

Design of a perfluorocarbon tracer based monitoring network to support monitoring verification and accounting of sequestered CO₂

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Abstract. The levels of CO₂ in the atmosphere have been growing since the beginning of the industrial revolution. The current level is 391 ppm. If there are no efforts to mitigate CO₂ emissions, the levels will rise to 750 ppm by 2100. Geologic carbon sequestration is one strategy that may be used to begin to reduce emissions. Sequestration will not be effective unless reservoir leak rates are significantly less than 1%. There must be rigorous monitoring protocols in place to ensure sequestration projects meet regulatory and environmental goals. Monitoring for CO₂ leakage directly is difficult because of the large background levels and variability of CO₂ in the atmosphere. Using tracers to tag the sequestered CO₂ can mitigate some of the difficulties of direct measurement but a tracer monitoring network and the levels of tagging need to be carefully designed. Simple diffusion and dispersion models are used to predict the surface and atmospheric concentrations that would be seen by a network monitoring a sequestration site. Levels of tracer necessary to detect leaks from 0.01 to 1% are presented and suggestions for effective monitoring and protection of global tracer utility are presented.

1. INTRODUCTION

There has been a growth in demand for energy since the beginning of the industrial revolution. The atmospheric concentration of CO₂ is increasing with this growth. The preindustrial atmospheric background level was 280 ppm; by 1958 this had risen to 315 ppm; and in 2005 it had risen to 379 ppm (1). The current atmospheric level is 391 ppm (2). The rate of emissions growth is also increasing. The quantity of CO₂ emissions grew by 1% per year in the period from 1980–2000. This rate had increased to greater than 3% per year in the period 2000–2005 (3). If there are no changes in these trends, the business as usual projection, the IPCC predicts that CO₂ emissions will increase to 77 Gt per year by the year 2100, there will be 9,000 Gt emissions of CO₂ into the atmosphere over the 21st century and the concentration will rise to 750 ppm by 2100 (1), (4), (3).

Stabilization of atmospheric levels of GHGs will require a mix of strategies (5), (6) including increasing energy efficiency, switching to energy sources that do not produce CO₂ such as nuclear and solar energy and wind power, and reducing the CO₂ emissions from fossil fuel energy production through carbon capture and storage (CCS). CCS will act as a bridging technology to facilitate a transition from fossil fuels to a sustainable energy based economy. Sequestration technology has been successfully used in commercial applications and numerous demonstration projects are in place to provide the research necessary for development and application of this technology. The focus of sequestration programs is large point sources of CO₂; there are 8,100 CO₂ point sources globally where CCS could be employed (4). Coal fired power plants are the largest, most common of these sources. They produce 40% of anthropogenic CO₂ emissions and supply approximately 50% of US energy generation. A 1000 mW coal fired plant will produce approximately 8.6 million tons of CO₂ per year over a 30-year lifetime (7). A minimum of 90% reduction of

CO₂ emissions from coal fueled power plants is required to stabilize atmospheric CO₂ levels. The goal of the US Department of Energy (DoE) sequestration program is to have advanced CCS technology ready for large scale demonstration in 2020 (8).

Monitoring Verification and Accounting (MV&A) at sequestration sites is necessary to insure regulatory compliance, health and safety of local populations and ecosystems, and ensure the global environmental benefit of sequestration projects. CCS will not gain acceptance as a climate mitigation strategy without robust MV&A protocols in place.

2. GEOLOGIC CO₂ SEQUESTRATION

Geologic Sequestration of CO₂ is the removal of CO₂ from combustion effluent and placing it in permanent storage deep underground. It consists of three parts:

- Capture of CO₂ from major stationary sources;
- Transporting it to a storage site, probably by pipeline; and
- Permanent storage of CO₂ underground.

Total geologic storage capacity for CO₂ is estimated at 1,100 to 3,400 Gt (4), (9).

Three types of geological formations are under consideration for storage.

The first type is mature and oil and gas fields. These natural reservoirs have stored hydrocarbons safely for millions of years. Supercritical CO₂ injection is used routinely by the oil and gas industry for enhanced oil recovery (EOR). Injection of the CO₂ decreases the oil viscosity and increases oil production while leaving CO₂ in the depleted oil reservoir (10). The extraction of otherwise inaccessible oil also increases the space available for CO₂ storage. EOR using CO₂ was begun in 1970s (7). Approximately 30 Mt of CO₂ per year is injected for EOR in the US (11).

The second type of geological formation is unmineable coal beds. It is expected that injection of CO₂ in these formations will also produce natural gas (12), (7).

The third type of geological formation under consideration is deep saline aquifers. These are formations 100s of meters to kilometers underground that are saturated with water which is not suitable for household or agricultural use because it contains high levels of dissolved salts. These formations are accessible globally over large areas – approximately 2/3 of land area in the US is located above deep saline formations. They have the most potential capacity for carbon storage of the three geological features under consideration and, because they are so geographically extensive, will allow storage of captured CO₂ near production sources (7), (12), (13).

3. RESERVOIR INTEGRITY

3.1. Leakage pathways

Leakage during transport or directly from the reservoir can reduce or eliminate the effectiveness of CCS. Reservoir Leakage pathways include pore systems in cap rock; openings in cap rock caused by natural fractures and faults; and, the most likely pathways, man-made faults in improperly sealed new or abandoned wells (14). The threat of abandoned wells is significant in places where CCS may be applied in conjunction with EOR. There are 350,000 existing wells in the Alberta Basin and 20,000 wells new drilled per year (7), (1). There have been 1.5 million oil and gas wells drilled in Texas (15). The location and condition of many of these wells may not be documented.

There are other effects that may compromise the integrity and reduce the maximum storage capacity of geologic reservoirs. The injection process may cause a rise in reservoir pressure that forces CO₂ to enter the cap rock pores or exceeds the pressure that will fracture the containing formation. Other undesirable effects may be the displacement and transport of the existing formation fluid to the oceans, to the atmosphere, or to subsurface formations such as mines, or basements. There also may be displacement of brine or other contaminants into aquifers (16).

3.2. Acceptable leak rates

The leak rate from geological storage reservoirs must be less than 1%. Hepple and Benson (6) determined that a 1% leak rate will result in the return on most of the sequestered carbon to the atmosphere after 400 years. They show that long term global performance requirement for stabilization of atmospheric levels at 350, 450, or 550 ppm required a leak rate less than 0.01%; that stabilization at 650 to 750 ppm required a leak rate less than 0.1%; and that rates of 0.01 to 0.1% are required to achieve mitigation of climate effects of atmospheric CO₂ (16). A 0.01% leak rate results in 90% retention for 1000 years while 0.001% results in 99% retention for 1000 years. They also assert that these rates are technologically achievable. The DOE performance target for demonstration projects is a leak rate less than 1% of stored amount (17).

4. MONITORING VERIFICATION AND ACCOUNTING

4.1. Goals of monitoring

Monitoring, Verification and Accounting (MV&A) is used to describe measurement and observations designed to support the research, health and safety, regulatory, and environmental goals of CCS programs.

The research goals identified by the US DoE MV&A program are:

- To understanding storage processes,
- To map CO₂ subsurface movement, and
- To evaluate CO₂ interactions with the target geological formation.

These goals are designed to further the understanding of sequestration processes and provide data for model development and validation.

The Health and Safety goals of the DoE MV&A program are designed to ensure that the local environment and human health are protected. Large CO₂ leaks can lead to health and safety issues. In 1986 a massive natural release of CO₂ from a lake bottom in Cameroon killed more than 1,700 people (18). Basements and confined spaces might be at risk from reservoir leaks along fault lines. Local groundwater may be at risk from displaced brine or contaminants released into aquifers by the chemical action of the sequestered CO₂.

The Global environmental goals of the DoE MV&A program are designed to ensure the achievement of long term greenhouse gas reduction targets (17), (19) and the regulatory requirements necessary to account for CO₂ stored for cap and trade, and treaty obligations.

MV&A programs will also provide a technical basis to assist in resolving legal disputes such as the alleged leaks from the disputes Weyburn EOR project (20).

4.2. Levels of monitoring

4.2.1. Sub surface

The geological formations where sequestration is proposed are hundreds of meters to kilometers underground. Mapping of the CO₂ pool in these reservoirs can be accomplished using 3-D seismic imaging (21), electrical resistivity tomography (22), gravitometry, and direct measurement of samples collected from monitoring wells (23).

4.2.2. Near surface

Near surface monitoring consists of soil gas analysis and testing ground water. Analysis of ground water can detect changes in the composition that may indicate leaks of CO₂ or brine into the local aquifers and can be used to identify natural or introduced tracer compounds. Inelastic neutron scattering can also be used to detect excess carbon in the soil (24). All these methods rely on pre-injection surveys to establish a baseline levels against which post-injection anomalies can be evaluated for indications of leaks.

4.2.3. Atmosphere

Detection of reservoir leaks by direct measurement of CO₂ at the surface will be difficult because of the high background levels and large variability of CO₂ in the atmosphere. This variability is a result of natural and anthropogenic sources as well as diurnal and seasonal effects. Eddy correlation methods have been proposed as a means to directly detect CO₂ leaks at the surface. This technique consists of fast response concentration measurements made in conjunction with 3-D wind data to determine surface CO₂ fluxes. This method is most effective when used in flat terrain with homogeneous vegetation. Other methods, including remote sensing using FTIR spectroscopy and satellite imagery have been proposed (17). Chemical compounds known as tracers can be used to tag the injected CO₂. When these compounds are detected they indicate the presence of tagged CO₂ and if the tagging ratio is known can be used to determine the size of the reservoir leak. Tracer compounds include natural isotopes that are unique to the sequestered CO₂ and introduced compounds such as noble gases, SF₆, and perfluorocarbon compounds (12), (24). Transport and dispersion along pathways both above and below the surface will significantly dilute the plume, so the quantity of tracer used to tag the CO₂ must be sufficient to allow detection at the levels necessary to ensure sequestration is effective.

5. DISPERSION MODELS

5.1. Subsurface

A model of subsurface transport is needed to determine the concentration of the tracer at the surface that will result from a leak in the cap rock. We developed a simple diffusion model with the assumptions that the rock above the reservoir cap acts as a porous medium and that fracture flow does not occur after the CO₂ escapes from the reservoir. If there was a subsurface fracture there would be a direct route to the surface and transport may be much faster.

The basic transport equation for diffusion controlled movement is:

$$\partial C / \partial t = D \nabla^2 C + \frac{Q}{\theta}.$$

Where C is concentration, D is the diffusion coefficient; Q is the release rate of the material being transported, and θ is the soil porosity.

5.1.1. Model results

The models were run with a diffusion coefficient $D = 110^{-2} \text{cm}^2/\text{s}$ and a source at depths from 100 m to 1 km. The calculated times for a leak to reach the surface with a dilution factor of 10^{-6} are given in Table 1.

Examining the results in Table 1, it is clear that unless there is a method to transport the tracer to within

Table 1. Time required for normalized concentrations near the surface to reach 10^{-6} .

Source Depth (m)	$D = 10^{-2} \text{cm}^2/\text{s}$ Time (years)
100	12
200	60
300	130
400	240
500	380
600	570
700	800
800	1150
900	1400
1000	1750

Table 2. Pasquill Gifford stability classes.

Stability class	Definition
A	very unstable
B	unstable
C	slightly unstable
D	neutral
E	slightly stable
F	stable

100 meters of the surface, the time required to be able to detect the leak at the surface will be tens to hundreds of years. Diffusion controlled point source leakage from faults in the cap rock is not a mechanism that will cause a significant loss of sequestered CO₂.

The diffusion coefficient used in the calculations is typical for sandy soils. Soils with high clay content may exhibit even lower diffusion coefficients and longer transport times. The model only considers the case of open porosity between the release depth and the surface. If there is an aquifer between the release and the surface, transport will be significantly different from the model results and it will be difficult to predict the transport effects. Monitoring must include ground water measurements.

5.2. Atmospheric dispersion model

A simple Gaussian Plume model was used to predict atmospheric dispersion (25). The concentration at any point downwind, x, and a distance y from the center line of the plume, is then given by:

$$\chi(x, y, z = 0, 0) = \frac{Q}{\pi u \sigma_y \sigma_z} \exp \left[-\frac{y^2}{2\sigma_y^2} \right].$$

The source and receptors were both at ground level, $z = 0$. The standard deviations in the z and y directions are determined by the horizontal and vertical fluctuations in the wind. The standard deviations have been parameterized according to a system of identifying the wind fluctuations, known as the Pasquill-Gifford stability classes (Table 2). The dilution isopleths for stability class D, neutral, are presented in Figure 1.

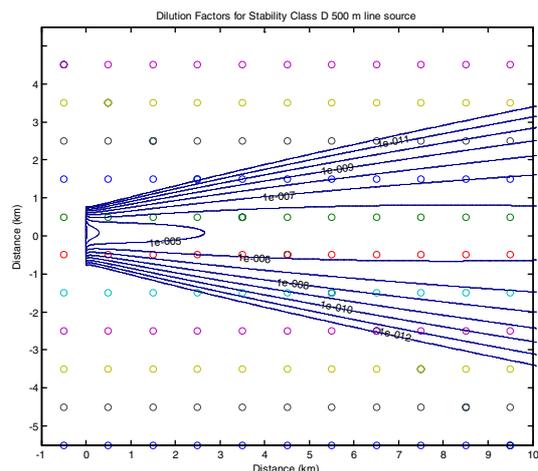


Figure 1. Isopleths of dilution factors for a 1 km line source and stability class D on a 10×10 km grid. Open circles represent the sampling sites.

Table 3. $[\text{CO}_2]$ at 1 km distance from source for a dilution factor of 10^{-5} .

Q	$\chi(\text{CO}_2)$	
leak rate	concentration	
(%year ⁻¹)	mixing ratio	(ppmv)
1.00%	4.2E-04	416
0.10%	4.2E-05	42
0.05%	2.1E-05	21
0.01%	4.2E-06	4

Table 4. PFTs commonly used as tracers.

Acronym	Chemical Name	Formula
PDCB	Perfluorodimethylcyclobutane	C ₆ F ₁₂
PMCP	Perfluoromethylcyclopentane	C ₆ F ₁₂
PMCH	Perfluoromethylcyclohexane	C ₇ F ₁₄
o-PDCH	Perfluoro-1,2-dimethylcyclohexane	C ₈ F ₁₆
i-PPCH	Perfluoroisopropylcyclohexane	C ₉ F ₁₈
PTCH	Perfluorotrimethylcyclohexane	C ₉ F ₁₈

The model illustrates the difficulty of directly measuring CO_2 at leak rates less than 1%. Atmospheric CO_2 levels undergo large diurnal, seasonal, and site specific fluctuations. One monitoring station has recorded 100 ppm changes over a single day (26). The results of the model for concentrations of CO_2 at a receptor 1 km from the source of the leak are given in Table 3. It is obvious that detection of a leak of less than 0.1% will be difficult to distinguish from typical variations caused by meteorology, natural cycles, and local combustion sources.

The tagging of the injected CO_2 with a tracer is a technique that can be used to overcome the difficulties of direct measurement. The detection limit for perfluorocarbon tracers is on the order of 100 fg (10^{-15} g) (24) and the background levels are in the parts per quadrillion level, 9 orders of magnitude less than CO_2 . The perfluorocarbon compounds commonly used as tracers are given in Table 4 and backgrounds and atmospheric loads for 5 PFTs are given in Table 5.

Table 5. Background atmospheric concentration and total atmospheric load of PFTs (24).

	PDCB	PMCP	PMCH	oPDCH	ptPDCH
Bkgd (ppqv)	3	8	8	1	7
Total Atmospheric load (metric tons)	140	430	500	71	500

Table 6. PFT tagging levels for detection at 1 km distance from the source and a dilution factor of 10^{-5} .

CO_2 leak rate (year ⁻¹)	PFT		
	Q PFT/QCO ₂ ppm	kg PFT year ⁻¹	tons PFT total
1.00%	1.2E-04	1	3.2E-02
0.10%	1.2E-03	10	3.2E-01
0.05%	2.4E-03	20	6.3E-01
0.01%	1.2E-02	110	3.2E+00

The extremely low detection limits and background levels make PFTs very useful in detecting leaks in the atmosphere.

A concept for a sampling network was designed using the following criteria and assumptions:

- Significant leaks will only occur from direct transport to the surface through faults or active or abandoned wells.
- The CO_2 source will be a 1000 MW coal fired power plant which will release.
 - 8.6 million tons of CO_2 per year,
 - Over a 30 year lifetime.
- 100 km² surface area above the storage pool will be monitored.
- The sampling grid will consist of:
 - Passive sampling,
 - 100 sampling locations,
 - 1 km spacing.
- Sample analysis will be monthly.
- Only a subset of samples will be analyzed.
- PFT background of 10 ppqv.
- Signal to background ratio of ~ 1 .
- Acceptable leak rate < 1% per year.

The locations of the passive sampling sites are shown relative to the leak plume as open circles in Figure 1. Table 6 shows the PFT levels necessary to tag sequestered CO_2 to detect leak levels from 0.01 to 1% of the total sequestered over the lifetime of a 1000 mW coal fired plant.

6. CONCLUSIONS

Perfluorocarbon tracers offer advantages over direct measurement of CO_2 for monitoring verification and accounting at CCS sites. The design of the monitoring network and the sampling strategy has to be carefully planned to take advantage of the unique properties of PFTs while accomplishing the goals of monitoring. A grid of

passive samplers with a 1 km spacing is the minimum necessary to be able to detect leaks at reasonable tagging levels. Monthly sample collection is necessary to be able to distinguish between background levels and a leak. A strategy for selectively analyzing samples from the grid should be developed based on the site meteorology. This can be used to select the samples most likely to be in the plume of a leak and reduce analytical costs.

A global agreement on the use of tracers for monitoring CCS projects should be developed. The utility of PFTs or any other tracer will be lost if the background levels are allowed to rise indiscriminately. Global background monitoring of tracer levels should be part of a comprehensive strategy of CCS MV and A.

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