Interpretation of Perfluorocarbon Tracer Data Collected During the Frio Carbon Dioxide Sequestration Test

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In October of 2004 over 1600 tons of CO_2 was injected into a brine-bearing sandstone unit within the Frio Formation. An injection well was used to introduce the CO_2 into the Frio at a depth of 1540 meters below the surface. A monitoring well located 31 meters updip from the injection well was used to sample formation fluids and detect the breakthrough of the CO_2 plume. Perfluorocarbon tracers (PFTs) were injected in three paired intervals at the beginning and middle of the CO_2 injection. The four PFTs selected for injection were perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH), and perfluorotrimethylcyclohexane (PTCH). The PFTs were used as a means to monitor CO_2 plume breakthroughs and aid in the interpretation of CO_2 flow path development. Fluid samples were collected at the monitoring well during and after the CO_2 and PFT injections. These samples were later analyzed in the laboratory to measure the concentration of PFTs. Laboratory analysis was performed using a gas chromatograph (GC) equipped with an electron capture detector (ECD). Standardization of the data set was achieved by dividing C by Cno (C/Cno), where C is the molar mass of PFT and CO_2 recovered and Cno is the initial molar mass of PFT and CO_2 injected. The C/Cno data showed the amount of PFT dilution that occurred between injection and collection. Analysis of the C/Cno data revealed three breakthrough peaks corresponding with the three PFT injections at 54, 157, and 173 hours after the start of CO_2 injection, with an average travel time of 51 hours for each injection. With each subsequent PFT peak a greater amount of PFT dilution was observed along with a broadening of the breakthrough peak. The first PFT breakthrough spans 10 hours, the second spans 20 hours and the third spans 24 hours. The increase in peak broadness observed in each subsequent breakthrough may have been caused by increased CO_2 saturation. Since PFTs are more soluble in CO_2 than in water, their dilution could indicate that additional CO_2 dispersed the injected PFTs. Additionally, further flow path development could also lead to broader PFT breakthrough peaks. Therefore, the C/Cno data shows that the travel time for each of the PFT injections was similar (~51 hours), but broadening of the peaks may represent increased CO_2 saturation or further developing flow paths.

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Interpretation of Perfluorocarbon Tracer Data Collected during the Frio CO_2 Sequestration Test

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Abstract (Ref. # 2990)

In October of 2004 over 1600 tons of CO_2 was injected into a brine-bearing sandstone unit within the Frio Formation. An injection well was used to introduce the CO_2 into the Frio at a depth of 1540 meters below the surface. A monitoring well located 31 meters updip from the injection well was used to sample formation fluids and detect the breakthrough of the CO_2 plume. Perfluorocarbon tracers (PFTs) were injected in three paired intervals at the beginning and middle of the CO_2 injection. The four PFTs selected for injection were perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH), and perfluorotrimethylcyclohexane (PTCH). The PFTs were used as a means to monitor CO_2 plume breakthroughs and aid in the interpretation of CO_2 flow path development. Fluid samples were collected at the monitoring well during and after the CO_2 and PFT injections. These samples were later analyzed in the laboratory to measure the concentration of PFTs. Laboratory analysis was performed using a gas chromatograph (GC) equipped with an electron capture detector (ECD). Standardization of the data set was achieved by dividing C by Cno (C/Cno), where C was the molar mass of PFT and CO_2 recovered and Cno was the initial molar mass of PFT and CO_2 injected. The C/Cno data showed the amount of PFT dilution that occurred between injection and collection.

Analysis of the C/Cno data revealed three breakthrough peaks corresponding with the three PFT injections at 54, 157, and 173 hours after the start of CO_2 injection, with an average travel time of 51 hours for each injection. With each subsequent PFT peak a greater amount of PFT dilution was observed along with a broadening of the breakthrough peak. The first PFT breakthrough spanned 14 hours, the second spanned 20 hours, and the third spanned 24 hours. The increase in peak broadness observed in each subsequent breakthrough may have been caused by increased CO_2 saturation. Since PFTs are more soluble in CO_2 than in water, their dilution could indicate that additional CO_2 dispersed the injected PFTs. Additionally, development of additional flow paths could also have led to broader PFT breakthrough peaks. Importantly, the C/Cno data showed that the travel time for each of the PFT injections was similar (~51 hours), but broadening of the peaks may represent increased CO_2 saturation or further developing flow paths.

Introduction

- 1600 tons of CO_2 injected to a depth of ~1500 m into a saline aquifer in the Frio Formation, Dayton, Texas (Figure 1).
- A monitoring well was situated 30 m updip from the injection well (Figure 2).
- Multiple organizations analyzed the geochemistry and geophysics of the CO_2 plume.
- Time stepped suites of CO_2 soluble perfluorocarbon tracers (PFTs) were injected alongside the CO_2.
- The PFTs were introduced at the injection well and recovered and stored at the monitoring well to be later analyzed using a gas chromatograph equipped with an electron capture detector (GC).
- The use of PFTs allowed for identification of CO_2 plume travel time, interpretation of flow path development, and added value to modeling.

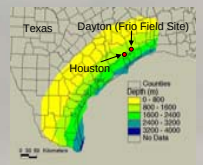

Figure 1: Depth of Frio Formation and location of CO_2 injection (modified from Galloway et al., 1982 and Texas Bureau of Economic Geology webpage)

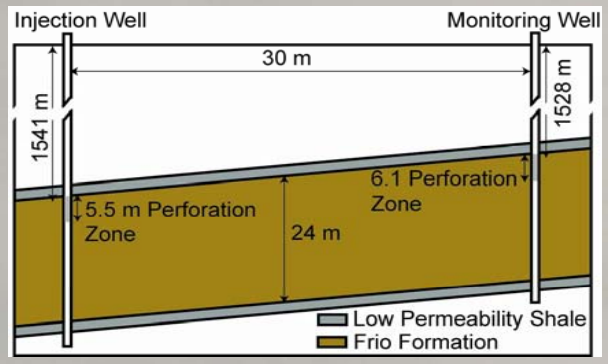

Figure 2: Cross section of the injection and monitoring well configuration and orientation of the Frio Formation (not to scale).

Materials and Methods

PFTs

- A total of 4 chemically inert and CO_2 soluble PFTs were selected as conservative tracers. The PFTs used were perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH), and perfluorotrimethylcyclohexane (PTCH).
- PFTs have low detection limits (femtoliter) (Dietz, 1986), are non-toxic, are stable up to 500°C, and can be used simultaneously (Phelps and Fredrickson, 2002).
- The variability in the molecular weight of each PFT allows for GC separation.

PFT Injection

- A total of 3 paired PFTs injections at the beginning, middle, and near end of CO_2 injection.
  - Injection 1 = 1.6 kg PMCH and 1.6 kg PTCH, 1.87 hours after start of CO_2 injection
  - Injection 2 = 0.17 kg PMCP and 0.18 kg PDCH, 102.75 hours after start of CO_2 injection
  - Injection 3 = 0.16 kg PMCH and 0.16 kg PTCH, 120.05 hours after start of CO_2 injection
- PFTs were introduced to the CO_2 stream at the injection well using a high performance liquid chromatography (HPLC) pump.

PFT Collection and Analysis

- High frequency fluid samples were collected at the monitoring well
- PFTs were independently detected using field based mass spectroscopy (MS) and laboratory based GC analysis.
- Samples for GC analysis were sealed and stored in glass vials for transport to the laboratory.
- Each GC sample vial was sub-sampled in 100 uL volumes for GC analysis.
- Interpretation of GC data provided PFT breakthrough curves.

C/Cno Standardization

- After GC analysis the PFT data was standardized using the C/Cno method, where:
  - C = (moles of PFT in sample vial)/(moles of CO_2 in sample vial)
  - Cno = (moles of PFT injected into well)/(moles of CO_2 injected during PFT injection)
- C/Cno provides a value that represents the change in PFT concentration from injection well to monitoring well.

Results

- After GC and MS analysis and C/Cno standardization a total of four PFT breakthroughs were identified (Figure 3). Three of the breakthroughs were associated with PFT suites injected by ORNL and the fourth was from a PFT injection by a collaborating party (National Energy and Technology Lab).

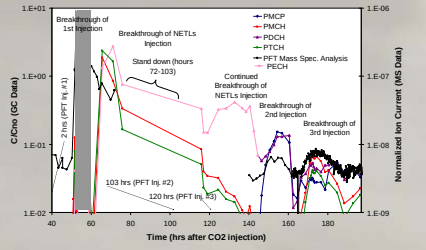

Figure 3: C/Cno data from GC and MS analyses of all PFTs for all breakthroughs. Shaded area represents the transition from liquid to gassy samples. Hours 72-103 represent stand down time.

Injection 1 Breakthrough

- Injection 1 introduced the largest volume of PFTs and its duration (4 hours) was longer than the subsequent injections.
- The first injection had travel times of 50 and 49 hours based on GC data and MS data respectfully (Figure 4 and Table 1)
- The MS data was deferred to for interpretation of Breakthrough 1 because a transition from liquid to gassy samples affected the PFT concentration of the GC samples.

Breakthrough 1 Peak Broadness

- The peak broadness, which measures the time in hours of the breakthrough peak, was 14 hours for both the MS and GC data (Figure 4 and Table 1).
- Breakthrough 1 represents the least broad peak of all PFT breakthroughs.

Table 1: PFT injection values for samples analyzed using GC and MS.

Injection #	Injection time (hours after CO2 start)	Injection Duration (hours)	Peak Arrival Time (hours)	PFT Travel Time (hours) (GC)	PFT Travel Time (hours) (MS)	PFT Peak Broadness (hours) (GC and MS)
#1 PMCH/PTCH	2	4	54	50	49	14
#2 PMCP/PDCH	103	0.6	157	52	49	20
#3 PMCH/PTCH	120	0.5	173	51	53	24

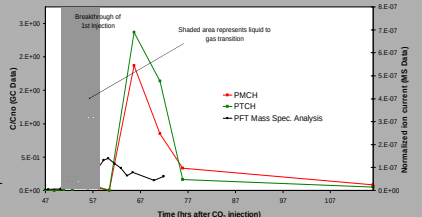

Figure 4: C/Cno data from GC and MS analyses for all major injected PFTs during the first breakthrough. Shaded area represents the transition from liquid to gassy samples.

Injection 2 Breakthrough

- Injection 2 lasted for 0.6 hours and introduced approximately one tenth the mass of PFT compared to the first injection.
- The second injection had travel times of 52 and 49 hours based on the GC and MS data respectfully (Figure 5 and Table 1).

Breakthrough 2 Peak Broadness

- The peak broadness was 20 hours for both the GC and MS data (Figure 5 and Table 1).
- Breakthrough 2 was intermediate in peak broadness relative to the first and third breakthroughs.

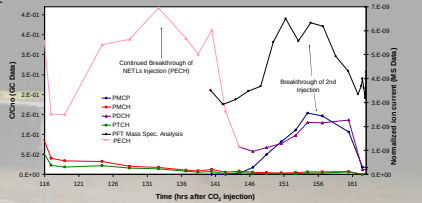

Figure 5: C/Cno data from GC and MS analyses for all PFTs during the second breakthrough. PECH is represented by the pink curve and was the PFT introduced by a collaborating party.

Injection 3 Breakthrough

- Injection 3 lasted for 0.5 hours and introduced approximately one tenth the mass of PFT compared to the first injection.
- The third injection had travel times of 51 and 53 hours based on the GC and MS data respectfully (Figure 6 and Table 1).

Breakthrough 3 Peak Broadness

- The peak broadness was 24 hours for both the GC and MS data (Figure 6 and Table 1).
- Breakthrough 3 represents the most broad peak of all PFT breakthroughs.

Summary of the C/Cno data

- The time of travel based on GC and MS data for the PFTs from injection well to monitoring well was a nearly constant 50.5 hours (sd = 1.6 hours) for all injections. In contrast the broadness of the breakthrough peaks increased from 14 to 20 to 24 with each successive breakthrough.

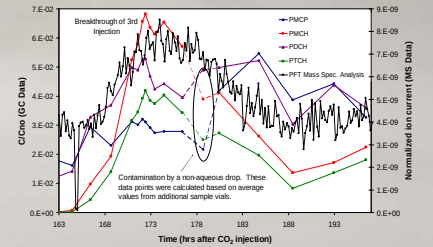

Figure 6: C/Cno data from GC and MS analyses for all PFTs during the third breakthrough.

Discussion

PFT Travel Time

The PFT travel time from injection to monitoring well remained fairly constant (50.5 ±1.6 hours) for all injections. This implied that a well developed CO_2 flow path was initially established. If the dominant flow path had changed then a standard deviation of travel time that was larger than 1.6 hours would have been expected.

PFT Peak Broadness

The PFT breakthrough peak broadness increased with each subsequent breakthrough. The increase in peak broadness implied that the PFTs were dispersing more in the CO_2 throughout the experiment and/or that minor flow paths continued to develop as the CO_2 injection progressed, which would also allow for more dispersion. As PFTs are soluble in CO_2 their dispersion would increase as more CO_2 becomes available and as flow develops.

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References

Dietz, R.N., 1986. Perfluorocarbon Tracer Technology. Regional and Long-range Transport of Air Pollution, Lectures of a course held at the Joint Research Centre, Ispra, Italy, S. Sandroni (Ed.), pp. 215-247.

Galloway, W. H., Hobday, D. K., and Magara, Kinji, 1982, Frio Formation of the Texas Gulf Coast Basin—depositional systems, structural framework, hydrocarbon origin, migration, distribution, and exploration potential: The University of Texas at Austin, Bureau of Economic Geology Report of Investigations No. 122, 78 p.

Phelps, T.J. and J.K. Fredrickson. 2002. Drilling, Coring, and Sampling the Subsurface Environment. *In*: Manual of Environmental Microbiology,C.J. Hurst (Ed.) ASM Press, Washington, D.C.

http://www.beg.utexas.edu/environqlty/co2seq/1frio.htm