

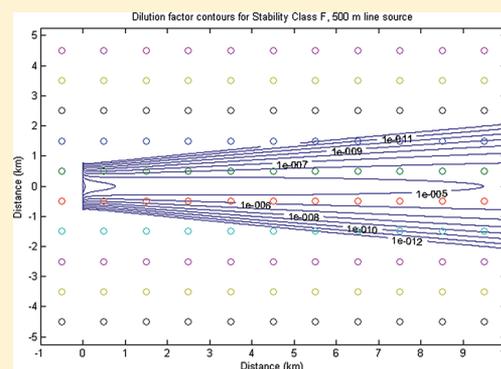
## Feasibility of a Perfluorocarbon tracer based network to support Monitoring, Verification, and Accounting of Sequestered CO<sub>2</sub>

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### S Supporting Information

**ABSTRACT:** Carbon capture and sequestration (CCS) will act as a bridging technology necessary to facilitate a transition from fossil fuels to a sustainable energy based economy. The Department of Energy (DOE) target leak rate for sequestration reservoirs is 1% of total sequestered CO<sub>2</sub> over the lifetime of the reservoir. This is 0.001% per year for a 1000 year lifetime of a storage reservoir. Effective detection of CO<sub>2</sub> leaks at the surface may require incorporation of a tracer tag into the sequestered CO<sub>2</sub>. We applied a simple Gaussian Plume model to predict dispersion of a direct leak into the atmosphere and used the results to examine the requirements for designing a perfluorocarbon (PFT) monitoring network and tracer tagging strategy. Careful consideration must be given to the climate implications of using these compounds. The quantity of PFTs needed for tagging sequestered CO<sub>2</sub> is too large to be practical for routine monitoring. Tagging at a level that will result in 1.5 times background at a sampler 1 km from a leak of 0.01% per year will require 625 kg per year of PFT. This is a leak rate 10 times greater than the 1000 year DOE requirement and will require 19 tons of injected PFT over the 30 year lifetime of a 1000 mega watt coal fired plant. The utility of PFTs or any other tracer will be lost if the background levels are allowed to rise indiscriminately. A better use of PFTs is as a tool in sequestration research. Instead, geological surveys of sequestration sites will be necessary to locate potential direct pathways and develop targeted monitoring strategies. A global agreement on the use of tracers for monitoring CCS projects should be developed.



### INTRODUCTION

Stabilization of atmospheric levels of greenhouse gases will require a mix of strategies, including increasing energy efficiency, switching to energy sources that do not produce CO<sub>2</sub> such as nuclear and solar energy and wind power, and reducing the CO<sub>2</sub> emissions from fossil fuel based energy production through carbon capture and sequestration (CCS). CCS will act as a bridging technology necessary to facilitate a transition from fossil fuels to a sustainable energy based economy. Monitoring, verification, and accounting (MV&A) at sequestration sites is necessary to ensure regulatory compliance, health and safety of local populations and ecosystems, and mitigation of the climate effects of anthropogenic CO<sub>2</sub>. CCS will not gain acceptance as a climate mitigation strategy without robust MV&A protocols in place.

Sequestration has been successfully used in commercial applications and there are numerous demonstration projects in place to provide the knowledge and experience necessary for application of this technology. There are an estimated 8100 large CO<sub>2</sub> point sources worldwide where CCS could be employed.<sup>1,2</sup> Coal fired power plants are the largest, most common of these sources of CO<sub>2</sub>. They produce 40% of anthropogenic CO<sub>2</sub> emissions and supply approximately 50% of U.S. energy generation. A 1000 mega watt (mW) coal fired plant will produce approximately 8.6 million tons of CO<sub>2</sub> per year over a 30-year lifetime.<sup>3</sup> A minimum reduction of 90% of

CO<sub>2</sub> emissions from coal fueled power plants is required to stabilize atmospheric CO<sub>2</sub> levels.<sup>4</sup>

Direct measurement of CO<sub>2</sub> at sequestration sites as a means to detect leaks is difficult because of the high background level of CO<sub>2</sub> and the large variations in the ambient concentration.<sup>5</sup> Therefore, a tracer is needed to detect leaks in sequestration reservoirs. Perfluorocarbon tracers (PFTs) are good candidates for this use because of their low background levels and existence of analytical methods for these compounds with limits of detection in the femtogram (10<sup>-15</sup> g) range. However, large quantities will be needed to tag the sequestered CO<sub>2</sub>. This paper will examine the requirements for the implementation of a perfluorocarbon tracer based surface monitoring network.

**Geologic CO<sub>2</sub> Sequestration.** Geologic Sequestration of CO<sub>2</sub> consists of capture of CO<sub>2</sub> from major stationary sources, transport to a storage site, and permanent storage of CO<sub>2</sub>. Total global storage capacity for CO<sub>2</sub> is estimated at approximately 2000 to 11 000 Gt CO<sub>2</sub>,<sup>1,2</sup> which is 22–120% of the high estimate of cumulative emissions predicted by the end of the 21st century.<sup>6</sup> Three types of geological formations are under consideration for storage. Mature oil and gas fields are

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natural reservoirs that have stored carbon safely for millions of years. Supercritical CO<sub>2</sub> injection is routinely used by the oil and gas industry in fields where production has declined in an operation known as enhanced oil recovery (EOR). Injection of the CO<sub>2</sub> decreases the oil viscosity and allows more oil to be extracted while sequestering the CO<sub>2</sub>.<sup>7</sup> EOR using CO<sub>2</sub> was begun in the 1970s<sup>3</sup> and approximately 30 million tons of CO<sub>2</sub> per year is injected for EOR in the U.S.<sup>8</sup> Unmineable coal beds have also been proposed as potential reservoirs for geologic CCS.<sup>9,2</sup> There are no current commercial or demonstration projects where CO<sub>2</sub> is being injected into these geological structures. Deep saline aquifers are formations hundreds of meters to kilometers underground saturated with water containing high levels of dissolved salts that are not suitable for household or agricultural uses. These formations are accessible over large areas of the U.S.—approximately two-thirds of the land area in the U.S. is located above deep saline formations. They have the largest potential physical capacity for carbon storage of the three geological structures under consideration.<sup>2,9,10</sup>

Successful pilot programs and commercial projects have demonstrated that geological sequestration of CO<sub>2</sub> is technologically feasible. Four commercial CO<sub>2</sub> sequestration programs are currently in operation. Over 20 million tons of CO<sub>2</sub> had been successfully injected at these projects by the end of 2008. These projects are examined in detail in Supporting Information (SI) 1.

Three projects sponsored by the DOE have tested PFTs as tracers. The West Pearl formation is a depleted sandstone oil field in southeast New Mexico. Three perfluorocarbon tracers were injected along with the CO<sub>2</sub> at 42 ppm by weight in 2002. The tracer subsurface data was used to estimate the leakage rate at approximately 0.0085% of the total CO<sub>2</sub> sequestered.<sup>11</sup> Leakage was believed to be occurring along the well casing. The first pilot injection of CO<sub>2</sub> into a saline aquifer in the U.S. was the Frio Brine Experiment conducted in 2004. PFTs, Krypton, Xenon, and SF<sub>6</sub> were used as tracers to monitor CO<sub>2</sub> plume migration. The CO<sub>2</sub> was tagged at 71 and 27 ppm PFT to CO<sub>2</sub> by weight.<sup>12–14</sup> The Zero Emissions Research and Technology (ZERT) test site was designed to study near surface CO<sub>2</sub> transport and monitoring techniques.<sup>15</sup> These techniques included passive sampling of perfluorocarbon tracers using tagging levels of 351 ppm in 2007,<sup>15</sup> 114 ppm in 2008,<sup>15,16</sup> and 162 ppm in 2009.<sup>17</sup>

**Reservoir Integrity.** Leakage from the storage reservoir will diminish the effectiveness of CCS. Leakage pathways include pore systems in cap rock; openings in cap rock caused by natural fractures and faults; and man-made pathways resulting from improperly sealed new or abandoned wells.<sup>18</sup> Small, persistent leaks over the thousands of years necessary for storage can eliminate the effectiveness of sequestration as a climate mitigation tool.<sup>19</sup> The threat of abandoned wells is significant in places where CCS may be applied in conjunction with EOR because of the large number of wells drilled in oil producing areas. There are 350 000 existing wells in the Alberta Basin and 20 000 new wells drilled per year.<sup>18,20</sup> One and a half million oil and gas wells have been drilled in Texas. The location and condition of many of these wells may not be documented.<sup>21</sup>

Studies on the effects of leakage from storage reservoirs have established that the overall leak rate from CCS must be less than 1% of total stored CO<sub>2</sub> per year and that rates of 0.01–0.1% per year are necessary to mitigate the climate effects of

atmospheric CO<sub>2</sub>,<sup>22,23</sup> particularly when the additional energy consumption necessary for CCS is taken into account.<sup>24</sup> Lindeberg<sup>19</sup> presents modeling results that suggest the minimal average residence time “should be at least 10 000 years”. Pacala<sup>23</sup> presents an analysis that shows individual sites in a heterogeneous reservoir system could have an annual mean leak rate of 1% of total sequestered CO<sub>2</sub> and still be effective. He estimates a reduction from the business as usual projection of 750 ppm by 2100 to a target of 450 ppm if there are other reservoirs in the system with lower leak rates. Ha-Dong and Keith<sup>21</sup> have determined that 0.1% per year is effective in reducing atmospheric levels, while a leak rate of 0.5% is not. Hepple and Benson<sup>25</sup> determined that stabilization at 350, 450, or 550 ppm required an annual leak rate less than 0.01% per year of total stored CO<sub>2</sub> and stabilization at 650–750 ppm required a leak rate less than 0.1% per year. These authors maintain that these rates are technologically achievable. The DOE goal is 99% retention of stored CO<sub>2</sub>.<sup>4,26</sup> If the lifetime of a reservoir is assumed to be 1000 years,<sup>8</sup> this is a leak rate of 0.001% of total stored CO<sub>2</sub> per year.

**Monitoring Verification and Accounting.** Monitoring verification and accounting describes a variety of measurement techniques designed to track the quantity, movement, and security of sequestered CO<sub>2</sub>. Surface and near surface monitoring techniques for monitoring are reviewed in detail by Klusman<sup>5</sup> and include direct measurement of CO<sub>2</sub>, eddy covariance, lidar, and use of tracer compounds to tag the CO<sub>2</sub>.<sup>26</sup> Tracers are elements or chemical compounds present in the reservoir CO<sub>2</sub>, that, when detected, indicate the presence of injected CO<sub>2</sub>. Tracers may be naturally occurring such as isotopes that are unique to the sequestered CO<sub>2</sub> or noble gases or radon that are displaced from the underground formations as the CO<sub>2</sub> is injected. They also may be compounds such as SF<sub>6</sub>, and perfluorocarbon compounds<sup>9,26</sup> that are introduced into the CO<sub>2</sub> before injection. Transport and dispersion along pathways both above and below the surface will significantly decrease the concentration of the plume, so the quantity of tracer in the CO<sub>2</sub> must be sufficient to allow detection after dispersion at the levels necessary to ensure sequestration is effective.

**CO<sub>2</sub> Monitoring Challenges.** Detection of reservoir leaks of 1% per year or less of sequestered CO<sub>2</sub> by direct measurement of CO<sub>2</sub> at the surface will be difficult because of the high background levels and large variability of CO<sub>2</sub> in the atmosphere.<sup>5</sup> This variability is a result of natural and anthropogenic sources as well as diurnal and seasonal effects. For example, the variation caused by anthropogenic sources can be seen in measurements across a power plant exhaust stack plume. The peak CO<sub>2</sub> measured in a plume, 7.5 km down-wind of the plant, was 22 ppm above background.<sup>27</sup> The combination of diurnal variability with anthropogenic emissions has been observed to exceed 100 ppm in isolated small town settings<sup>28</sup> as well as large urban settings.<sup>29,30</sup> Diurnal variations of 40 ppm have been observed at 30 and 50 m levels on rural towers in North Carolina and Wisconsin<sup>31</sup> and as high as 42 ppm at a mountain site in Colorado.<sup>32</sup> Diurnal variation of 20 ppm in winter and 60 ppm in spring has been observed in rural Spain.<sup>33</sup> McAlexander et al.<sup>34</sup> observed diurnal variations in ambient CO<sub>2</sub> background between 361 and 539 ppm. Eddy correlation methods have been proposed as a means to directly detect CO<sub>2</sub> leaks at the surface. This technique consists of fast response concentration measurements made on towers in conjunction with 3-D wind data to determine surface CO<sub>2</sub>

fluxes.<sup>24,25</sup> This method is most effective when used in flat terrain with homogeneous vegetation and is restricted to sampling a limited footprint that varies with the meteorological conditions.<sup>35</sup> Other methods, including remote sensing using FTIR spectroscopy and satellite imagery have been proposed,<sup>26</sup> but suffer from the same problems of discriminating natural variability from CO<sub>2</sub> coming from reservoir leaks. Klusman<sup>5</sup> came to the following conclusion: "...the gas concentration in the atmosphere and its natural variability set important limits on the above ground detection and measurement of gas microseepage by eddy covariance or open-path spectroscopic methods. Because of higher atmospheric concentration and high natural variability, CO<sub>2</sub> will be much more difficult to detect than a reservoir-derived natural-, or added tracer gas with a lower atmospheric concentration and less variance"

## MATERIALS AND METHODS

The monitoring network must detect leaks above a critical threshold in the range of 0.001 to 1% of total sequestered CO<sub>2</sub> per year. We applied simple models of subsurface and atmospheric transport and dispersion to predict the concentration levels that would occur from various leak rates to develop specifications for the performance of a PFT MV&A network.

**Subsurface Dispersion Model.** We applied a model of subsurface transport to determine the concentration at the surface that would result from a leak in the cap rock. The model assumes that overburden, the soil and rock above the reservoir cap, acts as a porous medium and that transport along direct channels resulting from fractures in the overburden does not occur after the CO<sub>2</sub> escapes from the reservoir. Our previous field work with PFTs in underground systems has shown that diffusion is the rate controlling process in porous media below ground level at depths greater than one meter.<sup>36</sup> Releases from the reservoir will be through fractures in the cap rock. The leaks may be driven by the pressure of the CO<sub>2</sub> in the reservoir which will force the supercritical liquid for some distance into the overlying porous media. At some point, the pressure difference will dissipate, the CO<sub>2</sub> will be in the gas phase, and the flow will become diffusion controlled. Point source leaks at a range of soil depths were examined with the model to explore the effects of pressure driven flows and consider the results of fractures of various lengths in the overburden.

The maximum depth from the surface to the cap rock that was modeled was 1000 m. Details of the subsurface diffusion model are presented in SI 2.

The model results are normalized to the maximum concentration so the values are expressed in terms of a dilution factor. The results are displayed as a function of radius from the release point in the X, Y plane. The time required for the CO<sub>2</sub> front, diluted by a factor of a million (10<sup>-6</sup>), to reach the surface from a point source leak in a cap rock 500 m below the surface is more than 425 years. The time required for the CO<sub>2</sub> front to reach the surface from a leak located 1000 m below the surface with the same dilution factor of 10<sup>-6</sup> is 1750 years.

Table 1 presents the normalized concentrations and travel time for the 10<sup>-6</sup> dilution front to reach the surface for source depths from 200 to 1000 m and diffusion coefficients<sup>36</sup> from 1 × 10<sup>-2</sup> to 5 × 10<sup>-2</sup> cm<sup>2</sup>s<sup>-2</sup>. The range of diffusion coefficients examined is typical for sandy soils. Soils with high clay content may exhibit even lower diffusion coefficients and subsequently longer transport times. The model results show that diffusion controlled transport to the surface from a leak in a cap rock

**Table 1. Time Required for Normalized Concentrations near the Surface to Reach 10<sup>-6</sup>**

source depth (m)	D = 10 <sup>-2</sup> cm <sup>2</sup> /s time (years)	D = 2 × 10 <sup>-2</sup> cm <sup>2</sup> /s time (years)	D = 5 × 10 <sup>-2</sup> cm <sup>2</sup> /s time (years)
200	60	30	12
400	240	120	48
600	570	290	110
800	1150	575	230
1000	1750	875	400

400–1000 m deep will take 240–1750 years to reach the atmosphere at a million to one dilution. The results in Table 1 show that unless there is a pathway from a fracture in the overburden or an improperly capped or abandoned well, transport time of detectable levels of the reservoir gas to the surface will be tens to hundreds of years for leaks at depths greater than 200 m. Even though the assumption of leak from a point source in the cap rock is somewhat unrealistic, changing the geometry to an area source or line source would not change the time of arrival. Diffusion controlled leakage from faults in the cap rock is not a mechanism that will cause a significant loss of sequestered CO<sub>2</sub>.

**Surface Dispersion Model.** The more likely mechanism of significant leaks is through fault systems or poorly sealed or abandoned wells providing a direct pathway for transport of sequestered CO<sub>2</sub> to the surface. We applied a simple Gaussian Plume model as presented by Turner<sup>37</sup> to model dispersion of a direct leak into the atmosphere. Details of the dispersion model are given in SI 3. The source and receptors were both set at ground level, z = 0. 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 is modeled as a line at the surface 500 m long. Dispersion is controlled by horizontal and vertical Gaussian parameters that are a function of the downwind distance and the Pasquill-Gifford stability class. The mean wind speed is assumed to be 2 ms<sup>-1</sup>.

The results are expressed in terms of an effective dilution factor expressed in units of sm<sup>-3</sup> (seconds and inverse cubic meters) and are calculated by dividing the concentration at the sampler or receptor point by the release rate. Results of the neutral case, stability class D, are presented in Figure 1 and SI 3. These data, and the results presented in SI 3, show that atmospheric dilution occurs rapidly over short distances. Class A is the worst case for detection of the leak at the surface because the mixing and therefore dilution are at a maximum and concentrations will be lowest. It can be seen in the data that 1 km from the release, the concentration of the plume has dropped by a factor of more than 10<sup>-6</sup>. The data for stability classes D and F, neutral, and very stable, show a minimum dilution factor of 10<sup>-5</sup> at distances up to 2 km for class D and 9 km for class F (SI 3, Figures 3 and 4, and Tables 8 and 9).

**Stability Class Frequency.** The frequency of occurrence of stability classes determined by observations and models from six investigations, as well as the mean and standard deviation of these frequencies is given in SI 3, Table 6. There are three broad classifications of atmospheric mixing: unstable or well mixed with the most dispersion; neutral or mixed with

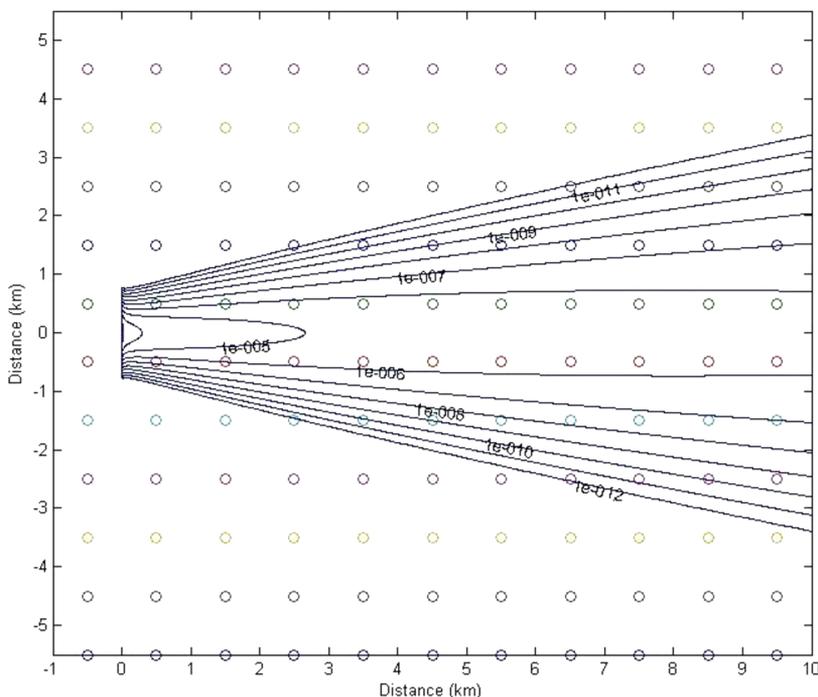


Figure 1. Isopleths of dilution factor for stability class D on a 10 × 10 km sampling grid.

moderate dispersion, and stable with the little dispersion. These data show that the three classifications occur with roughly the same frequency, although neutral may be somewhat more common, particularly in some geographical settings.<sup>38</sup>

**Monitoring Network Design.** A concept for a sampling network was designed using the assumptions that significant leaks will only occur from direct transport to the surface through faults or problems with active or abandoned wells and that the source is a reservoir containing the captured CO<sub>2</sub> produced by a 1000 mW coal fired power plant operating for 30 years for a total of 2.6 × 10<sup>8</sup> tons. The monitored area is a 100 km<sup>2</sup> surface area above the storage pool. The sampling grid will consist of 100 sampling locations with one km spacing and be sampled passively. We chose this coverage area and spacing as a compromise between spatial coverage and number of samples. The signal to background ratio should be approximately one and an acceptable leak rates are 0.001–1% per year of total stored CO<sub>2</sub> or 2.6 × 10<sup>3</sup> to 2.6 × 10<sup>6</sup> tons per year. The locations of the passive sampling sites are shown as open circles in Figure 1.

Samplers will be exposed to background levels for the entire sampling period. The time during which the plume from the leak will be sampled will be considerably less than the time that background levels will be sampled. They will only be exposed to the leak at concentrations significantly above background level for the time the wind is in a favorable direction and the meteorological conditions neutral or stable. Using the optimistic assumptions that the wind will be from a favorable direction 25% of the time, and that the stability class will be either neutral or stable 50% of the time, then the sampler will be in plume of the leak 12% of the sampling time. During this time the sampler will collect material from the plume in addition to the background. The other 88% of the time it will be sampling background levels.

The quantity of material seen on the sampler will be given by

$$m_s = S_r t [0.88B + 0.12(X + B)]$$

Where  $m_s$  ≡ quantity of analyte collected on the sample (mass units);  $S_r$  ≡ the sampling rate (unit volume, unit time<sup>-1</sup>);  $t$  ≡ the sampling time;  $B$  ≡ the background concentration of the analyte (mass units, volume<sup>-1</sup>); and  $X$  ≡ the concentration of the plume at the centerline resulting from the leak (mass units, volume<sup>-1</sup>)

If we assume that  $S_r t$  is equal to a unit volume, then the right side of the equation is in mass units. If the desired mass seen on the sampler is some factor,  $a$ , of the background level,  $B$ , it can be expressed as

$$m_s = aB$$

The concentration in the plume will be given by

$$X' = \frac{(a - 1)B'}{0.12}$$

The prime denotes the quantity of analyte in the collected sample volume in mass units.

Using this formulation, it can be seen that the concentration of analyte in plume must be eight times the background concentration to collect two times background level at the sampler. The critical factor in detecting the leak is not the detection limit of the analytical method, but the level of the ambient background of the target compound. The ratio of plume to background level,  $X'/B'$  necessary to have 1.5–10 times background quantities at the sampler are given in Table 2.

**PFT Tracers.** Perfluorocarbon compounds (PFTs) are good tracers because of their low background levels and excellent detection limits. They are used in a variety of research and practical applications. Details of their properties are given in Watson et al.<sup>39</sup> A brief summary will be given here. The perfluorocarbon tracer compounds (PFTs) are inert and very stable totally fluorinated alkylcycloalkane compounds consist-

**Table 2. Ratio of Concentration at Plume Centerline to Background Concentration Necessary to Collect a Factor of “a” Times Background Level at the Sampler**

a	1.5	2	3	4	5	10
X'/B'	4	8	17	25	33	75

ing of 4, 5, and 6 atom carbon rings. Background concentrations are several parts in  $10^{15}$  (parts per quadrillion by volume, ppqv) so the release of small amounts of PFT results in unambiguous signals. They are detectable at femtogram ( $10^{-15}$ g) levels PFTs typically used as tracers are given in SI 4, Table 10.

PFTs have no biological effects and, because they contain no chlorine atoms, do not deplete stratospheric ozone, but they are powerful greenhouse gases.<sup>40</sup> There are environmental concerns about releasing them into the atmosphere because the same characteristics that make them good atmospheric tracers cause them to have atmospheric lifetimes of thousands of years<sup>41,42</sup> and strong infrared absorption features.<sup>40</sup> The exact global warming potentials (GWP) of PFTs are currently being studied, but atmospheric lifetimes and GWPS can be estimated from similar compounds such as perfluorocyclobutane, with an atmospheric lifetime of 3200 years and 100 and 500 year GWPs of 10 090 and 14 740.<sup>41</sup> PFTs used in tracer applications have an insignificant impact on the global radiation budget because of the low ambient atmospheric levels, low release levels, and negligible growth rate in atmospheric concentration.<sup>39</sup> However, the potential for large effects from substantial releases make careful scrutiny essential when considering them for any large scale use such as widespread tagging of sequestered carbon. If the GWP is 14 740 the maximum tagging ratio that allows a lower impact from the PFTs compared to CO<sub>2</sub> is  $1/14\,740$  or 68 ppm. If tagging is done at a higher ratio, the PFT loss rate will have a larger effect on the radiation budget than the CO<sub>2</sub> loss from the reservoir.

The PFTs are soluble in hydrocarbons, so they are not conservative tracers in petroleum reservoirs. They will not be transported with the bulk flow of CO<sub>2</sub>, but the flow will be retarded with respect to the bulk flow rate.<sup>43,44</sup> There will also be PFT losses if the CO<sub>2</sub> is transported through some fault, abandoned well, or other direct pathway. The PFTs will be delayed with respect to the CO<sub>2</sub> and with respect to each other because of surface interactions with the rock, soil, or other solid substrate in the pathway. Two or three PFTs should be injected so the delays can be assessed.

## RESULTS AND DISCUSSION

**Modeling Application to CO<sub>2</sub> Monitoring.** We used the atmospheric model to predict the CO<sub>2</sub> levels that would be seen at a sampler that was located on the plume centerline and

1 km from a line source leak. The source is a reservoir containing  $2.6 \times 10^8$  tons of CO<sub>2</sub> or 30 years of emissions from a 1000 mW power plant. The data for stability classes D and F, neutral and very stable, show a minimum dilution factor of  $10^{-5}$  at distances up to 2 km for class D and 9 km for class F (SI 3 Figures 3 and 4, and Tables 8 and 9). The concentration, in the best case scenario, where the dilution factor is  $10^{-5}$ , is 420 ppm resulting in a leak contribution to background (X'/B') ratio of 1.1 or 10% higher than ambient levels (Table 3). The results for lower, more effective leak rates are even less. A leak rate of 0.01% results in a value of P'/B' of 0.01 or a signal 1% above background. This would be undetectable given the large variability in ambient CO<sub>2</sub> levels.

**PFT Tagging Calculations.** The starting point for calculation of the PFT tagging level is the PFT background, B'. We calculated this assuming a background level of 10 ppqv or one part in  $10^{-14}$  (SI 5) giving  $1.43 \times 10^{-10}$  g PFT m<sup>-3</sup> for the ambient background. We used this number to calculate the plume centerline concentration, X', necessary to see 1.5–10 times background level and the release rate from the leak necessary to get this plume concentration at the sampler for a dilution factor of  $10^{-5}$ . These calculations are made with the optimistic assumption that there are no losses or delays of PFT during underground transport. The results are given in Table 4. The tagging ratio can then be calculated for leak rates from 0.001 to 1.0% per year of the total CO<sub>2</sub> sequestered in the reservoir. Table 4 shows the PFT levels necessary to tag CO<sub>2</sub> to detect leak levels from 0.001 to 1% of the total sequestered over the lifetime of a 1000 mW coal fired plant. The tracer tagging ratio for the range of plume centerline concentrations is given in Table 5. The mass of PFT necessary to tag the CO<sub>2</sub> in kg per year is given in Table 6. The leak rates for the DOE Requirement of 1% loss of stored CO<sub>2</sub> from the reservoir with the assumption of a 1000 year lifetime is given in the 0.001% per year row in the tables.

It is clear that perfluorocarbon tracers offer advantages over direct measurement of CO<sub>2</sub> for monitoring verification and accounting at CCS sites. Direct measurement of CO<sub>2</sub> in the atmosphere for leak detection is impractical because of the large variations in the levels of ambient CO<sub>2</sub>. Perfluorocarbon tracers are one method to detect leaks in sequestration reservoirs and are the most practical compounds to use as tracers. However, a relatively large amount of material will be needed to tag the sequestered CO<sub>2</sub>. Tagging at a level that will result in 1.5 times background at a sampler 1 km from a leak of 0.01% per year will require 625 kg per year of PFT (Table 6). That is 19 tons of PFT over the 30 year lifetime of the plant. Currently PFT tracers cost about \$400 per kg. If economies of scale reduce this to \$10/kg, then the tracer cost of tagging at 0.07 ppm will be more than \$6 thousand per year or \$180 thousand over the lifetime of a single 1000 mW power plant.

**Table 3. Centerline Concentration of a CO<sub>2</sub> Plume for Reservoir Leak Rates from 0.01 to 1.0%, 1 km from the Leak Source under Neutral or Stable Conditions (D–F), and Ratio of Plume Concentration to Background**

leak rate (year <sup>-1</sup> )	leak rate (tons year <sup>-1</sup> )	X, leak contribution to plume concentration		total plume concentration B + X	X'/B'
		concentration (volume mixing ratio)	concentration (ppmv)		
1.00%	$2.3 \times 10^6$	$4.2 \times 10^{-4}$	420	796	1.1
0.10%	$2.3 \times 10^5$	$4.2 \times 10^{-5}$	42	422	0.1
0.05%	$1.15 \times 10^5$	$2.1 \times 10^{-5}$	21	401	0.05
0.01%	$2.3 \times 10^4$	$4.2 \times 10^{-6}$	4.2	384	0.01
0.001%	$2.3 \times 10^3$	$4.2 \times 10^{-7}$	0.42	380	0.001

Table 4. Centerline Plume Concentrations and Source Release Rates for PFT Tagging at 1.5–10 Times Ambient Background

a	1.5	2	3	4	5	10
X/B'	4	8	17	25	33	75
X (gm <sup>-3</sup> )	5.95 × 10 <sup>-10</sup>	1.19 × 10 <sup>-9</sup>	2.38 × 10 <sup>-9</sup>	3.57 × 10 <sup>-9</sup>	4.76 × 10 <sup>-9</sup>	1.07 × 10 <sup>-8</sup>
Q (gs <sup>-1</sup> )	5.95 × 10 <sup>-5</sup>	1.19 × 10 <sup>-4</sup>	2.38 × 10 <sup>-4</sup>	3.57 × 10 <sup>-4</sup>	4.76 × 10 <sup>-4</sup>	1.07 × 10 <sup>-3</sup>

Table 5. Mass Ratio of Tracer to CO<sub>2</sub>, Q<sub>PFT</sub>/Q<sub>CO<sub>2</sub></sub>, in Parts Per Million by Weight, Necessary to Have Plume Centerline Concentrations a Factor “a” Greater than Background at a Sampler 1 km Downwind of a Surface Leak

leak rate		Q <sub>PFT</sub> /Q <sub>CO<sub>2</sub></sub> (ppm)					
CO <sub>2</sub>	CO <sub>2</sub>	a					
(% year <sup>-1</sup> )	(gs <sup>-1</sup> )	1.5	2	3	4	5	10
1.00%	8.2 × 10 <sup>4</sup>	7.3 × 10 <sup>-4</sup>	1.5 × 10 <sup>-3</sup>	2.9 × 10 <sup>-3</sup>	4.4 × 10 <sup>-3</sup>	5.8 × 10 <sup>-3</sup>	1.3 × 10 <sup>-2</sup>
0.10%	8.2 × 10 <sup>3</sup>	7.3 × 10 <sup>-3</sup>	1.5 × 10 <sup>-2</sup>	2.9 × 10 <sup>-2</sup>	4.4 × 10 <sup>-2</sup>	5.8 × 10 <sup>-2</sup>	1.3 × 10 <sup>-1</sup>
0.05%	4.1 × 10 <sup>3</sup>	1.5 × 10 <sup>-2</sup>	2.9 × 10 <sup>-2</sup>	5.8 × 10 <sup>-2</sup>	8.7 × 10 <sup>-2</sup>	1.2 × 10 <sup>-1</sup>	2.6 × 10 <sup>-1</sup>
0.01%	8.2 × 10 <sup>2</sup>	7.3 × 10 <sup>-2</sup>	1.5 × 10 <sup>-1</sup>	2.9 × 10 <sup>-1</sup>	4.4 × 10 <sup>-1</sup>	5.8 × 10 <sup>-1</sup>	1.3
0.001%	8.2 × 10 <sup>1</sup>	7.3 × 10 <sup>-1</sup>	1.5	2.9	4.4	5.8 × 10 <sup>-1</sup>	13

Table 6. Mass PFT Per Year Required to Tag Sequestered CO<sub>2</sub> for a Range of Leak Rates

leak rate	mass of PFT (kg year <sup>-1</sup> )					
CO <sub>2</sub>	a					
(% year <sup>-1</sup> )	1.5	2	3	4	5	10
1.00%	6	13	25	38	50	113
0.10%	63	125	250	375	500	1126
0.05%	125	250	500	750	1001	2251
0.01%	625	1251	2502	3752	5003	11 257
0.001%	6250	12 510	25 020	37 520	50 030	112 570

Tagging at 13 ppm, the highest level satisfying the DOE requirement (Table 5), adds approximately 20% to the radiative effect relative to a CO<sub>2</sub> only leak because of the much higher GWPs of PFTs. The tagging levels at the demonstration projects where PFT methods were used to monitor transport and leakage of sequestered CO<sub>2</sub>, are 2–27 times greater than the maximum amount in Table 6.<sup>11–16,17</sup> The atmospheric burden of all the tracer compounds in current use is less than 2000 tons and is essentially stable.<sup>39</sup> Careful consideration must be given to the climate implications of using these compounds. Fugitive emissions from the manufacture, distribution, and handling of this quantity of PFT, particularly if they are to be used to tag a significant number of the 8000 point sources that are potential candidates for sequestration, could have significant effects on the global radiation budget. The quantity of PFTs needed for tagging sequestered CO<sub>2</sub> is too large to be practical for routine monitoring. A better use of PFTs is as a tool in sequestration research. PFTs can also be useful for monitoring for short periods during critical operations such as testing the integrity of new wells or verifying the seals of abandoned wells.

Higher resolution passive measurements where samplers will be closer to the source, or use of real time instruments for measurement of PFTs or other tracers will reduce the tagging levels necessary for leak detection by eliminating the accumulation of background levels on the passive sampler. But these techniques are not practical unless applied over areas that are substantially less than 100 km<sup>2</sup>. Leaks will result from faults or improperly sealed or abandoned wells that provide a pathway from the reservoir to the surface. High resolution surface or underground sampling is only practical if potential faults can be identified and a limited number of sampling

locations established. Geological surveys of sequestration sites will be necessary to locate potential direct pathways and develop targeted subsurface monitoring strategies.

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

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

More information on atmospheric trends in CO<sub>2</sub>, commercial and demonstration sequestration projects, subsurface and atmospheric modeling, perfluorocarbon tracers, and background perfluorocarbon tracer calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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