived compounds (Feng et al., 2010). The community structure ratios of fungi and gram positive and negative bacteria also changed, but this was more an influence of nitrogen changes and not CO_2 (Feng et al., 2010). Similar developments for detecting molecular markers for CO_2 and compounds mobilised by its release could be achieved at more concentrated conditions.

There are only a few examples world wide of the use of PCR studies related directly to CCS projects/natural analogue studies (Beaubein et al., 2008; Krüger et al., 2009; Morozova et al., 2011a; Oppermann et al., 2011). In the shallow monitoring environment, a natural analogue study in Italy showed greater activity of autotrophic methanogenic Archaea, methanotrophic bacteria and SRB near the CO_2 seep even through the actual cell numbers were lower than background (Oppermann et al., 2011). The use of ^{13}C isotopes confirmed that geothermal CO_2 was incorporated into the surface biological communities (Oppermann et al., 2011). Another natural analogue project in Germany showed bacteria were reduced near the CO_2 leak, but Archaea were more abundant (Krüger et al. 2009). This is believed to be a result of oxygen replacement in the soil by CO_2 forming microaerobic and then anaerobic conditions that would favour methane-producing Archaea and SRB. The change in microbial community function was also evident in the shift of nitrate- and nitrite-reducing bacteria (Krüger et al., 2009). The German study expanded the use of PCR further to isolate genes for these nitrogen- cycling bacteria. The study could not amplify some of the targeted genes, but did show that the specific nitrite-reducing bacteria gene *nirK* was indicative of the bacteria that were favoured in a higher CO_2 soil environment (Krüger et al., 2009). Thus, monitoring of this gene may show community shifts related to CO_2 leaks and associated soil changes, and could be used to develop specific biosensors. Identifying key groups of microbes to monitor is the first step towards a viable microbiological monitoring tool.

Deep biological monitoring has only been tested at Ketzin (647 m below surface). The techniques used to monitor the community structure were fluorescence in situ hybridisation coupled with rRNA-targeted oligonucleotide probes and PCR using both DGGE and SSCP of the 16S rRNA (Morozova et al., 2011a). The study showed changes in community structure post CO_2 injection in an environment dominated by SRB (*Desulfohalobium* sp and. *Desulfotomaculum* sp.) and fermentative halophilic bacteria (*Halanaerobium* sp.). After CO_2 injection, an increase in chemolithotrophic Archaea was detected which was believed to be a temporal and transient shift due to pH decrease as methanogenic Archaea out-competed the chemoorganotrophic SRB, that following a lag phase of many months, increased in number (Morozova et al., 2011a). Figure 18 illustrates the changes and physico-chemical measurements over time. These results are an important finding for deeper biological monitoring and correspond to similar changes (different species) in the shallow community and the natural analogue studies. The role of the methanogens and the SRB are probably the most important groups to consider in microbial monitoring for CCS projects.

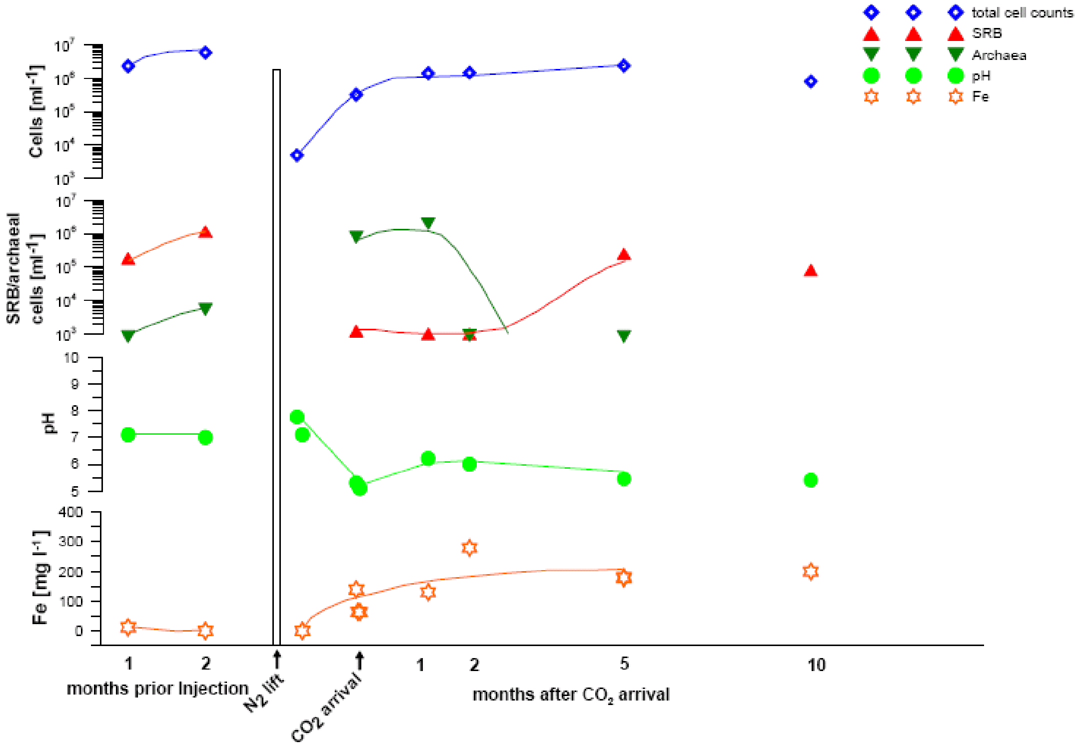


Figure 18 Total cell counts, SRB and Archaea cell counts, pH and Fe concentrations over time from deep microbial monitoring at Ketzin (from Morozova et al., 2011a).

Other studies have looked at deep brines and changes in the bacterial communities. Morozova et al. (2011b) used the same approaches as those at Ketzin to characterise microbial populations in a depleted gas reservoir at 3.5 km depth and found other species of H2-oxidising bacteria (*Hydrogenophaga* sp., *Acidovorax* sp., *Ralstonia* sp., *Pseudomonas* sp.) and thiosulfate-oxidising bacteria (*Diaphorobacter* sp.). Ehlinger et al. (2008), using PCR, showed a dominance of methanogenic bacteria in saline brines being tested for potential use in CCS. PCR-DGGE (Iwamoto et al., 2000) and other versions of PCR such as reverse-transcriptase methods (Han and Semaru, 2004) have also been adapted for better quantification of methanotrophs in soils and could be applicable to CCS M&V. Giese et al. (2009) used PCR SSCP to provide a DNA profile in the deeper monitoring of saline fluids. The dominant species were fermentative bacteria and SRB, agreeing with other studies reported herein. Most of these species are adapted to these extreme environments and could be used to assess changes at depth.

Although PCR methods are reported as quantitative in some cases, the error introduced through amplification can influence results. The techniques are slow and laborious and provide limited functional knowledge compared to microarrays.

3.2.10 Microarrays

Microarrays provide highly parallel-analysis of targeted DNA sequence information. Each array can contain information for thousands to millions of specific genetic regions, allowing detection of multiple organisms or functional gene targets in a single test. A microarray consists of multiple DNA oligonucleotide probes that are complementary to target genes in the sample of interest. The presence and/or abundance of genetic regions of interest are recorded, usually via a fluorescence signal. The number of functional genes and groups of microorganisms is dependent on the array. Techniques for assessing microbial communities that are cultivation-independent have been used to observe community shifts without the bias of methods previously mentioned. These techniques have revealed more microbial diversity than the previous time consuming and laborious techniques (Sessitsch et al. 2006).

Earlier microarray technology incorporated the use of ^{14}C isotope tracers to show the use of carbon sources directly being incorporated from the substrate into target nucleic acids and is independent of PCR amplification and the associated biases (Adamczyk et al., 2003), which may be valuable for tracing CO_2 and other C-containing compounds such as CH_4 from CCS into the microbial community. The latest development of these tools has enabled monitoring of entire microbial communities and directly linked the detected organisms to their specific functions in the ecosystem as predicted by Adamczyk et al. (2003).

These new Microbial Diagnostic Microarrays (MDM) comprise probes specific to microbial populations, for example different species of bacteria or gene functionality. These methods have been employed in other science fields, but have not been applied to CCS projects. However, because of the high complexity, biomass and number of substances that inhibit enzymatic reactions, many of the studies using MDMs are technique-based with respect to optimisation (Sessitsch et al. 2006), and the application to CCS could not have been applied much earlier.

Three categories of MDMs have been developed for use: 1) Phylogenetic oligonucleotide microarrays, 2) Functional gene arrays, and 3) Community genome arrays (Sessitsch et al. 2006). The well known MDMs are the phylogenetic16S rRNA oligonucleotide microarray (PhyloChip®) used for the analysis of phylotypes in a community and the functional gene array (GeoChip®) used for the analysis of functional genes.

3.2.11 PhyloChip®

The generation 2 PhyloChip® microarray can rapidly characterise prokyarotic community structure from a sample of DNA (Figure 19). The PhyloChip® contains ~500,000 probes which have coverage for 8741 known OTUs (Operational Taxonomic Unit) of bacteria and archaea. Probes are arranged in probe sets, whereby an average of 24 probe-pairs is present to enable detection of each OTU. The PhyloChip® can reveal greater diversity within a microbial community than traditional rRNA gene sequencing (Sanger sequencing) due to the placement of the entire gene product on the microarray compared with the analysis of up to thousands of individual molecules by traditional sequencing methods. The initial application of PhyloChip® arrays was to understand bacterial population dynamics during uranium redox chemistry in groundwater systems (Brodie et al., 2006). Recently, the

3^{rd} generation of PhyloChip® has been released. This array can now detect over 30,000 taxa and can be accessed for commercial and research applications.

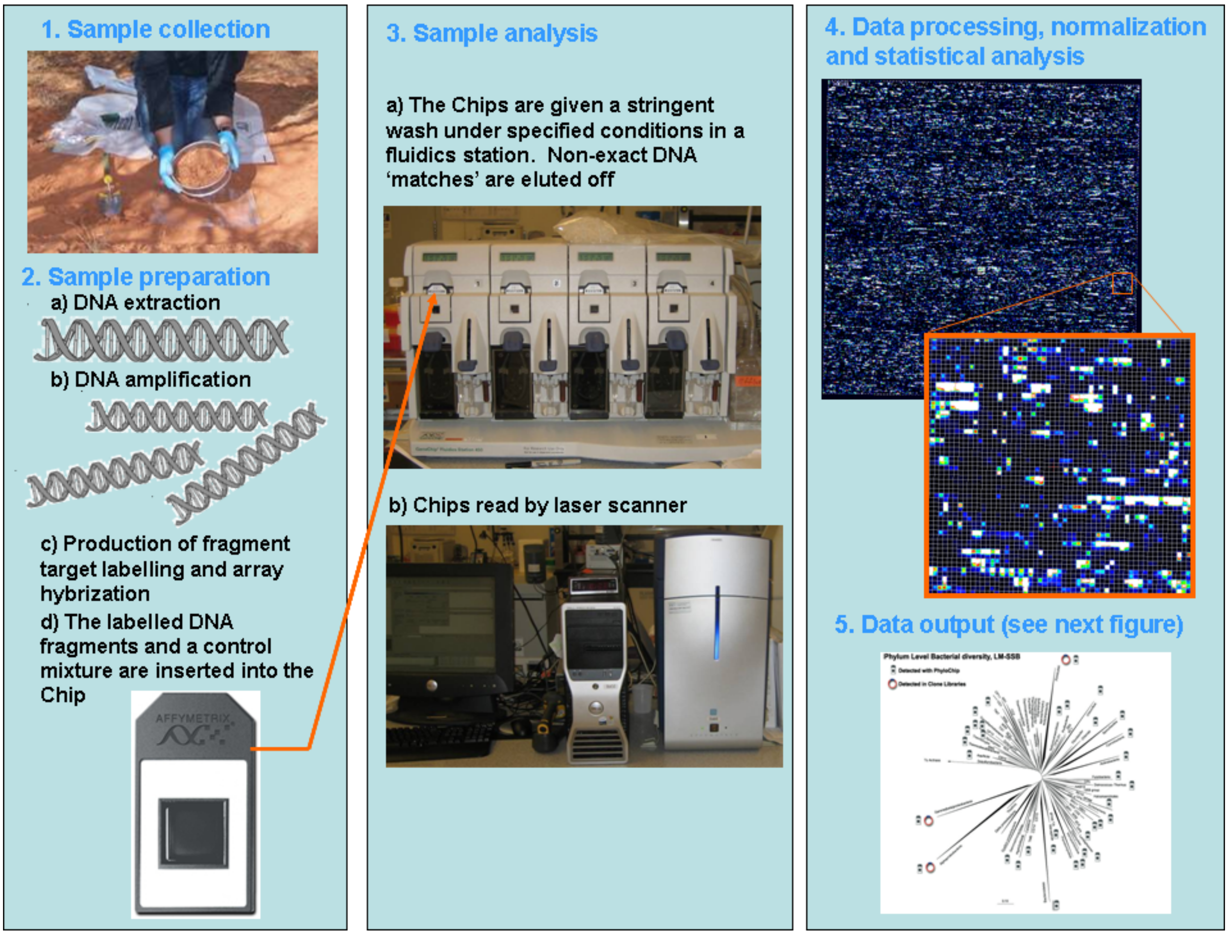


Figure 19 Schematic stages and photos of the PhyloChip® used to characterise microbial communities (Photos courtesy of S. Wakelin Pers. Comm., taken in 2008)

A phylogenetic microarray has been successfully used as a bio-indicator for TCE (at 1 ppm) in the soil (Nemir et al., 2010). Wakelin et al. (in press b) used PhyloChip® to show significant phylogenetic changes across soil subject to Zn enrichment (an example of a metal that could be mobilised by CO_2 induced acidification of the vadose zone). An example of the output generated from the PhyloChip® is shown in Figure 20 and similar type results could be adapted to CCS monitoring to see if fluctuations of the community structure can be detected around CO_2 leaks.

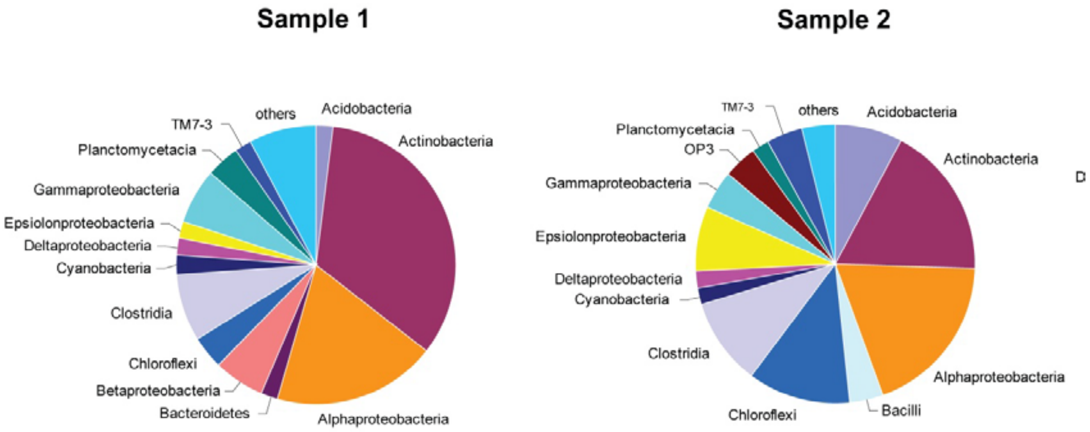


Figure 20 Examples of data generated from PhyloChip® analysis looking at the distribution of major classes of bacteria in two soil samples near a mine site (modified from Wakelin et al. in press (a)). For several taxonomical groups, such as Acidobacteria, Actino

3.2.12 GeoChip®

The GeoChip® functional gene array is an example of a microarray that dynamically identifies microbially-mediated processes of multiple members within a community. The arrays target functionally known genes. The initial version of GeoChip® contained 24,243 oligonucleotide probes covering more than 10,000 gene sequences in more than 150 functional groups that are related to C, N, S and P cycling, as well as genes associated with metal resistance and reduction, and organic contaminant degradation (He et al., 2007). The most recent version of the GeoChip® (3.0) has approximately 28,000 probes, 57,000 gene variants and 292 functional groups, providing even more information about microbial community functionality (He et al., 2010b).

The genes covered by GeoChip® include some of the sequences studies in PCR CCS natural analogue studies by Krüger et al. (2009) such as the *nirS* gene. By combining whole community genome amplification, the GeoChip® detection limits are as low as sub-nanogram quantities of soil community DNA (He et al., 2007).

GeoChip® can be a generic tool for microbial community analysis, and also link microbial community structure to ecosystem functioning. It is this multifunctionality and high throughput that make microarrays a viable tool for CCS M&V. If various metal mobilities are linked to CCS (Section 2.2), changes in the microbial cycling of these metals in the near surface environment can be assessed. Table 12 shows the gene categories covered by GeoChip® 3.0.

GeoChip® has been used for monitoring microbial communities in groundwater environments as it has probes for N, S and C cycling, metal resistance and contamination genes (Van Nostrand et al., 2009; Waldron et al., 2009), as well as soil microbial changes related to plant diversity (He et al., 2010b).

Other applications of microarray studies have successfully used a high through-put scenario for detecting functional activities of microbial communities in groundwater at a U-contaminated site (Gao et al., 2007; Van Nostrand et al., 2009) and soils contaminated with oil (Liang et al., 2009). These microarrays all examine functional genes related to encoding for specific enzymes.

Microarray research has looked at CO_2 sequestration from biological accumulation in woody tissue but not related to geological storage (Druart et al., 2006). Microarray testing of plant tissue under increased CO_2 conditions determined changes in gene expression leading to enhanced lignin synthesis in stems (Druart et al., 2006). This type of biological monitoring could be adapted in the future to CO_2 leakage, and the subsequent environmental changes, although this testing was based on increased atmospheric CO_2, not subsurface. Future research should look at these types of experiments in a CO_2 leakage context rather than a greenhouse gas/global warming scenario.

A move to field portable microarrays for monitoring microbial dynamics in subsurface environments has been developed by Chandler et al. (2010). Although used to show changes in Fe and SO4 reduction, the field portable unit was accurate and correlated with PCR results. The field portable unit provided results within 4 hours. The work by Chandler et al. (2010) is used for monitoring in situ remediation of U, but other adaptations to CO_2 leaks could be developed (U in some cases could be mobilised by CO_2-induced changes to the soil pH). Developments towards fully portable microarrays are progressing for miniaturized, stand-alone, multi-analyte biosensors that weigh < 6 kg (Sapsford et al., 2004). Unfortunately for CCS, the applications for this technology are currently directed towards biohazards, bioterrorism and remediation of major contaminant spills; not subtle chemical or microbiological shifts that may allow early detection of CO_2 leaks.

Despite the PhyloChip® and GeoChip® being restricted by only providing information about the genes present on the microarray, they deliver unbiased comparison of microbial communities as each community is tested against the same set of probes (Zhou et al., 2008).

It is important to realise that MDMs can be biased by the kind of DNA isolation method or PCR amplification procedures that may be used (Sessitsch et al. 2006). However, to understand the functions of microbial communities in spatial and temporal scales on a high-throughput tool, MDMs are an important new contribution to microbial ecology.

3.2.13 Next generation DNA sequencing (NGS)

Recent developments in DNA sequencing technologies, such as the Roche 454 pryosequencing platform, now allow for generation of massive amounts of DNA from environmental samples. Prominent applications are for genome sequencing and metagenomics. A study of microbial diversity on grassland soils had an entire data set of approximately 750,000 sequences, with 600,000 being classified below the domain level (Will et al., 2010). The distribution of the various phylogenetic groups was correlated to a number of soil properties and biomass. It is feasible that, as with the MDMs, if CO_2 leaks impact directly or indirectly on the microbial populations then this method will identify these changes. The advantage of NGS apart from the large number of sequences analysed is that small phylogenetic groups are also sampled and analysed, and not excluded as is the case in some other methods (Will et al., 2010). Many more unknown species will be included in the analysis and, although not dominant in normal cycles, the combined effects of a CO_2 leak on soil geochemical properties may trigger a substantial change in these species and in turn provide the biomarkers required to develop specific and sensitive biosensors of the future. The major problem with this technique is handling the massive amounts of data generated, and also analysis and interpretation with respect to microbial structure and environmental linkages. Also, at present the large-scale NGS can not classify bacterial taxa to the finest level, but this is expected to be less significant with future technology developments (Will et al., 2010).

Table 12 Summary of GeoChip® 3.0 probes and sequences (modified from He et al. 2010b). Bold numbers are major groups (subtotals) of gene categories).

Gene category	No. of genes or enzymes	No. of probes	Sequence-specific probes	Group-specific probes
Carbon cycling	**41**	**5196**	**1765**	**3431**
Carbondegradation	33	3777	1324	2453
Starch	8	772	263	509
Cellulose	4	305	151	154
Hemicellulose	5	505	182	323
Lignin	4	330	274	56
Chitin	3	574	227	347
Pectin	1	33	31	2
Others	8	1258	196	1052
Carbonfixation	4	1043	235	808
Acetogenesis	1	122	35	87
Methane metabolism	3	254	171	83
Methane production	1	136	84	52
Methane oxidation	2	118	87	31
Nitrogen (N) cycling	**16**	**3763**	**2148**	**1615**
N fixation	1	1224	764	460
Nitrification	2	111	69	42
Denitrification	5	1543	1061	482
Ammonification	2	315	87	228
Dissimilatory N reduction	2	262	85	177
Assimilatory N reduction	3	266	80	186
Anaerobic ammonium oxidation	1	42	2	40
Phosphorus (P) utilization	**3**	**599**	**183**	**416**
Organic P utilization	1	31	26	5
Inorganic P biosynthesis	1	182	90	92
Inorganic P degradation	1	386	67	319
Sulfur (S) cycling	4	1504	1083	421
S reduction	2	1123	881	242
S oxidation	1	195	66	129
Others	1	186	136	50
Energy process	**2**	**508**	**410**	**98**
Metal resistance	**41**	**4870**	**603**	**4267**
Aluminum	1	81	13	68
Arsenic	3	392	59	333
Cadmium	2	252	33	219
Cadmium and cobalt	3	1002	99	903
Chromium	1	543	55	478
Cobalt	1	49	6	4:03
Cobalt and nickel	3	7	1	6
Copper	5	804	71	733
Lead	3	33	3	30
Mercury	6	291	77	214
Nickel	1	35	3	32
Selenium	1	3	2	1
Silver	4	213	17	196
Tellurium	4	558	50	508
Zinc	2	589	103	486
Miscellaneous	1	18	1	17

Gene category	No. of genes or enzymes	No. of probes	Sequence-specific probes	Group-specific probes
Organic contaminant degradation	**173**	**8614**	**2165**	**6449**
Antibiotic resistance	**11**	**1594**	**265**	**1329**
Phylogenetic marker (gyrB)	**1**	**1164**	**629**	**535**
Total	**292**	**27812**	**9251**	**18561**

3.2.14 Ecological genomics (ecogenomics)

Although microbial methods have only been applied in limited cases for CCS M&V, their potential is significant. The development of large-scale, high-throughput metagenomics technologies along with these phylogenetic and functional gene arrays make it likely to generate community-wide temporal and spatial data on microbial communities. The biological monitoring toolbox includes those methods previously discussed and the more recent field of study - ecogenomics. Ecogenomics uses genomics to answer environmental questions by defining phylogenetic and functional biodiversity at the level of DNA, RNA and proteins. The methods include microarrays and NGS, which can be used to quantify microorganisms and to elucidate their functions and interactions within an ecosystem in relation to ecological and evolutionary processes (Maphosa et al., 2010). Ecogenomics aims to understand how genes determining function and community activity respond to environmental stimuli. An example of this could be metals mobilised from CO_2 leakage at CCS site, but this has not been tested. Studies of ecogenocmics have been applied elsewhere such as investigating the influence of organohalide pollutants (Maphosa et al., 2010). Ecogenomics has evolved because of the new technologies of high-throughput and - output available to address complex environmental problems. These technologies are considerably more unbiased, sensitive and responsive compared with other methods e.g. GeoChip® compared to plating. This toolbox (lower sections of Figure 21) comprises microbial techniques that yield information on: (i) DNA sequence diversity; (ii) expression of genes; and potentially (iii) linking genes to changes related to CCS monitoring of microbiological activity. Ecogenomics and other technologies mentioned for biological monitoring for CCS is depicted in (Figure 21). Developments of microbiological techniques are progressing and so too are the methods of interpreting the huge quantities of data generated. Bioinformatics is essentially this process and development step (Figure 21).

These new technologies are significantly reshaping the field of microbial ecology and problems associated with chemical cycling, climate change, bioenergy, agriculture, land use, ecosystem management, bioremediation and potentially CCS M&V.

Various monitoring tools and technology exists for studying biological communities at CCS sites. Potential and tested tools for biological monitoring are summarised in Table 13. Gaps are clearly evident (Table 13), but provide opportunities for further development and potentially new and significant progress can be made by closing these gaps and generating a more complete monitoring program for future CCS projects. The development of the technology to applied monitoring tools is time consuming research; however, this can be achieved in years, not decades, and should be pursued in the near future to ensure it is viable in the next decade when more and larger CCS projects start.

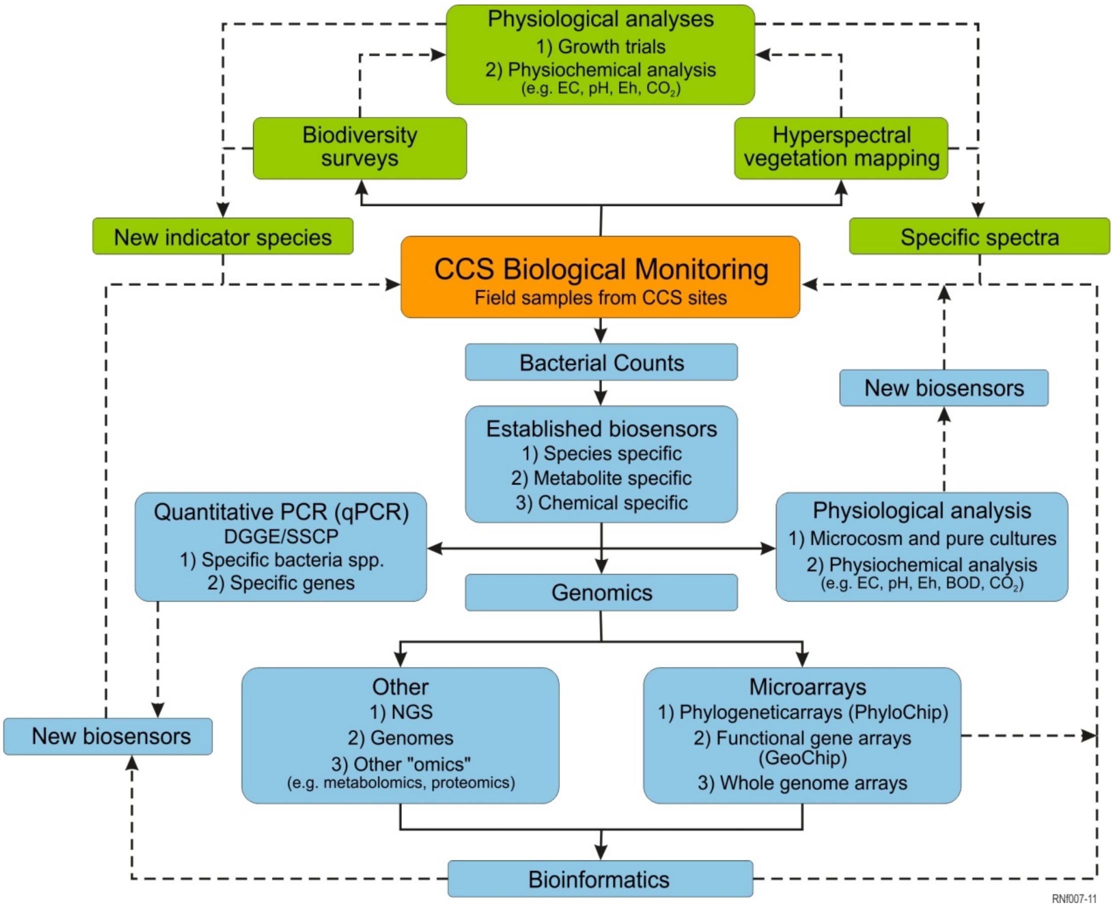


Figure 21 Biological monitoring approaches and developments steps discussed in this report. Blue boxes represent microbial methods and green show botanic methods. The structure of the microbial section is adapted from Maphosa et al. (2010).

Table 13 Biological monitoring tools and application to CCS.

	High throughput	Cost	Deep CCS	Shallow CCS	Tested Deep	Tested Shallow	Tested Analogue
Plant species survey	Y	L	X	🟥	X	⬛	⬛
Plant counts	Y	L	X	🟧	X	⬛	⬛
Hyperspectral plant monitoring	Y	L	X	🟧	X	⬛	⬛
Bacterial counts	Y	L	🟧	🟧	▒	⬛	⬛
Plating	N	L	🟧	🟧	▒	⬛	⬜
ATP activity	Y	L	🟧	🟧	▒	⬛	⬛
Metabolic profiles	N	L	🟧	🟧	⬛	⬛	▒
Biosensors	Y	L	🟥	🟥	⬜	⬛	⬜
Phospholipid Fatty Acid	Y	L	🟧	🟧	▒	⬛	▒
Microcosms	N	H	🟧	🟧	⬜	⬛	⬛
PCR	N	M	🟥	🟥	⬛	⬛	⬛
Microarrays	Y&N	M	🟥	🟥	▒	⬛	⬜
Pyrosequencing	Y&N	M	🟧	🟧	⬜	⬛	⬜
Ecogenomics	N	H	🟧	🟧	⬜	⬛	▒

Cost: H= High, M=Moderate, L=Low
For CCS applications: Red = suitable, orange = less suitable
For method development: Grey = tested, pale grey limited testing, white = untested
X= not applicable
Green = Botanical, Blue = Microbiological

3.2.15 Summary

Biological monitoring for CCS present challenges at depth, but is a relatively low cost and feasible option in the near surface environment. The gap in application of biological monitoring to CCS sites compared to chemical or geophysical methods is great, with only a few successful biological monitoring tests applied to natural analogues or shallow test injections. The most important finding in this section is the potential of newer monitoring tools for phylogenetic and functional gene characterisation of microbial communities that have not been tested in the "geosequestration realm" (Table 13). These tools offer rapid and more thorough microbial characterisation than older methods and have the potential to show changes in microbial communities due to CO_2 leakage and associated issues such as pH changes and mobilisation of potentially toxic metals and metalloids. Once a link can be established between species or functional genes that reflect CO_2 changes due to CCS leaks, refining specific microbiological signals into simple-to-use, field portable, rapid biosensors should become a reality (by 2020 or before). This is the next critical stage for advancing the science of biological monitoring for CO_2 geosquestration.

3.3 Geochemical effects: cations

The effects on mineral geochemistry by the addition of CO_2 in the subsurface have been studied extensively for both shallower groundwaters and deeper subsurface environments (petroleum reservoir diagenesis for example). The dissolution, mobilisation and precipitation (see Section 2.3) of new species caused by the addition of CO_2 to the system can be monitored through a variety of tools. What is most important in terms of monitoring changes in cation and anion concentrations in aquifers as a result of CO_2 sequestration is not initially the absolute values of the species in solution, but rather that there are changes outside of the normal range for a specific aquifer. The ability to discern changes overall rather than strict deviations from a theoretical background are also recognised as being challenging during pressure monitoring in similar environments (see Section 3.1).

During the investigation into potential monitoring tools for metals (cations and metalloids, it became clear that potentiometry, mainly in the form of ISE, was the most promising tool for in situ monitoring at CCS sites. ISE provides a platform that can allow multiple analytes to be measured in a bore at a reasonable cost (given the potential for multiple bores to be monitored). This would be one of the few methods which could provide similar amounts of analytical information that would be comparable with the isolation of a fluid sample (say, by U-tube) followed by a suite of analyses in a laboratory environment with IC, ICP-MS or –AES technologies. Hence the main focus in the cations section is a review of this technology.

3.3.1 Oxidation reduction potential (ORP)

In marine chemistry, sensors capable of being deployed to depths on the order of 5-6 km are used for the detection of hydrothermal plumes and location of sites of hydrothermal venting (Baker et al., 1994; Baker et al., 2003; de Ronde et al., 2003). For example, Walker et al. (2007) developed a new oxidation-reduction potential (ORP) sensor capable of deployment to between 3-6 km water depth. The sensor employs an AgCl and KCl saturated gel with an Ag/AgCl reference electrode and a platinum probe. Some of these probes have been in semi-continuous use for 18 months without calibration (Walker, Pers. Comm. 2011). The ORP sensor primarily responds to the Fe^{2+}/Fe^{3+} and HS^{-}/SO_4^{2-} couple; hydrothermal vents are enriched in the reduced species, which are oxidised on mixing with seawater. In practical terms, during deployment of the ORP sensors, the emphasis is placed on ΔmV, rather than consideration of absolute Eh readings (Figure 22).

3.3.2 In situ monitoring – Ion selective electrodes (ISE)

In situ monitoring for deep groundwater has a number of key features that are required for it to be feasible. These include ability to withstand elevated temperatures and pressures, long-term stability, ease or lack of calibration, small size for emplacement in a well, low detection limits and analyte specificity. There are only a small number of analytical techniques that are capable of more than a few of these features. Probably the analytical technique with the most promise for remote in situ monitoring of changes in alkali, alkaline earth, transition metal and metalloid concentration are ion selective electrodes (ISE). Although ISE have a relatively long history of development and application (e.g., Decher et al., 1971; Koebel, 1974; Rechnitz, 1974; Zipper et al., 1974), there has been a large number of studies in recent years investigating improvements in ISE design, performance, and material construction, with improvements on the order of 10^6 in detection limits and 10^9 in terms of selectivity (Pretsch, 2007; Abbaspour et al., 2010b). A further advantage of ISE is the ability to provide direct speciation of free metal species in solution, which few other methods readily achieve (Rachou et al., 2007). Improvements in ISE design have also meant that more analytes can be measured. New materials and new material combinations, such as the integration of imprinted polymers with potentiometric transducers, are also driving innovation in terms of selectivity and detection limits (Prasad et al., 2007; Prasada Rao and Kala, 2008; Prasad et al., 2010). Selectivity of ISE has been improved by up to 1000 fold through the use of pulsed chronopotentiometric ion selective sensors (pulstrodes; e.g., Perera and Shvarev, 2007; 2008). Considerations for long term monitoring include pH range, detection limit and analytical range, ability to handle variations in ionic strength, response time, and longevity of the probe. Many newly developed ISE that have been tested for longevity have shown that the electrodes are readily stable for at least three months (see below); a recently developed fluoride sensor was shown to be stable for 7 months (Pietrzak et al., 2007). Furthermore, the range of analytes that can be determined by ISE has increased over the last decade. Detection limits of the majority of these new ISE are in the range of 10^{-7} to 10^{-9} M; although other instrumentation such as inductively coupled plasma mass spectrometry can determine the same analytes to much lower detection limits, for in situ monitoring of metal and metalloid mobilisation as a result of CO_2 leakage, the key is to determine significant changes in water quality so that the relatively higher detection of ISE over other technologies is not an issue. In any case, advances in ISE technologies are continuously lowering detection limits, down to sub-nM levels in some cases (Bakker and Pretsch, 2005; Prasada Rao and Kala, 2008). For example, Rachou et al. (2007) have demonstrated a Cu-ISE that was used to determine Cu speciation at concentrations as low as 10^{-14} M.

Optimal use of long-term, remote monitoring with chemical sensors requires remote monitoring of the integrity and performance of the sensors. Radu et al. (2010) have recently shown that this sort of remote interrogation of ISE may be possible using electrochemical impedance spectroscopy (EIS). These authors suggest that EIS is a relatively simple electronic measurement, which can be used effectively to evaluate the functionality of membranes used in ISE membrane, providing predictive capabilities regarding the functionality of the ISE and calibration states. Such a system would be used to replace more conventional approaches to ISE testing (Radu et al., 2010).

One of the major challenges moving forward for in situ monitoring of aqueous metals and metalloids will be the ability to automate the analytical techniques. As noted, advances in ISE technologies are extending the time scales for deployment. However, ISE techniques commonly require matrix-matching, calibration, and in some cases addition of chemicals. Ohyama et al. (2009) recently reported a fully automated system for determination of B using an ISE. The B ISE was automated to perform the sampling and dispensing of the sample, the addition of chemicals, data acquisition and processing, rinsing of the measurement cell, and ISE electrode calibration (Ohyama et al., 2009). New designs raise the potential for recalibration-free, ion-selective chemical sensors through the use of exhaustive coulometry (Bakker et al., 2008; Bakker, 2011). Coulometry allows the design and construction of robust sensors that will be particularly useful for applications where in situ recalibration is difficult or undesirable (Grygolowicz-Pawlak and Bakker, 2010), such as in long-term deep borehole monitoring. For environmental analyses, ISE allow real-time remote water-quality monitoring, including use on remotely operated vehicles and other submersible applications with such features as backside calibration and switchtrodes that avoid the commonly used standard addition analysis, which commonly produces changes in analyte speciation (De Marco et al., 2007).

Materials research has resulted in significant improvements in terms of miniaturisation and microfabrication technology and ISE are becoming increasingly suitable for field-based and in situ environmental monitoring (Hanrahan et al., 2004). As noted by Hanrahan et al. (2004), ISEs are having a major impact upon the monitoring of priority pollutants because of their ability to be used in the field, as opposed to traditional sample collection and transport to a remote analytical facility. These new ISE are able to analyse dissolved aqueous species in complex matrices (such as formation waters and brines), combined with automation and rapid inexpensive construction (Hanrahan et al., 2004).

Some of the major disadvantages of ISE include interferences from competing ions, and, although great strides have been made in this regard, care must still be taken (Dimeski et al., 2010). One approach to this problem is the use of electronic tongues. The proliferation and miniaturisation of ion sensors based on polymeric or solid-state membranes means that they can be arranged in a sensor array, and electronic tongue (e.g., Ciosek and Wróblewski, 2007; Cai et al., 2009; Bratov et al., 2010; Witkowska et al., 2010; Winquist et al., 2011). These electronic tongue sensor arrays have been constructed using a variety of transduction techniques including polymer and solid-state membranes, solid-contact electrodes, which includes coated wire electrodes, ion-sensitive field-effect transistors and light addressable potentiometric sensors (Bratov et al., 2010). Issues of interference by competing ions are mitigated through the use of chemometric processing tools, such as principle component analysis and artificial neural networks (Mimendia et al., 2010). Smart sensor arrays can be equipped with blind source separation algorithms that allow more rapid discrimination of analytes, and greatly reduce the time-demanding calibration stages needed in the typical approaches (Duarte et al., 2009).

Electronic tongues are starting to see applications as automated remote environmental monitors in such areas as: 1) greenhouses, where ammonium, potassium, sodium, chloride, and nitrate ions were successfully monitored (Gutiérrez et al., 2008), 2) environmental monitoring of ammonium contamination and co-existing alkalis, and 3) the monitoring of heavy metals (i.e., Cu, Pb, Zn and Cd) in liquid waste and surface waters draining into the Gulf of Mexico (Mimendia et al., 2010).

Traditional ISEs (e.g. polymer-based, pH glass electrode) contain an internal filling solution and typically employ an Ag/AgCl reference electrode. The new classes of ISE that have been developed over the last few years are moving towards solid-state and polymeric-based electrodes. These newer electrodes have several advantages, including the lack of an internal reference solution, which removes transmembrane ion fluxes with consequent lower detection limits, lower cost, reduced electrode size and ability to operate at high pressure (Sutter et al., 2004; Wardak, 2011). Miniaturisation will also ultimately lead to electrodes capable of determining more than one analyte (Di Natale et al., 1996; De Marco and Martizano, 2008). As an example, De Marco and Martizano (2008) developed a bielectrode capable of simultaneous determination of free Cu^{2+} and Fe^{3+} to detection limits of 10^{-15} to 10^{-5} M for Cu^{2+} and 10^{-21} to 10^{-10} M for Fe^{3+} in a seawater matrix.

Developments in screen-printing technologies over the last decade means that electrolytic sensors can now be deposited on a variety of substrates (including paper; Dungchai et al., 2009) as thick layers with precise pattern control. The utility of the method is reflected in the relative simplicity, low-cost, high reproducibility and suitability to production at large-scales (Koncki et al., 2000; Parat et al., 2006; Tymecki et al., 2006; Sànchez et al., 2010).

3.3 3 Specific examples of recent developments in ISE

Alkalis and alkaline earths

ISE for the determination of Na, K, Ca and Mg, as well as Cs (Radu et al., 2006), Sr (Zamani, 2008), Li (Kang et al., 1997), and Rb (Hyun et al., 2004) have been developed and are commercially available for several decades. Research into extending the detection limits and dynamic ranges as well as miniaturization are driven in large parts by medical research for in vivo and in vitro monitoring (Dimeski et al., 2010; Sethi et al., 2011). There is also recognition for the need for ISE of these species in environmental monitoring, so that recent developments have produced ISE for the major cations in water with detection limits appropriate for both potable and saline aquifers (Radu et al., 2006; Şendil et al., 2009). A Sr sensor with an ionophore-based membrane was recently developed with detection limits at the 10^{-7} M level, and stable over a large range of pH (2.8 to 10.4) (Zamani, 2008)

Iron

Iron is a key analyte for monitoring of changes in aquifer pH. At circumneutral pH values and reducing condition, Fe^{2+} is stable in water, whereas under oxidizing conditions, Fe^{3+} is unstable and precipitates as $Fe(OH)_3$. Fe-oxyhydroxides possess strongly charged surfaces, depending on pH and degree of crystallinity, providing exchange sites, especially for As and Se. Pooyamanesh et al. (2007) developed an Fe^{3+} specific electrode with an analytical range of 10^{-6} to 10^{-1} M, at pH values of 2.2 – 4.8. The detection limit was determined to be around 6.8 x 10^{-7}, and the electrode was operated for up to 9 weeks. This Fe^{3+} ISE device is a PVC membrane with optimal results from a membrane composed of 30% poly(vinyl chloride), 65.5% nitrophenyl octyl ether, 2% sodium tetraphenyl borate and 2.5% AMMTO. The pH range for this electrode is optimal in terms of Fe^{3+} detection; at higher pH values, Fe^{3+} is unstable in most groundwaters, owing to formation of $Fe(OH)_3$ precipitates. Similar results have recently been reported for both PVC membrane and coated graphite Fe^{3+} ISE sensors by Motlagh et al. (2010) and by Masrournia et al. (2011). These sensors showed independence of pH over the range 1.8 to 5.6 and 2.3 to 3.4, respectively.

Lead

Given the toxicity of Pb and the interest in its fate in the environment from industrial processes and leaded gasoline, there have been a relatively large number of electrodes developed for the determination of Pb^{2+} in solution. Over the last three years a number of papers have reported new attempts to improve the detection limits and selectivity of Pb ISE, primarily through the use of polymeric membranes with PVC (Pouretedal et al., 1998; Pouretedal and Keshavarz, 2004; Yan et al., 2009; Abbaspour et al., 2010a; Abbaspour et al., 2010b). For example, Pilehvari et al. (2007) prepared a lead-selective electrode, which is based on a plasticized PVC membrane that contains 30% PVC, 67% ortho-nitrophenyloctylether and 3% ionophore that was coated on a graphite rod. Most of these new ISE are capable of measuring Pb at concentrations from around 1.0 x 10^{-7} to 1.0 x 10^{-1} mol/L, with typical detection limits of ~ 5.0 x 10^{-8} mol/L. The useful pH range for these electrodes is variable. Abbaspour et al. (2010a; 2010b) reported a useful pH range of 3.0 to 6.7 and Yaftian et al. (2006) pH of 3.5 to 5.0. By contrast, Nabi et al. (2008) found that their PVC-based Pb^{2+} ISE showed invariant response from pH 2 to 7. These Pb ISE typically have fast response times (10-20 seconds), good selectivity for other transition metals, REE, and alkali and alkaline earths. Most show minimal deterioration of electrode performance over periods of three to four months. These electrodes are not solid state, and improvements in detection limits to values closer to typically background values for Pb are likely to be attained in the near future.

Copper

Similar to the major cations, copper ISE have received a lot of attention in medical and pharmaceutical fields. However, as with Fe and Pb, developments in PVC-based membranes and solid-state detectors have resulted in lowering of detection limits. A review of new Cu^{2+} ISE sensors indicates that most have detection limits of 10^{-8} M at the low end, with variable pH ranges where the electrodes show optimal response, from for example, pH 3-8 (Kopylovich et al., 2011) and pH 4-6 (Masrournia et al., 2010; Shokrollahi et al., 2011). In most settings, it is unlikely that Cu concentrations would be perturbed sufficiently for these ISE sensors to be efficacious.

Mercury

ISE for the detection of free Hg^{2+} and Hg species in aqueous solution have been developed since the 1970's (Cattrall and Pui, 1976; Somer, 1981). As with other analytes of interest in terms of potential release from aquifer acidification, earlier Hg-specific electrodes were hampered by relatively large detection limits e.g., 10^{-4} M (Cattrall and Pui, 1976). Improvements in the last decade in terms of membrane construction and new ionophores has resulted in a number of Hg^{2+}-specific electrodes with improved detection limits and working ranges; most have detection limits in the 10^{-7} to 10^{-6} range, with improved selectivity compared to earlier generations (Mahajan et al., 2008; Zhang et al., 2008; Abu-Shawish, 2009; Kumar et al., 2010a; Puri et al., 2011). However, even lower detection limits have been reported with new ionophores (Tyagi et al., 2010) and, in particular through the use of ionic liquids. For example, Khani et al. (2010) developed a highly selective potentiometric ISE for the determination of Hg^{2+} in aqueous solutions. Development of this new electrode involved combining the ionic liquid 1-n-butyl-3-methylimidazolium tetrafluoroborate with multi-walled carbon nanotubes. The carbon nanotubes improved conductivity and transduction of the chemical signal to an electrical signal (Khani et al., 2010). This combination, along with an ionophore, produced significantly enhanced selectivity toward Hg^{2+} with a detection limit of 2.5 x 10^{-9} M. As with most new ISE, response times are short (~5s) and the electrode can operate for at least two months without any considerable divergence in electrode potential (Khani et al., 2010).

Rare earth elements (REE)

Improvements in ISE have also resulted in the ability to measure most of the REE in aqueous solutions (La, Ce, Pr, Dy, Tb, Eu, Lu, Nd, Gd, Sm, Ho, Er and Yb). These electrodes use ionophore binder-membrane sensors; here the active part of the sensor membrane is the ionophore, which forms the complex with the lanthanide of interest and determines the selectivity (Kumar et al., 2010b). For most of these electrodes, detection limits are generally in the 10^{-7} to 10^{-6} M range, although for some electrodes down to 10^{-10} M (Ganjali et al., 2009); although the REE are generally present at much lower concentrations than this in most groundwaters, the REE, as with many of the transition metals become increasingly soluble and mobile with decreasing pH (Johannesson and Lyons, 1995; Johannesson et al., 1996; Leybourne et al., 2000). Therefore, use of electrodes for analytes that are normally below detection could be a powerful tool; any detectable amount of the analyte would indicate significant change in the pH of the aquifer and adverse effects with respect to mobility of metals. Examples of recently developed lanthanide ISE include La (Ganjali et al., 2009), Dy (Prasad et al., 2006), Ce (Pouretedal et al., 2006; Abedi et al., 2008), Eu (Ganjali et al., 2007), Ho (Faridbod et al., 2010), Nd (Norouzi et al., 2006; Chandra and Singh, 2009; Menon et al., 2011), Er (Nekoei et al., 2009), Sm (Naddaf and Zamani, 2009), and Lu (Zamani et al., 2010).

3.3.4 Summary

Traditional ISE suffer from a number of drawbacks that make them largely unsuitable for long-term in situ monitoring of deep saline groundwaters. These disadvantages include issues of matrix matching, sensor drift, need for calibration, need for variable storage solutions for different analytes, use of internal reference solutions, and in some cases, detection limits that are too high for trace metals. The new advances discussed above, including solid-state electrodes, sensor arrays (electronic tongues), and thin and thick film deposition of sensors means that many of these problems are in the process of being solved, in particular detection limits, miniaturization, and reduction in the need for repeated calibration.

The most useful approach to long-term in situ monitoring for the alkalis, alkaline earths, transition metals and metalloids appears to lie in the area of ISE and ISE sensor arrays. The approach to take most likely involves identifying key analytes that represent a larger group of elements that typically have similar behaviour in groundwater and in response to changes in pH and aquifer mineralogy through carbonation reactions. Thus, Pb and Zn could be monitored as proxies for many of the transition metals. A La, Ce or Nd electrode would be suitable to monitor changes in REE and actinide concentrations (as these are commonly the most abundant REE in groundwater); many studies of the behaviour of the REE in solution are based on their ability to act as analogues of the actinides. An ISE for Fe would permit monitoring of dissolution and precipitation of Fe and Mn oxyhydroxides; these are key mineral phases that control the mobility and attenuation of many metals and metalloids (especially Cu, Pb, Co, Ni, As, Se). Finally, Ca, Na, Mg and K ISE, in conjunction with pH and $CO_{2(g)}$, would permit monitoring of the extent of water-rock interaction and carbonation.

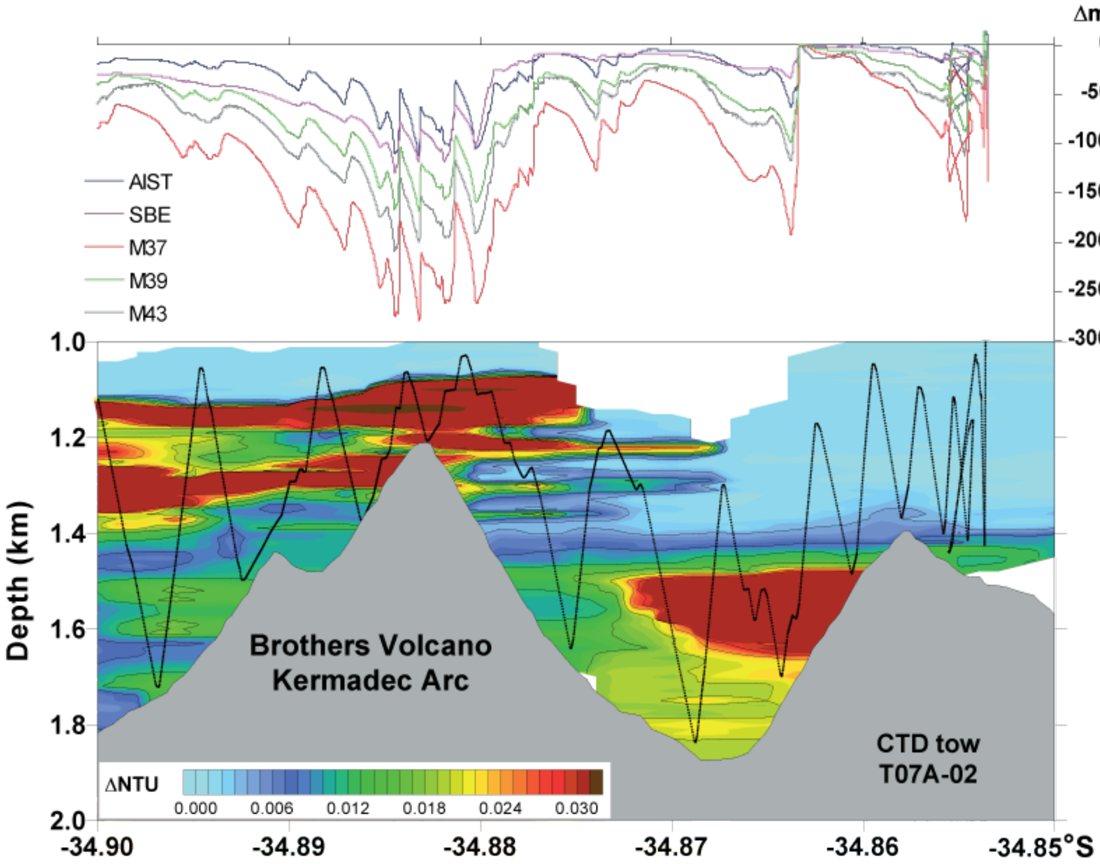


Figure 22 Cross section of Brothers volcano on the Kermadec arc, showing the hydrothermal plumes, as defined by changes in light scattering (ΔNTU) The top panel shows real-time changes in Eh (ΔmV) for five different ORP sensors deployed on the CTD. Figure from Walker et al. (2007).

3.4 Geochemical effects: Anions

Changes in anion concentration related to the presence of CO_2 could arise in a number of ways (Section 2.3), including: 1) mixing of freshwater with saline or brackish waters, which would increase Cl, Br, and I concentrations, 2) lowering of pH resulting in enhanced water-rock interaction, which could release anions, 3) lowering of pH may also result in increased adsorption of anions onto positively charged mineral surfaces, and 4) changes in redox conditions, resulting in changes in sulfide/sulfate values, reduction of nitrate or oxidation of ammonia. Thus, in situ measurement of key anionic species, i.e. Cl^-, H_2S/HS^-, SO_4^{2-}, F^-, I^-, Br^-, NO_3^-, PO_4^{3-} has significant potential for monitoring changes in formation water in the vicinity of a storage project.

3.4.1 In situ monitoring

Many anion sensors employ the potentiometric (i.e., electrochemical) transduction mechanism i.e., ISE. The majority of anion ISE tools use a polymer receptor/membrane and polyvinyl chloride (PVC) is common. In many cases, a plasticizer and ionophore is incorporated into the PVC membrane, and these are typically optimised to selectively interact with the anion of interest. Despite many displaying suitable analytical properties (i.e., sensitivity and selectivity), as with cation sensors there are problems related to drift and the need for calibration. Most polymer-based anion sensors have a relatively short lifetime (i.e., less than 3 months), which limits their application to long-term real-time monitoring. However, rapid progress is being made in miniaturization, extended life spans and lab-on-chip designs (Jang et al., 2011). These improvements are being driven by the needs of the medical community, but also by the increased recognition of the need to perform in situ monitoring for environmental purposes (Jang et al., 2011), including monitoring changes in water composition associated with concrete and cement (Antes et al., 2010; de Vera et al., 2010).

Chloride

Measurement of dissolved chloride may have application in detecting mixing of saline waters moving out of the storage site and into freshwater aquifers. It may also have potential as an indicator of cross-aquifer leakage by detecting the presence of pore fluids from aquitards (which attain elevated Cl concentrations through ultrafiltration processes; Zuber and Chowaniec, 2009). .Chloride ISE have been around for several decades (McWhirter, 1974; Doe and Kitagawa, 1982; Subrananian et al., 1984) and are commercially available. As with other ISE, advances have focused on a move to solid-state systems (e.g., Sjöberg-Eerola et al., 2004; Sjöberg-Eerola et al., 2007) with longer life spans and less need for constant calibration.

Pimenta et al. (2004) studied two quasi-independent systems to monitor real-time Cl concentrations within a flow system. These systems included both potentiometric and optical determination, using a membrane with an indium (III) octaethyl-porphyrin ionophore. Both systems provided Cl concentrations that were statistically indistinguishable from the reference analytical method. The potentiometric membrane permitted determination of Cl at the 10^{-5} to 10^{-2} M range, which would be suitable for groundwater studies. Further, the authors showed that the membrane showed essentially no drift over at least 4 months of operation (Pimenta et al., 2004).

Similarly, a chloride PVC-based membrane sensor based on a Ru^{3+} Schiff's base complex was developed by Ganjali et al. (2004). The sensor has a composition of 30% PVC, 62% benzyl acetate, 5% Ru^{3+} Schiff's base complex and 3% hexadecyltrimethyl ammonium bromide. The sensor is capable of determining Cl in aqueous solution over the concentration range 10^{-6} to 10^{-1} M, with a detection limit of 71 µg/L. The response of the electrode is independent of pH in the range of 4.0-10.0, with a life span of at least 2.5 months. The authors used the ISE to determine chloride concentrations in serum samples (Ganjali et al., 2004).

Gupta et al (2009) suggested that despite earlier studies and commercially available Cl-specific ISE, there was still a need for more work on Cl ISE. These authors developed a new potentiometric Cl sensor using an anion receptor [*2-(1-H-imidazo [4,5- f][1,10]phenanthroline-2-yl)-6methoxyphenol (HIPM)*] in a PVC matrix. The sensor extends the detection limit to 10^{-8} M Cl, albeit at a more limited pH range (6.5 to 8). However, these authors also showed that the sensor was capable of rapid Cl determinations even in mixed aqueous-methanol solutions (Gupta et al., 2009).

An alternative approach for aqueous Cl determination was used by Larson et al (2009). These authors monitored in situ changes in hydrothermal fluids at several vent sites to investigate phase separation at mid-ocean ridges. In this case, Cl was shown to change as a linear function of electrical conductivity (with changes in slope as a function of T), so that Cl concentrations were indirectly monitored with conductivity sensors (Larson et al., 2009).

Sulfide/Sulfate

Determination of dissolved sulfate and sulfide is important to understanding the influence of CO_2 sequestration and leakage on groundwater chemistry. The aqueous concentrations of these species reflects the redox state of the groundwater system, and can also be a key indicator of sulfide mineral oxidation (elevated sulfate), which can also produce increases in metal concentrations. Elevated concentrations of aqueous sulfide conversely would indicate important changes in redox state and would further indicate that base metal migration is likely to be limited owing to the low solubility of most metal sulfide minerals. Gulens (1978) discussed the problems of increasingly non-Nerstian responses on Ag_2S electrodes owing to build up of Ag metal at the electrode surface; newer sulfide sensors are finding novel ways of circumventing this problem. Sulfide ISE have been around for some time (Vesely et al., 1972) e.g., in metals processing (Jones and Woodcock, 1979).

Recently developed carbon nanotube (CNT) modified glassy carbon electrodes displayed both strong and stable electrocatalytic responses to dissolved sulfide, in particular compared to more standard carbon electrodes (by some 400 mV) (Lawrence et al., 2004). The electrode showed a wide linear concentration range (1.25-112.5 µM) with a detection limit of ~9 µg/L. The use of carbon nanotubes to promote the sulfide electron-transfer reaction should result in miniaturization of sulfide ISE (Lawrence et al., 2004).

A different approach was taken by Hassan et al., (2002). These workers used a PVC membrane-based sensor designed to react with the methylene blue cation. This sensor provided an analytical range of 10^{-7} to 10^{-4} M, at a buffered pH of 8.7. Compared to other sulfide ISE, this sensor allowed the determination of sulfide ions in samples with complex matrices, e.g. wastewaters (Hassan et al., 2002).

Rearick et al. (2005) reported a method for determining aqueous sulfide concentrations using coupled diffusive gradients in thin films (DGT) to solid-state ion-selective electrodes (ISE). Laboratory tests were performed for a series of solutions containing sulfide at concentrations ranging from 0.009 to 2.50 µM. The coupling of the DGT to the ISE results in a preconcentration of sulfide with consequent improvement in detection limits compared to other techniques (Rearick et al., 2005). Not discussed, however, is how well this method could be adapted to in situ borehole monitoring.

A highly sensitive sensor capable of determination of thiosulfate, sulfite, sulfide and dithionite was described by Salimi et al. (2002). The modified carbon ceramic electrode was doped with a Ru-complex and displays good reproducibility, responds rapidly to changes in analyte concentration and was stable for at least six months.

Whereas sulfide has received some attention in terms of ISE development, less emphasis has been placed on sulfate, despite its stability over a much broader range of Eh and pH compared to sulfide. Efforts were hampered primarily because of the highly hydrated nature of dissolved sulfate and consequent difficulties in terms of selectivity over other anions (Lomako et al., 2006). Morigi et al. (2001) described an ion-selective electrode (ISE) for sulfate based on a dispersion of hydrotalcite particles into a polymeric membrane using coated-wire (CW) with membranes made from either PVC or poly(dimethylsiloxane) (PDMS). Membranes constructed from PDMS showed the best response with detection of sulfate from 10^{-5} to 10^{-2} M. The PDMS-based electrode was highly selective to other anions compared to previous sulfate ISE, over a range of pH from 4-7. Practical use of a sulfate-selective electrode was shown by Lomako et al. (2006) using both mineral waters and seawater.

Fluoride

Ion selective electrodes for the detection of fluoride have been in use since the 1960's (Frant and Ross, 1966) and are commercially available with detection limits to 10^{-6} and 10^{-7} M. In most groundwaters, F concentrations are controlled by the low solubility of fluorite (CaF_2); however, higher pH, Na-rich, Ca-poor groundwaters can attain significant F concentrations owing to base-exchange reactions (Leybourne et al., 2008), evaporation of soda lakes (Gizaw, 1996) and geothermal fluid-groundwater mixing (Carrillo-Rivera et al., 2002; Edmunds and Smedley, 2005). Given the types of groundwater that display elevated F concentrations, an in situ F sensor would be most useful for groundwaters where F was already elevated (i.e., Na-Cl and Na-HCO_3 type groundwaters); the important change would be loss of F from solution, most likely following a lowering of pH.

Traditional fluoride ISE used rare earth, thorium and calcium fluoride membranes. More recently, development of fluoride ISE have focused on F ionophores (Perdikaki et al., 2002), and solid state sensors (Somer et al., 2010). For example, Somer et al (2010) developed a fluoride sensor constructed from 70% Ag_2S, 10% Cu_2S and 20% CaF_2 with a detection range of 10^{-6} to 10^{-1} molar. This sensor was found to be highly selective for fluoride compared to other common anions in groundwaters, and more significantly, had a life span of at least two years (Somer et al., 2010).

Nitrate

Nitrate ISE have been prone to issues related to selectivity and interference from competing anions (Di Gioia et al., 2010). Recent developments have focussed on miniaturization and development of microfluidic systems (Hassan et al., 2007). For example, Masadome et al. (2010) combined a NO_3 ISE (based on tetradodecylammonium bromide as an anion exchanger and 2-nitrophenyl octyl ether as a plasticizer) with a Na^+-ISE as a reference electrode onto a single microfluidic chip. The NO_3 ISE was useful over a concentration range of 10^{-6} to 10^{-1} M, a range that would be useful in monitoring changes in groundwater NO_3 concentrations. The microfluidic polymer chip was fabricated using polystyrene plates and stainless-steel wires. The chip designed by Hassan et al (Hassan et al., 2007) includes a sold-state NO_3 ISE with similar concentration ranges. The chip measures 13 x 3.5 mm and operates over a wide pH range.

3.4.2 Summary

As with cation ISE, anion ISE have traditionally suffered from a number of limitations that would hamper their use as long-term in situ monitors. However, along with rapid changes in ISE with respect to miniaturization and solid-state, lab-on-chip technologies, the key to in situ monitoring is likely to determine relative changes in aquifer chemical conditions, which would trigger more detailed sampling and laboratory analysis. It is most likely that these types of technologies would be applied in aquifers above the injection horizon. It is unlikely that there would be sufficient application to develop these to the point where they could be permanently deployed into a storage reservoir due to the risks associated with having an open wellbore, or the longevity issues associated with having them permanently cemented in place and the harsh environment of high pressures, temperatures and low pH, CO_2-rich formation water.

3.5 Monitoring of hydrocarbons and organics

The possibility of hydrocarbon contaminants being mobilised by CO_2 occurs where depleted oil and gas fields are used for CCS or CO_2 is used for EOR (e.g. Weyburn). There tends to be significant quantities of hydrocarbons remaining as “oil (or gas) -in-place” when using abandoned or uneconomic fields (e.g. Otway). The solubility of some hydrocarbons is much greater in CO_2 compared to water (Brudi and Schmieder, 1996) and this can play a significant role on their transport through the geological formation. Table 14 displays the chemical and physical properties of some hydrocarbons that are commonly monitored in the environment. More than 2000 papers and patents have been published in the last 5 years dealing with the monitoring of the hydrocarbons that are shown in Tables 15 & 16. Although there are many different types of hydrocarbons present in the environment, the focus here will be mainly on the monitoring of aliphatic and aromatic hydrocarbons, since these groups of compounds are derived from petroleum systems and are typically associated with geological formations. In addition, they are found at significant concentrations in the subsurface which makes it feasible for them to be monitored. There are more than 917 publications (both papers and patents) using various laboratory techniques for monitoring polycyclic aromatic hydrocarbons (PAH) (i.e. naphthalene, anthracene, phenanthrene, etc). The detection of PAH represents almost 50% of the total publications on hydrocarbon monitoring. The next most commonly monitored hydrocarbon was benzene (~20%) followed by methane (~11%), toluene (~11%), xylenes (~7%) and ethylbenzene (~4%). It is not surprising that there is significant interest in detecting PAHs and benzene since these compounds are considered to be highly toxic to humans and the environment.

Table 14 Some properties of various hydrocarbons measured in the environment (Aylward and Findlay, 1998; Lide, 2006).

Molecule	Molecular weight (g/mol)	Density at 25°C (g/cm^3)	Boiling temperature (°C)	Solubility in water (g/L) at 25 °C
Methane (CH_4)	16	0.423 (liquid)	-161.5	0.0227
Benzene (C_6H_6)	78.1	0.874	80.1	1.78
Toluene ($C_6H_5CH_3$)	92.1	0.862	110.6	0.53
Ethylbenzene ($C_6H_5CH_2CH_3$)	106.2	0.863	136.2	0.161
o-Xylene [$C_6H_4(CH_3)_2$]	106.2	0.876	144.4	0.171
m-Xylene [$C_6H_4(CH_3)_2$]	106.2	0.860	139.1	0.161
p-Xylene [$C_6H_4(CH_3)_2$]	106.2	0.857	138.4	0.181
Naphthalene ($C_{10}H_8$)	128.2	1.025^{20}	217.9	0.0316
Anthracene ($C_{14}H_{10}$)	178.2	1.28	340	0.000045
Phenanthrene ($C_{14}H_{10}$)	178.2	1.179	340	0.0011

3.5.1 Hydrocarbon sensor categories

Sensors for hydrocarbons are normally classed according to the type of transducer employed. The three most common types for the detection of hydrocarbon compounds are: 1) piezoelectric (i.e. mass/gravimetric), 2) optical (i.e. infrared, fluorescence, refractive index) and 3) electrochemical/electrical (i.e. resistance, potentiometric). The infrared and fluorescence transducers are the most widely used of the optical methods, whereas the resistance transduction mechanism is the most common of the electrochemical/electrical group. In terms of cost and portability, resistance transduction is one of the least expensive and has low power requirements.

Although cost and size are important criteria when selecting a sensor platform for a particular application, the sensitivity and selectivity are the parameters that determine if a sensor will be successful. Extensive research has been conducted on different hydrocarbon sensor technologies by many groups all over the world. A great deal of effort is focused towards improving the sensitivity and selectivity for hydrocarbons. The majority of the sensors can only detect down to parts per million (ppm) levels which represents a significant challenge when most hydrocarbon contaminants in the environment are present at parts per billion (ppb) concentrations. However, some of the sensors have been able to achieve ppb detection limits in laboratory based samples when certain experimental conditions are employed. It is important to note that the sensitivity of a chemical sensor is governed by both the type of transducer and the chemiselective material that is attached onto the transducer surface.

The methods employed during sensor fabrication and preparation (i.e. the nature and the amount of chemoselective material) play a significant role on sensitivity. However, some transduction methods are usually more sensitive for certain molecules compared to others. For instance, sensors based on fluorescence are highly sensitive for aromatic compounds, whereas electrochemical based sensors are generally more sensitive towards polar molecules. Selectivity is another important consideration when designing a chemical sensor and this is usually dictated by the type of chemoselective material employed. However, the transduction mechanism can also play a significant role on selectivity. Certain transduction mechanisms such as infrared spectroscopy (IR) is inherently selective since it is able to generate spectral data that is unique to an individual compound. By contrast, sensors that involve fluorescence detection respond to compounds with unsaturated functional groups such as benzene and PAHs. In the case of piezoelectric sensors, the chemoselective material, which is usually a polymer, is responsible for dictating selectivity by preferentially absorbing certain hydrophobic molecules.

3.5.2 Piezoelectric-based sensors

According to the International Union of Pure and Applied Chemistry (IUPAC), a piezoelectric sensor is a piezoelectric oscillator that responds to variations occurring in the environment with changes of the resonant frequency (fundamental or harmonic) or the wave speed (Buck et al. 2004). Piezoelectricity is a property of certain materials that generate an electrical polarization as a result of mechanical stress or, conversely, mechanical stress is produced by the application of an electric field. The piezoelectric sensors are usually distinguished by the mode of oscillation. The two common types are the thickness shear (TSM) mode or the shear horizontal surface acoustic wave (SH-SAW) mode. The TSM resonator, which is also referred to as the quartz crystal microbalance (QCM) or the quartz crystal resonator (QCR), is typically made from a thin disc of AT-cut quartz. Figure 23 shows a schematic diagram of a QCM sensing system for the detection of hydrocarbon compounds.

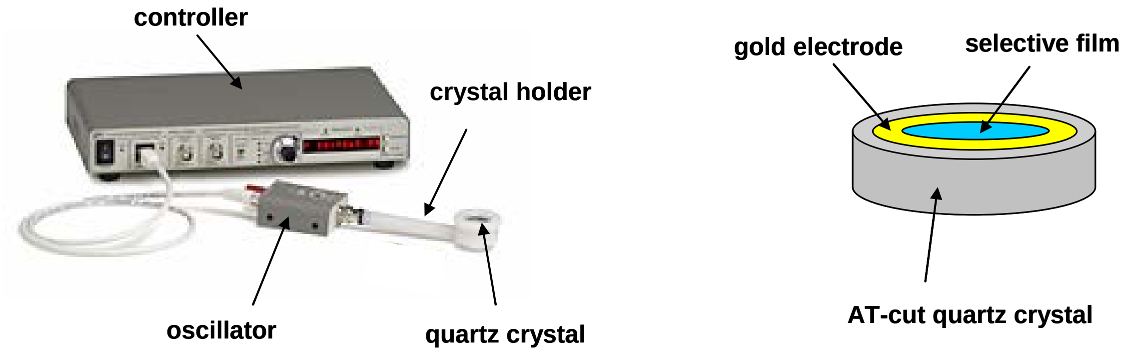


Figure 23 Typical QCM system used for hydrocarbon sensing.

The quartz crystal is commonly used for sensor measurements, however, there is some research in alternative piezoelectric materials such as lead zirconate titanate (Ferrari et al., 2000). A thin layer of gold or platinum (~100 nm thick) is printed on each side of the disk and is used to stimulate oscillations, to measure the resonance and to provide an inert surface layer for binding certain types of materials. An oscillating electric field is applied to the metal electrodes which results in an acoustic wave propagation perpendicular to the substrate surface. In the case of SH-SAW, it consists of an input and output interdigitated transducer which generates and detects the acoustic wave, respectively. When certain selective films are coated or attached onto the piezoelectric material, the device can then be used as a sensor for hydrocarbons. Generally, hydrocarbon-based molecules interact with the membrane material via a partitioning process and Sauerbrey's equation is used to relate the frequency shift (ΔF) as a function of the absorbed mass (Δm) (Thompson et al., 1991):

$$\Delta F = -\frac{2\Delta m f^2}{A\sqrt{\mu\rho}}$$

where f is the resonant frequency of the crystal (prior to the mass change), A is the surface area, μ is the shear modulus of quartz ($2.95\text{x}10^{11}$ g cm^{-1} s^{-1}), and ρ is the density of the quartz crystal (2.65 g cm^{-3}). It is important to note that there are other factors (i.e. solution viscosity, solution density, viscoelastic processes) that influence the resonant frequency of the crystal in contact with a liquid and the simple relationship between the measured frequency shift and the concentration of analyte in solution does not always hold (Thompson et al., 1991; Lucklum, 2005). However, some of these problems can be minimized by selecting certain coatings and using thin films (Patel et al., 2000).

3.5.3 Chemiresistor/resistance-based sensors

Resistance-based sensors or chemiresistive sensors come in various shapes and forms. Some of them consist of conductive particles (i.e. carbon) that are dispersed in an insulating material (i.e. polymer) and a film is deposited onto a set of interdigitated metal electrodes on a silicon based substrate. Others are based on a conducting (i.e. carbon nanotubes, polymer, gold nanoparticles) or semiconducting (i.e. metal oxides) material placed onto or sandwiched between two metal contacts or electrodes. Figure 24 summarizes some of the different types of resistance-based sensor configurations. When a hydrocarbon molecule is absorbed/adsorbed into a film or onto a conducting/semiconducting material a change occurs in its electrical resistance/impedance and this change is measured using an ohm meter or digital multimeter.

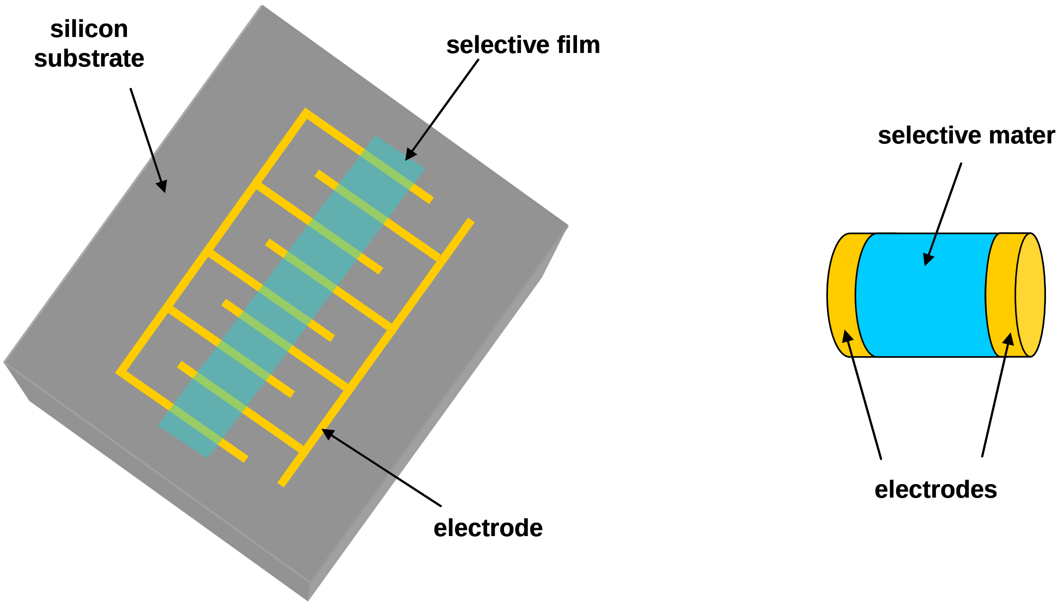


Figure 24 Typical chemiresistor sensors for hydrocarbon detection.

In the case of carbon black/polymer composites, the carbon particles are forced apart when the analyte diffuses into the film and the resistance change is proportional to the separation distance. The sensitivity depends on the type of polymer, the amount of conductive particles added to the polymer and the separation between the electrodes. The fundamental operation of the chemiresistor sensor system is quite simple and electrical resistance measurements are made using simple DC circuitry. The other advantage is the electronic components of the sensor can be easily miniaturized using microfabrication techniques, making these types of sensors highly portable.

3.5.4 Infrared-based sensors

Infrared based sensor systems have been increasingly applied in the detection of organic compounds in environmental samples (i.e. water, air). There are two types of infrared sensors commonly used for environmental monitoring and these are classed according to the region of the infrared spectrum. The mid-infrared (MIR) sensor typically uses a globar (i.e. SiC) radiation source to probe in the 2.5–25 μm region, whereas the near-infrared (NIR) sensor employs a tungsten halogen light source for probing the 0.80–2.5 μm range. Detection of the MIR radiation is achieved using either a mercury-cadmium-telluride (MCT) photoconductor or deuterated triglycine sulfate (DLaTGS) pyroelectric detector, whereas the NIR is normally detected with an indium-gallium-arsenide (InGaAs) diode. Figure 26 illustrates the infrared sensing principle noting that a spectrometer is used to assist during sensor measurements.

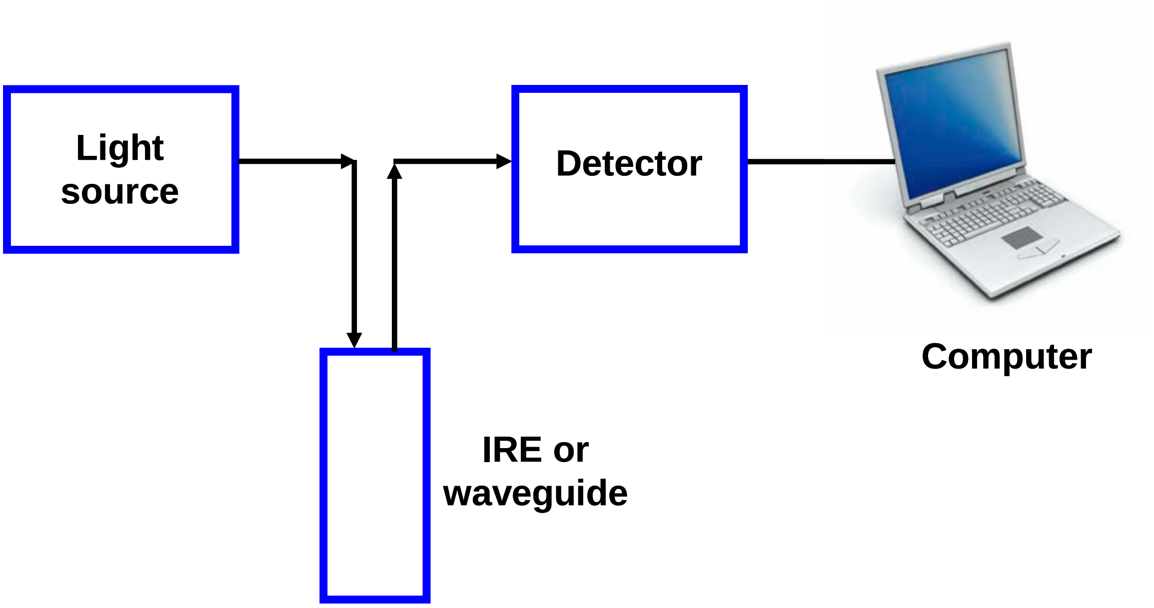


Figure 25 The principles of infrared sensing

The environmental monitoring of hydrocarbons at low levels (ppb to ppm range) has been made possible by employing the principles of attenuated total reflection (ATR) in conjunction with solid-phase micro extraction (SPME) techniques (Pejcic et al., 2009). When infrared radiation strikes an interface between two materials of different refractive indices, some of the light will be reflected and some will be transmitted. A standing wave normal to the reflecting surface is established in the denser medium and an evanescent non-propagating field in the rarer medium. An optically transparent material of high refractive index, known as the internal reflection element (IRE), is used to ensure that the IR beam propagates through a series of internal reflections at the sample/IRE interface. The IRE, or sometimes known as the waveguide, can be either in the form of a trapezoidal crystal (i.e. zinc selenide) that is typically 80 mm long and 4 mm thick or an optical fiber (i.e. silver halide, chalcogenide, quartz glass) that has a length ranging between 1 to 30 meters. Although complete internal reflection occurs at the interface, some of the radiation (evanescent wave) does penetrate into the sample where the sample is in direct contact with the IRE. Only molecules in the region of the evanescent wave will undergo interaction with the IR radiation, since the evanescent wave decays exponentially in amplitude with distance from the IRE surface into the adjacent sample. Generally, a hydrophobic material of less than 50 μm thickness is coated onto the IRE which helps to attract the organic molecules of interest while excluding water and other unwanted interfering molecules from the sensing surface.

3.5.5 Development of sensors for hydrocarbons

A number of reviews have been published prior to 2007 discussing various sensors for the environmental monitoring of hydrocarbons (Lawrence, 2006; Lieberzeit and Dickert, 2007; Pejcic et al., 2007). The analytical properties (sensitivity, selectivity and stability) of many different technologies have been compared and the following conclusions can be drawn from these reviews: a) a great deal of sensors are available for the detection of hydrocarbons and most of them have detection limits in the ppm range; b) the majority of the research effort has been directed towards the search for highly selective materials rather than the development of new transducers; c) many of the sensors are not completely selective and usually require some separation step or statistical processing (i.e. principal component analysis) to discriminate the various signals; d) most experiments have been conducted in the laboratory and very few field measurements have been performed. Although these reviews were thorough, they did not evaluate the performance and potential of the various sensor platforms for geosequestration applications. Furthermore, many papers and commercial sensing systems have appeared since 2007 and the suitability of these devices has not been properly examined.

Tables 15 and 16 compare the analytical performance of a number of sensors that have been used for the detection of hydrocarbon compounds in various environments (i.e. air, water). There are many different sensors available in both the scientific literature and commercially, and the intention is to highlight some monitoring tools that show promising results in terms of analytical performance (i.e. sensitivity, selectivity, robustness) and field readiness.

3.5.6 Gas sensing

The types of sensors available for the detection of hydrocarbons in the gas phase depend on the temperature that the sensor will be exposed to. Sensors for monitoring volatile hydrocarbons at room temperature usually employ a polymer as the sensing membrane, whereas metal (for example Pt, Pd) and metal oxide materials are commonly used when making measurements at elevated temperatures (i.e. >100 °C). Although the development of highly selective stable materials and membranes is a major area of research focus, there are some sensors available that show potential for monitoring in geological formations. The chemiresistor sensor developed by Ho and Hughes (2002) has been used to detect in real time volatile organic compounds (VOCs) in soil (Ho and Hughes 2002). It consists of a polymer coating loaded with conductive carbon particles and is housed in a stainless steel waterproof package that is ~3 cm in diameter (see Figure 26). The authors suggest that the device can be operated in either wet or dry environments. The detection limit of the sensor seems quite high suggesting that the device may not be sensitive enough for field monitoring. However, it has been shown that the sensitivity can be significantly improved down to parts per billion (ppb) levels when a microfabricated preconcentrator is attached to the sensor (Davis et al., 2005). Despite the promising sensitivity and highly stable sensor, there is some concern that it may not be able to completely distinguish between similar types of hydrocarbons, for example benzene, toluene and xylene. In addition, the sensor has not been thoroughly tested under high temperature and pressure conditions, and it is not known how the device will perform during long-term down-hole monitoring.

Figure 26 The chemiresistor developed at Sandia National Laboratories (Ho and Hughes, 2002).

The selectivity of membrane-based sensors for hydrocarbons can be tailored by carefully controlling the membrane composition with certain materials and various methods have been proposed to improve sensor performance (Pejcic et al., 2007). However, most environmental samples are complex and contain a mixture of hydrocarbons and other volatile interferences so that separation is often required. Zellers and coworkers (Whiting et al., 2001; Lu et al., 2003; Lu et al., 2006) have shown that combining gas chromatography (GC) and surface acoustic wave (SAW) polymer arrays into a portable analytical device is a far better approach for tackling the limited selectivity issue. It was demonstrated that over 30 different volatile compounds can be detected down to ppb levels in less than 10 mins. In another study, a gas chromatography-chemiresistor array was used which enabled parts per trillion (ppt) levels to be achieved (Cai and Zellers, 2002). The power demands of such systems are well known and the development of microfabricated gas chromatographs using MEMS technology has addressed this and other limitations (Lu et al., 2005). A handheld system that employs the SAW-GC sensor system (Canary-ThreeTM) is commercially available and is supplied by Defiant Technologies (http://www.defiant-tech.com). The SAW-GC is lightweight (760 g), small in size (7.5x5.25x2.25 inches) and can provide analysis within 2 minutes (Figure 27).

Monitoring aromatic (i.e. BTEX and PAHs) and chlorinated hydrocarbons in the environment is a significant area of sensor research. However, other groups have focused on the development of optical-based sensors for methane. Hennig and coworkers showed that methane can be detected down to ~10 ppm levels using a hand-held NIR tunable laser diode (Hennig et al., 2003), whereas Massie et al. (2006) designed a portable and robust NIR sensor that can be used over a wide temperature range (i.e. -20 to 50°C) (Massie et al., 2006). These infrared-based sensor systems have the ability to distinguish between many different volatile compounds. However, their poor sensitivity is an issue that requires further improvement if these devices are to be routinely deployed during CO_2 storage.

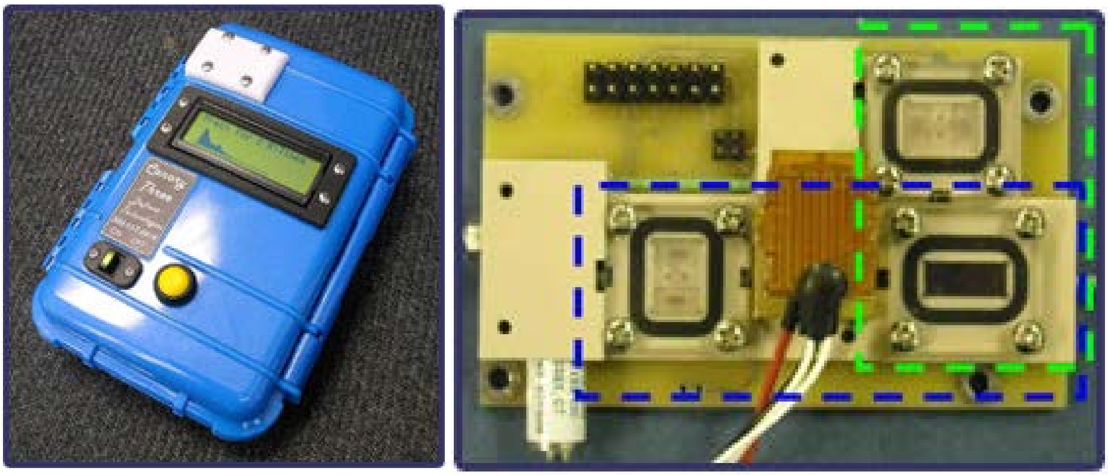


Figure 27 The SAW-GC supplied by Defiant Technologies (http://www.defiant-tech.com).

The automobile industry is under constant scrutiny and control from governments to ensure that the impact of hydrocarbons on the environment is minimal. A number of sensors based on electrochemical detection have been successfully used for monitoring a range of aliphatic hydrocarbons (i.e. propane, butane, etc) in automotive exhaust gas systems which has been recently reviewed (Moos, 2005). The majority of the research is tailored towards developing hydrocarbon sensors that are selective, chemically stable and can withstand high temperatures (Sahner et al., 2005; Sahner et al., 2006). Although most of the sensors are small, simple to operate and cheap, none of them have been used for CO_2 storage and down-hole monitoring applications. It seems that the main concern impeding their application is the poor selectivity and the ability to distinguish between many different compounds that are likely to exist in a typical geological formation.

Some commercial based sensors have been developed for hydrocarbon compounds in the gas phase. Leopold Siegrist GmbH supplies various types of portable devices for the measurement of gaseous and volatile components (http://www.siegrist.de/en/product-overview.html). The MECCOS AW2 is one particular sensor, which has been designed to detect BTX compounds (i.e. benzene, toluene, xylene) and consists of a stainless steel probe that contains a metal oxide semiconductor transducer housed behind a Teflon membrane. The membrane allows volatile components to diffuse through while protecting the metal oxide transducer from water. It is suggested that the device can be used for field deployment over periods of days to weeks for the monitoring of BTX concentrations in various environments such as streams, groundwater and sewerage. The membrane may require regular replacement depending on the condition of the environment to which it is exposed. Changing the membrane is a relatively straightforward procedure; however, it is important that exposure of the metal oxide transducer to air is minimized. Any exposure of the transducer to excess humidity or water is detrimental and will severely affect the sensor lifetime and performance. However, the system is lightweight (~2.6 kg) in total (including analyzer) and requires a 24 V power source (DC). Unfortunately, no studies have been reported in the literature that explicitly uses the MECCOS AW2 for field monitoring.

Table 15 A summary of some useful sensors for the detection of hydrocarbons in the gas phase.

Hydrocarbon	Transducer	Analytical range	Detection limit	Comments	Reference
Various aliphatic and aromatic compounds	Resistance	NA	~100 ppmv (gas)	Relatively cheap and has a temperature control feature. Portable. Very little information available of selectivity	Ho and Hughes (2002)
Various aliphatic and aromatic compounds	Surface acoustic wave	NA	ppb	Portable and compact. Low power. Excellent selectivity	Whiting et al. (2001); Lu et al. (2003); Lu et al. (2006)
Methane	Near infrared	10 ppm - 100 vol%	~ppm	Portable. Fast response time. Highly selective	Hennig et al. (2003)
Methane	Near infrared	NA	~100 ppm	Portable, rugged and fast response time. Highly selective	Massie et al. (2006)
Various aliphatic hydrocarbons	Potentiometric and Resistance	NA	~ppm	Portable, rugged and rapid response. Poor selectivity.	Moos (2005)
Benzene, toluene, xylene	Resistance	1-10 ppm	0.5 ppm (toluene)	Portable and compact. Low power. Affected by humidity.	Leopold Siegrist GmbH

NA: not available, ppmv: parts per million by volume.

3.5.7 Liquid sensing

The chemiresistor sensor developed by Ho and Hughes (2002) for measuring VOCs in the vapor phase has also been used for determining the concentration of VOCs in aqueous solutions. The sensor comprises a GORE-TEX® membrane that allows the passage of vapors, while protecting the sensor surface from water fouling processes (Ho and Hughes, 2002). Although the sensor is reasonably sensitive, the limited selectivity and stability under high temperature/pressure conditions may be a problem for long-term down-hole monitoring.

Other research groups have focused on the development of a fluorescence based sensor for the detection of polycyclic aromatic hydrocarbons (PAHs) in water (Fernandez-Sanchez et al., 2004). Sensors involving fluorescence transduction are particularly suited for monitoring aromatic hydrocarbons, since most of them fluoresce when excited by UV light. Generally, the fluorescence efficiency increases with the number of aromatic rings. It was shown that certain ions that are commonly found in water (e.g. bicarbonate or chloride) do not interfere with the sensor response. In addition, several drinking and waste water samples from different regions were tested and the sensor performed satisfactory. Despite some promising results, further work is needed to determine if the sensor can discriminate between the different types of PAH compounds.

A number of sensors have been developed over the past several decades to directly measure the concentration of hydrocarbons in water. Many of them are unsuitable for field monitoring since they struggle to clearly resolve and separate the signals arising from the presence of hydrocarbon compounds with similar chemical and structural properties. For instance, distinguishing between benzene, toluene and the xylenes is a significant challenge which cannot be easily accomplished by employing a selective membrane or pattern recognition/multicomponent analysis methods. However, the MIR sensor system developed by Mizaikoff and coworkers can simultaneously distinguish between these compounds down to ~0.1 ppm levels in less than 20 minutes (Karlowatz et al., 2004). The sensor uses an ethylene-propylene copolymer to extract the analytes of interest and separation. Quantification is achieved by integrating the individual characteristic infrared absorption frequencies and comparing them against standards. Figure 28 shows the main features of the MIR sensor used for underwater monitoring. Many publications have appeared that use the MIR sensor to monitor the sea and groundwater for a number of different hydrocarbons (Mizaikoff, 1999; Kraft, et al., 2002; Kraft et al., 2003; Steiner et al., 2003a; Steiner, et al., 2003b).

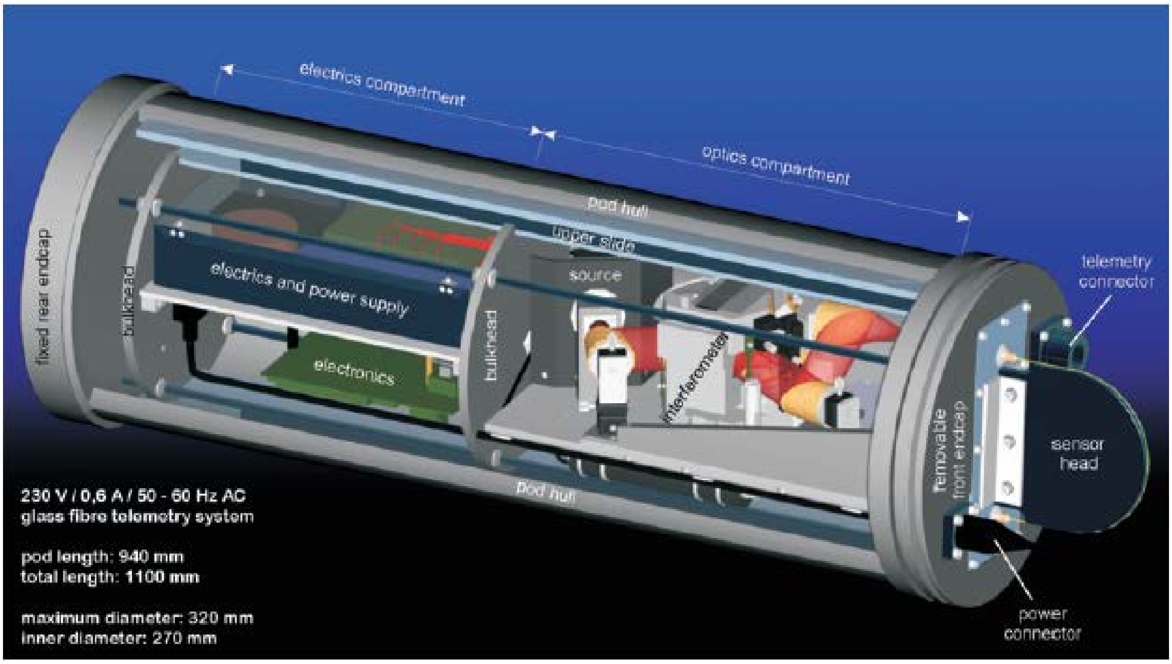


Figure 28 The MIR sensor developed for underwater monitoring (Kraft, et al., 2002).

The performance of the MIR sensor is comparable to other standard methods of analysis and experiments have been performed using both the ZnSe IRE and silver halide optical fibers. Various interferences (e.g. salinity, humic acids or turbidity) do not pose a significant problem (Kraft and Mizaikoff, 2000), suggesting that the MIR sensor behaves reliably during the assay of real water samples. The ability to distinguish between many different organic compounds simultaneously (i.e. aromatic, phenols or alkyl halides) makes the MIR sensor a unique and powerful tool for environmental monitoring. Although the MIR sensor is a promising analytical tool, there are some issues that need to be considered before this device can be used for geosequestration monitoring applications. The spectrometer cannot be operated without a 230 V power supply and it is relatively expensive compared to other technologies (>$10,000 US). The long term stability of the sensor has not been thoroughly evaluated and further work is needed to determine if soaking the sensor in water for extended periods (>1 day) influences its sensitivity. In the case of the MCT detector it needs to be cooled with liquid nitrogen and this presents a challenge when developing an autonomous device.

Various commercial sensors exist for monitoring hydrocarbon compounds in water. One particular sensor that seems useful for detecting hydrocarbons in water is the EFAS (Evanescent Field Absorption Sensor), which is supplied by Leopold Siegrist GmbH (http://www.siegrist.de/en/product-overview.html). The EFAS system consists of a portable photometer and a coiled optical fiber probe that is 15 or 30 meters in length. The optical fiber probe is treated with a polymer cladding and when the probe is exposed to an aqueous solution containing hydrocarbons, the hydrocarbon is absorbed into the cladding and detected by attenuation of NIR light. The sensor is designed for the detection of BTEX (benzene, toluene, ethylbenzene and xylene) compounds in water. The manufacturer states that the intended use is for in situ monitoring of landfill drainage water, surface water, groundwater and industrial waste waters. Due to its extremely fragile nature, the optical fiber probe is housed within a stainless steel mesh cowling for protection and details of the probes construction are presented elsewhere (Burck et al., 1998). A number of papers have been published describing the principle and specifications of the NIR sensor system (Burck, et al., 1998; Buerck, et al., 2001). In terms of portability, the EFAS system weighs ~6.5 kg (mainly due to the photometer unit) and requires a 230 V, 50 Hz power source. Although the probe can be submerged in water, it is recommended that it be used only in shallow waters. Depending on the water quality the EFAS sensor probe may become fouled and this will require regeneration by washing with solvent. Infrared absorption bands in the NIR region are typically broader and less intense compared to those in the MIR range. This usually requires the use of a long waveguide during NIR measurements in order to achieve a similar sensitivity. The fiber optical cable that connects the spectrophotometer to the probe can be fabricated to a significant length, although attenuation of light along the waveguide can also reduce sensitivity. However, some reports show that the limit of detection is improved significantly when using 30 m optical fiber waveguide compared to a 12 m waveguide (Burck et al., 1998). Another concern with the EFAS is the limited selectivity when exposed to a complex hydrocarbon mixture (i.e. petroleum). Though the sensor can perform measurements at two wavelengths, it is not selective to specific compounds and will provide an indication of the sum of hydrocarbons rather than a determination of an individual component.

Chelsea Technologies Group supplies a range of sensors for the detection of hydrocarbons in water (http://chelsea.co.uk/MarineSystems.htm). One particular sensor that may be applicable is the Aquatracka, which is a submersible fluorometer and is used to measure the concentration of PAHs in water (Figure 29). The unit comprises a xenon UV source to excite at a wavelength of ~239 nm and a detector measures the intensity of light at a wavelength of ~360 nm. The sensor is compact, robust (housed in titanium), lightweight (~5.5 kg) and intended for a wide range of environmental and oceanographic monitoring applications. The tool is intended to be submerged to depths of 500 m, however, the supplier’s website suggests that the equipment was rated to as high as 6000 m. The unit can be towed, deployed on a CTD rosette, or ocean glider, for profiling the PAH concentrations in water bodies, or used for long term measurements on fixed moorings. The Aquatracka requires a 12 volt DC power supply, and the xenon light source is stable for up to two years, however, this depends on usage. It is worth noting that the unit utilizes a reference beam in order to compensate for gradually decreasing lamp intensity during the lifetime of the instrument. A number of publications are available in the scientific literature that report the use of the Aquatracka for various environmental monitoring applications (Byrne et al., 1988; Lawford et al., 1990; Stagg et al., 1996; Whelan et al., 1998). There are some concerns that the sensor response is influenced by gas bubbles, turbidity and natural organic matter (i.e. humic acids). Natural organic matter is typically present in aquatic environments at ppm concentrations and the concentration can vary considerably from one region to another. It is recommended that the sensor is not subjected to shock and that the optical windows are not exposed to certain organic solvent (i.e. acetone) as this may cause the seals to leak when placed in water.

Figure 29 The fluorimeter sensor developed by Chelsea Technologies Group (http://chelsea.co.uk/MarineSystems.htm).

Table 16 A summary of some useful sensors for the detection of hydrocarbons in the aqueous phase.

Hydrocarbon	Transducer	Analytical range	Detection limit	Comments	Reference
Various aliphatic and aromatic compounds	Resistance	NA	~1 ppm (water)	Relatively cheap and has a temperature control feature. Uses a GORE-TEX® membrane to prevent water from fouling the surface of the chemiresistor. Portable. Very little information available of selectivity	Ho and Hughes, 2002
Benzene, toluene, xylenes, chlorinated hydrocarbons	Mid infrared	50-1000 ppb	20-100 ppb (varies with molecule)	Highly selective and sensor is unaffected by salinity and turbidity. Expensive and uses a spectrometer that requires high power.	Mizaikoff 1999; Kraft and Mizaikoff, 2000; Kraft et al., 2002; Kraft et al., 2003; Steiner et al., 2003a; Steiner et al., 2003b; Karlowatz et al., 2004
PAHs	Fluorescence	3-250 ng/l	~3 ng/l	Fast response time. Portable. Partially selective.	Fernandez-Sanchez, et al., 2004
Benzene, toluene, xylene	Near infrared	1-100 ppm	~1 ppm (toluene)	Portable and compact. Response time varies between 2 to 30 mins. Partially selective	Leopold Siegrist GmbH
PAHs	Fluorescence	0.001-10 µg/l	ng/l	Portable. Fast response time. Partially selective.	Chelsea Technologies Group

NA: not available.

3.5.8 Summary

Table 17 provides a summary of the most widely used analytical technologies for hydrocarbon detection. Although a great deal has been published on the development of sensor technologies and tools for monitoring hydrocarbons, very little has been applied to CCS monitoring applications. Some of the sensors (i.e. chemiresistor, quartz crystal microbalance, surface acoustic wave) that employ an absorbing membrane are not completely selective and usually require statistical treatment or other methods to separate the analyte signal from other molecules that are present. In addition, these sensors are generally less stable at high temperatures/pressures and over long monitoring periods given that the membrane material can degrade with time. Despite the shortcomings, the chemiresistor and piezoelectric-based sensors are particularly sensitive, simple to operate, small in size and have low power demands that field deployment would not be significant issue. By contrast, optical sensors based on fluorescence and mid-infrared detection tend to be more reliable and stable due to the robust nature of both the light source and the photometer. In addition, these sensors have been extensively used by a number of research groups around the world for monitoring various types of hydrocarbons in harsh corrosive environments (i.e. saline water) (Byrne et al., 1988; Lawford et al., 1990; Stagg et al., 1996; Whelan et al., 1998; Mizaikoff, 1999; Kraft et al., 2002; Kraft et al., 2003; Steiner et al., 2003a; Steiner et al., 2003b). In terms of analytical performance (i.e. quantification and selectivity in complex samples) the mid-infrared sensor is a promising tool for monitoring mobilised hydrocarbons in groundwater and geological formations. It has been shown that various chemical interferences (i.e. salinity, humic acids) do not pose a significant problem and the ability to distinguish many different molecules simultaneously makes the mid-infrared sensor a powerful technology. Although this sensor is capable of addressing many of the concerns in the M&V domain, there are some issues (stability at high temperatures and cost) that need to be considered before it can be routinely used for geosequestration monitoring applications. Furthermore, sensor performance in the geological formation over long periods of time it is not well known and it seems that the long-term stability (over a one year period) of this and other sensors have not been properly evaluated. Improving the long-term sensor stability is certainly one area of research that may need to be addressed in the future.

Table 17 Hydrocarbon monitoring tools and applications.

	High throughput	Cost	Suitability at high temperature & pressure	Down-hole monitoring	Groundwater monitoring	Shallow CCS	Deep CCS
Chemiresistor	Y	L	Y	🟩	🟩	🟥	🟥
Potentiometer	Y	L	Y	🟥	🟥	🟥	🟥
Quartz crystal microbalance	Y	M	🟨	🟥	🟥	🟥	🟥
Surface acoustic wave	Y	M	🟨	🟥	🟥	🟥	🟥
Mid-infrared	🟨	H	🟨	🟥	🟩	🟥	🟥
Near-infrared	🟨	H	🟨	🟥	🟩	🟥	🟥
Fluorimeter	Y	H	Y	🟥	🟩	🟥	🟥
Gas chromatography	Y	H	X	X	X	X	X
Mass spectrometry	Y	H	X	X	X	X	X

Cost: H= High, M=Moderate, L=Low
Y = Yes, N = No
Green = has been tested, Yellow = has potential but requires further testing, Red = untested
X= not applicable

3.6 CO_2 sensing tools

Although outside the scope of this report a number of CO_2 specific tools and sensors have been improved or updated since the earlier report by Ross et al. (2007). Geophysical tools have been discussed in earlier sections of this report, however, a number of additional tools were identified in this search that had not received significant attention in CCS M&V and could provide some additional information for future technology development.

3.6.1 Other geophysical tools

For major types of CO_2 monitoring the table from Chadwick et al. (2007) represents a general view of geophysical tools (Table 18). Down-hole geophysics are also technically considered “shallow” sensing with respect to the signal’s penetration depth, i.e. borehole tomography showing changes around the hole, but are considered a “deep” application in Table 18. Of the geophysical methods available (Table 18) and applied, the use of NMR (Nuclear Magnetic Resonance) also termed MRS (Magnetic Resonance Sounding), GPR (Ground Penetrating Radar) and magnetotellurics are not widely discussed or applied to CCS M&V, but could provide some additional CO_2 sensing tools.

Seismic, gravity and electromagnetics are the most studied methods with results from Fabriol et al. (2011) showing the comparison in CO_2 detection (Table 19) and are covered in Section 3.1.

Table 18 Potential monitoring tools for CO2 influences on both deep and shallow environments (modified from Chadwick et al., 2007).

🟨 Onshore only
🟦 Offshore only
🟩 Onshore & Offshore
🟥 Primary use
🟧 Secondary use
▨ New addition or change to table

			Deep	Shallow	Plume location/imigration	Fine-scale processes	Leakage	Quantification	New addition
Seismic		🟩 3D/4D surface seismic	🟥	🟧	🟥	🟧	🟧	🟥	
		🟩 Time lapse 2D surface seismic	🟥		🟥	🟧			
		🟩 Multicomponent seismic	🟥		🟥	🟥			
	Acoustic imaging	🟦 Boomer/Sparker		🟥	🟧		🟥		
		🟦 High resolution acoutstic imaging		🟥	🟧		🟥		
		🟩 Microseismic monitoring			🟧				
	Well-based	🟩 4D Cross-hole seismic	🟥		🟧	🟥		🟧	
		🟩 4D VSP	🟥		🟧	🟥			
Sonar Bathymetry		🟩 Sidescan sonar		🟥			🟥		
		🟩 Multi beam echo sounding		🟥			🟥		
Magnetics*		🟩 Airborne magnetic	🟧						▨
		🟩 Ground magnetic	🟧						▨
		🟩 Magnetic gradiometry	🟧						▨
Gravimetry		🟩 Time lapse surface gravimetry	🟥	🟧▨	🟧			🟧	
		🟩 Time lapse well gravimetry	🟥			🟧			
Electrical/Electro-magnetic		🟨 Surface EM	🟧	🟥	🟧		🟧		
		🟨 CSMT	🟥						▨
		🟩 Magnetotellurics	🟥						▨
		🟦 Sea bottom EM (CSEM)	🟥	🟥	🟧				
		🟩 Cross-hole EM/imaging	🟥		🟧▨	🟧			
		🟩 Permanenent borehole EM	🟥		🟧▨	🟧			
		🟩 Cross-hole ERT	🟥		🟧▨	🟧			
		🟨 ESP	🟥	🟧	🟥		🟧		
Remote sensing		🟨 Airborne hyperspectral imaging		🟥			🟥	🟧	
		🟨 Satellite interferometry	🟥		🟥				
		🟩 Airborne EM		🟥			🟥		
Others		🟩 Geophysical logs**	🟥		🟧▨	🟥		🟧	
		🟩 Pressure/temperature	🟥				🟥	🟧	
		🟩 Differential GPS	🟥		🟥				▨
		🟩 Tiltmeters	🟥	🟧	🟧	🟧			
		🟨 Magnetic Resonance Sounding		🟥	🟧	🟧			▨
		🟨 Borehole NMR	🟥		🟧	🟧			▨
		🟨 GPR - surface		🟥		🟧			▨
		🟨 GPR - borehole (tomography)	🟥			🟧			▨

*Used to map faults/potential leakage points
** Geophysical logs included gamma, resistivity, neutron, gamma-gamma, induction and magnetic susceptibility
CSMT = Controlled Source Magnetotellurics
CSEM = Controlled Source ElectroMagnetics

Table 19 Seismic, gravity and electromagnetic geophysical methods comparison for CCS M&V (modified from Fabriol et al., 2011).

Method	Verification: minimum quantity (reservoir depth > 800 m)	Leakage detection: minimum quantity (reservoir depth)	Leakage detection: minmum quantity in shallow reservoir (~250 m)	Limitations
4D sesmic	100s Kts	Few Kt	100s t	Reservoir: low porosity, layer thickness
EM	1 Mt	?	10s Kt	Low resistivity, thin layers
Gravimetry	1 Mt	?	10s Kt	Seasonal surface variations

Magnetotellurics

Electrical resistivities can be used to distinctly differentiate CO_2 from surrounding rocks, but depth of penetration is difficult with more established EM methods. Passive magnetotellurics use natural electromagnetic fields and have previously been used for very deep crustal studies. This method is severely limited by electromagnetic noise that occurs from man-made structures like railways and power lines. However, using a controlled source can reduce this interference and provide a method capable of mapping conductive and resistive structures. Controlled source magnetotelluric (CSMT) is similar to CSEM used in marine settings, and is more suitable for deep monitoring of CO_2 as it can penetrate to depths beyond most CCS injection levels.

Only one study has tested CSMT for application in CO_2 sequestration. Both 1D and 2D models were tested for potential to show CO_2 migration with CMST using a greatly simplified reservoir scenario based on the conditions at Ketzin (Streich et al., 2010).

Anomalies were clearly visible in the modelled data and were distinctly different for CO_2 thickness in the strata. Results indicate that surface measurements alone were not recommended due to signal dissipation through the atmospheric-half space, unlike the application on the deep sea floor that has a conductive saline water layer above. Installation of CSMT in shallow boreholes is recommended to produce a better signal and improve the value of this technique for monitoring (Streich et al., 2010). An example of the set up for CSMT is shown in Figure 30.

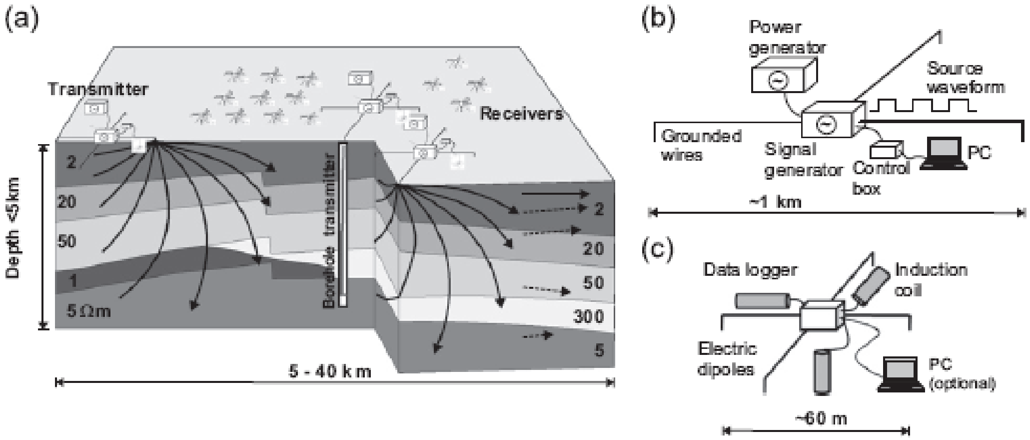


Figure 30 a) Example of CSMT layout from Streich et al. 2010. Numbers and shading relate to subsurface electrical resistivity. Passive MT current flow is indicated by the dashed arrows, whereas the solid arrows show CSMT current flow (3D); b) CSMT source; c) Receiver set up.

CSMT has not been applied previously primarily because of the logistical setup and the intensive data processing involved (Streich et al., 2010). Future studies of more complex geometries were recommended by Streich et al. (2010) before this technique could be applied, but CSMT has some potential as a CCS M&V tool.

Magnetic resonance sounding (MRS)

Nuclear Magnetic Resonance (NMR) equipment is generally classified according to the sample volume (Legchenko et al., 2002). Chemical NMR and biomedical MRI (Magnetic Resonance Imaging) applications that many are familiar with have great resolution, but only operate on small volumes. Using the same technology on a larger scale (a few 1000 m^3), MRS offers some potential applications in near surface monitoring, and is also valuable for down hole monitoring. Bore hole geophysical applications (dm^3) for MRS use Schlumberger and NUMAR tools, whereas HYDROSCOPE and NUMIS tools are examples for use from the surface (Legchenko et al., 2002).

Surface application of MRS can determine aquifer boundaries (depth, thickness and spatial extent), free water content and flow properties of water-bearing formations (Roy and Lubczynski, 2003). These measurements can be to a depth between 45 and 175 m, with a typical investigation depth of 100 m (Legchenko et al., 2002; Hunter, 2003). Unlike other geophysical techniques, MRS can differentiate between saturated (free) and unsaturated (bound) water (Roy, 2009). MRS has been applied with EM to studying intrusion of saline water into freshwater aquifers creating subsurface electrically conductive zones. Uncertainty associated with TEM measurements was insignificant in MRS results (Legchenko et al., 2008), but electromagnetics is the superior method for mapping saline intrusions that may occur in the form of displaced brine induced by CO_2 injection.

MRS is affected by conductive ground and groundwater, thickness (resistivity) of specific layers, interference from industrial installations and power lines, electrical storms and magnetic geology. Therefore, it is suited particularly to areas of consistent stratigraphy and absence of ambient noise (Legchenko et al., 2002; Hunter, 2003; Roy, 2009; Roy and Lubczynski, 2003). A compromise also exists between depth and spatial resolution. The deeper the investigation the lower the lateral resolution and, in turn, a greater probability that small leaks would not be observed near the surface.

The ability to map porosity changes could be valuable in mapping CO_2 leaks if mineral precipitation was considered a likely side effect. NMR was used down-hole at Ketzin to characterise the storage formation and calculate permeability (Norden et al., 2010). Down-hole NMR was sensitive to the borehole calliper in this study. NMR was used to understand CO_2 migration in porous rocks using supercritical CO_2 and conditions representative of 800m depth in an aquifer (Suekane et al., 2009).

NMR (small scale) can be used to observe isotopes of some elements such as H, C, P (Roy and Lubczynski 2003). Although not yet possible using present technology, it is feasible that MRS can differentiate between hydrogen and deuterium and could be used to map leaks if deuterium tracers were used. In the down-hole application other isotope tracers such as C^{13} tracers could also be used. The concentrations required to observe this isotopic tracer signal from the surface are unrealistically high with other interferences and depth of monitoring required, however this method would be a suitable test for a very shallow (few metres) CO_2 injection such as ZERT.

Ground penetrating radar

GPR has a limited depth of penetration compared to other geophysical techniques and is not likely to provide improved monitoring methods. However, using natural analogues for CO_2, Arts et al. (2009) demonstrated GPR showed a deeper penetration of the signal (with deeper reflectors) in the zone of CO_2 leakage. This coincided with loss of vegetation and an increase in surface water content that changes the soil electric/dielectric properties. With this example and others (Pettinelli et al., 2008), the correlation with GPR is *not* directly correlated, but does spatially map the zone of CO_2 at a shallow depth.

Using GPR technology down-hole (tomography), some beneficial data may be generated for monitoring in a similar manner to the MRS and other down-hole logging tools. All of these tools typically have depth of penetration of <60 cm (IEA, 2011). A number of other logging tools are potentially suitable for monitoring CO_2, including sonic, neutron, density, resistivity, and pulsed neutron logging tools, whereas radiometric geophysics (gamma logs, gamma-gamma logs) are less likely to be useful. These tools could provide information on changes in the subsurface properties related to CO_2 migration into the wellbore. In order to effectively assess the potential effects of CO_2 leakage for any of these methods, a pre-injection baseline is critical, followed by time-lapse logging during and post-injection.

3.6.2 Update on other CO_2 tools

The injection and storage of supercritical CO_2 in geological formations is a worthwhile process provided that the CO_2 leakage rates are negligible in terms of having no or very little impact on the biosphere. Migration of the supercritical CO_2 plume through the subsurface is a real possibility and the rate of CO_2 leakage will depend on a number of factors which have been previously discussed in section 2. The detection of CO_2 for the purpose of identifying a potential leak is an important aspect of the CCS monitoring and verification program. A significant number of papers and patents (>450 combined) have been published over the last two decades on tools for monitoring carbon dioxide. The majority of these articles relate to the atmospheric monitoring of CO_2 emissions from vehicles, agricultural, industrial and anthropogenic processes. In addition, there is a significant amount of research dealing with the detection of dissolved CO_2 in water and a number of reviews have been recently published on this topic (Johnson et al., 2007; Moore et al., 2009). Compared to atmospheric and water monitoring, very few articles have been found that explore the use of carbon dioxide sensors for geosequestration and CCS applications. However, this report will highlight potential sensing technologies that are available for monitoring CO_2 in the geological formation, noting that some of them are almost at a stage of being routinely deployed.

A range of sensors have been developed for the detection of carbon dioxide and Table 20 provides a summary of some of the technologies available. There appears to be considerable interest in developing either optical (i.e. infrared) or electrochemical (i.e. potentiometric) based sensing systems. The majority of the monitoring experiments have been tailored towards detecting carbon dioxide in the atmosphere for the purpose of studying the effects of global warming. However, some research has recently appeared (i.e. in the last several years) into sensor systems for monitoring underground carbon dioxide due to CO_2 storage. In particular, Barr et al. (2011) have used a laser-based near infrared instrument and monitored the concentration of carbon dioxide during a 30 day controlled release experiment performed at the zero emissions research and technology (ZERT) facility (Barr et al., 2011). Figure 31 shows the typical results obtained over the course of the 30 day release noting that the flow rate was maintained at 0.3 tCO_2/day (Barr et al., 2011).

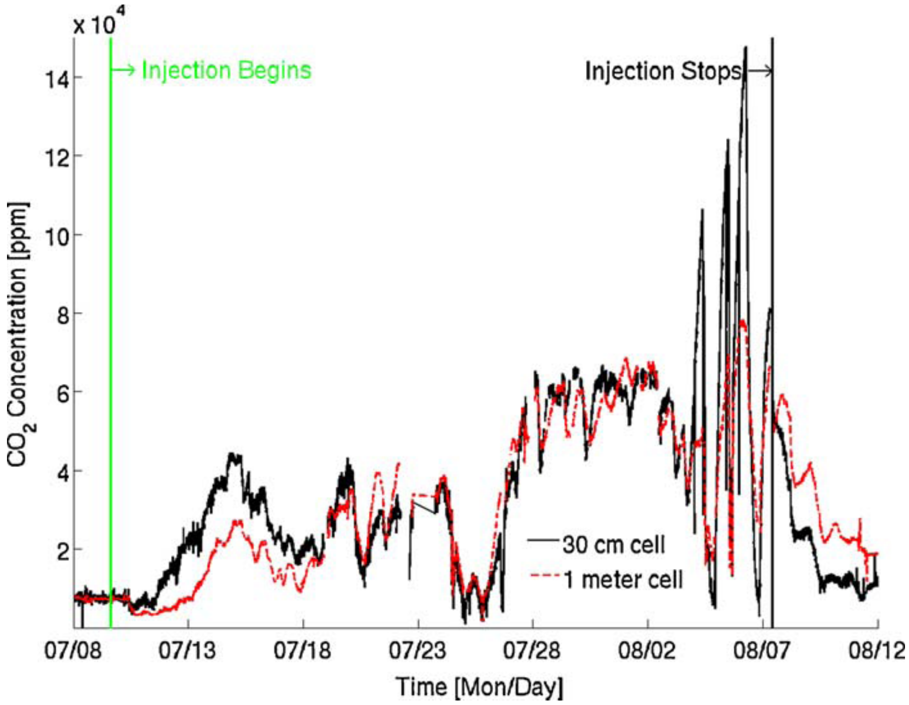


Figure 31 A plot of the CO2 concentration measured as a function of time with a fiber optic near infrared based sensor. Diagram taken from Barr et al., 2011.

Evidently, the laser-based near infrared instrument detected an elevated CO_2 concentration after injection of carbon dioxide. The authors have attributed some of the daily variations in the CO_2 level to events in the weather (i.e. rain) along with other above ground effects in the climate (i.e. temperature, pressure and wind speed). Although the instrument developed by Barr et al. (2011) is relatively stable and detected changes in the carbon dioxide levels underground (~0.75 m below the surface) (Barr et al., 2011), the authors do not provide any data on the limit of detection and the dynamic range. In addition, it is suggested that the sensor may only be suitable for detecting CO_2 down to ~1 km depths, since attenuation losses along the fiber optic is an issue and can lead to deterioration in the sensor sensitivity.

Other groups have designed an integrated multiple sensor system that monitors the level of carbon dioxide along with other physical and chemical properties of the reservoir fluid (Dong et al., 2008).

This tool provides real time measurements and is stable at high temperatures and pressures (Dong et al., 2008). Figure 32 shows a schematic diagram of the down-hole fluid analysis (DFA) tool that has been tested and developed by various organizations (i.e. Schlumberger, Shell, StatoilHydro, Eni Norge). However, Schlumberger have various patents on this technology and further information is provided in the following website http://www.slb.com/services/evaluation/wireline_open_hole/insitu_fluid/modular_formation_dynamics_tester/comp_fluid_analyzer.aspx). The carbon dioxide sensor is based on near infrared detection and it was shown that the sensor provides accurate data when compared to standard laboratory methods (Dong et al., 2008). However, no information has been provided on the limit of detection and sensor stability over long periods of monitoring (i.e. weeks to months). Despite the need for some further testing (i.e. detection limit and long-term stability), the DFA sensor system seems to have potential for long-term monitoring of carbon dioxide in relation to CCS applications.

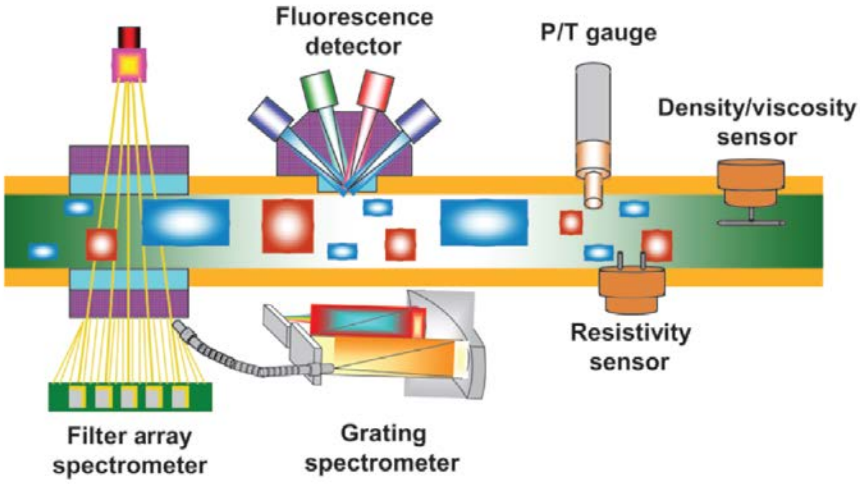


Figure 32 The down-hole fluid analysis (DFA) system developed for monitoring carbon dioxide along with other chemical and physical properties of reservoir fluids. Diagram taken out of (Dong et al., 2008).

3.6.3 Summary

Very little has been published on the application of carbon dioxide sensors to the high pressure/high temperature environments of CO_2 storage reservoirs. Of the sensors that have been developed commercially and in the scientific literature most of them cannot detect ppb levels as required for an acceptable CCS monitoring and verification program. In terms of achieving adequate selectivity (i.e. distinguishing between other compounds and interferences) and stability over long periods of measurement time, the optical based sensing systems seem to be the most promising. However, many of them are not robust and small enough (including spectrometer) to be placed directly in a high temperature and pressure slim-hole environment. Although the widespread use of optical fibers by the telecommunications industry suggests that this is not a significant limitation in the context of continuous monitoring in harsh and inaccessible environments. Indeed, there has been significant growth over the last decade in the use of fiber-optic chemical sensors for detecting a range of compounds and this has been recently reviewed (Wolfbels, 2008). However, further work is still needed to develop a relatively inexpensive device (<$5,000 US) that has low power requirements and can be operated autonomously with minimal user intervention. In addition, the long-term drift (over a one year period) of the various carbon dioxide sensors outlined in Table 20 have not been properly evaluated and this needs to be addressed in the future.

Table 20 A summary of some useful sensors for the detection of carbon dioxide.

Sensor	Transducer	Analytical range	Detection limit	Comments	Reference
Near-infrared	Optical	NA	NA	Rapid response time and robust. No data has been provided on the effect of other volatile compounds. Experiments were performed above and underground.	Barr et al., 2011
DFA (Near-infrared)	Optical	NA	NA	Stable at high temperatures and pressures. Robust and highly accurate. Provides additional chemical and physical information. Does not seem to require periodic calibration.	Dong et al., 2008; Schlumberger (http://www.slb.com/services/evaluation/wireline_open_hole/insitu_fluid/modular_formation_dynamics_tester/comp_fluid_analyzer.aspx)
Near-infrared	Optical	NA	NA	Suitable for both the detection of CO2 in the gas and liquid phase. Response is linear over the 0.1 to 1 bar range. The authors suggest that the sensor can be operated down to depths of ~800 m.	Orghici et al., 2008
Mid-infrared	Optical	10-100 vol%	0.5 vol%	Highly selective and fast response time (<1 min). Responds linearly over a wide concentration range. Experiments were performed in the laboratory at room temperature.	Charpentier et al., 2009
Mid-infrared	Optical	NA	350 ppm	Highly selective and robust. Cheap compared to other infrared-based sensors.	Mulrooney et al., 2007
Vaisala (Infrared)	Optical	0-20 % (0-200,000 ppm)	~ppm	Portable, robust and accurate. Has interchangeable probes for different concentration ranges. Tests have been conducted in a number of different waters. Can be used in the temperature range of -20 to 60 °C	Johnson et al., 2010 (http://www.vaisala.com/en/Pages/default.aspx)
Fluorescence	Optical	0-30 %	35 ppb	Sensor is reversible and responds within several minutes. Sensor has excellent sensitivity, however sensitivity depends on temperature. Unaffected by pH and flow	Wencel et al., 2010

Sensor	Transducer	Analytical range	Detection limit	Comments	Reference
				rate. Stable over a 7 day testing period.	
Potentiometric	Electrochemical	10-5000 ppm	~ppm	Based on a lithium-barium carbonate membrane and yttria-zirconia solid electrolyte. Fast response time and stable at high temperatures. Sensor signal durable over a 5 month testing period.	Bak et al., 2002
Potentiometric	Electrochemical	1000-106 ppm	100 ppm	Based on lithium a carbonate & LiSICON membrane. Fast response time and stable at high temperatures. Poor recovery time. Sensor sensitivity varies with carbon dioxide concentration. Unaffected by humidity.	Menil et al., 2005
VS-1000 (Infrared)	Optical	0-12,000 ppm	1 ppm	Measures dissolved carbon dioxide concentration. Unaffected by pressure (up to 10 bar), density and solution properties. Can be operated for more than 10,000 hrs without routine maintenance. Can be used within -2 to 85 °C	Vital Sensors Technologies (http://www.vitalsensorstech.com/PRODUCTS_new.html)
HydroC (Infrared)	Optical	0-1000 ppm 0-3000 ppm	1ppm	Lightweight (~6 Kg) and uses a 12 V power source. Fast response time. The supplier claims that it can be used at large depths (~6000 m) and temperatures between 3 to 30 °C. It is suggested that the sensor is stable over long term monitoring periods (12 months) and does not foul.	Contros (http://www.contros.eu/products-hydroC-CO2.html)

4. Application of study

4.1 Main observations from case studies and technology evaluation

The areas covered in this review of the feasibility of monitoring techniques for substances mobilised by CO_2 storage builds substantially on the earlier work by Ross et al, (2007). The approaches taken and workflow used have been equally useful in identifying new potential tools and also for confirming the earlier findings.

A conclusion made in the earlier report still appears to hold true, that is "few suitable sensing technologies, applicable to monitoring chemical changes associated with CO_2 storage down-hole, are available. This represents a significant gap in technology and is of particular importance when considering the requirement for new monitoring technologies that will be necessary for large scale implementation of carbon capture and storage" (Ross et al, 2007).

However, there is the potential for an increasing number of tools to be used to develop integrated multi-analyte sensors for real time qualitative and quantitative analysis, along with data acquisition and transfer. Some of the electrochemical and optical detection platforms appear more sited to adaptation and deployment as they are already relatively inexpensive, rugged, easily miniaturised, low in power requirement and sensitive. Solid state devices, such as new generation pH probes are beginning to have the sort of specifications required for deployment in deeper and more aggressive environments.

4.1.1 Physical parameters

Pressure measurement is a fundamental requirement of any CCS monitoring system. Pressure transients occur ahead of the migrating CO_2 plume potentially allowing the detection of changes some distance away from the source of $CO_{2.}$ This increases the coverage of the individual components (i.e. wells) of the monitoring system and increases the likelihood of early detection and remediation.

Complexities do arise however in the use of these and other tools and technologies (e.g. DTS and fibre optics) as they can produce large volumes of data. Interpreting the data can be highly complex and, in the case of pressure, it can be affected by numerous processes depending on deployment in the storage reservoir or overlying permeable aquifers (e.g. localised perturbations due to extraction of water or production of hydrocarbons, seasonal variations and unknown recharge rates). Calibrating the data to detect CO_2 related anomalies may require considerable understanding of the systems involved and extensive computing software, facilities and expertise. These issues arise not only for pressure data, but for all cases where considerable data acquisition occurs.

Capital costs of pressure instruments are variable and dependant on the sophistication of monitoring required. In general, this is a mature field and there are specific tools available depending on the monitoring environment (Table 10). Some of the newer technologies (for example fibre optics) may be expensive and their long term functionality and stability is unproven. For details of the technical specifications of selected pressure monitoring tools, refer to Section 3.1.

4.1.2 Geophysical tools

Addressed extensively in the IEA GHG report “Quantification Technologies for CO_2 Leakage” (2011), our review of geophysical monitoring has tended to focus on alternative technologies commonly employed in shallower environments using mineral exploration and agricultural approaches. Many techniques do work in both the shallower and deeper environments as evidenced by Chadwick et al., (2007) presented in Table 20 and the work summarised in the IEA GHG report Quantification Techniques for CO_2 leakage (2011).

Irrespective of the methods used to monitor the subsurface via geophysical methods, depth to “target” will always limit resolution for identifying leaks. As alternative approaches, electromagnetic and gravity surveys do appear to show some promise, as does magnetotellurics (though this method has not currently been tested in a CCS environment). Crosswell seismic methods are limited in their spatial extent though may be valuable for testing wellbores as potential leakage conduits.

In the near term, where possible 4D seismic remains of great value, closely followed by surface deformation monitoring techniques. Both of these have been successfully employed independently in CCS projects at commercial scale (Sleipner and In Salah respectively).

4.1.3 Biological technologies

Not surprisingly information on conducting extensive biological monitoring for CCS was limited. While this was found to be a challenging approach at depth, the relatively low cost of surface arrays (compared to geophysics) makes this technology appealing.

Few tests have been conducted (on vegetation or microbial systems) but there are successes from natural analogue and shallow release studies by way of “calibration”. As some of these tools have not yet been tested extensively in the CCS domain, the changes in vegetation or microbial community anticipated for these tools may not yet be identified and developed. Some tools e.g. phylogenetic chips, have shown potential after deployment in the mineral exploration domain and are anticipated to be of similarly good value to CCS. These tools could perform as low cost assurance monitoring tools, though testing is required to confirm their usefulness in other settings.

It is expected that the existing tools discussed in Section 3.2 and highlighted in Table 13, once calibrated to a CCS domain, will produce simple to use, field portable and rapid biosensors for future deployment.

4.1.4 Geochemical tools

The geochemistry of subsurface fluids has traditionally been characterised by direct fluid sampling. Advances, such as the use of the U-tube or other sampling methods to obtain pristine samples at reservoir conditions have been complemented by analysis in the field (e.g. mass spectrometry of gases and tracers) or in laboratory environments (e.g. use of ICP-MS or other techniques). Finding deployable tools that might compete with laboratory instrumentation in terms of specificity and sensitivity have tended to limit the availability of tools for inorganic geochemical monitoring (i.e. both cations and anions, and other species for that matter). This is because many in situ tools simply cannot detect species to the low levels that laboratory equipment can.

The advancement of ion selective electrodes (ISE) to sensitivities of the order of 10^6-10^9M allow for the consideration of these tools for deployment that will return similar results to laboratory testing.

Remote interrogation of these tools is possible, but automation of some of the chemical sensors remains challenging. There are some drawbacks however, as traditional ISEs currently suffer from sensor drift; the need for matrix matching; calibration requirements; the requirement of different storage solutions for different analytes; use of internal reference solutions and inappropriate detection levels for some species. But new advances in solid-state electrodes and sensor arrays have contributed toward improving some tools such that increased detection limits miniaturisation and reduced calibration times are occurring. Targeting the right group of species for a given site could allow for the building of a powerful array incorporating other monitoring tools looking specifically for changes in particular metal concentrations, pH and $CO_{2(g)}$.

The situation is similar for anion monitoring, with traditional ISEs suffering from the same suite of drawbacks as described above. However, these too are undergoing rapid advancements in technology with lab-on-chip solutions being developed to miniaturise tools for future deployment.

4.1.5 Hydrocarbon and organic sensors

Hydrocarbons and organic sensors were included due to their pervasive presence in the subsurface. In many situations, depleted oil and gas fields have and will continue to be targeted for CO_2 storage. Similarly EOR opportunities that aid in the economics of CO_2 storage (e.g. Weyburn or Cranfield) will mean that M&V will take place in locations with abundant hydrocarbon compounds present.

Many of the sensors available are not particularly selective to specific compounds; however this is not regarded as a concern for monitoring of depleted hydrocarbon reservoirs where a range of compounds may be present. However, it will be an issue if the sensor is required to monitor for a specific organic tracer compound (e.g. a perfluorocarbons).

Increased concerns about the mobilisation of organics (in particular BTEX compounds) into potable aquifers (related to recent coverage in coal seam gas [CSM] or shale gas activities) could become an issue for CCS. This means that tools or sensors may need to be deployed in shallow aquifers for public assurance at new or existing CCS sites. Furthermore, conflicts between competing activities in the same area could occur. In parts of eastern Australia (Great Artesian Basin), storage of CO_2 and recovery of coal seam gas may occur in proximity to one another. BTEX problems are already being encountered in the CSM industry in an area with potable groundwater causing considerable community concern.

While some small and relatively robust sensors for hydrocarbons are available, their long term drift and stability in aggressive environments may require further testing. It is anticipated that monitoring of overlying aquifers to show an absence of organics will be an increasing focus for assurance of potable water integrity. .

4.1.6 CO_2 Sensors

There is very little published work on deeper deployment of CO_2 sensors that can withstand the higher P/T conditions below 800m. Rather, many tools look at near surface or atmospheric monitoring. Many types of sensors do not have the sensitivities to ppb levels that may be necessary to identify first evidence of leakage or breakthrough. Nor are most tools easily miniaturised as yet, though optical fibres do show promise in this area. Drift and other operational aspects need to be considered before tools are ready for commercial deployment down-hole.

4.1.7 Capture contaminants

While many of the monitoring scenarios, such as pressure monitoring, relate to a specific location or depth interval, in the case of monitoring capture contaminants from gas streams, tools from many disciplines can be employed. The review in Section 2.5 illustrates that all manner of cations, anions organic species and inert gases may be entrained in the CO_2 stream to be injected underground. Knowing the composition of the CO_2 stream prior to injection is regarded as an important aspect of storage and monitoring. The benefit may be the application of the more quantitatively significant species (e.g. argon) to be used as a tracer for future M&V purposes. The tools then employed for subsurface monitoring would likely be applicable for periodic characterisation of the injectant as well as allow for identification where more than one effluent stream is co-mingled prior to disposal. This monitoring and characterisation may be important if keeping stream compositions within certain specifications where a change in composition may affect the compressibility, injectivity or significant reactive compounds could be identified prior to coming into contact.

4.2 Application of results to the IEA GHG CO_2 monitoring selection tool

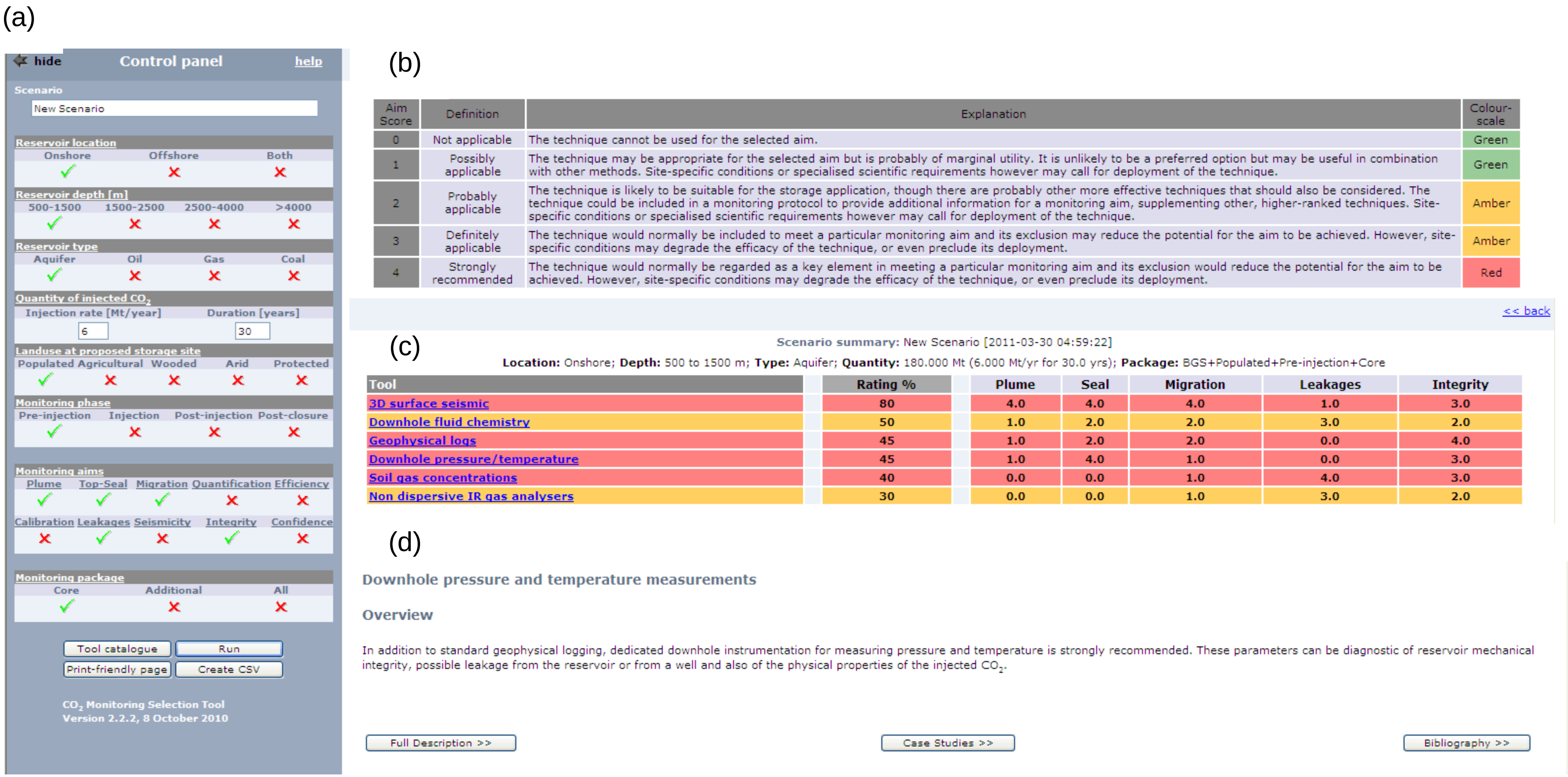
The IEA GHG CO_2 Monitoring Selection Tool[1] is an interactive program designed to aid in the building of a monitoring and verification program for new storage sites. It gives a variety of simple scenarios (onshore, offshore, populated, agricultural settings; [Figure 33]) that can be used to build a realistic, site specific monitoring and verification program.

General input data is inserted at the control panel (Figure 33a) and the simulation run. There is information to explain the traffic light colouring system (Figure 33b) to show which M&V tools or approaches might fit the scenario best. The output scenario summary (Figure 33c) using the traffic light colouring system, shows which tools are possible and their overall rating for both the scenario and for each of the monitoring aims. By clicking on the tool listed, for example “Down-hole Pressure and Temperature Measurements” (Figure 33c) the user is taken to a section that gives an overview (Figure 33d) of that tool/measurement and a series of additional pieces of information are presented including case studies and reference materials. The combination of obtaining case study information (Section 2.6) and some assessed new tools may be valuable information that can be used to update the Monitoring Tool. It is also possible to add new sections on tools that might be ready for testing, but have so far not been utilised due to either;

- Not used in a CCS environment to date
- Not adapted for high pressure/high temperature environments
- Not been deployed outside of a laboratory or other “clean” environment (e.g. food or beverage industry)

Where possible the technology evaluated in Section 3 has been accompanied by a table using a similar (but reversed) traffic light colour coding system (e.g. Table 19 hydrocarbon sensors). This has been conducted to complement the Monitoring Selection Tool (although the colour coding is reversed to match the work of Chadwick et al., 2007 and the IEA Report (Quantification Techniques for CO_2 leakage (2011)).

It is hoped that this summary of the technologies, is appropriate for input into the Monitoring Tool during its next update.



Scenario: New Scenario

Reservoir location

Onshore	Offshore	Both
✓	✗	✗

Reservoir depth [m]

500-1500	1500-2500	2500-4000	>4000
✓	✗	✗	✗

Reservoir type

Aquifer	Oil	Gas	Coal
✓	✗	✗	✗

Quantity of injected CO_2

Injection rate [Mt/year]	Duration [years]
6	30

Landuse at proposed storage site

Populated	Agricultural	Wooded	Arid	Protected
✓	✗	✗	✗	✗

Monitoring phase

Pre-injection	Injection	Post-injection	Post-closure
✓	✗	✗	✗

Monitoring aims

Plume	Top-Seal	Migration	Quantification	Efficiency
✓	✓	✓	✗	✗
Calibration	**Leakages**	**Seismicity**	**Integrity**	**Confidence**
✗	✓	✗	✓	✗

Monitoring package

Core	Additional	All
✓	✗	✗

CO_2 Monitoring Selection Tool
Version 2.2.2, 8 October 2010

Aim Score	Definition	Explanation	Colour-scale
0	Not applicable	The technique cannot be used for the selected aim.	Green
1	Possibly applicable	The technique may be appropriate for the selected aim but is probably of marginal utility. It is unlikely to be a preferred option but may be useful in combination with other methods. Site-specific conditions or specialised scientific requirements however may call for deployment of the technique.	Green
2	Probably applicable	The technique is likely to be suitable for the storage application, though there are probably other more effective techniques that should also be considered. The technique could be included in a monitoring protocol to provide additional information for a monitoring aim, supplementing other, higher-ranked techniques. Site-specific conditions or specialised scientific requirements however may call for deployment of the technique.	Amber
3	Definitely applicable	The technique would normally be included to meet a particular monitoring aim and its exclusion may reduce the potential for the aim to be achieved. However, site-specific conditions may degrade the efficacy of the technique, or even preclude its deployment.	Amber
4	Strongly recommended	The technique would normally be regarded as a key element in meeting a particular monitoring aim and its exclusion would reduce the potential for the aim to be achieved. However, site-specific conditions may degrade the efficacy of the technique, or even preclude its deployment.	Red

Scenario summary: New Scenario [2011-03-30 04:59:22]

Location: Onshore; **Depth:** 500 to 1500 m; **Type:** Aquifer; **Quantity:** 180.000 Mt (6.000 Mt/yr for 30.0 yrs); **Package:** BGS+Populated+Pre-injection+Core

Tool	Rating %	Plume	Seal	Migration	Leakages	Integrity
3D surface seismic	80	4.0	4.0	4.0	1.0	3.0
Downhole fluid chemistry	50	1.0	2.0	2.0	3.0	2.0
Geophysical logs	45	1.0	2.0	2.0	0.0	4.0
Downhole pressure/temperature	45	1.0	4.0	1.0	0.0	3.0
Soil gas concentrations	40	0.0	0.0	1.0	4.0	3.0
Non dispersive IR gas analysers	30	0.0	0.0	1.0	3.0	2.0

Downhole pressure and temperature measurements

Overview

In addition to standard geophysical logging, dedicated downhole instrumentation for measuring pressure and temperature is strongly recommended. These parameters can be diagnostic of reservoir mechanical integrity, possible leakage from the reservoir or from a well and also of the physical properties of the injected CO_2.

Figure 33 The IEA GHG Monitoring Selection Tool1 (a) initial control panel used to input the site circumstances (b) information to evaluate possible application of selected tools (c) recommendations and ratings of the tools for different aspects of the monitoring and (d) additional information that can be used to assess the potential of a particular M&V approach with case studies and source references.

[1] (http://www.ieaghg.org/co2tool_v2.2.2_product_joomla/co2tool_panel.php)

5. Conclusions & future work

5.1 Conclusions

The literature and web-based platforms used in this study contain significant information on the types of substances that might be mobilised or affected by CO_2 storage. Some of the background information and workflows we used are described in the introduction (Section 1) and in more detail in Appendix 2.

In Section 2, the following effects and parameters that could be monitored based on the impacts that CO_2 release might have on the subsurface have been identified and discussed in this study:

- Flow effects (including pressure, density, viscosity, temperature)
- Biological effects or changes (including changes to plant species, bacteria and general ecology, much of which has been drawn from the microbial ecology and mineral exploration literature as well as a few CCS studies where recent testing of these approaches has taken place)
- Geochemical effects (including the oxidation/reduction state of fluids and minerals, and the monitoring of changes to the metals, metalloids and anions. Species entrained in the capture gas are also considered)
- Hydrocarbons and Organics (including compounds that might be found in depleted oil and gas fields, or in EOR [enhanced oil recovery] environments, mobilisation of hydrocarbons removed by the solvent effects of supercritical CO_2 from organic matter [source rocks, coals or hydrocarbon reservoirs], organics entrained in the capture gases from fossil fuel processing or burning.
- CO_2 itself (where the Ross et al. (2007) report has been updated to include a review of potential monitoring tools for CO_2)

Some of the materials used were previous IEA GHG reports, some of which were in draft format or undergoing review. They were very useful sources of information and where possible we have avoided duplication of their work. Another major source of information was the use of case studies. Only pilot and research CO_2 storage sites employ comprehensive monitoring set ups that include geochemical sampling and other subsurface measurements such as pressure and temperature using monitoring wells. Commercial sites, on the other hand, largely rely on a range of geophysical and remote sensing techniques employed at the ground surface. Generally, standard petroleum industry monitoring equipment is used in existing projects for the injection interval (with the addition of a few novel tools such as the U-Tube sampling system) and standard groundwater industry tools are employed for shallow aquifer monitoring. An analogue system for the detection of displaced brines from CO_2 storage sites is the monitoring for the location of the seawater-freshwater interface in coastal areas. In most cases, direct monitoring of pressure, temperature and fluid chemistry is limited to the injection horizon and, for assurance purposes, in shallow groundwater aquifers. With the exception of Cranfield, above-injection zone monitoring is generally covered only by indirect methods. Unfortunately, it is difficult to get a hold of technical specifications of the employed sensors at individual sites and only well schematics showing the conceptual monitoring design and placement of tools are available through the published literature.

Substances that could be mobilised by CO_2 have been identified in Section 2 where possible though there can be ambiguity with respect to which substances are mobilised by CO_2 and which are measuring a combination of the mobilised substance and the CO_2 itself. The possibilites are many and a process of identifying the relevant substances for a given geological site should be assessed as a part of the overall M&V strategy.

In Section 3, where the potential tools and technologies are identified and evaluated, a small summary and table accompanying the results are presented to aid in the identification of the range of tools that are, or might become, available. Also discussed is whether these tools may have been used previously in a CCS domain or if they were deployed in another environment. The series of case studies presented in Section 2.6 further illustrates the application of certain types of tools and technologies. However, information on the type of equipment, technical specifications, actual deployment conditions and duration of project are often unpublished. For an overall summary of the evaluation of potential tools see Section 4.1.

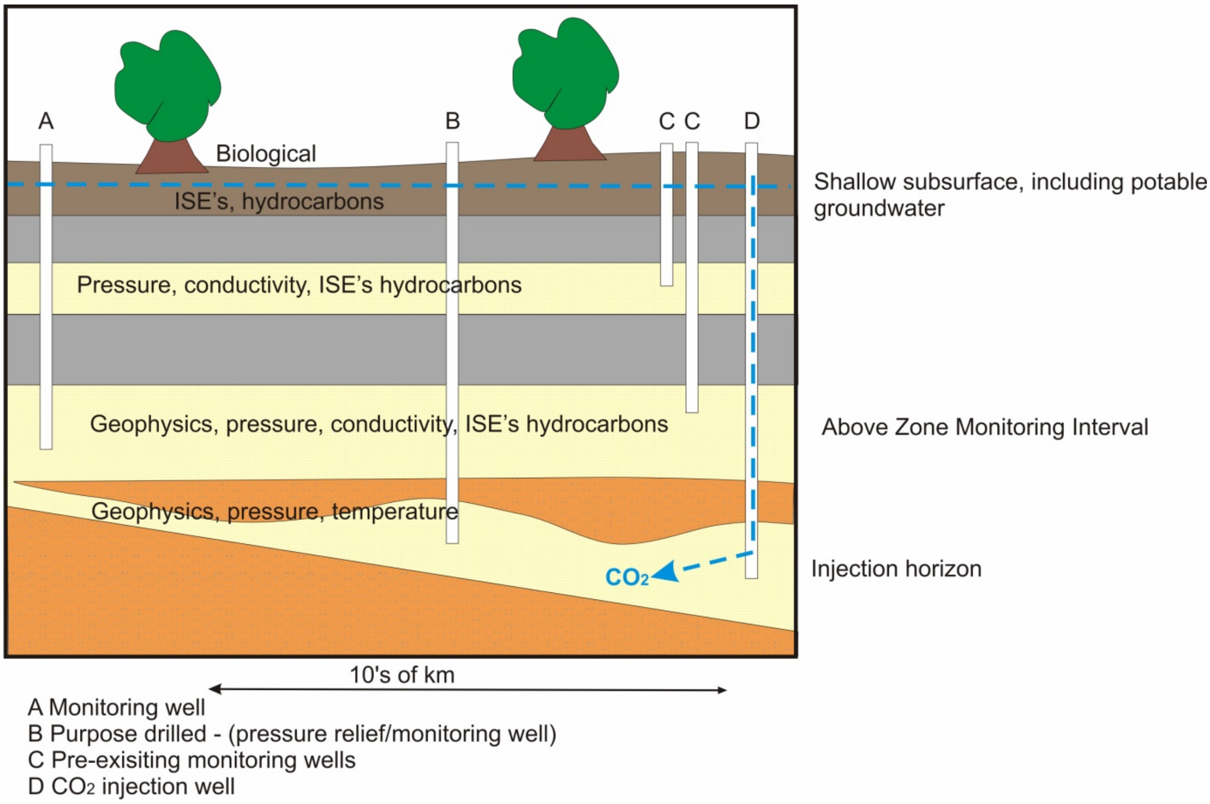


Figure 34 Summary of likely tools that could be deployed at descrete locations during monitoring.

Figure 35 is a schematic representation of the monitoring domains for which each set of monitoring tools reviewed in this report might be applied. The key physical parameter to be measured throughout the subsurface is pressure. Pressure disturbances due to CO_2 injection extend beyond the CO_2 plume itself and therefore can be detected over a larger area than for example, geochemical processes. Pressure monitoring is a mature technology in both shallow groundwater and petroleum reservoir applications that is cost-effective, sensitive and robust for long term installation. The cost of installation, data processing and interpretation increases with increasing complexity of the monitoring system and number of gauges installed. Therefore, monitoring objectives should be carefully considered for each specific injection case. Other monitoring tools like DTS and ERT have been successfully applied to CO_2 injection, particularly for environmental monitoring of the shallow groundwater. However, the longevity of these systems under reservoir conditions needs further testing and their cost may be prohibitive. Fibre optic technologies have the potential for quite sensitive monitoring of acoustic, flow and temperature properties, which produce large volumes of data that can be complex to handle, require sophisticated geological models to interpret, and considerable computing power to process.

Within the storage interval itself, geophysical techniques are the most commonly used and tend to be more advanced than other methods for delineating the presence of gases. 4D seismic is most valuable, but electromagnetics and gravity also have some use. Other seismic options such as microseismic, vertical seismic profiling will probably have more long-term value and use in future CCS projects to resolve CO_2 migration and enable continuous monitoring. Controlled source magnetotellurics have been identified a potential tool that has not been properly assessed at a real CCS project site. Of the other techniques mentioned, surface deformation monitoring is valuable, whereas other methods discussed such as MRS, GPR, magnetics, spectral and near surface gas fluxes do not appear to have extensive benefit towards CO_2 monitoring. However, with respect to substances mobilised by CO_2 this area of monitoring is much less well developed though some of the tools have been applied to anisotropy in rock properties or effective stresses from fluid pressure changes. Measurement of pressure, permeability, conductivity, porosity or temperature tend to be associated more with the shallow geophysical tools often used in agriculture or the minerals industry. These may include magnetic resonance sounding (MRS), ground penetrating radar (GPR), various magnetic (airborne, ground and gradiometry) and magnetotelleurics. Some of these tools look more at changes in metal contents, particle size, porosity, changes in sality or water contents of soils and formations and may be a way to look at subtances mobilised by CO_2 though can “see” CO_2 as well. Their ability to pentrate to only shallower intervals (say 45-175m in the case of MRS can be used in bore holes as well as from the soil surface. It is possible to test many of these tools at natural analogue sites as well for confirmation of their ability to detect substances mobilised by CO_2 prior to deployment.

Biological monitoring for CCS is a relatively low cost and feasible option in the near-surface environment, but requires more research and will present challenges if applied at depth. A significant gap in the development of chemical and geophysical monitoring compared to biological monitoring has been identified. Although biological monitoring techniques have shown some success on natural analogues and shallow injection studies, the use of newer and more powerful microbiological techniques in the form of phylogenetic and functional gene characterisation have been limited in the geosequestration sites. Tools such as GeoChip® and PhyloChip® offer rapid and more thorough microbial characterisation than previous studies with the potential to show changes in microbial communities due to CO_2 leakage and associated issues such as pH changes and mobilisation of potentially toxic metals and metalloids. Once a link can be established between species or functional genes that reflect CO_2 changes due to CCS leaks, refining specific microbiological signals into simple-to-use, field portable, rapid biosensors should become a reality. The few studies identified (In Salah and Ketzin to date) have shown mixed results with their approaches, partly due to the fact that only about 5% of any bacterial community may be cultured in a laboratory environment. Alternative approaches such as bacterial community structure analysis (Opperman et al., 2011) have been used to identify natural seeps. Specific target biosensors can also be develop to trace associated contaminants once these are identified (e.g., SO_x, SF_6, CH_4) as has been shown in BTEX biosensors from petroleum leaks (Beller et al., 2002; Baldwin et al., 2010).

During inorganic species monitoring, traditional ISE suffer from a number of drawbacks that make them largely unsuitable for long-term in situ monitoring of deep saline groundwaters. These disadvantages include issues of matrix matching, sensor drift, need for calibration, need for variable storage solutions for different analytes, use of internal reference solutions, and in some cases, detection limits that are too high for trace metals. New advances in ion selective electrode technologies, including solid-state electrodes, sensor arrays (electronic tongues), and thin and thick film deposition of sensors means that many of the problems associated with ISE (i.e., issues of matrix matching, sensor drift, need for calibration, need for variable storage solutions for different analytes, use of internal reference solutions, and in some cases, detection limits that are too high for trace metals) are in the process of being solved. Particularly pertinent advances to long term in situ monitoring include; improved detection limits, miniaturization, longer sensor life spans, and reduction in the need for repeated calibration. Thus, the most practical approach to long-term in situ monitoring for the major ions, trace metals and metalloids is in the area of ISE sensor arrays. The approach to take most likely involves identifying key analytes that represent a larger group of elements that typically have similar behaviour in groundwater and in response to changes in pH and aquifer mineralogy through carbonation reactions, and monitoring relative changes, rather than absolute concentrations. ISEs may also replace fluid sampling in deeper formations (such as use of the U-tube) though monitoring the injection interval may remain purely for academic purposes and during the initial R&D phases of CCS.

In the hydrocarbon sensor domain, there are a number of tools that might be applied to CCS monitoring and verification. The need for such monitoring will grow as a part of the assurance monitoring of BTEX and other hydrocarbons that might be mobilised by CO_2. In addition, the use of depleted hydrocarbon reservoirs or EOR stimulation activities means that organic compounds are likely to be mobilised. Hydrocarbons tend to be ubiquitous in the flue gases of all types of processing (from stripping CO_2 from high inert gas content hydrocarbon fields to the production of chemicals). The degree of selectivity of some tools may mean that there may be groups of compounds assessed rather than specific compounds. Stability of some tools may be limited at higher temperatures and pressures down-hole. Tools employing membrane-based technologies may degrade over time in these environments. By contrast, piezoelectric and fluorescence sensors are more sensitive, and while they are relatively robust they have not had sufficient long term deployment in geologic environments to date.

While there are numerous methods for monitoring CO_2 in the atmosphere and near surface environment, to date there has been little published on the application of CO_2 sensors in the high pressure and temperature environments of CCS storage reservoirs. Sensitivity is certainly one issue, where current down-hole tools are unable to reach ppb levels. The most promising method of detection in terms of selectivity and stability over longer periods is the use of optical sensor tools. These however, are required to be improved in terms of miniaturisation and ruggedization, though the surface deployment of optical fibres across many industries is demonstrating that many of these issues may be easily resolved. New R&D will be most likely directed towards the production of a lower cost tool that has suitably low power requirements for long term sentinel monitoring.

The tools/technologies identified together with the case studies provide updated information for the IEA GHG Monitoring Selection Tool. Section 4.2 discusses the compatibility of the work done here and its suitability for transfer to that tool.

The anticipated benefits, focusing where possible on near surface and down-hole monitoring tools or sensors relate to the following;

- Instrumentation in wells is still a costly business
- Reduction of capital costs, and associated operating and labour/processing costs are required

- Small scale tools or sensors deployment may be less risky relative to larger scale permanent down-hole tools

- Well interventions and re-entry may be reduced as replacement/changeover times extend thus reducing costs in the longer term

- In situ sensing can include inherent redundancy and provide continuous monitoring

- In situ sensors can compliment and aid in the optimisation of periodic sampling either in the longer term or as a part of a strategy to combine both methods of assurance

- Real-time data transmission versus sample collection and transfer to laboratories will reduce costs and increase the likelihood of timely intervention

- Telemetric data transfer can (a) reduce labour costs to site and (b) allow the transmission of instrument warnings and diagnostics.

5.2 Future considerations

While many tools and new technologies have been identified, many of these have not yet been tested either in a CO_2 storage environment, or even outside of a laboratory. Tools that have been deployed at previous and current sites have not been deployed across all sites. This may be due to costs and funding arrangements, or because they are not appropriate at some sites or there has been mixed experience with some tools or the datasets generated. Many of the current CCS sites have relied strongly on equipment from the oil and gas sector, where the tools are already appropriately rated for pressure and temperature, but may not always be tested in terms of longevity, ease of data retrieval or manipulating the extensive data generated.

In almost all cases, tools have been deployed to investigate the injection horizon, and some shallow aquifers, soil gas or atmosphere. Monitoring of the formation directly overlying the injection horizon has been limited to indirect measurements (i.e., geophysics). The one exception is at Cranfield where there is a specific monitoring zone above the first sealing unit because pre-existing wells in that zone could be equipped with monitoring tools relatively cost effectively More focus with selected tools sampling the zone directly overlying the injection horizon is needed, as this may provide early warning of leakage or detection of substances that might be mobilised by that leak.

There has been little discussion in this document about the location of some of the tools with respect to placement in the annulus or placement within or out-with the well casing. It is acknowledged that the development of smart or intelligent wells will provide more opportunity for investigating new approaches with placement of tools in the future.

Since the work done by Ross et al. (2007), it does appear that there is an ongoing drive towards miniaturisation, ruggedization, lower costs, lower detection levels and increasing electronic communications to report the data obtained. And yet, there are few tools that have been tested or deployed, and so, this must be a future goal of this sort of research. Identifying the longevity, stability and operational costs (retrieval, replacement of power supplies, data processing and manipulation etc.) must be a future goal for the CCS domain in order to quantify the true cost of M&V and also assess the relevance of different tools in different settings.

The work here also demonstrates that the tools can be split into different technology readiness levels TRL; Figure 35). For example, many seismic tools (Section 3.6.1) would be in the upper zone of TRL 7-9, where technology is mature, tested and deployed and only incremental improvements may be anticipated. By contrast, some tools, such as the biological tools (Section 3.2) would more likely fall into TRL 2-4 where the tools may have been tried for other applications reasonably successfully, but would require further research to prove the feasibility of the tools in CCS M&V applications. Evaluating tools in terms of their technology readiness might be a good way to flag tools that could be trialled alongside proven technologies during future storage operations.

Any mechanism that provides low cost, large spatial coverage of a CCS site and assures us that the CO_2 is safely stored is an important outcome for the CCS domain, however significant testing and augmentation of many tools may be required before we achieve a full toolbox of techniques that can fit any geological storage site.

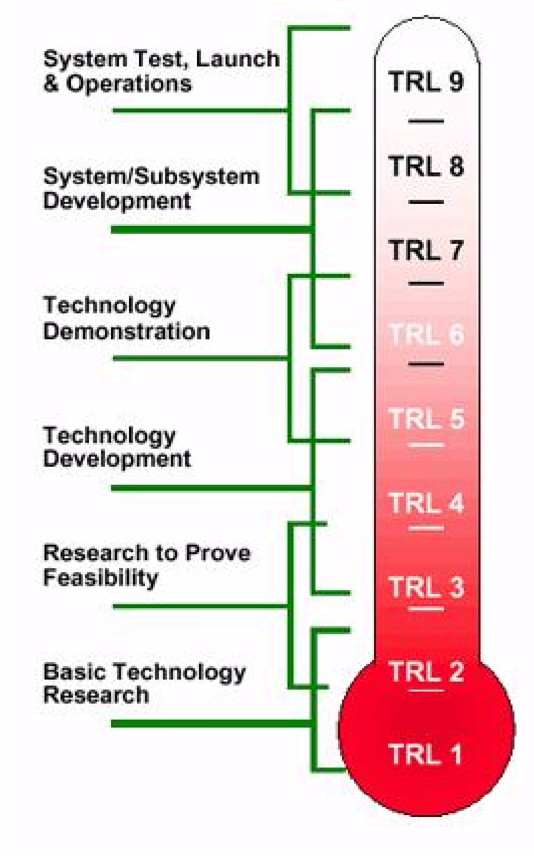


Figure 35 The NASA Technology Readiness Level tool for evaluating the maturity of evolving technologies.

Future research

The outcomes of the study suggest that any and all opportunities should be taken to test tools that might be appropriate currently, or appropriate following minor modification. By testing a number of tools, a data sheet of deployment characteristics could be prepared that can inform project teams of the temperature, pressure, storage scenarios (onshore, offshore, depleted gas field, sour gas presence etc) and specifications a tool can operate under, thereby providing useful details on stability, longevity, operational costs, ease of use and data transfer. This sort of information is difficult to obtain from either the previous case studies or during reviews of potential sensors. In many cases, failures of equipment are either not reported or merely mentioned in passing. A fuller review of the available information from these and other case studies would be of considerable benefit and add to the IEA GHG Monitoring Selection Tool.

Periodic reviews of the literature on this scale may be a worthwhile activity every 3-5 years and updates of field trials (of tools/sensors/storage sites etc.) would be helpful to monitor the state of the art.

An additional review of data transmission methods and associated difficulties with data processing and manipulation should be added to any future survey as telemetry and automation of site M&V will be advanced and hopefully reduce operational and travel costs.

Methods for adapting technologies that show promise (perhaps where a tool may not be functional in the presence of hotter environments but can tolerate higher pressures) should be investigated. Can oceanographic equipment be modified to be deployed in down-hole environments, for example?

The results of this report are planned to be presented as journal papers for the International Journal of Greenhouse Gas Control. One paper will cover general results for each of the sections investigated, while a second paper is envisaged to review the potential of biological tools identified during this project. This is one area that seems to have been used more in other applications (notably microbial ecology, agriculture, climate change and mineral exploration) and rarely in CCS domains. Further testing of these tools is being evaluated at a shallow release site and future storage sites where possible.

An abstract based on this work has been submitted to the TCCS 6 conference (Trondheim, Norway in June, 2011) and the team are awaiting notification of its acceptance (due 4th April).

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Appendices

Appendix 1

IEA GHG Tender document

Feasibility of Monitoring Techniques for Substances Mobilised by CO_2 Storage in Geological Formations

IEA/CON/10/182

Introduction

Monitoring programmes for geological storage of CO_2 have been focussed on techniques for detecting leakage of CO_2. However, it has been recognised that CO_2 may mobilise other substances and can cause displacement of saline water. All of which could have an environmental impact in the event of leakage from the geological storage formation to potable water, the water column, soil and the atmosphere.

Several regulatory regimes, including the guidelines for CO_2 storage in the London and OSPAR conventions, require that any effects of such substances mobilised by the CO_2 and any displaced saline water be included in the effects assessment and potentially monitored. Therefore it is necessary to review what the feasibilities and current capabilities are of techniques which can monitor movement of other substances in geological formations and in the event of leakage.

Technical background

The displacement of saline formation water may be caused by changes in formation pressure during CO_2 injection. This is particularly the case in deep saline formations. The extent of displacement is dependent on the geological setting and the injection scenario. A system may be considered to be ‘open’ or ‘closed’ depending on whether the target formation is compartmentalised by lateral flow boundaries (faults). In a ‘closed’ system, the boundaries limit fluid flow, whereas in an ‘open’ system there is a much greater pressure communication and hence fluid flow is more likely. It should be noted that many systems can be considered as ‘semi-closed’ with an intermediate pressure communication. Another factor is the number and location of injection wells, which may further complicate the resulting pressure fields within the formation.

Pressurisation could affect the caprock and fault integrity, and hence cause the creation of leakage pathways and it is possible that the displaced saline water may enter into an overlying potable aquifer.

The addition of CO_2 into a formation can cause changes in the pH and pE (redox potential) in the formation water. This may, in turn, cause changes in the solubility of various trace metals, especially those of redox sensitive metals, causing them to mobilise. Which substances are mobilised will depend upon the lithology of the target formation and that of the caprock, as well and the pH and pE. For example, in a poorly buffering (low $CaCO_3$) aquifer containing galena (PbS), it is likely that lead solubility, and possibly that of other toxic metals, will increase.

If leakage then occurs, the mobilised substances may enter the water column or soil, and may affect bacterial production and cause a significant change in the microbial community structure. The mobilised substances along with the CO_2 may also enter into any overlying potable aquifers, making them unusable.

It may also occur that additional substances, remaining from the capture process, may be injected into the target formation along with the CO_2. It is important to be able to monitor these in conjunction with the CO_2.

Scope of study

The scope of this study is in two parts. The first part is, by using the existing literature to identify what substances should be addressed, i.e. which are those that could be mobilised by injected and stored CO_2, as well as those contained in the CO_2 stream (incidental associated substances from the fuel, capture, transport and injection processes). For example, CO_2 can cause changes in pH in sediments which could mobilise trace metals and other compounds to a higher level of bioavailability. These substances should also include displaced saline water. Then the potential scale and effects of mobilisation of such substances be assessed, so as to identify those substances which are most likely to require monitoring.

Secondly, the main part of the study would review and assess potential technologies and techniques for their feasibility of detection of these substances, and for detection of any environmental impacts they might cause in the event of leakage. Potential technologies and techniques would include both direct sampling, including for down-hole applications, and remote monitoring techniques, and shall be reviewed for both onshore and offshore applications. The study should look at each technique and discuss its current and possible applications, which substances it applies to, sensitivity and resolution, costs and future developments.

It is expected that as well as a study report the contractor should be prepared to present the report and results at an IEA GHG Monitoring Network meeting.

The contractor should refer to the following recent IEA GHG reports relevant to this study, to avoid obvious duplication of effort and to ensure that the reports issued by the programme provide a reasonably coherent output:

- Development Issues for Saline Aquifer Storage, CO2CRC, Report 2008/12
- Assessment of Sub Sea Ecosystem Impacts, Report 2008/08
- Potential Impacts of Leaks from Onshore CO_2 Storage Projects on Terrestrial Ecosystems, Report 2007/3
- Environmental Impact Assessment for CO_2 Capture and Storage, Report 2007/1

The following active IEA GHG projects have strong links to this study and IEA GHG will manage and encourage contact between contractors to avoid duplication of effort or unnecessary discrepancies in findings:

- Pressurisation and Brine Displacement, Permedia, project commenced October 2009
- Effects of Impurities in CO_2 on Geological Storage, Natural Resources Canada, commenced December 2009
- Potential Impacts on Groundwater Resources of CO_2 Storage, currently out to tender.

This study will aim to provide the monitoring elements for the above studies and the results would be used to update the IEAGHG Monitoring Selection Tool.

Reporting

A draft report, containing the results of the study, will be produced. An unbound paper copy of the draft report and an electronic copy will be delivered by the date specified in the Instructions to Tenderers. The IEA Greenhouse Gas R&D Programme will send copies of the draft report to its expert review panel for their comments and they will be asked to deliver their comments to the IEA Greenhouse Gas R&D Programme within 1 month. Appropriate comments will be passed on to the contractor as soon as possible. The contractor will modify the report to take these comments into account and will deliver the final report within one month of receiving the comments.

Two copies of the final version of the report will be supplied on paper, one of which will be unbound. The final report will also be supplied electronically, on a PC CD-ROM or by electronic transfer, in Microsoft Word and PDF formats (including all diagrams, illustrations, tables etc.). All diagrams, pictures and illustrations must also be supplied as *.tif, *.jpg or *.gif files at a resolution no less than 300dpi, unless they have been created in Corel Draw, PowerPoint or Excel, in which case copies in the original format are acceptable. If pictures are inserted into PowerPoint then original *.tif files should also be supplied separately. Photocopies of photographs and illustrations are not acceptable.

The final report (and any material supplied with it, and including this specification) is the property of the IEA Greenhouse Gas R&D Programme and its contents must not be reported or published in any form, written or electronic, without the permission of the IEA Greenhouse Gas R&D Programme.

In addition to the final report, a paper (up to 10 pages) summarising the key findings of the study should be produced for open publication, either in a journal or for presentation at a conference. The conference or journal will be agreed in consultation with IEA GHG.

Progress meetings

Allowance should be made for up to three meetings (including a project launch meeting) at the offices of the contractor carrying out the study. These meetings may not be necessary given good progress and agreement of the various issues by fax, e-mail or other means. The contractor should indicate whether they would be able to hold progress meetings by video conference if required.

The contractor should nominate in their proposal their proposed frequency and mode of communication for the progress meetings. IEA GHG will be responsible for the costs of its representative attending the meetings.

Form of proposal

The proposal should include the names and qualifications of the persons to be involved in the work. A schedule of the proposed work should be described together with the fixed total cost (in UK pounds sterling) for the work described, together with a breakdown of each individual's contribution (in hours/weeks or days).

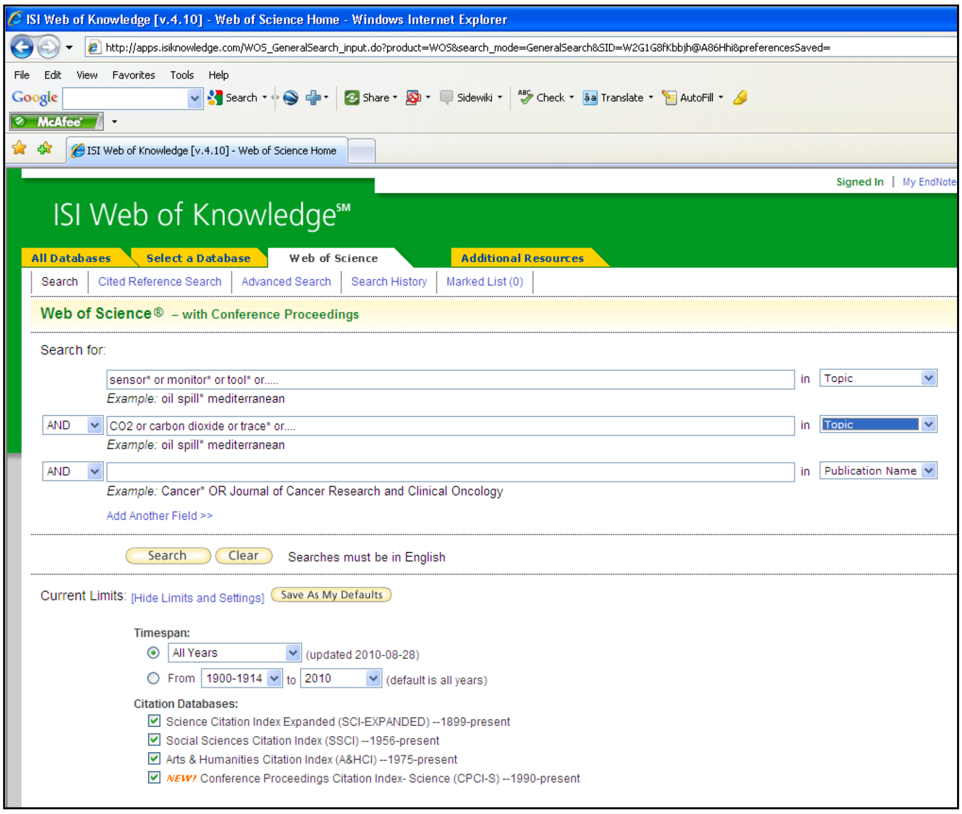
If the contractor has not previously carried out work for the IEA GHG programme, references should be given of two independent parties familiar with the work of those tendering for this contract.

Appendix 2

How the searches were conducted.

ISI and other search tools

Searches were mainly confined to those systems used in the 2007 report, i.e., ISI Web of Science, ISI Derwent Innovations Index and search engine Google, although others were used where deemed more appropriate. ISI Web of Science contains journals that tend to be higher impact European journals. The ISI system was also found to have simple functionality with EndNote and EndNote Web. This enabled the team to build up a database of relevant references on monitoring tools and their application (Figure 36).



http://apps.isiknowledge.com/WOS_GeneralSearch_input.do?product=WOS&search_mode=GeneralSearch&SID=W2G1G8fKbbjh@A86Hhi&preferencesSaved=

Web of Science® – with Conference Proceedings

Search for:

sensor* or monitor* or tool* or..... in Topic

Example: oil spill* mediterranean

AND CO2 or carbon dioxide or trace* or.... in Topic

Example: oil spill* mediterranean

AND in Publication Name

Example: Cancer* OR Journal of Cancer Research and Clinical Oncology

Add Another Field >>

Searches must be in English

Current Limits:

Timespan:

● All Years (updated 2010-08-28)

○ From 1900-1914 to 2010 (default is all years)

Citation Databases:

☑ Science Citation Index Expanded (SCI-EXPANDED) --1899-present

☑ Social Sciences Citation Index (SSCI) --1956-present

☑ Arts & Humanities Citation Index (A&HCI) --1975-present

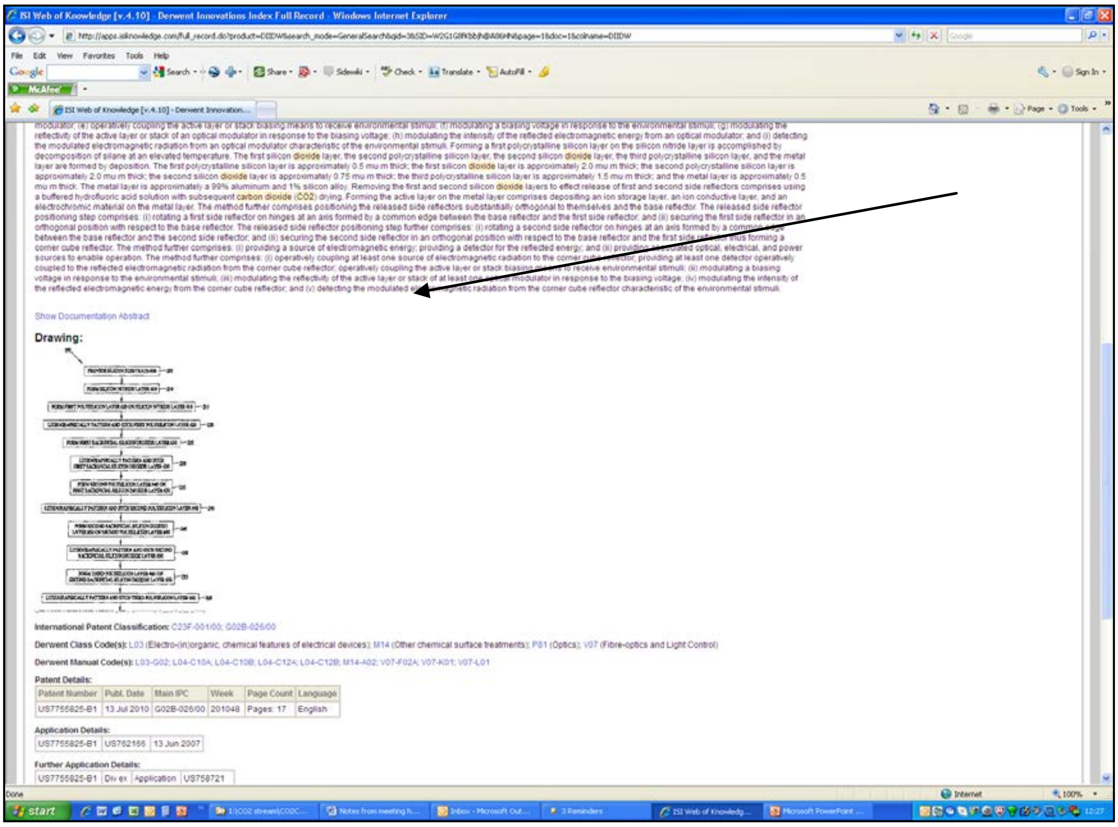
☑ NEW! Conference Proceedings Citation Index- Science (CPCI-S) --1990-present

Figure 36 Example of building a search in ISI web of science.

Where necessary, COMPENDEX was utilised, as that package contains more engineering references (e.g., SPE) and tends to have more of an Asia-Pacific focus.

For the main searches in ISI Web of Science longer searches were built from using keywords. For example, in Figure 37 a series of keywords could be added or excluded to build a single search which was encompassing and yet specific to the requirements of the project.

The same sorts of searches could also be performed using ISI Derwent Innovation Index as described above. This search tool also allowed for the definition of “Class Codes” which could be used to further refine searches in order to target information in a more detailed way (Figure 38).



modulator; (e) operatively coupling the active layer or stack biasing means to receive environmental stimuli; (f) modulating a biasing voltage in response to the environmental stimuli; (g) modulating the reflectivity of the active layer or stack of an optical modulator in response to the biasing voltage; (h) modulating the intensity of the reflected electromagnetic energy from an optical modulator; and (i) detecting the modulated electromagnetic radiation from an optical modulator characteristic of the environmental stimuli. Forming a first polycrystalline silicon layer on the silicon nitride layer is accomplished by decomposition of silane at an elevated temperature. The first silicon dioxide layer, the second polycrystalline silicon layer, the second silicon dioxide layer, the third polycrystalline silicon layer, and the metal layer are formed by deposition. The first polycrystalline silicon layer is approximately 0.5 mu m thick; the first silicon dioxide layer is approximately 2.0 mu m thick; the second polycrystalline silicon layer is approximately 2.0 mu m thick; the second silicon dioxide layer is approximately 0.75 mu m thick; the third polycrystalline silicon layer is approximately 1.5 mu m thick; and the metal layer is approximately 0.5 mu m thick. The metal layer is approximately a 99% aluminum and 1% silicon alloy. Removing the first and second silicon dioxide layers to effect release of first and second side reflectors comprises using a buffered hydrofluoric acid solution with subsequent carbon dioxide (CO2) drying. Forming the active layer on the metal layer comprises depositing an ion storage layer, an ion conductive layer, and an electrochromic material on the metal layer. The method further comprises positioning the released side reflectors substantially orthogonal to themselves and the base reflector. The released side reflector positioning step comprises: (i) rotating a first side reflector on hinges at an axis formed by a common edge between the base reflector and the first side reflector; and (ii) securing the first side reflector in an orthogonal position with respect to the base reflector. The released side reflector positioning step further comprises: (i) rotating a second side reflector on hinges at an axis formed by a common edge between the base reflector and the second side reflector; and (ii) securing the second side reflector in an orthogonal position with respect to the base reflector and the first side reflector thus forming a corner cube reflector. The method further comprises: (i) providing a source of electromagnetic energy; providing a detector for the reflected energy; and (ii) providing associated optical, electrical, and power sources to enable operation. The method further comprises: (i) operatively coupling at least one source of electromagnetic radiation to the corner cube reflector; providing at least one detector operatively coupled to the reflected electromagnetic radiation from the corner cube reflector; operatively coupling the active layer or stack biasing means to receive environmental stimuli; (ii) modulating a biasing voltage in response to the environmental stimuli; (iii) modulating the reflectivity of the active layer or stack of at least one optical modulator in response to the biasing voltage; (iv) modulating the intensity of the reflected electromagnetic energy from the corner cube reflector; and (v) detecting the modulated electromagnetic radiation from the corner cube reflector characteristic of the environmental stimuli.

Show Documentation Abstract

Drawing:

International Patent Classification: C23F-001/00; G02B-026/00

Derwent Class Code(s): L03 (Electro-(in)organic, chemical features of electrical devices); M14 (Other chemical surface treatments); P81 (Optics); V07 (Fibre-optics and Light Control)

Derwent Manual Code(s): L03-G02; L04-C10A; L04-C10B; L04-C12A; L04-C12B; M14-A02; V07-F02A; V07-K01; V07-L01

Patent Details:

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
US7755825-B1	13 Jul 2010	G02B-026/00	201048	Pages: 17	English

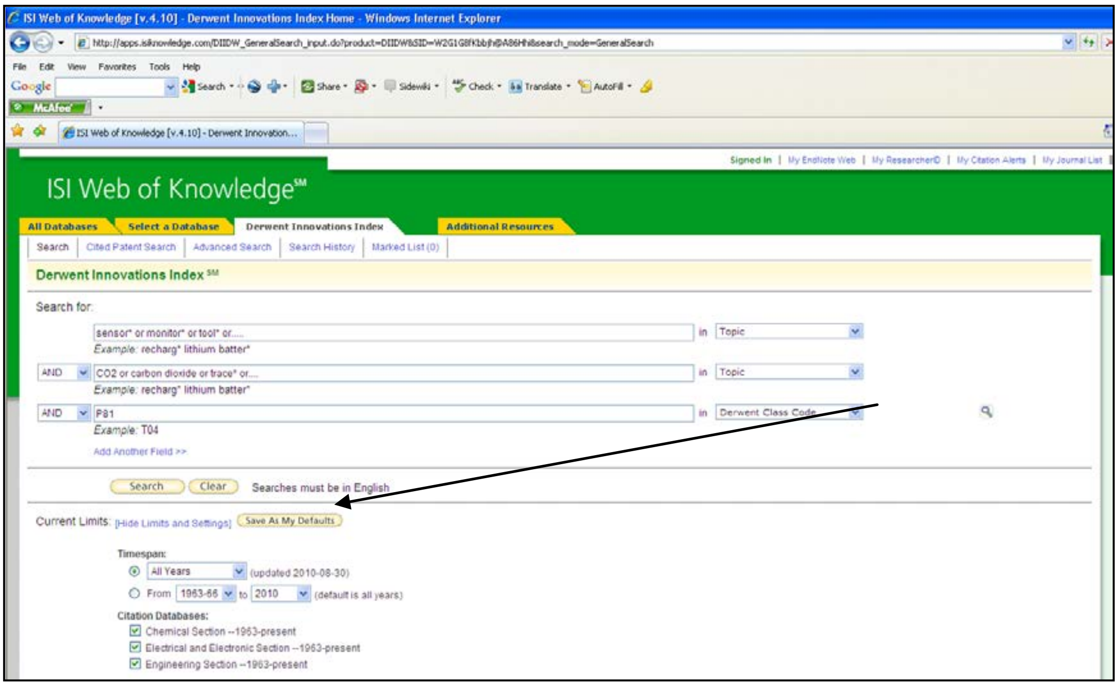
Application Details:

US7755825-B1	US762166	13 Jun 2007

Further Application Details:

US7755825-B1	Div ex	Application	US758721

Figure 36 Derwent Class codes show a code and meaning. These can be inserted into the next search if needed (see next figure).



Derwent Innovations Index ℠

Search for:

sensor* or monitor* or tool* or.... in Topic
Example: recharg* lithium batter*

AND CO2 or carbon dioxide or trace* or.... in Topic
Example: recharg* lithium batter*

AND P81 in Derwent Class Code
Example: T04

Searches must be in English

Current Limits:

Timespan:
● All Years (updated 2010-08-30)
○ From 1963-66 to 2010 (default is all years)

Citation Databases:
☑ Chemical Section --1963-present
☑ Electrical and Electronic Section --1963-present
☑ Engineering Section --1963-present

Figure 37 Derwent Class code for P81 (Optics) has been added to the search.

EndNote desktop and web

By uploading the original set of references identified in Ross et al, (2007) into EndNote web from its original EndNote file, all of the team could see the original list and be in a position to add to that list. From the original database, the team could then add important key references to the web version before downloading it to a file that has been added to the reported materials.

The sharing function was enabled by adding each person's email address and choosing the level of access they required. This was particularly helpful when some staff for the project were not at the same location.

The other useful feature of this software was that it was able to flag a reference that had already been saved to EndNote Web and avoided duplication.

COMPENDEX references could also be uploaded via the desktop version of EndNote and then transferred up to the web version.

ISI analyse function

The "analyse" function was used occasionally to illustrate some key points in the searches. For example, the ISI Derwent Innovation Index results for patent "assignee name" quickly illustrated that the main owners of patents in the "oil & sensor" search tended to be oil companies, service companies to oil companies or automotive companies (see previous section). Thus the "analyse" function was used selectively to illustrate key points in the search results.

Search quirks

The searches showed some interesting features, for example, where searches of "CO2 and Sensor" in ISI Web of Science gave 1462 hits whereas only 1081 hits were generated from a search for "Carbon Dioxide and Sensor" (see CO_2 Sensors below). Many of the papers will however be duplicates from each search. Few papers or patents were found that had a relationship with or been applied to "Sequestration" or "down-hole" environments. Another observation made during the repeat analysis in ISI Web of Science was that previous searches were carried out in with items in the singular in some instances and plural in others and this could have impact on the number of journal papers or patents identified. For example, if "Petroleum & Monitoring & Sensor" is searched for versus ""Petroleum & Monitoring & Sensors" (Table 21) different results are achieved (for a search during 2010). However, by truncating some key words and replacing them with the wildcard "*" to allow for searches of all variants of the words (Table 21), so that the searches returned significantly more hits. For example, if "Sensor" was replaced with "Sens*" then searches on sensor, sensors, sensing etc., would be carried out simultaneously and has been shown to result in significantly more hits and increases the chance of finding journal articles or patents of relevance in the new search.

Table 21 Comparison of search methods.

Search string	2007	2010
Petroleum & Monitoring & Sensors	12	19
Petroleum & Monitoring & Sensor		25
Petroleum & Monitoring & Sens*		97
Petroleum & Monit* & Sens*		122

Literature search information

As discussed briefly in Section 1.4, a comprehensive literature search was undertaken and a number of pieces of information were collected. While the body of the report deals with tools and sensors identified that might be deployed for monitoring of mobilized substances, we were also able to compare the overall results (i.e. number of papers identified in this search) with results from the previous study by Ross et al, 2007. Here follows a brief discussion on how the results compare and what they could be interpreted to say about the direction of some aspects of sensor and monitoring tool research in the last 3 years.

The analysis of the ISI Web of Science for some of the key research areas includes hydrocarbon sensors, tracers, CO_2 sensors, anions and cations. Briefly the use of the ISI Derwent Innovations Index is discussed and how it might too be used to identify tools for monitoring purposes. In some cases other databases were used as they were anticipated to be more appropriate and more likely to aid in the discovery of suitable information, tools or papers relevant to this study. This is discussed in general terms below.

Physical parameters

The Ross 2007 report previously discussed did not include searches for measuring physical parameters such as pressure and temperature. In this report a set of searches using these parameters (pressure, temperature, flow and density) were carried using the ISI Web of Science and ISI Derwent Innovations Index as above. As these parameters relate mostly to the engineering discipline, the Engineering Village database Compendex was also searched (http://www.engineeringvillage2.org). Compendex describes itself as "one of the most comprehensive engineering literature databases available to engineers, with 12 million records across 190 engineering disciplines. It includes millions of bibliographic citations and abstracts from thousands of engineering journals and conference proceedings". In addition many of the key references used in this section were sourced from the online library, OnePetro (http://www.onepetro.org/about.htm). According to their website, OnePetro contains a broad range of technical literature related to the oil and gas exploration and production industry, of particular interest in this study are the publications of the SPE (Society of Petroleum Engineers).

The results are included in this Apprendix. However, comparison of the number of returns from each database varies considerably depending on the term used. None of the databases searched consistently returned more results, even though the Compendex and OnePetro databases are specifically engineering and the OnePetro is specifically from the oil and gas industry where a lot of the sequestration technology is developed. There were also large differences depending on whether the term "carbon dioxide" or "CO_2" was used, again with neither term consistently returning the greater number. In summary, it would seem that a comprehensive search for these types of technology needs to encompass several databases, including scientific and technical publications.

Hydrocarbon sensors

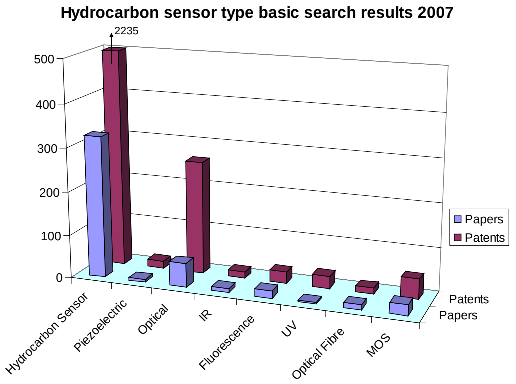
There were several reasons for investigating hydrocarbon sensors as part of the Ross et al, study in 2007. With the work commissioned by the CO2CRC, and a test commencing in a depleted gas field, methane gas, wet gases, and condensate compounds could all be regarded as materials that could be monitored for in the storage reservoir and in overlying zones of interest (groundwater aquifers, in the soil and atmosphere).

In 2007, many searches resulted in no findings in ISI Web of Science, and some of these searches included key words such as oil well, down-hole, piezoelectric, optical fibre UV and fluorescence. In 2010, there are fewer searches with no information, and most others increased. In one case “benzene

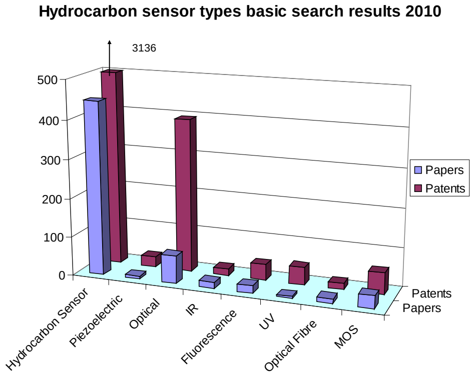
& sensor & water” leaped to 107 from zero, which suggests a typing error in the 2007 search rather than a massive leap in effort in this area (though this is difficult to check). However, the recent activity relating to groundwater quality impacts perceived to be caused by underground coal gasification (UCG) or coal seam methane (CSM) extraction, particularly in the area around the Great Artesian Basin of Queensland, Australia and parts of the US, indicates increasing awareness and monitoring of mobile organics (including BTEX) as potential contaminants mobilised into potable groundwater supplies.

At the other end of the scale, the largest number of papers found in this section was for “optical fibre & sensor” at 948 papers. However, there were 820 papers for “oil & sensor”, 470 for “methane & sensor” and 325 for “hydrocarbon & sensor” showing active research in this area (most likely related to oil and gas industry drivers). Where there were > 100 journal papers found for a search in 2007, R&D has continued to grow significantly, as is evidenced by the percentage increase in papers, (using [No. hits 2010 – No. hits 2007]/No. hits 2007*100) from nearly 25% (for “optical fibre & sensor”) to a 76% increase for “oil & sensor”. No doubt the increase in “oil & sensor” research is related to petroleum industry applications.

Significant increases have been observed in results from searches on “oil-, benzene-, toluene- and petroleum & sensor”. Of the more emergent areas, there has been a rapid increase in “MOS & oil” research (MOS = metal oxide semi-conductor sensors) by 76% (i.e., from 50 to 88 papers in the last 3 years). Of the largest areas of research, it would appear that optical and fluorescence sensors have had the largest relative increases of 51% and 99%, respectively.



	Hydrocarbon Sensor	Piezoelectric	Optical	IR	Fluorescence	UV	Optical Fibre	MOS
Papers	325	6	56	10	17	4	11	25
Patents	2235	17	261	15	27	29	14	47



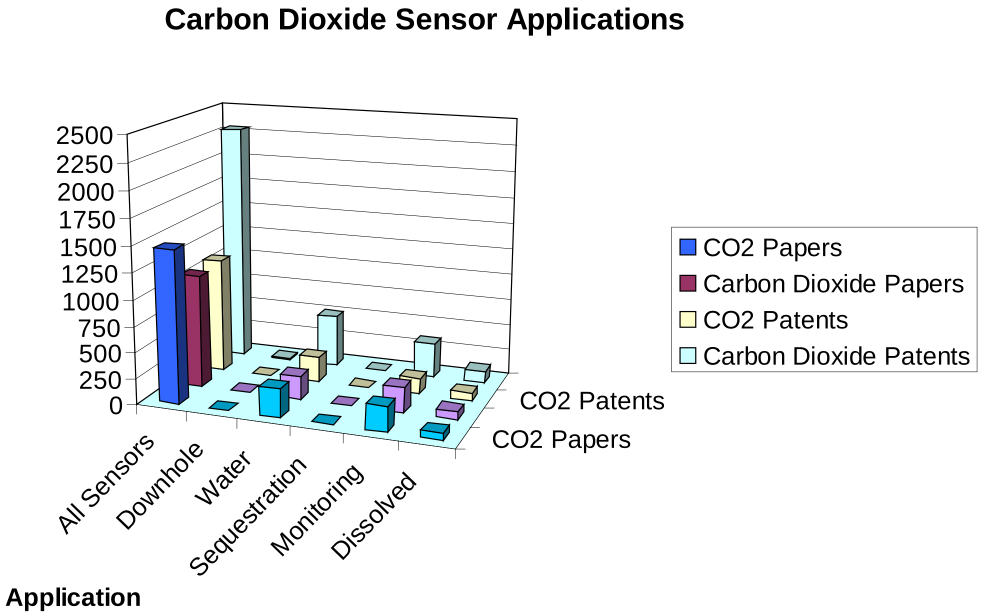
	Hydrocarbon Sensor	Piezoelectric	Optical	IR	Fluorescence	UV	Optical Fibre	MOS
Papers	446	7	72	16	20	5	12	33
Patents	3136	26	395	18	41	45	16	56

Figure 38 Hydrocarbon sensors

CO_2 sensors

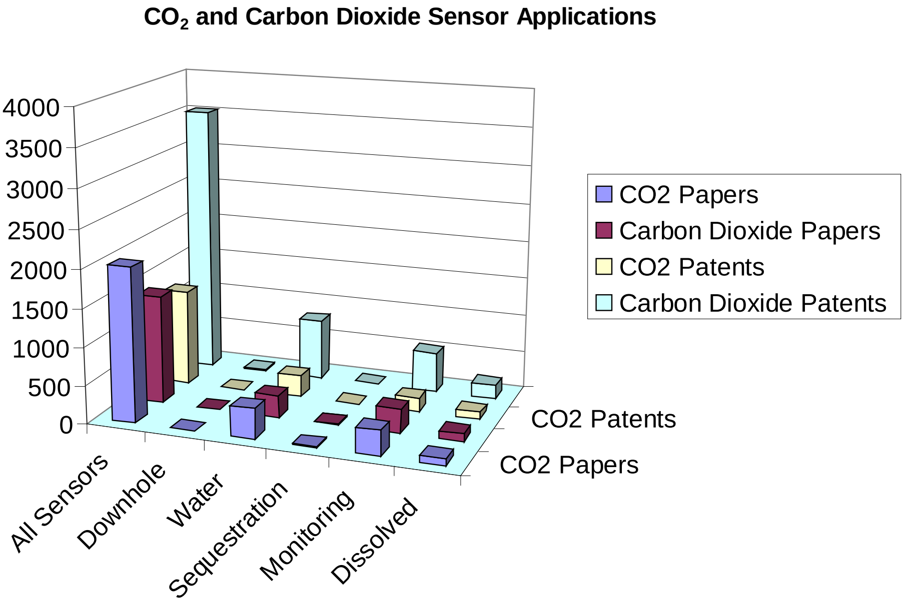
Twenty of the search parameters found no papers in 2007, and included key words such as “down-hole, amperometric, optical, piezoelectric, dissolved, IR, UV, fluorescence” etc. The word “sequestration” was also used in many of these search strings. However “carbon dioxide & sensor & sequestration” did return 3 papers in 2007 and 9 in 2010, while “CO_2 & sensor & sequestration” returned 6 papers in 2007 and 12 in 2010, showing increased interest at this early stage in the development of the research.

Naturally the largest number of papers found, at 1462 was for “CO_2 & Sensor” closely followed by “carbon dioxide & sensor” at 1081 hits. Of these, 271 papers related to “CO_2 & sensor & water indicating that this was a fairly important area of research within the subsections in the data table attached to Figure 40. showing a significant reduction in activity. Most CO_2 sensors according to the 2007 search appeared to be optical sensors.



	All Sensors	Downhole	Water	Sequestration	Monitoring	Dissolved
■ CO2 Papers	1462	0	271	6	240	63
■ Carbon Dioxide Papers	1081	0	218	3	241	77
□ CO2 Patents	1105	0	241	0	155	75
□ Carbon Dioxide Patents	2300	10	504	5	331	119

Figure 39 Example of one of the searches carried out in Ross et al., (2007) to identify use and application of CO2 or carbon dioxide sensors in the literature and patent applications.



	All Sensors	Downhole	Water	Sequestration	Monitoring	Dissolved
CO2 Papers	2023	1	396	12	330	86
Carbon Dioxide Papers	1418	1	283	9	314	99
CO2 Patents	1263	0	287	0	182	91
Carbon Dioxide Patents	3523	11	796	8	527	180

Figure 40 Equivalent search carried out in 2010 to demonstrate the relative change and increase in research in CO2 and carbon dioxide sensors in the literature and patent applications.

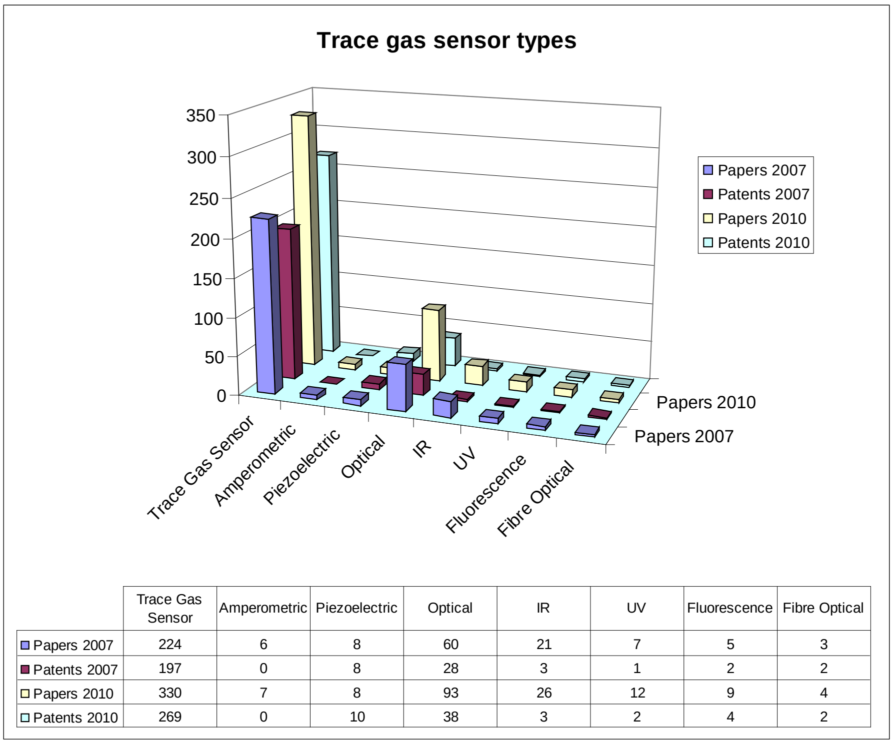
By 2010's search, only 11 categories had no papers associated with the searach criteria. Sensors for CO_2 and carbon dioxide have moved forward (both increasing by about a third) and rapid increases in R&D in optical and fluorescence sensors (increases of 50 and 100% respectively) have occurred. This may identify the best technologies currently available to apply as tools for the monitoring of CO_2 in CCS projects.

Tracers

The search for tracer specific sensors in Ross et al (2007) was based on the use of tracers at the CO2CRC Otway Project Stage 1, where SF_6, Kr and CD_4 (sulphur hexafluoride, krypton and fully deuterated methane) were used in the first tracer pulse (Stalker et al., 2009). Clearly, as compounds are applied to conduct tracer studies with different objectives, the types and numbers of tracer compounds will increase and a larger variety of sensors or monitoring tools will be required.

In 2007, the study showed that for the range of trace gases and sensors (Figure 42), optical sensors were most prevalent in the literature (60), followed by IR sensors (20). Some papers did contain reference to "CD4 & sensor" (20 papers in 2007 and 42 in 2010), but no papers for "deuterated methane & sensor" for either search which caused some suspicion. In this case, reviewing the journal titles and abstracts showed that "CD4" related to a type of cell measured in immunodeficiency illnesses and were therefore irrelevant. Hence, in Ross et al., (2007) these searches were labelled "not valid" in the supplementary materials (an excel sheet) and highlights the need to review the papers identified by this type of search.

Trace gas sensor papers were the most common in both 2007 and 2010 at 224 and 330 respectively. Of these, in 2007 it was optical sensors that were the most common, followed by SF_6 sensors. The largest increase in R&D activity for a single compound was in Kr sensors from 13 to 31 in the 3 year period.



	Trace Gas Sensor	Amperometric	Piezoelectric	Optical	IR	UV	Fluorescence	Fibre Optical
Papers 2007	224	6	8	60	21	7	5	3
Patents 2007	197	0	8	28	3	1	2	2
Papers 2010	330	7	8	93	26	12	9	4
Patents 2010	269	0	10	38	3	2	4	2

Figure 41 Trace gas sensors types.

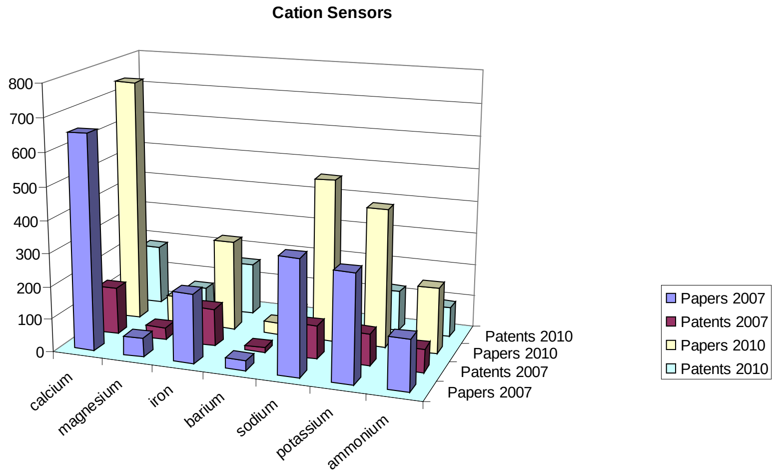
Anions and cations

This section of the search in the Ross et al., (2007) report was by no means comprehensive, but did give a flavour of the options available and potentially useful tools for the Otway Project. The variety of sensors covered here reflects the different applications required such as the monitoring of groundwaters, potable water supply and industry processes or even oceanographic applications.

In 2007, by far the most common sensor in this group was “pH & Sensor” with 5180 papers found. In the last 3 years, this has increased to 7436 and may potentially relate more to the application of the tool than any new tool/sensor developments, pH being one of the most common chemical measurements likely to be made. The next most common sensor is for calcium (1849 papers in 2007) followed by chloride (1527 papers) and sodium (1445 papers). Carbonate & Sensor (239 in 2007) and bicarbonate & sensor (78 in 2007) measuring dissolved CO_2 are far less common.

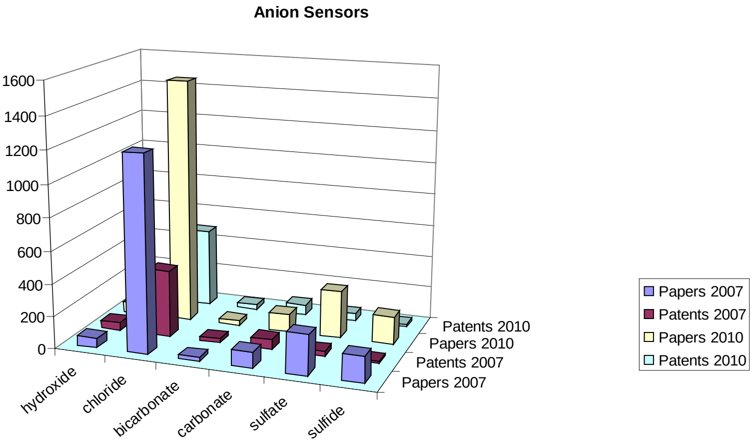
By 2010, the most rapid increases in the number of journal papers (and by inference R&D) has been on iron &-, potassium &- and magnesium & sensor applications (all have increased by > 50%). This may relate to specific areas of interest on the rise, for example in mineral exploration and processing.

The general review of changes to the number of results between 2007 and 2010 for Ross et al, (2007) report has shed some light on how the searches were done, how they could be done better and some of the pitfalls of carrying out these searches, but also gives insight into changes in R&D focus over the last 3 years.



	calcium	magnesium	iron	barium	sodium	potassium	ammonium
Papers 2007	654	58	212	31	351	327	156
Patents 2007	144	37	114	14	101	97	71
Papers 2010	747	81	276	36	497	423	201
Patents 2010	183	63	158	26	136	124	92

Figure 42 Cation Sensors comparison over the last three years.



	hydroxide	chloride	bicarbonate	carbonate	sulfate	sulfide
Papers 2007	58	1204	25	100	246	162
Patents 2007	49	413	26	61	32	12
Papers 2010	66	1509	31	110	292	172
Patents 2010	64	487	29	66	46	16

Figure 43 Cation Sensors comparison over the last three years.

ISI Derwent Innovation Index

The same process of re-running the searches that had been conducted in 2007 by Ross et al., were performed in late August, 2010 on ISI Derwent Innovation Index. This database searches exclusively for patents. Here we include the example of hydrocarbon sensors to illustrate the sort of information that can be gleaned from a thorough search in this database to help identify key players in the commercial field of sensor research.

Hydrocarbon sensors

In the 2007 report, by far the largest number of patents were in “oil & sensor” at 10,783. By 2010 there has been a 50% increase in the number of patents in this domain. An analysis (Figure 45) of the assignees of these patents in 2010 (on “oil & sensor”), shows that a significant number of the patents are held by various divisions of Schlumberger (950), while the nearest competitors are car manufacturers (Hyundi with 358 and Nissan with 344 patents). Analysis of the subject areas shows that the patents in the “oil & sensor” domain are predominantly engineering, instruments & instrumentation, chemistry, transportation and energy & fuels. This information can be used to identify possible tools or manufacturers that could provide off-the-shelf monitoring equipment that is either directly suitable for monitoring hydrocarbons in general or specific groups or compound series. In the case of the car manufacturing industry, it may be possible to identify tools that may work at atmospheric pressure but higher temperatures that could be modified to cope with the higher pressure conditions in the deep subsurface, or could be deployed in shallow groundwater monitoring settings.

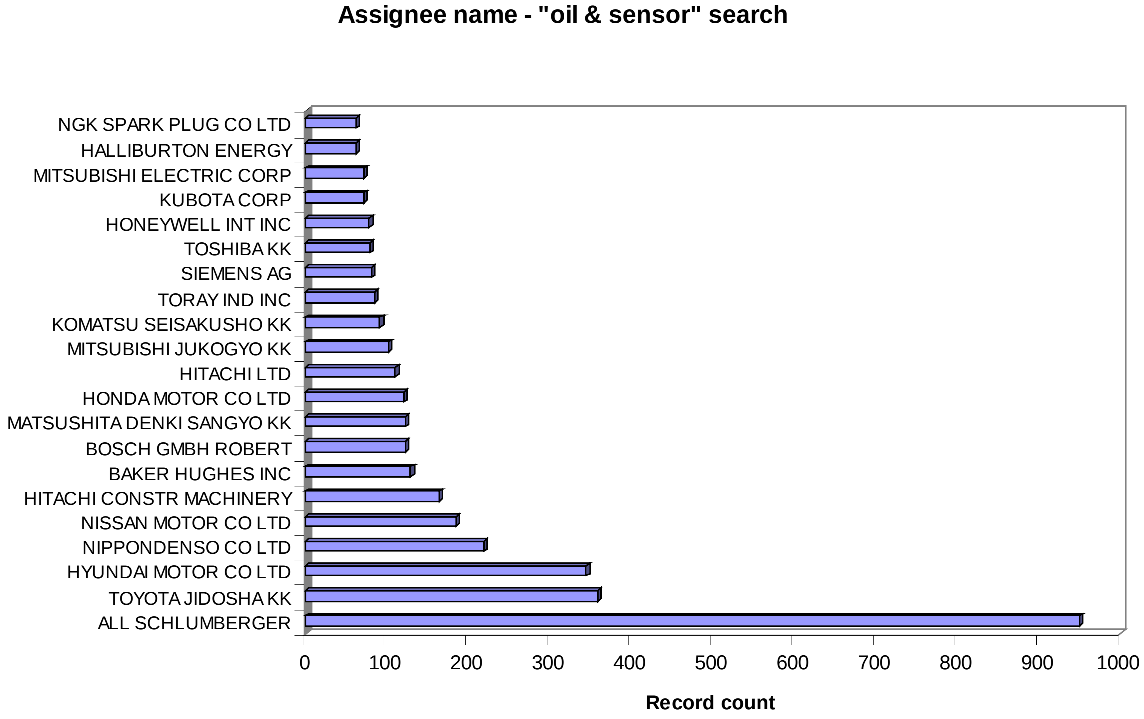


Figure 44 Dominance of oilfield service companies and vehicle industries in oil and sensor technologies.

Other searches similar in nature to “oil & sensor” such as “hydrocarbon & sensor”, “petroleum & sensor”, “methane & sensor”, “hydrocarbon and gas and sensor” all show similar percentages of increased patents in the 3 years since the last search.

There are 2 other areas that seem to be of interest by showing some increases of note in the search; optical sensors and sensors that monitor for a specific chemical (in this case toluene and benzene).

While “optical fibre and sensor” has not increased much since 2007 (only 4.4% increase in the number of patents) this translates to an increase of 225 on the 5066 patents from 2007, and therefore indicates significant activity. The subgroup of “optical & hydrocarbon & sensor” has had a > 50% increase in patents (i.e. up by 134) in the last 3 years and suggests that this may be a suitable technology to evaluate further for hydrocarbon sensors and the list of assignees was examined (Table 22). Assignees to this technology include various oilfield service companies, photographic/chemical/analytical instrumentation manufacturers, chemical/industrial chemical manufacturers, oil industry and some research institutes. These sorts of evaluations of who holds the rights to patents within a particular domain can give some information on likely organsiations or manufacturers/industries most likely to produce suitable or adaptable monitoring tools and from there more detailed evaluations can be conducted.

Table 22 Assignees and business type for those holding patents from "optical & hydrocarbon & sensor"

Assignee	Record count (of a total of 400)	Business type
KONICA CORP	15	Optics, medical, analytical equipment
FUJI	25	Optics, medical, analytical equipment
SCHLUMBERGER	35	Oilfield services
TORAY IND INC	10	Chemicals, plastics, fibres
SUMITOMO CHEM CO LTD	9	Industrial chemicals, alumina products, optics
SENSOR HIGHWAY LTD	8	Oilfield services
DOKURITSU GYOSEI HOJIN SANGYO GIJUTSU SO	7	Research institute
KONICA MINOLTA OPTO KK	7	Optics, medical, analytical equipment
WEATHERFORD/LAMB INC	7	Oilfield services
BAKER HUGHES INC	6	Oilfield services
KANEKA CORP	6	Chemicals
UNIV OSAKA	6	Research institute
ASAHI DENKA KOGYO KK	5	Oil refining & plastics
CHEN Y	5	?
IDEMITSU KOSAN CO LTD	5	Petrochemicals & petroleum exploration
JAPAN ENERGY CORP	5	Petroleum exploration
MERCK PATENT GMBH	5	Chemicals & pharmaceuticals
MITSUBISHI CHEM CORP	5	Chemicals, industrial materials, health
MITSUI CHEM INC	5	Petrochemicals, plastics, car parts
SEKISUI CHEM IND CO LTD	5	Chemical, medical, plastics

Benzene/toluene

Another example of a patent search for further information or the types of organisations developing tools for measuring different species was conducted by searching ISI Derwent Innovations Index for “benzene and sensor or toluene and sensor”. Results (Table 23) show that there are differences in the types of industries involved in research or development of sensors of this type, relative to those involved in optics and hydrocarbon sensors (Table 22). Table 23 shows that those most involved in the research and development of these tools are not oilfield service companies, but rather organisations making chemicals, involved in photography and printing, electronics and some car part manufacturing. Again, this suggests a need for a wide ranging search for tools that exist and can be adapted to suit CCS monitoring.

Table 23 Assignees and business type for those holding patents from "benzene & sensor or toluene & sensor"

Assignee	Record count (of a total of 1736)	Business type
MITSUI CHEM INC	67	petrochem, plastics, car components
IDEMITSU KOSAN CO LTD	37	petrochem & petroleum exp
MATSUSHITA ELEC IND CO LTD	35	electronics
NEC CORP	35	electronics
RICOH KK	34	printers & optics
CANON KK	27	printers & optics
JSR CORP	26	plastics, electronics, optics
TOSHIBA KK	26	plastics, electronics, optics, automotive
SHARP KK	25	plastics, electronics, optics
MERCK PATENT GMBH	23	chemicals & pharm
SUMITOMO CHEM CO LTD	22	Industrial chemicals, alumina products, optics
DOKURITSU GYOSEI HOJIN SANGYO GIJUTSU SO	18	National Institute of Advanced Industrial Science and Technology
FUJITSU LTD	17	electronics, optics, automotive
FUJI	29	optics/medical/analytical
HITACHI LTD	15	electronics, optics, automotive
MITSUBISHI DENKI KK	15	electronics, automotive
SAMSUNG ELECTRONICS CO LTD	15	electronics, chemical, medical, engineering
US SEC OF NAVY	15	?
JAPAN SCI & TECHNOLOGY AGENCY	13	institute
TORAY IND INC	13	textiles, plastics, chemicals
UNIV CALIFORNIA	13	institute
AGENCY OF IND SCI & TECHNOLOGY	12	institute
KANEKA CORP	12	chemicals
NISSAN CHEM IND LTD	12	chemicals, materials, pharmaceuticals

Summary

Conducting searches such as those described in this Appendix have been the primary method of starting to find suitable tools and techniques that could be used to monitor varying types of substances mobilised by CO_2 (including the CO_2 itself). The information can be used to validate which direction research may be heading in these areas, such as the focus on ion selective electrodes in the monitoring of cations and anions that may be as good as other laboratory based techniques compared with laboratory analysis as an equivalent. Reviews of the literature can direct us towards that information and provide good sources of evaluation and information to show previous deployment, testing and applicability of these varied tools.

Table 24 Physical properties searches

	Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro		Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro
Pressure sensors					**Flow Meter**				
pressure & sensor*	>100,000	23093	25295	2802	flow & meter*	45909	8715	10706	4977
pressure & sensor* & carbon dioxide	1240	476	404	149	flow & meter* & carbon dioxide	599	98	104	307
pressure & sensor* & CO2	437	614	40	2802	flow & meter* & CO2	213	161	14	4977
pressure & sensor* & downhole	608	59	256	2802	flow & meter* & downhole	154	0	82	2802
pressure & sensor* & downhole & carbon dioxide	11	1	5	59	flow & meter* & downhole & carbon dioxide	3	0	0	112
pressure & sensor* & downhole & CO2	1	1	2	931	flow & meter* & downhole & CO2	0	0	0	451
pressure & sensor* & in situ	7117	688	671	2802	flow & meter* & in situ	7117	239	632	4977
pressure & sensor* & in situ & carbon dioxide	7117	24	15	44	flow & meter* & in situ & carbon dioxide	dns	1	8	104
pressure & sensor* & in situ & CO2	7117	50	2	254	flow & meter* & in situ & CO2	dns	4	0	406
Pressure gauge					**Density Sensor**				
pressure & gauge*	21537	5763	4612	2051	density & sensor*	17269	14922	15333	2802
pressure & gauge* & CO2	158	84	6	2051	density & sensor* & carbon dioxide	277	122	105	64
pressure & gauge* & carbon dioxide	348	64	47	152	density & sensor* & CO2	84	202	12	426
pressure & gauge* & downhole	165	42	233	2051	density & sensor* & downhole	84	9	46	1114
pressure & gauge* & downhole & CO2	0	1	1	745	density & sensor* & downhole & carbon dioxide	4	1	3	37
pressure & gauge* & down-hole & carbon dioxide	3	0	3	61	density & sensor* & down-hole & CO2	0	1	1	150
pressure & gauge*	7117	186	145	0	density & sensor* & in	dns	584	432	571

	Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro		Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro
& in situ					situ				
pressure & gauge* & in situ & CO2	7117	2	0	201	density & sensor* & in situ & carbon dioxide	dns	4	6	39
pressure & gauge* & in situ & carbon dioxide	7117	2	2	37	density & sensor* & in situ & CO2	dns	12	0	60
Temperature sensors					**Density Meter**				
temperature & sensor*	>100000	46679	53318	2802	density & meter*	6653	3458	3499	4977
temperature & sensor* & carbon dioxide	1733	838	836	111	density & meter* & carbon dioxide	155	48	62	162
temperature & sensor* & CO2	467	1326	92	887	density & meter* & CO2	44	57	6	708
temperature & sensor* & downhole	328	58	212	1339	density & meter* & downhole	22	9	10	990
temperature & sensor* & downhole & carbon dioxide	13	1	4	55	density & meter* & downhole & carbon dioxide	2	0	0	99
temperature & sensor* & downhole & CO2	1	2	1	418	density & meter* & downhole & CO2	0	0	0	3
temperature & sensor* & in situ	7117	1919	1921	1014	density & meter* & in situ	dns	131	115	952
temperature & sensor* & in situ & carbon dioxide	7117	36	29	41	density & meter* & in situ & carbon dioxide	dns	2	2	101
temperature & sensor* & in situ & CO2	7117	83	2	131	density & meter* & in situ & CO2	dns	7	1	120
Temperature gauge					**Temperature sensors**				
temperature & gauge*	6648	8828	4068	2051	permanent downhole gauge*	5	12	141	349
temperature & gauge* & carbon	182	41	29	81	permanent downhole gauge* & carbon	0	0	1	186

	Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro		Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro
dioxide					dioxide				
temperature & gauge* & CO2	61	66	3	704	distributed temperature s* (or sensor)	1136	invalid search	16270	111
temperature & gauge* & downhole	45	20	115	1051	distributed temperature s* & carbon dioxide	0	invalid search	186	3
temperature & gauge* & downhole & carbon dioxide	3	0	1	42	acoustic & downhole	511	67	250	46
temperature & gauge* & downhole & CO2	0	0	0	345	acoustic & downhole & carbon dioxide	0	0	1	0
temperature & gauge* & in situ	7117	183	132	774	thermal conductivity & downhole & carbon dioxide	0	0	0	9
temperature & gauge* & in situ & carbon dioxide	7117	3	2	36	DTS				147
temperature & gauge* & in situ & CO2	7117	2	0	84					
Flow Sensor									
flow & sensor*	>100,000	22858	24062	2802					
flow & sensor* & carbon dioxide	1138	319	228	125					
flow & sensor* & CO2	339	445	20	2802					
flow & sensor* & downhole	477	37	184	2802					
flow & sensor* & downhole & carbon dioxide	8	1	1	59					
flow & sensor* & downhole & CO2	0	2	1	659					
flow & sensor* & in situ	7117	719	632	2802					

	Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro		Derwent Innovations Index	Web of Science (w CP)	Compendex - 1969-2011	OnePetro
flow & sensor* & in situ & carbon dioxide	dns	8	8	45					
flow & sensor* & in situ & CO2	dns	18	0	180					

Table 25 Geophysics Searches

Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid or useful
Keyword string used				Keyword string used			
Geophysical monitoring				**Geophysical monitoring**			
seismic & CO2	ISI Web of Science (WoS)	388	N	seismic & CO2	Derwent Innovations Index (DII)	8	Y
seismic & CO2 sequestration	WoS	43	Y	seismic & CO2 sequestration	DII	1	N
seismic & CO2 monitoring	WoS	118	Y	seismic & CO2 monitoring	DII	2	N
seismic & sensor	WoS	839	N	seismic & sensor	DII	1968	N
seismic & CO2 monitoring & sensor	WoS	7	Y	seismic & CO2 monitoring & sensor	DII	0	N
microseismic & CO2 monitoring	WoS	9	Y	microseismic & CO2 monitoring	DII	0	N
microseismic & CO2 sequestration	WoS	2	Y	microseismic & CO2 sequestration	DII	0	N
microseismic & sensor	WoS	17	N	microseismic & sensor	DII	19	N
electromagnetic & CO2	WoS	333	N	electromagnetic & CO2	DII	284	N
electromagnetic & CO2 sequestration	WoS	5	Y	electromagnetic & CO2 sequestration	DII	0	N
electromagnetic & CO2 monitoring	WoS	17	Y	electromagnetic & CO2 monitoring	DII	13	N
electromagnetic & sensor	WoS	3213	N	electromagnetic & sensor	DII	18324	N
electromagnetic & CO2 monitoring & sensor	WoS	2	N	electromagnetic & CO2 monitoring & sensor	DII	31	N
resistivity & CO2	WoS	330	N	resistivity & CO2	DII	115	N
resistivity & CO2 sequestration	WoS	6	Y	resistivity & CO2 sequestration	DII	0	N
resistivity & CO2 monitoring	WoS	20	Y	resistivity & CO2 monitoring	DII	2	N
resistivity & sensor	WoS	1064	N	resistivity & sensor	DII	1524	N
resistivity & CO2 monitoring & sensor	WoS	2	Y	resistivity & CO2 monitoring & sensor	DII	0	N
conductivity & CO2	WoS	1953	N	conductivity & CO2	DII	575	N
conductivity & CO2 sequestration	WoS	30	Y	conductivity & CO2 sequestration	DII	2	N
conductivity & CO2 monitoring	WoS	71	Y	conductivity & CO2 monitoring	DII	30	N
conductivity & sensor	WoS	4127	N	conductivity & sensor	DII	7774	N
conductivity & CO2 & sensor	WoS	142	N	conductivity & CO2 & sensor	DII	40	N
conductivity & CO2 monitoring & sensor	WoS	9	Y	conductivity & CO2 monitoring & sensor	DII	5	N
"self potential" & CO2	WoS	21	Y	"self potential" & CO2	DII	0	N
"self potential" & CO2 sequestration	WoS	0	N	"self potential" & CO2 sequestration	DII	0	N
"self potential" & CO2 monitoring	WoS	4	Y	"self potential" & CO2 monitoring	DII	0	N
"self potential" & sensor	WoS	2	N	"self potential" & sensor	DII	4	N
"self potential" & CO2 & sensor	WoS	0	N	"self potential" & CO2 & sensor	DII	0	N

Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid or useful
Keyword string used				Keyword string used			
"self potential" & CO2 monitoring & sensor	WoS	0	N	"self potential" & CO2 monitoring & sensor	DII	0	N
gravity & CO2	WoS	542	N	gravity & CO2	DII	299	N
gravity & CO2 sequestration	WoS	53	Y	gravity & CO2 sequestration	DII	3	N
gravity & CO2 monitoring	WoS	27	Y	gravity & CO2 monitoring	DII	9	N
gravity & sensor	WoS	4637	N	gravity & sensor	DII	4086	N
gravity & CO2 & sensor	WoS	6	Y	gravity & CO2 & sensor	DII	4	N
gravity & CO2 monitoring & sensor	WoS	2	Y	gravity & CO2 monitoring & sensor	DII	1	N
spectral & CO2	WoS	3490	N	spectral & CO2	DII	137	N
spectral & CO2 sequestration	WoS	22	Y	spectral & CO2 sequestration	DII	1	N
spectral & CO2 monitoring	WoS	167	N	spectral & CO2 monitoring	DII	14	N
spectral & sensor	WoS	10943	N	spectral & sensor	DII	3250	N
spectral & CO2 & sensor	WoS	190	N	spectral & CO2 & sensor	DII	11	N
spectral & CO2 monitoring & sensor	WoS	23	N	spectral & CO2 monitoring & sensor	DII	2	N
magnetic resonance & CO2	WoS	1340	N	magnetic resonance & CO2	DII	124	N
magnetic resonance & CO2 sequestration	WoS	17	Y	magnetic resonance & CO2 sequestration	DII	0	N
magnetic resonance & CO2 monitoring	WoS	43	Y	magnetic resonance & CO2 monitoring	DII	11	N
magnetic resonance & sensor	WoS	2386	N	magnetic resonance & sensor	DII	1596	N
magnetic resonance & CO2 & sensor	WoS	11	N	magnetic resonance & CO2 & sensor	DII	3	N
magnetic resonance & CO2 monitoring & sensor	WoS	2	Y	magnetic resonance & CO2 monitoring & sensor	DII	0	N
ground penetrating radar & CO2	WoS	15	Y	ground penetrating radar & CO2	DII	0	N
ground penetrating radar & CO2 sequestration	WoS	1	Y	ground penetrating radar & CO2 sequestration	DII	0	N
ground penetrating radar & CO2 monitoring	WoS	1	Y	ground penetrating radar & CO2 monitoring	DII	0	N
ground penetrating radar & sensor	WoS	280	N	ground penetrating radar & sensor	DII	28	N
ground penetrating radar & CO2 & sensor	WoS	1	N	ground penetrating radar & CO2 & sensor	DII	0	N
ground penetrating radar & CO2 monitoring & sensor	WoS	0	N	ground penetrating radar & CO2 monitoring & sensor	DII	0	N
topography & CO2	WoS	558	N	topography & CO2	DII	6	N
topography & CO2 sequestration	WoS	25	Y	topography & CO2 sequestration	DII	0	N
topography & CO2 monitoring	WoS	14	N	topography & CO2 monitoring	DII	0	N

Literature searches Keyword string used	Search engine/ database	Number of hits	Useful	Patent searches Keyword string used	Search engine/ database	Number of hits	Valid or useful
topography & sensor	WoS	1174	N	topography & sensor	DII	347	N
topography & CO2 & sensor	WoS	7	N	topography & CO2 & sensor	DII	1	N
topography & CO2 monitoring & sensor	WoS	1	N	topography & CO2 monitoring & sensor	DII	0	N
geophysic* & CO2	WoS	371	N	geophysic* & CO2	DII	2	N
geophysic* & CO2 sequestration	WoS	25	Y	geophysic* & CO2 sequestration	DII	0	N
geophysic* & CO2 monitoring	WoS	60	Y	geophysic* & CO2 monitoring	DII	1	Y
geophysic* & sensor	WoS	941	N	geophysic* & sensor	DII	486	N
geophysic* & CO2 & sensor	WoS	8	Y	geophysic* & CO2 & sensor	DII	0	N
geophysic* & CO2 monitoring & sensor	WoS	3	Y	geophysic* & CO2 monitoring & sensor	DII	0	N

Table 26 Biological searches

WWW search	Search engine/ database	Number of hits	Valid ?	Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid?
Keyword string used				Keyword string used				Keyword string used			
Biosensor	Google	2740000		Biosensor	ISI Web of Science (WoS)	22196	N	**Biosensor**	Derwent Innovations Index (DII)	5548	Y
Biosensor & CO2	Google	248000		Biosensor & CO2	WoS	112	Y	Biosensor & CO2	DII	25	Y
Biosensor & CO2 & monitoring	Google	7100		Biosensor & CO2 & monitoring	WoS	19		Biosensor & CO2 & monitoring	DII	6	Y
Biosensor & Sensor & CO2	Google	9610		Biosensor & Sensor & CO2	WoS	49	Y	Biosensor & Sensor & CO2	DII	11	Y
Biosensor & sequestration	Google	58400		Biosensor & sequestration	WoS	11		Biosensor & sequestration	DII	0	Y
Biosensor & soil	Google	364000		Biosensor & soil	WoS	266	Y	Biosensor & soil	DII	52	Y
Biosensor & soil & monitoring	Google	219000		Biosensor & soil & monitoring	WoS	49	Y	Biosensor & soil & monitoring	DII	11	Y
Biosensor & groundwater	Google	189000		Biosensor & groundwater	WoS	61	Y	Biosensor & groundwater	DII	2	Y
Biosensor & down hole	Google	563		Biosensor & down hole	WoS	62		Biosensor & down hole	DII	18045	Y
Biosensor & in situ	Google	111000		Biosensor & in situ	WoS	654	N	Biosensor & in situ	DII		N
Biosensor & in situ & monitoring	Google	67600		Biosensor & in situ & monitoring	WoS	139	N	Biosensor & in situ & monitoring	DII		N
Biosensor & in situ & monitoring & CO2	Google	51900		Biosensor & in situ & monitoring & CO2	WoS	1	N	Biosensor & in situ & monitoring & CO2	DII		N
Biosensor & in situ & monitoring & groundwater	Google	11300		Biosensor & in situ & monitoring & groundwater	WoS	5	Y	Biosensor & in situ & monitoring & groundwater	DII		N
DNA fingerprint	Google	95500		DNA fingerprint	WoS	2423	N	**DNA fingerprint**	DII	448	Y
DNA fingerprint & CO2	Google	3360		DNA fingerprint & CO2	WoS	2	Y	DNA fingerprint & CO2	DII	0	Y
DNA fingerprint & CO2 sequestration	Google	62		DNA fingerprint & CO2 sequestration	WoS	0	N	DNA fingerprint & CO2 sequestration	DII	0	Y
DNA profile	Google	127000		DNA profile	WoS	12167	N	DNA profile	DII	1993	Y
DNA profile & CO2	Google	3560		DNA profile &	WoS	25		DNA profile & CO2	DII	18	Y

WWW search	Search engine/ database	Number of hits	Valid ?	Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid?
Keyword string used				Keyword string used				Keyword string used			
				CO2							
DNA profile & CO2 sequestration	Google	126		DNA profile & CO2 sequestration	WoS	0	N	DNA profile & CO2 sequestration	DII	0	Y
DNA fingerprint & groundwater	Google	1660		DNA fingerprint & groundwater	WoS	4		DNA fingerprint & groundwater	DII	0	Y
DNA profile & groundwater	Google	868		DNA profile & groundwater	WoS	12	Y	DNA profile & groundwater	DII	0	Y
DNA fingerprint & soil	Google	11700		DNA fingerprint & soil	WoS	116		DNA fingerprint & soil	DII	3	Y
DNA fingerprint & soil & monitoring	Google	813		DNA fingerprint & soil & monitoring	WoS	7		DNA fingerprint & soil & monitoring	DII	0	Y
DNA profile & soil	Google	6180		DNA profile & soil	WoS	277		DNA profile & soil	DII	25	Y
DNA profile & soil & monitoring	Google	6410		DNA profile & soil & monitoring	WoS	10		DNA profile & soil & monitoring	DII	3	Y
DNA fingerprint & sequestration	Google	644		DNA fingerprint & sequestration	WoS	1	N	DNA fingerprint & sequestration	DII	0	Y
DNA profile & sequestration	Google	728		DNA profile & sequestration	WoS	8	N	DNA profile & sequestration	DII	1	Y
PCR & CO2	Google	1550000		PCR & CO2	WoS	630	N	**PCR & CO2**	DII	257	Y
PCR & CO2 sequestration	Google	1560		PCR & CO2 sequestration	WoS	3	Y	PCR & CO2 sequestration	DII	0	Y
PCR & CO2 & monitoring	Google	49300		PCR & CO2 & monitoring	WoS	9	Y	PCR & CO2 & monitoring	DII	14	Y
PCR & groundwater	Google	121000		PCR & groundwater	WoS	363	N	PCR & groundwater	DII	7	Y
PCR & groundwater & monitoring	Google	16000		PCR & groundwater & monitoring	WoS	68	Y	PCR & groundwater & monitoring	DII	2	Y
PCR & soil	Google	1840000		PCR & soil	WoS	4382	N	PCR & soil	DII	484	Y
PCR & soil & monitoring	Google	68000		PCR & soil & monitoring	WoS	249	N	PCR & soil & monitoring	DII	64	Y
PCR & soil & monitoring & in situ	Google	18100		PCR & soil & monitoring & in situ	WoS	36	Y	PCR & soil & monitoring & in situ	DII	6797	Y
Microarray	Google	31300000		Microarray	WoS	51449	N	**Microarray**	DII	5577	Y
Microarray & CO2	Google	176000		Microarray & CO2	WoS	112		Microarray & CO2	DII	39	Y

WWW search	Search engine/ database	Number of hits	Valid ?	Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid?
Keyword string used				Keyword string used				Keyword string used			
Microarray & CO2 sequestration	Google	1010		Microarray & CO2 sequestration	WoS	2	N	Microarray & CO2 sequestration	DII	0	Y
Microarray & CO2 & monitoring	Google	16500		Microarray & CO2 & monitoring	WoS	3	Y	Microarray & CO2 & monitoring	DII	6	Y
Microarray & groundwater	Google	323000		Microarray & groundwater	WoS	27	Y	Microarray & groundwater	DII	2	Y
Microarrary & soil	Google	241000		Microarrary & soil	WoS	280	N	Microarrary & soil	DII	43	Y
Microarray & soil & monitoring	Google	21000		Microarray & soil & monitoring	WoS	20	Y	Microarray & soil & monitoring	DII	7	Y
Microarray & soil & in situ	Google	55100		Microarray & soil & in situ	WoS	24	Y	Microarray & soil & in situ	DII	5576	Y
Phylochip	Google	18100		Phylochip	WoS	0	N	Phylochip	DII	0	Y
Bacteria	Google			Bacteria	WoS	>100000	N	**Bacteria**	DII	>100000	Y
Bacteria & monitoring & down hole	Google			Bacteria & monitoring & down hole	WoS	10	Y	Bacteria & monitoring & down hole	DII	18045	Y
Bacteria & monitoring & in situ	Google			Bacteria & monitoring & in situ	WoS	406	N	Bacteria & monitoring & in situ	DII		N
Bacteria & monitoring & in situ & groundwater	Google			Bacteria & monitoring & in situ & groundwater	WoS	63	Y	Bacteria & monitoring & in situ & groundwater	DII		N
Bacteria & monitoring & in situ & groundwater & sensor	Google			Bacteria & monitoring & in situ & groundwater & sensor	WoS	0	N	Bacteria & monitoring & in situ & groundwater & sensor	DII		N
Bacteria & monitoring & in situ & soil	Google			Bacteria & monitoring & in situ & soil	WoS	77	Y	Bacteria & monitoring & in situ & soil	DII		N
Bacteria & monitoring & in situ & soil & sensor	Google			Bacteria & monitoring & in situ & soil & sensor	WoS	0	N	Bacteria & monitoring & in situ & soil & sensor	DII		N
Fluorescence & sensor & CO2	Google			Fluorescence & sensor & CO2	WoS	190		Fluorescence & sensor & CO2	DII	32	Y
Fluorescence &	Google			Fluorescence &	WoS	25	Y	Fluorescence &	DII	10	Y

WWW search	Search engine/ database	Number of hits	Valid ?	Literature searches	Search engine/ database	Number of hits	Useful	Patent searches	Search engine/ database	Number of hits	Valid?
Keyword string used				Keyword string used				Keyword string used			
sensor & CO2 & monitoring				sensor & CO2 & monitoring				sensor & CO2 & monitoring			
Fluorescence & sensor & CO2 & soil	Google			Fluorescence & sensor & CO2 & soil	WoS	1	Y	Fluorescence & sensor & CO2 & soil	DII	1	Y
Fluorescence & sensor & CO2 & groundwater	Google			Fluorescence & sensor & CO2 & groundwater	WoS	0	N	Fluorescence & sensor & CO2 & groundwater	DII	0	Y
Dissolved Organic Carbon & sensor	Google			Dissolved Organic Carbon & sensor	WoS	56	Y	Dissolved Organic Carbon & sensor	DII	185	Y
Dissolved Organic Carbon & sensor & CO2	Google			Dissolved Organic Carbon & sensor & CO2	WoS	11	Y	Dissolved Organic Carbon & sensor & CO2	DII	0	Y
DNA & sensor & CO2	Google			DNA & sensor & CO2	WoS	16	N	DNA & sensor & CO2	DII	8	Y
Metabolic profile & sensor & CO2	Google			Metabolic profile & sensor & CO2	WoS	2	N	Metabolic profile & sensor & CO2	DII	0	Y

Table 27 Cation Searches

WWW search	Search engine/ database	Number of hits	Literature searches	Search engine/ database	Number of hits	Search engine/ database	Number of hits	Patentent searches	Search engine/ database	Number of hits
Keyword string used			Keyword string used					Keyword string used		
Cations	Google		**Cations**	ISI Web of Science (WoS)		Scopus		**Cations**	Scopus Patents (SP)	
Cation & CO2	Google	2,250,000	Cation* & CO2	WoS	4532	Scopus	6806	Cation* & CO2	SP	63922
Cation & CO2 + monitoring	Google	1,290,000	Cation* & CO2 + monitoring	WoS	61	Scopus	89	Cation* & CO2 + monitoring	SP	17589
Cation & sensor* & CO2	Google	1,050,000	Cation* & sensor* & CO2	WoS	188	Scopus	155	Cation* & sensor* & CO2	SP	12350
"Cation* sensor*" & CO2	Google	2,790,000	"Cation* sensor*" & CO2	WoS	7	Scopus	9	"Cation* sensor*" & CO2	SP	8
Cation* & sequestration	Google	794,000	Cation* & sequestration	WoS	432	Scopus	621	Cation* & sequestration	SP	6774
Cation* & "CO2 sequestration"	Google	53,700	Cation* & "CO2 sequestration"	WoS	13	Scopus	15	Cation* & "CO2 sequestration"	SP	79
Cation* & in situ & monitoring	Google	2,170,000	Cation* & in situ & monitoring	WoS	138	Scopus	172	Cation* & in situ & monitoring	SP	32524
Cation* & in situ & monitoring & CO2	Google	995,000	Cation* & in situ & monitoring & CO2	WoS	8	Scopus	8	Cation* & in situ & monitoring & CO2	SP	10041
Calcium & sensor*	Google	10,400,000	Calcium & sensor*	WoS	8420	Scopus	11602	Calcium & sensor*	SP	11602
"Calcium sensor*"	Google	620,000	"Calcium sensor*"	WoS	979	Scopus	832	"Calcium sensor*"	SP	546
"Calcium sensor*" & in situ	Google	95,300	"Calcium sensor*" & in situ	WoS	23	Scopus	22	"Calcium sensor*" & in situ	SP	231
"Calcium sensor*" & monitoring	Google	94,500	"Calcium sensor*" & monitoring	WoS	11	Scopus	14	"Calcium sensor*" & monitoring	SP	321
Calcium & sensor* & in situ & monitoring	Google	710,000	Calcium & sensor* & in situ & monitoring	WoS	15	Scopus	24	Calcium & sensor* & in situ & monitoring	SP	14946
"Ion specific electrode" (ISE)	Google	47,100	"Ion specific electrode" (ISE)	WoS	104	Scopus	342	"Ion specific electrode" (ISE)	SP	595
"Ion specific electrode" & CO2	Google	21,100	"Ion specific electrode" & CO2	WoS	1	Scopus	5	"Ion specific electrode" & CO2	SP	67
"Ion specific electrode" & calcium	Google	36,300	"Ion specific electrode" & calcium	WoS	18	Scopus	61	"Ion specific electrode" & calcium	SP	293
"Ion specific electrode" & cation*	Google	19,300	"Ion specific electrode" & cation*	WoS	8	Scopus	36	"Ion specific electrode" & cation*	SP	202

WWW search	Search engine/ database	Number of hits	Literature searches	Search engine/ database	Number of hits	Search engine/ database	Number of hits	Patentent searches	Search engine/ database	Number of hits
Keyword string used			Keyword string used					Keyword string used		
Potentiometry & sensor*	Google	865,000	Potentiometry & sensor*	WoS	947	Scopus	3042	Potentiometry & sensor*	SP	780
Potentiometry & sensor* & monitoring	Google	421,000	Potentiometry & sensor* & monitoring	WoS	74	Scopus	336	Potentiometry & sensor* & monitoring	SP	336
Potentiometry & sensor* & in situ	Google	183,000	Potentiometry & sensor* & in situ	WoS	28	Scopus	106	Potentiometry & sensor* & in situ	SP	169
Potentiometry & sensor* & metal*	Google	586,000	Potentiometry & sensor* & metal*	WoS	301	Scopus	686	Potentiometry & sensor* & metal*	SP	660
Fe-III OR Fe-II OR iron & monitoring	Google	19,400,000	Fe-III OR Fe-II OR iron & monitoring	WoS	3148	Scopus	9743	Fe-III OR Fe-II OR iron & monitoring	SP	65732
Fe-III OR Fe-II OR iron & monitoring & in situ	Google	2,440,000	Fe-III OR Fe-II OR iron & monitoring & in situ	WoS	239	Scopus	393	Fe-III OR Fe-II OR iron & monitoring & in situ	SP	17086
Fe-III OR Fe-II OR iron & borehole	Google	480,000	Fe-III OR Fe-II OR iron & borehole	WoS	134	Scopus	251	Fe-III OR Fe-II OR iron & borehole	SP	5434
Groundwater & monitoring & metal*	Google	7,600,000	Groundwater & monitoring & metal*	WoS	285	Scopus	773	Groundwater & monitoring & metal*	SP	2417
Groundwater & monitoring & cation*	Google	2,790,000	Groundwater & monitoring & cation*	WoS	67	Scopus	162	Groundwater & monitoring & cation*	SP	694
Groundwater & monitoring AND barium OR Ba2+	Google	204,000	Groundwater & monitoring AND barium OR Ba2+	WoS	6	Scopus	41	Groundwater & monitoring AND barium OR Ba2+	SP	161
Manganese & groundwater & monitoring	Google	318,000	Manganese & groundwater & monitoring	WoS	37	Scopus	242	Manganese & groundwater & monitoring	SP	643
Mercury & groundwater & monitoring	Google	819,000	Mercury & groundwater & monitoring	WoS	24	Scopus	91	Mercury & groundwater & monitoring	SP	618
Lead & groundwater & monitoring & sensor*	Google	1,330,000	Lead & groundwater & monitoring & sensor*	WoS	6	Scopus	17	Lead & groundwater & monitoring & sensor*	SP	1017
Lead OR Pb & groundwater &	Google	483,000	Lead OR Pb & groundwater &	WoS	14	Scopus	30	Lead OR Pb & groundwater &	SP	979

WWW search	Search engine/ database	Number of hits	Literature searches	Search engine/ database	Number of hits	Search engine/ database	Number of hits	Patentent searches	Search engine/ database	Number of hits
Keyword string used			Keyword string used					Keyword string used		
monitoring & in situ			monitoring & in situ					monitoring & in situ		
Zinc OR Zn & groundwater & monitoring	Google	848,000	Zinc OR Zn & groundwater & monitoring	WoS	105	Scopus	286	Zinc OR Zn & groundwater & monitoring	SP	751
Zinc OR Zn & groundwater & monitoring & in situ	Google	237,000	Zinc OR Zn & groundwater & monitoring & in situ	WoS	9	Scopus	10	Zinc OR Zn & groundwater & monitoring & in situ	SP	503
Cadmium OR Cd & groundwater & monitoring	Google	1,310,000	Cadmium OR Cd & groundwater & monitoring	WoS	77	Scopus	213	Cadmium OR Cd & groundwater & monitoring	SP	725
Cadmium OR Cd & groundwater & monitoring & in situ	Google	283,000	Cadmium OR Cd & groundwater & monitoring & in situ	WoS	12	Scopus	9	Cadmium OR Cd & groundwater & monitoring & in situ	SP	444
Arsenic & groundwater & sequestration	Google	44,500	Arsenic & groundwater & sequestration	WoS	23	Scopus	16	Arsenic & groundwater & sequestration	SP	193
Arsenic & groundwater & monitoring	Google	516,000	Arsenic & groundwater & monitoring	WoS	107	Scopus	427	Arsenic & groundwater & monitoring	SP	502
Arsenic & groundwater & monitoring & in situ	Google	99,000	Arsenic & groundwater & monitoring & in situ	WoS	6	Scopus	30	Arsenic & groundwater & monitoring & in situ	SP	324
Iron & groundwater & sequestration	Google	84,000	Iron & groundwater & sequestration	WoS	42	Scopus	30	Iron & groundwater & sequestration	SP	360
Iron & groundwater & sequestration & monitoring	Google	109,000	Iron & groundwater & sequestration & monitoring	WoS	4	Scopus	4	Iron & groundwater & sequestration & monitoring	SP	303
Metal & groundwater & sequestration	Google	96,600	Metal & groundwater & sequestration	WoS	27	Scopus	36	Metal & groundwater & sequestration	SP	417
Mercury OR Hg & groundwater & sequestration	Google	63,300	Mercury OR Hg & groundwater & sequestration	WoS	7	Scopus	3	Mercury OR Hg & groundwater & sequestration	SP	244
Cadmium OR Cd & groundwater & sequestration	Google	76,000	Cadmium OR Cd & groundwater & sequestration	WoS	5	Scopus	6	Cadmium OR Cd & groundwater & sequestration	SP	253
Lead OR Pb &	Google	165,000	Lead OR Pb &	WoS	22	Scopus	36	Lead OR Pb &	SP	417

WWW search	Search engine/ database	Number of hits	Literature searches	Search engine/ database	Number of hits	Search engine/ database	Number of hits	Patentent searches	Search engine/ database	Number of hits
Keyword string used			Keyword string used					Keyword string used		
groundwater & sequestration			groundwater & sequestration					groundwater & sequestration		
Monitored natural attenuation	Google	107,000	Monitored natural attenuation	WoS	275	Scopus	264	Monitored natural attenuation	SP	18
"Ion specific electrode" OR "ion selective electrode"	Google	101,000	"Ion specific electrode" OR "ion selective electrode"	WoS	2976	Scopus	8658	"Ion specific electrode" OR "ion slective electrode"	SP	3963
"Ion specific electrode" OR "ion selective electrode" & CO2	Google	32,700	"Ion specific electrode" OR "ion selective electrode" & CO2	WoS	58	Scopus	152	"Ion specific electrode" OR "ion selective electrode" & CO2	SP	400
"Ion specific electrode" OR "ion selective electrode" & monitoring	Google	47,100	"Ion specific electrode" OR "ion selective electrode" & monitoring	WoS	174	Scopus	623	"Ion specific electrode" OR "ion selective electrode" & monitoring	SP	1298
"Ion specific electrode" OR "ion selective electrode" & in situ	Google	22,800	"Ion specific electrode" OR "ion selective electrode" & in situ	WoS	82	Scopus	176	"Ion specific electrode" OR "ion selective electrode" & in situ	SP	542
"Ion specific electrode" OR "ion selective electrode" & metal*	Google	184,000	"Ion specific electrode" OR "ion selective electrode" & metal*	WoS	694	Scopus	1424	"Ion specific electrode" OR "ion selective electrode" & metal*	SP	2592
"Ion specific electrode" OR "ion selective electrode" & iron OR Fe-III OR Fe-II	Google	45,200	"Ion specific electrode" OR "ion selective electrode" & iron OR Fe-III OR Fe-II	WoS	101	Scopus	230	"Ion specific electrode" OR "ion selective electrode" & iron OR Fe-III OR Fe-II	SP	786
"Ion specific electrode" OR "ion selective electrode" & copper	Google	49,000	"Ion specific electrode" OR "ion selective electrode" & copper	WoS	312	Scopus	643	"Ion specific electrode" OR "ion selective electrode" & copper	SP	959
"Ion specific electrode" OR "ion selective electrode" & mercury	Google	34,800	"Ion specific electrode" OR "ion selective electrode" & mercury	WoS	108	Scopus	228	"Ion specific electrode" OR "ion selective electrode" & mercury	SP	500

Table 28 Anion Searches

WWW search	Search engine/ database	Number of hits	Literature searches	Search engine/ database	Number of hits	Search engine/ database	Number of hits	Patent searches	Search engine/ database	Number of hits
Keyword string used			Keyword string used					Keyword string used		
Anions			**Anions**	ISI Web of Science (WoS)				**Anions**	Scopus Patents (SP)	
Anion* & CO2	Google	5,550,000	Anion* & CO2	WoS	3351	Scopus	4380	Anion* & CO2	SP	51624
Anion* & CO2 + monitoring	Google	6,790,000	Anion* & CO2 + monitoring	WoS	40	Scopus	57	Anion* & CO2 + monitoring	SP	12122
Anion & sensor* & CO2	Google	4,150,000	Anion & sensor* & CO2	WoS	89	Scopus	72	Anion & sensor* & CO2	SP	5468
"Anion* sensor*" & CO2	Google	19,400,000	"Anion* sensor*" & CO2	WoS	2	Scopus	3	"Anion* sensor*" & CO2	SP	18
Anion* & sequestration	Google	610,000	Anion* & sequestration	WoS	232	Scopus	246	Anion* & sequestration	SP	5607
Anion* & "CO2 sequestration"	Google	40,100	Anion* & "CO2 sequestration"	WoS	7	Scopus	7	Anion* & "CO2 sequestration"	SP	57
Anion* & in situ & monitoring	Google	1,170,000	Anion* & in situ & monitoring	WoS	138	Scopus	142	Anion* & in situ & monitoring	SP	22054
Anion* & in situ & monitoring & CO2	Google	1,360,000	Anion* & in situ & monitoring & CO2	WoS	5	Scopus	6	Anion* & in situ & monitoring & CO2	SP	6163
Chloride & sensor*	Google	6,820,000	Chloride & sensor*	WoS	4629	Scopus	9413	Chloride & sensor*	SP	118759
"Chloride sensor*"	Google	620,000	"Chloride sensor*"	WoS	58	Scopus	128	"Chloride sensor*"	SP	143
"Chloride sensor*" & in situ	Google	4,000	"Chloride sensor*" & in situ	WoS	9	Scopus	4	"Chloride sensor*" & in situ	SP	16
"Chloride sensor*" & monitoring	Google	11,000	"Chloride sensor*" & monitoring	WoS	13	Scopus	14	"Chloride sensor*" & monitoring	SP	78
Chloride & sensor* & in situ & monitoring	Google	3,820,000	Chloride & sensor* & in situ & monitoring	WoS	29	Scopus	49	Chloride & sensor* & in situ & monitoring	SP	16259
"Ion specific electrode" (ISE)	Google	47,100	"Ion specific electrode" (ISE)	WoS	104	Scopus	342	"Ion specific electrode" (ISE)	SP	595
"Ion specific electrode" & CO2	Google	21,100	"Ion specific electrode" & CO2	WoS	1	Scopus	5	"Ion specific electrode" & CO2	SP	67
"Ion specific electrode" & chloride	Google	65,500	"Ion specific electrode" & chloride	WoS	11	Scopus	58	"Ion specific electrode" & chloride	SP	430
"Ion specific electrode" & anion*	Google	20,200	"Ion specific electrode" & anion*	WoS	1	Scopus	20	"Ion specific electrode" & anion*	SP	222
Potentiometry &	Google	865,000	Potentiometry &	WoS	947	Scopus	3042	Potentiometry &	SP	780

sensor*			sensor*					sensor*		
Potentiometry & sensor* & monitoring	Google	421,000	Potentiometry & sensor* & monitoring	WoS	74	Scopus	336	Potentiometry & sensor* & monitoring	SP	336
Potentiometry & sensor* & in situ	Google	183,000	Potentiometry & sensor* & in situ	WoS	28	Scopus	106	Potentiometry & sensor* & in situ	SP	169
Potentiometry & sensor* & anion*	Google	163,000	Potentiometry & sensor* & anion*	WoS	282	Scopus	441	Potentiometry & sensor* & anion*	SP	253
Groundwater & monitoring & anion*	Google	1,820,000	Groundwater & monitoring & anion*	WoS	63	Scopus	145	Groundwater & monitoring & anion*	SP	670
Groundwater & monitoring & sulfate OR SO42-	Google	1,100,000	Groundwater & monitoring & sulfate OR SO42-	WoS	232	Scopus	467	Groundwater & monitoring & sulfate OR SO42-	SP	1015
Fluoride & groundwater & monitoring	Google	1,230,000	Fluoride & groundwater & monitoring	WoS	32	Scopus	120	Fluoride & groundwater & monitoring	SP	230
Bromide & groundwater & monitoring	Google	120,000	Bromide & groundwater & monitoring	WoS	61	Scopus	146	Bromide & groundwater & monitoring	SP	306
Iodide & groundwater & monitoring	Google	69,200	Iodide & groundwater & monitoring	WoS	11	Scopus	19	Iodide & groundwater & monitoring	SP	151
Phosphate & groundwater & monitoring	Google	1,040,000	Phosphate & groundwater & monitoring	WoS	59	Scopus	199	Phosphate & groundwater & monitoring	SP	846
Nitrate & groundwater & monitoring	Google	1,690,000	Nitrate & groundwater & monitoring	WoS	505	Scopus	1087	Nitrate & groundwater & monitoring	SP	801
Sulfate & groundwater & sequestration	Google	172,000	Sulfate & groundwater & sequestration	WoS	14	Scopus	10	Sulfate & groundwater & sequestration	SP	239
Anion & groundwater & sequestration	Google	97,000	Anion & groundwater & sequestration	WoS	1	Scopus	2	Anion & groundwater & sequestration	SP	45
Fluoride & groundwater & sequestration	Google	185,000	Fluoride & groundwater & sequestration	WoS	0	Scopus	0	Fluoride & groundwater & sequestration	SP	81
Nitrate & groundwater & sequestration	Google	679,000	Nitrate & groundwater & sequestration	WoS	16	Scopus	13	Nitrate & groundwater & sequestration	SP	112
Phosphate &	Google	77,200	Phosphate &	WoS	6	Scopus	7	Phosphate &	SP	109

groundwater & sequestration			groundwater & sequestration					groundwater & sequestration		
"Ion specific electrode" OR "ion selective electrode"	Google	101,000	"Ion specific electrode" OR "ion selective electrode"	WoS	2976	Scopus	8658	"Ion specific electrode" OR "ion slective electrode"	SP	3963
"Ion specific electrode" OR "ion selective electrode" & CO2	Google	32,700	"Ion specific electrode" OR "ion selective electrode" & CO2	WoS	58	Scopus	152	"Ion specific electrode" OR "ion selective electrode" & CO2	SP	400
"Ion specific electrode" OR "ion selective electrode" & monitoring	Google	47,100	"Ion specific electrode" OR "ion selective electrode" & monitoring	WoS	174	Scopus	623	"Ion specific electrode" OR "ion selective electrode" & monitoring	SP	1298
"Ion specific electrode" OR "ion selective electrode" & in situ	Google	22,800	"Ion specific electrode" OR "ion selective electrode" & in situ	WoS	82	Scopus	176	"Ion specific electrode" OR "ion selective electrode" & in situ	SP	542
"Ion specific electrode" OR "ion selective electrode" & anion*	Google	105,000	"Ion specific electrode" OR "ion selective electrode" & anion*	WoS	636	Scopus	1107	"Ion specific electrode" OR "ion selective electrode" & anion*	SP	1487
"Ion specific electrode" OR "ion selective electrode" & Chloride	Google	67,000	"Ion specific electrode" OR "ion selective electrode" & Chloride	WoS	886	Scopus	2056	"Ion specific electrode" OR "ion selective electrode" & Chloride	SP	2642
"Ion specific electrode" OR "ion selective electrode" & sulfate	Google	38,200	"Ion specific electrode" OR "ion selective electrode" & sulfate	WoS	244	Scopus	274	"Ion specific electrode" OR "ion selective electrode" & sulfate	SP	1060
"Ion specific electrode" OR "ion selective electrode" & nitrate	Google	37,300	"Ion specific electrode" OR "ion selective electrode" & nitrate	WoS	280	Scopus	509	"Ion specific electrode" OR "ion selective electrode" & nitrate	SP	868