

Workbook for Developing a Monitoring Plan to Ensure Storage Permanence in a Geologic Storage Project, Including Site-specific Tool Selection

by

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Abstract

This workbook illustrates a methodology for developing a site-specific and fit-to-purpose monitoring plan for geologic storage of CO₂. The monitoring plan must be aligned with project goals, which may vary from project to project. Early geologic storage projects have had research and demonstration goals; because mature and full-scale projects have different goals, the monitoring plan must then be different in response. Design of an effective monitoring plan requires development of quantitative goals for the project; implicit in these goals is the possibility of failure to meet the goals, which is designated a material impact. By the time the project is advanced to the stage of monitoring-plan design, characterization, modeling, and engineering design will have greatly diminished the risk of such impact. To increase project certainties beyond this stage, an assessment of a low-probability material impact (ALPMI) is undertaken, by modeling the response to outlier conditions possible in the characterization data. Only scenarios in which uncertainties combine to create material impacts are retained; other unexpected outcomes that do not lead to material impact can be disregarded.

Development of hypothetical ALPMI scenarios allows design of monitoring plans that are site specific. ALPMI's provide discrete thresholds that are indicators of or trends toward material impact; monitoring is designed to detect these conditions. Different sites lead to different ALPMIs, choices which in turn lead to selection of different monitoring parameters.

A second parameter that defines what monitoring is optimal is site-specific tool sensitivity. In addition to conventional tool optimization, ALPMI allows a quantitative assessment of whether the tool is sensitive to perturbation under site-specific conditions. We assess a sample of site-specific variables related to seismic, pressure, thermal, and geochemical monitoring to illustrate the need to for extensive forward modeling and evaluation by a team of experts to design tools that can provide robust assurance of the expected negative outcome: that the material impact is not occurring.

A third site-specific parameter especially important in designing for a response that is not expected is an assessment of noise and repeatability. This is conventionally recommended for 3-D seismic surveys, but this assessment is equally or even more important for other surveys with a time-lapse element, such as pressure and geochemistry. Noise evaluation is needed both to provide assurance that the material impact can be detected above noise by the planned method and to avoid triggering concern by ambient variability unconnected to material impact.

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Acronyms

AoR	area of review
AZMI	above-zone monitoring interval
ALPMI	assessment of low probability material impact
CCS	carbon capture and storage
DIC	dissolved inorganic carbon
EOR	enhanced oil recovery
USDW	underground sources of drinking water
VSP	vertical seismic profile

1 Introduction

1.1 Overview of Geologic Storage

Geologic storage is the last step in carbon capture and storage (CCS), a process by which CO₂ that is now being emitted to the atmosphere is captured, transported, and injected into the subsurface for storage (IPCC, 2005; World Resources Institute, 2008). The goal of geologic storage is that the rate of increase of CO₂ in the atmosphere and oceans will be diminished or reversed. Under market scenarios, the cost of CCS may incentivize other emissions reductions, such as conservation, efficiency, or fuel switching to low- or no-carbon energy.

For pragmatic reasons, the major location of CO₂ capture is from large stationary sources; scattered or mobile sources are not generally seen as feasible because of the value of efficiency of scale to both capture and storage. Sources that produce large volumes of CO₂ as a result of oxidation of carbon-based fuels (coal, oil, gas, biofuel, etc.) such as power plants or refineries are major targets for carbon capture. CO₂ from other large-volume emitters, for example CO₂ stripped from natural gas or produced as a by-product of cement manufacture, can also be captured.

The value of a geologic storage project is in providing assurance that injected CO₂ will be stored over long time frames so that the benefit to the atmosphere is attained (Lindeberg, 2002). The main mechanism to provide assurance of long-term storage is site selection (U.S. Department of Energy, National Energy Technology Laboratory, 2010). The hydrologic and petrophysical properties of the natural subsurface system provide the large-volume containment required. CO₂ is injected below and isolated from freshwater resources that in the U.S. are protected by the Safe Drinking Water Act (U.S. Environmental Protection Agency, 2012). Isolation of the injection zone from the atmosphere and freshwater resources is initially assessed through numerical modeling of fluid flow using measured rock and fluid characteristics.

Abundant experiences with long-term trapping in natural accumulations of methane, oil, and CO₂ in the subsurface as well as similar engineered conditions for oil and gas production, fluid waste disposal, injection of CO₂ for enhanced oil recovery (EOR), and a number of well-studied CO₂ storage tests allow predictive modeling of the system response to injection to be conducted with high confidence (for example, U.S. Department of Energy, National Energy Technology Laboratory, 2011). Numerical modeling is required to make predictions of the system performance to accept and retain the planned volume of CO₂ at the planned rate, for the planned duration, and to retain the CO₂ for a long time frame. However, predictive modeling intrinsically has uncertainties derived from 1) extrapolation of measurements made in parts of the storage volume to the entire storage volume and for time scales much longer than the observation periods and 2) model simplifications, such as upscaling pore-scale processes to large grid blocks needed to run fluid flow models.

To reduce uncertainties, additional measurements can be made during injection. Such measurements fall into two categories. *Conformance monitoring* is designed to confirm the correctness of the model prediction of the system response to injection. A database of observations can be accumulated as

injection continues; a series of refinements can be made to the predictive model that result in decreased uncertainty in model prediction. Conformance monitoring over long time periods is conducted for measurement of groundwater aquifers and in hydrocarbon reservoirs, and is needed in geologic storage to predict the long-term fate of injected CO₂ in the reservoir. *Assurance monitoring*, in contrast, is designed to detect if any undesirable or unacceptable responses are occurring during the monitoring period. Assurance monitoring can also be designed to measure any trends that indicate that undesirable or unacceptable responses may occur in the system in the future. Assurance monitoring is more challenging than conformance monitoring because it undertakes to document a negative finding, that is, no unacceptable effects or trends toward unacceptable outcomes are occurring.

1.2 Purpose of this workbook

Regulations and protocols for monitoring have emphasized the need to match the monitoring plan design to the geologic storage site (Det Norske Veritas, 2009; U.S. Environmental Protection Agency, 2010; United Nations Framework Convention on Climate Change, 2011; McCormick, 2012). However, details on how to conduct this matching are sparse. This workbook illustrates a workflow to fill the gap between the intent to make the plan specific to the site and the implementation of such a plan (Fig. 1).

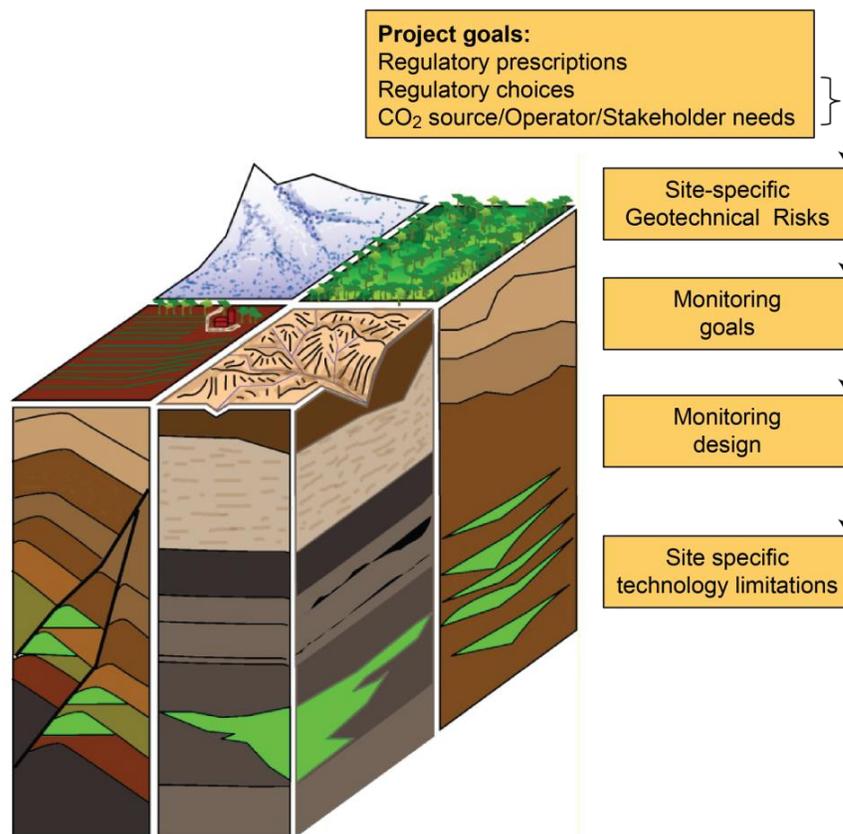


Figure 1. Project goals interact with site-specific geotechnical risks and site-specific technologies' limitations, which creates a need for site-specific monitoring goals and plans.

A geotechnical team with expertise in diverse science and engineering components is needed to design a monitoring plan, and this workbook in no way substitutes for a qualified design team. This workbook provides background information to participants whose different types of expertise are needed to develop a CCS project, from financiers who provide the investment, to regulators who ensure that standards are met to assure the public that public health and safety and environmental and other resources are conserved, to members of the local community who need assurance that outcomes will not adversely impact quality of life in the storage areas, to consumers who pay for the value of carbon-emissions reduction in terms of higher costs of energy supply. Representatives of stakeholders may need to evaluate the project plan and its execution. This workbook provides guidance and examples of a method to critically evaluate the design of the monitoring plan. After reviewing the test cases, stakeholder representatives should have the tools to ask a series of key questions of the geotechnical design team to determine the extent to which the plan is fit-to-purpose.

This workbook can provide examples of only a small subset of monitoring techniques that have been considered as having value for CCS (for examples, see British Geological Survey, 2006; World Resources Institute, 2008; U.S. Department of Energy, National Energy Technology, 2009, Det Norske Veritas, 2009, Cooper and CCP team, 2009). Further, each of the selected subset of techniques has a large number of possible variations and optimizations. Beyond the currently available techniques, we anticipate that many more improvements and valuable variations will be proposed in future projects. This workbook is therefore designed as a method that can be adapted to assess a wide range of technologies.

2 Methodology to evaluate a site-specific, fit-to-purpose geologic storage monitoring design

2.1 Components of storage assurance

Creating a successful geologic storage project requires integration of a series of interlocking steps: goal setting, site selection, geologic characterization, geotechnical risk assessment/retention assurance, monitoring design and execution, and closure. The focus of this workflow is on developing the fit-to-purpose monitoring component. However, to design the monitoring component requires analysis of the interlock with the other steps.

2.1.1 Goal setting

Goal setting has a critical interlock with the monitoring design in that it defines the goal that a fit-to-purpose monitoring plan will meet (Hovorka, 2012). Most CCS projects have a series of high-level goals; however, as part of monitoring design, goals have to be set that are specific and quantitative. Different goals may result in a different monitoring design. Failure to meet the goals is referred to as a *material impact*.

Examples of project goals that might drive the monitoring program are shown in Table 1.

Table 1. Selected example project goals that might be related to the monitoring design.

Goal:	Set quantitative standard:	Drives monitoring to:
Specified in protocol	Determined by protocol	Comply
Accept the planned mass at the planned rate	Determine factors that limit the rate at which CO ₂ would be accepted	Design monitoring with detection limits required to meet this expectation
Demonstrate retention of CO ₂ in the subsurface (not emitted to the atmosphere)	Set a standard for retention	Design monitoring with detection limits required to meet this expectation
Avoid damage to groundwater	Calculate the rate and volume of CO ₂ and brine that would be defined as damaging	Design monitoring with detection limits required to meet this expectation
Avoid damage to resources	Enumerate and calculate the rate or volume of CO ₂ or brine that would be defined as damaging	Design monitoring with detection limits required to meet this expectation
Avoid human health and safety risk	Calculate the emissions rates at site specific conditions that could imperil human health or safety	Design monitoring with detection limits required to meet this expectation
Avoid ecosystem damage	Calculate the emission rates at site-specific conditions that could damage the ecosystem	Design monitoring with detection limits required to meet this expectation
Avoid felt seismicity	Calculate the geomechanical stress differential that could lead to felt seismicity at site-specific conditions	Design monitoring with detection limits required to meet this expectation
Demonstrate the validity of numerical models for predicting fluid flow (in the research context)	Determine the parameters needed to validate models	Deploy instruments capable of collecting the needed parameters at adequate sensitivity
Demonstrate the appropriateness of monitoring tools	Design situations to test tool response	Deploy instruments capable of collecting the needed parameters at adequate sensitivity
Other concern	Measurement made to meet stakeholder need	

The first case listed in Table 1 is one in which regulations or other best practice protocols provide concrete guidance about monitoring tools to be used, frequency of data collection, calibration and precision, reporting standards, and other specifications. Where this is the case, the workflow presented here is not needed; direct negotiations between the operator and the regulator are sufficient. In related cases, the regulations require certain types of measurement, and the expectation is that the project designer will negotiate with the regulator on some of the needed details. However, in other cases, where a non-prescriptive approach has been taken, as in the U.S. Environmental Protection Agency

(EPA) class VI regulation and guidance (U.S. CFR, 2010b, U. S. Environmental Protection Agency, 2013) the workflow is valuable to optimize the negotiations with respect to site-specific conditions.

Capacity for the selected site to accept the planned volume of CO₂ at the planned rate is a critical project goal (Table 1, second goal). The simplicity of the metric obscures the difficult aspect of goal setting, which is to define the conditions under which injection could not continue at the planned rate. A depth-dependent limit on the acceptable injection pressure at the perforated section of the well is the most common limit on injection rate (Bruce, 2002; Railroad Commission of Texas, 2012). Regulations set the maximum allowable injection pressure with respect to failure criteria, which may be set as fracturing the reservoir or the confining system. Rock type, pre-existing weakness such as partings or fractures, stress state, well construction, and injection and formation temperatures can have an impact on failure, which can drive the need for sophisticated characterization. However, once the acceptable maximum pressure at the perforations is determined, monitoring is relatively straightforward. The largest difficulty in obtaining accurate measurements is that CO₂ density and viscosity have strong temperature dependence, and the evolution of temperature within injection wells as the system reaches a new equilibrium is difficult to model. This difficulty can be overcome by making downhole measurements near the perforations until the conditions are adequately constrained. If bottomhole pressure at the injection well increases on a trajectory that will intersect the maximum allowable pressure, this should trigger an ALPMI, and a remediation such as increasing the perforated interval, drilling an additional injection well, or withdrawing fluid from the far-field to decrease pressure should be considered. Such measures have been deployed at Statoil's CO₂ injection project at Snøhvit field in the North Sea (Hansen and others, 2013), and planned at Chevron's CO₂ injection project at Gorgon field, Northwest Australia (Flett and others, 2009).

Bottom-hole pressure is a widely used and robust measure of conformance, with pressure used to demonstrate that fluid flow models are predictive. Because pressure integrates over a large rock volume, far-field reservoir conditions such as no-flow boundaries or open flow-paths that connect multiple units can be detected by trends in pressure evolution, and augmented by fall-off testing (Johnson and Lopez, 2003).

Pressure conditions distant from the injection well can also have an impact on the acceptable pressure increase. Examples of distant pressure limits include anisotropies in the rocks such as transmissive fracture systems and well completions that do not isolate zones (Birkholzer and others, 2013). If pressure exceeds the limit, these features may fail hydraulically, resulting in fluids conveyed to Underground Sources of Drinking Water (USDW), or may fail geomechanically, resulting in rupture at weaknesses, potentially creating seismicity or opening pathways. The potential for failure and the pressure at which failure can occur can be difficult to determine during characterization (IEAGHG, 2013). Additional complications in far-field pressure can occur as a result of injection into a strongly dipping reservoir, where confining pressure is decreased away from the injection well, or by accumulation of a thick column of buoyant CO₂. Strategies to determine sensitivity of the system to far-field pressure increase are precursors to development of monitoring strategies to provide assurance that the system is responding within the boundaries set.

Retention is implicit in the term storage and is the focus of cases explored in this workbook (Table 1, line 3). In order to meet a retention goal, a quantitative expression of project ambitions is needed. In some cases (Texas House Bill 469, 2009), the IPCC (2005) expectation that it is probable that 99% of the CO₂ will be stored in the subsurface for a duration of 1000 years may be the goal. Using this definition, the monitoring program can be designed to detect a leakage rate calculated by dividing the total volume planned to be injected by the desired storage duration. Another approach is used by the European Union is to quantify emissions and surrender allowances (Official Journal of the European Union, 2009), in this case an emission rate that is considered negligible must be quantified, and calculated in the same way. Project developers may want to demonstrate that retention is occurring during the early stages of project to demonstrate the value of the site early on; this would result in a different type of calculation and a different metric.

Documentation of retention by direct measurement of the mass of CO₂ stored is problematic because of a lack of precision of *in situ* measurements of CO₂ volume. Given that CO₂ occurs in the reservoir complexly admixed with water and rock, measurements of CO₂ volume range from 5 to 25%, which is lower than most retention goals. Conformance measurements showing that CO₂ has not and will not migrate to areas where known or suspected leakage paths exist may be of value in documenting that the retention standard is met. Such an approach relies on confidence in characterization of the quality of confinement in the area where the injection is planned; it cannot test for the presence of unknown migration pathways.

To assess for unknown migration pathways, an assurance method is required. Care must be used in development of a monitoring strategy because leakage is not expected; the design should be sufficiently robust that if leakage occurs, a report of “no material impact” can be made. Potential flaws in confinement, such as wells with flawed engineering or fractures that provide transmissive pathways, will have been tested during characterization and mitigated such that the operator and regulator have confidence that the system will isolate injected CO₂ so that a permit can be obtained. To demonstrate that leakage of CO₂ out of the designated interval is not occurring is a negative conclusion. Such a conclusion is most manageable by setting up a series of scenarios in which leakage greater than that specified by goals is unlikely but possible (low probability) and testing each scenario via modeling to see if the outcome is possible in the context of the available data, including uncertainty, and then collecting additional data during characterization or monitoring to continue to test if the low- probability scenario is still possible.

The next five goals in Table 1 are focused on avoiding damages or other undesirable outcomes. Assessments of scenarios that might lead to damage could be complex, as they may need to consider both fluids from the failure of storage and attenuation. Attenuation processes might be dilution or rock-water-CO₂ interactions. In most cases the retention goal may be sufficient to provide assurance that no resource damage is occurring, which may allow the numerous goals shown in Table 1 to collapse into a few, most stringent goals.

Other goals listed in Table 1 are research-oriented objectives. Many monitoring projects completed to date have had, in part, research-oriented objectives. It is important to make explicit if this is part of the

design because research needs may drive monitoring toward high- resolution, high-frequency, or redundant measurements that are not appropriate for a commercial project. For example, at the Frio test (Hovorka and others, 2006), research-oriented goals resulted in a design that called for two closely spaced wells between which crosswell seismic measurements and high- precision “U-tube” emplaced tracer samples could be collected. Such an array was fit-to-purpose to meet research objectives, but it is clearly unsuitable for meeting other types of objectives.

A last category of goals is goals specific to stakeholders, who may have concerns that can be met by providing certain types of information. Meeting this need may be integrated with other types of goals, but it is possible that the specific type of monitoring needed to assure stakeholders is beyond the scope of this workflow.

It is important that the goals be set to be attainable through available methods at the selected site. An iteration through the stages of design may be needed to determine what is attainable. Quantitative project goals allow definition of information important to the project, because not all information is equally valuable, and previous experience in a rapidly maturing technology may not be a good guide. Outcomes that have a material impact on the project goals are elevated; other types of variability that fall of the range of acceptable performance are given less importance. Such an assessment allows justification of investment in some measurements but not others, and for different measurements to be made at different sites. If the value of the material impact can be specified, for example in terms of a penalty for loss of CO₂ from storage in a specified volume, a formal value of information assessment can be conducted to evaluate characterization and monitoring investments.

To discuss providing assurance of project success requires detailed consideration of the inverse: outcomes that would not be acceptable. Only with a quantitative and pragmatic definition of the boundary between an acceptable and unacceptable outcome is it possible to document achieving a successful outcome. Tolerance for uncertainties can be substantively different depending on context. For example, many geologic storage projects conducted so far have had a significant research element, which motivates the monitoring program and requires an intensive monitoring program to meet their objectives. Other project objectives may be met very simply, for example via a simple mass accounting as is done for most types of disposal and production wells. This workflow is designed for cases in which project goals require a more elaborate plan for confirmation, for example as outlined in the Clean Air Act subpart RR (U.S. Environmental Protection Agency, 2010) or in the U.S. EPA’s Class VI rules for injection of CO₂ into saline formations (U.S.CFR, 2010b).

2.1.2 Site Selection

Site selection is the most critical stage of the project in terms of accepting the planned volumes of CO₂ at the planned rate and of retaining it to the planned standard while avoiding any unacceptable ancillary effects (Official Journal of the European Union, 2009; Det Norsk Veritas, 2009; U.S. Department of Energy, National Energy Technology Laboratory, 2010; U.S. CFR, 2010b; CSA Group, 2012). In this workflow, we assume that the site has been selected using the best available methods. It is worth noting that the characteristics of the site have a strong impact on the methods by which it can be monitored and on the sensitivity of those methods. If the site characteristics cause an important detection method

to be relatively insensitive, a site that was otherwise acceptable might be downgraded during site selection.

2.1.3 Geologic Characterization

In the context of monitoring, geologic characterization is the critical data source to provide input into predictive models, risk assessment, and sensitivity analysis. The properties of rocks and fluids needed for characterization are relatively well known. Many general examples (Van Riel, 2000; Slatt, 2006; Lucia, 2007) are augmented by CO₂ storage-specific reviews (Det Norsk Veritas, 2009; U.S. Department of Energy, 2010; U.S. CFR, 2010b, CSA Group, 2012) However, examining the interlock between characterization and monitoring brings out several important aspects that have previously not been widely considered.

Not all characterization data are equally important to the goals set by the project. In an assessment workflow, we suggest that early and approximate characterization data be taken through a preliminary modeling, risk assessment, and modeling scenario to determine the precision with which reservoir properties need to be characterized to meet project goals. Risk assessment and modeling can then be used interactively with characterization to optimize data compilation, as described in the next section.

Characterization and monitoring are linked, and many activities can fall into either category. To complete a quantitative characterization, it is usually necessary to energize the reservoir system by injecting or withdrawing fluids to obtain reliable data on the hydrological properties of the reservoir. Other elements, such as the performance of the confining system including the adequacy of well penetrations in providing isolation, the nature of reservoir boundary conditions, and the geomechanical response of the reservoir to pressure increases, may also be critical needs prior to completing the risk assessment and designing a monitoring program. Some data about the performance of the two-phase (water and CO₂) system are needed for modeling, for example residual water saturation, relative permeability, and residual CO₂ saturation. These data can be collected in the laboratory on small samples; however the best practice from CO₂ EOR projects is to conduct a CO₂ injection pilot prior to committing to a full-scale injection (Teletzke and others, 2010).

In converse to the issue of injection as part of characterization, many monitoring techniques rely on collection of a suite of static measurements prior to perturbation of the system by injection. Such measurements are typically described as *baseline*. Baseline plays several important roles: it is important to correctly define the purpose of the survey for assessment of trends and noise, to assess signal strength, to determine repeatability, or to collect a pre-injection stable baseline from which later changes can be subtracted. The last goal, having a stable baseline against which to detect change, is a derivative from assessment of trends, noise and repeatability.

One major role of preinjection measurement is to collect data on the ambient variability of the system prior to introducing the perturbation. For example, in a 3-D seismic survey, noise is produced by events such as wind, traffic, thunder, equipment, and quarry blasts. Prior to design of the 3-D survey, a site-specific assessment of noise is conducted (Pevzner and others, 2011). Similar data on noise are needed for other types of monitoring. For example, pressure variability can originate from tides, ongoing

injection or production of water or other fluids, and recovery from past geologic or engineered perturbations. It is important in preparation for collection of time-lapse data to assess any trends in the preinjection conditions. For example, groundwater systems can be actively perturbed by local or distant injection or extraction, in recovery from past such activities, or in slow re-equilibration from basin-scale events such as glaciation. Groundwater systems can be stable or highly variable, as can vadose-zone gas saturations, with the possibility of varying trends in daily, seasonal, cyclic, and long-term land use and ecosystem evolution. Such a noise determination is one of the most critical site-specific impacts on the sensitivity of monitoring. Measurements can be made at a quiet site where the signal is stable that would be obscured at a noisy site. It is possible to design methods to remove noise and improve data quality. Methods include making measurements at locations isolated or shielded from noise, setting up an array of measurements over time and space that can be used to extract signal from noise, and treating data statistically.

A second element of characterization needed for monitoring design is the strength of the signal. In this workbook we illustrate some examples of factors that influence signal strength. However, a best practice is to make measurements at the site to determine experimentally the strength of the signal. For a 3-D seismic survey, this assessment can be made by testing the response of an array of geophones placed in a well to various types of seismic sources at the surfaces. Such a test can be part of a vertical seismic profile (VSP) and is a well-known important part of designing a 3-D survey. Similar tests of sensitivity are recommended for pressure and temperature. Sensitivity tests for pressure might be an injection-fall off test to calibrate pressure response to a rate of injection and recovery. A sensitivity test for detection of CO₂ in groundwater might be a push-pull test, in which a small, controlled release of CO₂ is tested to determine the signal produced by rock-water-CO₂ interaction (Yang and others, 2013c).

A third element of characterization test program is repeatability, which can usually be collected at the same time as signal strength. If a time-lapse measurement is to be made, it is important to repeat the test several times to determine how accurately the test can be duplicated. In a seismic survey, repeatability can be formally determined by collecting statistics (Kinkela and others, 2011). Similar tests of repeatability are recommended for hydraulic pressure and thermal perturbation tests. Tests of repeatability are classically conducted for geochemical analysis programs using duplicates and blanks; it is important for gas-liquid systems such as CO₂ in water to test the repeatability of the field sampling protocols as well as the laboratory analysis.

After the first three elements have been measured and determined to be favorable, it is reasonable to proceed to collect a pre-injection stable baseline survey of 3-D seismic, pressure, temperature, groundwater chemistry, or other parameters from which later changes can be subtracted to determine change or no change. Time-lapse techniques are very powerful in assessing geologic storage, in which an allochthonous fluid is substituted and pressure systematically changed during the project timeframe. In most geologic applications, change from geologic processes or from human perturbation has already occurred.

2.1.4 Risk assessment/Retention assurance

Risk assessment is a mature method for managing risks in financial, industrial, nuclear, oil and gas, health and safety, and environmental operations. Diverse theoretical and applied methods have been developed for geologic storage applications (for example, U.S. Department of Energy, National Energy Technology Laboratory, 2011; CSA Group, 2013; Det Norsk Veritas, 2013; Quintessa, 2013). Much geotechnical risk can be mitigated by management techniques including targeted characterization followed by design and management of injection operations.

Monitoring is one element that augments both characterization and reservoir management. As is well known in geoscience operations, the intersection of an engineered system with the complexity of the subsurface is impossible to completely predict (Cooper and Staff of Carbon Capture Project, 2009). No matter how much work is done to characterize the reservoir and other relevant parts of the geologic system, some uncertainties will remain in predicting how the system will perform when the system is perturbed, in this case when CO₂ is injected. Risk assessments can be used to determine which uncertainties will remain at the end of characterization; these are called *material uncertainties*, and reducing them becomes the target for monitoring and for achieving the goals of the project. In this workbook, focused on designing a monitoring program for an individual site, we disregard the probabilistic aspects of risk assessment. We assume that high-probability risks are removed by site selection, injection design, and management prior to permitting the site. Our objective is identifying low-probability but possible material impacts, and designing a monitoring program to provide additional assurance that the failure of concern is not relevant.

In the context of this workbook, a distinctive type of risk assessment is needed. A range of acceptable outcomes was quantitatively specified in during goal-setting; acceptable risks are the opposite of risks of concern. The novel modeling needed to support this workflow is to explicitly model the conditions that would result in failure to reach the project goals. We describe this as an *assessment of low probability material impact (ALPMI)*.

Figure 2 illustrates the concept of exploring the range of acceptable outcomes in order to design a monitoring program. The parameters plotted in Figure 2 are each of the quantitative performance metrics defined as a result of goal setting. Table 2 provides a few illustrative examples of the parameters that might be used in Figure 2.

A predicted range (central box of Figure 2) based on characterization and modeling is the typical value presented during project development and to regulators. A best practice is to present a range of prediction uncertainty that is implicit in characterization and modeling, also shown in Figure 22. The critical step proposed in this workbook is setting the acceptable range of each parameter, which defines an ALPMI. Values greater than the range of uncertainty are not expected, however only values or trends reaching the ALPMI are of concern with regard to failure to meet project objectives. Figure 2 also illustrates a component emphasized in this workbook, that measurements have a range of error and uncertainties that must be considered in project design.

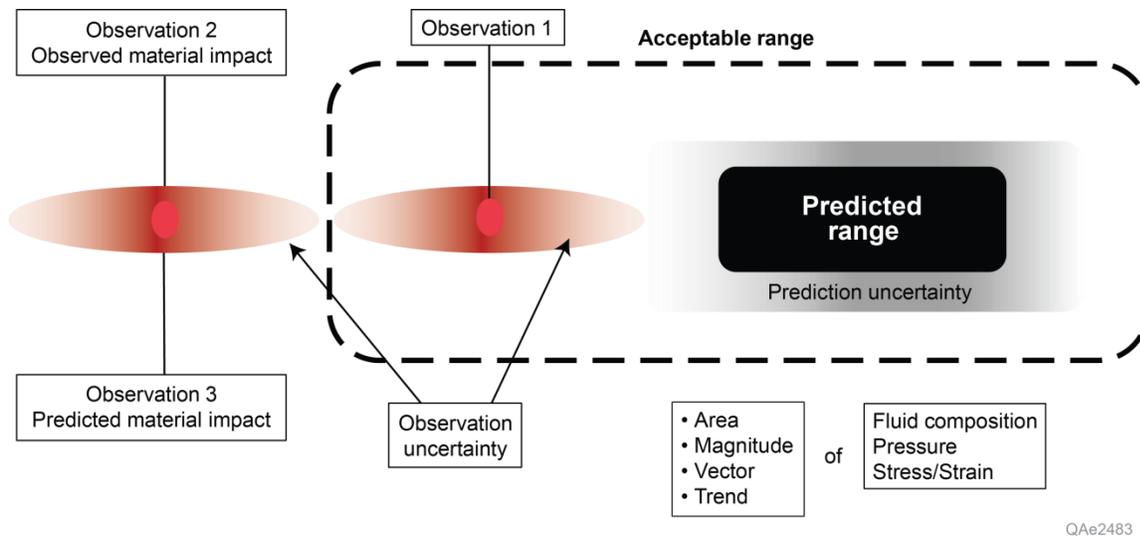


Figure 2. Nomenclature of outcomes of injection. The figure illustrates any important parameter that is set as a monitoring goal (examples in Table 2). Normally, modelers report the predicted range of reservoir response (black), which can be augmented with an expression of uncertainty (gray). For monitoring design, however, the critical range is that which is acceptable. Outside the acceptable range is the potential for material impact on the project goals. A parameter or trend measured inside the acceptable range, even if unexpected, does not cause concern. However, a measurement outside of the range triggers additional evaluation and reporting. Note that measurements also are assigned a range of uncertainty.

Table 2. Examples of parameters that define an acceptable response to injection.

	Parameter	Material Impact: Out of acceptable range indicates:
Conformance	Maximum pressure elevation in the reservoir	Trend too high – reservoir may not be able to continue to accept injection at the planned rate and stay below fracture pressure. Trend too low – fluids are migrating into parts of the geologic system that are not planned.
	Area in the reservoir where pressure is elevated such that brine could be lifted to fresh water through an open pathway	Preferential flow; need to qualify additional area (repair any wells), or to manage pressure through changing injection or adding withdrawal.
Assurance	Pressure in Above Zone Monitoring Interval (AZMI) – upward trend; greater than expected geomechanical response	Increasing trend above noise – out-of-zone fluid flow
	CO ₂ or CO ₂ -linked chemical parameters increasing above noise in groundwater, soil gas, or atmosphere	Escape of CO ₂ , concern for damage or perturbation of water or ecosystem resources

Maximum pressure elevation is a common reservoir management parameter, and it is regulated during injection. The upper limit on injection pressure is related to rock strength for the purposes of avoiding inducing fracturing of the confining system or inducing seismicity in a way that might be unacceptable.

An ALPMI is always done for the injection project to determine the maximum allowable surface injection pressure. In the context of ALPMI, a lower-than-predicted pressure increase in the reservoir may indicate that fluid flow is accessing parts of the reservoir that were not considered, for example by leaking vertically or horizontally. The maximum pressure elevation can be modeled using analytical or geocellular fluid flow methods. Major components shown in Figure 3 include the permeability of the flow unit (Fig. 3A), the thickness of the flow unit (Fig. 3B), and the extent to which the flow unit has open or closed boundary conditions far from the injection site (Fig. 3C). These data can be extracted from characterization data, using standard statistical approaches. Other fluid parameters can be considered, for example by hydrologic characterization of the top and bottom of the flow unit (Fig. 3D), by characterization of the well and near-well conditions, and by two-phase permeability studies. The outcome of a probabilistic intersection of these inputs for a good site is illustrated in Figure 3E. The accuracy of the probability distributions in the ALPMI may be poor, but accuracy of probability is not critical to the method; the most important consideration is that the possible *range* of characterization data be expressed, thus allowing development of sets of models of *material uncertainties*, those that lead to unacceptable outcomes.

The area underlain by pressure elevation such that brine could be lifted to freshwater resources through an open pathway in U.S. EPA Underground Injection Control regulation defines the Area of Review (AoR), which defines the area where a regulator would require assessment of potential pathways for upward fluid migration into protected resources, such as well bores (U.S. CFR, 1983). An ALPMI can be applied to determine which sets of conditions would lead to elevated pressure extending outside the planned area. A larger AoR would increase leakage risk or increase monitoring cost and could result in other unacceptable outcomes, such as interference with other types of subsurface projects.

In the context of assurance monitoring, an ALPMI would consider several aspects of out-of-zone migration of CO₂. One case of out-of-zone migration would result in failure to meet the retention standard. The implications of such a failure have not been completely defined, however in some future policy and regulatory environments the value assigned to storage that meets the retention standard would be lost. A value to retention has not yet been set by U.S. policy, but it might take the form of credits, offset, or access to captured CO₂. The EPA's Clean Air Act subpart RR (U.S. CFR, 2010a) provides a mechanism to begin accounting for storage quality but does not assign a value for storage or a penalty for failure of storage. A protocol for accrediting storage value is provided through the Railroad Commission of Texas (Texas Administrative Code, Title 16, part 1, chapter 5, subpart B, 2010), and proposed accounting protocols have been developed (McCormick, 2012). Figure 4 provides an ALPMI for a reservoir top seal that includes discrete transmissive features such as fractures or imperfectly constructed wells. Site characterization expends significant effort in determining that an adequate confining system exists to isolate injected CO₂ from freshwater and from the atmosphere; however, some possibility that flaws are not detected should be considered. The flux across part of the confining system can be estimated in an ALPMI by considering the spacing of possible pathways and the range of possible permeabilities that could exist in in features (Nicot and others, 2013; Sun and Nicot, 2012; Sun and others, 2013a, 2013b).

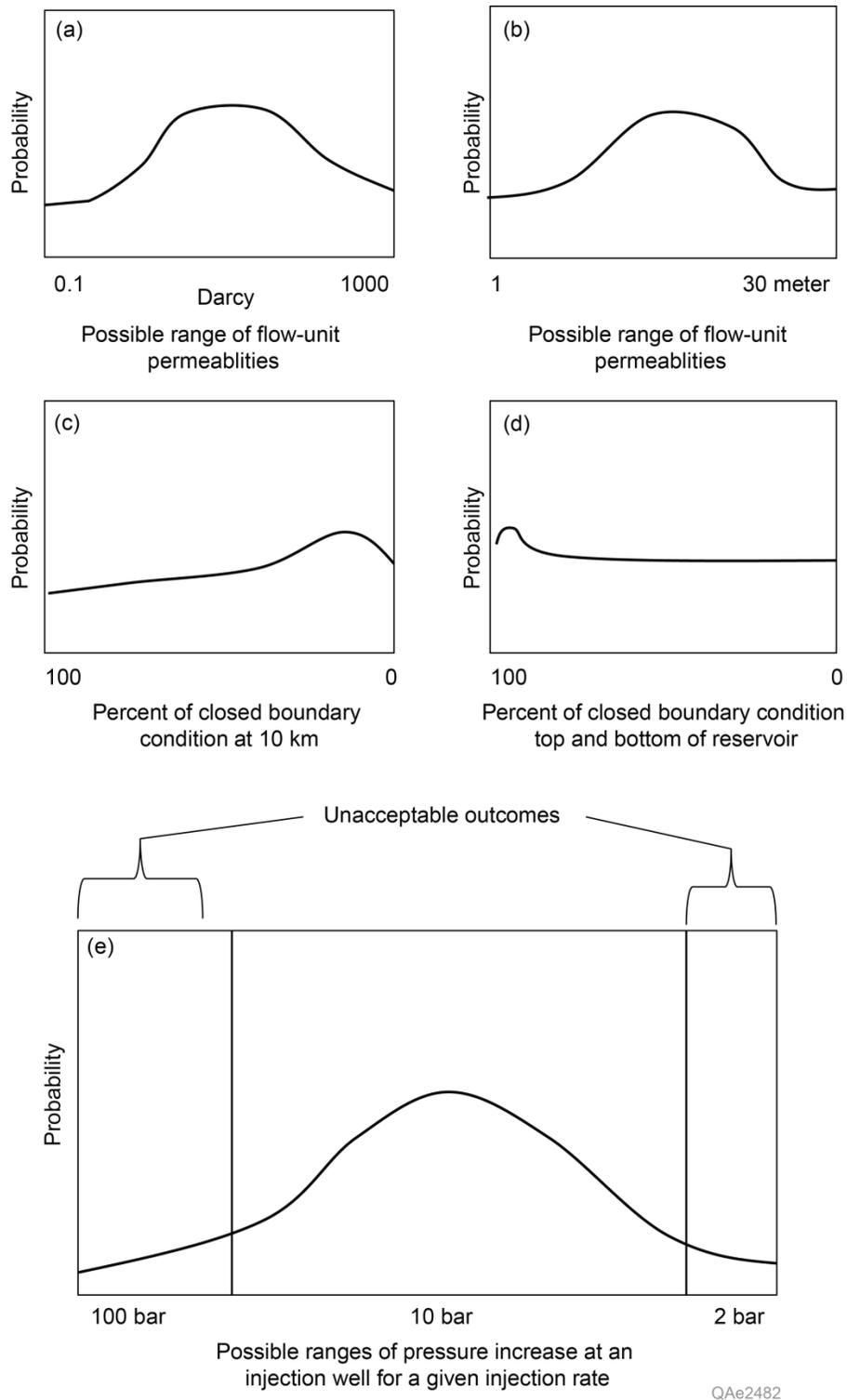


Figure 3. Characterization uncertainties such as (3A) range of possible flow-unit permeabilities, (3B) range of possible flow-unit thickness, (3C) percent of closed boundary conditions at 10 km, and (3D) percent of closed boundary conditions at the top and bottom of a reservoir can be modeled to assess the ranges of system responses, for example (3E), range of pressure increase possible at an injection well for a given injection rate.

Damage to freshwater resources resulting from out-of-zone migration of either brine or CO₂ has been widely considered, both in research (for example, Carroll and others, 2009, Zheng and others, 2009, Apps and others, 2010; Keating and others, 2010) and in regulations (U.S. Environmental Protection Agency, 2010; 2012). CO₂-rock-water reaction might release constituents with low maximum contaminant levels in drinking water. Damage to ecosystems from higher-than-ambient CO₂ flux has also been considered (McGee and others, 1998; Blackford and others, 2009). The detection mechanism could be related to change in CO₂ or CO₂-linked parameters above the ambient variability of the system. CO₂-linked parameters might include more sophisticated chemical indicators such as process-based methods (Romanak and others, 2012a). We have been experimenting with a powerful tool using pressure change in an above-zone monitoring interval (AZMI) that produced greater than the expected geomechanical response.

During all projects, characterization data are used to model the likely project outcomes (Fig. 2), and techniques to generate an associated uncertainty in the predicted project outcomes are also important to preserve project credibility. Experience with history matching predictive models leads to an expectation that as additional data on response of the system are collected, model refinement is possible and expected, and this has been built into some CCS rules; for example, the U.S. EPA class VI rule for geologic storage of CO₂ (U.S. CFR, 2010b) explicitly requires model updating. In common applications related to resource extraction, the mean and high-probability outcomes receive the highest attention. Discriminating among these high probability outcomes may be valuable, for example, in optimizing well placement or well completion to improve recovery. In contrast, in risk assessment for geologic storage at a good site, many of the possible outcomes would be acceptable. The differences among acceptable outcomes are not material to the outcome of the project, and time spent differentiating among them has little value in achieving project objectives. In the ALPMI method of evaluating the project against its goals, possible but low-probability outcomes that fall outside the acceptable range are the ones that need to be the focus of monitoring. This may mean that ends of the endpoints of distribution of characterization statistics need more careful evaluation than the variance near the mean.

A key element in the workflow is to create a quantitative and explicit boundary between what is acceptable and what is unacceptable performance of the geologic system in response to injection. The following step is to model the possible ends of distributions of characterization data to determine if any unacceptable outcomes are possible. Figure 3 illustrates a case assessing uncertainty in basic hydrologic parameters of permeability, flow unit thickness, and boundary conditions. Only a few possible outcomes are unfavorable, and it is likely that some outcomes could be eliminated by a hydrologic test program prior to the commissioning of the project for CO₂ storage. However, large-scale and long-duration injection may probe parts of the reservoir that are not completely tested during the pre-injection characterization. Figure 3E shows how an ALPMI method can use a basic monitoring (bottom hole pressure increase at an injection well under constant injection rate) to diagnose conditions that may lead to material impact, such as (Fig. 3 B) a thin flow unit, which might cause development of an unacceptably large plume; (Fig. 3C) closed boundary conditions, which might lead to inability of the reservoir to accept the planned volume of injection without unacceptable pressure increase, or (Fig. 3D)

an unexpectedly low increase in pressure, which might signal that fluids are migrating out of the intended zone. Plotting the trend in bottom-hole pressure at an injection well to test a trend toward the values unacceptable values shown in Figure 3E is a traditional method for screening the performance of an injection. This approach is different from some geologic storage protocols, in that even if the pressure response is different from expected, there is no expectation of a need to recalibrate the numerical models if the value lies within the acceptable range. If the value is trending to fall outside of the acceptable range, a need for additional diagnostic measurements is triggered to determine if the risk of material impact is real or an error in characterization, monitoring, and measurements, and, if real, to identify cause and mitigation.

Figure 4 shows an example of such a follow-up measurement, regarding the quality of confinement, in which the characteristics of flaws in the confining system are assessed to determine if the flux is significant with regard to project goals. This flux could be calculated from losses from the injection zone, or measured directly by thermal measurements, but most likely it would be measured as a function of hydraulic connectivity between the reservoir and the AZMI.

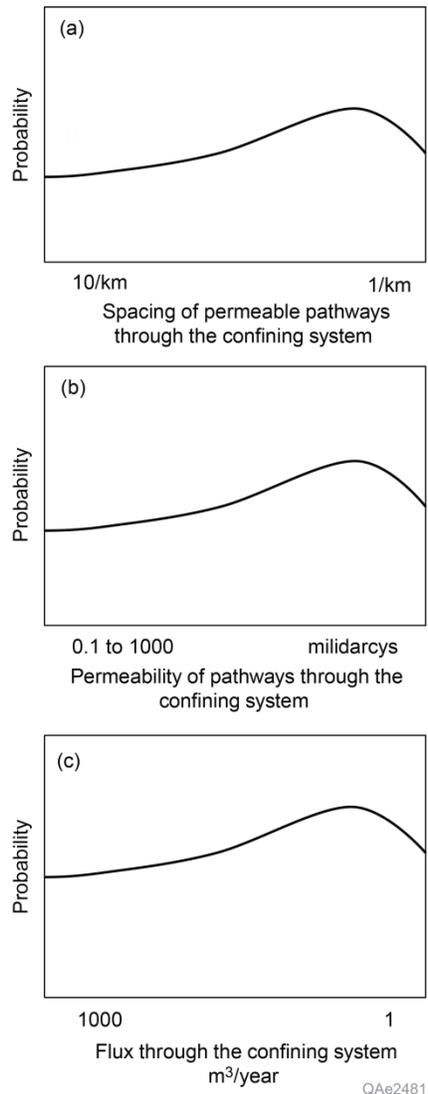


Figure 4. Frequency of flaws in the confining system (4a) and the aperture of those flaws (4b) can be used to calculate flux (4c). Other parameters such as the attenuation of pressure in the reservoir near the leakage point and the pressure response of the zone that receives the flow must also be considered (Zeidouni and Pooli-Davish, 2012a, b).

Figure 5 illustrates quantifying another project risk factor, long-term stabilization. If the CO₂ is injected in a domal structure, the main long-term migration risk is to provide assurance that all the CO₂ remains within the structure during the injection period. Any spillage out of the structure would occur during injection when plume development would be partly radial away from injection wells. At the end of injection, the pressure gradient driving CO₂ away from the injection wells will quickly equilibrate, and buoyancy of low-density CO₂ in brine will cause migration of the CO₂ upward to the top of the structure, mimicking the natural charge of oil and gas reservoirs. However, if injection is into a large system with regional dip, the CO₂ plume will migrate laterally and upward beneath low-permeability zones. The rate and ultimate extent of migration may need to be determined as part of assuring storage, for example to

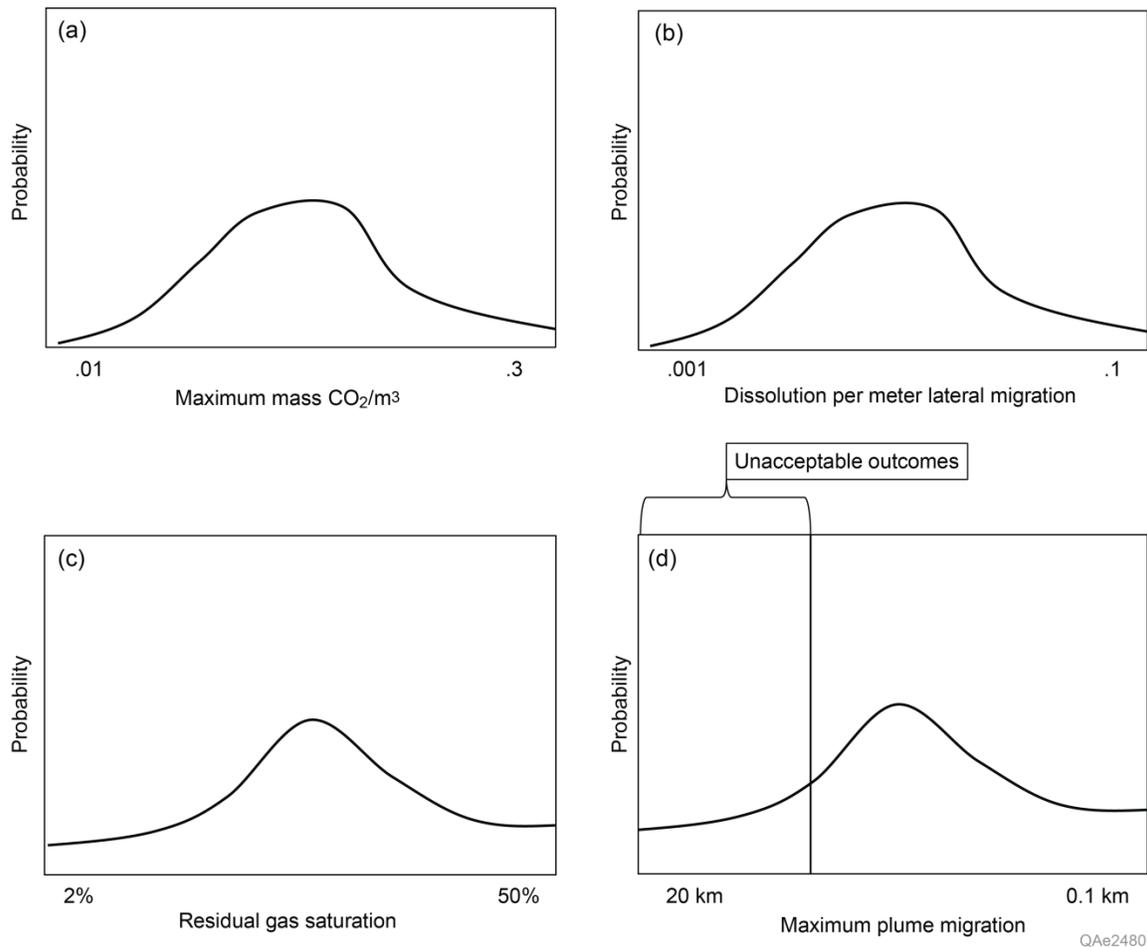


Figure 5. Long-term stabilization depends on three variables: (5A), the maximum saturation attained during injection, (5B), the residual saturation, and (5C) the rate of CO₂ dissolution. The extent to which these variables are uncertain during characterization impacts the extent to which uncertainty remains in the modeled performance in settings where post-injection migration may have a material impact (5d). An ALPMI process leads to definition of material uncertainty prior to CO₂ injection (5d), which can guide a fit-to-purpose monitoring program.

avoid arrival of CO₂ at leakage points at the basin margin or at resources within the basin. Examples of assessments of stabilization are for the long-running injection at the Sleipner gas field beneath the North Sea (for example, Chadwick and Noy, 2010; Cavanaugh, 2013), for proposed injection at the Gippsland Basin (Gibson-Poole and others, 2008), and for small-scale injection at the Frio site, South Liberty, Texas (Hovorka and others, 2006).

2.1.5 Monitoring design and execution

Monitoring is a component of a systematic process designed to achieve the project goals. It is essential for different projects to deploy different monitoring strategies, which is recognized in rules such as EPA's class VI rule requiring non-prescriptive site-specific monitoring programs. Three elements interact to create diversity: 1) the goals and the way these goals are phrased may be diverse, 2) the impact of site characteristics on risk of not attaining the goals may differ site-to-site, and 3) the characteristics of the site that control feasibility of making a certain type of measurements may be different among sites.

Different types of goals have a profound effect on monitoring needs. A prominent example in current monitoring experience is the need for research-oriented monitoring, which provided a strong drive toward certain types of data collection; in fully commercial future projects this need may be reduced or eliminated. Other goal-driven differences come from previous experiences of the regional regulators or project financiers; for example, concern about microseismic response to injection might fall in this category. The way the goals are stated also has a surprisingly important impact on the monitoring program. For example, a retention statement phrased in terms of documenting that 99% of the total injected volume will be retained for 1000 years can leave an expectation that very long-term monitoring is needed. A statement that leakage of less than 0.001 % of injected volume must be detected creates a very high standard of retention during early stages of the project when only a small amount of CO₂ has been injected; this might not be a feasible goal to reach at any site. Another type of goal might be to reach an early degree of certainty that major flaws in the system do not exist. This could be accomplished by focusing on the performance of the storage site during its first decade. Another type of goal, one to document permanence, would focus on validation of numerical modeling that shows long-term retention. Figure 6 illustrates three examples of retention goals intersecting three hypothetical sites.

Risks of failure to meet the project goals are strongly dependent on site-specific characteristics. Figure 6 illustrates three different types of retention risk. At site A, CO₂ is injected into a dipping regional aquifer. Modeling shows that the plume will stabilize by capillary trapping and dissolution before reaching a distant outcrop. The risk emphasized here is that the model might not be correct, and a thin finger of CO₂ might migrate preferentially, reaching the outcrop, as illustrated in Figure 5d. Site B is a saline formation forming a domal structure. The long-term migration uncertainty is absent at the site because CO₂ will migrate toward the top of the domal structure. Retention uncertainty at this site will consider the possibility that the confining system over the top of the domal structure is flawed, allowing CO₂ that accumulates in the top of the structure to migrate out vertically, as explored in Figure 4. Site C is a depleted hydrocarbon field; the uncertainty about the quality of the seal that is dominant at site B is greatly reduced because of the geologic duration of hydrocarbon retention. At site C the principal uncertainty in retention performance may be the performance of well penetrations.

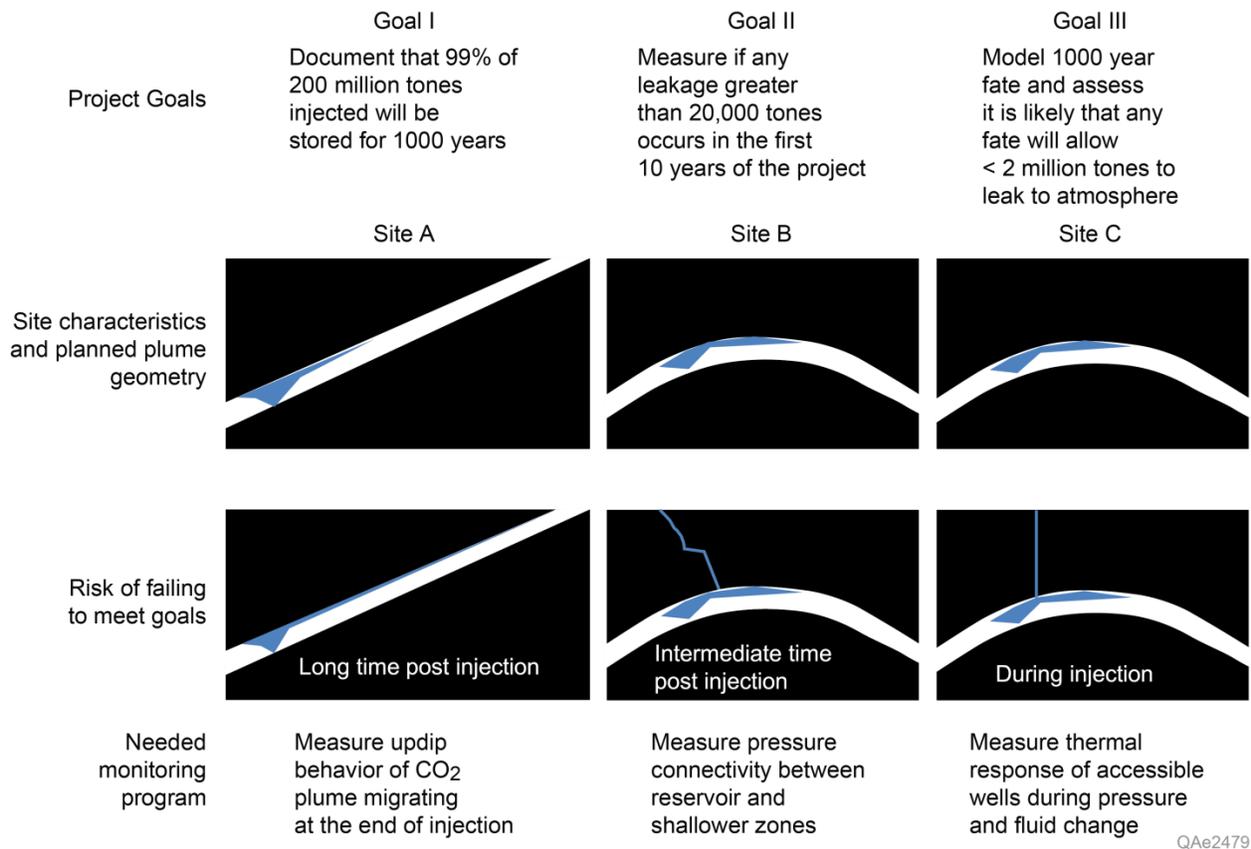


Figure 6. Three different statements of retention goals intersecting three different sites. The intersection of different goal statements with different site characteristics results in different risks of failure to meet goals. For example, goal statement II, with its focus on short-term measurement, might be highly effective in assessing retention uncertainties at sites B and C but miss the uncertainties at site A. Goal statement III would be needed to consider the non-retention uncertainty at site A.

In some protocols, the idea of risk is stated very simply, in terms of monitor the “potential seepage pathways” (United Nations Framework Convention on Climate Change, 2011). However, such an approach results in conflict between the operator and the regulator. By the stage of project development in which the operator is presenting a monitoring plan to the regulator, much investment in managing and reducing risk will have taken place, and the operator can say to the regulator with high confidence that all the potential seepage pathways have been eliminated by characterization or by engineering design. A more sophisticated approach, outlined in the previous section on ALPMI, to identify outcomes that are low probability but that remain possible, is recommended.

ALPMI has an important component beyond identification of monitoring targets; the range of magnitude of events that would lead to failure to meet project objectives must be modeled in order to design an effective monitoring program. The threshold against which failure is defined has an important impact on the possible strategies to determine whether or not the project is successful. For example, a goal of zero leakage is pragmatically impossible to confirm. However, no pragmatic atmospheric or other environmental goal requires obtaining zero leakage; an intersection of the desired goal with what is

pragmatically possible to measure can be undertaken to set a monitoring standard. Situations where a zero probability or material impact is needed may show that either the project or the site is unacceptable.

An essential stage of designing a monitoring program that is not often described with respect to geologic storage monitoring plan design is to match the sensitivity of the planned detection method with the quantitative goal (last row, Figure 6). Sensitivity study is a required stage of a scientific study and is widely practiced for some types of monitoring, for example in designing a seismic survey. However, in the expectation of documenting a negative measurement, “no leakage signal was detected,” it is especially important to formally document the sensitivity of the methods. In this workbook we illustrate the mechanism for determining site-specific sensitivity of monitoring tools.

2.1.6 Closure

The nature of geologic storage is linked to an expectation that storage will be long-term. Demonstrating the validity of this expectation is problematic, as it relies upon a predictive model. Regulatory approaches have also been somewhat problematic; for example, EPA’s class VI rule sets a post-injection site care (PISC) expectation having a default of 50 years. The type of activity to be conducted during this period has not been deeply explored. Several protocols have discussed “plume stabilization” or prediction of stabilization as being among the goals of the PISC (for example U.S. Environmental Protection Agency, 2010).

An ALPMI approach along with assessment of site determine sensitivity of tools can improve feasibility of increasing confidence in a predictive model at the end of injection in the same way that it can provide assurance during injection. In fact, with suitable goal setting and monitoring design, much uncertainty about the post-injection performance of the plume can be reduced during characterization or during injection. This approach would perhaps avoid the need for an extended period of observation after the end of injection.

3 Exercises in site-specific monitoring design

This workbook illustrates the ideas presented. We use a small and theoretical subset of possible goals, site characteristics, and monitoring strategies to illustrate the approach. An encyclopedic approach to integrating is impossible because of substantive differences among project goals and sites, and especially because of the great variability of monitoring tools available. Indexes of monitoring tools (British Geological Survey, 2006; U.S. Department of Energy, National Energy Technology Laboratory, 2009) provide an overview of dozens of tool types. However, they do not inventory the variability in sensitivity resulting from variants of the tools and options in tool use such as frequency of data collection. Only a site-specific plan designed by a team with substantive expertise in each monitoring tool and their use for geologic storage applications can create a robust plan. Our workbook, however, can guide reviewers in asking the design team questions by illustrating the limitation of various tools, and it can provide perspective on how much or little investment in characterization, baseline, design, and execution of monitoring is needed to meet the project’s goals. This kind of review is needed even

for simple plans at very secure sites so that the tools selected are fit-to-purpose, because documenting a finding of “no leakage” is challenging.

3.1 Goal setting

For these exercises we consider a high-level goal storage goal of 99% of 100 million tons of CO₂ injected is stored in isolation from the USDW and from the atmosphere. To frame this goal as a quantitative monitoring goal, we will restate it as an intent to detect CO₂ migration greater than 1 million tones into or across the selected monitoring locations. In this case, we set monitoring locations such that either leakage that might occur during the monitoring period or trends toward possible long-term leakage are detected. We simplify the consideration of variables such as attenuation over time. In a real case, deeper investment would result in a more sophisticated approach, and other goals mentioned in Table 1 could be similarly set.

3.2 Site characterization

For our exercise, we assert that prior to selecting and permitting these sites, an excellent team collected state-of-the-art characterization data, including high-resolution 3-D seismic analysis using advanced technologies, intensive stratigraphic and hydrologic testing of injection zones, overlying confining system, and overlying permeable saline and fresh-water-bearing zones.

Very simple data are presented about each site so that the evaluation can be made quickly in a workbook context. Several nearly identical sites are assessed to allow us in the exercise to focus on how each parameter changes the monitoring design. The base case, with the modeled predicted distribution of CO₂ at 1000 years after the end of injection, is illustrated in Figure 7. In all cases, the injection target is three sandstone intervals, designated from top to bottom as Q, S, and U. Sandstones are 100 m thick and have permeability ranging from 100 to 1000 mD, with some low-permeability muddy sandstone zone interbeds. Sandstones are separated by mudstone zones characterized as barriers to CO₂ migration. Sandstone Q, S, and U are deformed into a broad anticline with 4-way closure. The injectivity is high, and the boundary conditions are open on the north, south, and west. On the southeast, the anticline has a fault boundary with an adjacent structure that produces gas from the U sandstone. The gas production history is interpreted as indicating that the fault is sealing across this zone. Good records suggest that gas production wells were properly plugged and abandoned. A variable-thickness mudstone, unit P, overlies the deeper structures unconformably. Shallower zones M, N, and O have different characteristics in different sites (Table 3). Sandstone O is characterized as being regionally extensive and quite homogeneous, but it varies in thickness from location to location. Mudstone N confines the O sandstone and defines the base of USDW. Sandstone M hosts the USDW; it is 100 m thick and confined by a muddy surface unit. It has 20% porosity and varies regionally from being a clean quartz sandstone to having 1% carbonate grains.

Table 3. Variable site characteristics

Site	Sandstone O	USDW sandstone M
Figure 8	10 m thick	Quartz sandstone
Figure 9	100 m thick	Quartz-calcite sandstone
Figure 10	10 m thick	Quartz-calcite sandstone

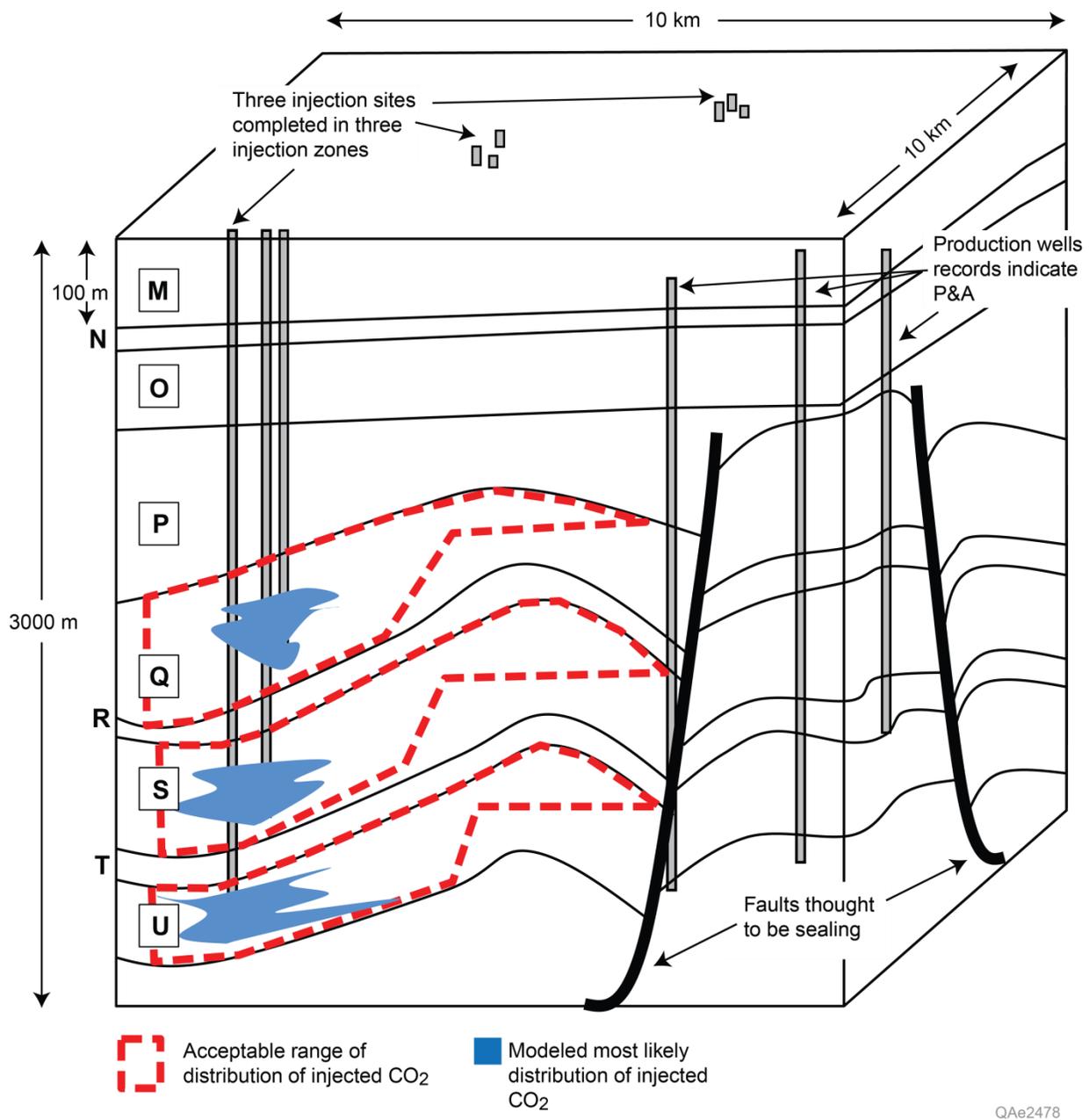
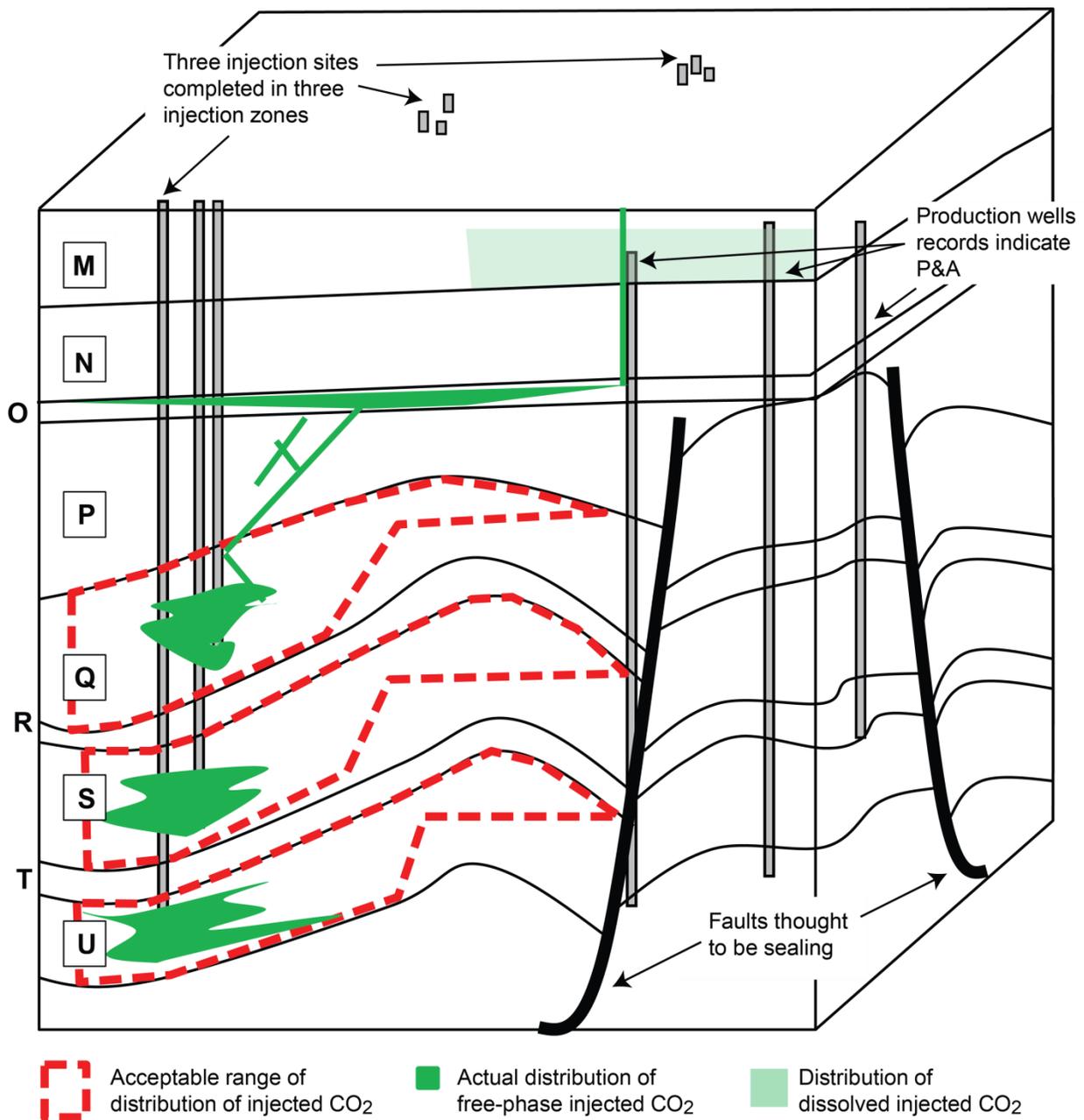


Figure 7. Hypothetical storage complex. The predicted free-phase CO₂ extent is shown in blue, and the maximum acceptable extent to ensure meeting the project's retention goals is in red dashes.



QAe2477

Figure 8. An ALPMI case (hypothetical) where CO₂ has unexpectedly migrated outside of the acceptable limits through an undetected transmissive fracture system, entering the 10-m-thick area above zone unit O, and migrating to a well with an unidentified flawed surface casing cement, which allowed it to migrate to zone M, the USDW.

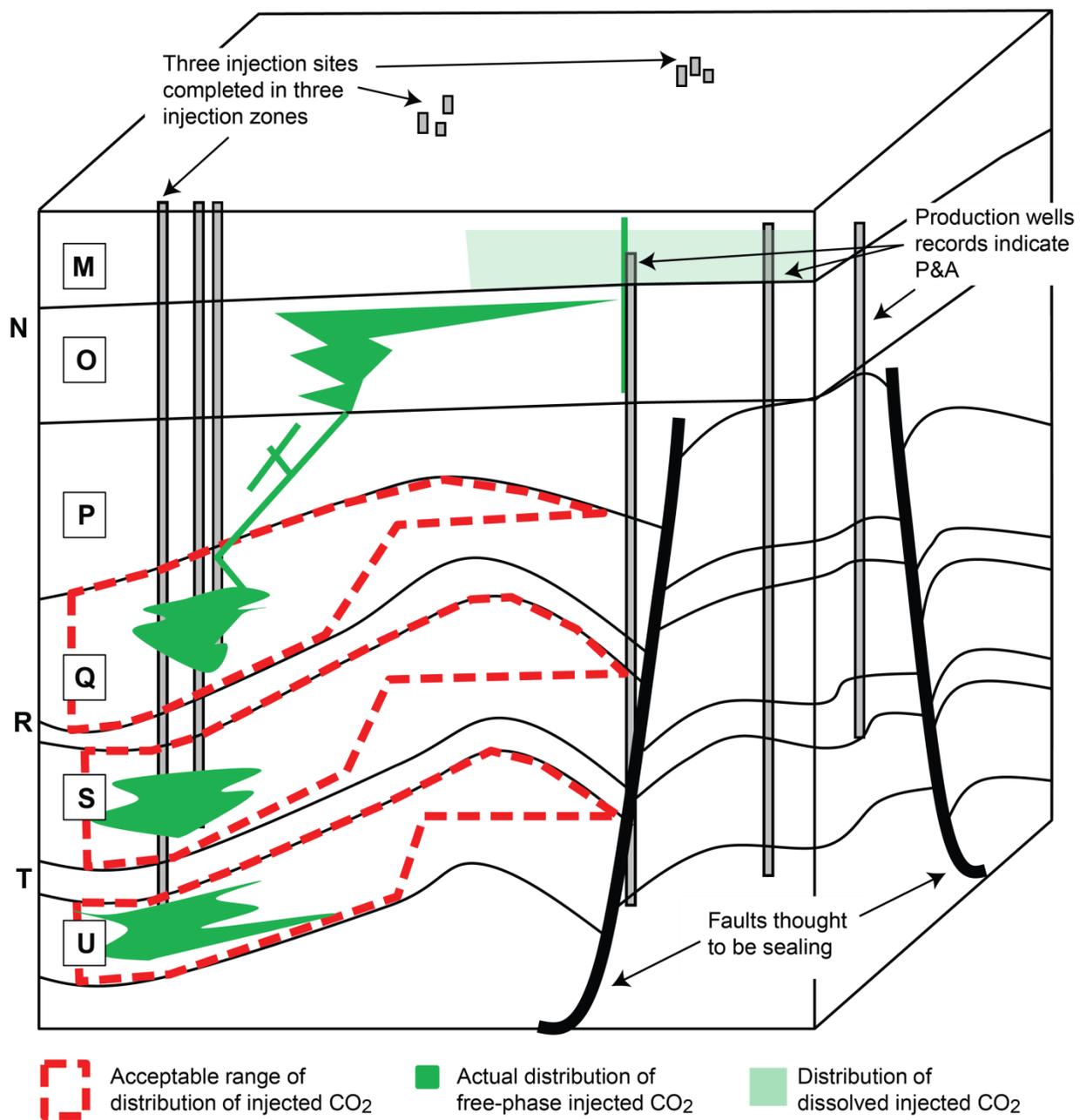
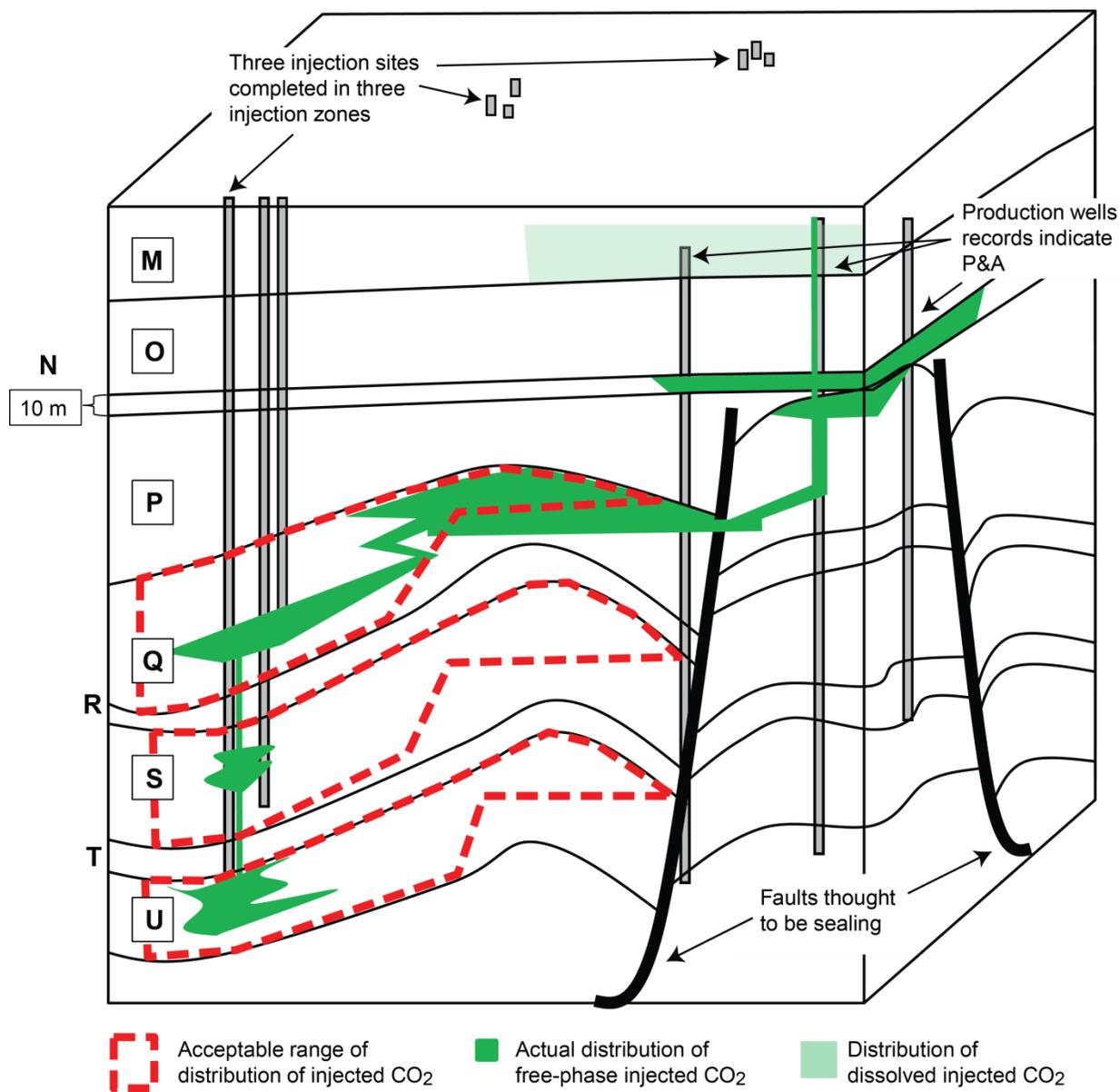


Figure 9. An ALPMI case(hypothetical) similar to that show in Figure 8, except that zone O, into which CO₂ has unexpectedly migrated, is 100 m thick and USDW zone M the contains 1% carbonate.



QAe2475

Figure 10. An ALPMI case (hypothetical) where CO₂ has migrated outside of the acceptable limits. In this case the flaw that allows failure is unexpected connectivity among stacked injection zones, which allowed more CO₂ than planned to accumulate in zone Q. This allowed the CO₂ to migrate further than expected, where it crosses a fault and encounters the same flawed surface casing cement as in the Figure 8 case.

3.3 Injection and predictive model

The CO₂ will be injected into a geologic storage site through nine wells, such that the annual injection is 3 million metric tons/year, for 33 years. Wells are clustered on the flank of the structure, such that each cluster has a Q, S, and U injection well capable of accepting 1/3 million tons CO₂ per year under supercritical conditions. Modeling of the planned free phase CO₂ plume development shows that CO₂ will occupy a compact area near the injection wells, and the nine plumes will be isolated from each other vertically and horizontally.

3.4 Risk assessment and assessment of low probability of material impact

Excellent characterization and good injection design and implementation will not remove all uncertainties that could lead to failure to retain CO₂. In this workbook, we conduct three example ALPMI's. In cases shown in Figures 8 and 9, we model an undetected transmissive fracture system that crosses the confining zone P above the planned injection site and allows injected CO₂ to migrate into transmissive zone O. In Figure 8, zone O is 10 m thick; in Figure 9 zone O is 100 m thick. In these ALPMI, we consider that CO₂ migrates laterally until it finds a flaw in confining zone N, which in these cases is considered to be a former gas production well with poor cement along the surface casing. CO₂ then migrates into aquifer M, the USDW, and from there escapes into the atmosphere. For simplicity in the workbook setting, we assume that the aquifer is well mixed over an area of 10 km². For a real case, a flow and transport model would be needed. In the ALPMI considered, M in Figure 8 is fairly clean quartz sandstone, whereas in Figure 9, it is identical except for 10% carbonate.

In the case shown in Figure 10, connectivity in the casing-rock annulus of a flawed injection well is considered, such that cross-formational flow allows much more CO₂ to accumulate in reservoir Q than planned. This would still have no material impact, so to create the ALPMI we assume that the fault is non-sealing where it crosses formation Q, and that the CO₂ then encounters that same well with poor cement along the surface casing, as in Figures 8 and 9, which similarly allow CO₂ to migrate into aquifer M, where it is similarly well mixed.

For a real-world case, a number of additional ALPMI's might be considered.

3.5 Monitoring design

The monitoring design should efficiently and surely conduct the assessment part of the ALPMI, to systematically determine if each unlikely but possible flaw is or is not present in the system. In our experience with experimental and commercial tests, the design of monitoring requires a team of dozens of technology experts having many months and many interactions to consider, model, and optimize using the available tools. In this workbook, we consider only four tools in simple form (time-lapse 3D seismic, pressure monitoring, thermal monitoring, and groundwater geochemistry), and only a sample subset of site-specific parameters to provide examples. In a real -world case, a longer period of study and a much larger portfolio of tools, as well as enhancements and protocols for optimizing the tools, would be needed.

3.5.1 Time-lapse 3D seismic

Time-lapse 3D seismic, in which one survey is collected prior to injection of CO₂ followed by one or more surveys at critical times for the project, can be an ideal tool for conformance as well as assurance

monitoring. As CO₂ migrates and replaces brine, the resulting change in seismic velocity through the area of changed fluid can be identified by subtracting the survey parameters before injection from the survey after injection. The difference can be interpreted as a result of fluid substitution.

Time-lapse seismic surveys are very powerful technologies, and deep investment in their use allows them to be optimized in many ways (Lumley, 2010). For this workbook, we consider three fundamental limitations. The magnitude of the change created by fluid substitution varies depending on 1) the elastic properties of the rock matrix, 2) the thickness of the zone of fluid change, and 3) the porosity of the zone of fluid change. If the magnitude of the change in signal corresponding to fluid substitution is small, it may be masked by noise or limitations on repeatability. Technology developments can reduce noise and increase repeatability; for example, collection of data in a water body can improve signal, or stacking signal from permanent receivers, or sources can improve statistics and reduce repeatability error (Daley and others, 2007). In this workbook, we assume current technology maturity and an onshore site, and we use simple, basic design. In a real site, various technology enhancements in data collection and especially in processing could be considered, but the methods presented would be used to evaluate the improvements. The detailed calculations and field examples from which the simple relationships presented in the workbook are drawn are presented in Hovorka and others (in press).

Rock physics is used to define the elastic properties of rock. Figure 11 shows a simple depth-dependent model of a dry rock (no fluids considered) in which the velocity of the P wave (V_p) varies depending on the effective pressure placed on the same rock. A normal hydrostatic pressure gradient might be 0.433 psi/ft (9.8 mPa/km), so that the pressure range in Figure 11 roughly corresponds to depths from surface to 8 km. This change in rock physics is used to model the response to fluid substitution shown in Figure 12. In Figures 12 and 13, we hold the porosity and saturation constant and favorable at 30% porosity and 20% saturation.

Figure 12 shows that the change in P-wave velocity as a result of fluid substitution is large, 24%, at shallow depths of 2 km. However, as depth increases, the magnitude of the velocity change decreases, such that by a depth of 3.5 km, the change is reduced by 2/3, to 7%. A 7% change is probably large enough to be detected, but this calculation considers only the effect of confining pressure; other factors that might limit detection that increase with depth such as attenuation of energy, noise from crossing more layers, and possible other changes in rock properties such as fracturing or cementation will be added. Depth is shown to be a limiting factor on seismic detectability in time-lapse fluid substitution.

Figure 13 shows a similar result in the response of reflectivity of P-waves as effective pressure increase with depth. This plot is quite idealized in terms of geometry and rock properties, using a thick reservoir with and overlying confining system so that a half-space assumption is valid. In a real site, this calculation should be repeated with site-specific data. However, this simple calculation illustrates a valuable lesson, showing that a technique that worked well at shallow depth may be less diagnostic in a deeper setting.

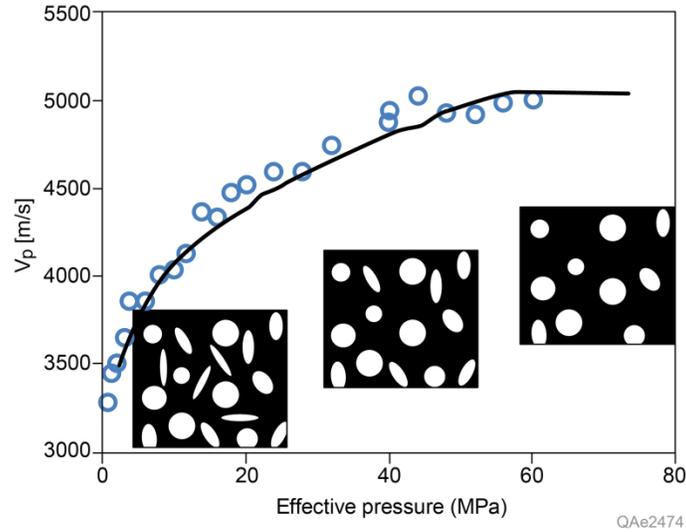


Figure 11. Rock physics model developed using self-consistent approximations (Berryman, 1995) plotted against experimental data from Purcell and Harbert (personal communication, 2013, University of Pittsburgh).

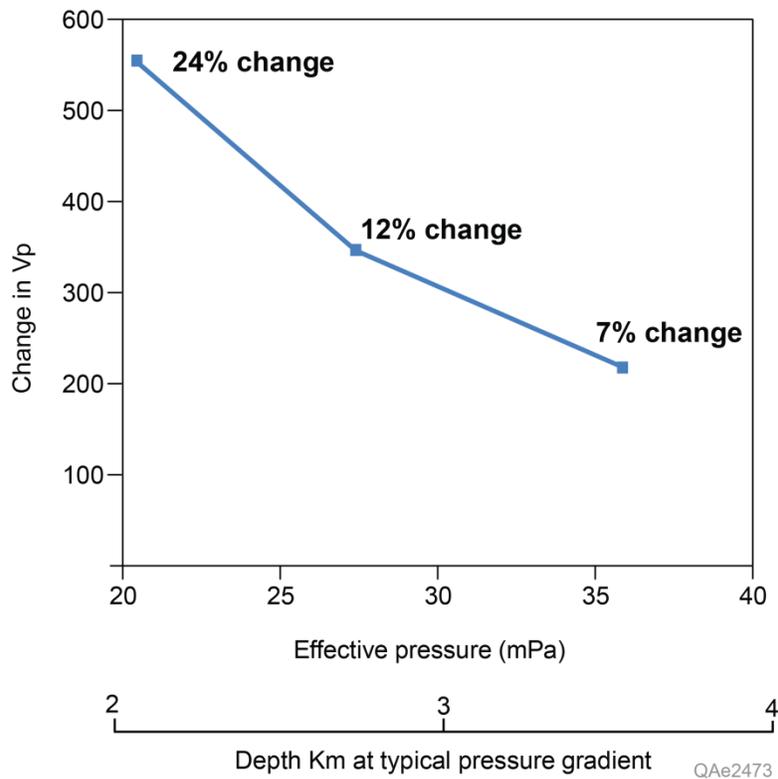


Figure 12. Modeled change in P-wave velocity as a result of fluid substitution for the same rock at different effective pressures. The model is based on work by Reuss (1929) and uses rock with average elastic properties from Gassmann's (1951) theory, 30% porosity, 20% fluid substitution CO₂ for brine, no changes to minerals during injection, fluids do not support shear (see Hovorka and others, in press, for details).

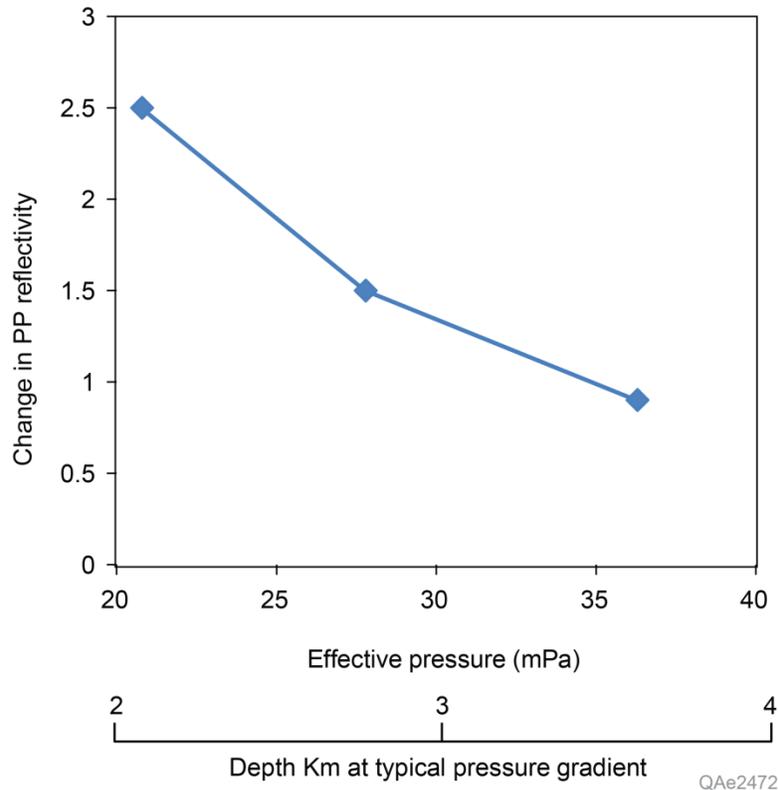


Figure 13. Change in reflectivity with increase in effective pressure for the same rocks with the same geometry calculated with Zoeppritz's (1919) equation, using a half space assumption (thick reservoir and seal with set petrophysics) and 20% fluid substitution of CO₂ for brine (see Hovorka and others, in press for details).

Bed thickness is a classic issue for seismic imaging, and Figure 14 shows a model of impact of the thickness of the zone in which fluid substitution occurs. Note that the relevant parameter is the thickness of the flow unit that is accessed by CO₂, which can be much less than the entire reservoir, especially of concern in cases where thin and narrow pathways also CO₂ to migrate farther than expected. In this model set-up (described in detail in Hovorka and others, in press) a bed thickness of less than 20 feet shows a sharp decrease in percent change in amplitude to less than 5%, which is likely not detectable above noise and repeatability error. Advanced techniques can be used to improve thin-bed detection (for a CO₂ example, see Williams and Chadwick, 2012).

Another type of variable that has an important impact on whether fluid substitution is detectable is rock and fluid properties. Many variables have important and complex effects, and expensive assessment is part of the normal tools of forward modeling a seismic survey. For this example we vary porosity (Fig. 15) from 10 to 30%. For all porosities, acoustic impedance (density times velocity) increases with compressibility, the same effect shown in Figure 12. Figure 15 shows that the 10% porosity rock in this case fails to produce a signal above a 5% detection threshold.

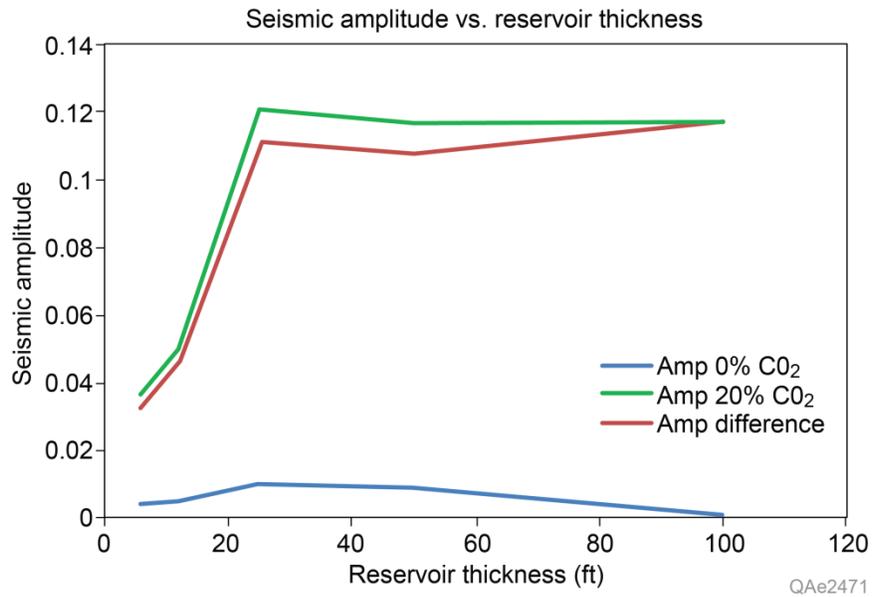


Figure 14. Modeled seismic amplitude versus reservoir thickness as fluids are changed from no CO₂ to 20% CO₂. Model set-up described in Hovorka and others, in press.

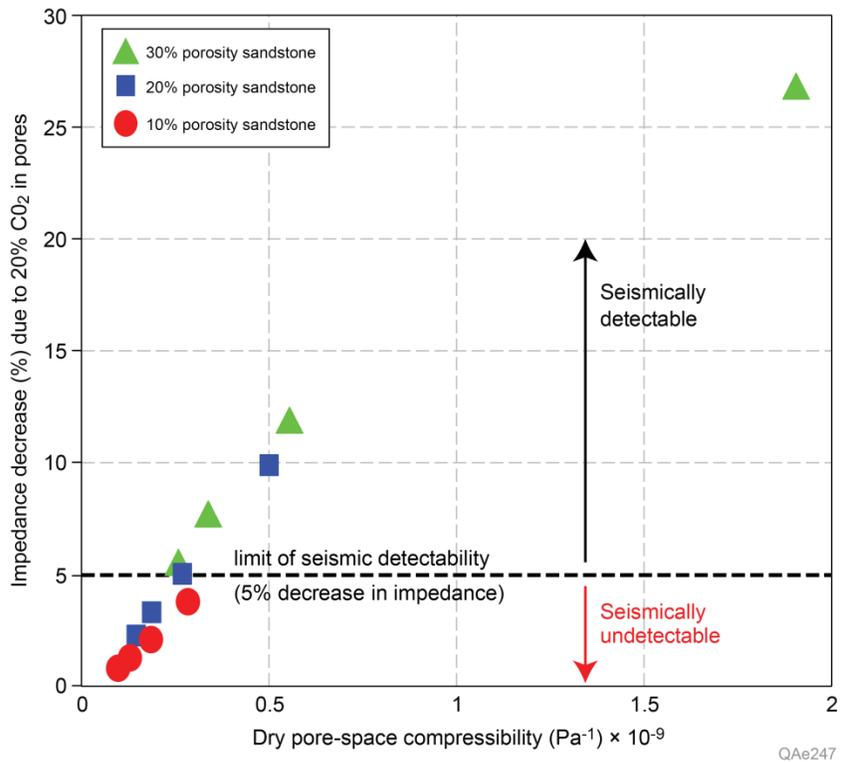


Figure 15. Modeled acoustic impedance versus dry pore-space compressibility as porosity of the rock is changed from 10 to 30%. Model set-up described in Hovorka and others (in press).

A full assessment of seismic sensitivity will consider many other variables, such as site-specific rock physics, fluid compressibility, site specific noise and repeatability, and the impact of pressure increase resulting from injection.

Limitations in time-lapse seismic sensitivity may be more significant in assurance monitoring, for which the time-lapse survey will undertake to show no change from fluid migration, than in conformance monitoring, for which the survey confirms the area occupied by the fluid substitution. Case studies illustrate this relationship. The surveys at Sleipner, which have served as a prototype for the use of time-lapse seismic, were collected at shallow (1000-m) depths, in highly porous and compacted sandstone, in a marine setting (Arts and others, 2004). Multiple repeats of the survey have been beneficial in improving statistics and optimizing the interpretation (A. Chadwick, British Geologic Survey, personal communication, 2013). This set of 3-D surveys has been used extensively in conformance mode where the observed reservoir response in terms of fluid replacement is compared used to validate numerical models, but can also be used in assurance mode to demonstrate no migration outside of the planned areas (A. Chadwick, British Geologic Survey, personal communication, 2013). Another survey collected at the Snøhvit field, offshore Norway, provides an excellent case of successful assessment of the location of the injected CO₂ in conformance mode, as an amplitude bright spot is centered on the injection well (Eiken and others, 2011). However, using this survey in assurance model is problematic, as time-lapse change is observed in patches over a wide area. It is difficult to separate any thin paths of CO₂ from signal resulting from pressure increase and from error and noise.

The highly regarded Weyburn, Saskatchewan 3-D survey has also been considered successful in conformance mode (White, 2013). This survey was collected in more challenging conditions, onshore, at depths of 1400 m, in a thin zone of carbonates that are relatively stiff. The survey has been repeated several times, improving statistics. However, use in assurance mode is more problematic. Horizontally, the survey is cropped close to the injection patterns, and cannot therefore be used to map the plume edge. Vertical migration has been considered, and possible out-of-zone migration above background may have been detected.

A deep survey (3 km) at Cranfield Field, Mississippi, shows the difficulty of working near the maximum depth for detection of fluid substitution. A clear time-lapse signal is detected in many regions where CO₂ replacement of reservoir fluids is expected (Zhang and others, 2013). A complicating effect is the presence of methane in some areas of the field, which suppresses the Vp change when CO₂ is introduced as a compressible fluid already present in the pores (Urosevic and others, 2011). In addition, the small signal produced by the injection is close to the magnitude of the noise and repeatability errors (Al-Jabri and Urosevic, 2010), so that it is difficult to use the data to demonstrate that CO₂ has not migrated laterally or vertically into areas where it is not expected. No suspicious geometries have been detected; however, it is impossible to use the 3-D to affirm that retention is occurring. Work continues to optimize this survey.

Similar effects from time-lapse 3-D surveys in terms of useful conformance results but inability to use the survey for assurance of retention have been acquired in at other sites, such as West Pearl Queen field (Pawar and others, 2006).

3.5.2 Pressure monitoring

Pressure monitoring is the workhorse of both conformance and assurance monitoring for many applications from hydrocarbon production to waste disposal to aquifer resource management. Pressure is a valuable tool because it is collected locally using a relatively simple, robust, and low cost gauges, and is highly quantitative, so that results are immediately available and trends can be quickly and easily analyzed and reported using classical diagnostic plots (Bourdet, 2002; Renard and others, 2009). It is valuable because the response at one point can be robustly extrapolated to other parts of the geologic system using well-understood hydrologic equations. Extrapolation of diffusive hydrologic response requires a series of linked assumptions that are derived from characterization and improved through a series of hydrologic measurements. Injection/fall-off tests, for example, are a basic tool to assess how the system responds to flow perturbations. Pressure also is a key tool for understanding geomechanical signals; this is somewhat less mature than hydrologic testing (for geologic storage examples of geomechanical assessments see Rutqvist and others, 2008; Kim and Hosseini, 2013).

In this workbook we explore one of the many pressure-based methods with potential high value for assurance monitoring at geologic storage sites to document retention goals. If a suitable permeable layer can be identified above the injection zone (designated an AZMI), measuring fluid pressure in this zone can provide assurance of no measurable fluid migration out of the injection zone.

To use AZMI pressure to document **no** leakage, three conditions must be met:

- 1) Low-probability migration paths must be hydrologically connected to the AZMI. For example, if fluid migration occurs within a well casing that is intact across the AZMI, no pressure response will occur in the AZMI. If the AZMI is hydrologically discontinuous, pressure may not propagate to the monitoring points.
- 2) The noise created by ambient pressure variations in the AZMI must be below leakage signal to be detected. Noise can be from tides, from distant production and injection wells, and from geomechanical response of the AZMI to injection (Kim and Hosseini, 2013).
- 3) Gauge placement must be engineered to respond correctly and with adequate sensitivity to pressure response of the AZMI. Issues to be considered are spatial heterogeneity (Sun and others, 2013a), well spacing (Sun and others, 2013b), interval perforated, and gauge placement in the well. Pressure will propagate long distances; however it may fall below noise or below gauge sensitivity if the measurement points are too far from the source of signal or if the hydrologically interconnected interval is too thick. Gauge placement is important in sampling the interval to be assessed properly as well as not confusing the signal by connecting disparate zones at the well. In addition, if several fluids can access the wells, the effect of different fluid densities on pressure measurement must be considered. Targeted characterization of the potential AZMI is needed, both by collecting pressure profiles to assess the ambient characteristics and by well-designed injection/fall-off testing in the AZMI. One way to provide additional assurance is to monitor at one or more levels within the confining system to document that fluid flow through the confining system is attenuated such that the retention can be quantified and the goal met.

AZMI can be either fresh or saline. Some monitoring protocols, such as US EPA's class VI rule (U.S. CFR, 2010b), require geochemical sampling of AZMI's, focusing on the lowest USDW's. However, modeling

recently conducted by Porse (2013) shows that pressure signal is propagated faster and farther than a geochemical signal; thus, AZMI pressure monitoring is the more sensitive method, where the conditions for its use are met. In addition, fluids migrating upward under pressure gradient will preferentially enter deeper zones, causing a delayed and attenuated signal in shallow zones (Nordbotten and others, 2004; Zeidouni, 2012).

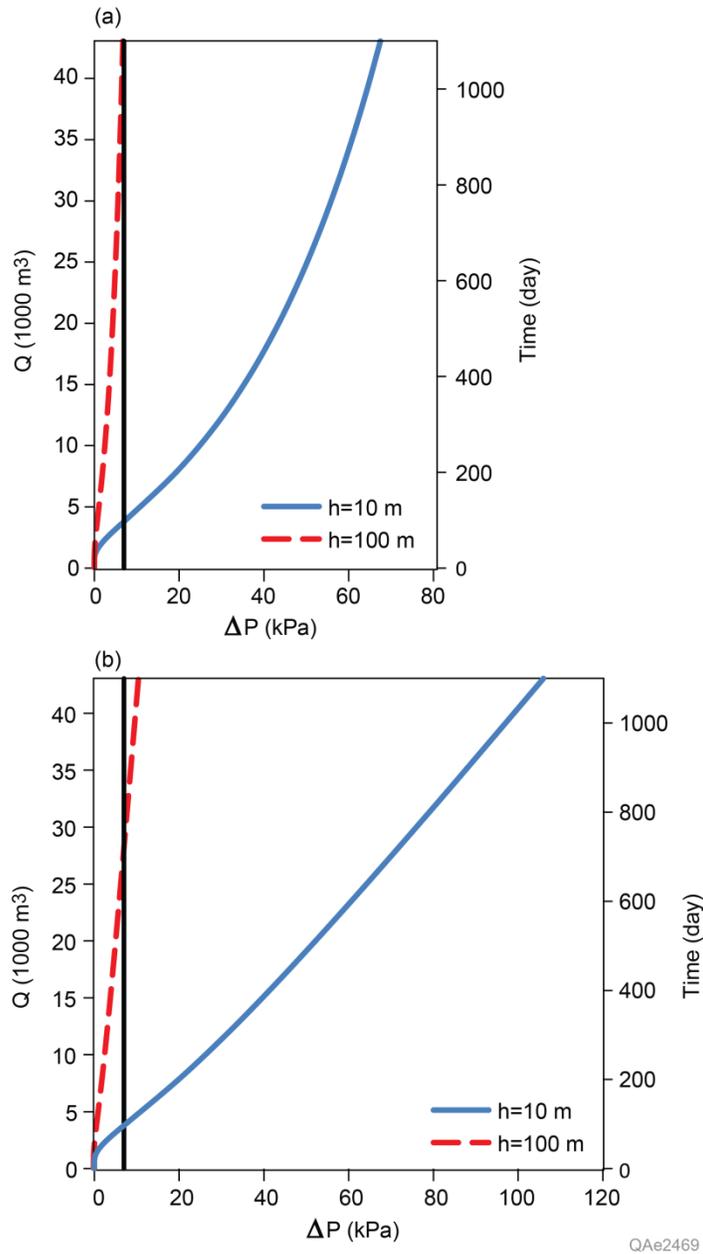


Figure 16. Impact of thickness and boundary conditions on detection of flow into an AZMI. Part a shows the difference in response between an AZMI thickness of 10 m and a thickness of 100 m in a zone with infinite-acting boundary conditions, and a distance from leakage point to pressure monitoring well of 6 km. Part b shows the same model, but with closed boundary conditions at 12 km.

The hydrologically connected thickness of the AZMI has an important control on the sensitivity of detection. Figure 16 shows a subset of hydrologic variables, focusing on two important ones, AZMI thickness and boundary conditions. In this model, we hold the leakage rate constant. This is a simplification of the coupled reservoir-AZMI models (Zeidouni, 2012; Zeidouni and Pooladi-Darvish, 2012a) where leakage energizes the AZMI, leakage into that zone may decrease before reaching a steady-state constant rate. In a multi-layer system this feedback energizes shallower permeable zones more as leakage continues, until flow can reach the near surface. The impact of AZMI thickness is strong, with the signal in the thinner zone above a noise threshold of 5 psi within 100 days of from the start of leakage and migration of 3000 m³. The thicker zone does not rise to this detectable threshold until 1000 days have elapsed and 40,000 m³ of leakage has occurred. Volume is used as the unit, because the leaking fluid could be either brine or CO₂. Closed boundary conditions (Fig. 16B) increase the magnitude of signal in the AZMI significantly, especially at later times.

With information about the hydrologic properties of the AZMI and the desired signal above noise, an optimization program can be run to place the minimum number of monitoring wells to be effective in detection (. Objectives for AZMI monitoring may be in conflict with each other. For example, reducing detection time generally requires more monitoring wells. Therefore, optimal monitoring solutions only exist in the Pareto-optimal sense. Sun and others (2013b) formulated and solved a multi-objective programming problem to determine the optimal AZMI monitoring locations. An important notion introduced in Sun and others (2013b) is the notion of maximum detection time, which has both practical and regulatory significance. Only when the maximum detection time is clearly defined and incorporated into a site-specific risk management plan can the efficacy of a monitoring program be measured. A design that skips this step of monitoring network optimization runs the risk of setting up monitoring that is not sufficiently sensitive to leakage.

AZMI pressure monitoring is used commercially in gas storage contexts, but applications to geologic storage of CO₂ are sparse. A test program using several different installations has been reported from the Southeast Regional Carbon Sequestration Partnership (SECARB) Program at Cranfield, Mississippi, which successfully differentiated between geomechanical and fluid flow signals and evaluated near-field versus far-field signal sources (Kim and others, 2013; Meckel and others, 2013; Tao and others, 2013). Other variants of AZMI installations, at PCOR installations at Bell Creek field, Montana, the Illinois Basin Decatur project, and Denbury's Hastings field, are reportedly in testing.

3.5.3 Thermal monitoring

Another classic leakage indicator is thermal signal, caused by transport of hotter fluids from depth that exchange heat with surrounding rock and fluids. In the case of CO₂ leakage, leakage to a shallower zone results in decreased pressure, which expands CO₂, producing a strong and distinctive Joule-Thomson cooling effect. Thermal monitoring at the point of upward migration distant from CO₂ injection points will produce a distinctive heating trend when water is the phase that is migrating, followed by cooling trend when CO₂ is the phase that is migrating, which could be of high value in discriminating which phase is migrating (Fig. 17).

Although temperature gauges are typically combined with pressure gauges, the uses of the two measurements for monitoring are fundamentally different. Pressure perturbation propagates over large distances; because of the thermal mass of rocks and fluids, temperature is strongly localized (Fig. 18). The thermal mass of rock and fluid attenuates thermal signal over short distances, so this method is valuable only where the low-probability leakage path can be probed directly, within a meter or less. Thermal monitoring is sensitive to flow rate; slow flow will equilibrate during migration, resulting in inability to detect signal. Thermal monitoring can be used to test if wells are transmitting fluid behind casing. We are testing applications where faults are penetrated by many wells.

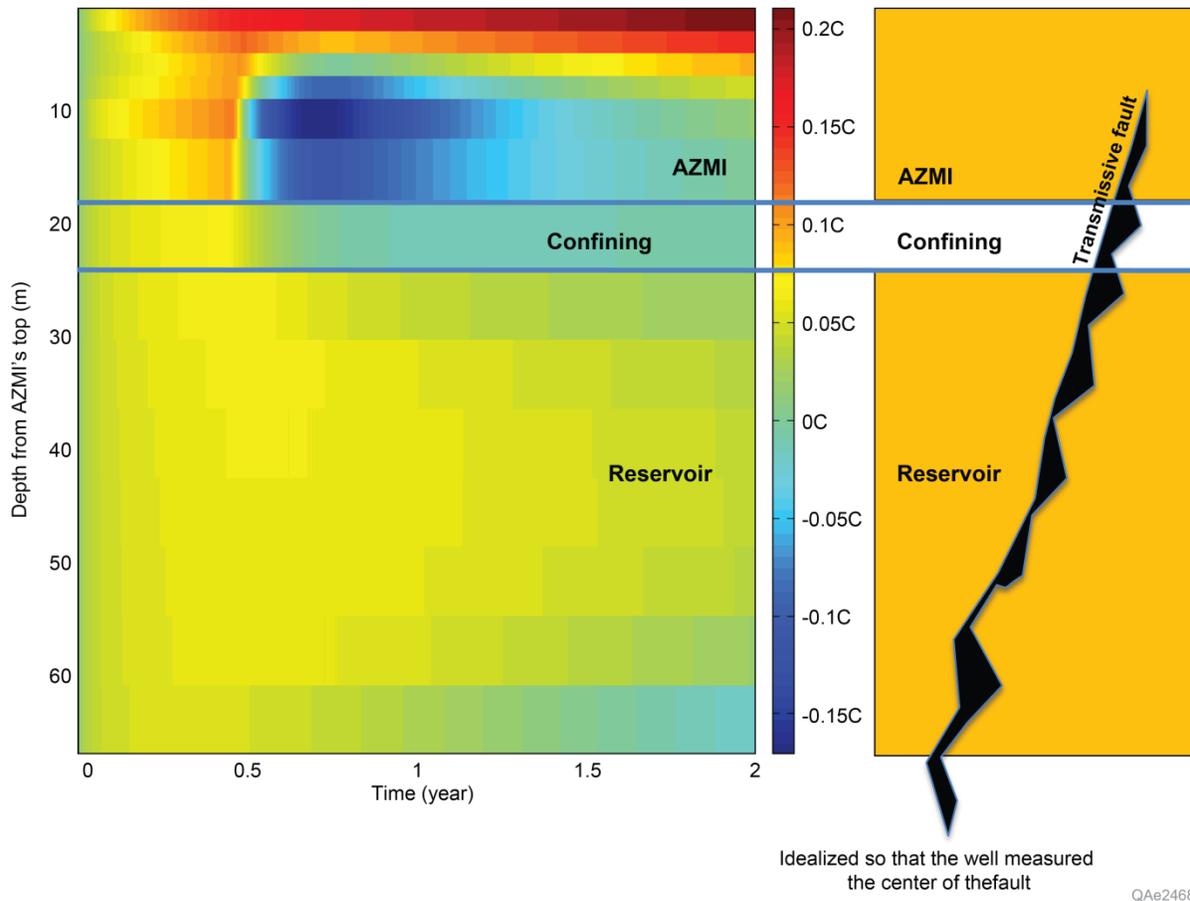


Figure 17. Modeled thermal response showing temperature change with time along a vertical conduit with the geometry of a fault. The measurements are made as if the each point along the center of a 2-m-wide permeable fault zone was instrumented, although in reality measurements might be made along many vertical wells that penetrate somewhat inclined faults. The modeled transmissive fault is 200 m from the injection point, so that initially brine is lifted from the injection zone to the AZMI as a result of pressure increase. When the CO₂ plume increases in diameter to reach the transmissive fault, CO₂ becomes the phase to migrate. Response is sensitive to all reservoir properties and geometries; details provided in Zeidouni and others (in press, 2014).

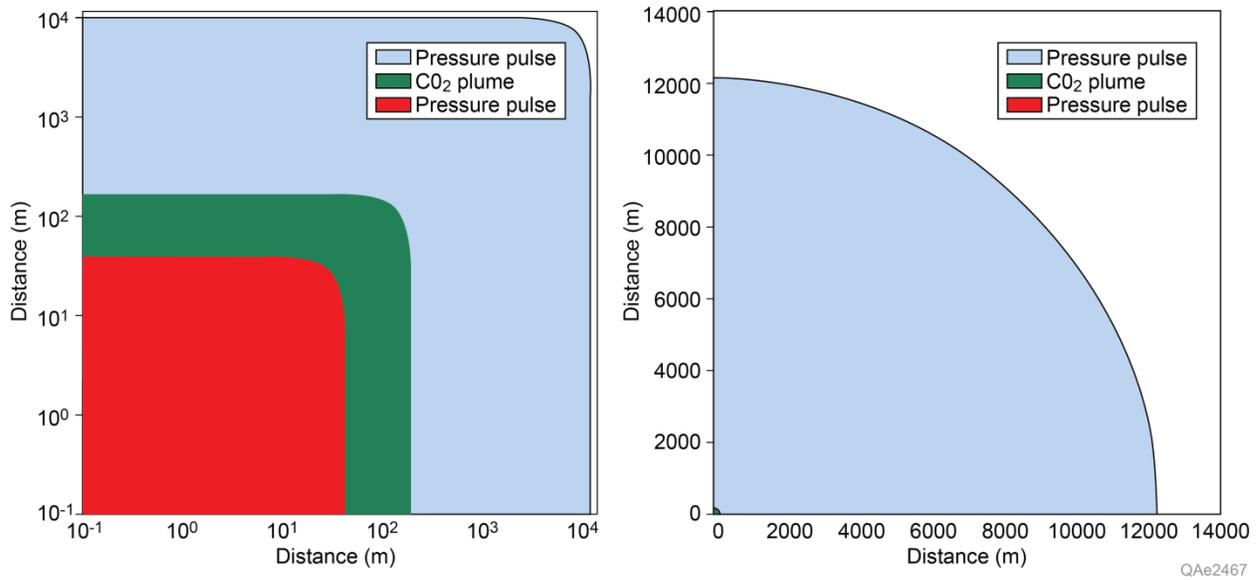


Figure 18. Thermal signal is diagnostic but highly localized compared to the extent of CO₂ and extent of pressure. Areas shown are a 0.15°C increase in temperature and a 1 kPa increase in pressure. Part A has a log scale for area and part B has a linear scale.

The magnitude of the diagnostic Joule-Thomson cooling is sensitive to the depth at which the migration takes place. Figure 19 shows that large changes of 6 °degrees C occur where CO₂ is migrating near the transition to gas phase; deeper migration leads to smaller change.

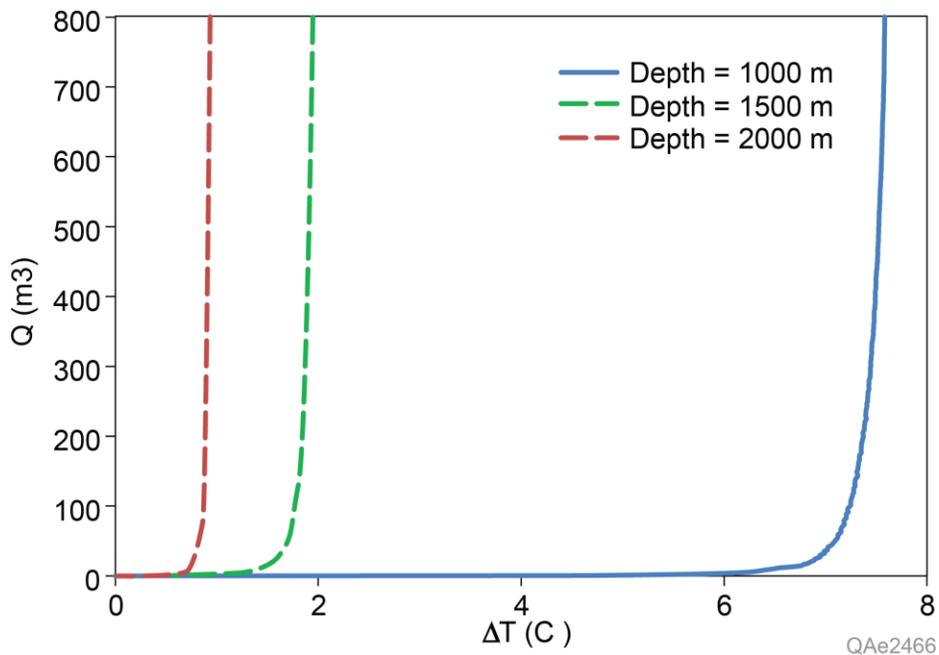


Figure 19. Comparing temperature change in °degrees C with flow rate at three different depths, showing non-linear expansion of CO₂ with depth.

Thermal methods are conventionally used for behind-casing well leakage detection, where they can be combined with noise logging (McKinley, 1973) and advanced programs such as radioactive tracers or oxygen activation logging. Thermal assessment has recently been used in a CO₂ project to document that the well measured was not allowing fluid flow (Tao and others, 2013). A program for testing feasibility of assessing fluid migration along with numerous well penetrations crossing low-angle faults with time-lapse thermal monitoring is in development.

3.5.4 Groundwater geochemistry

In many settings, monitoring groundwater geochemistry is an important parameter for reducing risk of groundwater contamination. For example, at a landfill or a chemical spill, an array of wells for sampling aqueous geochemistry of groundwater can be used to provide assurance that mitigation is effective and that contaminants are not migrating into the regional groundwater. The same approach has been proposed to provide assurance that the injected CO₂ is retained and has not migrated to groundwater (for example, Wilkin and DiGiulio, 2010).

However, monitoring groundwater for injected CO₂ is different from monitoring a known contaminant, for three reasons:

- 1) Only in case of a low-probability failure would any migration occur; groundwater monitoring is conducted mostly a matter of seeking to prove a negative, that no leakage to groundwater is detected.
- 2) CO₂ is naturally present in groundwater and the amount present in the non-impacted system may vary over space and time.
- 3) CO₂ is reactive with the rock-water system.

Designing a groundwater monitoring plan requires deep investment. One critical step is to determine what the geochemical result of interaction of CO₂ with the groundwater would change, and how this change would be detected above natural variability. This requires a modeling or conducting at batch reactions (Lu and others, 2009; Mickler and others, 2013). We find that given the complexity of the natural system an *in situ* test program may be advisable (Trautz and others, 2012; Barrio and others, 2013; Mickler and others, 2013; Yang and others, 2013b).

As in each of the monitoring methods, ambient variability is a critical parameter for determining site-specific sensitivity. Groundwater pH, alkalinity, dissolved inorganic carbon (DIC), and dissolved CO₂ in aquifers show spatial and temporal variations. These variations are the equivalent of noise in a geophysical measurement, and if a CO₂ leakage signal cannot be reliably separated from the ambient variability, detecting leakage with groundwater chemistry monitoring is not fit-to-purpose.

In addition, sampling and analytical processes in geochemical data collection are well known limitations for geochemical applications, analogous to poor repeatability in geophysical measurements. EPA projects manage data quality with a Quality Assurance Project Plan (U.S. Environmental Protection Agency, 2001), but much of the effort is focused on laboratory analysis. In the case of geochemistry focused on a dissolved gas such as CO₂, even collection of repeatable samples is difficult because sampling can cause depressurization, temperature change, and turbulence, which strongly modify the dissolved gas and associated chemical parameters. For example, DIC measured in a laboratory can be

deviated from the measurements in the field because of degassing during the process of sampling, preservation and transportation (Yang et al., 2013b).

As an example of the ambient noise and unreducible inconsistency introduced sampling in a groundwater system, measurements of groundwater pH and alkalinity in the 30 groundwater wells at the Ogallala and Dockum shallow aquifer over an area in Scurry County, of 450 km² from June 2007 to August 2008 (Smyth et al., 2010) are shown in Figures 20 and 21. The standard deviation and average values are calculated based on Texas, using the measurements of pH and alkalinity. Calculated coefficients of variation for pH and alkalinity are 0.064 and 0.304, respectively. Since DIC and dissolved CO₂ were not collected in the field, the coefficient of variation of alkalinity is used also for DIC and dissolved CO₂. Variations in groundwater pH, alkalinity, DIC and dissolved CO₂ for the simulated case are calculated according to the following equations:

$$P_L = P_i - P_i \times \alpha \quad (2)$$

$$P_U = P_i + P_i \times \alpha \quad (3)$$

where P_i is the initial value of groundwater pH, alkalinity, DIC, and dissolved CO₂ used in the model, and α is their coefficient of variation. P_L is the lower boundary and P_U is the upper boundary. Calculated P_L and P_U are shown in Figures 22-25 for comparison to modeled change groundwater pH, alkalinity, DIC, and dissolved CO₂.

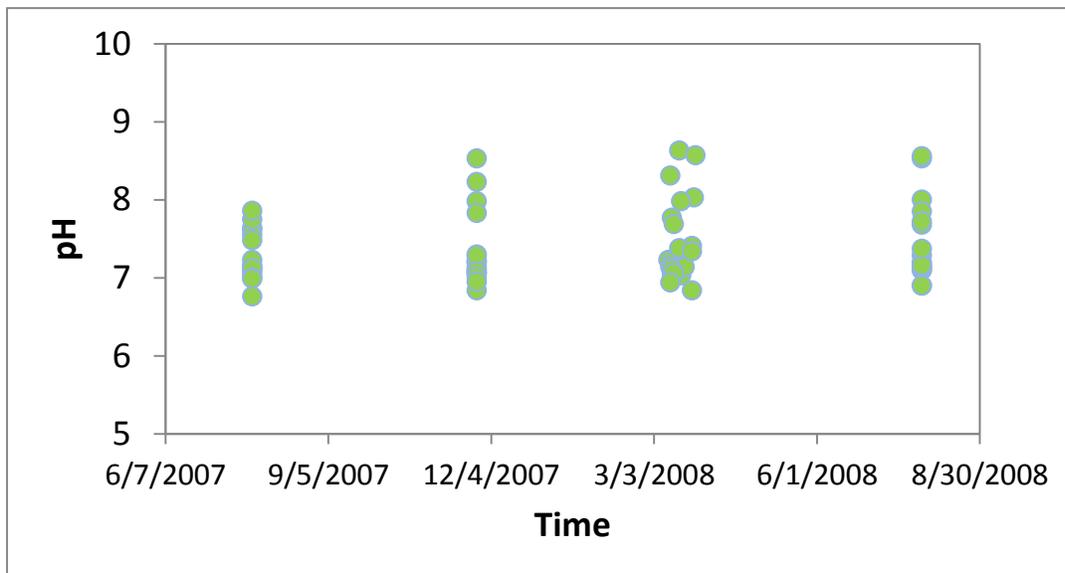


Figure 20. Groundwater pH measured in about 30 groundwater wells over an area of 450 km² in the Ogallala-Dockum shallow aquifer in Scurry County, Texas, from June 2007 to August 2008.

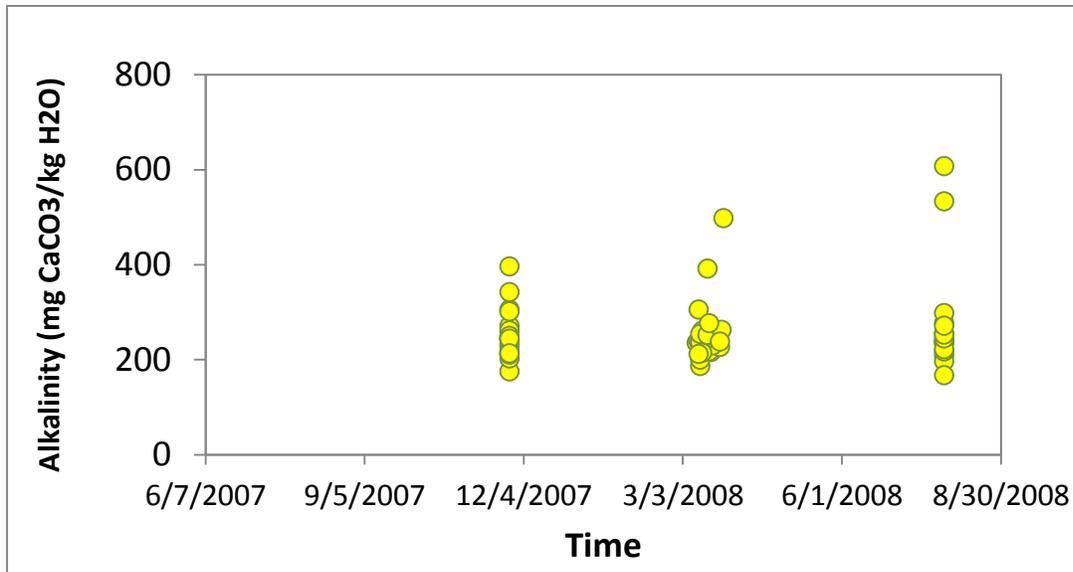


Figure 21. Alkalinity measured in about 30 groundwater wells in the Ogallala-Dockum fresh water aquifer over an area of 450 km² in Scurry County, Texas, from June 2007 through August 2008.

An important and difficult question to be answered as part of an ALPMI is how much CO₂ would have to migrate into the aquifer to create a signal that would be detectable above noise. The most important variable is the extent to which the aquifer is confined. Confined aquifers would retain CO₂; unconfined aquifers would rapidly outgas resulting in a minimal and localized impact. Flow and transport also have an important effect on mixing of the CO₂ with aquifer water, creating either a dispersed or a focused signal. A dispersed signal is easier to detect because it is spread over a large area, but more difficult to detect because it is attenuated. Few CO₂ monitoring projects have completed a detailed fate and transport model for CO₂ introduced into an aquifer, as the modeling could be even more complex than modeling in the reservoir because of temporally and spatially dynamic characteristics of the aquifer.

For an example in the workbook we consider the impact of aquifer rock properties on determining which geochemical properties are sensitive indicators of leakage. Responses of groundwater pH, alkalinity, dissolved inorganic carbon, and dissolved CO₂ in groundwater to unexpected CO₂ leakage from the storage formations to the potable aquifer are modeled. For simplification, we neglect both single and multiphase flow by assuming that CO₂ entering the aquifer is immediately well-mixed with groundwater over the model domain (Fig. 22). The leaked CO₂ is assumed to be dissolved into groundwater and reacting with rock minerals. No free CO₂ gas phase is assumed in the aquifer. PHREEQC is used to simulate the responses of groundwater pH, alkalinity, dissolved inorganic carbon, and dissolved CO₂ (Parkhurst and Appelo, 1999).

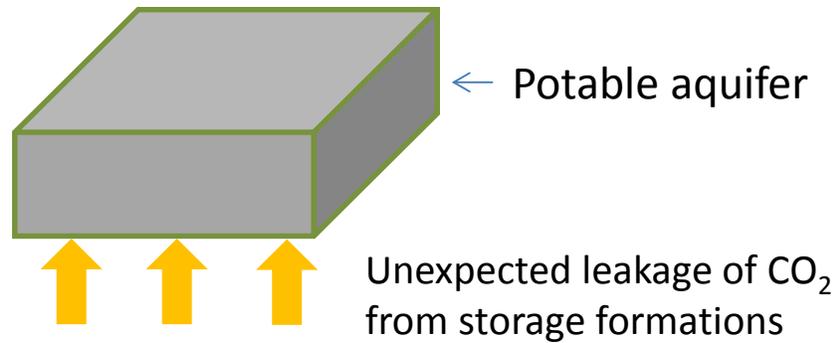


Figure 22. Conceptual model for geochemical response to CO₂ migration into an aquifer. The leakage rate is 1 million metric tons per year uniformly distributed over an area of 10 km² of the potable aquifer (USDW). The aquifer is confined and has a thickness of 100 m. Porosity of the aquifer is 0.2.

Two simplified cases are tested: a carbonate-poor aquifer in which aquifer sediments are represented with 95% quartz +5% albite, and a carbonate-bearing aquifer that the aquifer sediments are represented by 99% quartz + 1% calcite. Once CO₂ is leaked into the aquifer, groundwater pH will be decreased and will further drive dissolution of reactive minerals, albite in the carbonate-poor aquifer and calcite in the carbonate-bearing aquifer. Mineral reactions caused by CO₂ leakage are simulated with the kinetic theory. Detailed information about configuration of kinetic mineral reactions can be found (Yang et al., 2013a). Water compositions from the shallow ground water of the Ogallala –Dockum aquifer of Scurry County, TX above the SACROC field (Romanak and others, 2012b) are used as initial water chemistry in the geochemical model; however, assessment by Yang and others (2013) shows that outcomes are relatively insensitive to initial water chemistry. Time simulated is 10 years.

Modeling shows, as expected, that groundwater pH decreases because of CO₂ dissolution (Fig. 23). Groundwater pH decreases faster in the carbonate-poor aquifer (blue-open circle line) than in the carbonate-bearing aquifer (the red-solid triangle line). After 10 years, groundwater pH in the carbonate-poor aquifer is about half a unit smaller than that in the carbonate-bearing aquifer. The pH change above noise occurs in 1 year in the carbonate-poor aquifer but takes 4 years in the carbonate-bearing aquifer, and plateaus close to the region of noise for the model period. The pH sensitivity is shown to be strongly dependent on aquifer rock composition.

Alkalinity calculated is shown in Figure 24. Alkalinity increases much faster in the carbonate-bearing aquifer than in the carbonate-poor aquifer. After 10 years, alkalinity in the carbonate-bearing aquifer is about 3 times that in the carbonate-poor aquifer because of calcite dissolution. The modeled slight increase in alkalinity in the carbonate-poor aquifer is attributed to albite dissolution. Alkalinity is more sensitive to CO₂ leakage in the carbonate-bearing aquifer; in a carbonate-free aquifer the change in alkalinity never increases out of the range of normal variability.

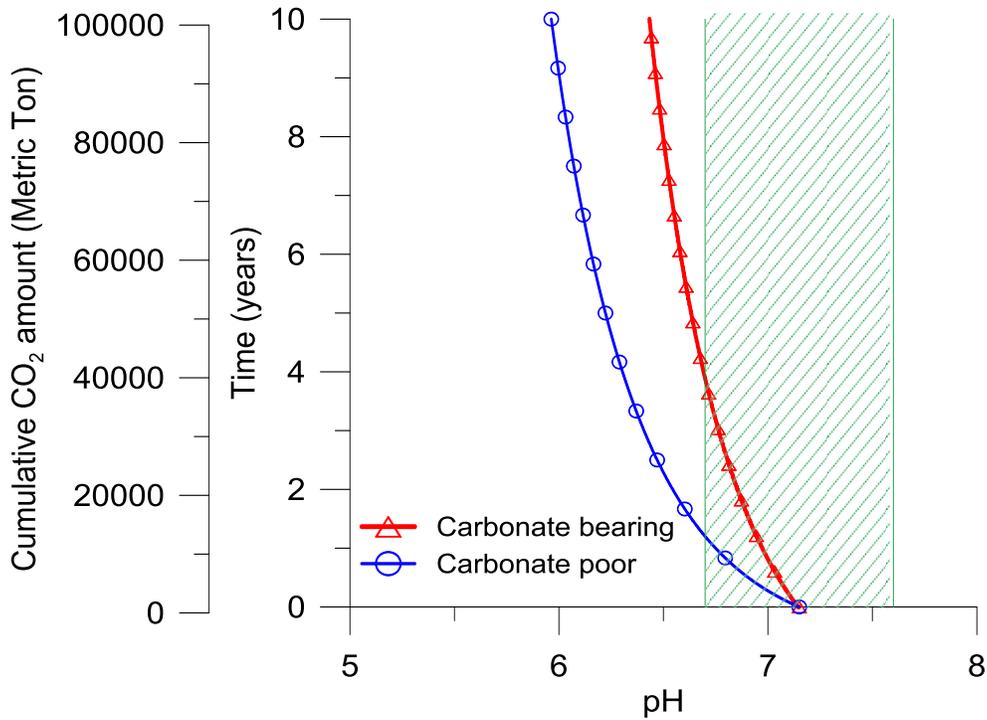


Figure 23. Plot of pH calculated in the carbonate-poor and carbonate-bearing aquifers (the shaded area represents spatial and temporal variability of pH from data shown in figure 20).

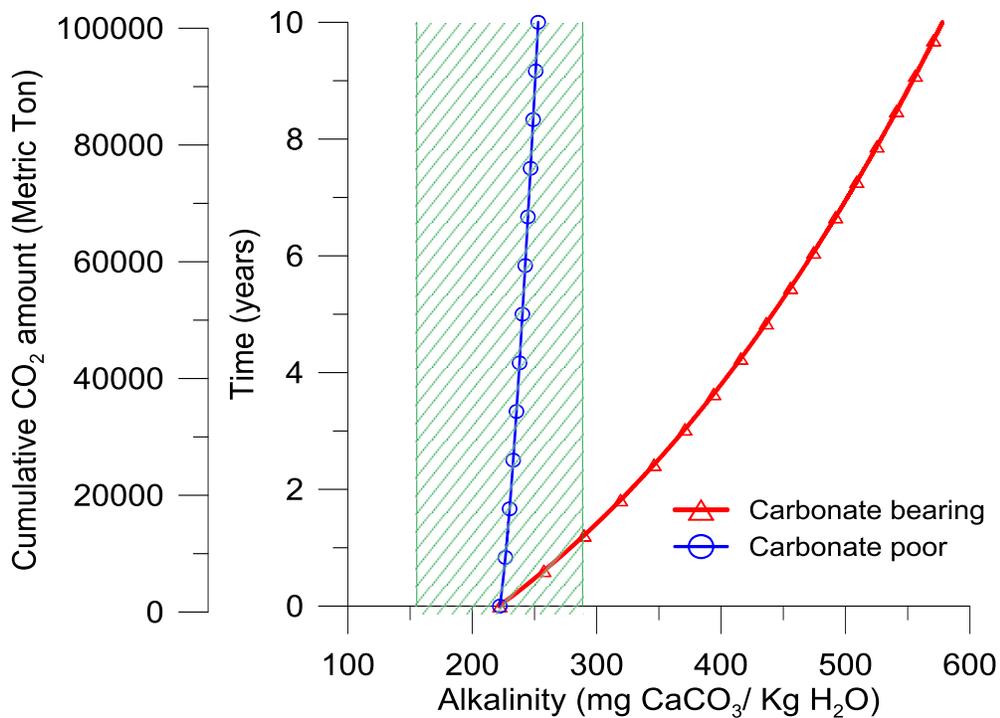


Figure 24. Plot of alkalinity calculated in the carbonate-free and carbonate-bearing aquifers. The shaded area represents spatial and temporal variability of alkalinity from the data shown in Figure 21.

Dissolved inorganic carbon (DIC) is a summation of concentrations of dissolved CO_2 , HCO_3^- , and CO_3^{2-} . Once CO_2 is leaked into the aquifer, DIC increases quickly, regardless of the carbonate-poor or carbonate-bearing nature of the aquifer (Fig. 25). DIC calculated in the carbonate-bearing aquifer is slightly higher than that in the carbonate-poor aquifer. This is due to dissolution of calcite in the carbonate-bearing aquifer according to the following reaction,



Dissolved CO_2 in groundwater is shown in Figure 26. Dissolved CO_2 in groundwater increases as more CO_2 is leaked into the potable aquifer. Note that dissolved CO_2 apparently increases faster in the carbonate-free aquifer than in the carbonate-bearing aquifer (Fig. 26). The reason is that some dissolved CO_2 reacts with calcite and is converted to be bicarbonate (Eq. 1).

Simulated DIC in both carbonate-poor and carbonate-bearing aquifers are beyond the variation after about 1 year in the carbonate-bearing aquifer and 1.5 years in the carbonate-poor aquifer, suggesting that DIC could be used as an indicator for CO_2 leakage detection.

Dissolved CO_2 , as shown in Figure 26, shows the earliest signals above noise, about few months after CO_2 is leaked into the aquifer. Note that variation in dissolved CO_2 shown in Figure 26 is calculated based on that of alkalinity. Variation in dissolved CO_2 would be more realistic with measurements of dissolved CO_2 . Repeatable methods of obtaining dissolved gas measurements would appear to be a high-value target for this type of monitoring, irrespective of aquifer mineralogy.

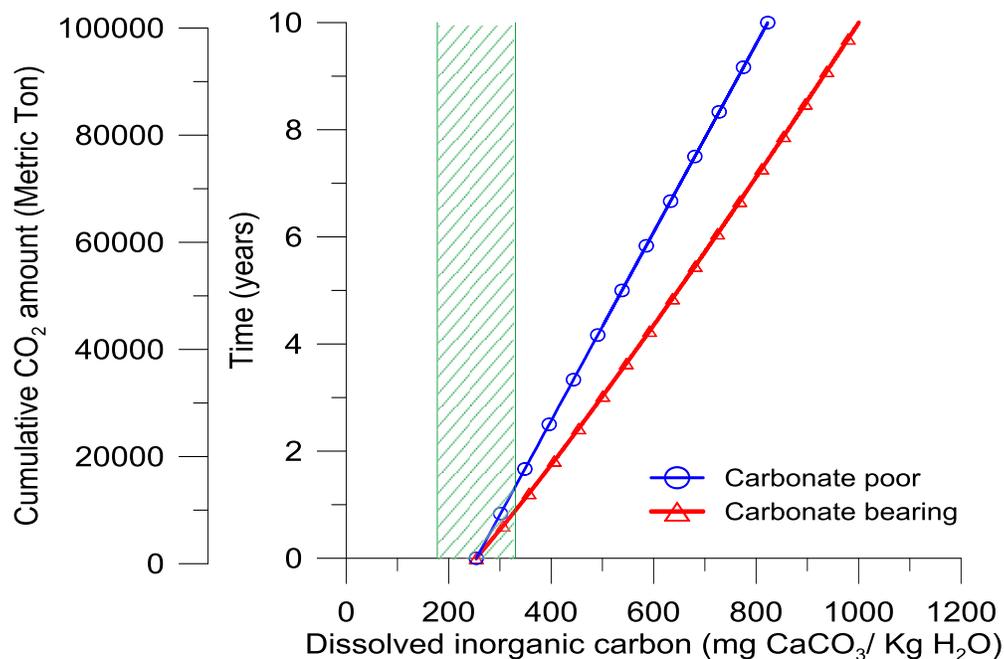


Figure 25. Plot of DIC calculated in the carbonate-poor and carbonate-bearing aquifers. The shaded area represents spatial and temporal variability of DIC calculated from observed data shown in Figures 20 and 21.

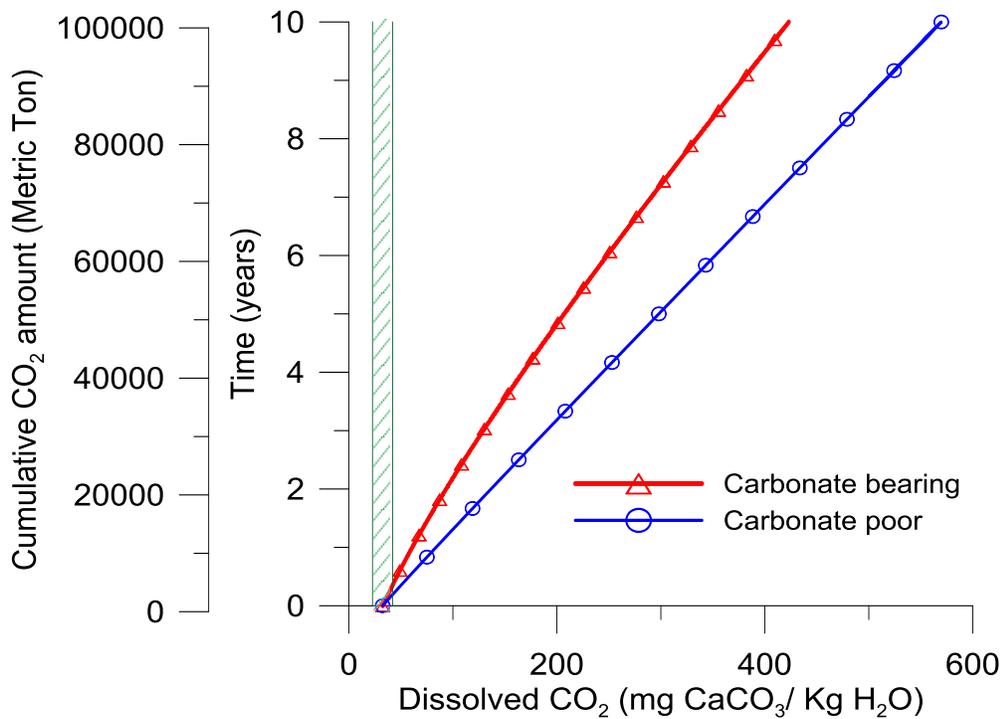


Figure 26. Plot of dissolved CO₂ in groundwater calculated in the carbonate-poor and carbonate-bearing aquifers. The shaded area represents spatial and temporal variability of dissolved CO₂ in groundwater, which is assumed to be same as the observed variability in alkalinity shown in Figure 21.

Monitoring groundwater geochemistry at geologic storage sites has begun and experience is being gained. The study of the Ogallala and Dockum aquifer chemistry over a multi-decade CO₂ injection project at SACROC field, Texas, identified no signal indicative of CO₂ leakage. However, that study documented a large number of complexities that require evaluation to separate natural variation from a leakage trend (Smyth and others, 2010; Romanak and others, 2012a, 2012b). Other studies of groundwater above geologic storage sites are reporting similar responses that indicate a need for detailed characterization as well as improved definition of the expected and measurable signal that would indicate leakage.

3.6 Application of four test monitoring methods to the ALPMI cases

In this section we illustrate optimization of tool sets for three low-probability cases of material impact shown in Figures 8-10 and Table 3. The cases are illustrative, not comprehensive. In a real case, this section might be quite long, considering, weighing, and evaluating many scenarios. However, a few idealized cases may be of value in preparation for real projects.

The differences among the cases are in 1) the mechanism of leakage and 2) the opportunities for detection of leakage because of geometries of the overburden. Figures 8 and 9 show leakage as hypothesized through confining zone P uppermost above the uppermost injection zone Q. In Figure 10 the leakage results from failure to isolate the three injection zones, such that, post injection, more CO₂ than planned migrates to the uppermost injection zone Q, and CO₂ migrates laterally further than expected. In each of these cases, the first failure mechanism results in trapping in a secondary reservoir,

O, which can then serve as the AZMI, responding as an early warning system prior to any material impact as defined in the project goals. Material impact would occur if leakage continued unchecked, in Figures 8 and 9, resulting in the CO₂ plume's migrating laterally to find a well with unacceptable construction flaws in the surface casing. In Figure 10, an additional failure is required, which is that the fault, known to be sealing at depth, is transmissive at O, so that migration to the same poor surface casing occurs.

As is typical in good sites, material impact is low probability. For this exercise, we set a condition that the project or regulator has required that the ALPMI process proceed to monitoring design and deployment to further reduce risk of material impact. The monitoring design should use the site-specific information provided to identify the conditions that might lead to a material impact (trend toward migration of greater than 1 million tons of CO₂ into the atmosphere in less than 1000 years).

In Figures 8 and 9, which hypothesize that loss might occur through an undetected transmissive fracture system, we reject pressure and seismic measurements made in the injection zone as unlikely to be sufficiently sensitive to detect loss of the CO₂ from the intended location. Remaining uncertainty about two-phase flow and boundary conditions in reservoir Q remains moderate and creates sufficient uncertainty that mass balance is insufficient to conduct ALPMI by comparing measured and modeled mass and pressure. Inaccuracy would be especially high during early stages of injection, when it would be of highest value.

Direct detection of the fracture system is likewise rejected. We postulate that it was not detected during excellent characterization. Perhaps the fracture aperture is enhanced by geomechanics during injection in this scenario. It is possible that advanced acoustic imaging (e.g., Pérez and others, 1999) might detect a change in the seismic characteristics of layer P. However, in the ALPMI situation of trying to obtain a negative response to document no impact, these methods may fall short of being reliable enough in many geometries and rock types. Thermal methods of detecting fracture flow are rejected, because the location of the hypothesized fracture system is unknown, so that making measurements close enough for detection would not be possible.

Detection of the migrated CO₂ as it perturbs layer O, serving as an AZMI, is considered a highly reliable method, but the detection mechanism would vary between cases. Looking at Figures 12 and 14, we see that time-lapse seismic methods would be sensitive at the moderate depth of 1500 m. However, in the case in Figure 8, where the bed O is only 10 m thick, if the CO₂ plume did not access the heterogeneous reservoir, the saturated thickness might be below detectability, whereas in the thick O zone in Figure 9, the chance that vertical migration will create a detectable signal is good. For pressure-change detection, the optimization is reversed. Figure 16 shows that the thin O zone in Figure 8 would respond distinctly to pressure increase, whereas the 10-ft-thick zone might be slow and might fall below the noise threshold.

Pressure monitoring and seismic monitoring at depth are both more desirable and more robust than monitoring USDW zone M. Deep monitoring is desirable, because detection would occur early in the project, allowing more effective mitigation and avoiding any impact to USDW or loss to the atmosphere. Deep monitoring is generally more sensitive also, because noise from the near surface is reduced.

Thermal surveillance would be effective in assessing the condition of the well completions penetrating zone N. Should CO₂ migration occur at these shallow depths, it would create a strong thermal signal (Fig. 19). However, it might be cost prohibitive to reenter wells that have been plugged and abandoned and that appear, based on records, to be properly constructed and plugged.

Geochemical monitoring would be effective in aquifer M because it is confined. To complete the exercise, we compare a simplified and idealized geochemical monitoring program for zone M using the sensitivity diagrams in Figures 23-26. If dissolved CO₂ can be detected with high repeatability, using an advanced sampling method, this is the most sensitive geochemical tool in all cases, followed by DIC. Note that the successful scenarios presume a CO₂ migration rate. Another way to consider this is that the monitoring well spacing is small, so that the sample is collected close to the leakage point. Since M is confined, pressure measurement would likely show a leakage signal before a geochemical method (Porse, 2013). However, if the aquifer recharge and discharge are dynamic and variable, pressure noise might be too high for leakage detection.

The ALPMI depicted in Figure 10 is more difficult, because the impact might not be evident until the end of injection, when buoyancy becomes dominant. During injection, pressure distribution would cause cross-formational flow to other zones also under injection to be small compared to within-zone flow. However, over long time frames, vertical CO₂ migration to unit Q might allow CO₂ to migrate beyond the acceptable area. The best way to provide assurance that the case shown in Figure 10 does not exist is to test the connectivity between zones during the commissioning of the wells, by late-stage hydraulic testing. However, for this exercise let us assume that uncertainty about connectivity remains.

Methods discussed for cases 8 and 9 are relevant, but this scenario would require a prolonged monitoring period. However, testing of the lateral connectivity of zone O into the area of old wells is feasible during the injection using pressure methods, and if connectivity does not exist the ALPMI can be reduced to negligible. If connectivity exists, this might trigger a reentry and testing program for the old wells to reduce the need for post injection monitoring.

3.7 Workflow

A workflow focused on developing fit-to-purpose monitoring is presented in Appendix I.

4 Conclusions

An optimized monitoring program provides assurance that the project goals are being met. We note that many geologic storage projects conducted previously have had research goals to test models and tools. Fully commercial projects have quite different goals, and therefore different monitoring programs are required. To conduct optimization of monitoring for a site, project goals are re-expressed in terms of quantified material impacts.

After high-quality characterization and injection design, the likelihood of such impact has been greatly reduced. However, because of the large scale and complexity of the geologic system, it may not be possible to completely eliminate some possibility of certain types of unacceptable outcomes, which is expressed as an assessment of low-probability material impacts (ALPMI). Ranges of possible but unlikely

outcomes are created by modeling the tails of possible distributions from characterization, and those outcomes that fail to meet quantitative project goals are highlighted for reduction by additional characterization and monitoring. The ALPMI process will highlight different material impacts at different sites, which will result in turn in different monitoring designs. Unlike risk assessment methods that attempt to assign probability and impact in terms of cost, the ALPMI method is used to design a site-specific monitoring program, although the two approaches are complementary and could be combined to create a formal value of information assessment that could be used to allocate monitoring resources.

In this methodology, we note that characterization is iterative and segues without a sharp boundary into monitoring. Items that are intermediate between characterization and monitoring are 1) energizing the system to measure response prior to full-scale start of injection, such as hydrologic testing, and 2) collecting data on noise and repeatability relevant to each prospective monitoring tool. These activities are often considered for geologic storage projects under the heading of preinjection baseline, but without clearly stating the goals of this activity, the value may be lost. Monitoring can be unsuccessful either if it fails to detect a material impact, or if signal with no impact on goals are flagged, resulting in loss of confidence. Project investors, developers, regulators, and other stakeholders need to require sufficient investment to avoid unsuccessful outcomes to monitoring.

From characterization and modeling the ALPMI, the site-specific sensitivity of monitoring tools can be formally assessed. Deep expertise is available in conducting such an assessment; however, it is important that stakeholders and investors make sufficient investment in design, rather than following a precedent or a protocol.

In this workbook, we highlighted a few selected aspects of monitoring that are sensitive to site parameters. These examples are only illustrations; they cannot substitute for a detailed site-specific evaluation by a team that provides substantive experience with possible monitoring approaches. An intense and interactive period of optimization prior to monitoring deployment will be effective in increasing assurance that goals are met, as well as cost-cutting because ineffective methods are not used in the field.

Time-lapse seismic surveys are a powerful tool for geologic storage, because CO₂ that replaces water can be mapped in 3-D. Seismic survey design typically involves substantive field testing to optimize sources and measure noise and forward modeling to assess the likely magnitude of the signal. It is important, however, that the whole project design team take the limitations of seismic data seriously. We provide three simple examples of limits on seismic sensitivity:

- 1) where the rock frame is stiff, for example, because of high effective pressure at deep burial (e.g., 3 km),
- 2) the fluid substitution has a small impact on seismic velocity
- 3) thin beds (<20 ft) and low porosity (<10%) are also modeled to illustrate reduced detectability using standard seismic methods.

Pressure is a well-known and robust method to monitor an injection. A gas-storage method of monitoring pressure in an above-zone monitoring interval (AZMI) is readily adapted for geologic storage

applications. Noise measurement and forward modeling are needed to document that the planned installation is adequate to be sensitive to leakage rate and leakage volume defined by the goals at the relevant hydrodynamic conditions. Such an assessment may not be triggered by conventional uses of pressure, such as for model calibration and history matching.

Thermal methods are also used conventionally to assess migration of hot fluid from depth along a pathway. Where CO₂ is the migrating fluid, pressure expansion as a result of decreased pressure at shallower depths produces a diagnostic signal. This signal is strong at shallow depths near 1 km; at greater depth non-linear CO₂ behaviors creates a weak signal. Thermal signal does not propagate far from the source. The intensity of the cooling is strongly depth-dependent.

Sophisticated methods are available to assess the detection limit of constituents in an aqueous phase contaminant plume. Since in the ALPMI the impact is hypothetical, investment in sufficient data collection for such an assessment may be overlooked, resulting in poor design. An example case of the impact of minor amounts of calcite in the aquifer on detection of leakage via geochemical monitoring was analyzed using geochemical modeling. Calcite suppresses sensitivity of pH and enhances sensitivity of using alkalinity for CO₂ leakage detection. DIC and dissolved CO₂ are sensitive to leakage in calcite-bearing and no-calcite aquifers; however, methods to ensure sampling repeatability are needed for these parameters.

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6 References

- Al-Jabri, Y., and Urosevic, M., 2010, Assessing the repeatability of reflection seismic data in the presence of complex near-surface conditions, CO₂CRC Otway Project, Victoria, Australia: *Exploration Geophysics*, v. 41, no. 1, p. 24-30.
- Apps, J., Zheng, L, Zhang, Y., and others, 2010, Evaluation of potential changes in groundwater quality in response to CO₂ Leakage from deep geologic storage: *Transport in Porous Media*, v. 82, p. 215-246.
- Arts, Rob, Eiken, Ola, Chadwick, Andy, Zweigel, Peter, van der Meer, Bert, and Zinszner, Gary, 2004, Monitoring of CO₂ injected at Sleipner using time-lapse seismic data: *Energy*, ISSN 0360-5442, 07/2004, v. 29, Issue 9-10, p. 1383 – 1392.
- Barrio, Maria, Querdez, Etor, and Jordan, Michael, 2013, CO₂ Field Lab: CSLF CO₂ monitoring Interactive Workshop, 18 April 2013, Rome, <http://www.cslforum.org/publications/documents/rome2013/Barrio-Workshop-Rome0413.pdf>
- Berryman, J. G., 1995, Mixture theories for rocks: *In Rock Physics and Phase Relations: A Handbook of Physical Constants*, ed. T. J. Ahrens. Washington, DC: American Geophysical Union.

- Birkholzer, Jens, Cihan, Abdullah, and Bandilla, Karl, 2013, A tiered area-of-review framework for geologic carbon sequestration: *Greenhouse Gas Science and Technology*; 1-16; DOI: 10.1002/ghg.
- Blackford, J., Jones, N., Proctor, R., Holt, J., Widdicombe, S., Lowe, L., and Rees, A., 2009, An initial assessment of the potential environmental impact of CO₂ escape from marine carbon capture and storage systems: *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, May 1, 2009, v. 223, no. 3, p. 269-280.
- British Geological Survey, 2006, Interactive Design of Monitoring Programmes for the Geological Storage of CO₂, released October 18, 2006, http://www.CO2captureandstorage.info/CO2tool_v2.1beta/index.php.
- Bruce, Bob, 2002, Pore pressure terminology, *The Leading Edge*, v. 21, no. 2, p. 170-172. doi: 10.1190/1.1.452607
- Bourdet, D. (2002), *Well test analysis: the use of advanced interpretation models*, Elsevier Science, Amsterdam.
- Carroll, Susan, Hao, Yue, and Aines, Roger, 2009, Geochemical detection of carbon dioxide in dilute aquifers: *Geochemical Transactions*, v. 10, p. 4067-4866.
- Cavanaugh, Andrew, 2013, Benchmark calibration and prediction of the Sleipner CO₂ plume from 2006 to 2012: *Energy Procedia*, v. 37, p. 3529–3545.
- Chadwick, R. A., and Noy, R.J., 2010, History-matching flow simulations and time-lapse seismic data from the Sleipner CO₂ plume, Geological Society, London, *Petroleum Geology Conference series 2010*, v. 7, p. 1171-1182, doi:10.1144/0071171.
- Cooper, Cal (editor) and Members of the CO₂ Capture Project, 2009, A technical basis for carbon dioxide storage, carbon capture project, Published in the UK by CPL Press, Tall Gables, The Sydings, Speen, Newbury, Berks RG14 1RZ or available online at http://www.co2captureproject.org/co2_storage_technical_book.html.
- CSA Group, 2012, *Geological Storage of Carbon Dioxide, Z741-12*, Canadian Standards Association, first edition.
- Daley, T.M., Solbau, R.D., Ajo-Franklin, J.B., and Benson, S.M., 2007, Continuous active-source monitoring of CO₂ injection in a brine aquifer: *Geophysics*, v. 72, no 5, p. A57–A61, doi:10.1190/1.2754716.
- Det Norske Veritas, 2009, CO₂QAULSTOR guidelines and qualification of sites and projects for geological storage of CO₂, DNV Report No. 2009-1425.
- Det Norske Veritas, 2013, CO₂RISKMAN Guidance on effective risk management of safety and environmental major accident hazards from CCS CO₂ handling systems. DNV Report No.: I3IJLJW-2 http://www.dnv.com/binaries/CO2riskman%20guidance%20-%20level%201%20rev%201b_tcm4-536360.pdf.
- Eiken, Ola, Ringrose, Philip, Hermanrud, Christian, Nazarian, Bamshad, Torp, T.A., and Høier, Lars, 2011, Lessons learned from 14 years of CCS operations: Sleipner, In Salah and Snøhvit: *Energy Procedia*, Volume 4, 2011, p. 5541-5548, <http://dx.doi.org/10.1016/j.egypro.2011.02.541>.
- Flett, M., Brantjes, J., Gurton, R., McKenna, J., Tankersley, T., and Trupp, M., 2009, Subsurface development of CO₂ disposal for the Gorgon Project: *Energy Procedia* v. 1, p. 3031-3038.
- Gassmann, F., 1951, On the elasticity of porous media: *Veierteljahrsschrift der Naturforschenden*

- Gesellschaft in Zurich, v. 96, p. 1-23.
- Gibson-Poole, C. M., Svendsen, L. Underschultz, J., Watson, M. N., Ennis-King, J., van Ruth, P. J., Nelson, E. J. Daniel, R. F., and Cinar, Y., 2008, Site characterisation of a basin-scale CO₂ geological storage system: Gippsland Basin, southeast Australia, *Environmental Geology*, v. 54, p. 1583-1606, DOI: 10.1007/s00254-007-0941-1.
- Hansen, Olav Gilding, Douglas, Nazarian, Bamshad, Osdal, Bård, Ringrose, Philip, Kristoffersen, Jan-Boye, Ola, Eiken, and Hansen, Hilde, 2013, Snøhvit: The history of injecting and storing 1 Mt CO₂ in the fluvial Tubåen Fm, *Energy Procedia*, v. 37, p. 3565-3573.
- Hovorka, S. D., 2012, In quest of robust and commercial CO₂ monitoring. *Greenhouse Gas Science and Technology*, 2: 145–147. doi: 10.1002/ghg.1290.
- Hovorka, S. D., Doughty, Christine, Benson, S. M., Freifeld, B. M., Sakurai, Shinichi, Daley, T. M., Kharaka, Y. K., Holtz, M. H., Trautz, R. C., Nance, H. S., Myer, L. R., and Knauss, K. G., 2006, Measuring permanence of CO₂ storage in saline formations: the Frio experiment: *Environmental Geosciences*, v. 13, no. 2, p. 105–121.
- Hovorka, S.D., Zeidouni, Mehdi, Sava, Diana, Remington, R. L., and Yang, Changbing, in press, Site-specific optimization of selection of monitoring technologies, in *Carbon dioxide storage in deep saline formations*, v. 4, CPL Press and BP.
- IEAGHG, 2013, Induced Seismicity and its Implication for CO₂ Storage Risk, 2013/09, http://ieaghg.org/docs/General_Docs/Reports/2012-02.pdf, 132 pages.
- IPCC, 2005, IPCC Special Report on Carbon Dioxide Capture and Storage, prepared by Working Group III of the Intergovernmental Panel on Climate Change, Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.), New York: Cambridge University Press.
- Johnson, Ken, and Lopez, Suzie, 2003, The nuts and bolts of falloff testing, EPA Region 6, <http://www.epa.gov/safewater/dwa/pdfs/2%20uic%20modules/dwaUIC-2003falloffseminar.pdf>
- Jordan, P. D., Oldenburg, C. M., and Nicot, J.-P., 2013, Measuring and modeling fault density for CO₂ storage plume-fault encounter probability estimation: *American Association of Petroleum Geologists Bulletin*, v. 97, no. 4, p. 597-618, doi:10.1306/10011211181.
- Keating, E. Fessendon, J., Kanjorski, N., Koning, D., and Pawar, R., 2010, The impact of CO₂ on shallow groundwater chemistry: observation: *Environmental Earth Science*, v. 60 p. 273-284.
- Kim, S. H., and Hosseini, S.A., 2013, Above-zone pressure monitoring and geomechanical analyses for a field-scale CO₂ injection project, Cranfield, MS: *Greenhouse Gases: Science and Technology*, doi: 10.1002/ghg.1388.
- Kinkela, J., Pevzner, R., and Urosevic, M., 2011, Ground roll repeatability analysis - CO₂CRC Otway Project case study, in 73rd European Association of Geoscientists and Engineers Conference and Exhibition Incorporating SPE EUROPEC 2011, May 23-25, 2011. Vienna, Austria: EAGE.
- Lindeberg, Eric, 2002, The quality of a CO₂ repository: what is the sufficient retention time of CO₂ stored underground?: *Proceedings of 6th International Conference on Greenhouse Gas Control Technologies*, p. 255-260.
- Lu, Jiemin, Partin, J. W., Hovorka, S. D., and Wong, Corinne, 2009, Potential risks to freshwater resources as a result of leakage from CO₂ geological storage: a batch-reaction experiment: *Environmental Earth Sciences*, v. 60, no. 2, p. 335–348. doi 10.1007/s12665-009-0382-0.
- Lucia, F. J., 2007, *Carbonate reservoir characterization: an integrated approach*: Springer, 341 p.

- Lumley, David, 2010, 4D seismic monitoring of CO₂ sequestration: *The Leading Edge*, v. 29, no. 2, p. 150–155. doi: 10.1190/1.3304817.
- McCormick, Mike, 2012, A greenhouse gas accounting framework for carbon capture and storage: Center for Climate and Energy Solution, <http://www.c2es.org/docUploads/CCS-framework.pdf>.
- McGee, K. A. and Gerlach, T. M., , 1998, Annual cycle of magmatic CO₂ in a tree-kill soil at Mammoth Mountain, California; implications for soil acidification: *Geology*, v. 26, no. 5, p. 463-466.
- McKinley, R.M., 1973, The structure and interpretation of noise from flow behind cemented casing: *Journal of Petroleum Technology*, v. 25, p. 329-338.
- Meckel, Timothy, Zeidouni, Mehdi, Hovorka, S. D., and Hosseini, S. A., 2013, Assessing sensitivity to well leakage from three years of continuous reservoir pressure monitoring during CO₂ injection at Cranfield, MS, USA: *International Journal of Greenhouse Gas Control*, v. 18, p. 439-448.
- Mickler, P., Yang, Changbing, Scanlon, B. R., Reedy, R. C., and Lu, Jiemin, 2013, Potential impacts of CO₂ leakage on groundwater chemistry from laboratory batch experiments and field push-pull tests: *Environmental Science & Technology*, v. 47, p. 10694-10702, doi: 10.1021/es401455j.
- Nicot, J. -P., Oldenburg, C. M., Houseworth, J., and Choi, Jong-Won, 2013, Analysis of potential leakage pathways at the Cranfield, MS, U.S.A., CO₂ sequestration site: *International Journal of Greenhouse Gas Control*, v. 18, p. 388-400.
- Nordbotten, J. M., Celia, M. A. and Bachu, S., 2004, Analytical solutions for leakage rates through abandoned wells: *Water Resources Research*, v. 40, no. 4. W04204, doi: 10.1029/2003wr002997.
- Official Journal of the European Union, 2009, EU Directive on the Geological Storage of Carbon Dioxide; <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0114:0135:EN:PDF>.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2)— a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey, Water-Resources Investigations Report 99-4259.
- Pawar, R. J., Warpinski, N.R., Lorenz, J. C., Benson, R.D., Grigg, R. B., Stubbs, B. A., Stauffer, P. H., Krumhansl, J. L. Cooper, S. P., and Svec, R.K., 2006, Overview of a sequestration field test in the West Pearl Queen reservoir, New Mexico: *Environmental Geoscience*, v. 13, pp. 163–180. http://www.es.ucsc.edu/~phlip/LDRD_ER/Pawar_EnvironmentalGeoscience.pdf.
- Pérez, M., Grechka, V., and Michelena, R., 1999, Fracture detection in a carbonate reservoir using a variety of seismic methods, *Geophysics*, v. 64, no. 4, p. 1266–1276, doi: 10.1190/1.1444633.
- Pevzner, Roman, Shulakova, V., Kepic, A. and Urosevic, Milan, 2011, Repeatability analysis of land time-lapse seismic data: CO₂CRC Otway pilot project case study: *Geophysical Prospecting*, v. 59, p. 66-77.
- Porse, S. L., 2013, Using Analytical and Numerical Modeling to Assess Deep Groundwater Monitoring, Parameters at Carbon Capture, Utilization, and Storage Sites: The University of Texas at Austin, Master's thesis, 144 p
- Quintessa, 2013, CO₂ FEP database, <http://www.quintessa.org/CO2fepdb/>.
- Railroad Commission of Texas, updated 2012, Injection/disposal well permit testing and monitoring manual, technical discussion of injection pressure issues, <http://www.rrc.state.tx.us/forms/publications/HTML/tech-psi.php>.
- Renard, P., D. Glenz, and M. Mejias (2009), Understanding diagnostic plots for well-test interpretation,

- Hydrogeol J, 17(3), 589-600.
- Reuss, A., 1929, Berechnung der Fließgrenzen von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle, *Zeitschrift für Angewandte Mathematik und Mechanik*, v. 9, p. 49-58.
- Romanak, K. D., Bennett, P. C., Yang, C., and Hovorka, S. D., 2012a, Process-based approach to CO₂ leakage detection by vadose zone gas monitoring at geologic CO₂ storage sites, *Geophysical Research Letters*, v. 39, L15405, doi:10.1029/2012GL052426.
- Romanak, K. D., Smyth, R. C., Yang, C., Hovorka, S. D., Rearick, M., and Lu, J., 2012b, Sensitivity of groundwater systems to CO₂: application of a site-specific analysis of carbonate monitoring parameters at the SACROC CO₂-enhanced oil field: *International Journal of Greenhouse Gas Control*, v. 5, no. 1, p. 142–152.
- Rutqvist, J., Birkholzer, J.T., and Tsang, C.-F., 2008, Coupled reservoir–geomechanical analysis of the potential for tensile and shear failure associated with CO₂ injection in multilayered reservoir–caprock systems: *International Journal of Rock Mechanics and Mining Sciences*, v. 45, p. 132-143.
- Slatt, R. M., 2006, Stratigraphic reservoir characterization for petroleum geologists, geophysicists, and engineers, 1st ed., *Handbook of Petroleum Exploration and Production*, ISBN 0444528180, v. 6, 478 p.
- Smyth, R., Hovorka, S., Lu, J., Romanak, K., Partin, J., Wong, C., and Yang, C., 2010, Assessing risk to fresh water resources from long term CO₂ injection—laboratory and field studies: *Energy Procedia*, v. 1, no. 1, p. 1957-1964.
- Sun, A. Y., and Nicot, J. -P., 2012, Inversion of pressure anomaly data for detecting leakage at geologic carbon sequestration sites: *Advances in Water Resources*, v. 44, p. 20–29.
- Sun, A. Y., Zeidouni, Mehdi, Nicot, J. -P., Lu, Jiemin, and Zhang, D., 2013a, Assessing leakage detectability at geologic CO₂ sequestration sites using the probabilistic collocation method: *Advances in Water Resources*, v. 56, p. 49–60.
- Sun, A.Y., Nicot, J. -P., 2012, and Zhang, X., 2013b, Optimal design of pressure-Based, leakage detection monitoring networks for geologic carbon sequestration repositories: *International Journal of Greenhouse Gas Control*, 19, p. 251–261.
- Tao, Q., Bryant, S.L., and Meckel, T.A., 2013, Above-zone measurements of pressure and temperature for monitoring CCS Sites: *International Journal of Greenhouse Gas Control*, v. 18, p. 523-530, <http://dx.doi.org/10.1016/j.ijggc.2012.08.011>.
- Teletzke, G.F., Wattenbarger, R.C., and Wilkinson, J.R., 2010, Enhanced oil recovery pilot testing best practices: *SPE Reservoir Evaluation & Engineering*, v. 13, p. 143-154.
- Texas House Bill 469, 2009, <http://www.legis.state.tx.us/billlookup/text.aspx?LegSess=81R&Bill=HB469>.
- Texas Administrative Code, Title 16, part 1, chapter 5, subpart B, 2010, Geologic storage and associated injection of anthropogenic carbon dioxide (CO₂), RULE §5.201.
- Trautz, R.C., Pugh, J.D., Varadharajan, Charuleka, Zheng, Liange, Bianchi, Marco, Nico, P. S., Spycher, N.F., Newell, D. L., Esposito, R.A., Wu, Yuxin, Dafflon, Baptist, Hubbard, S. S., and Birkholzer, J.T., 2012, Effect of dissolved CO₂ on a shallow groundwater system: a controlled release field experiment: *Environmental Science and Technology*, v. 47, p. 289-305.
- United Nations Framework Convention on Climate Change, 2011, Draft decision-/CMP.7: Modalities and procedures for carbon dioxide capture and storage in geological formations as clean

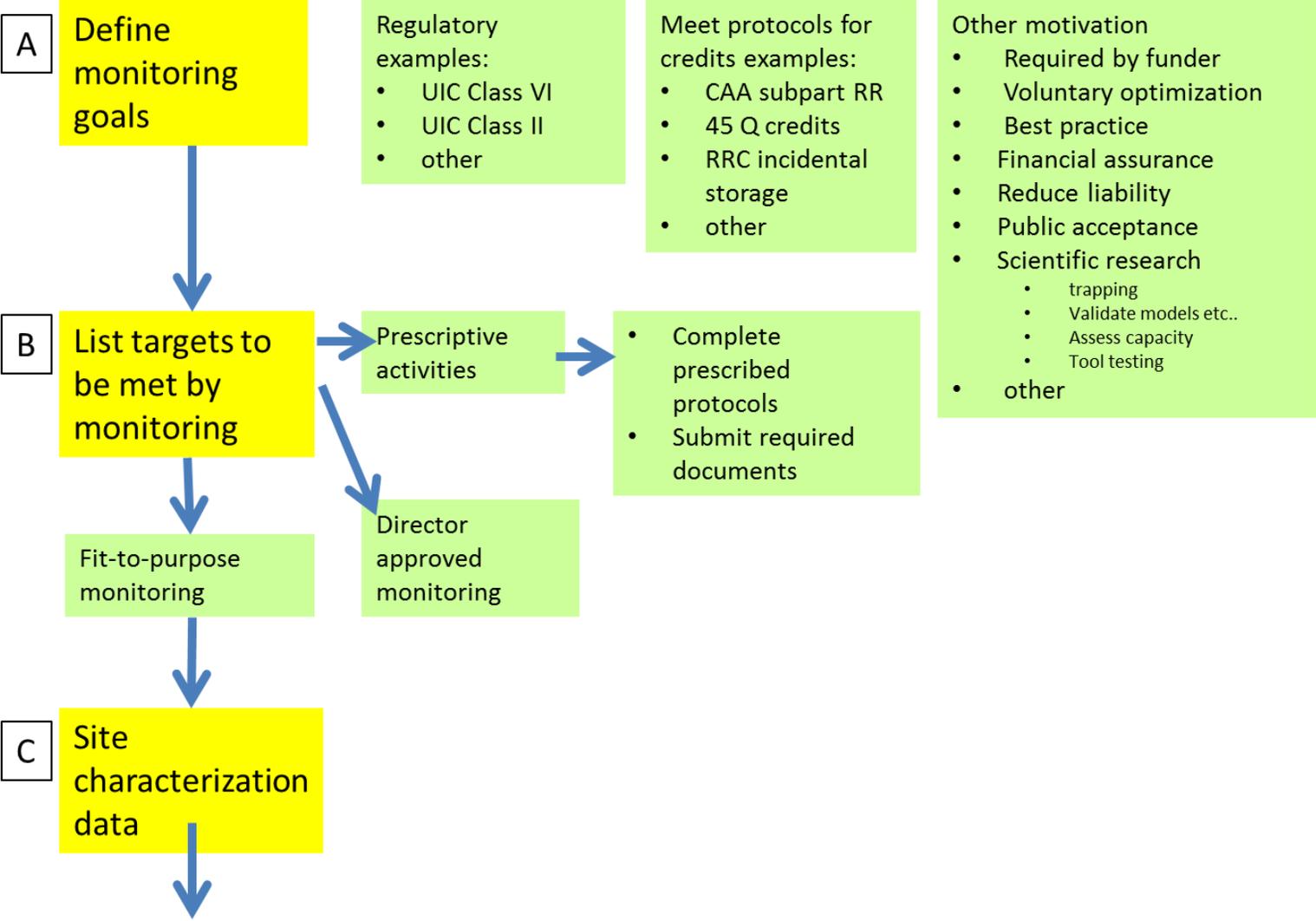
- development mechanism project activities;
http://unfccc.int/files/meetings/durban_nov_2011/decisions/application/pdf/cmp7_carbon_storage_.pdf
- Urosevic, M., Pevzner, R., Shulakova, V., Kepic, A. Caspari, E., and Sharma, S., 2011, Seismic monitoring of CO₂ injection into a depleted gas reservoir – Otway Basin Pilot Project, Australia: *Energy Procedia*, v. 4, p. 3550-3557.
- U.S. CFR, 1983, Code of Federal Regulations, 40 CFR 146.23. Part 146—Underground Injection Control Program: Criteria and standards. Subpart C—Criteria and Standards Applicable to Class II Wells. 146.23 Operating, monitoring, and reporting requirements, p. 31404.
- U.S. CFR, 2010a, Code of Federal Regulations, 40 CFR Parts 72, 78, and 98. Mandatory Reporting of Greenhouse Gases: Injection and Geologic Sequestration of Carbon Dioxide., p. 75060-75089.
- U.S. CFR, 2010b, Code of Federal Regulations, 40 CFR Parts 124, 144, 145, 146, and 147. Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (CO₂) Geologic Sequestration (GS) Wells. Final Rule. EPA Docket: EPA–HQ–OW–2008–0390 FRL–9232–7, p. 77230-77303.
- U.S. Department of Energy, National Energy Technology Laboratory, 2009, Monitoring verification, and accounting of CO₂ stored in deep geologic formations: DOE/NETL-311/081508.
- U.S. Department of Energy, National Energy Technology Laboratory, 2010, Best practices for site screening, selection, and initial characterization for storage of CO₂ in deep geologic formations, 110 p, http://www.netl.doe.gov/technologies/carbon_seq/refshelf/BPM-SiteScreening.pdf.
- U.S. Department of Energy, National Energy Technology Laboratory, 2011, Risk analysis and simulation for geologic storage of CO₂, DOE/NETL-2011/1459.
- U.S. Environmental Protection Agency, 2001, Requirements of quality assurance project plans, EPA/240/13-10/003, March 2003, <http://epa.gov/quality/qs-docs/r5-final.pdf>
- U.S. Environmental Protection Agency, 2012, Protecting drinking water through underground injection control, Office of Water (4606M), EPA 816-K-10-004, http://water.epa.gov/type/groundwater/uic/upload/pocketguide_uic_protecting_dw_thru_uic.pdf
- U.S. Environmental Protection Agency, **2013**, Geologic Sequestration of Carbon Dioxide: Underground Injection Control (UIC) Program Class VI Well Testing and Monitoring Guidance (PDF), 142 p. EPA 816-R-13-001, March 2013
<http://water.epa.gov/type/groundwater/uic/class6/gsguidedoc.cfm#complete>
- Van Riel, Paul, 2000, The past, present and future of quantitative reservoir characterization: The Leading Edge, v. 19, p. 878-881.
- White, Don, 2013, Seismic characterization and time-lapse imaging during seven years of CO₂ flood in the Weyburn field, Saskatchewan, Canada: *International Journal of Greenhouse Gas Control*, v. 16S, p. S95-S102.
- Wilkin, R.T., and DiGiulio, D.C., 2010, Geochemical impacts to groundwater from geologic carbon sequestration: Controls on pH and inorganic carbon concentrations from reaction path and kinetic modelling: *Environmental Science & Technology*, v. 44, no. 12, p. 4821-4827.
- Williams, G., and Chadwick, A., 2012, Quantitative seismic analysis of a thin layer of CO₂ in the Sleipner injection plume: *Geophysics*, v. 77, no. 6, R245–R256, doi: 10.1190/geo2011-0449.1.

- World Resources Institute, 2008, Guidelines for Carbon Dioxide Capture, Transport, and Storage; <http://www.wri.org/publication/ccs-guidelines>.
- Yang, Changbing Hovorka, Susan, and Trevino, Ramon, 2013a, Geochemical sensitivity to CO₂ leakage: detection in potable aquifers at carbon sequestration sites (submitted): *Greenhouse Gas: Science and Technology*.
- Yang, Changbing Mickler, P.J., Reedy, Robert, Scanlon, B.R., Romanak, K.D., Nicot, J.-P., Hovorka, S.D., Trevino, R.H., and Larson, Toti, 2013b, Single-well push-pull test for assessing potential impacts of CO₂ leakage on groundwater quality in a shallow Gulf Coast aquifer in Cranfield, Mississippi: *International Journal of Greenhouse Gas Control*, v. 18 p. 375-387, <http://dx.doi.org/10.1016/j.ijggc.2012.12.030>.
- Yang, Changbing, Romanak, Katherine, Hovorka, S. D., and Treviño, R. H., 2013c, Modeling CO₂ release experiment in the shallow subsurface and sensitivity analysis: *Environmental & Engineering Geoscience*, v. 19, no. 3, p. 207–220.
- Zeidouni, Mehdi 2012, Analytical model of leakage through fault to overlying formations: *Water Resources Research*, 48, W00N02, doi:10.1029/2012WR012582.
- Zeidouni, Mehdi and Pooladi-Darvish, M., 2012a, Leakage characterization through above-zone pressure monitoring: 1—inversion approach: *Journal of Petroleum Science and Engineering*, v. 98-99, p. 95–106.
- Zeidouni, Mehdi , and Pooladi-Darvish, M., 2012b, Leakage characterization through above-zone pressure monitoring: 2—design considerations with application to CO₂ storage in saline aquifers: *Journal of Petroleum Science and Engineering*, v. 98-99, p. 69–82.
- Zeidouni, Mehdi, Nicot, J-P., and Hovorka, S. D., (in accepted ms2014, press 2014) Monitoring above-zone temperature variations associated with CO₂ and brine leakage from the storage aquifer, Accepted in *Environmental Earth Sciences*.
- Zhang, Rui, Ghosh, Ranjana, Sen, Mrnal, and Srinivatsan, Sanjeay, 2013, Time-lapse surface seismic inversion with thin bed resolution for monitoring CO₂ sequestration: A case study from Cranfield, Mississippi, *International Journal of Greenhouse Gas Control*, v. 18., p. 430-438, <http://dx.doi.org/10.1016/j.ijggc.2012.08.015>
- Zheng, L., Apps, J.A., Zhang, Y., Xu, T., and Birkholzer, J.T., 2009, On mobilization of lead and arsenic in groundwater in response to CO₂ leakage from deep geological storage: *Chemical Geology*, v. 268, p. 281-297.
- Zoeppritz, K., 1919, *Erdbebenwellen VIII B*, On the reflection and propagation of seismic waves: *Gottinger Nachrichten*, v. I, p. 66-84.

Appendix 1

The following four panels should be understood a single flow chart describing the design of a fit-to-purpose monitoring system.

Designing Fit-to-Purpose Monitoring (1)



Designing Fit-to-Purpose Monitoring (2)

D Assessment of Low Probability Material Impacts (ALPMI)

Recommended process: Model characterization uncertainties that lead to material impact. This can be a conceptual model, analytical model, or full geocellular model. Goal: concrete realization of what impact would look like, trace to early signals that would diagnose condition

Identify characterization uncertainties that might lead to material impact and (preferably) identify events preceding material impact

Identify operational actions lead to material impact and (preferably) identify events preceding impact

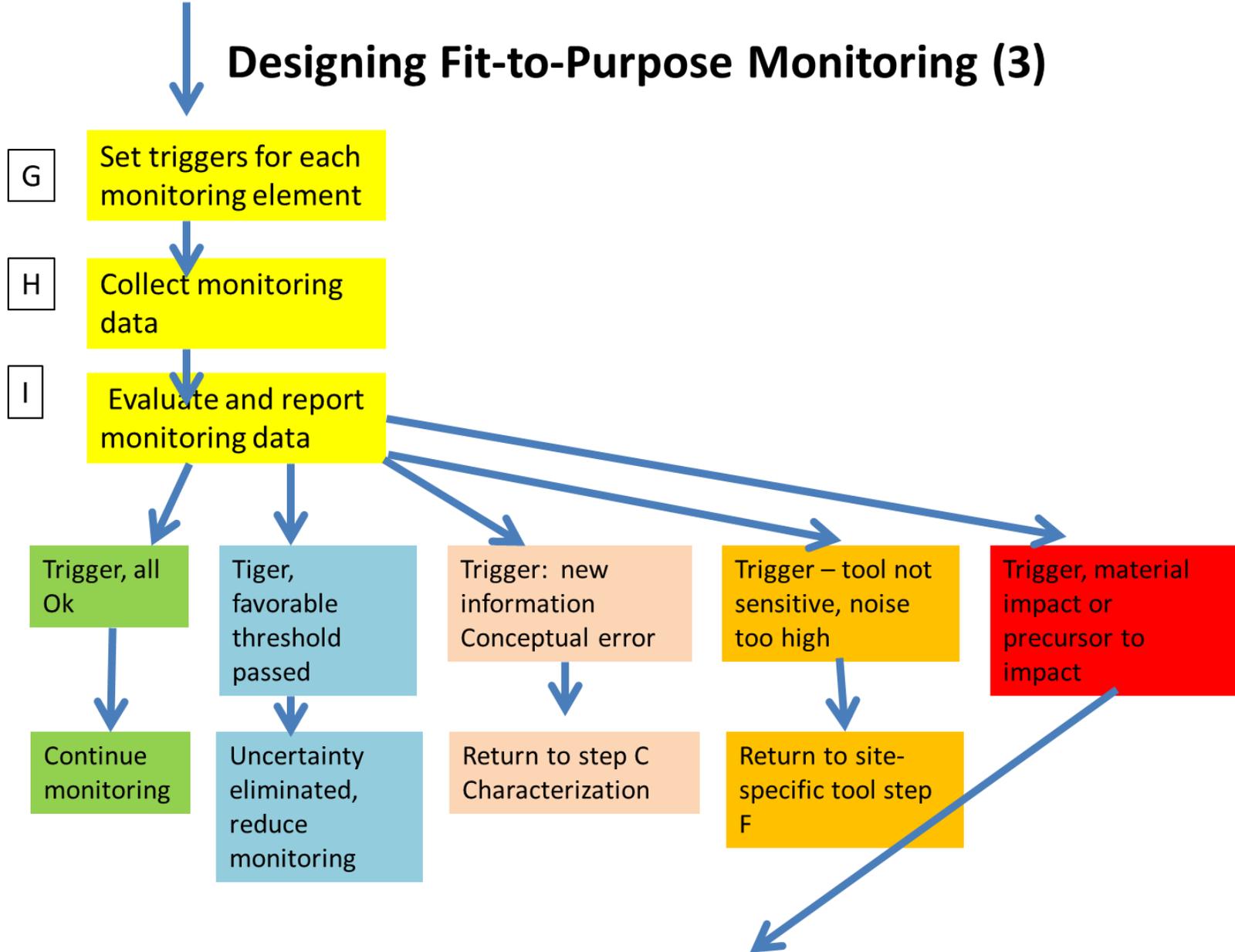
E Monitoring approach to detect ALPMI

Determine what monitoring approaches are sensitive to the possible material impact to obtain retention, or preferably to events preceding impact.

F Site specific tool sensitivity

Test each mentoring tool sensitivity to detect material impact above measurement noise. Design data density and sampling frequency to provide statistically valid measurements of events.

Designing Fit-to-Purpose Monitoring (3)



Designing Fit-to-Purpose Monitoring (4)

