High Pressure Flow-Through Apparatus for Assessing Subsurface Carbon Sequestration

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Abstract

Deep subsurface formations are of particular interest for geologic sequestration. However, hydrodynamic and geochemical processes affecting the fate and transport of geologically sequestered CO_2 are poorly understood. The potential residence time of added CO_2, the reservoir storage capacity, and the effectiveness of sequestration are among the important questions that need to be addressed. These questions can be investigated using an experimental flow-through test system and then validated in field tracer studies. Interactions between injected CO_2 with natural and added conservative tracers, with native subsurface media, and with representative brine or hydrocarbon-containing solutions can be examined in a flow-through test system at Oak Ridge National Laboratory. Effects of pressures (up to 300 bar), temperatures (up to 90°C), and materials typical of potential reservoirs are being examined.

Introduction

Concern over rising atmospheric CO_2 levels has prompted the exploration of multiple pathways for the storage or sequestration of carbon. Geologic sequestration of carbon dioxide into deep subsurface formations is of particular interest for several reasons; 1) knowledge from the petroleum industry demonstrating that subsurface CO_2 injections successfully enhance oil recovery (Bachu et al. 1994); 2) deep subsurface formations, such as depleted oil and gas reservoirs provide pressure and temperature parameters that would allow the conditions for supercritical phase to be met for CO_2 (Omerod et al. 1994); and 3) underground storage of CO_2 has the potential for long-term sequestration in diverse settings, such as brine formations, unmineable coal seams, and depleted oil and gas reservoirs (Tanaka et

al. 1995, Omerod et al. 1994, Stevens et al. 1998, van der Meer 2002, Gale 2002, Moberg et al. 2002). However, hydrodynamic and geochemical processes affecting the fate and transport of geologically sequestered CO_2 are poorly understood. Such factors include advection, dispersion, diffusion, dissolution, partitioning into hydrocarbons, sorption onto mineral phases, biogeochemical reactions, and potential escape. These issues should be addressed in order to ensure that geological carbon sequestration is implemented in a safe, affordable, and effective manner.

The rigorous analysis of natural and added conservative tracers is one possible strategy to identify and quantify potential processes affecting CO_2 in subsurface environments. Such results would be beneficial to modelers prior to field injection scenarios, would help validate models designed to describe results, and may enable better predictive codes. Similarly, the monitoring of natural and added conservative tracers could provide a means for evaluating the transport, geochemcial (abiotic; biotic) reactions, loss, or escape of injected CO_2.

To enable these studies, a high-pressure and temperature controlled flow-through apparatus was designed, constructed, and put to use for laboratory-scale assessments of long-term carbon sequestration. The geo-sequestration simulator was designed with the capability to measure conditions under brine and hydrocarbon environments with pressures up to 300 bar and temperatures up to 90°C. A series of bench-scale experiments utilizing representative site media have been designed to examine the physical, geochemical, and transport characteristics of CO_2 injection into native fluids and brines.

Select chemically inert perfluorocarbon tracers (PFTs) were chosen as conservative tracers for the geo-sequestration simulator experiments. PFTs have been used extensively in numerous scientific applications, including studies relating to the subsurface hydrogeology (e.g., Dietz and Senum 1998, Ghafurian et al. 1998, Senum et al. 1990, Senum and Fajer 1992, Sullivan et al. 1998, Dugstad et al. 1992, Dietz 1986, Galdiga and Greibrokk 1997 and 2000), subsurface microbial sampling, (Phelps and Fredrickson 2002, McKinley and Colwell 1996, Smith et al. 2000, Russell et al. 1992), and atmospheric monitoring (O'Mahony et al. 1993, Lagomarsimo 1996, D'Ottavio et al. 1986, Cooke et al. 2001). Characteristics that make PFTs a good choice for conservative tracers include their stability at temperatures up to 500°C (Senum et al. 1989), low detection limits at femtoliter levels within minutes using routine gas chromatography (GC) (Galdiga and Greibrokk 2000, Dietz 1986), non-toxic (McKinley

and Colwell 1996), and multiple PFTs can be used simultaneously (Dugstad et al. 1992, Galdiga and Greibrokk 2000). In addition, PFTs exhibit variable partition coefficients when exposed to hydrocarbons and variable sorption coefficients in clays (Dugstad et al. 1992). The differing molecular weights, solubilties, and physical attributes of selected PFTs enable chromatographic separation of several PFTs upon co-injection into a GC. Four PFTs have been selected for analysis in this study. These include perfluoromethyl cyclopentane (PMCP), perfluoromethyl cyclohexane (PMCH), perfluorodimethyl cyclohexane (PDCH), and perfluorotrimethyl cyclohexane (PTCH) (F2 Chemicals, Lancashire, England).

The objectives of the on-going project are to: 1) conduct bench-scale flow experiments to systematically test the ability of selected tracers to isolate transport processes under field conditions; 2) identify transport mechanisms with the use of multiple tracers to assist geophysical interpretations, testing, and validating and improving models; 3) determine physical, geochemical, and transport-related interactions between tracers and CO_2 with reservoir materials; and 4) test the use of periodically introduced tracers for enhancing the ability to predict breakthrough behavior at monitoring stations.

Experimental Details

Tracer Preparation

The selected tracer suite is used in paired stepwise injections to differentiate mass transfer and specific transport processes in selected media (Figure 1) on a Hewlett Packard 5890 gas chromatograph (Agilent Technologies, Wilmington, DE). Single and paired-tracer standards were prepared by injecting a known volume of PFTs (F2 Chemicals, Lancashire, England) into 40ml EPA vials. The vials were then placed in a water bath and heated to 70°C. It was empirically determined that an equilibration time of 90 minutes was sufficient for headspace samples to be injected. A 10-ml headspace sample of a 0.1mg/L standard was drawn using a gas-tight syringe that was heated to 70°C and injected under vacuum into the simulator (Figure 2) for homogenization in the gas homogenization reservoirs (GHRs). The system was then pressurized with nitrogen carrier gas at an experimental pressure of 48 bar under an ambient temperature of 19°C. Samples were allowed to homogenize overnight to ensure thorough mixing with carrier gas.

Flow-system design:

Design and construction of the geo-sequestration simulator can be categorized into five main areas: injection, column, tracers, fluids, and data collection (Table 1, Figure 2).

Table 1: Overview of geo-sequestration simulator capabilities and design.

Injection:
Multiple gas homogenization reservoirs (95ml, 150ml, 300ml) allow for continuous sampling
Metered flow rates from 0.01ml/min to 10ml/min
Column:
Constructed of corrosion resistant Monel (brine injection areas) and 2507 stainless steel with Swagelock valves and tubing; 20 feet in length
Working pressure range up to 344 bar (~5000psi)
Working temperature up to 100°C
Temperature measurements by type T thermocouples
Pressure measurements using piezoelectric transducers (0-6000psi)
Helium used to measure substrate porosity
Tracers:
Conservative tracers include stable isotopes, noble gases, nonreactive salts, and perfluorocarbons
Fluids:
Ability to add hydrocarbons and/or brine conditions to column
System can operate with CO_2 as a gas, liquid, or supercritical fluid
Data Collection:
System can be remotely operated via internet connection
Valco sample valve injects gaseous effluent directly into HP 5890 gas chromatograph with an electron capture detector
Data continuously monitored using Labview

Injection:

The injection area of the apparatus was designed to allow continuous flow operations. The use of two 300mL-GHRs allows the tracer gases to mix with carrier gases for equilibration. Extra GHR volumes include one 95ml and two 150ml cylinders. Flow though the GHRs can be switched back and forth to allow simultaneous loading and injection into the system. Upstream pressure is maintained by the use of an HPLC pump (Varian Instruments, Walnut Creek, CA) with a built-in pressure transducer, while downstream pressures are regulated by the use of a backpressure regulator (Temco Inc., Tulsa, OK).

Experimental flow rates are established using the HPLC to direct tracers from the GHRs into the flow-column through a series of valves. To verify flow rate, a digital balance continuously measures the weight of the water pumped from the HPLC. The experimental flow rate for the HPLC can be set between 0.01ml/min to 10ml/min. The flow rate was set for 3mL/min for our preliminary runs in this paper. In addition, the simulator allows for the use of either nitrogen or liquid CO_2 as a carrier gas. Nitrogen was selected as the carrier gas for the preliminary experiments.

Column Design:

A 20-foot length coiled flow-column, packed with representative geologic media as substrate is housed within a temperature-controlled oven. An oven-bypass line serves as a control for all tests. Similarly, columns of varying length containing other geologic media under consideration can also be substituted (e.g., sample cores from the Frio formation field demonstration). The current column, packed with Ottawa sand (~0.6 to 0.85 mm grain diameter), is 6m long with a 6.89mm internal diameter, is made of 2507 stainless steel, and is rated for pressures up to 689 bar.

After gas homogenization, the tracers enter the oven-column unit through a series of valves and are allowed to react with the substrate to identify hydrodynamic processes. The experimental flow rate established upstream by the HPLC pump and the column pore volume determines the time-scale of tracer exposure to the substrate. Hydrodynamic processes resulting from the interaction of tracers with solid and liquid phases that can be examined include adsorption, partitioning into brines and hydrocarbons, and diffusion. Modeling of such processes utilizes the breakthrough times of tracers. The behavior of CO_2 and noble gases of argon, helium, and xenon during transport and interaction with the carbon and oxygen isotopes in the substrate can also be measured in samples obtained from a side loop designed for quick release. Stable isotope samples are taken separately from this loop and can be analyzed off-line with a gas-source isotope ratio mass spectrometer.

Exposure to brine and hydrocarbon phases:

A unique feature of the flow-through simulator is the ability to load brine and/or hydrocarbons into the sediment-bearing flow-column prior to initiating tracer flow. Up to 75mL of brine fluids are sparged with low-pressure helium before injection into the flow-through column. This construction includes the use of two sample gas cylinders to sparge, mix, and inject a known amount of fluid into the system under high pressures up to 97 bar. After brine and/or hydrocarbon fluids flow through the column, a series of condensation traps collect excess fluids to prevent crossover to the GC.

Detection and Data Acquisition:

A Hewlett-Packard 5890 gas chromatograph (Agilent Technologies, Wilmington, DE) equipped with an electron capture detector (ECD) was used to quantify peak separation of perfluorocarbons. GC parameters included the use of an alumina plot (Restek, Bellefonte, PA) column (50m length, 0.53mm ID), 51 ml/min split vent, 2.6 ml/min septum purge, 11.5 ml/min column flow, 250°C ECD detector temperature, and 90°C injector temperature. Oven parameters followed a temperature ramp program by setting the initial temperature to 120°C and increased 50°C (per 40 seconds) to reach a final temperature of 170°C. Samples are retrieved either every 15 minutes for tracer pair 1 or every 7 minutes for tracer pair 2 through a 10-inlet Valco gas-sampling valve containing a 250 L sample loop. Sample times are based upon retention times of perfluorocarbon standard curves. Analysis conducted using the standard curve (Figure 3) determined an instrument detection limit of 1.5 10^{-14}g.

Preliminary Results

The injection of PDCH into one of the 300mL GHRs was 2ng, thus 7pg/mL of PFT was allowed to homogenize within the GHR. Upon exiting the flow-through column filled with Ottawa sand, PFT sample concentrations were determined to be 0.1pg (Figure 4), corresponding to our predictions. The resulting concentration approached the instrument detection limit, but was approximately 10 above the baseline.

Summary

Further experiments utilizing PFT concentrations 100 times our preliminary experiments are planned in addition to helium porosimetry measurements for the determination of substrate porosity. Our plans include a series of runs using brine and hydrocarbons under a variety of experimental pressures and temperatures. Upon completion of these experiments, the current Ottawa sand column will be replaced with a column containing material from the Frio Formation, a formation planned for a subsequent field CO_2 injection experiment. As part of the GEO-SEQ project (http://esd.lbl.gov/GEOSEQ/), one of the proposed intentions is to make the expertise and ORNL geo-sequestration simulator facilities available for

other CO_2 sequestration projects, including the use of additional subsurface materials for hydrodynamic process analysis.

Results from our preliminary experiments using the geo-sequestration simulator have demonstrated a working system that is reproducible, sensitive to low levels of detection, and is capable of distinguishing physical and geochemical parameters effecting long-term sequestration of CO_2.

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References:

Bachu, S., W.D. Gunter, and E.H. Perkins. 1994. Aquifer Disposal of CO_2: Hydrodynamic and Mineral Trapping. Energy Convers. Mgt. 35:269-279.

Cooke, K.M., P.G. Simmonds, G. Nickless, and A.P.W. Makepeace, 2001. Use of capillary gas chromatography with negative ion-chemical ionization mass spectrometry for the determination of perfluorocarbon tracers in the atmosphere. Anal. Chem. 73:4295-4300.

D'Ottavio, T.W., R.W. Goodrich, and R.N. Dietz. 1986. Perfluorocarbon Measurement Using an Automated Dual-Trap Analyzer. Environ. Sci. Technol. 20:100-104.

Dietz, R.N. 1986. Perfluorocarbon tracer technology. *In* Regional and Long-range Transport of Air Pollution, S. Sandroni (Ed.). Lectures of a course held at the Joint Research Centre, Ispra, Italy, 15-19 Sept., 1986, Elsevier, Amsterdam (also BNL-38847, Brookhaven National Laboratory), 215-247.

Dietz, R.N. and G.I. Senum. 1998. Detection of Interstate Liquids Pipeline Leaks: Feasibility Evaluation. Brookhaven National Laboratory, BNL-65970.

Dugstad O., T. Bjornstad, and I.A. Hundere, 1992. Construction of a slim-tube equipment for gas tracer evaluation at simulated reservoir conditions. Appl. Radiat. Isot. 43:527-535.

Galdiga, C.U., and T. Greibrokk, 1997. Simultaneous determination of trace amounts of sulfur hexafluoride and cyclic perfluorocarbons in reservoir samples by gas chromatography. Chromatographia 46:440-443.

Galdiga CU, and T. Greibrokk, 2000. Ultra trace detection of perfluorocarbon tracers in reservoir gases by adsorption/thermal desorption in combination with NICI-GC/MS. Fresenius J. Anal. Chem. 367:43-50.

Gale, J. 2002. Geological Storage of CO_2: What's Known, Where are the Gaps, and What More Needs to be Done? GHGT Conference Proceedings, Abstract A1-1, 1-4 October, Kyoto, Japan.

Ghafurian, R., R.N. Dietz, T. Rodenbaugh, J. Dominguez, and N. Tai. 1998. Leak Location in Fluid-Filled Cables Using the PFT Method. Brookhaven National Laboratory, BNL-65959.

Lagomarsino, R.J. 1996. An improved gas chromatographic method for the determination of perfluorocarbon tracers in the atmosphere. J. Chromatog. Sci. 34:405-412.

McKinley, J.P. and F.S. Colwell. 1996. Application of perfluorocarbon tracers to microbial sampling in subsurface environments using mud-rotary and air-rotary drilling techniques. J. Microbiol. Meth. 26:1-9.

Moberg, R., D.B. Stewart, and D. Stachniak. 2002. The IEA Weyburn CO_2 Monitoring and Storage Project. GHGT Conference Proceedings, Abstract A1-3, 1-4 October, Kyoto, Japan.

O'Mahony, T.K.P., A.P. Cox, and D.J. Roberts. 1993. Gas Chromatographic Separation of Perfluorocarbons. J. Chromatography 637:1-11.

Omerod, W. 1994. IEA Greenhouse Gas R & D Programme, Carbon Dioxide Disposal from Power Stations, 1994, IEA/GHG/SR3.

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.

Russell, B.F., T.J. Phelps, W.T. Griffin, and K.A. Sargent. 1992. Procedures for Sampling Deep Subsurface Microbial Communities in Unconsolidated Sediments. Groundwater Monitoring Rev. 12:96-104.

Senum, G.I., E.A. Cote, T.W. D'Ottavio, and R.N. Dietz, 1989. Hydrocarbon Precombusting Catalyst Survey and Optimization for Perfluorocarbon Tracer Analysis in Subsurface Tracer Applications. Brookhaven National Laboratory, BNL-4276934.

Senum, G.I., R.N. Dietz, T.W. D'Ottavio, R.W. Goodrich, E.A. Cote, and D.J. Spandau. 1990. A perfluorocarbon tracer transport and dispersion experiment in the North Sea Ekofisk Oil Field. Brookhaven National Laboratory, BNL 43811R.

Senum, G.I., and R. Fajer, 1992. Petroleum reservoir characterization by perfluorocarbon tracers. SPE/DOE 24137, 337-344.

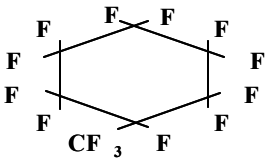
Smith et al., 2000. Tracer-based estimates of drilling-induced microbial contamination of deep sea crust. Geomicrobiology 17:207-219.

Stevens, S.H., V.A. Kuuskraa, D. Spector, and P. Riemer. 1998. CO_2 Sequestration in Deep Coal Seams: Pilot Results and Worldwide Potential. GHGT Conference Proceedings, 30 August-2 September, Interlaken, Switzerland.

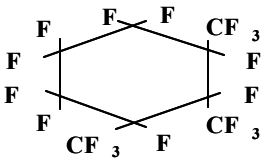
Sullivan, T.M., J. Heiser, A. Gard, and G. Senum, 1998. Monitoring subsurface barrier integrity using perfluorocarbon tracers. J. Env. Tech. 124:490-497.

Tanaka, S., H. Koide, and A. Sasagawa. 1995. Possibility of Underground CO_2 Sequestration in Japan. Energy Conservs. Mgmt. 36:527-530.

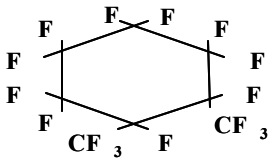
Van der Meer, L.G.H. 2002. CO_2 Storage in the Subsurface. GHGT Conference Proceedings, Abstract A1-0, 1-4 October, Kyoto, Japan.



Pair 1



Perfluoromethyl cyclohexane (PMCH) and perfluorotrimethyl cyclohexane (PTCH)



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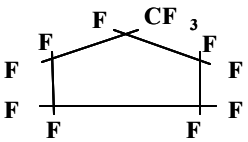

Perfluorodimethyl cyclohexane (PDCH) and perfluoromethyl cyclopentane (PMCP)

Figure 1. Selected pairs of perfluorocarbon tracers used for analyses in geo-sequestration simulator.

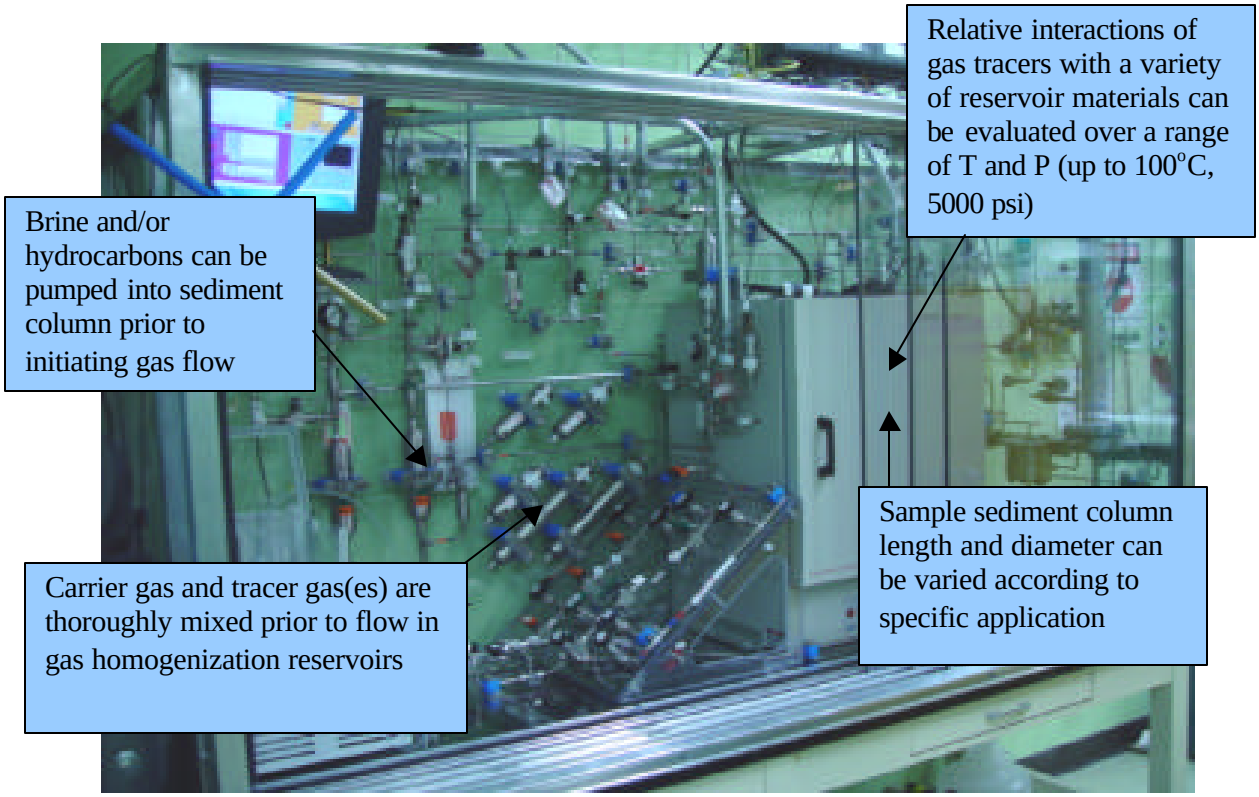

Figure 2: Geo-sequestration simulator housed at Oak Ridge National Laboratory

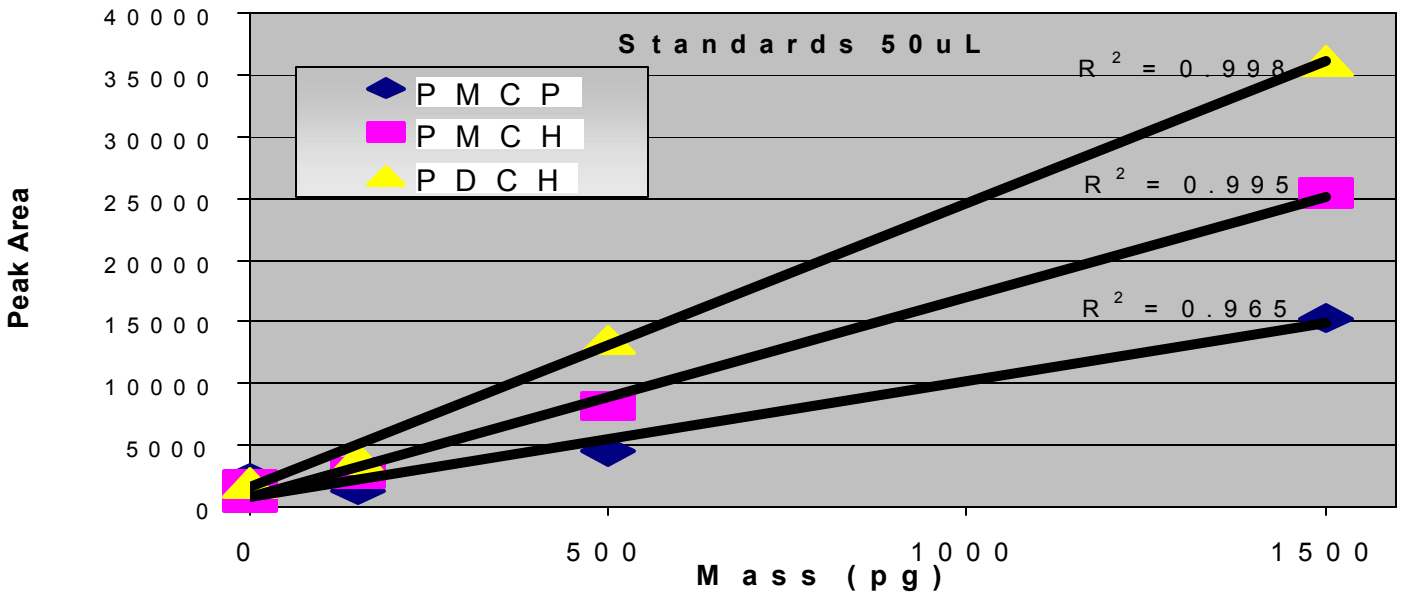

Figure 3: Standard calibration curve (pg) for determination of PFTs.

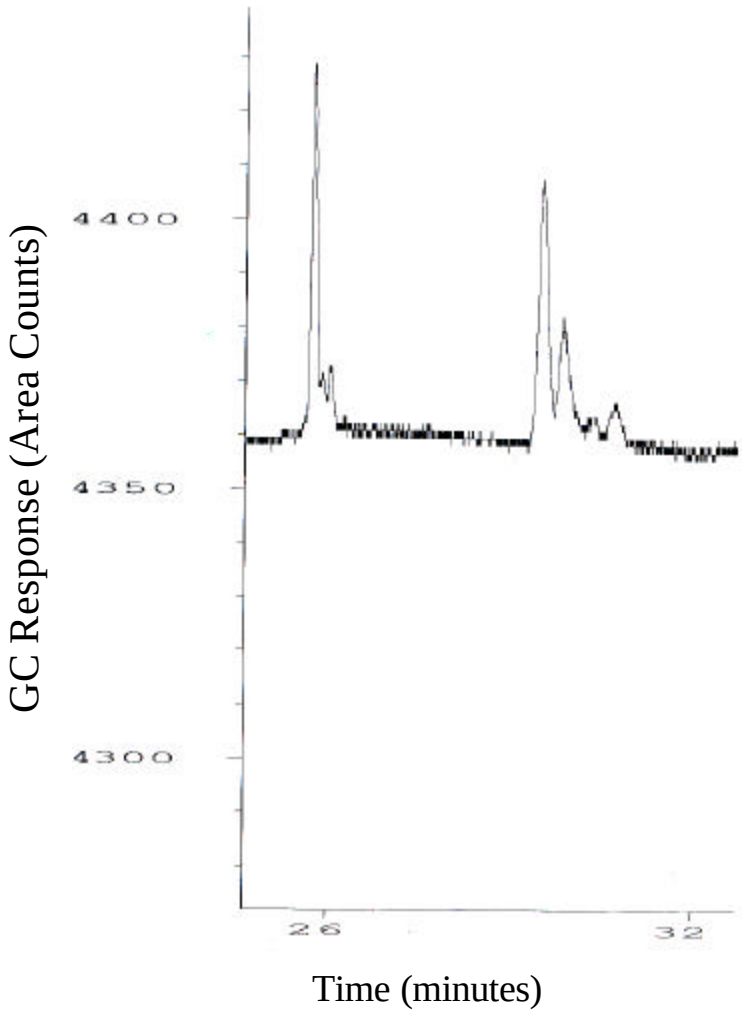

Figure 4: GC Response for PDCH determined from preliminary PFT injections on flow-through system sampled from gas sample valve.