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GCCC Digital Publication Series #05-04n

S. D. McCallum  
D. E. Riestenberg  
D. R. Cole  
B. M. Freifeld  
R. C. Trautz  
S. D. Hovorka  
T. J. Phelps



**Keywords:**

Perfluorocarbon Tracers (PFTs), Gas Chromatography, Electron Capture Detector (ECD)

**Cited as:**

McCallum, S.D., Riestenberg, D.E., Cole, D.R., Freifeld, B.M., Trautz, R.C., Hovorka, S.D., and Phelps, T.J., Monitoring geologically sequestered CO<sub>2</sub> during the Frio Brine Pilot Test using perfluorocarbon tracers: presented at the National Energy Technology Laboratory Fourth Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 2-5, 2005. GCCC Digital Publication Series #05-04n, pp. 1-9.

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<sup>1</sup>McCallum, S.D., <sup>1</sup>Riestenberg, D.E., <sup>1</sup>Cole, D.R., <sup>2</sup>Freifeld, B.M.,  
<sup>2</sup>Trautz, R.C., <sup>3</sup>Hovorka, S.D., and <sup>1</sup>Phelps\*, T.J.

<sup>1</sup> Oak Ridge National Laboratory, 1505 Bethel Valley Road, Oak Ridge, TN, 37831-6036 USA

<sup>2</sup> Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720-90R1116, USA

<sup>3</sup> Texas Bureau of Economic Geology, The University of Texas at Austin, University Station, Box X, Austin, Texas 78713-8924, USA

\*Corresponding author and presenter (phelpstj@ornl.gov)

## **Abstract**

A suite of gaseous perfluorocarbon (PFT) conservative tracers were successfully employed to monitor migration of the CO<sub>2</sub> plume during the Frio Brine Pilot Test. The conservative tracers enabled quantification of plume breakthrough and transport times, added value to model validity testing, and are providing insight into the saturation behavior of the CO<sub>2</sub> plume. Specific pairs of tracers were introduced at chosen times alongside the injected CO<sub>2</sub> stream. These tracers were transported through the formation and then collected at a monitoring well approximately 30 meters up-dip. A novel U-tube design allowed for high frequency sampling at the monitoring well. The PFTs introduced at the onset of CO<sub>2</sub> injection appeared at the monitoring well 50.3 hours after injection and coincided with the initial CO<sub>2</sub> breakthrough. A second and third set of PFT pairs were introduced 102 and 120 hours after the initial CO<sub>2</sub> injection. The breakthrough times for the second (51.7 hours) and third (51.2 hours) PFT sets indicated little change in the overall saturation of the CO<sub>2</sub> plume, between the injection and monitoring location. The rapid establishment of well developed flow paths demonstrates the importance in understanding preferential flow for assessing the storage efficiency of geologic CO<sub>2</sub> sequestration sites.

## Introduction

CO<sub>2</sub> is a known greenhouse gas that has been released into the atmosphere in increased quantities since the industrial revolution. Geologic sequestration of CO<sub>2</sub> has been proposed as a method for storing CO<sub>2</sub>, which could serve to alleviate some of the effects of global warming. Geologic formations have the ability to hold approximately 920 Gt in depleted oil and gas reservoirs, 400 – 10,000 Gt in deep saline aquifers, and greater than 15 Gt in unminable coal seams (IEA, 2001). The Frio Injection Test is a field scale experiment that aims to evaluate the capability of saline aquifers to sequester CO<sub>2</sub>. The CO<sub>2</sub> was injected into an approximately 6 m thick high permeability sandstone interval within the Frio formation in south east Texas that was confined by low permeability shale layers.

The objective of this research was to track the plume of injected CO<sub>2</sub> using a suite of perfluorocarbon tracers (PFTs). In addition to monitoring the CO<sub>2</sub> plume the PFTs also served to quantify CO<sub>2</sub> plume breakthrough, added value to model validity testing, and provided insight into the saturation behavior of CO<sub>2</sub>. This paper describes the methods used to inject, collect, and analyze PFTs during the Frio Pilot CO<sub>2</sub> injection and reports the results.

## Material and Methods

PFTs are conservative gaseous tracers that are non-depositing, non-scavenged, non-reactive, have low atmospheric background, limited industrial use, and detectable at the femtogram (Dietz, 1986) to picogram level. Due to the properties of PFTs they have been used extensively for atmospheric (Dietz, 1986; Lagomarsino, 1996; Straume, 1998) and subsurface studies (Senum et al., 1990; McKinley and Colwell, 1996; Sullivan et al., 1998; Phelps, 2001).

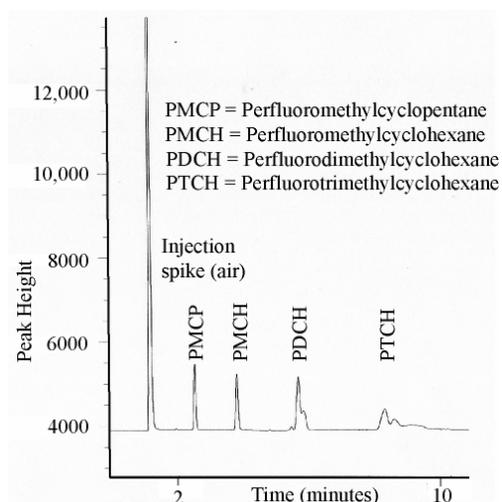


Figure 1. Gas chromatograph showing the 4 PFTs used during the Frio Injection and their relative elution times

Of the nearly one dozen varieties of PFTs available for tracer studies four were selected to use during the Frio injection. The tracers used were perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH), and perfluorotrimethylcyclohexane (PTCH). These four PFTs were selected because of their volatility and their favorable gas chromatographic (GC) separation and elution time, which ranged from 1 to 2 minutes between each PFT (Figure 1). Using PFTs with spaced elution times allows multiple PFTs to be examined in a single GC injection. Detection of the PFTs was sensitive to the picogram level when using a Hewlett Packard 5890 GC equipped with an electron capture detector (ECD).

After selecting the PFTs to be used for the Frio Test an injection scenario was devised that would allow the PFTs to be introduced during the CO<sub>2</sub> injection at the injection well. In order to do this a high performance liquid chromatography pump (HPLC) that operated at pressures in excess of the Frio formation pressure (~13 MPa) was used. A total of 3 PFT injections were performed consisting of a pair of PFTs injected at a specific volume. Injection 1 occurred just after the beginning of the CO<sub>2</sub> injection (1.9 hrs, 10/04/2004), lasted for 3.9 hrs, and introduced 900 mL (1.6 kg) of PMCH and 860 mL (1.6 kg) of PTCH. The second injection occurred just after the beginning of the second CO<sub>2</sub> injection (102.8 hrs, 10/08/2004), lasted for 0.6 hrs, and introduced 100 mL (0.2 kg) of PMCP and 100 mL (0.2 kg) of PDCH. The third injection occurred at 120.1 hrs, lasted for 0.5 hrs, and introduced 90 mL (0.2 kg) of PMCH and 85 mL (0.2 kg) of PTCH.

The injected PFTs were introduced via the injection well to an approximately 6 m thick interval of the Frio Formation. This interval was bounded by low permeability shale that constrained the vertical flow of CO<sub>2</sub> and PFTs. The lateral flow from the injection well followed an up-dip direction for at least 30 m where sampling occurred at a monitoring well. High frequency samples were collected at the monitoring well using a U-tube, described in detail by Freifeld et al. (manuscript submitted). The U-tube was a 'U' shaped tube that was inserted to the sampling depth (~1530 m) and was equipped with a series of one way check valves at the cusp of the 'U' bend in the tube. The pressure in the U-tube could be decreased below formation pressure which would permit

sample fluids to enter the tube through the check valves. The U-tube pressure would then be increased using compressed nitrogen gas and the sample would be rapidly transported to the surface where subsampling would be accomplished.

Samples that had been transported to the surface by the U-tube system were subsampled for PFTs by filling 150 mL Monel steel high pressure cylinders (Hoke Incorporated, Spartanburg, SC) with formation fluid (brine, CO<sub>2</sub>, and PFTs). The cylinders remained pressurized and were further subsampled using a 0.4, 1.0 mL, or 10 mL sample loop (Figure 2), which also remained pressurized. At each sampling time 58 and 158 mL serum vials were injected with between 0.4 and 10 mL of formation fluids from pressurized sample loops. The fluid was introduced to each serum vial by piercing the Teflon septa and injecting the fluids from the sample loop. The introduction of pressurized formation fluids caused gasses to exsolve from solution at atmospheric conditions and pressurized the glass sample vial slightly above atmospheric pressure (< 0.03 MPa excess of atmospheric pressure). After the injection an additional ~2 mL of distilled



Figure 2. Sample loop (1 mL) used to inject fluid samples into glass vials for transport and analysis

water was used to flush the sample loop into the vial and assist in sealing the vial. These samples were classified as pressurized samples. An alternate sampling technique used a 10 mL sample loop to collect a subsample from the Monel cylinder. The sample loop would then be vented into a 58 mL (and then 158 mL) glass serum vials at atmospheric pressure. The sample loop was flushed with distilled water and the glass vial was sealed with an aluminum cap and septa. These samples were classified as unpressurized samples. Therefore, at each sampling time four subsamples were collected, pressurized samples in 158 and 58 mL vials and unpressurized samples in 158 and 58 mL vials. In total over 200 samples were collected over a 9 day period. The samples were transported off-site for PFT analysis using a GC-ECD.

The GC used for sample analysis was equipped with a 50 m RT-Alumina (Restek Corporation, Bellefonte, PA) capillary column and an ECD. Each of the samples was analyzed in a GC using duplicate 100 uL injections. Standards were analyzed at the beginning and end of each GC working day to ensure accuracy throughout the analysis. GC detection of PFTs was reported as an area count which could be converted to a concentration based on standard curves. Due to variation in original PFT injection volumes at the injection well, variable sized sample vials, and multiple PFTs, it was necessary to standardize and display the data as concentration divided by maximum concentration (C/C<sub>max</sub>) for each injection.

After GC analysis was complete the data were viewed graphically as C/C<sub>max</sub> versus time. Time was displayed in hours after the start of the first CO<sub>2</sub> injection (0 hrs, 10/04/04). PFT breakthrough times were calculated based on the peak arrival time of a given PFT minus the injection time minus the mean injection duration minus the U-tube travel time (1.83 hr) (see eq. 1). As the U-tube travel time varied during the experiment it was necessary to subtract the U-tube travel time from the 2<sup>nd</sup> and 3<sup>rd</sup> breakthroughs, but not the 1<sup>st</sup>. PFT breakthrough times were used in calculations of a simple radial flow model, which was used to estimate the level of CO<sub>2</sub> saturation within the Frio and interpret the ability of CO<sub>2</sub> to bypass the denser and lower mobility brine.

$$B = p - i - d - u \quad (\text{eq. 1})$$

B = PFT breakthrough time

p = peak arrival time

i = injection time

d = mean injection duration

U = U-tube travel time (2<sup>nd</sup> and 3<sup>rd</sup> breakthroughs)

## Results

Breakthrough times for the 3 PFT injections are summarized in Table 1. The variability in breakthrough times was minimal for all three injections. However, the 12 hr perfluoroethylcyclohexane (PECH) injection performed by the National Energy and Technology Laboratory (NETL) was introduced prior to a 31 hour stand

down in CO<sub>2</sub> injection. Table 2 shows that the breakthrough time varied from 50.3 to 51.5 hours (except for the PECH breakthrough). Duration time was 3.9 hours during injection 1 because a total of 1760 mL (3.2 kg) of PFTs were injected at 6 to 8 mL/min compared to approximately 200 mL (0.4 kg) of PFTs injected at the same rate during injections 2 and 3. Approximately 500 mL (0.9 kg) of PECH were injected at a rate of < 1 mL/min which resulted in a 12 hour injection period.

Table 1. Injection time, injection duration, peak arrival time, and breakthrough time for PFT injections. Injection time and peak arrival time is given in hours after the start of the first CO<sub>2</sub> injection.

Injection #	Injection time (hrs)	Injection Duration (hrs)	Peak Arrival Time (hrs)	Breakthrough <sup>i</sup> Time (hrs)
#1 (PMCH/PTCH)	1.9	3.9	54.1	50.3
#2 (PMCP/PDCH) <sup>ii</sup>	102.8	0.6	156.6	51.7
#3 (PMCH/PTCH) <sup>ii</sup>	120.1	0.5	173.4	51.2

<sup>i</sup> Breakthrough time is calculated by subtracting the injection time and mean duration from the peak arrival time.

<sup>ii</sup> In order to calculate breakthrough time an additional 1.83 hours was subtracted from the peak arrival time to account for U-tube travel time.

The breakthrough times for the complete dataset can be graphically viewed as a C/C<sub>max</sub> versus time graph (Figure 3) showing each PFT before, after, and during breakthrough. PMCH and PTCH were introduced during injection 1. However, PMCP and PDCH which had not been introduced appear at low levels during the first breakthrough due to the use of the technical grade PFT solution (data not shown). A stand down time occurred from hours 72 to 103 in which both the injection and monitoring well were not operated in order to observe pressure

transients and perform geophysical tests. The PECH breakthrough (NETL injection) was also detected. Breakthrough of injection 2 (PMCP/PDCH) appeared as a well defined peak that spanned less than 20 hours. The 3<sup>rd</sup> injection breakthrough is partially overlain by the PFTs of injection 2, but also spans approximately 20 hours.

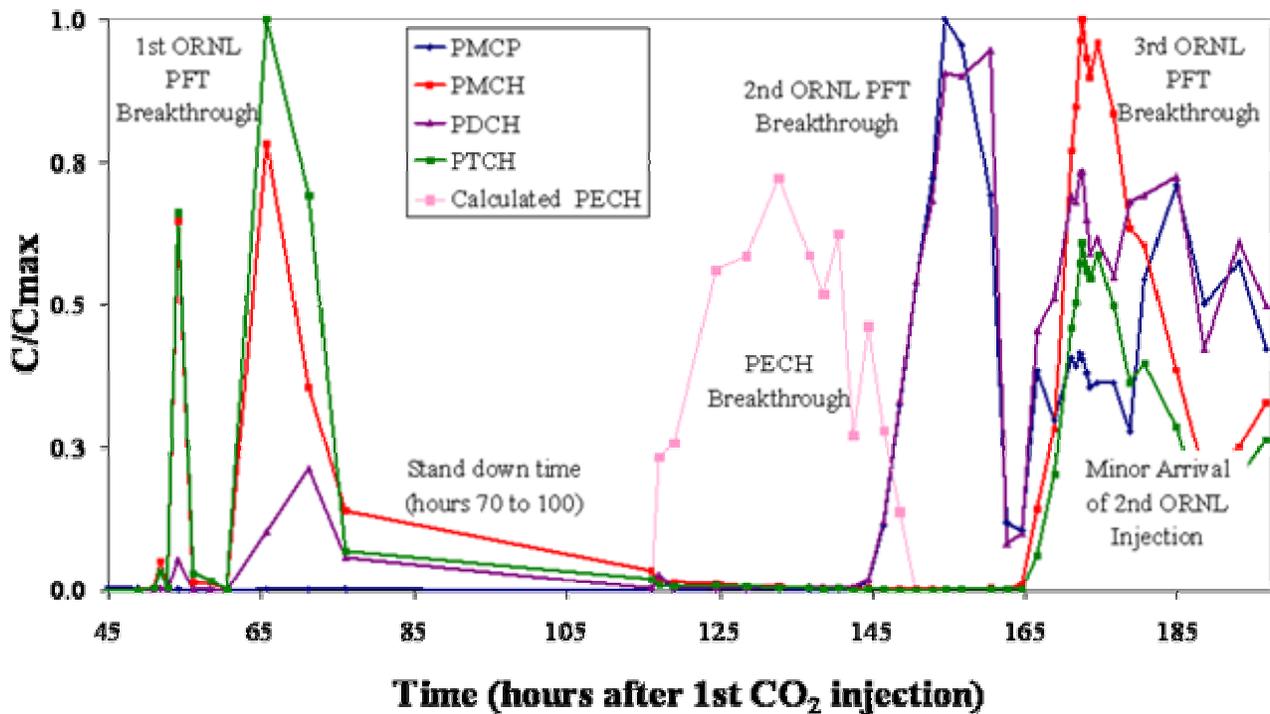


Figure 3. Dataset showing C/C<sub>max</sub> versus Time (hours after first CO<sub>2</sub> injection) for the first, second, and third injection breakthroughs as well as the PECH breakthrough (NETL injection).

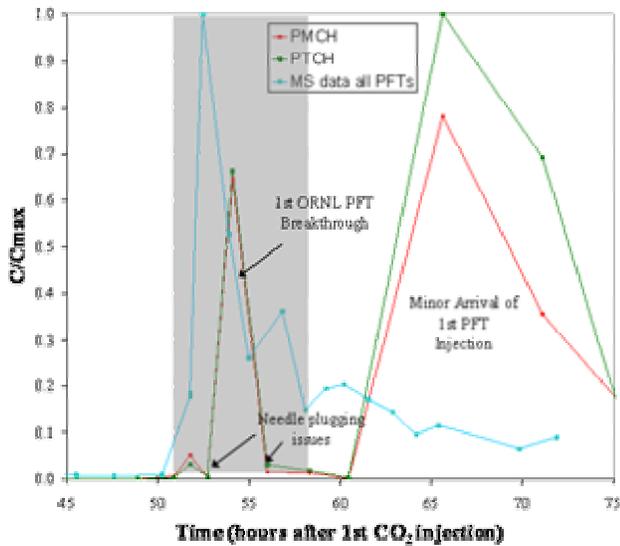


Figure 4. C/Cmax versus time in hours after the start of the CO<sub>2</sub> injection. Area shaded in gray corresponded to the transition from liquid to gassy samples.

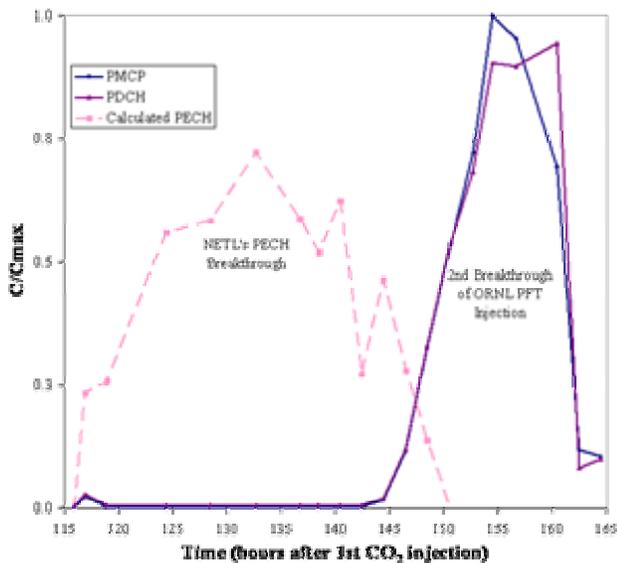


Figure 5. C/Cmax versus time in hours after the start of the CO<sub>2</sub> injection. PECH injected by NETL was identified.

PMCH and PTCH were introduced during injection 1, and their travel time was 50.3 hrs. Analysis of the first injection breakthrough (Figure 4) revealed a minor arrival that appeared larger and followed the first breakthrough. It is likely that the first breakthrough was smaller than the minor arrival due to the transition from liquid to gassy production at the monitoring well. The gassy samples arriving during the minor arrival (hours 60 plus) provided more concentrated PFT samples than the liquid samples that arrived prior (hours 50 to 60). Mass spectrographic (MS) data provided a more complete record during the liquid to gas transition. Inspection of the MS results revealed a larger initial breakthrough followed by a minor arrival of the PFT injection.

A stand down time lasting from hours 72 to 103 persisted after the breakthrough of the 1<sup>st</sup> injection. The second injection introduced PMCP and PDCH and was initiated after the stand down (Figure 5). The travel time for these PFTs (51.7 hours) was similar to that of the first injection. The breakthrough of PECH was observed prior to the second injection breakthrough. PECH exhibited a similar and largely overlapping elution time as PDCH. Identification of the PECH breakthrough peak was based on 1) the recognition of the chromatographic profiles of the PDCH peak, 2) the simultaneous arrival off PMCP and PDCH versus a single peak for PECH, 3) the earlier arrival time of PECH at the monitoring well, 4) and the peak broadening of PECH.

As with the first injection breakthrough, the breakthrough of the second injection also revealed a minor arrival at a later time. Minor arrival from the second injection overlapped the breakthrough of the third injection. For the sake of clarity the conflicting PFTs have been removed from Figure 6. Prior to hour 179 a dashed line indicates a data point that was estimated based on the PFT ratios within 3 out of 4 vials because one of the sample vials had been contaminated and skewed the original trajectory.

The travel times of the 3 injections could be used to calculate CO<sub>2</sub> saturation using a simple radial flow model. This model treated the CO<sub>2</sub> flow as a uniform disk expanding outward in a geologic formation. The model was expressed by:

$$S_{CO_2} = (Q t) / (\pi r^2 l \phi_f) \quad (\text{eq. 2})$$

Where:

- ‘S<sub>CO<sub>2</sub></sub>’ is percent saturation of CO<sub>2</sub>
- ‘Q’ is volumetric flow
- ‘t’ is travel time
- ‘r’ is distance from well to well
- ‘l’ is formation thickness
- ‘φ<sub>f</sub>’ is percent porosity

Using known values for  $Q$  ( $19.9 \text{ m}^3/\text{hr}$ ),  $r$  (30 m),  $l$  (6.1 m), and  $\phi_f$  (0.35) from the Frio formation and the PFT travel times from the 3 injections  $\text{CO}_2$  saturation maintained approximately 17% saturation from the first breakthrough to the third breakthrough (Table 2).

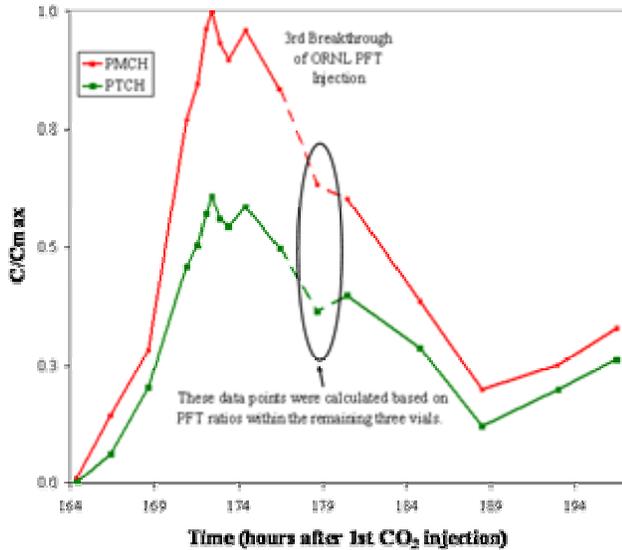


Figure 6.  $C/C_{max}$  versus time in hours after the start of the  $\text{CO}_2$  injection. Circled area indicates data points that were calculated based on PFT ratios within 3 out of 4 vials.

PFT suites provided data for identification of multiple breakthroughs. Multiple travel times for each injection varied between 50.3 and 51.7 hours.

The travel times for each injection provided data to estimate the  $\text{CO}_2$  saturation using a simple radial flow model. The low variance in travel times led to a low variance in calculated  $\text{CO}_2$  saturation of approximately 17%. The lack of variability in  $\text{CO}_2$  saturation from the first to third injection implied that saturation and  $\text{CO}_2$  flow paths were rapidly established and persisted throughout the injection. This flow model does not take into account parameters such as buoyancy, relative permeability, and capillary pressure-saturation which more sophisticated models incorporate (e.g. Bachu et al., 2004) and are being used by other contributors for more detailed analysis of the Frio project.

### Lessons Learned

A variety of sample collection methods were used to increase the likelihood of capture and transport of PFT subsamples. Samples were collected in 58 and 158 mL vials and identified as pressurized or unpressurized. It was later found that the pressurized samples had a tendency to leak before they could be analyzed even though the pressure in the vials was less than 0.03 MPa over atmospheric pressure. This was in part due to the punctures in the Teflon septa of the pressurized vials. The septa were punctured when the sample was transferred from the sample loop to the serum via needles. The small pin hole created by the needle provided an escape route for fluids within the vial. Vials that contained leaks were identified by a fluid level below the mineral rim, or if no fluid was present, or if external mineral precipitation was identified. It was also found that the needles would often clog or partially clog with particulates, which would result in fluctuations in concentration between samples. Future experiments need not use pressurized vials or needles and 58 mL vials could be used exclusively and could be collected in triplicate. Unpressurized vials avoided these problems and showed less fluctuation between vials. The use of this sampling technique was efficient and has become more streamlined. This method could readily be scaled from the 200 samples collected to handle larger sampling scenarios in the range of greater than 1000 samples.

Table 2. Percent  $\text{CO}_2$  saturation calculated using a simple radial flow model and the travel time at each injection

Injection #	Travel Time (hrs)	Estimated $\text{CO}_2$ Saturation ( $\text{SCO}_2$ )
#1 (PMCH/PTCH)	50.3	17
#2 (PMCP/PDCH)	51.7	17
#3 (PMCH/PTCH)	51.2	17

### Discussion

Multiple PFT tracer suites were introduced via an injection well at three separate times during the Frio Test. The PFTs were then sampled at a monitoring well 30 meters up-dip. GC analysis was used to detect the injected PFTs and generate breakthrough profiles for each injection. The use of

## **Acknowledgements**

We acknowledge the collaborative support of the entire Frio Project team especially the Texas Bureau of Economic Geology. We are particularly grateful to Edward A. Miller for the organization and oversight of the field operations. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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