GENERAL TECHNICAL SUPPORT DOCUMENT FOR INJECTION AND GEOLOGIC SEQUESTRATION OF CARBON DIOXIDE: SUBPARTS RR AND UU

GREENHOUSE GAS REPORTING PROGRAM

Office of Air and Radiation
U.S. Environmental Protection Agency
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Disclaimer

The Environmental Protection Agency (EPA) regulations cited in this technical support document (TSD) contain legally-binding requirements. In several chapters this TSD offers illustrative examples for complying with the minimum requirements indicated by the regulations. This is done to provide information that may be helpful for reporters' implementation efforts. Such recommendations are prefaced by the words "may" or "should" and are to be considered advisory. They are not required elements of the regulations cited in this TSD. Therefore, this document does not substitute for the regulations cited in this TSD, nor is it a regulation itself, so it does not impose legally-binding requirements on EPA or the regulated community. It may not apply to a particular situation based upon the circumstances. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Note that this document only addresses issues covered by 49 CFR part 98, subpart RR and subpart UU, which are being promulgated under EPA's authorities under the Clean Air Act (CAA). Other statutory and regulatory requirements, such as compliance with Safe Drinking Water Act (SDWA) and Underground Injection Control (UIC) Program requirements[1], are not within the scope of this TSD. Please see section I.D. of the preamble to the final rule for more information on the relationship between subpart UU, subpart RR and the UIC Program.

[1] Please refer to EPA's UIC Web site for more information: http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm.

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Acronyms and Abbreviations

2-D	Two-Dimensional
3-D	Three-Dimensional
4-D	Four-Dimensional
ACZ	Above Confining Zone
AMA	Active Monitoring Area
AMR	Annual Monitoring Report
ASTM	American Society for Testing and Materials
bbl	Barrel
CCS	Carbon Dioxide Capture and Geologic Sequestration
CFR	Code of Federal Regulations
CH_4	Methane
CO_2	Carbon Dioxide
CO_{2FI}	Total annual CO_2 mass emitted (metric tons) as equipment leaks or vented emissions from equipment located on the surface between the flow meter used to measure injection quantity and the injection wellhead.
CO_{2FP}	Total annual CO_2 mass emitted (metric tons) as equipment leaks or vented emissions from equipment located on the surface between the production wellhead and the flow meter used to measure production quantity.
CO_3^{--}	Carbonate
CZ	Confining Zone
DIAL	Differential Absorption Light Detection and Ranging
DIC	Dissolved Inorganic Carbon
DOE	Department of Energy
e-GGRT	Electronic Greenhouse Gas Reporting Tool
EOS	Equation of State
EM	Electromagnetic
EOR	Enhanced Oil Recovery
EPA	Environmental Protection Agency
ER	Enhanced Oil and Gas Recovery
FTIR	Fourier Transform Infrared
GHG	Greenhouse Gas
GPA	Gas Processors Association
GPS	Global Positioning System
GS	Geologic Sequestration
H_2CO_3	Carbonic Acid
H_2S	Hydrogen Sulfide
HCO_3^-	Bicarbonate
HCPV	Hydrocarbon Pore Volume
He	Helium
InSAR	Interferometric Synthetic Aperture Radar
IOGCC	Interstate Oil and Gas Compact Commission
IRGA	Infrared Gas Analyzer
IZ	Injection Zone

km	Kilometer
LIDAR	Light Detection and Ranging
mcf	Thousand Cubic Feet
MIT	Mechanical Integrity Testing
MMA	Maximum Monitoring Area
MRV	Monitoring, Reporting, and Verification
NIST	National Institute of Standards and Technology
O&GJ	Oil and Gas Journal
PFC	Perfluorocarbons
ppm	Parts Per Million
ppmv	Parts Per Million by Volume
psi	Pounds Per Square Inch
SDWA	Safe Drinking Water Act
STP	Standard Temperature and Pressure
TDL	Tunable Diode Laser
TSD	Technical Support Document
UIC	Underground Injection Control
U.S.	United States
USDW	Underground Source of Drinking Water
ZERT	Zero Emissions Research and Technology

1. Source Description

Preliminary estimates indicate that the amount of carbon dioxide (CO_2) captured from industrial processes, including combustion and chemical manufacturing, and produced from naturally occurring subsurface CO_2 reservoirs is approximately 44 million metric tons carbon dioxide equivalent .[2,3] Currently more than 95 percent of this CO_2 supplied to the economy is injected underground for enhanced oil and gas recovery (ER).[2] CO_2 may be injected underground for geologic sequestration (GS). GS is the long-term containment of a CO_2 stream in subsurface geologic formations and is a key component of a set of climate change mitigation technologies known as carbon dioxide capture and geologic sequestration (CCS). CCS has the potential to enable large emitters of CO_2 such as coal fired power plants to significantly reduce greenhouse gas (GHG) emissions.

1.1 *Overview of Source Categories*

Three sectors were considered for inclusion in this rule: injection of CO_2 underground for GS, injection of CO_2 underground for ER, and end uses of CO_2 by other industries.

1.1.1 Geologic Sequestration

Underground geologic formations that can be used for GS include deep saline formations, oil and natural gas reservoirs, and unmineable coal seams. In addition, CO_2 may be injected into other types of subsurface geologic formations, such as basalt formations. The UIC program, which is authorized by Part C of the SDWA, regulates underground CO_2 injection.

Geologic sequestration occurs through a combination of structural and stratigraphic trapping, residual CO_2 trapping, solubility trapping, mineral trapping, and preferential adsorption trapping. These mechanisms are functions of the physical and chemical properties of CO_2 and the geologic formations into which the CO_2 is injected. For more background information on GS trapping mechanisms, see the Vulnerability Evaluation Framework for Geologic Sequestration of Carbon Dioxide.[4]

1.1.2 Enhanced Oil and Gas Recovery

CO_2 is currently being injected into subsurface geologic formations in the United States (U.S.) for ER. The CO_2 currently being used in ER is primarily produced from naturally occurring underground CO_2 reservoirs but is also captured from industrial processes, including combustion and chemical manufacturing.

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[2] U.S. EPA. 2010. Inventory of U.S. Greenhouse Gas Emissions and Sinks, 1990-2008, EPA 430-R-10-006. Available at: http://epa.gov/climatechange/emissions/usinventoryreport.html.
[3] The estimated 44.2 million metric tons of CO_2 does not include biogenic CO_2.
[4] Vulnerability Evaluation Framework for Geologic Sequestration of Carbon Dioxide (see docket ID No. EPA-HQ-OAR-2009-0926)

ER involves injecting CO_2 into oil or natural gas reservoirs via injection wells for the purposes of increasing crude oil production or to enhance recovery of natural gas. The crude oil and CO_2 mixture is produced from production wells and sent to a two-phase separator where the crude oil is separated from the gaseous hydrocarbons and CO_2. The gaseous CO_2-rich stream then is typically dehydrated, recompressed, and reinjected into the oil or natural gas reservoir to further enhance recovery. If the concentration of hydrocarbons in the CO_2 stream from the dehydrator is significant, then an acid gas recovery unit is used to separate the hydrocarbons from the CO_2.

Injection of CO_2 into unmineable coal seams may result in displacement of methane (CH_4) from the coal seam and subsequent production of the methane as a product (or enhanced coal bed methane).

There are currently 80 ER fields operating in the United States where CO_2 is being injected for the purposes of ER.[5] ER projects operating in the United States range from new pilot-scale projects with one or two injection wells to CO_2 floods that commenced operation in the 1970s and that have hundreds of injection wells. Approximately 44 million metric tons of CO_2 was received for injection underground for ER in 2008. Of this amount approximately 80 percent was produced from naturally occurring underground CO_2 reservoirs and 20 percent was captured from industrial processes, including combustion and chemical manufacturing.[6]

Natural gas processing plants and wellhead treatment units condition incoming natural gas from the wellhead to meet sales and natural gas pipeline specifications. In some fields the natural gas may contain a significant quantity of hydrogen sulfide (H_2S) or CO_2, which is separated from the natural gas by the processing plants and treatment units. Because of the highly corrosive nature of this stream, the combination of H_2S and CO_2 separated from the natural gas is called acid gas. The composition is quite variable and can range from 2 percent H_2S and 98 percent CO_2 to about 85 percent H_2S and 15 percent CO_2.[7] Most acid gas is disposed of by underground injection under a UIC Class II permit. These permits may allow for disposal of other oil and gas production wastes, including brine, well completion and work-over fluids, and spent dehydration unit fluids, in addition to the acid gas.

1.1.3 Other Industries That Use CO_2

[5] See Appendix B of this technical support document.
[6] U.S. EPA. 2010. Inventory of U.S. Greenhouse Gas Emissions and Sinks, 1990-2008, EPA 430-R-10-006. Available at: http://epa.gov/climatechange/emissions/usinventoryreport.html.
[7] S. Bachu and W.D. Gunter. 2004. Overview of Acid Gas Operations in Western Canada. In: *Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume 1: Peer-Reviewed Papers and Plenary Presentations*.

EPA identified and considered a total of 22 commercial end use sectors[8] that use gaseous, liquid, or solid CO_2, excluding ER and GS. These end use sectors are summarized in Appendix C. EPA received comments to subpart PP suggesting that at least one of these end-uses – precipitated calcium carbonate production – may be a non-emissive use. At proposal for this rule, EPA sought comment on whether applications, such as precipitated calcium carbonate and some cement production, permanently sequester CO_2 and if so, which industries this would include; how many facilities operate in each of these industries; how much of the CO_2 consumed in each industry would be sequestered; whether a sequestration factor would be reasonable in any case; and what methodologies could be used to verify this sequestration. These sectors were not included in this final rule. Please refer to the Response to Comments document for further information.[9]

1.2 Delineation of Facility

For CO_2 received by pipeline, the point of measurement for reporting the amount of CO_2 received at a facility will often be identified by a change in ownership (or custody) of the CO_2. The transfer of custody of the CO_2 is the basis of sales contracts and revenue reporting, and is generally measured with meters that conform to state oil and gas board regulations and industry standards. The question arises of how to delineate a facility when collecting data on CO_2 received. Subparts RR and UU rely on the definition of "facility" in 40 Code of Federal Regulations (CFR) 98.6, which states that "a facility means any physical property, plant, building, structure, source, or stationary equipment located on one or more contiguous or adjacent properties in actual physical contact or separated solely by a public roadway or other public right-of-way and under common ownership or common control..." To illustrate how EPA applies this definition of facility to injection wells under subparts RR and UU, six example scenarios are presented in Figure 1-1 through Figure 1-6.

[8] This count includes the various chemical, pharmaceutical, and other processes that use CO_2 as an end product and excludes intermediate CO_2 processors. After CO_2 is captured from production process units or produced from natural reservoirs for subsequent commercial application, it is generally purified, compressed, and liquefied before being delivered for a multitude of end use commercial applications. This processing is done so that end users can input the CO_2 into their processes in the necessary state; e.g., food grade CO_2 used for food and beverage production. Intermediate processors often receive the produced CO_2 from the production process units or natural reservoirs, purify, compress, and/or liquefy it, and then deliver it to end users. Intermediate processors are not discussed further in this TSD.

[9] See docket ID No. EPA–HQ–OAR–2009–0926.

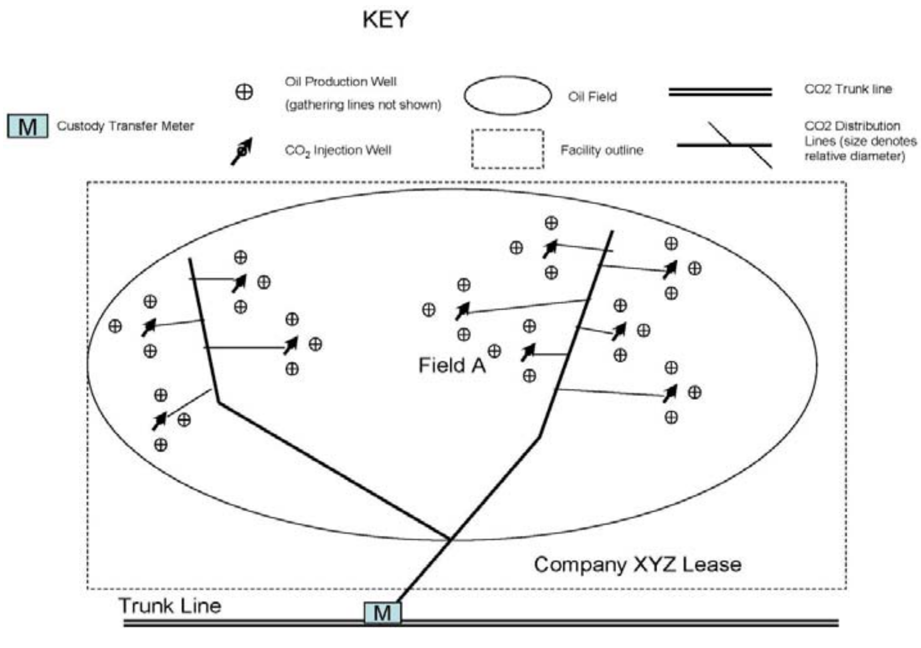

Figure 1-1: Facility Example 1

In the first example (Figure 1-1) an operator is conducting CO_2-ER operations in a field that is fully contained within one leased area. A large-diameter CO_2 supply pipeline (trunk line) owned by a third party supplies all the CO_2 used in the field. The CO_2 is delivered to the field from the trunk line via a distribution line owned by the field operator. The custody of the CO_2 is transferred to the field operator at the meter where the distribution line begins. Once the field operator takes possession of the CO_2, it is transported over some distance and further distributed and injected into the wells in the field. Although not shown on the figure, there would likely be gathering lines from the producing oil wells that lead to facilities that capture and re-process the CO_2 for re-injection downstream of the custody transfer meter. In this scenario the field is one facility because it is under common control, and the meter reading at the custody transfer point is the amount of CO_2 received.

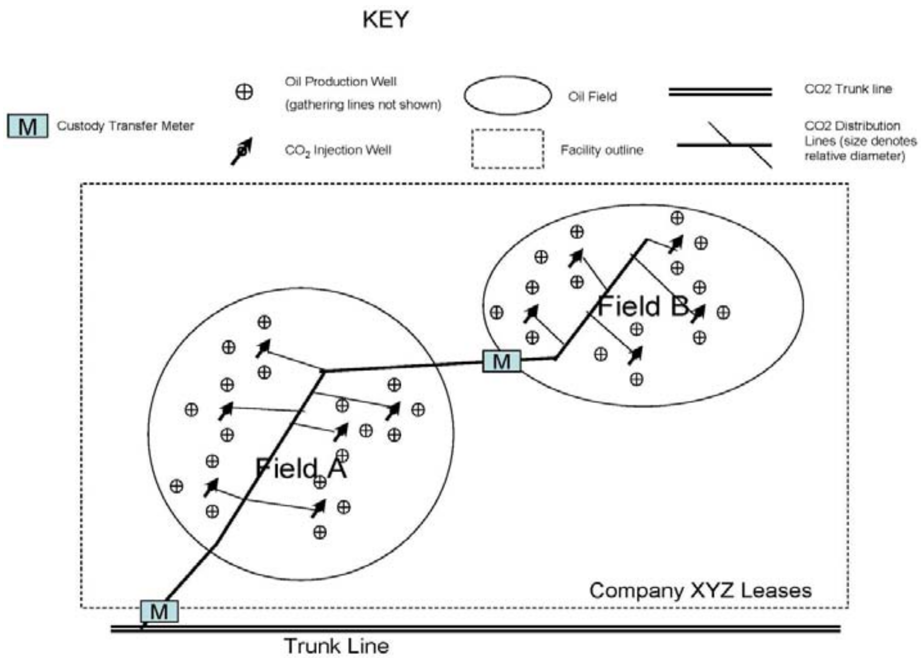

Figure 1-2: Facility Example 2

In the second example, Figure 1-2, two fields under common control are fed by a continuous CO_2 distribution line that passes through Field A and terminates in Field B. The operator has placed a meter at the upstream end of Field B to assist with state oil and gas board reporting requirements and reservoir management. In this case, whether this scenario is one or two facilities depends on site specific conditions. Reporters should review the definition of facility carefully and decide whether to report as one or two facilities in their specific situation.

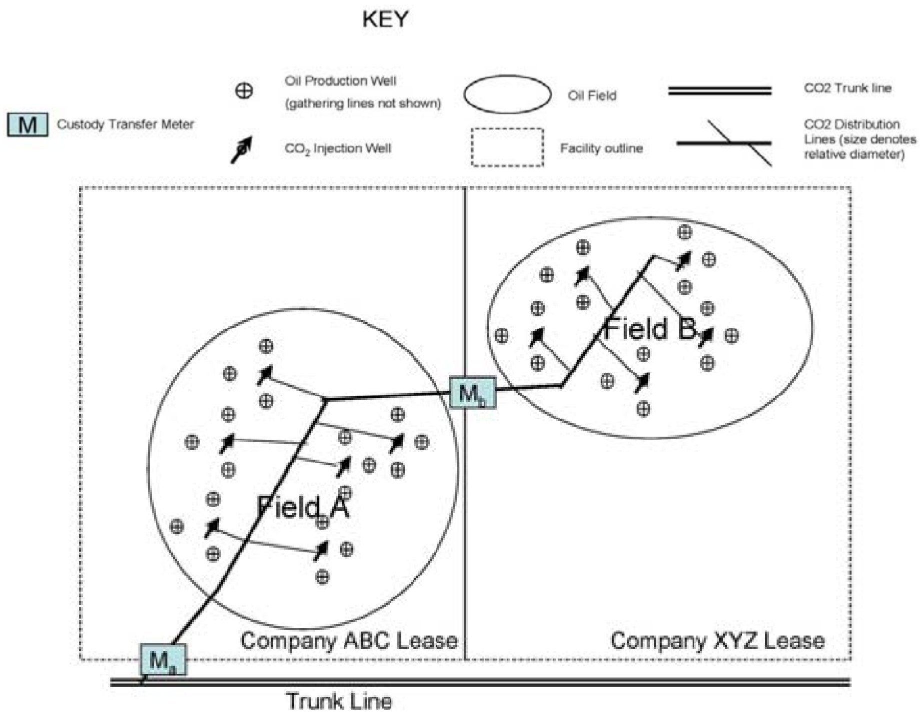

Figure 1-3: Facility Example 3

An example similar to Figure 1-1 is shown in Figure 1-3. In this instance, Fields A and B are on different leases and operated by different entities, but fed by a single CO_2 distribution line from the main trunk line. Ownership of the CO_2 is transferred at the meter between Fields A and B. In this example because Field A and Field B are under different ownership and control, they represent two different facilities. The amount of CO_2 passing through meter A (at the trunk line) represents the total amount of CO_2 supplied to both fields; therefore the owner of Field A should report the total amount at meter A less the amount at meter B (the amount of CO_2 provided to Field B).

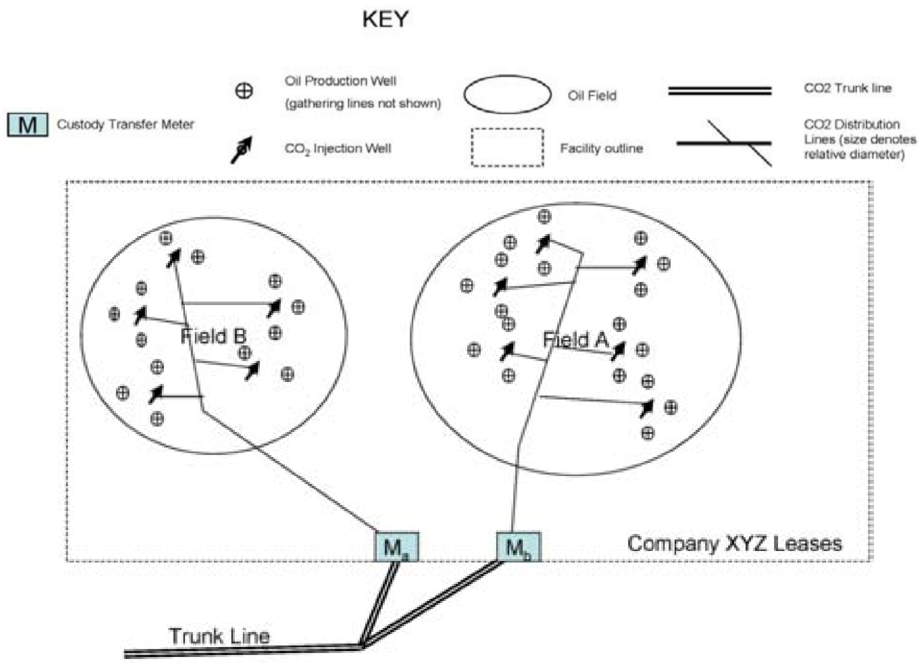

Figure 1-4: Facility Example 4

Figure 1-4 shows a trunk line that splits and supplies two different fields operated by the same entity, and thus are under common control. Custody of the CO_2 is transferred at the meters that connect the distribution line to the trunk line. This example is similar to the second example, in that the determination of whether this situation represents one or two facilities depends on site-specific conditions. Reporters should review the definition of facility carefully and decide whether to report as one or two facilities in their specific situation.

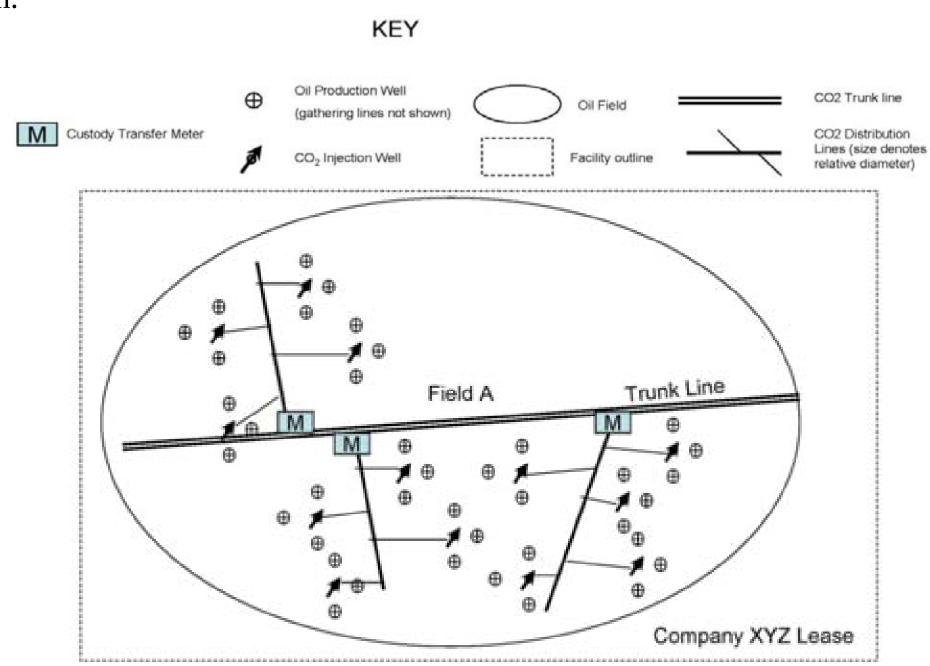

Figure 1-5: Facility Example 5

In large ER operations in a single field operated by the same entity, the trunk line may pass directly through the field and connect to multiple distribution lines (Figure 1-5). Custody of the CO_2 is transferred to the operator at each meter. Even though there are many custody meters, the entire field is under common ownership and would be considered a single facility. To determine the total amount of CO_2 received at the facility, the reporter would sum the CO_2 amounts from all meters within the field.

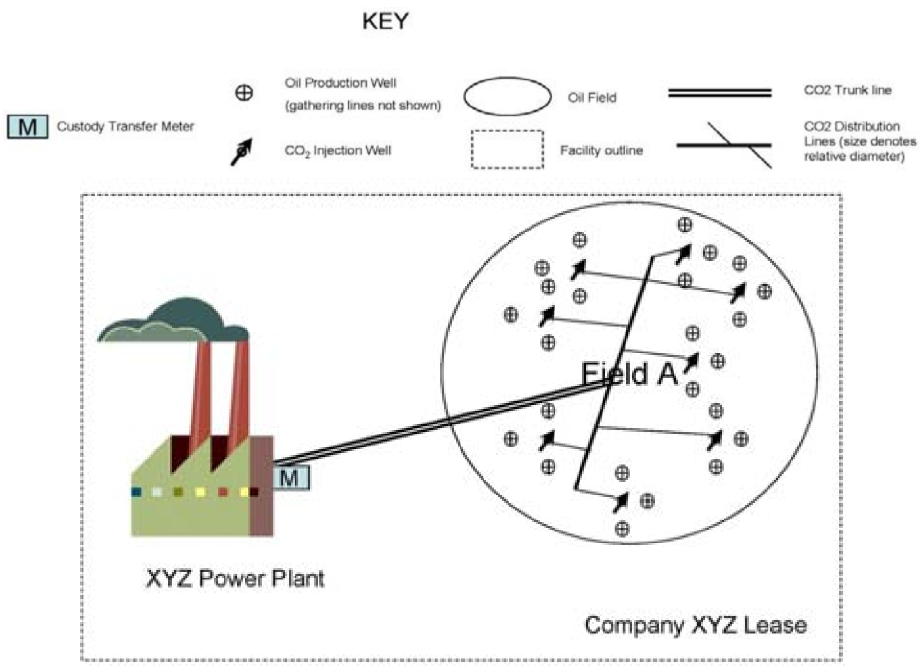

Figure 1-6: Facility Example 6

In the last example, Figure 1-6, a CO_2 generator supplies CO_2 to an ER project that it operates. The generation facility and ER operation are located on the same property and are connected by a dedicated transmission line. In this example the generating facility, the transmission line, and the ER operation are under common ownership and are located on the same property and therefore are considered a single facility under subpart RR. The CO_2 received is the amount passing through the meter at the point of generation in this example. A third-party pipeline company that owns and operates the transmission line, but does not take custody of the gas or operate the injection facility, is not a facility or operator under subpart RR.

2. Reporting Threshold Analysis

To determine the appropriate threshold for reporting, EPA considered a threshold based on the amount of CO_2 emitted, a threshold based on the amount of CO_2 injected, and a threshold based on the amount of CO_2 received by the facility. EPA concluded that an emissions-based threshold would be problematic because of the lack of data on the incidence and scale of surface emissions and leakage from facilities that conduct GS and all other facilities that inject CO_2 underground. EPA also concluded that the amount of CO_2 injected one year is not a good indicator of the amount of CO_2 injected the following year, and that injected CO_2 may be produced and recycled at some facilities. EPA accordingly analyzed injection facilities based on the quantity of CO_2 received by the facility.

EPA conducted the threshold analysis based on the quantity of CO_2 received at the facility (not including CO_2 being recycled onsite) and considered whether a threshold on CO_2 received should apply. EPA evaluated a no threshold option (i.e., all facilities that inject CO_2 would be required to report), 1,000 metric tons per year, 10,000 metric tons per year, 25,000 metric tons per year, and 100,000 metric tons per year of CO_2 received per facility. Only facilities expected to be operating in 2011, the first year of reporting under this proposal, were considered in the analysis. For this analysis it was assumed that all of the CO_2 received by the facility was injected for ER.

To establish a facility count, EPA relied on data reported in the Oil and Gas Journal (O&GJ) *Enhanced Oil Recovery Survey* published in April 2008.[10] These data come from the results of a voluntary survey of oil producers reporting miscible and immiscible CO_2 projects in the U.S. operating as of the end of 2007. The O&GJ survey asked for the production figures “as of the end of 2007.” For projects that were active throughout 2007 the value represents annual production (12 months). Several of the projects started mid-year, or had scheduled downtime in 2007, so the reported annual 2007 production may represent only a partial year of production. Production data were not pro-rated to come up with an annual estimate. Some projects starting late in the year did not see any increase in crude oil production due to ER operations, or were unable to measure it. These were noted as "TETT" (Too Early To Tell) in the O&GJ survey. In a few cases, companies did not report crude oil production data to the O&GJ. The O&GJ did not specify how the production data were to be calculated by the reporting facilities, so most of the data are based on internal oil company reporting, which is consistent with state oil and gas commission reporting requirements.

The O&GJ left it up to the companies to define a “project” when they reported data. Most projects are defined based on production reporting requirements to state oil and gas commissions, based on the unit or pool. Some state oil and gas commissions finely divide the production zones in order to manage resource conservation. In one operation in Michigan, for example, the fields are very small (2–5 wells each) because they target pinnacle reefs that are limited in their extent. The company reported two “projects” separately to the O&GJ even though they are located in the same field, because it appears

[10] Enhanced Oil Recovery Survey. 2008. *Oil and Gas Journal*, Volume 105, Issue 15.

that they target different producing zones within the same formation. A somewhat different situation exists for the Seminole field in West Texas, where several projects are listed. These projects are in different geographic locations within the large Seminole field, and target different parts of the reservoir (i.e., main oil pay or residual oil) using different CO_2 injection technologies. These are identified as “pilot tests” in the O&GJ data, so the company considers them separate projects for evaluation purposes. Depending on how “project” or “facility” is defined, they could be separate or combined.

The use of CO_2 in ER has increased significantly since 2004 (Figure 2-1), and is expected to increase further in the next five to 10 years. The O&GJ survey is the latest and most complete data set of active ER projects in the U.S. EPA believes that the 2007 data presented in the O&GJ survey are representative of the type and scope of ER projects that will be operating in 2011.

For this analysis, EPA compiled all the projects listed for miscible and immiscible CO_2 floods[11] reported in the O&GJ survey. The list of active projects represents a wide cross-section of several geologic basins in 10 states, ranging from relatively recent pilot-scale projects with one or two injection wells to CO_2 floods started in the 1970s with hundreds of injection wells. The Wasson Field in the Permian Basin is the largest user of CO_2, and has six active CO_2 ER projects managed by two operators.

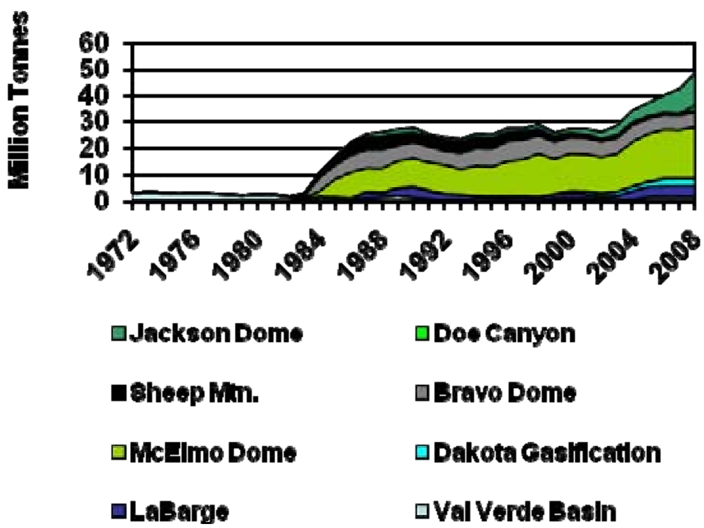

Figure 2-1: Total CO_2 used in ER showing growth since 2004. Graph based on data from specified anthropogenic and natural CO_2 sources.

Data based on sales. Source: Kinder Morgan CO_2 Company, CCS briefing to EPA June 3, 2009[12]

[11] A miscible CO_2 flood injects CO_2 as a liquid at high pressure to completely mix with oil and make it flow more easily. An immiscible CO_2 flood uses lower pressures of CO_2 to swell the oil and provide additional gas pressure to move the oil.

[12] Note that the CO_2 being produced by Dakota Gasification Plant in North Dakota is being injected into an ER project in Canada.

A total of 105 active ER projects operated by 23 different companies were reported in the O&GJ survey. In some cases multiple projects were reported by the same company in an oil field, reservoir, or operator unit. For the purposes of this analysis, EPA grouped these reported projects by field and by owner or operator to align with the definition of facility at 40 CFR 98.6. This computation results in 80 facilities that conduct ER. EPA further grouped the fields by their source of CO_2 as determined from geographic location, U.S. DOE pipeline maps, and operator-published information. As of 2008, four natural sources (Jackson Dome, MS; Bravo Dome, NM; Sheep Mountain, CO; and McElmo Dome, CO) and five anthropogenic CO_2 sources (Antrim Gas Plant, MI; LaBarge/Shute Creek Gas Plant, WY; Enid Fertilizer Plant, OK; U.S. Energy Partners Russell, KS Plant; and Val Verde Gas Plants, TX) supply CO_2 for ER that is conducted in the United States.[13]

The O&GJ survey does not provide the specific volume of CO_2 used in each of the active ER projects, but does provide the total oil production attributed to the ER process. To calculate the estimated volume of CO_2 received by each ER project, EPA determined the total amount of CO_2 used daily for ER based on data from the U.S. EPA 1990–2007 Inventory of U.S. Greenhouse Gas Emissions and Sinks[14] (Inventory). According to the Inventory, approximately 2.08 billion cubic feet per day of CO_2 from natural and anthropogenic sources is received (purchased) for ER. The threshold analysis was performed two ways, one based on total daily CO_2 received combined for all fields in the U.S., and one based on the total from each source of CO_2 received for ER (natural or anthropogenic). The daily average CO_2 production from each source was apportioned among the projects supplied by the source based on an average value for the fractional production of oil attributed to ER as presented in the O&GJ survey and normalized on an annual basis (see Appendix B). The analysis was further complicated because anthropogenic gas from the Val Verde Gas Plants is mixed with natural CO_2 in the pipeline carrying the CO_2 to the Permian Basin; therefore the specific projects supplied by the Val Verde Gas Plants could not be determined. To accommodate the mixture of sources in the Permian Basin, the CO_2 from the Val Verde Gas Plants was apportioned based on the total crude oil production in the Permian Basin and the known quantities of CO_2 supplied from natural sources. The CO_2 from the Val Verde Gas Plants represents approximately 5.39 percent of the CO_2 used in Permian Basin Enhanced Recovery projects.

EPA recognizes that this is likely an oversimplification of the actual volume of CO_2 received by each facility, but notes that it follows the principle that higher production is a function of higher CO_2 injection volumes. The volume of CO_2 received by a particular ER project is a function of many factors, including:

[13] DOE/NETL, 2009. Carbon Dioxide Enhanced Oil Recovery, Untapped Domestic Energy Supply and Long Term Carbon Storage Solution. U.S. Department of Energy, National Energy Technology Laboratory, September 2009. page 11. Available at: http://www.netl.doe.gov/technologies/oil-gas/publications/EP/small_CO2_eor_primer.pdf

[14] U.S. EPA. 2009. Inventory of U.S. Greenhouse Gas Emissions and Sinks, 1990-2007, EPA 430-R-09-004. Available at: http://epa.gov/climatechange/emissions/downloads09/GHG2007entire_report-508.pdf.

- Reservoir characteristics: Heterogeneity is a significant design consideration, along with porosity, permeability, oil gravity, production history, depth, and reservoir pressure.
- Flood design: The injection design (e.g., continuous, simultaneous water and gas, water alternating gas), and number of injector wells are major factors in overall CO_2 use. Injection well pattern, miscible or immiscible processes, CO_2 saturation target as a percent of hydrocarbon pore volume (HCPV), and use of surfactants and additives also influence CO_2 use.
- Project age: The stage of the project is a significant factor in determining CO_2 use. New CO_2 floods use more purchased CO_2 and produce less oil because the CO_2 has not fully penetrated the reservoir. It may take 6–12 months to see an increase in oil production upon initiation of injection. As the reservoir becomes saturated with CO_2, the amount of new CO_2 added to the project is reduced, and the majority of the injected CO_2 is recycled from producing wells.

The calculation of CO_2 utilization in the threshold analysis presented in this chapter is based on the volume of new (purchased) CO_2 for ER obtained from the Inventory. The value represents the "Net CO_2 Utilization" in thousand cubic feet (mcf)/barrel (bbl). "Gross CO_2 Utilization" is the total amount injected, including purchased and recycled CO_2. Gross CO_2 Utilization was not analyzed in this threshold analysis because the total injection data were not available.

To evaluate the reasonableness of the approach, EPA compared the calculated Net CO_2 Utilization from the threshold analysis to field-specific values for 12 field-scale projects published by DOE.[15] Values for individual projects showed variance; however, overall the average values were consistent (7.53 mcf/bbl in the Threshold Analysis, versus 6.48 mcf/bbl in the DOE report).

As a secondary check on the reasonableness of the estimates in the threshold analysis, EPA compared the average age of the projects to the Net CO_2 Utilization. EPA performed this comparison because the age of the project is one of the most significant factors in determining Net CO_2 Utilization. The threshold analysis evaluated ER projects by CO_2 source (essentially by producing basin) and resulted in Net CO_2 Utilization estimates by basin. The results provided support that the estimates of CO_2 use were reasonable. For example:

- The Permian Basin has the oldest EOR projects (70 percent started before 2000) and the Threshold Analysis shows the lowest Net CO_2 Utilization (7.2 mcf/bbl) for this basin.

[15] DOE. 2006. Evaluating the Potential for "Game Changer" Improvements in Oil Recovery Efficiency from CO_2-Enhanced Oil Recovery, Prepared by Advanced Resources International for DOE NETL, February 2006. Available at: http://fossil.energy.gov/programs/oilgas/eor/Game_Changer_Oil_Recovery_Efficiency.html.

- The Mississippi Interior Salt Basin has the youngest CO_2 EOR projects (15 percent started before 2000) and the Threshold Analysis shows the highest Net CO_2 Utilization (19.2 mcf/bbl) of any basin.

Based on the analysis described above, the simplified estimation using production-apportioned CO_2 volumes shows a good correlation with independent data and is an appropriate estimation of the amount of CO_2 received by the facility.

Analysis of the ER injection data showed five fields with no enhanced production, which were correspondingly allocated to no CO_2 use. One additional field showed near zero production. Two of the six fields reported the projects as having "just started," and four reported projects at the "nearing completion" stage. This demonstrated to EPA that injection activity generally follows a curve that can slowly increase in the beginning, as the project moves from a pilot test to a larger scale, or slowly decrease toward the end of operations. Development of a full-scale CO_2 ER project requires extensive testing and ramping up over many years. Additionally, EPA determined that some ER production operations inject CO_2 and water in alternating pulses rather than continuously over years to maximize production, and the CO_2 injection periods and the corresponding (alternating) water injection periods may last from several months to two years or more. Therefore, the annual snapshot of data compiled for ER does not necessarily represent the typical operating conditions of full-scale projects expected in the future, as the number of ER operations increase.

The Interstate Oil and Gas Compact Commission (IOGCC) noted that acid gas is injected at approximately 20 sites in Michigan, New Mexico, North Dakota, Oklahoma, Texas, and Wyoming.[16] Many of the acid gas injection well locations are within oil fields that are listed in the O&GJ EOR survey, and inject into oil producing zones, suggesting the acid gas is being used for ER and not being injected solely for the purposes of disposal. Other acid gas injection locations identified by the IOGCC that are not associated with ER include one in Michigan, two in North Dakota, two in the Palo Duro basin of Texas, one in the Permian Basin in New Mexico, and one in Utah. These sites generally inject the acid gas for disposal into permeable strata below the deepest currently producing oil zone. EPA could not find any data to estimate quantity of CO_2 received for injection, so these facilities are not included in the threshold analysis.

Table 2-1 shows that nearly all facilities (92.5 percent) received greater than 1,000 metric tons of CO_2 per year**.** At a reporting threshold of up to 25,000 metric tons of CO_2 received per year, essentially all CO_2 (100 percent) received would be included, but not all facilities would report. At a reporting threshold of 25,000 tons of CO_2 received per year, 65 of the 80 facilities (81 percent) would report. At a 100,000 metric tons of CO_2

[16] Interstate Oil and Gas Compact Commission, 2005, Interstate Oil and Gas Compact Commission. 2005. Carbon Capture and Storage: A Regulatory Framework for States – Final Report January 2005. Available at:
http://groundwork.iogcc.org/topics-index/carbon-sequestration/executive-white-papers/ccgs-task-force-phase-i-final-report-2005

received per year threshold, 97.4 percent of all CO_2 used in ER would be reported from 60 percent of the facilities. The majority of the 40 percent of facilities not covered are characterized in the O&GJ Survey as pilot projects, projects that have just started, or projects nearing completion.

Table 2-1: Threshold Analysis Based on Amount of CO_2 Received by a Facility

Threshold Level (metric tons/yr of CO_2 received)	Total National (metric tons/yr of CO_2 received)	Total Number of U.S. Facilities	Amount of CO_2 Received		Number of Facilities	
			Metric tons/yr of CO_2 Received	Percent Covered	Number of Facilities Covered	Percent Covered
All In	40,111,639	80	40,111,639	100.0%	80	100.0%
1,000	40,111,639	80	40,111,115	100.0%	74	92.5%
10,000	40,111,639	80	40,099,065	100.0%	71	88.8%
25,000	40,111,639	80	40,005,238	100.0%	65	81.3%
100,000	40,111,639	80	39,065,039	97.4%	48	60.0%

Since the proposed subpart RR rule and March 2010 General TSD[17] were published, a new O&GJ survey of ER projects was published. The 2010 O&GJ Worldwide Survey of Enhanced Oil Recovery projects was conducted by O&GJ and published on April 19, 2010 (Volume 108 Issue 14). The data were collected and presented in the same manner as the 2008 survey that EPA used in the Threshold Analysis and described in the March 2010 General TSD.

The 2010 survey reflects the status of CO_2 ER projects at the end of 2009, and shows that the popularity of CO_2 ER is growing. There was a 14 percent increase in the number of fields employing CO_2 flooding, a 4 percent increase in the acreage of projects, and a 2 percent increase in the acreage of the fields. The projects included in the 2010 O&GJ survey are generally being operated by the same companies and in the same states as was the case in the 2008 survey. The projects appear to be more successful, producing 14 percent more oil per project with only a 3–5 percent increase in the number of producing and injection wells. This is likely due to the increased volumes of CO_2 being used for flooding.[18]

In the threshold analysis described in the March 2010 General TSD, EPA estimated the CO_2 use for each field identified in the 2008 OG&J survey of ER projects operating as of the end of 2007 using the apportioned amount of CO_2 used daily for ER based on the 2007 data from the 1990–2007 U.S. GHG Inventory. The 2009 data from the 1990–2009 U.S. GHG Inventory is not available at this time; therefore the Threshold Analysis cannot be updated to reflect the new 2010 O&GJ Survey data which identifies ER projects as of the end of 2009. However, producers of natural sources of CO_2 are increasing

[17] U.S. Environmental Protection Agency, General Technical Support Document for Injection and Geologic Sequestration of Carbon Dioxide, Proposed Rule for Mandatory Reporting of Greenhouse Gases, March 2010 (see docket ID No. EPA–HQ–OAR–2009–0926).
[18] DOE. 2009. Electricity Use of Enhanced Recovery with Carbon Dioxide (CO_2 –EOR), U.S. Department of Energy, DOE/NETL 2009-1354, January 26, 2009.

production[19,20,21] in response to the growing demand for CO_2 in new and existing ER projects. The 2008 Inventory shows an increase from 2007 of approximately 3 million metric tons of CO_2 production from natural sources. Additionally, as noted above, the volume of CO_2 used in each field is increasing, as is the Net CO_2 Utilization.

[19] Denbury Resources 2009 Annual Report page 20 shows a 7.2 percent increase in production of CO_2 over the previous year, and page 48 reports a production increase of 17 percent over 2009 in February 2010.
[20] Kinder-Morgan Analysts Conference, January 28, 2010, Slide 14 showing Permian Basin CO_2 Deliveries increasing 23 percent from 2007 to 2009.
[21] The 1990-2008 U.S. GHG Inventory (containing 2008 data) is available at: http://epa.gov/climatechange/emissions/usinventoryreport.html.

3. Monitoring Methods for CO_2 Received and CO_2 Injected

This chapter presents monitoring methods for determining the amount of CO_2 received (subparts RR and UU) and the amount of CO_2 injected (subpart RR).

CO_2 is a gas whose volume is typically reported at standard temperature and pressure (STP). The behavior of CO_2 at low pressure and high temperatures can be satisfactorily approximated by the ideal gas law. The ideal gas law is simple to apply in practice, but the behavior of CO_2 deviates from ideal gas with an increase in pressure or decrease in temperature as the assumptions made in deriving the ideal gas equation begin to deviate from actual gas behavior. The GHG Reporting Program addresses CO_2 equipment leaks, vented CO_2 emissions, and combustion CO_2 emissions as well as CO_2 streams, which can be at a wide range of temperatures and pressures. In addition, the program also covers facilities that conduct GS and all other facilities that inject CO_2 underground, which may use mixtures of several fluids that predominantly contain CO_2. The ideal gas law is only applicable to fluids in the gas phase; therefore significant error will occur if it is used to calculate densities for liquids and supercritical fluids.

Measuring CO_2 in gas phase should be performed differently from CO_2 in the supercritical phase. In supercritical phase, CO_2 behaves much like a liquid, and other gases can dissolve into supercritical-phase CO_2. This means the volumetric reading of supercritical phase CO_2 stream can be misleading if there is any significant amount of impurities dissolved in the CO_2 stream. The discussion below describes different measurement and calculation methods that may be required to accurately measure the different phases of CO_2.

3.1 Determining the Amount of CO_2 Received Using Data from Sales, Contracts, Invoices, or Manifests Associated with Commercial Transactions

In order to determine the amount of CO_2 received, a facility would measure the flow rate of the CO_2 at the custody transfer meter at the facility boundary prior to any subsequent processing operations at the facility, use flow rate data from the sales contract associated with CO_2 received from a one-time commercial transaction, use data from invoices or manifests for CO_2 received from an ongoing commercial transaction, or measure the flow rate at the equivalent of a custody transfer meter, following the provisions of subpart PP, for CO_2 supplied from a production process that is part of a facility. Also, for commercial transactions for which the sales contract specifies a range of CO_2 concentration, and if the supplier of the CO_2 sampled the CO_2 stream and measured its concentration per the sales contract terms, the reporter can use the average CO_2 concentration data from the sales contract or the seller's measured value.

Information concerning the use of mass or volumetric flow meters for measurement of the amount of CO_2 received is included below under Chapter 3.2 concerning the use of data from sales contracts, invoices, or manifests associated with commercial transactions is discussed in this chapter.

For a one-time commercial transaction between a CO_2 supplier and a CO_2 recipient (i.e., the reporter) there would generally be a sales receipt indicating the amount of CO_2 that was supplied by the supplier and that was received by the recipient in the commercial transaction.

For an ongoing commercial transaction between a CO_2 supplier and a CO_2 recipient (i.e., the reporter) involving a series of discrete shipments, there would generally be invoices or manifests indicating the amount of CO_2 that was supplied by the supplier and that was received by the recipient. Each individual invoice or manifest would cover a specific period of time (e.g., one month; one quarter) over which CO_2 was received, or may cover one individual transaction in the series of discrete shipments.

To minimize errors in reporting data from sales receipts or invoices and manifests associated with one-time and ongoing commercial transactions, the sales receipts, invoices, and manifests provided by the CO_2 supplier should report the amount of CO_2 supplied (and the amount of CO_2 received) in the same physical units (mass units) as are required to be reported under the subpart, and using the same standard conditions (STP) and conversion factors as are required to be used under the subpart. This will minimize errors by the reporter in converting the amount of CO_2 received from one set of units (e.g., volumetric units) to the units (i.e., mass units) that are required to be used under the subpart. If the commercial transaction is actually tied to a different set of measurement units (e.g., volumetric units) the sales receipt, invoice, or manifest should report the amount of CO_2 supplied in both the units to which the transaction is tied and the units that are required to be reported under the subpart. The units of CO_2 concentration measurements provided by the CO_2 supplier in sales contracts used by the reporter to determine the CO_2 content should also be in the same units as required to be used under the subpart, and the methodology used by the CO_2 supplier to measure the CO_2 concentration should be consistent with the methodology specified under subpart PP for CO_2 suppliers.

For ongoing transactions, the reporter should compare invoices and manifests received for CO_2 supply transactions from one period to the next (e.g., monthly, quarterly) or should compare the invoices or manifests from one shipment to the next, to assess the variability of the amount of CO_2 supplied. Unanticipated variation in the amount of CO_2 supplied (and received) between one invoice/manifest period and the next could indicate a reporting error on the part of the CO_2 supplier, for example.

3.2 Determining the Amount of CO_2 Received, Injected, or Produced Using Mass Flow Meters or Volumetric Flow Meters

In order to determine the amount of CO_2 received, injected, or produced (at ER or other fluid production operations), a facility would measure the flow rate using either a mass flow meter or a volumetric flow meter. To determine the mass, the facility would either multiply the mass flow rate by the concentration of CO_2 in that flow or multiply the volumetric flow rate at STP by the concentration of CO_2 in the flow and by the density of

CO_2 at STP. Either a continuous mass flow meter or a continuous volumetric flow meter would most accurately account for the fluctuations over time of flow rate.

To minimize the error in calculating the mass from CO_2 volumetric readings, the application of an equation of state[22] (EOS) more accurate than the ideal gas law is recommended. The EOS proposed by Span and Wagner[23] represents the state of science in theoretical prediction of gas phase CO_2 properties. This EOS predicts density of CO_2 within ± 0.03 percent to ± 0.05 percent for pressures up to 4,350 pounds per square inch (psi) and temperatures up to 482°F. At the same time, the Span and Wagner EOS may be too complex to be directly applied by reporters. Therefore, EPA recommends using the database of thermodynamic properties developed by the National Institute of Standards and Technology (NIST). This online database, available at http://webbook.nist.gov/chemistry/fluid/, provides density of CO_2 using the Span and Wagner EOS at a wide range of temperature and pressures.

The following generic protocol is recommended to calculate CO_2 mass from volumetric measurements, with the assumption that the gas stream is predominantly CO_2:

- Obtain volumetric measurements using consensus standards at operating conditions;
- Determine the density of CO_2 at operating conditions using the Span and Wagner EOS from NIST tables;
- Calculate the mass of CO_2 in the required units by multiplying the density by the volumetric measurements of CO_2.
- Obtain species and their mass fraction information by sampling the stream of CO_2. The sample can be analyzed using standards from consensus standards organizations for methods such as chromatography or mass spectroscopy to identify all chemical constituents and their mass fractions. With knowledge of the mass of CO_2 calculated, the masses of the other individual species present may be evaluated knowing their individual mass fractions in the CO_2 stream.

The density of liquid or supercritical phase[24] CO_2 depends significantly on process conditions as well as mixture composition. Therefore, available theoretical models to calculate density of CO_2 may not be robust enough to span all potential process conditions. Furthermore, theoretical methods, where available, may be too cumbersome for reporters to implement in practice. EPA has not identified standards from consensus-based organizations that are suited for the purpose of measuring the density of CO_2 in liquid or supercritical state. Therefore, EPA recommends the following generic protocol

[22] An equation of state is a mathematical expression that describes the relationship between thermodynamic properties of chemical species.
[23] Span, R. and W. Wagner. 1996. A New Equation of State for Carbon Dioxide covering the Fluid Region from the Tripe-point Temperature to 1100 K at Pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, Vol 25.
[24] Supercritical CO_2 refers to CO_2 with both pressure and temperature greater than their critical values. Critical temperature of a gas is the temperature above which the gas cannot be liquefied at any pressure. This temperature for CO_2 is 88°F. Critical pressure is the pressure required to liquefy the gas at its critical temperature. Critical pressure for CO_2 is 1072 psi.

to calculate density of CO_2 in liquid or supercritical state at process conditions or conditions at the point of transfer/measurement:

- Collect a representative sample of liquid or supercritical CO_2 mixture from process equipment in a high-pressure sampling container.
- Determine the volume of the sampling container from manufacturer specifications.
- Determine the mass of the sample by weighing the sampling container before and after taking the sample.
- Send the sampling container to an analytical laboratory for compositional analysis. The laboratory may expand the contents in sampling container to testing conditions. A sub-sample is analyzed using standards from consensus standards organizations for methods such as chromatography and mass spectroscopy to identify all chemical constituents and their mass fractions.
- Determine the mass of each individual chemical species in the sampling container by the known mass of the sample and mass fractions. Mass of CO_2 in the process volumes from volume readings is determined by using volume of the sampling container and mass of individual species in each of the container; i.e., CO_2 Mass flow rate = CO_2 Volume flow rate *(Mass of Representative Sample / Volume of Sample Container) * Mass fraction of CO_2 in the sample.

It is important to note that the sampling of liquid or supercritical CO_2 should be performed so the sample represents the process fluid. Some American Society for Testing and Materials (ASTM) standards that detail procedures for sampling liquids, especially hydrocarbons such as liquefied natural gas, may be applicable to conduct this sampling. In addition, weighing scales may be sensitive to temperature difference between the empty container and the container with the sample. Care must be taken to minimize such error.

Facilities subject to the UIC program for permitting of injection wells would already have flow meters installed to measure the flow rate of the CO_2 stream injected for purposes of compliance with their UIC permits. It is common industry practice to use volumetric rather than mass flow meters.

In order to determine the portion of the CO_2 stream that is CO_2, the facility would sample the stream and analyze it for its CO_2 concentration. EPA has identified three industry standards that provide methods to quantify CO_2 that may be applicable to CO_2 streams. Facilities may use any standard method published by a consensus-based standards organization if such a method exists, or an industry standard practice.

<u>Gas Processors Association (GPA) Standard 2261-00. Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography</u>
This standard describes a method for the compositional analysis of natural gas and similar gaseous mixtures that also contain CO_2, in addition to other gaseous constituents, and various hydrocarbons. The method consists of physically separating the gaseous

constituents by gas chromatography with a thermal conductivity type detector. Procedures are outlined for component concentrations by mathematical procedures and using calibration data from a reference standard. The method is applicable to mixtures that confirm to component concentrations as outlined in the standard.

<u>GPA Standard 2177-03. Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography</u>
This standard describes a method for the compositional analysis of demethanized liquid hydrocarbon streams that also contain CO_2, in addition to nitrogen and various hydrocarbons. The method consists of physically separating the liquid mixture constituents by gas chromatography having a thermal conductivity type detector. Procedures are outlined for component concentrations by mathematical procedures and using calibration data from a reference standard. The method is applicable to mixtures that confirm to component concentrations as outlined in the standard.

<u>ASTM E1747-95 (re-approved 2005). Purity of Carbon Dioxide Used in Supercritical Fluid Applications</u>
This ASTM standard defines purity standards for CO_2 for use in chemical extraction and chromatography applications. The guide defines standards for impurities in CO_2 used in extraction and chromatography and it suggests methods of analysis for quantifying these impurities using gas chromatography with an electron capture detector and flame ionization detector.

EPA recognizes that these standards are not specifically designed for the analysis of CO_2 for use in ER or GS applications. The GPA standards note that the methods use gas chromatography to separate and identify compositional characteristics of the constituents of the gas/liquid mixtures; however, they are recommended and applied for mixtures with a relatively low concentration of CO_2 (less than 20.0 mol percent in the case of GPA Standard 2261-00, and less than 5.0 mol percent in the case of GPA Standard 2177-03). Typical applications of CO_2 for ER or sequestration may have CO_2 concentrations greater than 95 percent. There does not seem to be any indication in the standards themselves that the standards would be inaccurate or even biased for high CO_2 streams, but the reporter should evaluate the suitability of these methods if they are used.

Using the operating temperature and pressure, the volume of CO_2 can be converted into STP conditions and, using a STP density value for CO_2, from the NIST online database (0.0018682 grams per milliliter or 0.11663 lb/ft^3) one can calculate the CO_2 quantity in metric tons. A facility would apply the same method in order to calculate the quantity in metric tons of CO_2 received.

Measurements of CO_2 volume may be taken at actual pressure and temperature conditions and may therefore need to be converted to STP conditions for the purposes of reporting under subpart RR. If the CO_2 is not in a liquid or supercritical state the reporter may apply the Ideal Gas Law to convert measurements at actual temperature and pressure conditions to STP conditions. Standard Temperature is defined in the Rule as 60 degrees Fahrenheit. Standard Pressure is defined in the Rule as 1.0 atmosphere.

For example, if a CO_2 volume of 1,000 actual cubic feet was measured at an actual temperature of 300 degrees Fahrenheit and an actual pressure of 1.1 atmospheres, the calculation to convert the measurement to the volume of CO_2 at STP would be as follows:

Volume Conversion using the Ideal Gas Law

The Ideal Gas Law is: P x V = n x R x T in which:

> P = Pressure
> V = Volume
> n = mass (number of lb-moles)
> R = Gas Constant
> T = Temperature

For pressure in units of atmospheres, volume in units of cubic feet, and temperature in degrees Rankine, the Gas Constant R = 0.730 atm ft3 / lb-mol deg. R.

Degrees Rankine is defined as Degrees Fahrenheit + 459.67.

From the Ideal Gas Law:

$P_1 \times V_1 / T_1 = P_2 \times V_2 / T_2$

Where:

> P_1 = Actual pressure
> T_1 = Actual temperature
> V_1 = Actual volume
> P_2 = Standard pressure
> T_2 = Standard Temperature
> V_2 = Volume at Standard Conditions

For the example of a measurement of 1,000 cubic feet of CO_2 at actual temperature and pressure conditions of 1.1 atmospheres and 300 degrees Fahrenheit, the values for the Ideal Gas Law equation would be as follows:

> T_1 = Actual Temperature = 300 + 459.67 = 759.67 Deg R
> P_1 = Actual Pressure = 1.1 atmosphere
> T_2 = Standard Temperature = 60 + 459.67 = 519.67 Deg R
> P_2 = Standard Pressure = 1.0 atmosphere
> V_1 = Actual Volume = 1,000 cubic feet

The equation $P_1 \times V_1 / T_1 = P_2 \times V_2 / T_2$ would then be solved for the variable V_2.

> $V_2 = (P_1 \times V_1 / T_1) / (P_2 / T_2)$

$$V_2 = [(1.1 \text{ atm}) \times (1{,}000 \text{ ft}^3) / (759.67 \text{ Deg R})] / [(1.0 \text{ atm}) / (519.67 \text{ Deg R})]$$

Therefore:

V_2 = 752.48 cubic feet at standard temperature (60 degrees F) and pressure (1.0 atm)

For CO_2 that is in a supercritical state, the Ideal Gas Law is not applicable and therefore a different equation of state is needed to calculate the volume of the CO_2 at standard conditions.

In such cases, the reporter may apply the NIST Thermophysical Properties of Fluid Systems (accessible at http://webbook.nist.gov/chemistry/fluid/) to look up the density of supercritical CO_2 at actual temperature and pressure conditions.

For example, for supercritical CO_2 at an actual temperature of 140 degrees Fahrenheit (60 degrees Celsius or 333.15 degrees Kelvin) and an actual pressure of 100 atmospheres (10.13 MPa or 1470 lb/in^2) the NIST Thermophysical Properties database shows the density of the supercritical CO_2 to be 18.614 lb/ft^3.

Temperature (F)	**Pressure (atm)**	**Density (lbm/ft^3)**	**State**
140	100	18.614	supercritical

At the standard temperature of 60 degrees Fahrenheit and standard pressure of 1.0 atmosphere, the density of CO_2 is 0.11663 lb/ft^3.

So if a volume of 1000 ft^3 of supercritical CO_2 was measured at actual pressure and temperature conditions of 100 atmospheres and 140 degrees Fahrenheit, that volume of CO_2 would be equivalent to: 1000 ft^3 x 18.614 lb/ft^3 = 18,614 lb of CO_2.

The density of CO_2 is 0.11663 lb/ft^3 at STP. Therefore, 18,614 lb of CO_2 at a density of 0.11663 lb/ft^3 = 18,614 lb / 0.11663 lb/ft^3 = 159,598.7 ft^3 CO_2 at STP.

Therefore, the volume of the 1,000 ft^3 of CO_2 at actual conditions would be reported as 159,598.7 ft^3 CO_2 under standard conditions.

4. Overview of Monitoring Technologies for CO_2 Leakage Detection and Quantification

This chapter describes technologies for monitoring of the injection well, subsurface CO_2 plume, vadose zone[25], soil zone and vegetation, and atmosphere and how they may be applied to detect and quantify movement of CO_2 to the surface at GS sites. Table 4-1 provides a list of monitoring methods that are being used at CCS projects.[26]

Table 4-1: Monitoring Technologies as Deployed at 10 Existing CCS Projects

Technology	Description	Characterization	Injection	Post-Closure	CO2SINK	In Salah	Nagaoka	Sleipner	Snohvit	Weyburn	Frio
Surface-based seismic (2D / 3D / 4D)	Surface-based sources used to impart energy into thesubsurface. Surface-based receivers collect energy waves that have been reflected and refracted through the deep subsurface, and these travel time data are processed and analyzed to resolve structures at depth. 2D seismic produces a single "slice" image of the subsurface, while 3D produces a three-dimensional image. So-called "4D" timelapse seismic data are acquired at multiple discrete periods in time to resolve changes in the subsurface over time.	X	X	X	X	X		X	X	X	X
Lithology logging / core	Initially performed for site characterization and project / operational design, these tests are crucial to understanding the fine-scale characeristics of the formation at depth. In particular, core samples can be analyzed in the laboratory for critical storage formation and caprock parameters, including information on the ability of the rock to transmit fluids and its ability to withstand injection pressures.	X			X	X	X	X		X	X
Wireline logging	Performed by introducing a set of tools into the well to measure geophysical and electrical properties of the storage formation, caprock and other zones of interest. Initial logging is often done in an uncased well, although some logs (e.g., cement bond log) are routinely performed through casing. These logs are used for initial characterization and project design, and many are useful for ongoing monitoring as well. Note that logging of the injection well requires that injection cease in order to introduce the logging tool string.	X	X	X	X	X	X	X		X	X
Geochemical sampling & analysis	Collection of fluid samples from the storage zone, as well as overlying and possibly underlying aquifers via monitoring wells to screen for changes in chemistry that could suggest movement of formation fluids from the storage zone.	X	X	X	X	X	X	X		X	X
Pressure & injection rate monitoring	Standard field management tools used to monitor formation and well integrity.	B	X	X	X	X	X	X	X	X	X
Electromagnetic surveys	Introduce EM energy into the subsurface and measure the response. Can be used as an accessory to seismic surveys.	X	X	X							X
Electrical resistance tomography	Inexpensive but lower resolution that seismic. ERT uses an electrode in the subsurface (the wellbore may be used as the electrode) to measure resistitivity. Data can be acquired often and via remote, making this a good option for filling in between higher-resolution but more expensive discrete seismic surveys.	X	X	X	X	X				X	
Crosswell seismic	Uses sources and receivers placed in the wells, which allows for greater resolution in the subsurface, but only between the wells.	X	X	X	X		X			X	X
Microseismic / passive seismic	Uses permanent geophones in monitoring wells and/or on the surface to monitor for very, very small geomechanical changes in the storage formation as the CO_2 moves.	X	X	X		X	X	X		X	
Gravitational surveys	Measures changes to the gravitational field in order to resolve changes in formaiton fluid density as CO_2 displaces brine in the formation over time.	B	X	X		X		X			
Magnetic surveys	Excellent aerial technique for identifying existing (cased) wellbores. Less mature as a CO_2 monitoring technique.	X									
Tiltmeters	Resolves small changes in elevation of the ground surface resulting from CO_2 injection at depth using tiltmeters on the ground.	B	X			X					
InSAR / DInSAR	Uses satellite-based radar to measure changes in the elevation of the ground surface resulting from CO_2 injection at depth.	B	X	X		X					
Soil gas / vadose zone / shallow aquifer monitoring	Monitoring wells in the shallow subsurface are used to collect samples to check for changes in CO_2 concentrations, as well as changes in isotope ratios, concentrations of tracers, and other markers that might indicate CO_2 leakage.	B	X	X	X	X				X	X
Tracers	Impurities that are highly detectable at low concentrations and not naturally present in the subsurface or the CO_2 stream are introduced into the injectate prior to injection. Detectors used at the surface and in intermediate water-bearing zones can look for these trace gases to determine if CO_2 is leaking from the storage interval.		X	X		X					X
Atmospheric monitoring	Monitoring of the wellhead and other areas above the plume. This can include eddy covariance, LIDAR and other forms of CO_2 detection.	B	X	X		X				X	X

B: Baseline needed for future phases.

(Source: J.J. Dooley, CL Davidson and RT Dahowski. 2009. An Assessment of the Commercial Availability of Carbon Dioxide Capture and Storage Technologies as of June 2009. Joint Global Change Research Institute. Pacific Northwest National Laboratory. June 2009. PNNL-18520)

While technologies for quantifying CO_2 surface leakage from GS sites are continuously being refined, it is generally recognized that, when properly planned and implemented, monitoring methods will be effective at detecting surface leakages.[27, 28] A wide range of

[25] The vadose zone is the relatively shallow zone beneath the surface that is not saturated with groundwater.
[26] J.J. Dooley, CL Davidson and RT Dahowski. 2009. "An Assessment of the Commercial Availability of Carbon Dioxide Capture and Storage Technologies as of June 2009." Joint Global Change Research Institute. Pacific Northwest National Laboratory. June 2009. PNNL-18520.
[27] Benson, S.M. 2006. Monitoring Carbon Dioxide Sequestration in Deep Geological Formations for Inventory Verification and Carbon Credits. Society of Petroleum Engineers Paper 102833, 14pp. http://www.onepetro.org/mslib/servlet/onepetropreview?id=SPE-102833-MS&soc=SPE (at cost).
[28] FutureGen Alliance. 2006. Mattoon Site Environnemental Information Volume. December, 2006. http://www.futuregenalliance.org/.

techniques for monitoring GS have been used at GS sites as well as for a number of years in other applications, including oil and gas production, ER, and plant and soil science. These techniques may be used at a GS site to monitor the injected CO_2, the surrounding rocks and fluids, wells and equipment, and the surface conditions. EPA has concluded that a GS facility would be able to propose a site-specific monitoring, reporting, and verification (MRV) plan for leak detection and quantification based on the current availability of monitoring technologies. In addition, it is expected that site characterization and screening will lead to selection of sites that are suitable for long-term sequestration, and that incidences of leaks to the surface may be infrequent at well-selected and well-managed sites.

4.1 Monitoring of the Injection Well

Mechanical Integrity Testing (MIT) is commonly used at UIC permitted injection wells to demonstrate that the injection wells can resist the high pressures of injection, as well as the potentially corrosive nature of the injected CO_2. Please refer to the UIC program Web site for information on requirements related to monitoring of UIC permitted injection wells, including MIT.[29]

Periodic *external MIT* checks the area between the cement and the formation in the long string casing to detect gaps or fluid flow.[30] Should there be a break in the bond between the cement and the rock of the wellbore, the injected CO_2 can make its way vertically to access shallow formations, and possibly escape to the surface. External MIT is a reliable and effective method commonly carried out using wireline logs or pressure tests.

Wireline logs are subsurface measurements of the wellbore taken by lowering an instrument on a wire into the well, and recording the log response continuously as the tool is pulled upward. This generates a detailed picture of the borehole and nearby rock. There are numerous types of wireline logs used in the oil industry; the primary focus is on determination of reservoir properties such as lithology, porosity, and fluid content (oil, gas or water). Other types of tools are used to evaluate the integrity of the casing and cement in a cased well. Wireline logs can be run in the open hole of a newly drilled well, and may be used to evaluate conditions in injection wells or monitoring wells. Common wireline logs used for external MIT are the cement bond log, the temperature log, and the noise log. The cement bond log is a sonic (sound-wave) based tool that is used to evaluate the bond between the casing and cement, and between the cement and the formation.[31, 32] The temperature log helps identify hot spots due to flow from deeper

[29] http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm.

[30] Koplos, Jonathan, B. Kobelski, A. Karimjee, C.H. Sham. 2006, UIC Program Mechanical Integrity Testing: Lessons for Carbon Capture and Storage. Fifth Annual Conference on Carbon Capture and Sequestration, May 8-11, DOE/NETL, 2006. http://www.netl.doe.gov/publications/proceedings/06/carbon-seq/Tech%20Session%20139.pdf.

[31] Duguid, Andrew, and John Tombari. 2007. Technologies for Measuring Well Integrity in a CO_2 Field. Sixth Annual Conference on Carbon Capture and Sequestration. DOE/NETL, May 2007. Available at: http://www.netl.doe.gov/publications/proceedings/07/carbon-seq/data/papers/tue_064.pdf.

formations, while the noise log detects the sound of CO_2 flow behind the pipe. To some extent, the log response might be used as a qualitative measure of the amount of leakage. Other external integrity tests include the oxygen activation log and radioactive tracer surveys, which indicate lack of fluid migration behind the casing.

Internal MIT of the injection well checks the integrity of the well materials: the tubing, packers, and long string casing. During injection operations, there can be continuous monitoring of the annulus fluid pressure, which is typically maintained at a higher pressure than that of the injected CO_2. A drop in the annulus pressure may indicate cracks or holes in the long string casing, or may also indicate a leak in the tubing or packers. This would not necessarily be an indication of a CO_2 leak to the atmosphere. In addition to continuous pressure monitoring in the annulus, internal well damage can be monitored with periodic wireline logs, including caliper tools, radioactive tracer tests, and downhole video. Logs can detect corroded or damaged tubing or casing even before a leak occurs. All of these methods are commonly used in the oil and gas industry.

In certain circumstances, new technologies allow well logging to be conducted while drilling using small, sophisticated tools.

4.2 Monitoring of Subsurface CO_2 Plume

The location and size (areal extent) of the injected CO_2 plume can be evaluated using several approaches. These include the acquisition of active seismic data, passive seismic data, gravity data, and information from monitoring wells. This information can be used in concert with reservoir modeling to predict subsurface CO_2 plume movement. Please refer to the UIC program Web site for information on requirements related to tracking and monitoring the CO_2 plume.[33]

The *active seismic* geophysical technique involves the generation of sound waves that propagate downward or laterally through the subsurface, are reflected off of geological layers, and are subsequently detected and analyzed at the surface by advanced instrumentation. The method is used to evaluate the structural or spatial configuration of the subsurface, and can also be used in some cases to determine reservoir properties and fluid content, including the presence of free-phase (but not dissolved) CO_2. In conventional active seismic, both sound sources and detectors are located on the surface. In *vertical seismic profiling*, the source is on the surface and the detector is downhole. In another arrangement called *cross-well seismic*, both source and detector are downhole in different wells. Periodic acquisition of *active seismic* data can in some cases be used to detect subsurface CO_2 movement within and outside of the injection zone (IZ). This may include leakage from or around the injection well, from or around older pre-existing wells, or through geological zones of weakness in the confinement zone (CZ).

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[32] DOE/NETL. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. Available at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

[33] http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm.

A variety of active seismic methods are in use today in the oil and gas industry, and can be used for CO_2 plume monitoring. These include *two-Dimensional (2-D) seismic*, *three-Dimensional (3-D)/four-Dimensional (4-D) seismic*, *vertical seismic profiling*, and *cross-well* seismic. Surface seismic data may be either 2-D, 3-D or 4-D. *2-D seismic* is obtained with a linear surface arrangement of receivers. The acoustic energy source is from small explosive charges or from "vibro-seis" trucks. 3-D seismic may provide better resolution, accuracy, and tracking of the CO_2 if it migrates from the storage reservoir into the overburden. *3-D seismic* evaluates a large volume of the subsurface, has high resolution, and is more complex and more costly to obtain and analyze. Surface receivers are laid in a grid pattern, and large amounts of data are simultaneously recorded and subsequently processed. Sophisticated software allows the conversion of this raw information into a detailed subsurface representation. 3-D data are being increasingly used in the oil industry, as they allow the mapping of structural details, small faults, rock properties, and fluid properties. *4-D seismic* is time-sequenced 3-D. The technique is the same as 3-D, but it is acquired over time. In this way, one can evaluate fluid movement over time.

Vertical seismic profiling uses sensors deployed in a borehole to measure sound propagation in the immediate vicinity of the well.[34] It is a high-resolution method that evaluates a small volume of the subsurface adjacent to a single well. A variation of vertical seismic profiling is "walk-away" profiling, in which the source is sequentially moved away from the well. This creates a mini-2-D seismic line away from the injection well. *Cross-well seismic*, as mentioned above, involves the transmission of acoustic waves between wellbores, and also evaluates a small rock volume. *Vertical seismic profiling* and *cross-well seismic* methods are used to develop a very high-resolution image of conditions relatively near the injector or monitoring wells, due to the short distance between seismic sources and receivers. These methods can also be used to calibrate the acoustic signature of the CO_2 plume under very controlled conditions. This calibration can then be used to better interpret the 2-D and 3-D seismic, which cover a much larger area.

All these types of active seismic methods can be used to image the free-phase portion of a CO_2 plume under certain subsurface conditions. These methods are known to be effective in many cases where CO_2 is injected into a saline reservoir and has a good density contrast with the saline fluid. The ability to image and track a CO_2 plume depends upon factors such as lithology (sandstone, limestone, coal, or shale), porosity (pore space), fluid content, and depth.[35] Seismic detection of a CO_2 plume in a carbonate (CO_3^{--}) (limestone or dolomite) reservoir may be a challenge due to low porosity and other factors. Seismic detection of CO_2 in a depleted oil reservoir may be more challenging than monitoring a saline reservoir due to lower average fluid density contrast (both oil

[34] DOE/NETL. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. Available at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

[35] IPCC. 2005. Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change, pg. 237. Available at: http://www.ipcc.ch/publications_and_data/publications_and_data_reports_carbon_dioxide.htm.

and free-phase CO_2 are less dense than saline water). Studies have been undertaken to evaluate seismic plume monitoring in coal beds.[36]

Active seismic methods including 2-D, 3-D/4-D, and cross-well seismic can achieve high plume detection resolution, and therefore can be used to develop a first-order estimate of plume dimensions for leakage quantification; a drawback is that seismic methods only image free-phase CO_2 in the reservoir and not the dissolved CO_2 component. In addition, the amplitude of the seismic signal (which is used to detect the CO_2) is only partially related to the concentration and therefore cannot fully quantify even the free-phase part of the CO_2. However, amplitude anomalies have been observed in CO_2 sequestration monitoring that have been related to CO_2 concentration. Such amplitude effects have been observed at the Sleipner and Weyburn projects.[37] To be detectable, the CO_2 accumulation must have lateral and vertical dimensions sufficient to produce a discernible seismic response. One study based on theoretical resolution considerations[38] has suggested that CO_2 buildups as small as 10,000 to 20,000 metric tons may be detectable at typical injection depths, but amounts would be difficult to quantify, as saturation would remain a key uncertainty. In practice, results from the Sleipner time-lapse surveys suggest that repeatability noise (which depends on the accuracy with which successive surveys can be matched), rather than resolution, may be the key parameter in limiting the detection of small changes of seismic signature due to leakage. Under favorable conditions, such as those at Sleipner, Weyburn and Frio, accumulations on the order of 1,000 to 10,000 metric tons of CO_2 are detectable at depths less than 1,000 meters (m), and smaller accumulations could be detected at shallower depths.[39]

Passive seismic methods, which use only receivers (no active acoustic sources), monitor the sound waves that are emitted from high-pressure injection sites with sophisticated instrumentation and decipher the results using computational methods. As the pressurized CO_2 moves through the reservoir, it creates microfractures that release acoustic energy that is detected in 3-D space. Passive seismic methods can be used to track the subsurface plume and the areas of high pressure. They can also be used to detect where fractures are occurring that might signal breaks in the CZ or activation of old faults.

Gravity surveys measure the earth's gravitational field at a series of points over a subsurface target of interest. Gravity surveys have been used since the early 1900's in oil exploration, and are now being evaluated for use in GS sites. Changes in the earth's

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[36] Lawton, Don. 2002. A 3C-4D Surface Seismic and VSP Program for a Coalbed Methane and CO_2 Sequestration Pilot – Red Deer, Alberta. CREWES Research Report 14. Available at: http://www.crewes.org/ForOurSponsors/ResearchReports/2002/2002-64.pdf.

[37] DOE. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. Available at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

[38] Myer, L. R., Hoversten, G. M., and Gasperikova, E. 2002. Sensitivity and Cost of Monitoring Geologic Sequestration Using Geophysics. In: Gale, J. & Kaya, I. (eds.) *Greenhouse Gas Control Technologies*. Elsevier, 377 – 382. Available at: http://www.sciencedirect.com/science/book/9780080442761.

[39] Benson, S.M.. 2006. Monitoring Carbon Dioxide Sequestration in Deep Geological Formations for Inventory Verification and Carbon Credits. Society of Petroleum Engineers Paper 102833, 14pp. Available at: http://www.energy.utah.gov/Utah_Actions/documents/dec2006/spe102833.pdf.

gravitational field are caused by changes in density in the underlying rock layers. Because CO_2 is usually less dense than native fluids and petroleum, reservoirs that fill with CO_2 will appear as lower gravity areas. Gravity surveys are performed in a time lapse mode like 4-D seismic, to evaluate plume movement. Data processing is complex and involves removal of several external influences from the data set prior to creating a model of the gravity field. Studies at Sleipner site indicate the method shows promise to help constrain the reservoir simulation models[40]. This technology is still in early stages of field testing and model development.

Downhole instrumentation is used in *monitoring wells* to measure temperature, pressure, conductivity/salinity, and fluid characteristics. The individual measurements are quite reliable and accurate, but their limitation is that they represent a single point in time and space. The monitoring wells can be logged periodically with *wireline logs* that can be used to detect the presence and depth of CO_2. Certain wireline tools may be used to collect a fluid sample under reservoir pressure and temperature conditions, and retrieve the sample to the surface for laboratory analysis.[41] They can also be used for *cross-well seismic* data acquisition, in which seismic signals are broadcast from one well and detected in an adjacent well to characterize the formation between the wells. Monitoring wells can be designed to allow testing of the CO_2 reservoir, or of units above the reservoir. *U-tube devices* can be used to retrieve pressurized samples for laboratory testing. Based on the specific (electric) conductance and the pH of the pressurized samples, the concentration of dissolved inorganic carbon (DIC) can be determined using complex algorithms. DIC includes aqueous CO_2, carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and CO_3^{--}. CO_2 leakage from the reservoir can be detected long before the CO_2 can escape to shallower zones or to the surface.

Geochemical sampling of the fluid from monitoring wells can also be used to detect natural or artificial "tracers" in the injected CO_2. Monitoring to gather additional data may be necessary if the instrumentation indicates a significant anomaly relative to background levels.

Intermediate monitoring wells can be used to test zones within a depth range of approximately 200 to 2,000 feet below the surface. As with the deeper wells, downhole instruments can measure pressure, temperature, and conductivity/salinity. Further monitoring may be implemented when readings depart from background levels; for example, a 3-D seismic survey may be undertaken if the anomaly is within an appropriate depth range.

Surface deformation monitoring is currently being tested as a rapid cost effective method to identify plume movement and potential leakage pathways in the subsurface. As CO_2 is injected the ground surface may be raised a minute amount in response to the addition of fluids to the subsurface. Highly sensitive tiltmeters (much like a highly sensitive

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[40] Arts, R., Chadwick, A., Eiken, O., Thibeau, S., Nooner, S., 2008. Ten years' experience of monitoring CO_2 injection in the Utsira Sand at Sleipner, offshore Norway, *First Break*, Volume 26, January 2008
[41] FutureGen Alliance. 2006. Mattoon Site Environnemental Information Volume. Available at: http://www.futuregenalliance.org/news/fg_mattoon_eiv_v1_master_rev1.pdf.

electronic carpenters level) and Differential Global Positioning Systems can be used to measure ground movements over small areas, and specialized radar (Interferometric Synthetic Aperture Radar (InSAR)) can be used to survey large areas from the air. Tiltmeters are capable of detecting changes in slope on the order of one millimeter (mm) over 1000 kilometers. InSAR satellite images are collected monthly and can cover from 2,500 to 10,000 square kilometers (km) with accuracy in the millimeter range.[42] When combined with tiltmeter and global positioning system (GPS) data, accuracy and resolution can be improved. Surface deformation at In Salah was monitored using InSAR from 2003 to 2008[43] and showed ground swelling on the scale of 3 to 14 mm per year near the injection wells, and several millimeters of subsidence near the natural gas production wells. The data can be used to infer underground pressure gradients and fluid movements from the changes in surface deformation over time. Surface deformation surveys are influenced by vegetation, frost heaves and other natural conditions that can be removed from the data set with additional information.

4.3 Vadose Zone Testing

The vadose zone is the relatively shallow zone beneath the surface that is not saturated with groundwater. Due to absence of water, monitoring in this zone therefore is limited to testing the chemistry of the gases contained within the pore space. The CO_2 concentration of gas samples taken in this zone can be measured using commercially available *infrared gas analyzers* (IRGAs), which measure the absorption of specific portions of the infrared spectrum to determine the concentration of CO_2 (or other gases) in the sample. Background levels must first be measured to determine the statistical variations of CO_2 concentration accounting for sample temperature, seasonal variations, diurnal variations, and the like. Later, a presumptive leak is detected if the monitored CO_2 concentration exceeds a value corresponding to a very high (e.g., exceeds the 99 percentile) prediction for the natural CO_2 concentration accounting for sample temperature, seasonal variations, diurnal variations, etc. Should significant anomalies be detected, an expanded soil or atmospheric testing program may provide additional information. In addition to the use of IRGAs for CO_2 concentration, vadose zone sampling can include testing for tracers, should they be used, and for sampling for carbon and oxygen isotopes, to determine whether the CO_2 is that which is being injected or naturally occurring CO_2.[44] As with data collected in monitoring wells, these individual measurements are quite reliable and accurate, but their limitation is that they represent a single point in time and space.

4.4 Soil Zone and Vegetation Testing

The soil zone is generally present within the first few inches to possibly tens of feet beneath the surface, the uppermost layer of the vadose zone. The soil zone is the fertile

[42] McColpin, L. 2009. Surface Deformation Monitoring as a Cost Effective MMV Method. Energy Procedia, 1, (2009) pp. 2079-2086
[43] Onuma, T, and Ohkawa, S. 2009 Detection of surface deformation related with CO_2 injection by D InSAR at In Salah, Algeria Energy Procedia, 1, (2009) pp. 2177-2184
[44] FutureGen Alliance. 2006. Mattoon Site Environmental Information Volume. Available at: http://www.futuregenalliance.org/news/fg_mattoon_eiv_v1_master_rev1.pdf

portion that can retain water (i.e., topsoil). A monitoring program in the soil zone can detect the vertical CO_2 flux. It is especially important in the soil zone that background levels (which vary with time of day and season) be determined to provide a well-characterized baseline against which statistically significant anomalies can be detected and estimated.

Accumulation chambers can be used to estimate CO_2 flux from the ground surface to the atmosphere, and be used to directly detect and quantify the mass of CO_2 leaking from the subsurface.[44] The approach may consist of a grid of accumulation chambers in which the CO_2 flux is periodically measured.[45] Commercially available accumulation chamber instrument packages are currently being used to track seasonal variations in CO_2 flux as part of climate change studies. The accumulation chamber is a method of measuring soil CO_2 flux that involves the placement of a collection chamber directly on or into the soil surface, with the rate of CO_2 accumulation measured periodically with an IRGA. The rate of change in CO_2 concentration defines the rate of flux. The calculated rate of flux can be used as a standalone quantification method if CO_2 leakage is detected. This type of measurement could be used to quantify leakage that is moving up through the soil zone across a wide area, as opposed to point sources such as a leaking injection well. To account for local variations in the underlying geologic, soil characteristics, and soil moisture levels, several accumulation chambers would have to be distributed over the area to quantify the leakage rate. CO_2 flux measurement systems based on accumulation chambers are commercially available and can provide a measurement of anomalous CO_2 flux at a point, with a precision better than 5 micrograms per square meter per second. That point measurement precision corresponds to a leak rate of 25,000 metric tons per year distributed across an area of 150 square kilometers.

Surface leaks detected in the soil zone may also be quantified through tenting methods, in which large tents (made of impermeable material) are used to capture and accurately measure the CO_2 leakage from a much larger soil surface area. Tenting methods have been used to detect CH_4 leaks from natural gas pipelines and could also be used for CO_2 quantification. Variations of this method are commonly used in measuring CH_4 flow rates from equipment leaks.[46] A tent or bag is constructed above a known leakage site. An inert gas such as nitrogen is conveyed through the bag at a known flow rate. Once the carrier gas attains equilibrium, a gas sample is obtained from the bag and the CH_4 content of the sample is determined. The leak flow rate is calculated from the purge flow rate through the enclosure and the concentration of CH_4 in the outlet stream. Table 4-2 illustrates the general approach to quantify the leak.

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[45] Oldenburg, C.M., Jennifer L. Lewicki, and Robert P. Hepple. 2003. Near-Surface Monitoring Strategies for Carbon Dioxide Storage Verification. Earth Sciences Division, Lawrence Berkeley National Laboratory, publication LBNL-54089. Available at: http://www.osti.gov/bridge/servlets/purl/840984-dTw752/native/840984.pdf.

[46] Envirotech Engineering. 2007. Review and Update of Methods Used for Air Emissions Leak Detection and Quantification. February 5th, 2007. Available at: http://eipa.alberta.ca/media/31357/1666%20review%20and%20update%20of%20methods%20used%20for%20air%20emissions%20leak%20detection%20and%20quantification%20-%20final%20report.pdf

Table 4-2: Example Leak Quantification Using Tenting and Known Test Gas Flow[47]

Inlet Flow of Conveyed Test Gas (cu. ft./minute)	Measured CO_2 Concentration at Outlet (%)	Calculated Outlet Flow Rate (cu. ft./minute)	Calculated CO_2 Leak Rate (cu. ft./minute)
10	50%	20	10
10	10%	11.1	1.1

This approach is limited to sampling a point source or small area of leakage. However, if the site of the leakage can be mapped by airborne methods such as are described below, it should be possible to set up a number of tent measurement locations such that the leaks over a large area can be quantified using statistical sampling. However, the cost and time to set up a large number of tents and/or accumulation chambers might favor the development and use of innovative mobile quantification methods (e.g., radial plume mapping with path-integrated optical remote sensing).

CO_2 in the shallow subsurface can also be detected through *shallow wells* drilled to sample the groundwater. Such wells may be on the order of only several hundred feet deep. Water samples collected from the wells are analyzed for a wide range of parameters that may reflect changes due to the presence of CO_2. Some indicator parameters such as pH, alkalinity, electrical conductance and dissolved oxygen can be measured in the field, and other parameters (trace metals, dissolved organic carbon, organic compounds and isotopes) are submitted to a laboratory for analysis. Pilot tests and controlled release experiments demonstrate that the rapid and significant changes in chemical parameters were observed in response to the presence of CO_2.[48] As with soil testing, background levels must first be established in order to detect changes that may indicate CO_2 leakage.

Vegetative stress can also be a leakage indicator. Vegetative stress can be detected through tower-mounted or airborne imaging instruments, such as digital color infrared orthoimagery or hyperspectral and multispectral imaging, to detect changes to vegetation coloration in the visible, infrared, and ultraviolet spectrum. These are relatively new technologies with uncertainty in the interpretation of the results. Recent work has shown that vegetation in the vicinity of a leak may be negatively affected, but vegetation farther from a leak may be positively affected.[49] A controlled release experiment at the Zero Emissions Research and Technology (ZERT) facility in Montana reported that the surface area of CO_2 leakage hot spots could be delineated to within 2.5 meters using portable hyperspectral imagers. The plant response was dependent on plant species but was discernable when soil concentrations reached 4 to 8 percent CO_2 concentration.[50]

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[47] The Calculated Outlet Flow Rate (cu. ft./minute) is inlet flow volume divided by concentration. The Calculated CO_2 Leak Rate (cu. ft./minute) is calculated as outlet flow minus inlet flow.

[48] Kharaka, Y., J. Thordsen, E. Kakouros, G. Ambats, W. Herkelrath, S. Beers, J. Birkholzer, J. Apps, N. Spycher, L. Zheng, R. Trautz, H. Rauch, and K. Gullickson 2009. Changes in the Chemistry of Shallow Groundwater Related to the 2008 Injection of CO_2 at the ZERT Field Site, Bozeman Montana. Environ. Earth Sci. (2010) 60:273-284

[49] Rouse, J.H. 2008. Measurements of Plant Stress in Response to CO_2 Using a Three-CCD Imager. Montana State University. Available at: http://etd.lib.montana.edu/etd/2008/rouse/RouseJ1208.pdf

[50] Male, E.J., W.L. Pickles, E.I. Silver, G.D. Hoffmann, J. Lewicki, M. Apple, K. Repasky, and E.A. Burton, Using hyperspectral plant signatures for leak detection during the 2008 ZERT CO_2 sequestration

4.5 Atmospheric Monitoring

The atmosphere above a GS site may be monitored with an array of CO_2 detectors (closed-path point measurements and open-path line measurements), tracer gas and CO_2 isotopic measurements, eddy covariance methods, Raman LIDAR (Light Detection and Ranging), or Differential Absorption LIDAR (DIAL). In all methods, CO_2 concentration data are integrated with data on wind speed and direction to determine the vertical CO_2 flux and locate the CO_2 leakage footprint. As noted previously, establishing baselines are important to distinguish between natural CO_2 fluxes and CO_2 flux due to leakage from geologic storage.[51]

CO_2 detectors are commercially available for short closed-path and short open-path (point) measurements, as well as long open-path (radial line) measurements. Similar detectors have been integrated into stationary, mobile, and airborne monitoring packages that are commonly used in combination with high-resolution GPS to detect and quantify CH_4 leaks in areas with road access. While these packages have not been widely tested for CO_2, various types of CO_2 monitors are commercially available, generally relatively low cost, reliable, and could be used in these applications. The technologies include IRGAs (including Fourier transform infrared (FTIR) and non-dispersive infrared analyzers), tunable diode lasers (TDLs), cavity ring-down techniques, and others. The sample path can range from 10 cm to 1 km, by reflecting a laser beam off retro-reflecting mirrors. These devices measure the gas concentration, and, when packaged with measurements of wind speed and wind direction, they measure the total gas flow. The method is described in detail in EPA Other Test Method 10 —Optical Remote Sensing for Emission Characterization from Non-Point Sources.[52] The protocol describes three methodologies, each for a specific use:

- Horizontal radial plume mapping (for locating the source of emissions or hot spots);
- Vertical radial plume mapping (for estimating the rate of gaseous emissions from an area fugitive emission source); and
- One-dimensional radial plume mapping (for profiling pollutant concentrations along a line-of-sight which is downwind of an emission source).

These methodologies use an open-path path-integrated optical remote sensing system in multiple beam configurations to measure path-integrated concentration data. The protocol suggests four scanning systems:

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field experiment in Bozeman, MT. Environmental Earth Sciences, 60, 251-261, doi: 10.1007/s12665-009-0372-2, 2010.

[51] David Etheridge, Ray Leuning, Donald de Vries, Kevin Dodds, Cathy Trudinger, Colin Allison, Paul Fraser, Fred Prata, Cirilo Bernardo, Mick Meyer, Bronwyn Dunse and Ashok Luhar. 2005. Atmospheric monitoring and verification technologies for CO_2 storage at geosequestration sites in Australia. CO2CRC Report No: RPT05-0134, Prepared by CSIRO Marine and Atmospheric Research for CANSYD Australia and the CRC for Greenhouse Gas Technologies (CO2CRC). Available at: http://www.co2crc.com.au/publications/index.php.

[52] http://www.epa.gov/ttn/emc/prelim.html.

- Open-Path FTIR Spectroscopy;
- Ultra-Violet Differential Optical Absorption Spectroscopy;
- Open-Path TDL Absorption Spectroscopy; and
- Path-Integrated Differential Absorption LIDAR.

EPA is also testing mobile versions of these systems for methane leak detection, in which the detectors are integrated onto ground or airborne vehicles with high-resolution GPS to aim the lasers at the retro-reflectors and correctly locate the methane leak.

Other atmospheric monitoring for leakage detection and quantification approaches include *tracer gases* and *CO_2 isotopic measurements*. The incorporation of trace amounts of chemical compounds into the injected CO_2 may be useful in circumstances in which a suitable baseline for a natural parameter (e.g., soil CO_2 flux or surface-to-atmosphere CO_2 flux) cannot be established due to the parameter's wide and unpredictable natural variation. In such cases, tracers could be added to the injected CO_2 and continuous or periodic monitoring could be conducted to determine if the tracer could be identified outside the IZ in water, soil or air. The UIC Class VI rule does not require the use of tracers.

Tracers can be manmade molecules such as perfluorocarbons (PFCs) and sulfur hexafluoride, or noble gases such as helium (He), argon (Ar), and xenon (Xe), including specific isotope concentrations. Tracers can be detected at levels of a few parts per billion or even parts per trillion.

PFC tracers have been applied in several pilot studies and experimental tests and appear to have good detection capabilities for leakage detection and potentially for quantification in both soil gas[53] and the atmosphere.[54] The CO_2 injection pilot test at West Pearl Queen ER site in New Mexico used PFC tracers to detect and quantify leakage from injection wells at soil gas monitoring points within 300 meters of the injection well.[55] PFC tracer analysis has also been used in monitoring wells in the IZ to map the location of the advancing CO_2 plume[56] in the Frio Brine Test, and to monitor for potential surface leakage at the Zama Acid gas injection project in Alberta.[57]

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[53] Strazisar B.R., Wells A.W., Diehl J.R. (2009) Near surface monitoring for the ZERT shallow CO2 injection project. Int J Greenh Gas Control 3(6):736–744. doi:10.1016/j.ijggc.2009.07.005

[54] Wells, Arthur, Strazisar, B., Diehl, J., and Veloski, G. 2010. Atmospheric tracer monitoring and surface plume development at the ZERT pilot test in Bozeman, Montana, USA, Environ. Earth Sci. Volume 60, Number 2, 299-305, DOI: 10.1007/s12665-009-0371-3

[55] Arthur W. Wells, J. Rodney Diehl, Grant Bromhal, Brian R. Strazisar, Thomas H. Wilson, Curt M. White. 2007. The use of tracers to assess leakage from the sequestration of CO_2 in a depleted oil reservoir, New Mexico, USA. *Applied Geochemistry*, Volume 22, Issue 5, May 2007, Pages 996-1016, ISSN 0883-2927. Available at: http://www.sciencedirect.com/science/article/B6VDG-4N3GFGS-3/2/f16a133a1eda34353e1cbcc8dd05c917.

[56] McCallum, S.D., Riestenberg, D.E., Cole, D.R., Freifeld, B.M.,Trautz, R.C., Hovorka, S.D., and Phelps, T.J. 2005. Monitoring Geologically Sequestered CO_2 during the Frio Brine Pilot Tests Using Perfluorocarbon Tracers. Fourth Annual Conference on Carbon Capture and Sequestration, May 2005.

[57] Smith, Steven A., J.A. Sorensen, A.A. Dobroskok, B. Jackson, D. Nimchuck, E. N. Steadman, and J. A. Harju. 2009. Injection of Acid Gas (CO_2/H_2S) into a Devonian Pinnacle Reef at Zama, Alberta, for

The amount of tracer added to the injected CO_2 will depend on the minimum detectable amount within the medium to be monitored and the probable leakage volumes and dispersion patterns for the relevant leakage pathways. It also depends on how the tracers will move along the leakage pathway relative to the leaking CO_2. Therefore, if tracers are proposed to be used, the monitoring strategy should consider the proposed tracers characteristics in terms of:

- dissolution in water more/less than CO_2;
- sorption into coals/shales more/less than CO_2;
- chemical reactions with fluids and rocks; and
- physical separation due to differences in molecular size and weight.

In some cases, tracers can move more quickly than the CO_2 and will reach sensors or sample collection points well before any CO_2 leak. In other instances a tracer might be trapped along the leakage pathway, reducing its effectiveness. Certain tracers are GHGs and if leaked, would contribute to total GHG emissions.

Another consideration for tracers is the possibility of contamination of sensor locations or sample collection point through:

- spills during transport and loading of the tracer;
- equipment leaks and vented emissions from surface equipment;
- equipment (tubing) brought to surface for repair and replacement;
- fluid retrieved from IZ for analysis; and
- old leaks that have been repaired.

Therefore a monitoring strategy that includes the use of tracers should include ways of preventing contamination by misplaced tracers through careful design of where and how tracers are injected and how equipment and fluids that contact the tracers are handled. Considerations should be made on what could be done in the event of contamination including options for:

- moving sampling point away from contaminated locations (e.g., from surface to subsurface);
- changing type of tracer used; and
- measuring a tracer “baseline” and looking for deviations from the baseline.

Alternatively, CO_2 isotopic measurements are able to distinguish between CO_2 derived from fossil fuels and naturally occurring atmospheric and underground CO_2. Researchers in Australia note that even relatively large leaks at the well could dissipate rapidly away from the source and be indistinguishable from background concentrations of CO_2. They suggest that the use of radioactive tracers or natural carbon isotope ratios in the sequestered fluids will improve detection sensitivity. [58] Field studies of carbon ratios in injected and recovered CO_2 have been conducted at Weyburn-Midale CO_2 Monitoring and Storage Project (Saskatchewan), the Pembina Cardium CO_2 Monitoring Project (Alberta), and the Lost Hills oil field (California). Recently a commercially available carbon isotope instrument was modified for portable use and deployed during the controlled release field tests at the ZERT site in Bozeman Montana.[59] The advantage of the technique is that it provides essentially real time results of the carbon isotope concentrations across a potential leak location. The results showed that the portable instrument was capable of real time spatially distributed measurements of carbon isotopes to detect leakage for a subsurface source. The authors note that other techniques would need to be used to quantify the leakage rate and background fluxes may complicate the interpretation of results.

Eddy Covariance systems can measure the vertical CO_2 flux in the atmosphere. They combine an open-path IRGA on a tower alongside a sensitive, high-speed, 3-D anemometer, a device used for measuring instantaneous wind speed and direction. Time series data are recorded and evaluated using computer methods. The size and shape of the sampling footprint (the surface area that is sampled by the instrument) is derived mathematically from the anemometer data. A typical station consists of sensors mounted on a tower from several meters to 30 meters or more high. The stations can be operated with solar power and can be set up for data telemetry for transmission to a central facility. Deployment of a grid of such detectors over an area provides information regardless of wind direction. CO_2 concentration data are integrated with meteorological data including wind speed and direction, relative humidity, and temperature.

Such methods have the ability to measure CO_2 concentration in the atmosphere over relatively large areas. A limitation of the method is that it assumes a horizontal and homogeneous surface to interpret the data. Variations in plant cover, land use, and topography may create challenges. As with soil sampling, the rate of leakage of CO_2 from the site must be a statistically significant anomaly above the background variability. Therefore, to provide the required precision, eddy covariance towers would have to collect data over an appropriate time period to provide a baseline which includes diurnal and seasonal variations. With careful installation and the collection of baseline data, the eddy covariance method can potentially provide a precise average of CO_2 flux over a large surface area. Although eddy covariance systems are currently research tools assembled from a variety of commercially available components, the eddy covariance method may eventually provide the anomalous CO_2 flux averaged over a large surface area, with an precision less than 50 micrograms per square meter per second, which

[58] Paul Steele, Zoë Loh, David Etheridge, Ray Leuning, Paul Krummel, Aaron Van Pelt. 2008. Continuous Greenhouse Gas and Isotopic CO_2 Measurements via WS-CRDS-based Analyzers: Investigations in Real Time Monitoring at CO2 Geological Storage Sites. Presented at American Geophysical Union, Fall Meeting 2008, abstract #U41C-0024, poster available at: http://www.picarro.com/assets/docs/AGU_poster_sequestration.pdf

[59] Krevor, S., Perrin, J.-C., Esposito, A., Rella, C., Benson, S., 2010. Rapid detection and characterization of surface CO_2 leakage through the real-time measurement of [delta]13 C signatures in CO_2 flux from the ground. International Journal of Greenhouse Gas Control 4, 811-815.

corresponds to a leak rate of 25,000 metric tons per year distributed across an area of 17 square kilometers.

Another potential technology for measurement of CO_2 in air is Raman *LIDAR*. LIDAR is the optical analog of radar, and it is based upon the use of laser radiation to measure various compounds in the air, including CO_2. The Raman LIDAR method involves transmitting laser light into the atmosphere and then detecting the scattered laser radiation that has been shifted in wavelength due to interaction with the target scattering molecules (e.g., CO_2) along the resolved path length. By comparing the Raman signal of the CO_2 to the Raman signal of nitrogen or oxygen, a direct measurement of CO_2 concentration can be obtained.

A similar method, *DIAL*, would use two wavelengths of laser light to measure the CO_2 concentration in the atmosphere. The wavelengths used are specific to CO_2. One wavelength is selected to correspond to a CO_2 spectral absorption line, while the other is a non-absorbing wavelength. The average CO_2 concentration over the path length can be determined from the ratio of the backscatter signals for the two laser wavelengths. The instrumentation for both methods (Raman LIDAR and DIAL) can be ground, truck, helicopter, or airplane mounted and can provide similar precision at similar cost. Truck methods can cover up to tens of square kilometers per day. Helicopter and airplane mounted platforms can cover a much larger area.

Airborne DIAL methods are currently in use for methane leakage detection along natural gas pipelines.[60] Instrumentation includes the LIDAR, a digital mapping camera, a color video system, and an optical guidance system. The airplane flies a survey over the pipeline at an altitude of about 1,000 feet, approximately perpendicular to the wind direction. The LIDAR instrumentation measures the concentration of methane by measuring how much of the reflected laser pulse has been absorbed. These data could be integrated with real time wind direction and velocity to define the leakage footprint and estimate a leakage rate.

While DIAL is commercially available for methane, Raman LIDAR and DIAL are currently under development for commercial CO_2 applications. Etheridge[61] reports that ground-based and airborne LIDAR and DIAL technologies appear to be feasible technologies when used in conjunction with other sources of information, however additional research is needed to improve precision for measuring and monitoring leaks at geosequestration sites. Researchers at Montana State University are developing and testing a portable DIAL with the ability to monitor several square kilometers at a

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[60] Brake, D. 2005. Detection and Measurement of Fugitive Emissions Using Airborne Differential Absorption Lidar (DIAL). EPA Gas Star Program Annual Implementation Workshop. Available at: http://www.methanetomarkets.org/expo_china07/docs/postexpo/oag_brake.pdf

[61] Etheridge, D, Leuning, R, de Vries, D, Dodds, K, Trudinger, C, Allison, C, Fraser, P, Prata, F, Bernardo, C, Meyer, M, Dunse, B and Luhar, A, 2005. Atmospheric monitoring and verification technologies for CO2 storage at geosequestration sites in Australia. Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia, CO2CRC Publication Number RPT05-0134. 83pp. Available at: http://www.co2crc.com.au/publications/index.php.

resolution on the order of 100 m.[62] Airborne methods may also be integrated with ground methods to provide the best approach for quantification. Airborne methods could be used to map out the surface leakage area, and ground methods (such as accumulation chambers and tents) could be installed on the surface leakage area to measure the combined background and anomaly CO_2 flux and outside the surface leakage area to measure just the background CO_2 flux.

4.6 Leakage Detection and Quantification in the Offshore Environment

Reservoir modeling and monitoring techniques, such as seismic and monitoring wells, can also be applied to the detect leakage in subsurface geologic formations and shallow ocean bottom sediments located offshore. However, the fate of the CO_2 entering the ocean from an offshore geologic formation is dependent on the temperature, pressure, and CO_2 flux, and may result in the formation of CO_2 hydrates, may dissolve into the seawater, or may be released into the atmosphere. Shallow monitoring systems aim to detect and quantify CO_2 that has migrated into the shallow sediments and related water bearing strata or seabed, and, ultimately, into the seawater or atmosphere. Shallow monitoring includes those methods that detect and measure CO_2 in the subsurface (e.g., potable aquifers, soil, sub-seabed) and those that actually measure CO_2 in the water column or atmosphere.[63]

Sparker surveys detect reflections of acoustic signals produced from electro-capacitive sources that penetrate several hundred meters beneath the seafloor. *Boomer* surveys detect reflections of acoustic signals produced from electromagnetic (EM) sources that penetrate about 100 meters beneath the seafloor. Both methods can potentially resolve bed thickness of a meter or less, and would likely have considerable potential for resolving small amounts of gas. However sparker and boomer data are acquired along 2-D profiles, which render them less effective for systematic areal detection of undiscovered leaks. Their main use may lie in high-resolution imaging of shallow features previously detected on 3-D conventional data.

Shallow sedimentary deposits can also be examined using *high-resolution acoustic imaging*. The technique should reveal anomalous features in the top 100 meters beneath the seafloor as well as direct imaging of rising gas bubbles in the water column. Transducers such as Compressed High Intensity Radar Pulse Sonars, operating at frequencies between 2 and 8 kilohertz, have been widely employed on the continental margins, and have also been used to map glacial and other sedimentary deposits in shallow water. These techniques are potentially very useful for shallow storage monitoring. They offer high-resolution profiling of seabed morphology but also have sufficient depth penetration to identify anomalous features in the subsurface; for example,

[62] DOE/NETL, 2010, Development and Deployment of a Compact Eye-safe Scanning Differential Absorption Lidar (DIAL) for Spatial Mapping of Carbon Dioxide for MVA at Geologic Carbon Sequestration Sites, Project 642, March 2010 http://www.netl.doe.gov/publications/factsheets/project/Project642.pdf

[63] Cleaner Fossil Fuels Programme, 2005. Monitoring Technologies for the Geological Storage of CO_2. Technology Status Report, DTI/Pub URN 05/1032, Didcot, Oxfordshire, UK, March 2005. Available at: http://www.co2net.eu/public/reports/tsr025abc.pdf.

zones of acoustic blanking interpreted as signifying high gas saturations. The techniques can also permit direct imaging of gas plumes in seawater.

Several *acoustic sonar bathymetric systems* have been developed to provide area mapping of sea bed bathymetry, resolving features as small as 1 cm, such as pockmarks on the seafloor and free gas in the water column. Naturally occurring pockmarks and shallow gas chimneys may act as potential pathways for CO_2 leakage. Two principal types are available: *sidescan sonar* using piezoelectric transducers mounted on towfish,[64] and *multibeam echo sounding* using magneto-restrictive transducers from ships.

Multibeam echo sounders integrate bathymetric and backscatter information and can provide a highly efficient way of obtaining very useful views of the sea floor. A multi-beam echo sounder may be considered as a series of around 100 single-beam echo sounders, mounted in a fan-shaped array on either side of a ship collecting echoes from the entire swath width as the ship advances. The fan is narrow in the fore and aft direction, typically 1.5 degrees, and wide in the port and starboard direction—around 120 degrees. For each beam, the system reports depth and the echo maximum amplitude over time. This allows the detailed mapping of the seafloor bathymetry and inferences about the nature of the sediment.

Electrical and EM methods offer the theoretical potential for low-resolution, low-cost, site monitoring. The techniques utilize the propagation of electrical or EM fields within the earth to map subsurface variations in electrical conductivity. A distinction can be made between electric methods that use zero frequency (DC) or very-low-frequency methods, where no EM induction occurs, and EM techniques that use frequencies where time-variant source fields induce secondary electrical and magnetic fields that carry information about subsurface electrical structure. CO_2 is resistive, so electrical/EM methods are likely to be suitable for monitoring storage in saline formations where CO_2 is displacing more conductive formation waters. Placing the electrical sources or receivers (or both) in the subsurface, within or around the storage reservoir, radically increases spatial resolution while reducing power requirements. Downhole configurations seem to offer the greatest potential for useful offshore application.

Recent developments of *sea floor EM systems,* previously used (typically) for deep-water tectonic studies, have led to "direct-detection-of-hydrocarbons" systems. Two of the most advanced systems are referred to as SeaBed Logging[65] and Offshore Hydrocarbon Mapping[66]. The systems consist of towed Controlled Source transmitters and static sea-bed receiver arrays. The source is a horizontal electric dipole, towed behind an

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[64] A towfish is an underwater equipment package towed a few hundred feet above the seafloor using an umbilical cable connected to a support craft.

[65] Ridyard, D. 2007. Seabed Logging – A Proven Tool for Offshore Exploration and Development. Summarized from a Presentation given to AAPG European Region. Search and Discovery Article #40277 (2008) Posted January 31, 2008. Available at: http://www.searchanddiscovery.net/documents/2008/08008ridyard/images/ridyard.pdf.

[66] Greer, A. MacGregor, L. Weaver, R. 2003, Remote mapping of hydrocarbon extent using marine Active Source EM Sounding EAGE 65th Conference & Exhibition — Stavanger, Norway, 2 - 5 June 2003.

instrumented towfish on a neutral buoyant streamer. During a survey the source is towed around and through the array of receivers that each measure 2 or 3 orthogonal components of the electric field. The technique is sensitive to thin resistive anomalies at depths between several tens of meters and several kilometers. Recent surveys have successfully determined the presence and absence of hydrocarbons within reservoirs. Direct detection of resistive CO_2 zones within more conductive lithologies would, theoretically, be possible.

Technologies to monitor surface *seawater geochemistry*, coupled to hydrographic and meteorological conditions advanced significantly in the 1990s in an effort to understand the role oceans play in global carbon budgets and the relative size and directions of carbon (mainly CO_2) fluxes between the sea, the atmosphere and the sediment. These technologies are relatively well tested and are deployed extensively across the world, often routinely on ships regularly crossing oceans. A sensitive pH sensor for marine studies has recently been developed in the United Kingdom and would be useful to monitor changes in seawater pH resulting from CO_2 leaks. Four parameters are typically measured that, together with ancillary information such as temperature, pH, and salinity etc., can be used to describe the CO_2 system in a given sample. These parameters are: total DIC (a measure of the concentrations of CO_2 (aq), H_2CO_3 (aq), HCO_3^{-} and CO_3^{2-}), total alkalinity (a form of mass-conservation relationship for the hydrogen ion), fugacity of CO_2 in equilibrium with seawater (a measure of the partial pressure of CO_2), and total hydrogen ion, primarily controlled by total sulfate concentration.

Seawater samples obtained at depth, which are more appropriate to the needs of monitoring for CO_2 escape, require the pressure to be maintained in order to ensure that degassing does not occur. One such gas-tight sampling device has been developed to obtain fluids samples (both waters and gases) at elevated temperatures and pressures. A key feature is that fluid within the chamber is maintained at seafloor pressures during sampling, allowing fluid aliquots to be withdrawn for an almost unlimited number of analytical techniques without degassing the remaining fluid.

4.7 Detection Range, Accuracy and Precision of Various Monitoring Technologies

Each of the monitoring methods discussed above involves the application of technologies to detect and quantify CO_2 leakage. Monitoring is effective in detecting the presence of both subsurface and atmospheric leakage. Methods of surface leak quantification continue to be an active research area.

The ability to detect or quantify a plume or leak is dependent upon factors such as the rate of leakage, its depth and location, the atmospheric background CO_2 variability, the number and distribution of sampling stations, and the limits of the technology itself. Each technology typically has strengths and weaknesses, and only a combination of approaches is expected to ensure reliable monitoring and leak detection.

To evaluate the capabilities of monitoring technologies, one must look at the theoretical limits of CO_2 detection, the size of anomaly that can be detected, and the precision and accuracy of the method. Table 4-3 presents this information for a number of technologies that can potentially be used for leak quantification. [67, 68, 69, 70] The terminology in the table is as follows:

- Sampling rate. The frequency of sampling.
- Detection range. The instrument detection limit or a range of instrument detection limits in appropriate units for the instrument.
- Anomaly detection threshold. The size of the CO_2 anomaly that can be detected under typical background conditions.
- Precision. The degree of mutual agreement among a series of individual measurements.
- Accuracy. The degree of conformity of a measured quantity to its actual value.

Table 4-3: Detection Range, Accuracy, and Precision of Various Monitoring Technologies

Technology	Reference	Sampling rate	Detection Range	Anomaly Detection Threshold	Precision	Accuracy	Comments
Pressure gauges in monitoring wells	1, 4	Continuous	NA	0.1 psi change	NA	NA	Established and reliable.
3-D seismic	1, 4	Periodic surveys	NA	1,000 to 10,000 metric ton accumulations	NA	+/-20% of plume vol.	Established technology; expensive, resolution decreases with depth. Cannot image dissolved CO_2.
Eddy Covariance	1, 2, 4	Continuous	>10 microgram / m^2/ sec	>45 microgram/sq. m/sec	5 - 30% of the CO_2 flux	NA	Commercially available technology used in other fields; signal to noise challenges
CO_2 Detectors (closed path and open path)	2	1 - 10 Hz during sampling	0 - 3,000 ppmv	NA	0.2 ppm at 350 ppm CO_2 concentration	NA	Established technology; Portable and inexpensive.
Accumulation Chamber	2, 3, 4	Continuous	>0.46 micrograms/ m^2/ sec	NA	10% of the CO_2 flux	12.5% of the CO_2 flux	Commercially available technology;

[67] Benson, S.M. 2006. Monitoring Carbon Dioxide Sequestration in Deep Geological Formations for Inventory Verification and Carbon Credits. Society of Petroleum Engineers Paper 102833, 14pp. Available at: http://www.energy.utah.gov/Utah_Actions/documents/dec2006/spe102833.pdf.
[68] Oldenburg, C.M., J.L. Lewicki, and R.P. Hepple. 2003. Near-Surface Monitoring Strategies for Geologic Carbon Dioxide Storage Verification. Report #LBNL 54089, Lawrence Berkeley National Laboratory, Berkeley, CA, October 30, 2003. Available at: http://www.osti.gov/bridge/servlets/purl/840984-dTw752/native/840984.pdf.
[69] IPCC. 2006. 2006 IPCC Guidelines for Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change, Simon Eggleston, ed. Available at http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html.
[70] DOE. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. Available at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

							Many sampling stations needed; average data from multiple chambers; samples small area; signal to noise challenge.
Raman LIDAR and DIAL	2, 4	Continuous or periodic	<1ppmv to several % CO_2	**NA**	1 - 5% of the CO_2 concentration	**NA**	Technology available for methane; CO_2 technology under development; Very large sampling area; long range; Precision of 3-27 ppm at 1 km path length

References:
1. Benson, S.M. 2006. Monitoring Carbon Dioxide Sequestration in Deep Geological Formations for Inventory Verification and Carbon Credits. Society of Petroleum Engineers Paper 102833, 14pp. Available at: http://www.energy.utah.gov/Utah_Actions/documents/dec2006/spe102833.pdf.
2. Oldenburg, C.M., J.L. Lewicki, and R.P. Hepple. 2003. Near-Surface Monitoring Strategies for Geologic Carbon Dioxide Storage Verification. Report #LBNL 54089, Lawrence Berkeley National Laboratory, Berkeley, CA, October 30, 2003. Available at: http://www.osti.gov/bridge/servlets/purl/840984-dTw752/native/840984.pdf.
3. IPCC. 2006. 2006 IPCC Guidelines for Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change, Simon Eggleston, ed. Available at: http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html.
4. DOE. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. Available at: http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

5. Monitoring, Reporting, and Verification Plans

Facilities conducting GS are required to develop and implement an EPA-approved MRV plan that includes the following five major components (which are identified at 40 CFR 98.448):

- Delineation of the maximum monitoring area (MMA), and active monitoring areas (AMAs);
- Identification of the potential surface leakage pathways and an assessment of the likelihood, magnitude, and timing of surface leakage of CO_2 through these pathways;
- Strategy for detection and quantification of surface leakage;
- Approach for establishing the expected baselines; and
- Considerations made to calculate site-specific variables for the mass balance equation.

Chapters 5.1 through 5.5 describe these MRV plan requirements and present considerations for developing site-specific MRV plans. For each requirement, the chapter lays out key information that may address the requirement, and provides illustrative examples and metrics to help the reporter determine the level of performance necessary to design and implement a system that meets the regulatory requirements. Examples are provided throughout the chapter to illustrate how these requirements may be addressed under different scenarios.

In the MRV plan, the reporter should show that the approach taken to address each MRV plan component provides an adequate level of assurance that the regulatory requirement will be met. This assurance could include a demonstration that the statistical basis of the monitoring strategy or the quantification method meets a certain level of performance. In some cases the MRV plan may not include specific details of implementation because there are many site-specific or event-specific factors that will influence the selection of a particular method or technology. For example, prior to writing the plan the reporter will not know the exact location or cause of a future surface leak, and therefore should provide a description of the process and tools used to detect and quantify the potential leaks. The reporter should provide the process and decision rationale for how such event-specific decisions will be made.

EPA is taking this site-specific flexible approach for three reasons. First, each facility will have a unique set of geologic, environmental, and operational conditions that are best addressed with site-specific solutions to satisfy each MRV requirement. Second, as projects mature, reporters will collect new information and may choose to improve their conceptual site models and modify their monitoring, modeling, and evaluation techniques. Third, EPA recognizes that the uncertainties and inherent variability in the natural systems will necessitate modifications to the selected methods and approaches over time and in response to unexpected events.

The site-specific approach also allows the reporter to leverage the site characterization, modeling, and monitoring approaches (e.g. monitoring of injection pressures, injection well integrity, groundwater quality and geochemistry, and CO_2 plume location, etc.) developed for their UIC permit. The UIC Class VI permit (including the Testing and Monitoring plan) and subpart RR MRV plan have separate monitoring objectives. Requirements under the UIC program are focused on demonstrating that underground sources of drinking water (USDWs) are not endangered as a result of CO_2 injection into the subsurface, while requirements under the GHG Reporting Program through subpart RR will enable reporters to quantify the amount of CO_2 that is geologically sequestered. However, monitoring approaches and technologies employed for these two objectives may overlap. The MRV plan submitted for subpart RR may describe (or provide by reference to the UIC permit) the relevant elements of the UIC permit (e.g. assessment of leakage pathways in the monitoring area) and how those elements satisfy the subpart RR requirements.

Beyond describing how the existing or planned UIC monitoring procedures form the basis for fulfilling the subpart RR leakage detection requirements, the subpart RR MRV plan should show how any detected anomalies would be further studied to verify and then quantify leakage. Leakage verification and quantification could include more frequent monitoring, denser spatial coverage, or the deployment of additional monitoring technologies.

For more information on UIC regulations, including requirements and guidance documents, please go to http://water.epa.gov/type/groundwater/uic/index.cfm.

5.1 Delineation of the MMA and AMA

The MRV plan must include a delineation of the area that will be monitored. The maximum areal extent of the plume area of the life of the project should be determined using a reservoir simulator model informed by site characterization data and monitoring results. Reservoir modeling or simulation is a powerful mathematical tool that is used to evaluate the movement of injected CO_2 in the reservoir, to predict the size and location of the plume, and is an integral aspect of project design, planning, site characterization, and monitoring program design.[71] An initial model can be used to forecast how the plume is expected to move and change. After the beginning of injection, the data from the injection well and data from the other types of monitoring should be used to calibrate and history-match the model.

Reservoir modeling has been in use for decades in the oil and gas industry, and is used to design the development of fields, and is applied at GS sites. The model is a 3-D construct of the subsurface reservoir, and uses a numerical approach in which the reservoir is divided into a large number of discrete 3-D volumes for analysis. Input data include reservoir thickness, depth, pressure, porosity, permeability, fluid saturations, and other

[71] DOE. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

parameters. Each 3-D volume has its own specific characteristics. In the case of GS, the model is set up using all available data, and the model is run to estimate future movement of CO_2 through the reservoir. The model is then calibrated and updated through time as the injection proceeds. This is accomplished through history-matching of actual subsurface data, such as pressure or the detection of CO_2.

There are three general types of simulation models used for GS: multiphase fluid flow models, reactive transport models, and geomechanical models.[72] The simulators allow the prediction of the following:

- Temporal and spatial migration of the plume;
- Geochemical reactions;
- CZ and wellbore integrity;
- Potential leakage pathways and estimates of travel times for these routes;
- Effects of unplanned hydraulic fracturing;
- Potential leakage near the injector well; and
- Consequences of wellbore failure.

Like all numerical models, reservoir simulation models for GS are not an exact representation of the subsurface reality, but provide an approximation of the conditions throughout the reservoir based on the given input values and the computational codes used in the simulation. Some uncertainty is inherent in the model output as a result of uncertainties related to the construction of the underlying governing equations, and uncertainties in the values used to represent the actual site conditions[73]. The accuracy of the model will improve as model input parameters more accurately reflect the actual subsurface conditions within the modeled area. It is important, therefore, for reporters to evaluate the accuracy of the model, and identify the input parameters which are most sensitive to the model output. Developing accurate input values for the most sensitive parameters will improve the models predictive accuracy. The model input parameters may need to be updated often to reflect new information gained from the operation of the GS project.

A recent evaluation of advances in numerical modeling by Michael et al.[74,75] notes that significant improvements have been made in the numerical models particularly in the linking of geochemical, geomechanical, and flow models to predict reservoir performance. The authors also note, however, that relative permeability and residual CO_2 saturation are sensitive input parameters for accurate reservoir models and need to be better constrained with data from current projects. The evaluation also notes that there is

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[72] DOE. 2009. Best Practices for Monitoring, Verification, and Accounting for CO_2 Stored in Deep Geologic Formations. U.S. Department of Energy, National Energy Technology Laboratory. http://www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf.

[73] US EPA, 2003. Draft Guidance on the Development, Evaluation, and Application of Regulatory Environmental Models. Prepared by The Council for Regulatory Environmental Modeling.

[74] Michael, K., Arnot, M., Cook, P., Ennis-King, J., Funnell, R., Kaldi, J.G., Kirste, D., Paterson, L., 2009. CO_2 storage in saline aquifers I—current state of scientific knowledge. Energy Procedia 1, 3197–3204.

[75] Michael, K., Golab, A. Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S., and Aiken, T.2010. Geological storage of CO_2 in saline aquifers – A review of the experience from existing storage operations

limited data from post injection monitoring to calibrate models for the long term assessment of reservoir conditions.

As described below, subpart RR requires that two monitoring areas be delineated: the MMA and the AMAs.

5.1.1 Maximum Monitoring Area (MMA)

Under 40 CFR 98.448(a)(1) the reporter will need to establish the maximum areal extent of the injected CO_2 over the life of the project, including the post-injection period, to define boundaries for monitoring leakage. This boundary is used to help define the MMA. The MMA is defined as equal to or greater than the area expected to contain the free-phase CO_2 plume until the CO_2 plume has stabilized, plus an all-around buffer zone of at least one-half mile. The buffer is intended to encompass leaks that might migrate laterally as they move towards the surface. EPA has determined that a buffer zone of at least one-half mile will have an acceptable probability of encountering leaks in many circumstances. In some cases the use of a one-half mile buffer zone may not account for uncertainties in the subsurface conditions, or may not incorporate potential leakage risks from faults and fractures that extend into the edge of the modeled MMA, and the buffer zone should be expanded.

For example, if there is a specific leakage pathway or a pronounced regional dip that might carry a leak further, the buffer zone should be expanded beyond one-half mile. The reporter should derive the MMA from site characterization, monitoring, and models. The MRV plan should describe the rationale for how the MMA was determined, including a discussion of the uncertainties of the models and buffer zones.

In order to determine the MMA, the reporter should estimate, by modeling, the future area of the free-phase plume. The geometry of the free-phase plume will be a function of the amount and rate of CO_2 injected, as well as the geologic characteristics of the IZ including the CZ geometry, IZ thickness, permeability, and porosity, and the amount of anisotropy within the IZ. The resolution of the reservoir model used to predict plume behavior will also influence the delineation of the area of free-phase CO_2. A model that can predict characteristics of thin layers at the upper boundary of the IZ, or predict the presence of lower CO_2 saturations, may be able to resolve a larger area of free-phase CO_2. The reporter should describe the rationale for defining the free-phase plume boundary by presenting the results of the reservoir simulation including the minimum CO_2 saturation that defines free-phase, and the thickness of the zone over which the saturation is estimated. The determination of both minimum saturation and saturated thickness help define the plume edge.

Plume stabilization is the basis of the free phase plume boundary and depends on the rate of movement of the free-phase CO_2 and the moderation of pressures within the free-phase plume. The reporter should define what criteria will be used to determine when the free-phase plume is to be considered stable. For example, this could be stated in terms of when the rate of movement of free phase CO_2 is less than a certain value (X foot per year), in any direction, greater than the natural (or not influenced by the site) hydrodynamic movement of the IZ, and the pressure change within the reservoir is less than a certain value (Y psi per year). The values of fluid movement and pressure would be generated from runs of the reservoir model. The values that define plume stability should be consistent with the proposed monitoring and modeling methods.

The reporter should redefine the MMA to reflect changes to the plume area if observations of the plume extent are significantly different from the modeled or expected extent and should also resubmit the MRV plan (see Chapter 6.7).

5.1.2 Active Monitoring Area (AMA)

It may not be practical or cost-effective to implement a full-scale monitoring program for the entire MMA when in the early years of operation the free-phase plume covers only a small portion of the MMA. The deployment of monitoring locations may be phased in over time to include those areas where the potential leakage may occur. The AMA is the part of the project area that will employ the monitoring methods and systems described in the MRV plan for a period of time less than the life of the project but greater than a year. Over the life of the project there will likely be several monitoring phases, each with an AMA that will increase in size as the plume expands. The MRV plan should describe the area and duration of each AMA as defined by the reporter, and should be determined using the most recent monitoring and characterization data available. The MRV plan should include a description of how the AMA was determined.

To ensure that the proposed leak detection monitoring systems provide adequate coverage, the AMA must extend beyond the modeled plume position at the end of the monitoring period. The AMA is established by superimposing two areas: the first is a one-half mile buffer zone around the outline of the anticipated plume location at the end of the AMA period, and the second is the area projected to contain the free-phase CO_2 plume five years after the end of the AMA. The area encompassed by either or both of the two areas will represent the AMA.

Subpart RR requires that the AMA be larger than the projected free-phase plume, for two reasons. First, there may be uncertainty in the projected plume location, given uncertainties in the characteristics of the IZ. The biggest element of uncertainty may be the “storage efficiency” of the IZ, or what portion of the pore space will be filled with CO_2 versus the portion that still will contain naturally occurring saline fluids. This uncertainty will be greatest at the start of injection and will be reduced over time as the reservoir simulation models are calibrated through history-matching of observed plume migration. The initial AMA must encompass the area that the free-phase plume is expected to occupy five years beyond the end of the initial monitoring period, so as to account for this IZ-related uncertainty in reservoir characteristics.

The second reason why the AMA needs be larger than the expected free-phase plume area is that any CO_2 leaks from the IZ will not necessarily follow a straight path upward to the surface. The flow path of leaking CO_2 will be influenced by buoyancy forces that move the CO_2 laterally in an up-dip direction, via hydrogeologic pressure differences. The leaked CO_2 will tend to follow formation fluid movements, or geologic features such as reservoir heterogeneities or faults that may produce circuitous upward leakage pathways. Therefore, a monitoring buffer around the free-phase plume needs to be applied. To account for sites where lateral movement of the plume will be controlled by structural features (and where the free-phase plume five years past the end of the active monitoring period will be nearly the same location as at the end of the long-term monitoring period), EPA has determined that a monitoring buffer of at least one-half mile will have an acceptable probability of encountering leaks in many circumstances. At sites where there are known geologic features that may carry leaks laterally more than one-half mile beyond the free phase plume, then that monitoring buffer zone should be extended to encompass those specific leakage pathways.

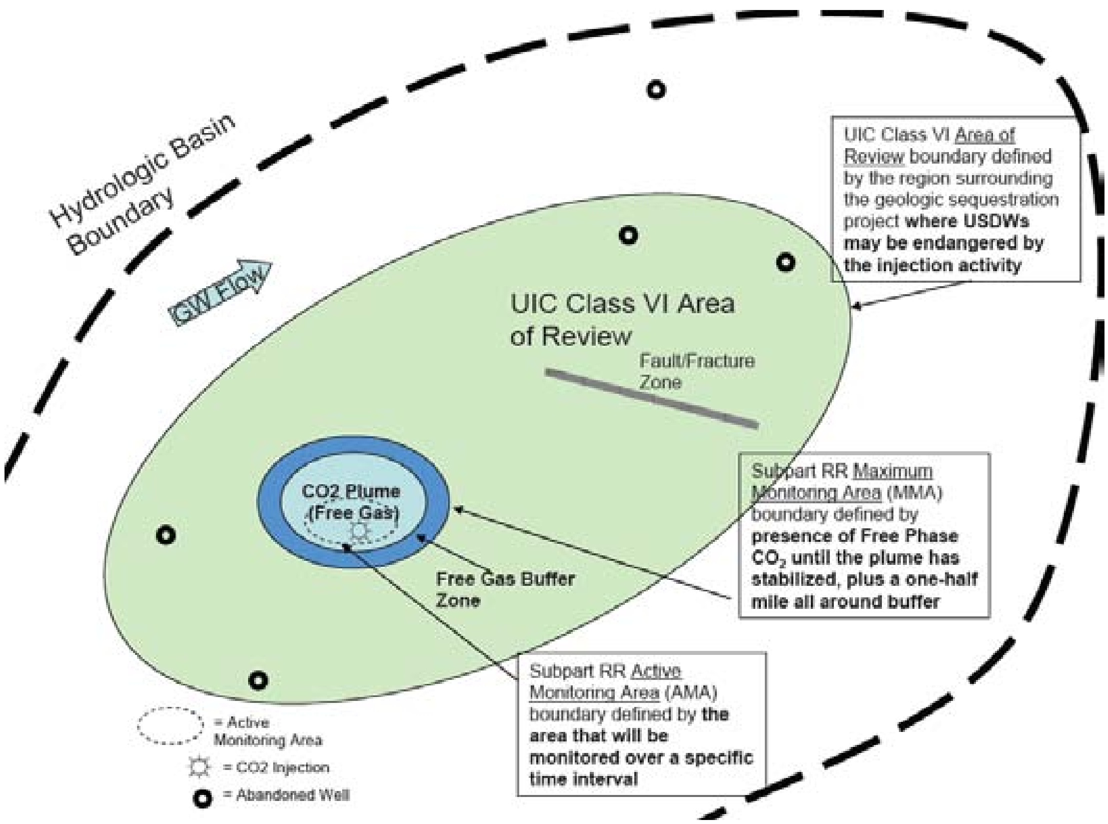

Figure 5-1: Monitoring Areas as They Relate to UIC Class VI and subpart RR Requirements

5.2 Assessment of the Risk of Potential Leakage of CO_2 to the Surface

Reporters are required to evaluate the risk for leakage of CO_2 through all potential pathways within the monitoring area described in Chapter 5.1. As discussed in Chapter 5.1, leakage pathways outside the monitoring area should be evaluated if the pathway has the potential to carry a leak outside the monitoring area. Once a potential leakage risk pathway is identified, it should be evaluated to determine the likelihood, magnitude, and timing of potential leakage. Each leakage pathway should be numerically identified and referenced in the MRV plan. The evaluation of leakage pathways will likely be qualitative in nature. If a reporter has sufficient information to develop a quantitative analysis of the likelihood, magnitude, or timing of leakage risk, it may be presented in the MRV plan. One example of a quantitative analysis of leakage risk is presented in the Risk Assessment appendix to the Final Environmental Impact Statement for the FutureGen project.[76] Another method of quantifying leakage risk was developed by Oldenburg, Bryant and Nicot who applied their methodology to a GS site in the Gulf Coast. [77]

One or a combination of physical phases of CO_2 that have varying chemical and physical properties could be present in leakage from a GS system. These phases of CO_2 include:

- Dry supercritical CO_2;
- The wetted portion of the supercritical CO_2 plume;
- Native fluids in the IZ in which high concentrations of CO_2 are dissolved; and
- Fluids above the confining zone (ACZ) that mix with CO_2-containing fluids migrating from the GS system.

Fluids in these phases may be present in the IZ or adjacent geologic layers, and could come into contact with the potential subsurface leakage pathways. Escape of any of these CO_2-containing substances to the surface could constitute a reportable release requiring quantification by the reporter. While the nature of individual GS systems can be expected to differ with respect to site-specific geologic attributes, potential release pathways at GS sites could be:

- Wells;
- Fractures, faults, and bedding plane partings;
- Competency, extent, and dip[78] of the confining system.[79]

Please refer to relevant UIC regulations[80] for information on suitable sites for GS, and the Vulnerability Evaluation Framework[81] for further background information on potential leakage pathways.

5.2.1 Assessment of the Risk of Potential Leakage of CO_2 through Wells

Of the potential conduits for CO_2 leakage, abandoned wells are the most likely conduits for leakage of CO_2 from the IZ.[82] The presence of oil, gas, and water wells completed

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[76] U.S. Department of Energy (DOE). 2007. FutureGen Environmental Impact Statement.
[77] Oldenburg, C. Bryant, S., and Nicot, J., 2009. Certification Framework Based on Effective Trapping for Geologic Carbon Sequestration. International Journal of Greenhouse Gas Control Volume 3, Issue 4, July 2009, Pages 444-457
[78] Dip is the angle at which the rock unit is included from horizontal.
[79] Leakage related to the CZ can occur if the CZ allows CO_2 to pass though it via permeable zones or fractures, or if the CZ is not continuous across the plume area and CO_2 escapes around the CZ. Leakage may also occur if the CZs is at an angle and CO_2 moves up the incline to the surface or to other permeable zone.
[80] http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm
[81] US EPA. 2008. Vulnerability Evaluation Framework for Geologic Sequestration of Carbon Dioxide. U.S. Environmental Protection Agency Technical Support Document EPA430-R-08-009, July 10, 2008.

and/or abandoned over the last century poses a risk for CO_2 leakage due to the potential for casing and cement failure, as well as the potential for incompetent bonding between cements and either well casing and/or the confining formation.[83] Abandoned oil and gas wellbores and exploratory boreholes may be present at GS sites located in depleted or active oil and gas fields, or in formations near current or historic petroleum exploration or production.

Well plugging and abandonment methods have evolved over time from makeshift plugging with available materials to a regulated, documented process with quality control measures. Gasda et al.[83] describe the possibility of improperly cemented and abandoned wellbores to function as conduits for CO_2 due to a variety of mechanisms, including:

- Degradation of cement and piping by corrosive fluids from the GS system;
- CO_2 flow through degraded cements;
- CO_2 flow along the borehole wall;
- CO_2 flow along the interface of the casing and cement; and
- CO_2 flow through holes in the casing or annular seals.

As a depleted oil and gas reservoir is repressurized by GS activities, potentially to pressures exceeding those present at the start of the field's development, risks posed by weak well seals can be expected to increase significantly. Newer wells constructed specifically for service in CO_2 environments are less likely to show cement and casing deterioration than older oil and gas production wells. Recent studies of cement cores from a 52 year old well exposed to CO_2 ER in the Permian Basin for 30 years[84], and a 30 year old CO_2 production well in Colorado[85] showed effective sealing ability of the cement. These studies concluded that although the cement reacted with the CO_2 it was not compromised possibly due to re-mineralization of the cement into impermeable materials.

Although relatively rare, blowouts from operating oil and gas wells can occur as a result of injection. A study of the rate of oil well blowouts in California's southern San Joaquin Valley between 1991 and 2005, indicated that approximately one-third of the blowouts occurred at active producing wells, most of which were in fields undergoing thermally

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[82] Gasda, S.E., S. Bachu, and M.A. Celia. 2004. The potential for CO_2 leakage from storage sites in geological media: Analysis of well distribution in mature sedimentary basins. *Environmental Geology* 46(6-7):707–720.

[83] Gasda, S.E., S. Bachu, and M.A. Celia. 2004. Spatial Characterization of the Location of Potentially Leaky Wells Penetrating a Deep Saline Aquifer in a Mature Sedimentary Basin. *Environmental Geology* 46, 707–720.

[84] Carey, J.W., M. Wigand, S.J. Chipera, G. WoldeGabriel, R. Pawar, P.C. Lichtner, S.C. Wehner M.A. Raines and G.D. Gutherie Jr., "Analysis and Performance of Oil Well Cement with 30 Years of CO2 Exposure from the SACROC Unit, West Texas, USA", preprint submitted to International Journal of Greenhouse Gas Control, October 18, 2006

[85] W. Crow, B. Williams, D. Carey, J.W. Celia, S. Gasda, "Wellbore integrity analysis of a natural CO_2. producer, Energy Procedia, Vol 1 (1), Proceedings GHGT- 9, Washington, D.C., (2008).

enhanced oil recovery[86]. However, the study also showed that the number of blowouts per year declined by 80 percent, which the authors attribute to improved industry operational and safety practices.

As part of an MRV plan, the reporter should identify the risk of leakage to the surface through abandoned wells by considering the location, depth, type and age of well, and reviewing the available documentation to evaluate the quality of construction and effectiveness of the closure methods. The associated risks should be described in terms of the relative likelihood, magnitude, and timing for surface leakage. The rationale for estimating likelihood, magnitude and timing of each pathway should be presented.

Injection and monitoring wells of the GS project are potential leakage pathways but are also the conduits over which the facility will have the highest level of control. The UIC program regulates injection well construction and integrity testing. Please refer to the UIC program Web site for information on requirements related to monitoring of permitted UIC wells, including MIT.[87] Injection and monitoring well construction, evaluation, and leakage risk is also an active area of research.[88, 89, 90]

Injection wells pose a potential CO_2 leakage risk because they will be subjected to high pressures and flows of CO_2. Monitoring wells in the IZ may also pose a risk for potential CO_2 leakage because they will be within the area of increased pressure from the injection wells, and could be in contact with native fluids containing CO2 which may affect cement integrity. Additionally, nearby monitoring wells within the IZ will experience extended periods of exposure to corrosive mixtures of resident fluids and CO_2 as the CO_2 plume migrates outward from the injection wells. The combination of potential corrosion and high pressures will increase risks associated with monitoring wells in the IZ. Injection and monitoring wells constructed of materials that can withstand the pressures and the corrosive environments can minimize risk of an accidental release. Mechanical integrity testing of cement, cement bonds, casing, tubing, packers, valves, and piping can ensure that injection and monitoring wells are capable of withstanding the pressures and geochemical conditions anticipated to occur during GS injection and post-injection period.

[86] P. Jordan and S. M. Benson, 2009. Well blowout rates in California Oil and Gas District 4: update and trends. Exploration and Production: Oil and Gas Review.
[87] http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm.
[88] Chabora, Ethan and Benson, S. 2008. Monitoring Pressure Transients in Zones Overlying CO_2 Storage Reservoirs as a Means of Leak Detection and Diagnosis. Poster presented at 7th Annual Conference on Carbon Capture and Sequestration - Pittsburgh, PA, May 7, 2008.
[89]Nordbotten, J.M., D. Kavetski, M.A. Celia, and S. Bachu. 2009. Model for CO_2 leakage including multiple geological layers and multiple leaky wells. *Environmental Science and Technology* 43: 743–749.
[90] Celia, Michael A., Bachu, S., Nordbotten, J., Gasda, S., Dahle, H. 2004. Quantitative Estimation of CO_2 Leakage from Geological Storage: Analytical Models, Numerical Models and Data Needs. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, September 5-9 2004, Vancouver, B.C.

The MRV plan should describe and reference construction and MIT methods to be used for GS system injection and monitoring wells,[91] and include an analysis of the likelihood and magnitude of releases from wells.

5.2.2 Assessment of the Risk of Potential Leakage of CO_2 through Fractures, Faults, and Bedding Plane Partings

Fractures, faults, and partings along bedding planes are potential leakage pathways in a GS system. Fractures are breaks in the rock caused by compression or stress, which result in areas of weakness in the rock that can also serve as conduits for fluid movement. Individual fractures are often part of a larger group of similarly oriented fractures resulting from regional and local stresses. Faults are features in the earth at which the rock has broken and along which movement has occurred. Depending on the properties of the strata in which a fault occurs, nature of the movement, and subsequent mineralization or dissolution, faults may function as conduits for fluids moving through the subsurface or as barriers to fluid movement. Bedding plane partings are naturally occurring areas of weakness, often found between poorly bonded sedimentary layers, which may be laterally extensive and intersect vertical migration pathways. Fractures, faults, and bedding plane partings can be forced open by fluids whose pressures exceed the fracture/fault reactivation pressure.

These features may not be observed at the surface or be apparent during geologic site characterization, due to overburden or insufficient offset to be observed by standard geophysical imaging. Additionally, due to the significantly lower viscosity of supercritical CO_2 relative to water, these features may not be observed during site characterization hydraulic testing of the CZ and the ACZ. Risk presented by these features exists due to the ability of CO_2 to move along open fractures and faults, and the ability of pressurized fluids to open faults,[92] fractures, and bedding plane partings.[93] These potential conduits can be identified from core samples and various geophysical and hydraulic testing methods. Once identified, these features should be monitored for early detection of leaks, in accordance with the approved MRV plan. Please note that for GS wells permitted by the UIC Class VI program, there are extensive site characterization and suitability requirements, including that the CZ must be free of transmissive faults and fractures.

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[91] Please see http://water.epa.gov/type/groundwater/uic/wells_sequestration.cfm for UIC program MIT requirements and guidance documents. Additional guidance is provided at the EPA Region V UIC Web site: http://www.epa.gov/r5water/uic/techdocs.htm.

[92] Evans, D.J. 2007. An appraisal of Underground Gas Storage Technologies and Incidents, for the Development of Risk Assessment Methodology. British Geological Survey. (OR/07/023), Nottingham, UK, Available via http://nora.nerc.ac.uk/7877/.

[93] Watney, Willard L., Byrnes, Alan P. Bhattacharya, Saibal, Nissen, Susan E., and Anderson, Allyson K. 2003. Natural Gas Explosions in Hutchison, Kansas: Geologic Factors. Geological Society of America, North-Central Section - 37th Annual Meeting, Kansas City, Missouri, March 24–25. Updated presentation available from: http://www.kgs.ku.edu/Hydro/Hutch/GSA_Watney_updated082004.pdf

The possibility of induced seismicity from fluid injection[94] compounds the risks associated with the above leakage pathways. Seismic events (e.g. small earthquakes) resulting from overpressure in the IZ, CZ, or well materials can cause fracturing and create preferential pathways for CO_2 movement. While induced seismicity may occur along pre-existing faults identified during site characterization, it may also occur along features that were not detected prior to injection, and be activated as a result of increased pore pressure from injection.

The MRV plan should describe the leakage risk from known and inferred faults and fracture systems based on their extent, depth and historical data. The analysis of risk should consider the possibility of lateral transmission of CO_2 and splays in the fault and fracture systems as well as offsets within the subsurface. The evaluation of faults and fractures should encompass a large enough area to account for plume movement that is different from the predicted reservoir simulation model.

Existing data sets may need to be supplemented and updated with measurements specific to the needs of understanding CO_2 leakage. For example, existing or new geophysical survey data may need to be re-processed and re-interpreted to evaluate the extent of faults and fractures, the competency of the CZ or the current location of the CO_2 plume. In areas where there is limited geological information from exploration wells, reporters may need to increase the density of data sampling.

5.2.3 Assessment of the Risk of Potential Leakage of CO_2 based on the Competency, Extent, and Dip of the Confining Zone

The CZ overlying a GS system performs a critical function of preventing the upward migration of highly buoyant supercritical CO_2 into the ACZ. The risk of a release of CO_2 into the ACZ and subsequently into the atmosphere is greatly dependent on the competency, extent, and slope of this rock unit.

The presence of fractures, faults, interconnected bedding plane partings, susceptibility to degradation by CO_2 and impacted native fluids, or low capillary entry pressures[95] could render the CZ capable of transmitting CO_2 from the IZ into the ACZ. These properties should be evaluated during site characterization, and any potential conduits should be monitored during baseline data collection and facility operation. In addition, anticipated injection pressures should be compatible with the geomechanical properties of the CZ to prevent fracturing and creation of conduits to the ACZ. Geochemical, hydraulic, and geomechanical testing of the CZ materials should be performed as part of GS system characterization and facility construction.[96]

[94] Ingebritsen, S. E , Sanford, W. E, Neuzil, C. E. 2006. Groundwater in Geologic Processes. Cambridge University Press, p. 29.

[95] Capillary entry pressure is defined in the Vulnerability Evaluation Framework as the added pressure that is needed across the interface of two immiscible fluid phases (e.g., supercritical CO_2 and water or brine) for CO_2 to enter the confining system. If the IZ pressure exceeds the capillary entry pressure, CO_2 could be forced out of the IZ into the CZ.

[96] US EPA. 2008. Vulnerability Evaluation Framework for Geologic Sequestration of Carbon Dioxide. U.S. Environmental Protection Agency Technical Support Document EPA430-R-08-009, July 10, 2008.

The lateral extent of the CZ should be sufficient to contain the CO_2 plume as it spreads and migrates laterally, during and after injection, until physical and geochemical trapping mechanisms can sequester the CO_2. General CZ extent and thickness should be available from previous oil and gas or ER studies or regional geologic studies used in the GS system siting. These data can be supplemented by well logging performed during injection and monitoring well drilling, records from oil and gas exploration and production drilling, and geophysical studies. At sites where the CZ is not laterally extensive, an increased risk of leakage around the edge of the CZ may be present.

The dip of the confining system is an important component of the GS system. Due to the buoyancy of supercritical CO_2, until geochemical trapping mechanisms sequester the CO_2, the injected fluid can be expected to move in an up-dip direction until a structural or stratigraphic trap[97] is encountered or the lateral extent of the confining unit is reached and the plume moves upward into the ACZ. A relatively steep dip of the overlying CZ may result in the need for a more laterally extensive confining system to prevent the escape of CO_2 to the ACZ and subsequently to the atmosphere. The risk of leakage at the up-dip locations should be considered a potential leakage pathway for sites with steeply dipping CZ without structural closure. GS system modeling studies including simulation of multiphase fluid flow may be performed to determine expected travel times and evaluate the potential for the confining system to retain supercritical, and subsequently dissolved-phase, CO_2 until geochemical and structural trapping mechanisms can effectively sequester the $CO_{2.}$ The likelihood, magnitude, and timing of the risk of releases through the CZ should be assessed and presented in the MRV Plan.[98] The MRV plan should present an assessment of the risk of leakage from the CZ with supporting information for how the risk was determined. The description should evaluate the uncertainties in the risk evaluation and consider movements of the plume throughout the lifecycle of the sequestration.

5.3 Strategy for Detecting and Quantifying any CO_2 Leakage to the Surface

5.3.1 Detecting Leakage

After the potential leakage pathways in the MMA have been identified, the reporter will design a strategy to assess the pathways for conditions that could indicate leakage from the AMA within specified time intervals. The strategy should be designed so that potential leakage pathways are monitored in a comprehensive manner that allows for timely and accurate identification of leaks. Subpart RR requires quantification and reporting of leakage to the surface; however, the reporter's leakage detection program may rely on subsurface measurements to detect leaks (such as may be implemented for compliance with a UIC permit). A leak may be initially detected in the subsurface in

[97] A stratigraphic trap is caused by changes in the permeability or porosity of the reservoir rock that restrict flow. An example of a stratigraphic trap would be a sand lens that is surrounded by silt or clay.
[98] K. P. Saripalli, N. M. Mahasenan, and E. M. Cook. 2002. Risk and hazard assessment for projects involving the geological sequestration of CO_2. In Kaya et al. *GHGT-6: Sixth International Conference on Greenhouse gas control technologies*, Kyoto, Japan, September 30–October 4 2002. Elsevier.

which case subsequent verification and quantification analysis will be needed to determine if the leak has reached or is likely to reach the surface (described in Chapter 5.3.2 and 5.3.3).

The strategy for detecting CO_2 leakage to the surface could include taking measurements on a continuous basis, such as pressure readings in injection and monitoring wells, or continuously reading eddy covariance monitoring. The leakage detection strategy could also include regularly scheduled periodic monitoring events and surveys designed to evaluate conditions at a snapshot in time. Regularly scheduled monitoring events could include periodic sampling of water chemistry, MIT of injection and monitoring wells, or whole-area airborne surveys conducted at regular intervals. The area covered by the leakage detection measurements may change over time as the plume expands, and the AMA is expanded, or new wells are added, but the practices would likely remain the same.

The detection capability of leakage detection monitoring systems should be described in the MRV plan. Reporters should develop a robust monitoring system that ensures adequate detection capability. In determining the detection capability, the reporter should consider:

- The accuracy and precision of the instruments used to measure data that will be quantified.
- The statistical variability of the expected baselines against which the measurements will be compared.
- The time required for a leak to be transmitted to a monitoring station or measurement point.
- The ability to use the monitoring program to reliably recognize leaks of the targeted magnitude.

The identification and influence of site characteristics such as topography, land use, weather, and climate on the detection methods should be presented in the MRV plan as part of the assessment of adequacy for detection methods. The considerations for the approach and techniques are described below.

Part of the suite of leakage detection monitoring should include MIT of injection wells, using a suite of well logs that are capable of determining leakage under the site-specific conditions. Such logs may include but are not limited to noise logs; cement bond/variable density logs; mechanical, electrical, or acoustical caliper tools; tracer logs; and other specialized well inspection tools. MIT utilized for satisfying UIC requirements could be described as part of the leakage detection strategy in the MRV plan. Although there are no UIC requirements for performing MIT on monitoring wells, it may be prudent for reporters to include in their MRV plans a periodic evaluation of the integrity of monitoring wells that penetrate the IZ. The reporter’s process for selecting and interpreting MIT should be provided in the MRV plan. Additional information on the use of these and other monitoring techniques is provided in Chapter 4 of this TSD.

The process and technologies for detecting leakage through CZ or spill points should be presented in the MRV plan. In some cases, changes to the ACZ will likely be a result of leakage through the CZ or structural spill points, which are detectable in the monitoring wells and with other subsurface imaging technologies. For example, pressure changes observed in multiple monitoring wells can be used to locate the general area of leakage through triangulation. The process and technologies for detecting leakage through CZ or spill points should be presented in the MRV plan. The reporter should determine the targeted leak size and estimate the reliability of its detection for the proposed monitoring technologies and procedures.

Faults, natural fracture systems, and abandoned boreholes are potential leakage pathways, where a range of different monitoring technologies could detect leakage, depending on site-specific conditions. Near-surface monitoring devices may include eddy covariance, LIDAR, accumulation chambers, soil gas surveys, isotopic analysis of CO_2 at the surface or in shallow wells, and monitoring for tracers injected with the CO_2. Leakage from the ground into surface water, such as a leaking fault that intersects a lake, may require different approach to monitoring and flux calculation.[99]

The reporter should consider the characteristics of the GS site and the capabilities of the monitoring systems to analyze what leak sizes or surface CO_2 fluxes are detectable using the proposed methodology. Subpart RR does not have a specific leak detection minimum volume or reliability standard. Instead, it is requested that reporters compute the statistical reliability of the monitoring element given one or more targeted leak rate(s). Note that a GS project operating under a UIC permit will have separate UIC requirements if a leak is detected that may include reporting of the leak, ceasing injection, and taking corrective action.

The targeted leak rates for the probability calculations in the MRV plan should be appropriate to the site, and for example could be on the order of thousands or tens of thousands of metric tons per year as measured in the subsurface. There is little published research on measured subsurface leakage rates for GS sites, so the reporter should provide a justification for selection of the target rate. The reporter may wish to review the risk assessment performed for the proposed FutureGen project[100] which tabulated surface emissions rates from 28 locations including natural CO_2 sources (domes, volcanic, and hydrothermal sites) and ER/GS sites. The surface emissions ranged over eight orders of magnitude, but all of the ER and GS sites had surface flux of less than one micromole per square meter per second. The reporter may also wish to review the design of studies conducted at the Zero Emissions Research and Technology Center in Bozeman Montana where controlled release experiments were performed to simulate low-level seepage in order to test the detection capability of several monitoring methods[101].

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[99] Oldenburg, C.M., and J.L. Lewicki. 2006. On leakage and seepage of CO_2 from geologic storage sites into surface water. *Environmental Geology*, 50(5), 691-705 LBNL-59225

[100] U.S. Department of Energy (DOE). 2007. FutureGen Environmental Impact Statement.

[101] Spangler, L.H., Dobeck, L.M., Repasky, K.S., Nehrir, A.R., Humphries, S.D., Barr, J.L., Keith, C.J., Shaw, J.A., Rouse, J.H., Cunningham, A.B., Benson, S.M., Oldenburg, C.M., Lewicki, J.L., Wells, A.W., Diehl, J.R., Strazisar, B.R., Fessenden, J.E., Rahn, T.A., Amonette, J.E., Barr, J.L., Pickles, W.L., Jacobson, J.D., Silver, E.A., Male, E.J., Rauch, H.W., Gullickson, K.S., Trautz, R., Kharaka, Y.,

For the evaluation of near-surface monitoring techniques, these leak rates should be translated to surface leak areas and fluxes based on dispersion modeling or calculated factors to be discussed below. It should be understood that these leak rate assumptions are not intended as predictions of actual leaks or limits on what leaks can or should be detectable. Rather, they are benchmarks against which the performance of the leak detection strategy can be measured using statistically valid techniques. The performance would generally be stated in terms of a leak rate target, a time period, and percent probability of detection.

For example a plan to detect leaks with pressure monitoring using wells in the ACZ might have a performance evaluation concluding that it can detect “leaks of X metric tons of CO_2 per year within Y days with a probability of Z percent.” The performance estimate does *not* mean that leaks smaller or larger than this cannot be detected. Smaller leaks can be detected, but they may take more time or will be detectable with less reliability; larger leaks may be detectable in less time with greater reliability.

A consideration in designing a leakage detection strategy (and in establishing expected baselines) for the MRV plan is ensuring adequate data resolution to cover a range of points in space and time. A non-representative data set that contains too few samples at too few times of day/year from too few locations will generate a biased picture and result in erroneous decision making. A sampling program should be designed to ensure that it considers the appropriate frequency of sampling, aerial extent of sampling, and sample size. The MRV plan is likely to include approaches that involve collecting data at one or more locations within the MMA.[102] For example, CO_2 isotope ratios in soil gases might be measured throughout the entire AMA as one leak detection method. The MRV plan could present the statistical coverage adequacy of a given sampling program (i.e., the probability a given size of leak will be detected). Please refer to Appendix E for further discussion of this topic.

5.3.2 Verifying Leakage

The MRV plan should describe the strategy to verify and confirm the location and source of leakage that has been detected. The leak verification process is intended to be a quick and cost effective step to help the reporter focus efforts on deviations from expected measurements that would need to be quantified. The MRV plan should describe the methods and criteria for determining how an anomalous reading or condition will be evaluated to determine if it represents a leak, for verifying the location and source of the leak, and what level of accuracy is anticipated. This description should include details of the approach for determining how readings will be distinguished from background or

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Birkholzer, J., and Wielopolski, L.,, A shallow subsurface controlled release facility in Bozeman, MT, USA, for testing near surface CO2 detection techniques and transport models. Environmental Earth Sciences, 60, 227-239, doi:10.1007/s12665-009-0400-2, 2010

[102] Jones, David. 2009. Ground surface monitoring of CO_2 and associated gases. Presented at CO_2 GeoNet Open Forum, March 2009, Venice, Italy.

operational variability (see Chapter 5.4 for a detailed presentation of this topic). If possible, the MRV plan should provide criteria that will be used to identify the presence of a leak. Monitoring systems for each pathway are likely to employ different technologies at different measurement frequencies. For example, ACZ pressure monitoring may be conducted continuously at several locations over a broad part of the CO_2 plume however, leak detection at active or abandoned wells may be performed using a truck-mounted laser scanning survey that is conducted once per year at specific well locations within the AMA. Likewise, leak detection and verification methods will vary with the monitoring technology. Since each monitoring system will be different, and the monitoring systems may change location over time as the plume changes, the reporter may simplify the presentation of the leak detection and verification process in the MRV by describing the leak detection and verification in a flowchart or process diagram.

The verification steps may include:

1. Verification that the reading is accurate and truly representative of the condition. This may require repeating the measurement, recalibrating the measurement device and repeating the measurement, taking a second measurement with a redundant device or a different device of greater accuracy or higher precision, or evaluating other data and measurements that may be affected by the condition. Verification of the reading may also necessitate collecting measurements for a longer period of time to determine if the anomalous reading is of a short duration or part of a longer or continuous trend of anomalous readings. For very large leaks that are manifested at the surface, direct visual observation of ice crystals, vapor plumes, or gas bubbles in well cellars may provide adequate verification of a large leak.

2. Identification of the location or the source of a suspected leak. Once the accuracy of the measurement is confirmed, other methods may be used to further refine the location of a leak, including triggered or episodic monitoring that takes place after a leak is suspected. For example, if a release of CO_2 from a fault zone is suspected based on fixed location eddy covariance data, a soil gas survey of the fault area could be performed to more accurately define the location of the leak. Resolution of the source can also be made with surface measurements by using a denser sampling grid or more frequent time scale to improve the resolution of the source area. For subsurface leakage in the injection or monitoring wells, mechanical integrity well logs can be used to help define the area and pathway of leakage.

5.3.3 Quantifying Leakage

The MRV plan must include a discussion of how leaks will be quantified once they are detected and verified.[103] Given the uncertainty concerning the nature and characteristics of leaks that will be encountered, EPA expects that this section of the MRV plan will

[103] Any leakage detected would constitute a failure of mechanical integrity and would necessitate the cessation of injection in accordance with the UIC permits.

provide a list of possible quantification methods and a discussion of when and how those methods might be employed for each risk pathway identified in the leakage pathway assessment. To the extent possible, the expected accuracy of the techniques should also be discussed. EPA understands that it may be difficult to measure CO_2 leakage quantities and that modeling and estimation processes with possibly wide margins of error may be utilized.

In some cases the leak volume or rate may be estimated using near-surface parameters, and quantification will reflect a mass of CO_2 leaked to the surface that is then reported to EPA. In other cases, the estimation process will employ subsurface parameters, and the initial estimates will be of the subsurface leak rate and amount. These subsurface leakage rate and amount estimates then need to be translated to an estimate of the mass of CO_2 leaked to the surface, and reported to EPA. The choice of quantification methods in an MRV plan will be site specific. They could include but are not limited to:

1. Estimation of leakage in the subsurface by material balance, using known injected quantities and monitored pressures in the IZ. Since leaks will cause monitored pressure in the IZ to be lower than expected, leaked quantities might be estimated as those amounts that bring the modeled IZ pressure down to measured values. Given the uncertainty and variability in IZ reservoir conditions, this technique would be expected to have a very wide margin of error, particularly in the early phases of injection when pressure differences above background levels are small and reservoir characteristics have not been confirmed/adjusted by history-matching. The estimated leaked amounts will be reported in volume of fluids (e.g., cubic feet or cubic meters) and should be broken out into the amounts of water versus amounts of CO_2. Then the amount of subsurface CO_2 leakage must be converted to the amount of CO_2 that has leaked or will leak to the surface. (See discussion below on these two estimation steps.)
2. Estimation of subsurface leakage by material balance using monitored pressures in the ACZ. Leaks through the CZ likely will cause monitored pressure in ACZ to be higher than expected. This second technique should be more accurate than the first technique using IZ pressures, because there should be less uncertainty determining the value of "normal" pressure in the ACZ. However, a wide margin of error will exist because of the given uncertainty in ACZ reservoir characteristics. The volume of fluids leaked will have to be converted to CO_2 leaked to the surface.
3. Estimation of leakage by reservoir simulation that triangulates leak location and calculates leak rate by interpreting pressures in ACZ at three or more monitoring wells. When several wells in the ACZ record pressure increases, it will be possible to locate and estimate volumes of a leak that is concentrated at one location (i.e., not made up of several scattered leaks). The volume of fluids leaked will have to be converted to CO_2 leaked to the surface.
4. Estimation of leakage by measuring CO_2 flux at several locations on the surface with eddy covariance, accumulation chamber, tenting, etc., can be used in extrapolating the entire area of leak. This process would involve identifying that

the surface area through which the leak is occurring and directly measuring the leak rate at a sample of locations at or near the surface. The accuracy of this technique will depend on the shape and size of the leak at the surface, the sample footprint size, (i.e., point sampling for accumulation chambers versus a measurement area for an eddy covariance tower), density of sampling, and the ability to distinguish leak volumes from natural flux rates.

5. Estimation of a leak by remote sensing or ground surveys of the effects of leaked CO_2 on vegetation[104]. It may be possible to approximate the surface extent and rate of leakage by looking at vegetative effects. This option is likely to have a very uncertain accuracy. It may best be used to estimate the areal extent of the leak or to determine whether subsurface leak has reached the surface.
6. Estimation of the plume size and location using seismic survey by mapping the primary plume size and density in the IZ and the subsurface leakage plume in the ACZ. Under favorable geologic circumstances, it will be possible to use periodic seismic surveys to track movements of the CO_2 plume in the IZ through time. Under those same circumstances, it might be possible to use the seismic surveys to estimate how much of the CO_2 plume is still located in the IZ and how much has leaked into the ACZ.

Though the state of the science does not currently support using existing logging techniques to quantify leakage in wells, estimation of well leakage through interpretation of mechanical integrity well logs of injection wells or monitoring wells drilled into the IZ can help to bound leakage estimates. When logs indicate the leak of fluids along the wellbores, it might be possible to estimate the extent of leakage by analyzing those logs or supplemental logs. For example, the rate of fluid movement may be indicated by the analysis of the frequency of sound signals from noise logs. The analysis of the velocity of radioactive tracers up a borehole could also indicate rate of fluid leaks. In addition, an analysis of dimensions of damaged well materials (e.g., gaps in cement or corroded casing) determined from sidewall cores and pressure drawdown tests might be used to constrain of the size of leaks. The volume of fluids leaked will have to be converted to CO_2 leaked to the surface.

When leaks are quantified in the subsurface as volumes of CO_2 or fluids, it will be necessary to convert this value to an estimate of the amount of CO_2 that has leaked to the surface. One method to estimate CO_2 volume leaked at the surface would be to apply one or more of the near-surface options listed in items #4, #5, and #6 above to measure CO_2 leak flux and leakage area, and then estimate the leak volume by multiplying leakage area by flux and duration. Alternatively, the reporter can choose to use techniques such as modeling to more directly estimate what portion of the subsurface leak is CO_2 that has or will reach the surface. When the leak has been measured as total volume of fluids, the amount of the leak that is CO_2 versus water may be inferred by analysis of where the leak occurs relative to the position of the plume. The reporter may determine that leaks far

[104] Keith C.J., Repasky K.S., Lawrence R.L., Jay S.C., Carlsten J.L. (2009) Monitoring effects of a controlled subsurface carbon dioxide release on vegetation using a hyperspectral imager. *International Journal of Greenhouse Gas Control* 3(5):626–632. doi:10.1016/j.ijggc.2009.03.003

outside of the plume area are assumed to be 100 percent water and no CO_2. Leaks through the CZ within the plume area might be estimated based on the relative modeled CO_2/water saturation levels at the point of the leak and modeled flow characteristics through the CZ.

The quantification of leakage should include consideration of the time at which the leakage began and when the monitoring system first detected the leak. Subsurface leaks may be identified relatively quickly if they occur near a monitoring well, but may take months or years to reach the surface. Leak quantification methods should also consider the effect of time on leakage rates because the leakage rate at the surface is likely to increase over time.

The portion of CO_2 that leaks through the CZ, out of structural spill points, or along boreholes that will ultimately reach the surface may also be estimated using modeling. This will include careful characterization of the rocks and fluids to be encountered by the CO_2 along the leakage pathways to the surface. If any part of the leak is modeled as trapped in a USDW, the assumption should be made that the water with the trapped CO_2 may eventually be produced from the USDW, and therefore counted as a leak to the surface, unless the reporter demonstrates that the CO_2 will not be emitted to the atmosphere. Alternatively, the reporter may report to EPA that 100 percent of the subsurface leak has reached the surface. Note that if the injectate reaches a USDW, the reporter will be in violation of their UIC permit.

5.4 Strategy for Establishing the Expected Baselines

Baseline monitoring is essentially the first step in implementing the leakage detection and quantification monitoring strategy. The primary goal of establishing expected baselines is so that the reporter can discern whether or not the results of monitoring are attributable to leakage of injected CO_2. This chapter describes considerations for developing expected baselines that will ensure adequate leakage detection capability within the monitoring system.

Leakage of sequestered CO_2 may result in detectable deviations from the expected baseline values in one or more of a number of environmental conditions, such as subsurface pressure, groundwater chemical composition, the concentration of CO_2 in air, soil, surface or near-surface CO_2 flux rates, surface CO_2 isotope ratios, and other geophysical and geochemical parameters, or deviations from expected operational conditions, such as the injection pressure and the annular pressure in the well. The MRV plan leakage detection and quantification strategy may include monitoring a selection of these indicator parameters to detect potential CO_2 leakages. To judge whether a set of measured parameter values obtained during GS operations presents a cause for concern, reporters should know what those parameter values would be expected to be in the absence leaks. In the MRV plan, reporters should credibly explain how an expected baseline that represents the most probable range of the indicator parameters will be obtained. Once the expected baseline has been established, reporters would then have a basis for statistically evaluating if the measured parameter values obtained during GS operations are of a level that suggests a leakage of injected CO_2.

In most cases seepage fluxes will far exceed background;[105] however, some natural systems, especially the concentration of CO_2 in near-surface soil and air, are quite variable and are affected by many factors, making prediction of baseline difficult. There may be situations where conditions limit the ability to collect or model representative conditions, either for baseline or monitoring applications. For example, in the subsurface, heterogeneity may create complex pressure pathways between the injection well and the monitoring well that can result in anomalous or unexpected readings that cannot be correlated to the injection well pressure. In ER areas with multiple stages of primary, secondary, and tertiary production and reservoir manipulation, pressure transients and well stimulation practices may make pressure monitoring unreliable.

5.4.1 Approaches for Establishing an Expected Baseline

The baseline approach described in the MRV plan should be reliable, representative of the site conditions, and provide enough resolution such that an anomalous reading can be identified without an unacceptable level of false negative or false positive results. Inaccuracies in establishing the expected baseline could lead to erroneous conclusions. If the baseline is inaccurately determined to be too low, then "false positives" would result; in other words, CO_2 leakages would be detected even when they were not occurring. On the other hand, if the baseline is inaccurately determined to be too high, then "false negatives" would result; that is, CO_2 leakages would not be detected even when they were in fact occurring.

In the MRV plan submittal, the reporter should provide a description of the baseline monitoring that demonstrates the statistical validity of the selected approach for each monitoring method proposed. This discussion should include documentation of the environmental variability and instrument capability, and a determination of the probability of detecting a leak of the targeted size(s). The identification and influence of site characteristics such as topography, land use, weather, and climate on the monitoring methods for baseline should be addressed in the MRV plan as part of the assessment of adequacy and potential for variability in conditions.

Pre-injection Monitoring of Environmental Parameters

Optimally the indicator parameters would be measured at the proposed locations prior to injection. Given the seasonal variability of some parameters, such as CO_2 flux, this historical baseline may need to encompass a range of seasonal and climatic conditions. An advantage of this approach is that the operational stage and pre-injection values are derived from the same location, thus minimizing variance derived from geographical differences. Using the same geographic location for baseline and measurements will

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[105] Benson, S. 2004. Monitoring Protocols and Life-Cycle Costs for Geologic Storage of Carbon Dioxide. Presentation at Carbon Sequestration Leadership Forum meeting in Melbourne Australia. September 13-15, 2004.

eliminate one potential source of error and variability in the determination of anomalous readings and potential leakage. However, the disadvantage is that operational stage and pre-injection values are measured at different points in time, resulting in possible variance from temporally varying factors such as weather.

Contemporaneous Monitoring of Environmental Parameters

There are two potential approaches involving contemporaneous monitoring of environmental parameters. One approach involves contemporaneous monitoring of the indicator environmental parameters at a site similar to the sequestration facility, but at an offsite location that is unaffected by the CO_2 injection. This reference site should be established to be similar to the MMA in terms of all the relevant environmental parameters so that it serves as a proxy for what conditions would have been like in the MMA had the CO_2 facility not been built and the CO_2 not been injected. The advantage of this method is that the reference site readings are contemporaneous to the monitoring zone readings and would therefore be matched in terms of weather conditions and season (provided the reference site is fairly close to the MMA). The disadvantage of this approach is that it is usually difficult to find a reference site that is a perfect proxy for the facility site in every respect. For this reason it may be necessary to use data from the reference site indirectly in predictive models of the expected baseline values.

A second approach involves contemporaneous monitoring of the indicator environmental parameters at reference points within the maximum monitoring area. These reference points are expected to be currently unaffected by the CO_2 injection, although they lie within the maximum monitoring area of the sequestration facility. The advantage of this approach is that it is likely to be cost-effective to implement. However, it suffers from the drawback that the reference sites may unexpectedly be affected by the leakage, which would result in false negative determinations.

Use of Predictive Models

A predictive model for the baseline is a mathematical model, usually developed through regression analysis, that estimates the expected baseline as a function of other variables (e.g., predicting expected CO_2 flux in soils as a function of season, time of day, recent rainfall, and temperatures). Predictive models may be useful when there may be bias in the historical data, or when the variation of the monitored parameters is very wide and when it is known that certain measurable influences, such as weather, account for much of that variation. The creation of predictive models adds to the complexity and cost of the MRV plan development and implementation, but may improve the statistical reliability of a monitoring strategy. If the MRV plan relies on predictive models, then the plan should lay out how the predictive model will be developed and how the model will change the bias and variance in the expected baseline. The MRV plan should describe how the predictive model is based on available monitoring data. Examples of predictive models used to calculate flux can be found in recent studies of natural CO_2 releases, ER and sequestration sites.[106, 107]

5.4.2 Considerations in Establishing Expected Baselines

Adjustments for a Shifting Baseline

Changing natural and land-use factors may necessitate revisiting the expected baseline. In the case of a baseline defined by pre-injection historical environmental data, changes in land use in the surrounding region could affect current measured parameter values, biasing them in a certain direction and increasing the possibility of a false positive or negative. To prevent this, either the pre-determined baseline would have to be adjusted to factor in the effect of the current land use change, or the measurement of the current environmental parameter values would have to be adjusted to factor out the effect of the land use change.

For a baseline defined by contemporaneous reference data, natural or land use changes in the reference area that do not influence the monitoring area would be a cause for concern. In such a situation, reporters would need to define a new reference site more reflective of original conditions at the monitoring area and create a new baseline there, or they would need to factor out the influence of the natural/land use changes at the existing reference site. Depending on the particular influence of the change, failure to make these adjustments could lead to either false negative or false positive determinations.

If adjustments are made to the strategy for establishing the expected baseline after the MRV plan is approved by EPA, the reporter must describe the changes in the annual report. Changes to baseline may result in a material change and would require the MRV plan to be re-submitted.

Uncertainty and Variability in Baseline Data: The Choice of a Monitoring Method

In the choice of monitoring methods for leakage detection and quantification, the reporter should consider the issues posed by uncertainty and variability in both the baseline and the measured operational data. Certain environmental parameters such as CO_2 flux are likely to be harder to measure accurately than others. For example, surface-to-atmosphere CO_2 flux varies considerably by time of day, by season, and by location. A number of

[106] Etheridge D., R. Leuning, A. Luhar, D. Spenser, S. Coram, P. Steele, M. van der Schoot, S. Zegelin, C. Allison, P. Fraser, C.P. Meyer and P. Krummel. 2007. Atmospheric monitoring and verification of geosequestration. At the CO2CRC Otway Project 2007 Annual Report, Report # RPT07-0735.

[107] Stephanie Trottier, William D. Gunter, Bernice Kadatz, Mark Olson, Ernie H. Perkins. 2009. Atmospheric monitoring for the Pembina Cardium CO_2 Monitoring Project using open path laser technology, Energy Procedia, Volume 1, Issue 1, Greenhouse Gas Control Technologies 9, Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), 16-20 November 2008, Washington DC, USA, February 2009, Pages 2307-2314. Available at: http://www.sciencedirect.com/science/article/B984K-4W0SFYG-BM/2/e8c3fb1745fea4010531f65c351bd233.

variables influence surface-to-atmosphere CO_2 flux, many of which are associated with measurement error. The measurement of surface-to-atmosphere flux using eddy covariance is reported to have a precision of up to 30 percent, with short-term error of 7 to 12 percent.[108] There is also uncertainty about the statistical model that converts wind and CO_2 concentration readings to flux and the values of the coefficients in the model. This suggests that CO_2 flux estimates may have sizeable confidence intervals or error bars.[109] In a study of the CO_2 leakage potential from the ER operations at the Rangely oil field in Colorado, Klusman found that CO_2 flux and carbon isotope ratios varied significantly at reference locations and over the suspected source areas.[110] A predictive model based on regression analysis of the historical data could predict expected baseline flux as a function of weather and other conditions.

A sampling program that measures an environmental parameter with a considerable error bar or confidence interval is likely to be difficult to discriminate from baseline conditions. High error bars in either or both the operational stage monitoring estimates or the baseline estimates will increase the probability of false negative readings, thus potentially leading to erroneous conclusions. An environmental parameter with a low error bar is preferable to alternative indicators that are associated with high error bars.

Predictive models have been applied at ER and sequestration pilot tests to compare background CO_2 flux and concentrations to measured values.[111, 112, 113, 114] These studies demonstrate the use of predictive models and the challenges[115] of discriminating natural conditions from leakage especially over small areas or with low leakage rates.

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108 Oldenburg, C.M., and J.L. Lewicki. 2003. Near-surface monitoring strategies for geologic carbon dioxide storage verification, Lawrence Berkeley National Laboratory Report LBNL-54089, October 2003.

109 Confidence intervals or error bars are used to describe the most probable range of values with which a measured reading should be associated. Readings that closely match the actual values will have narrow confidence intervals or error bars; readings with high variability will have wide confidence intervals or error bars.

110 Klusman, R., 2003. A geochemical perspective and assessment of leakage potential for a mature carbon dioxide-enhanced oil recovery project as a prototype for carbon dioxide sequestration; Rangely field, Colorado. AAPG Bulletin V. 87, No. 9 pp 1485-1507

111 Lewicki, J.L., G.E. Hilley, and C.M. Oldenburg. 2005. An improved strategy to detect CO_2leakage for verification of geologic carbon sequestration. *Geophysical Research Letters*, 32 (19), L19403, doi:10.1029/2005GL024281.

112 Loh, Z., Leuning, R., Zegelin, S., Etheridge, D., Bai, M., Naylor, T., Griffith, D. 2009. Testing Lagrangian atmospheric dispersion modelling to monitor CO_2 and CH_4 leakage from geosequestration. *Atmospheric Environment* doi: 10.1016/j.atmosenv.2009.01.053

113 Benson, S. 2004. Monitoring Protocols and Life-Cycle Costs for Geologic Storage of Carbon Dioxide, http://www.cslforum.org/documents/benson_sally_wed_Pal_AB_0915.pdf.

114 Lewicki, J.L., G.E. Hilley, M.L. Fischer, L. Pan, C.M. Oldenburg, L. Dobeck, and L. Spangler. 2009. Detection of CO_2 leakage by eddy covariance during the ZERT project's CO_2 release experiments. *Energy Procedia*, 1, 2301-2306.

115 Etheridge, D, Leuning, R, Luhar, A, Spencer, D, Coram, S, Steele, P, Van der Schoot, M, Zegelin, S, Allison, C, Fraser, P, Porter, L, Meyer, C and Krummel, P. 2007. Atmospheric monitoring and verification of geosequestration at the CO2CRC Otway Project 2007 Annual Report to the CO2CRC. Cooperative Research Center for Greenhouse Gas Technologies, Canberra, Australia, CO2CRC Publication Number RPT07-0735. 14pp.

Statistical Methods for Comparing Operational Stage Measurements and Expected Baseline Data

In the MRV plan, the reporter may propose to use a statistical approach to conclude if the operational stage measurements differ from the expected baseline. Using statistics, the reporter can infer about a population using data from a sample. In many cases a statistical approach is advisable because environmental parameters tend to be inherently variable- even the best sampling program would only generate an estimate of the true value of a parameter. This sampling estimate could be mathematically expressed as a statistical probability distribution, which represents the most probable range of values for the parameter based on the sample data. A range of statistical tests are available to determine if the measured operational stage data differs significantly from the baseline. Heterogeneous populations should be split into homogeneous subdivisions to ensure that like quantities are being compared and the statistical comparisons are meaningful. For more information, see EPA's Data Quality Assessment statistical guidance.[116]

Using the Regional Hydrologic Evaluation to Determine Expected Conditions in the Monitoring Zones

An understanding of the regional hydrogeologic characteristics in which the GS facility is situated will provide the context for conceptual site model development, and may be used to help quantify potential leaks from a GS reservoir. As an example, the presence of small-scale structural, stratigraphic, or geochemical features, such as faults, trapping structures, or mineral deposits, are often indicated by the broader geologic setting of an area. However, these features, which could impact geochemical monitoring parameters, may not be observed during site-specific investigations. IZ hydrogeologic and geochemical conditions should be evaluated during development of an expected baseline to anticipate the movement of injected CO_2 after injection has begun. As part of baseline data collection, data could be gathered to establish the ambient pressures, direction, velocity, and geochemical nature of native fluids in the reservoir and ACZ prior to GS facility operations. These data can be used to predict CO_2 plume migration, assist calibration of reservoir models, and during periodic reviews to quantify differences between observed changes in the hydrologic regime and predicted effects. The regional model can also be combined with the site characterization model to assist siting of monitoring infrastructure.

In the strata comprising the ACZ, determination of baseline hydraulic and geochemical conditions may allow determination of the presence and magnitude of any leakage that may be occurring. If strata in the ACZ are in hydraulic communication with a USDW, pumping regime changes in the USDW may cause pressure fluctuations that could be misinterpreted as being indicative of a release from the reservoir. With a sufficient period of baseline monitoring, seasonal fluctuations in ACZ pore pressures can account for seasonal trends in groundwater pumping, resulting in regular increases and decreases in ACZ fluid pressures.

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[116] US EPA. 2006. Data Quality Assessment: Statistical Methods for Practitioners (EPA QA/G-9S, 2006)

Geochemical data are also an important part of baseline data collection, as naturally occurring localized mineral deposits or the presence of organic constituents such as natural gas or naturally occurring CO_2 may mimic or obscure conditions indicative of a CO_2 release. Depending on the site and on the proposed monitoring strategy, the GS reservoir and ACZ geochemistry could be measured as part of a baseline assessment, due to the possible presence of naturally occurring CO_2, metals that may mobilize in the event of a GS reservoir leak such as iron and manganese, or naturally occurring constituents that could also be introduced by the CO_2 stream such as argon, nitrogen oxide, hydrogen sulfide, and methane.

5.5 Site-Specific Variables for the Mass Balance Equation

The mass balance equations RR-11 or RR-12 are used to calculate the amount of CO_2 that is reported as sequestered and include the terms CO_{2FI} and CO_{2FP}. CO_{2FI} is defined as the total annual CO_2 mass emitted (metric tons) as equipment leakage or vented emissions from equipment located on the surface between the flow meter used to measure injection quantity and the injection wellhead. CO_{2FP} is defined as total annual CO_2 mass emitted (metric tons) as equipment leakage or vented emissions from equipment located on the surface between the production wellhead and the flow meter used to measure production quantity. The MRV plan should include a summary of considerations made to calculate equipment leaks and vented emissions from surface equipment between the flow meters and either injection or production wellheads, and the quantity of CO_2 that is produced with oil and water.

The mass balance equation assumes that all CO_2 measured at the flow meter is injected at the wellhead. In most cases this will provide an accurate estimate of injection volume. However, if additional surface equipment is located on the injection line after the point of flow/mass measurement, and before the injection well, there is a potential for equipment leaks and vented emissions that will not be included in the mass balance. Similarly, the measurement point for produced CO_2 (at the flow meter immediately downstream of the gas-liquid separator) is assumed to represent the amount of CO_2 exiting the wellhead. However if additional surface equipment other than the separator is located between the production wellhead and point of CO_2 measurement, an estimate of equipment leaks and vented emissions from that equipment must be made in accordance with the monitoring methods in §98.233 of the Petroleum and Natural Gas Systems Reporting Rule (subpart W of the GHG Reporting Program).[117]

The following table lists the surface CO_2 emission sources at an injection facility that may be located between the point of transfer onsite and the injection wellhead (selected from the list of all emissions sources under onshore petroleum and natural gas production at §98.232) and describes the methodologies provided in §98.233 of subpart W. Note that the compressors may or may not be a part of this operation depending on how the individual site configures its recycle stream. Compressors are used to compress the recycle stream, which is eventually converted to critical phase CO_2 that is mixed with the critical phase stream coming from outside facility boundary. In the event that there are

[117] http://www.epa.gov/climatechange/emissions/subpart/w.html

other vented or fugitive CO_2 emissions sources that are between the flow meter and the wellhead, the Reporter will need to use the respective monitoring methods for such sources as provided in §98.233.

Table 5-1: Surface Components as Potential CO_2 Emissions Sources at Injection Facilities

Emissions Source	Engineering Estimates[1]	Direct Measurement[2]	Equipment Count and Population Factor[3]
Natural gas pneumatic high bleed device venting[4]			X
Natural gas pneumatic low bleed device venting[4]			X
Natural gas pneumatic intermittent bleed device venting[4]			X
Natural gas driven pneumatic pump venting[4]			X
Reciprocating compressor rod and packing venting			X
EOR injection pump			X
EOR injection pump blowdown	X		
Centrifugal compressor wet seal oil degassing venting			X
Other equipment leaks (valve, connector, open-ended line, pressure relief valve)			X

(1) The engineering calculation methods use monitored process operating parameters and either engineering calculations (in the case of EOR injection pumps) or emission factors provided by the equipment manufacturer (in the case of pneumatic device or pneumatic pump).
(2) Direct measurement involves use of rotameters, turbine meters, or other meters, as appropriate, for emissions measurement directly from the vent stack. This would be repeated once each year to establish a site-specific, equipment-specific emission factor for use between repeat measurements.
(3) For the use of population factors, the relevant emission factors would be applied to all components using a count of the sources.
(4) ER operations that power pneumatic equipment by instrument air rather than natural gas would not have natural gas pneumatic emissions sources.

Equipment leaks and vented CO_2 emissions at an ER operation can also occur from surface components located between the production well and the point of CO_2 measurement. Between these two points, an injection facility will typically have valves, connectors, meters, and headers (which are large pipes that mix the oil stream from multiple wellheads). The procedures provided in subpart W for determining CO_2 emissions from all of these sources are equipment count and population factor.

The MRV plan must provide the basis for calculations of equipment leaks and vented emissions estimates from these points and include the emissions in the mass balance equations RR-11 or RR-12.

Fluids, including oil and water, produced at GS facilities may contain CO_2 that is not captured in the gas phase CO_2 measurement downstream of the gas-liquid separator. The CO_2 is present as dissolved gas in the oil and water phase of the produced fluids. To account for the amount of produced CO_2 that is not sequestered, the reporter must tailor the mass balance equation to account for the mass of CO_2 in all produced fluids. Equation RR-9 describes the mass balance of CO_2 at the gas-liquid separator where $CO_{2,P}$ represents the total mass of CO_2 in the incoming production stream (oil, water and CO_2), and $CO_{2,W}$ represents the amount of CO_2 in the separated gas stream. The value of “X” is the percent of CO_2 expected to remain with the produced oil and gas when referenced to the CO_2 separated for recycle or reuse.

The MRV plan must describe how the volume of CO_2 in produced fluids will be determined, and how the value of “X” will be calculated. The reporter should describe how the analysis of CO_2 in produced fluids will be performed. Commercial laboratories perform crude oil analyses and separator liquid analyses that can include quantification of CO_2 as a component. Because separators operate under pressure, the CO_2 saturation in water and oil inside the separator is higher than it would be at atmospheric conditions. Care must be taken to ensure the measured CO_2 concentration is representative of the pressure conditions at the measurement location. For analysis, the water and oil may need to be separated and analyzed using different methods. Several steps would be needed in order to estimate the quantity of CO_2 produced with oil, water or gas. The oil or gas stream of a production well at an ER operation is first separated into liquid phase and gas phase; the liquid phase is further separated into a water fraction and an oil fraction. CO_2 may be found in the following three streams following the gas-water-oil separation phase: 1) CO_2 in oil, 2) CO_2 in water, and 3) CO_2 in gas phase (along with other produced hydrocarbons). The amount of CO_2 in the oil (or water) can be estimated by multiplying the gas-to-oil (or gas-to-water) ratio by the volume of oil (or water) produced. The gas-to-oil (or gas-to-water) ratio can be determined using any standard test method (the ratio determination as well as chromatography are well understood techniques). A method to determine the amount of CO_2 in gas phase is to use a mass flow meter or volumetric flow meter to measure mass or volumetric flow rate of the produced gas stream that contains CO_2, take a sample of the stream, and analyze the stream for CO_2 composition, which can be done using chromatography.

A total fluids analysis from the separator liquid stream can also be performed to determine the amount of dissolved CO_2 in the oil and produced water. The total fluid analyses are often a combination of several ASTM or other methods. The selected sampling and analytical method(s) should consider the pressure at which the fluid is separated from the gas and differences in CO_2 solubility in oil and water. EPA has not identified consensus-based or industry standard analytical methods specifically for determining the amount of CO_2 in mixed produced fluids (oil and water); however, two potentially applicable methods for CO_2 in hydrocarbons were identified:

ASTM D2597 - 94(2004) Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

GPA Standard 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

To measure the CO_2 content in water co-produced with the oil, the reporter may use the following potentially applicable method:

ASTM D2513 - 06 Standard Test Method for Total Dissolved Carbon Dioxide in Water

The reporter must describe the analytical methods used and demonstrate the applicability of the methods in the MRV plan.

It is common in centralized production collection and processing sites receiving production from dozens of surrounding wells to have a “test trap.” This is a small gas/oil/water separator, outfitted with accurate flow measuring devices on all streams in/out, and manifolded to divert any one well through the test trap to gauge gas/oil/water ratio of each well. This is important in balancing the extraction of production between wells. If a well is drawing too much water, it can be slowed down and adjacent wells increased in production. This is where gas/oil/water production would be monitored for each well individually and regularly. Therefore, it is not necessarily the case that the sample point would involve a single CO_2 stream from a single well. There may be an aggregate point of monitoring from a collection of wells.

At some geologic sequestration sites where oil is not produced, saline water may be removed from the IZ to manage the pressure and capacity of the CO_2 storage system. The amount of dissolved CO_2 in the saline water removed from the IZ may be measured using ASTM D2513 - 06 Standard Test Method for Total Dissolved Carbon Dioxide in Water, or other consensus-based or industry standard methods. The MRV plan should describe the fate of the produced water and account for all CO_2 in the produced water.

5.6 Quality Assurance and Quality Control

To ensure accuracy in reporting the data from natural and engineered systems, reporters should document their quality assurance program for data collection and analysis. The MRV plan should define what quality assurance and quality control procedures will be implemented for each technology applied in the leak detection and quantification process. For example, the plan should describe how the reporter will ensure that sensor readings are correct, and describe (or reference) the quality control measures that are in place to ensure precision, accuracy, representativeness, completeness, and comparability of data.

Examples of quality control measures that may be described in the MRV plan include standard operating procedures, calibration requirements, redundancy of the sensor or measurement, criteria for equipment selection, maintenance schedules and procedures, and surveillance of subcontracted surveys or vendor materials.

5.7 Missing Data

Missing data procedures for the quarterly values of mass or volume, density, and concentration for both CO_2 injected and CO_2 received are provided at 40 CFR 98.445. Procedures are also provided for missing data on CO_2 production and for equipment leaks and vented emissions.

The rule does not require the reporter to develop missing data procedures for monitoring data described in the MRV plan. However, if leakage is detected for which a quantification approach is not outlined in the plan, information on the quantification approach should be included in the annual report. Similarly, if additional leakage pathways are identified, they should be assessed in accordance with the procedures in the "Assessment of potential surface leakage pathways" section of the MRV plan, and included in the annual report. Procedures for developing missing leak quantification data should be included in the MRV plan.

6. MRV Plan Approval Process Overview

If a facility is subject to subpart RR, the MRV plan must be submitted:[118]

- By June 30, 2011 if the facility was issued a UIC permit authorizing CO_2 injection on or before December 31, 2010.
- Within 180 days of receiving a final UIC permit (or offshore authorization) authorizing CO_2 injection.
- Any time if injecting CO_2 to enhance oil and gas recovery and not permitted under UIC Class VI.

Facilities will be allowed one extension of up to an additional 180 days. After submission of the MRV plan, the following review and approval process steps apply:

- Notification of receipt of MRV plan.
- Completeness check.
- Technical review.
- Issuance of EPA decision.

This chapter describes each step of the MRV plan approval process.

6.1 Suggested Outline for the MRV Plan

A suggested outline for the MRV plan may be found in Appendix D. The reporter may choose to modify this outline to meet site-specific requirements. The MRV plan outline addresses characteristics within the MMA; however, the plan may include information on geologic, topographic, cultural, and potential CO_2 source conditions outside the MMA, where appropriate, to assist EPA in developing a full understanding of potential influences on the proposed monitoring strategy.

6.2 Notification of Receipt of MRV Plan

EPA will accept MRV plan submittals from reporting entities that have established a "Certificate of Representation" through the GHG Reporting Program's Electronic Greenhouse Gas Reporting Tool (e-GGRT). All MRV plans must be submitted by the reporter electronically through e-GGRT. EPA has provided information and directions on how to electronically submit MRV plans on the subpart RR Web site: http://www.epa.gov/climatechange/emissions/subpart/rr.html. Upon MRV plan submittal, EPA will send a notice of receipt to the reporter within 15 days to acknowledge that EPA has received the MRV plan submission.

6.3 Completeness Check

[118] Please refer to http://www.epa.gov/climatechange/emissions/data-reporting-system.html for information on electronic data reporting.

EPA will first conduct a completeness check of the MRV plan submittal based on the regulatory requirements identified in Table 6-1. In addition, if a facility uses their UIC permit to fulfill or provide the basis for certain MRV plan requirements, the reporter should clearly identify relevant sections of the UIC permit as well as reference this information clearly in the MRV plan. EPA will determine if the MRV plan is complete within 45 days of the notice of receipt and will notify the reporter whether the plan is complete or incomplete.

EPA will issue a written notice that either requests additional information from the reporter or provides notice to the reporter that the MRV plan is complete and that the technical review will commence. In the case that the MRV plan is incomplete, the notice would specify the MRV plan requirements that were deemed to be incomplete, what additional information is needed, and the rationale for why such additional information is needed. If incomplete, the reporter must submit an updated MRV plan within 45 days of EPA notification unless otherwise specified by EPA.

Note that the completeness check is not a substitute for the technical review process. EPA will initiate the technical review process only upon determination of the completeness of the MRV plan.

Table 6-1: Completeness Check Criteria for MRV Plan Submittals and Resubmittals

Requirement	Subpart RR Section
The facility holds a certificate of representation	40 CFR 98.448(g)
Delineation of the maximum monitoring area and the active monitoring areas as defined in §98.449	40 CFR 98.448(a)(1)
Identification of potential surface leakage pathways for CO_2 in the maximum monitoring area and the likelihood, magnitude, and timing, of surface leakage of CO_2 through these pathways	40 CFR 98.448(a)(2)
A strategy for detecting and quantifying any surface leakage of CO_2	40 CFR 98.448(a)(3)
A strategy for establishing the expected baselines for monitoring CO_2 surface leakage	40 CFR 98.448(a)(4)
Summary of considerations to calculate site-specific variables for mass balance equation	40 CFR 98.448(a)(5)
If a well is permitted or is to be permitted under the UIC Program, the well identification number in the permit or permit application and the UIC permit class	40 CFR 98.448(a)(6)
If an offshore well is not subject to SDWA, any well identification number and any identification number used for the legal instrument authorizing GS	40 CFR 98.448(a)(6)
Proposed date to begin collecting data for calculating total amount sequestered according to equation RR-11 and RR-12 of subpart RR	40 CFR 98.448(a)(7)
For MRV plan revisions, the reason for resubmission	40 CFR 98.448(d)

6.4 Technical Review

After the determination of completeness, EPA will initiate technical review of the MRV plan. After 60 days of technical review, EPA will send the reporter a written request for additional information, including clarifying technical questions, if necessary. The reporter will be encouraged to provide a response to this request within 15 days; however, EPA recognizes that there may be circumstances where additional time is needed for the reporter to collect the information requested.

6.5 Issuance of EPA Decision

Within a reasonable period of time, EPA will issue a final MRV plan as submitted, or with revisions. EPA will post the approved MRV plan on a public Web site, subject to any limitations or requirements in its CBI determination.[119]

6.6 Appeals Period

If the reporter, or any interested person, objects to EPA's final decision, it may be appealed to EPA's Environmental Appeals Board. See Section II.B of the preamble for more information on the appeals process and see http://www.epa.gov/climatechange/emissions/subpart/rr.html for information on joining the interested person list.

6.7 Resubmittal of MRV Plans

An MRV plan may require revision and resubmittal if a material change was made to monitoring and/or operational parameters that was not anticipated in the original plan, if there has been a change in the permit class of the reporter's UIC permit, if the reporter is notified by EPA of errors in their MRV plan or annual monitoring report, or if the reporter chooses to revise their MRV plan for any other reason.

Examples of material changes include but are not limited to: large changes in the volume of CO_2 injected; the construction of new injection wells not identified in the MRV plan; failures of the monitoring system including monitoring system sensitivity, performance, location, or baseline; changes to surface land use that affects baseline or operational conditions; observed plume location that differs significantly from the predicted plume area used for developing the MRV plan; a change in the maximum monitoring area or active monitoring area; or a change in monitoring technology that would result in coverage or detection capability different from the MRV plan.

The reporter must submit a revised MRV plan if notified by EPA of errors in the MRV plan or annual monitoring report (AMR). A suggested format is provided in Appendix D.

[119] At the time of publication of this TSD, the CBI determination rulemaking for the GHG Reporting Program is not finalized (see Section II.B of the final preamble for a brief description of the CBI determination rulemaking). Please refer to http://www.epa.gov/climatechange/emissions/CBI.html for more information.

7. Annual Monitoring Report and Records Retention

Under the GHG Reporting Program, all reporters are required to electronically submit an annual GHG report to EPA that includes general reporting elements that are common across all sectors covered under the GHG Reporting Program,[120] as well as reporting elements that are specific to each subpart. This chapter outlines information to be included in the subpart RR annual monitoring report (AMR), per 40 CFR 98.446(f)(12). AMRs will be submitted each year by reporting entities through the e-GGRT system with other GHG data, and will summarize monitoring activities conducted in the past year. Reporters must include four components in AMRs:

- A narrative history of the monitoring effort conducted;
- A description of any non-material changes made to the MRV plan;
- A narrative history of any monitoring anomalies that were detected in the previous calendar year and how they were investigated and resolved; and
- A description of surface leakages, if any.

These four components are described in this chapter. Appendix D provides a suggested outline of an AMR. This outline includes all the key elements required to be included in an AMR, and is intended to be a suggestion for reporters to follow. The reporter may choose to modify this outline to meet site-specific requirements. Other information that reporters may deem as necessary to include in an AMR can and should be included as well.

7.1 Narrative History of Annual Monitoring Efforts

The first required component of an AMR is a narrative history of the monitoring effort conducted over the reporting year, including a listing of all monitoring equipment that was operated and its period of operation and any relevant tests or surveys that were conducted. This narrative history may include, for example, a general discussion cross-walking the monitoring activities implemented during the reporting year with the activities outlined in a facility MRV plan. Reporters may include a table that presents all the monitoring equipment used during a reporting period and the related information.

7.2 Report of Non-Material Changes to the MRV Plan

The second component required to be included in the AMR is a detailed report of any non-material changes made to the MRV plan over the course of the reporting year. Non-material changes to the MRV plan are those that do not warrant the submission of a revised MRV plan to EPA. Non-material changes to an MRV plan may include, for example, the use of newer versions of a technology that are already included as part of the EPA-approved MRV plan, or changes in the location of equipment that do not alter the coverage of detection capability of monitoring. To present this information in the AMR, a reporter could include a description of the non-material changes made to the

[120] Please refer to EPA's GHG Reporting Program Web site at: http://www.epa.gov/climatechange/emissions/ghgrulemaking.html

MRV plan, including an identification of the part of the MRV plan affected by the non-material change, supporting information for why the change is non-material, the purpose of the change, when the non-materials change occurred, and if it affected facility operations. To articulate non-material changes in the AMR, it may be useful for reporters to identify, in a list or table, the conditions that were used to determine what constituted a non-material change to their EPA-approved MRV plan. (See Appendix D)

7.3 Narrative History of Monitoring Anomalies

The AMR must also contain a narrative history of monitoring anomalies that were detected in the year and how they were investigated and resolved. This discussion could include a detailed description of all monitoring anomalies detected, and how the anomalies were investigated in line with the methods in the EPA-approved MRV plan, to determine if they represent a leak. This part of the AMR may also contain a description of how the monitoring anomalies were resolved. As an example, if an anomalous pressure reading at a monitoring well, that is later found out to be caused by a vent line obstruction, is detected, a reporter would include the following information in the AMR: a description of the pressure anomaly detected, a description of the steps taken to further investigate the reason for anomalous pressure reading and evaluate if it represents a leak (i.e., how the obstruction in the vent line was identified). The reporter may also include a description of the actions the reporter has taken/is planning to take to rectify the obstruction in the vent line. Reporters could also present this information along with other monitoring information presented in a table format. (See Appendix D)

This section of the AMR should also include a qualitative discussion of any unexpected operational or maintenance issues that caused down-time for the equipment. If the evaluation and investigation of a monitoring anomaly did result in the detection and quantification of a leak, reporters should include information discussed in Chapter 7.4.

7.4 Description of Surface Leakage

The fourth required component of the AMR is a description of surface leakages that happened during the reporting year (if any). Reporters must provide a description of any surface leakages of CO_2, including a discussion of all methodologies and technologies involved in detecting and quantifying the surface leakages and any assumptions and uncertainties involved in calculating the amount of CO_2 emitted.

In this section of the AMR, as part of the discussion of the methodologies and technologies involved in detection and quantifying the surface leakages, reporters could provide EPA with a demonstration showing that the methods and technologies used for leak detection and quantification followed the methods specified in the facility's MRV plan. This section might include, for instance, monitoring measurement records that showed monitoring anomalies that resulted in the reporter having to confirm the detection of a leak and quantify the leakage in that reporting year. If non-material deviations are made from the leakage detection and quantification approaches specified in the MRV plan it must be documented in the AMR. (See Chapter 7.2.)

This component of the AMR may also include qualitative descriptions and quantitative identifications (i.e., if a leak rate were assumed) of the assumptions that went into each leakage calculation. Reporters may also provide information demonstrating the assumptions' validity. Information on uncertainties may include a qualitative analysis of the uncertainty around the amount of CO_2 emitted. For instance, such an analysis may include a description of how variables such as the accuracy and precision of measurement instruments may have affected calculating the quantity of leakage determined, and how uncertainty in baseline conditions may have affected calculations as well. Reporters may also, if feasible, include a detailed quantitative analysis of the uncertainty around the quantity of leakage calculated. If a quantitative analysis is done, reporters should include examples of all calculations made, and descriptions of the statistical methodologies and parameters used.

In the AMR, reporters should show the verification of the quantity of leakage in accordance with the methods in the EPA-approved MRV plan. Reporters should provide calculations used to determine the quantity of leakage.

7.5 Records Retention Requirements for MRV Plans

Subpart RR requires facilities to retain records specified for retention in the MRV plan. These may include data that support the development and implementation of the MRV plan. Such records may be required to provide an auditable record of documentation in the event of an EPA-requested audit. The records to be retained should be sufficient to document the rationale of the decision-making process and demonstrate the completeness and accuracy of the data and calculations used in the detection and quantification of leaks to the surface. The MRV plan should state which documents are to be retained, and the format and/or location of the records. The duration for retention is 3 years per 40 CFR 98.3(g). Examples of records to be retained may include, but are not limited to, operational data, data sets used to construct expected baseline conditions, data relating to the detection or quantification of surface leakage, logs of mechanical integrity tests and pressure tests, and field books and photographs that record observations of field conditions.

Appendix A: Glossary

Above Confining Zone (ACZ): The geologic formation that is immediately above the caprock or CZ.

Active Monitoring Area (AMA): The area that will be monitored over a specific time interval from the first year of the period (n) to the last year in the period (t). The boundary of the AMA is established by superimposing two areas: 1) the area projected to contain the free-phase CO_2 plume at the end of year t, plus an all-around around buffer zone of one-half mile or greater if known leakage pathways extend laterally more than one-half mile; and 2) the area projected to contain the free phase CO_2 plume at the end of year t+5. (40 CFR 98.449)

Carbon dioxide (CO_2) plume: The extent underground, in three dimensions, of an injected CO_2 stream. (40 CFR 146.81(d))

Carbon dioxide (CO_2) stream: CO_2 that has been captured from an emission source (e.g. a power plant) plus incidental associated substances derived from the source materials and the capture process, and any substances added to the stream to enable or improve the injection process. (40 CFR 146.81(d))

Confining Zone (CZ): A geologic formation, group of formations, or part of a formation stratigraphically overlying the IZ(s) that acts as a barrier to fluid movement. For UIC Class VI wells operating under an injection depth waiver, CZ means a geologic formation, group of formations, or part of a formation stratigraphically overlying and underlying the IZ(s). (40 CFR 146.81(d))

Equipment leak: Those emissions that could not reasonably pass through a stack, chimney, vent, or other functionally-equivalent opening. (40 CFR 98.449)

Expected baseline: The expected baseline is the anticipated value of a monitored parameter that is compared to the measured monitored parameter. (40 CFR 98.449)

Formation or **geological formation**: A layer of rock that is made up of a certain type of rock or a combination of types. (40 CFR part 144 and part 146)

Free-phase CO_2 plume: That part of the CO_2 plume in which the injected CO_2 stream exists in gaseous, liquid or supercritical free phase. The precise definition will be stated by the reporter in the MRV plan based on site characteristics and the proposed methods of monitoring and modeling.

Free-phase CO_2 plume area: The 2-D vertical projection onto the surface of the free-phase CO_2 plume. The free phase CO_2 plume area is included within the AMA and MMA.

Geophysical surveys: The use of geophysical techniques (e.g., seismic, electrical, gravity, or EM surveys) to characterize subsurface rock formations. (40 CFR part 144 and part 146)

Injectate: The fluids injected (40 CFR part 144 and part 146). For the purposes of this rule, this is also known as the CO_2 stream.

Injection Zone (IZ): A geologic formation, group of formations, or part of a formation that is of sufficient aerial extent, thickness, porosity, and permeability to receive CO_2 through a well or wells associated with a GS project. (40 CFR 146.81(d))

Maximum Monitoring Area (MMA): The area that must be monitored under this regulation and is defined as equal to or greater than the area expected to contain the free phase CO_2 plume until the CO_2 plume has stabilized plus an all-around buffer zone of at least one-half mile. (40 CFR 98.449)

Mechanical integrity (MI): The absence of significant leakage within the injection tubing, casing, or packer (known as internal mechanical integrity), or outside of the casing (known as external mechanical integrity. (40 CFR part 144 and part 146)

Mechanical Integrity Test (MIT): A test performed on a well to confirm that a well maintains internal and external mechanical integrity. MITs are a means of measuring the adequacy of the construction of an injection well and a way to detect problems within the well system. (40 CFR part 144 and part 146)

Operational stage: The operational stage of a GS system includes the period of time during injection.

Pore space: Open spaces in rock or soil. These are filled with water or other fluids such as brine (i.e., salty fluid). CO_2 injected into the subsurface can displace pre-existing fluids to occupy some of the pore spaces of the rocks in the IZ. (40 CFR part 144 and part 146)

Separator: means a vessel in which streams of multiple phases are gravity separated into individual streams of single phase. (40 CFR 98.449)

Stratigraphic zone (unit): A layer of rock (or stratum) that is recognized as a unit based on lithology, fossil content, age, or other properties. (40 CFR part 144 and part 146)

Subsurface CO_2 Leakage: Subsurface leakage is injected CO_2 that is present outside the IZ but has not reached the surface.

Surface CO_2 Leakage: The movement of the injected CO_2 stream from the IZ to the surface, into to the atmosphere, indoor air, oceans, or surface water. (40 CFR 98.449)

Vented emissions: intentional or designed releases of CH_4 or CO_2 containing natural gas or hydrocarbon gas (not including stationary combustion flue gas), including process designed flow to the atmosphere through seals or vent pipes, equipment blowdown for maintenance, and direct venting of gas used to power equipment (such as pneumatic devices). (40 CFR 98.449)

Appendix B: U.S. Oilfields Using CO_2 Injection for Enhanced Oil Recovery

*Note that this table is a based on data summarized from the Oil & Gas Journal Enhanced Oil Recovery Survey published in April 2008 and April 2010 with permission of the publisher. Any other use of these data may be subject to copyright restrictions.
NR indicates that no production data were reported in the Oil & Gas Journal Survey.

Field	Operator	State	Incremental Production (bbl per day)
Rangely Weber Sand	Chevron	CO	11,600
Hall-Gurney (removed 2010)	Murfin Drilling	KS	3
Lockhart Crossing	Denbury Resources	LA	NR
Charlton 30-31	Core Energy	MI	75
Charlton 6	Core Energy	MI	10
Chester 2 (added 2010)	Core Energy	MI	NR
Dover 33	Core Energy	MI	75
Dover 35	Core Energy	MI	286
Dover 36	Core Energy	MI	195
Brookhaven	Denbury Resources	MS	3,100
Cranfield (added 2010)	Denbury Resources	MS	10,150
East Mallalieu	Denbury Resources	MS	1,800
Eucutta	Denbury	MS	3,000
Lazy Creek	Denbury Resources	MS	250
Little Creek	Denbury Resources	MS	1,650
Martinville	Denbury	MS	830
McComb	Denbury Resources	MS	1,650
Smithdale	Denbury Resources	MS	600
Soso	Denbury Resources	MS	1,700
Tinsley	Denbury Resources	MS	NR
West Heidelberg (added 2010)	Denbury Resources	MS	2,050
West Mallalieu	Denbury Resources	MS	6,200
North Hobbs	Occidental	NM	6,300
Vacuum	Chevron	NM	2,950
Vacuum	ConocoPhillips	NM	5,200
Bradley Unit	Merit Energy	OK	600
Camrick	Chaparral Energy	OK	1,175
Northeast Purdy	Merit Energy	OK	1,800
Postle	Whiting Petroleum	OK	4,500
Postle Expansion	Whiting Petroleum	OK	1,700
Sho-Vel-Tum	Chaparral Energy	OK	1,170
Abell (added 2010)	Fasken	TX	85
Adair San Andres Unit	Hess	TX	900
Adair Wolfcamp Unit (added 2010)	Apache	TX	420

Albert Spicer Unit (added 2010)	Chaparral Energy	TX	NR
Anton Irish	Occidental	TX	4,000
Booker Trosper Unit (added 2010)	Chaparral Energy	TX	NR
Cedar Lake	Occidental	TX	2,860
Central Mallet Unit	Occidental	TX	2,100
Cogdell	Occidental	TX	5,900
Cordona Lake	XTO Energy Inc.	TX	400
Dollarhide (Clearfork "AB") Unit	Pure Resources (Chevron 2010)	TX	1,970
Dollarhide Devonian Unit	Pure Resources (Chevron 2010)	TX	124
East Ford	Orla Petco	TX	128
East Penwell (SA) Unit	Energen Resources	TX	450
El Mar	Occidental	TX	270
Frazier Unit	Occidental	TX	925
Garza	George R. Brown	TX	NR
GMK South	Occidental	TX	375
Goldsmith	XTO Energy Inc.	TX	20
Gramstorff Unit (added 2010)	Chaparral Energy	TX	NR
Hanford	Fasken	TX	300
Hanford East	Fasken	TX	45
Hanford San Andres (added 2010)	Fasken	TX	NR
Hansford Marmaton	Stanberry Oil	TX	102
Igoe Smith	Occidental	TX	440
Levelland	Occidental	TX	950
Mabee	Chevron	TX	2,000
Means (San Andres)	ExxonMobil	TX	8,700
Mid Cross-Devonian Unit	Occidental	TX	296
N. Cross-Devonian Unit	Occidental	TX	835
North Cowden Demo.	Occidental	TX	80
North Dollarhide	Occidental	TX	1,000
North Perryton	Chaparral Energy	TX	170
North Ward Estes	Whiting Petroleum	TX	700
Reinecke	Pure Resources (Chevron 2010)	TX	830
River Bend (Devonian) (added 2010)	Fasken	TX	20
S. Cross-Devonian Unit	Occidental	TX	5,790
SACROC	Kinder Morgan	TX	24,227
Salt Creek	Occidental	TX	6,600
Seminole San Andres Unit - Main Pay and ROZ	Hess	TX	24,350
Sharon Ridge	Occidental	TX	400
Slaughter	Apache	TX	4,580
Slaughter (5 Units)	Occidental	TX	3,800
Slaughter Sundown	Chevron	TX	4,747
South Cowden	ConocoPhillips	TX	250

South Welch	Occidental	TX	865
T-Star (Slaughter Abo)	Occidental	TX	2,100
Twofreds	Great Western Drilling	TX	170
Wasson (Cornell and Mahoney Units)	XTO Energy Inc.	TX	2,250
Wasson (4 Units)	Occidental	TX	44,325
West Welch	Occidental	TX	0
Yates	Kinder Morgan	TX	6,280
Greater Aneth	Resolute Natural Resources	UT	400
Greater Aneth Area	ExxonMobil	UT	3,000
Beaver Creek (added 2010)	Devon	WY	2,425
Lost Soldier	Merit Energy	WY	7,221
Patrick Draw Monell	Anadarko	WY	3,000
Salt Creek	Anadarko	WY	6,000
Sussex	Anadarko	WY	NR
Wertz	Merit Energy	WY	4,019

Appendix C: Summary of Other End Uses of Captured or Produced CO_2

The following is a summary of end uses of captured or produced CO_2 (with the exception of ER and GS).

Cement. While not a common practice in the cement industry, some companies are currently working to employ a cement manufacturing process that uses captured CO_2.[121] The process will convert CO_2 into carbonic acid, which will be made into CO_3^{--}. The CO_3^{--} will be combined with calcium and magnesium from seawater to make calcium carbonate and magnesium carbonate for the cement.[122] EPA does not have enough information to conclude whether cement production using this CO_2 capture method permanently sequesters CO_2.

Precipitated Calcium Carbonate (PCC). PCC is produced through a chemical reaction process that utilizes calcium oxide (quicklime), water, and CO_2. The CO_2 used to manufacture the PCC is in some cases captured from lime kilns operated at pulp and paper manufacturers. The PCC is available in numerous crystal morphologies and sizes, which can be tailored to optimize performance in specific applications. EPA does not have enough information to conclude whether PCC production using this CO_2 capture method permanently sequesters CO_2.

Food and Beverage Manufacturing. The food and beverage industry is one of the largest consumers of manufactured and captured CO_2 in the U.S. CO_2 is used widely throughout the food and beverage industry for a variety of applications including:

- Carbonation of soft drinks;
- Beer and wine production;
- Decaffeination of coffee and tea;
- pH adjustment and shelf life lengthener for dairy products;
- Frozen food production; and
- Canning.

Pulp and Paper Manufacturing. CO_2 is used in the pulp and paper industry in production processes to control pH, decrease calcium levels, increase de-watering, buffer the paper making system, and recover chemicals in the mill process.[123, 124]

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[121] Engineering News-Record. 2009. New Green-Concrete Process Combines Seawater, Flue Gas, February 18, 2009, http://64.62.167.123/images/uploads/news/press-coverage/enr.pdf (accessed July 26, 2009).
[122] Biello, David. 2009. *Cement from CO_2: A Concrete Cure for Global Warming?*, Scientific American, http://www.scientificamerican.com/article.cfm?id=cement-from-carbon-dioxide (accessed July 26, 2009).
[123] Linde Gas, AGA and the Pulp and Paper Industry. http://www.aga.fi/international/web/lg/aga/like35agacom.nsf/docbyalias/nav_pulp_paper (accessed October 25, 2010)
[124] US Patent 6200416 - Recycled paper production process which incorporates carbon dioxide, March 2001 http://www.patentstorm.us/patents/6200416/description.html (accessed July 26, 2009).

Industrial and Municipal Wastewater Treatment. Industrial and municipal wastewater treatment facilities use CO_2 to control pH levels in the water and treat soft water by dissolving lime.[125]

Metal Fabrication. CO_2 is used for metal fabrication to enhance the hardness of casting molds; CO_2 is also used during welding and cutting of metal as a shielding gas to prevent the molten metal from oxidation.

Greenhouse Uses for Plant Growth. CO_2 is used to increase plant growth in greenhouses that produce flowers to full growth, nursery plants in early developing stages, and some produce (e.g., tomatoes).

Fumigants and Herbicides. CO_2 is used in the agricultural sector as an herbicide for organic produce that successfully kills insects and increases storage life; and as a fumigant for grain storage to control insects in the storage facility.

Medical Treatment. For medical treatment, CO_2 is added to oxygen to stimulate breathing and balance CO_2/O_2 levels in patients.

Construction. In the construction and manufacture industry, CO_2 is used on a large scale as a shield gas in metal inert gas (MIG) welding and metal active gas (MAG) welding, where the gas protects the weld puddle against oxidation by the surrounding air.[126] A mixture of argon and CO_2 is commonly used to achieve a higher welding rate and reduce the need for post-weld treatment. Additionally, dry ice pellets are used to replace sandblasting when removing paint from surfaces. Dry ice aids in reducing the cost of disposal and cleanup.

Rubber and Plastic Industry. CO_2 cleaning, also known as dry ice blasting, is a method of cryogenic cleaning. Dry ice is used to remove flash from rubber objects by tumbling them with crushed dry ice in a rotating drum. Almost all major tire manufacturers use CO_2 cleaning in their rubber molds. Shoe companies as well as gasket and other small rubber companies have successfully been using CO_2 cleaning as part of their routine machine maintenance. Additionally, in the production of polymer foams, liquid CO_2 is used as a blowing agent instead of environmentally hazardous substances. CO_2 is a physical blowing agent with properties desired for ideal foaming, while simultaneously fulfilling many requirements related to quality, efficiency, and the environment.

Fire Suppression. CO_2 fire extinguishers are used for Class B fires (involving flammable and volatile liquids) and Class C fires (involving electrical equipment).

Cleaning and Solvent Use. Liquid CO_2 is used a solvent for cleaning a variety of products during manufacturing processes, e.g., electronics cleaning and metal cleaning. Liquid

[125] Linde Industrial Gases, Products and Supply, Wastewater. http://www.linde-gas.com/en/products_and_supply/water_treatment/index.html (accessed October 25, 2010).
[126] Metal inert gas (MIG) welding and metal active gas (MAG) welding are two subtypes of gas metal arc welding (GMAW).

CO_2's solvent potential has been employed in some dry cleaning equipment as a substitute for conventional solvents.

Refrigeration and Cooling. Liquid and solid CO_2 are important refrigerants, especially in the food distribution industry, where they are employed during the transportation and storage of ice cream and other frozen foods, primarily in small retail food stores. In those cases, the CO_2 may be stored on-site or be provided by refrigerant technicians at the time of recharging.

Transportation and Storage of Explosives. CO_2 is used in the transportation and storage of explosives as it reduces the explosion risk.

Algae Production. Algae plantations for the production of biofuels have recently been under the spotlight, primarily with respect to potential capture of CO_2 from electric power and chemical production projects. The biofuel production from captured CO_2 represents a potential GHG/carbon sink. Also of strong interest is the use of algae as a source of feedstock material for the production of biodiesel, and perhaps fermentation. CO_2 is an ingredient used by algae for normal growth, during photosynthesis. The process is being studied at various pilot projects in the U.S. and elsewhere.

Pressurized Gas. CO_2 is used as an inexpensive, nonflammable pressurized gas. Compressed CO_2 gas is used in life jackets (stored inside canisters), in air guns, in paintball markers, and for inflating bicycle tires.

Chemical processes. CO_2 is currently used for various processes in the chemical industry, including but not limited to, the production of:

- Urea (from ammonia);
- Methanol;
- Ethanol; and
- Sodium Bicarbonate.

Pharmaceutical Processes. Pharmaceutical processes may use CO_2 as a less toxic alternative to organochlorides or more traditional solvents.

Appendix D: Suggested Outlines for MRV Plans, MRV Plan Resubmittals, and Annual Monitoring Reports

<u>Suggested Outline for MRV Plan and MRV Plan Resubmittals</u>

1) Facility Information
    i) Reporter number
    ii) UIC permit class
    iii) UIC injection well identification numbers
    iv) Authorization for CO_2 injection if an offshore well not subject to SDWA
    i) MRV plan identification number (for resubmittals)
    ii) Date most recent MRV plan approved by EPA (for resubmittals)
    iii) Reason for re-submittal (for resubmittals)
2) Project Description
    a) Project characteristics
        i) Estimated years of CO_2 injection
        ii) Estimated tons CO_2 received over lifetime of project
    b) Environmental Setting of the MMA
        i) Surface and subsurface boundary of the MMA
        ii) Geology and hydrogeology
        iii) Historical use of subsurface and surface
        iv) Available reference sites (near but outside project area for development or adjustments to baselines)
    c) Description of the Injection Process
        i) Variability of CO_2 composition
        ii) Number, location and depth of injection wells
        iii) Compression/pumping, conditioning and pipelines at the facility
    d) Reservoir Characterization and Modeling
        i) Simulation model(s) used
        ii) Modeling objectives
        iii) Modeling procedures
        iv) Data inputs, sources, quality control, update process
        v) Model outputs
        vi) Grid size and resolution
        vii) Model calibration process and sensitivity analysis
3) Delineation of the monitoring areas
    a) MMA
        i) Determination of free phase plume extent
        ii) Determination of buffer zone
    b) AMA(s)
        i) Initial monitoring period, area and time frame
        ii) Future monitoring periods, areas and time frames
4) Evaluation of Leakage Pathways
    a) Well pathway(s)

    b) Fractures, faults and bedding plan parting pathway(s)
    c) Confining system pathway(s)
    d) Other identified pathways(s)
5) Detection, Verification and Quantification of Leakage
    a) Leakage detection methods
        i) Process for detecting leakage for each pathway
        ii) Performance measures for leak detection
    b) Leakage Verification and Quantification Methods
        i) Process for verifying and quantifying leakage for each pathway
        ii) Performance measures for verifying and quantifying leakage
6) Determination of Expected Baselines
    a) Monitoring method A expected baseline method
    b) Monitoring method B expected baseline method
    c) Monitoring method C expected baseline method
7) Site Specific Modifications to the Mass Balance Equation
    a) Equipment leaks and vented emissions from surface equipment downstream of injection flow meter
    b) Equipment leaks and vented emissions from surface equipment downstream of production well flow meter (if applicable)
    c) CO_2 produced in oil and other fluids
8) Estimated Schedule for implementation of MRV plan
    a) Timing for expected baseline determination
    b) Timing of implementation of leakage detection and quantification monitoring
    c) Proposed date to begin collecting data for calculating total amount sequestered according to equation RR-11 or RR-12 of this subpart.
9) Quality Assurance Program
10) Records Retention
11) Appendices

Suggested Outline for Annual Monitoring Report to EPA-approved MRV plans

1) Executive Summary
   a) Date MRV plan approved by EPA
   b) MRV plan identification number
2) Summary Table of Monitoring Activities (suggested format Table D-1)
3) Narrative History of the Monitoring Effort Conducted
   a) Listing of all monitoring equipment, period of operation, and relevant tests or surveys conducted (see also suggested table format above)
   b) Cross walk of annual monitoring activities with approved MRV plan
4) Non-Material Changes to EPA-Approved MRV Plan
5) Narrative History of Monitoring Anomalies Found
   a) Monitoring anomalies detected, resulting investigations, and resolutions (see also Table D-1)
6) Description of Surface Leakage
   a) Methodologies and technologies used
      i) Description of alignment with EPA-approved MRV plan
      ii) Non-material deviations from the leakage detection and quantification approaches specified in the MRV plan
      iii) Measurement records showing detection of monitoring anomalies
   b) Assumptions Involved in Calculating the Quantity of CO_2 Emitted
      i) Assumption identification and supporting information
   c) Uncertainties Involved in Calculating the Quantity of CO_2 Emitted

Table D-1: Suggested Format for Listing of Monitoring Equipment

	Monitoring Equipment	Period of Operation	Tests/Surveys Conducted	Test/Survey Results	Monitoring Anomaly Investigation	Resolutions After Monitoring Anomaly
1	[Equipment technology type, make and model number]	[Dates of operation]	[Identification of tests/surveys conducted]	[Brief summary of survey results and identification of any anomalies detected]	[If anomalies were identified, a brief summary of action taken to evaluate and investigate the anomaly and the related results (i.e., if it is concluded that the anomaly represents a leak)]	[A brief summary of the follow-up actions taken after anomalies are further evaluated an investigated]
2	Monitoring well Number T31NR14WS23-IZ, Paine model 213-36-940 Pressure Transducer	Continuous from August 1, 2011 through December 31, 2011	Hourly recording of pressure in IZ @ 5020 feet	September 23-28, 2011, increased pressure (up to 2180 psi) detected at this location. Exceeded baseline expectation by 21 psi	Secondary pressure transducer at this location did not read elevated pressure. Investigation revealed that vent line was obstructed.	Vent line obstruction corrected on September 29, 2011.

Appendix E: Sampling Considerations for Designing a Monitoring Strategy

A consideration in designing a leakage detection strategy and also in establishing an expected baseline is ensuring adequate data resolution to cover a range of points in space and time. A non-representative data set that contains too few samples at too few times of day/year from too few locations will generate a biased picture and result in erroneous decision making. A sampling program may be designed to ensure consideration of the appropriate frequency of sampling, aerial extent of sampling, and sample size.

Frequency of Sampling

If the environmental factor being measured incurs considerable intra-day and/or seasonal variation, the sampling program may be designed to capture these fluctuations. An example of a parameter that shows high intra-day and seasonal variation is near-surface CO_2 flux. A program based on CO_2 flux monitoring would need a high frequency of sampling across the year. On the other hand, if the environmental parameter being monitored is not known to show a substantial intra-day or seasonal variation, the sampling program could rely on a lower frequency of sampling. An example of such a parameter may be fluid pressure in a deep confined reservoir to be used for ACZ monitoring. To account for different monitoring technologies or variability in the monitoring area, the reporter may employ different frequencies within the monitoring area to achieve adequate baseline definition. The MRV plan should clearly define the frequency of baseline sampling and provide a rationale for the chosen frequency.

Areal Extent of Sampling and Subdividing Maximum Monitoring Area

The specific method used for the measurement of the monitored environmental parameter will produce values representative of a certain area. Eddy covariance towers are known to produce flux estimates representative of a radius equal to approximately 50 times the height of the tower.[127] If cost-effective, it would thus be possible to construct as many eddy covariance towers as necessary to ensure coverage of the entire monitoring area. On the other hand, if the method employed produces representative values for a small range, it may be necessary to rely on statistical techniques to balance cost and coverage. Accumulation chambers are an example of a technique that measures a very small area (tens of cm^2). Expert judgment based on modeling results may be used to focus sampling in higher CO_2 leakage risk areas and limit sampling in lower risk areas. Modeling inputs and sensor placement should be updated periodically with the results from the monitoring program to redefine the areal sampling plan as necessary. The MRV plan should present the rationale for selecting the areal extent of sampling and demonstrate that it provides adequate coverage to determine a representative baseline. If the monitored parameter is expected to vary by subdivisions of the MMA, then the proposed subdivisions and the process for preparing expected baselines for each should be presented in the plan.

[127] Campbell Scientific, Inc. 2004-2006. Open Path Eddy Covariance System Operator's Manual CSAT3, LI-7500, and KH20. Available at: http://www.campbellsci.com/documents/manuals/opecsystem.pdf

Sample Size

An adequate sample size will ensure greater ability to detect differences between prevailing conditions and the expected baseline. Approximate knowledge of sampling variation in the measured parameter (potentially based on prior sampling experience) could be used to estimate the number of samples needed to limit the occurrence of false positives and false negatives to the desired level. Frequently, cost considerations place limitations on the number of samples that may be gathered such that reporters should estimate the probability of occurrence of false positives and false negatives to better guide decision making. For instance, if calculations show a high probability of a false negative at a given location for a given sample size, the reporter could initiate a program for securing more samples from that area before taking a decision. Knowledge of the expected sampling variation in a parameter will improve with each successive sampling phase, which in turn will improve the accuracy of the predicted sample size for the specified error rates. The MRV plan should demonstrate that the sample size is adequate to account for the observed variability in the measured parameter.

Coverage Adequacy of a Sampling Program

The MRV plan is likely to include one or more leakage detection or quantification monitoring techniques that involve collecting data at one or more locations within the MMA. This appendix explains how the statistical coverage adequacy of a given sampling program (i.e., the probability a given size of leak will be detected) can be computed and presented in an MRV plan.

The overall probability that a given leak will be detected is the probability that the leak will be physically encountered by the sampling program times the probability the leak will be recognized once encountered. In equation form this is:

$$P_d = P_e \times P_r \qquad \text{(Equation 1)}$$

Where:
P_d = overall probability leak will be detected
P_e = probability leak will be encountered by a sampling program
P_r = probability leak will be recognized once encountered

The probability that the leak will be recognized after it is encountered (P_r) can be computed given the mean and standard deviation in the expected environmental or operating baseline, and the mean and standard deviation of the measured parameter. As noted earlier, P_r is equal to one minus the chance of false negatives. As discussed below, the probability of any given monitoring element encountering the leak, P_e, is a function of the size of the monitoring area, the size and shape of the leak area, the size and shape of the sample coverage, and the number and pattern of sampling.

The “leak area” may be specified in terms of how much total area the expected leak will encompass. It may also be useful to know, if possible, how many separate pieces or segments the leak area will be in at the surface (or other monitoring zone), and what shape (maximum length of the leak in one dimension) those segments might take. The leak area can be estimated by hypothesizing a size of leak to be examined and estimating the expected dispersion pattern to the surface (or to another monitoring zone such as a shallow USDW) for a given leakage pathway. The dispersion pattern for leaks along artificial penetrations and faults would be expected to be more easily defined, and probably have smaller footprints compared with CZ leaks, which can meander and break apart traveling upward. The dispersion modeling would indicate the expected area of the leak in units such as square meters and the surface flux in units such as micrograms of CO_2 per square meter per second ($\mu g\ m^{-2}\ s^{-1}$). The probability of encountering the leak is related to the leak area, while the probability of recognizing the leak once encountered is often related to the flux.

The term “sample coverage” refers to the physical area over which the monitoring method provides a representative measurement of the parameter. Common types of sample coverage are: point, linear, and area. For example, a soil gas sample typically would provide a “point sample coverage” for a limited area without a significant length or width. A closed-path remote sensing sample consisting of a laser beam bounced off a mirror would have a “linear sample coverage,” which is an area with length but no significant width. An eddy covariance survey would typically have an “area sample coverage,” which is a roughly circular area with a given radius. An example of the effect of leakage footprint size on eddy covariance detection station density is presented by Cortis et al.[128]

[128] Cortis, A., Oldenburg, C.M., and Benson, S.M. 2008. The role of optimality in CO2 seepage detection for geological carbon sequestration sites. *International Journal of Greenhouse Gas Control*, Vol. 2(4) Special Issue: Sp. Iss. SI, 640-652. doi:10.1016/j.ijggc.2008.04.008.