Application of tracers to measure, monitor and verify breakthrough of sequestered CO₂ at the CO2CRC Otway Project, Victoria, Australia

Linda Stalker^{a&b*}, Chris Boreham^{a&c}, Jim Underschultz^{a&d}, Barry Freifeld^e, Ernie Perkins^{a&f}, Ulrike Schacht^{a&g}, Sandeep Sharma^{a&h}

Affiliations;

^aCO2CRC, GPO Box 463, Canberra, ACT 2601, Australia (info@co2crc.com.au)

^bCSIRO, PO Box 1130, Bentley, WA 6102, Australia (linda.stalker@csiro.au)

^cGeoscience Australia, GPO Box 378 Canberra ACT 2601 Australia

(chris.boreham@ga.gov.au)

^d Now at: Sustainable Minerals Institute, University of Queensland, Brisbane, QLD 4072, Australia (j.underschultz@uq.edu.au)

^eLawrence Berkeley National Laboratory, MS 90-1116, 1 Cyclotron Rd., Berkeley, CA 94720, USA (bmfreifeld@lbl.gov)

^fAlberta Innovates, Carbon Conversion, Capture and Storage, 250 Karl Clark Road, Edmonton, Alberta, Canada, T6N 1E4 (ernie.perkins@albertainnovates.ca)

^gAustralian School of Petroleum, U. Adelaide, SA 5005, Australia (Ulrike.schacht@adelaide.edu.au)

^hNow at: Carbon Projects Pty Ltd, Perth, Australia (sharmass@bigpond.com)

*Corresponding author:

linda.stalker@csiro.au

CSIRO, PO Box 1130, Bentley, WA 6102, Australia

Phone +61 8 6436 8909

Fax +61 8 6436 8555

Abstract

At the Cooperative Research Centre for Greenhouse Gas Technology's (CO₂CRC) field site in the Otway Basin of Victoria, Australia, investigations into the storage of CO₂-rich gas in a depleted hydrocarbon gas field have been conducted in the Waarre C reservoir. The injected gas from the nearby Buttress field contained 75 mol% CO₂, 21 mol% CH₄ with the remaining balance being a mixture of wet hydrocarbons, condensate and nitrogen. Chemical tracers (sulphur hexafluoride, SF₆; krypton, Kr; perdeuterated methane, CD₄) were added on the basis of literature surveys and small volume trials at the Frio II Brine experiment in Texas. The aim of the project was to measure, monitor and verify the presence of injected CO₂ in a depleted gas field and that the arrival of tracers was a major component of demonstrating breakthrough of CO₂ at the monitoring well, Naylor-1. The paper focuses on methods developed for the injection, recovery and analysis of samples collected at the Naylor-1 well. Results of tracer analysis compare well with other data collected (including pH and density measurements) to demonstrate breakthrough.

A slip-stream injection system was designed to deliver the tracers mixed with the CO₂-rich gas into the subsurface at the CRC-1 well. The tracers were added to the gas stream 17 days after the start of injection (CO₂ injection commenced 18th March, 2008) into the depleted natural gas field at Naylor. A U-tube system was used to retrieve the samples from the Naylor-1 monitoring well. Collected gas and formation water samples were analysed in detail for gas composition, tracers, isotopes (¹³C CO₂ mainly) and inorganic geochemistry for the broader project. The tracer results confirm that CO₂ breakthrough at the monitoring well occurred within the predicted times. However the interval between samples taken from the U-tubes was too coarse to resolve detailed differences in arrival times between the CO₂ and tracers.

Of the three tracers used, SF₆ provided the clearest evidence of breakthrough at U-tube 2. Kr, because of its abundance in air, and its potential to be present in the subsurface, was more prone to contamination and had higher background levels prior to breakthrough. CD₄ was expected to provide some more unique data based on the presence of abundant CH₄ in the reservoir interval. With hindsight, larger volumes should have been injected to facilitate comparisons with the other tracers and add value to the data set. The test of CD₄ however acted as a suitable proof of concept that CD₄ could be used in such a high background of CH₄.

60 Further work is ongoing to generate data for partition coefficients between
61 supercritical CO₂, CH₄ and water under the injection conditions.

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63 Keywords: Otway Stage 1 Project; carbon storage; geosequestration; depleted
64 reservoir; tracers; gas geochemistry

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1. Introduction and history

The CO₂CRC Otway Project has utilised a depleted gas reservoir to demonstrate carbon storage in the Otway Basin, Victoria, Australia. As such, it was the first depleted gas reservoir demonstration site for solely geosequestration purposes. The project site, approximately a 300 km drive WSW from the Victorian state capital, Melbourne, is just inland from the tourist region known as the Great Ocean Road (Figure 1). The Otway Project utilises a former production well, Naylor-1, which has been re-completed as a monitoring well. An injection well, CRC-1, was drilled in 2007. This is connected by a ~2 km pipeline to the gas source at Buttress-1 which produces a gas from the Turonian age (~ 90 Ma) Waarre C Formation which contains 75 mol% CO₂, 21 mol% methane and the remaining balance being a mixture of wet hydrocarbon gases, condensate and nitrogen (Boreham et al., 2011). Injection of gas commenced on the 18th March, 2008 into the sandstone of the Waarre “C” Formation at approximately 2 km depth and ceased on the 29th August, 2009 after 65,445 tonnes of gas were injected. Various methods, many adopted from the petroleum industry, were deployed to monitor the migration of the CO₂-rich plume over a distance of 300 m from the CRC-1 injector to the Naylor-1 monitoring well that sits near the top of the structure.

A key performance indicator often used to show the successful storage of carbon dioxide during pilot or demonstration projects for carbon capture and storage (CCS) is the ability to measure, monitor and verify the presence of the injected CO₂ in the reservoir. As identified by the Frio I and II Brine Pilot Tests (Hovorka et al, 2006; Sakurai et al. 2006), run by the Bureau of Economic Geology at the University of Texas, it is necessary to:

- Demonstrate to the public, government regulators and other stakeholders that CO₂ can be injected into a brine formation without adverse health, safety, or environmental effects,
- Measure subsurface distribution of injected CO₂ using diverse monitoring technologies,
- Test the validity of conceptual, hydrologic, and geochemical models.

Since CO₂ is a commonly occurring gas in the subsurface (at both deep and shallow levels), it may be difficult to unequivocally confirm that CO₂ measured by a

monitoring system is the CO₂ injected. One of the most obvious ways to circumvent this is to add chemical tracers to the injected gas that are not otherwise found in the subsurface to verify its presence and safe storage. Tracers have also played a role in assurance monitoring of the atmosphere (Etheridge et al., 2005), soil gas (Watson et al., 2006; Watson et al., 2009) and ground water (Hennig et al., 2008; de Caritat et al., 2009).

Aside from the observed gross enrichment in CO₂ concentration in the injection horizon, the carbon isotopic signature of injected CO₂ could be a key monitoring parameter if different from indigenous CO₂ isotopic signatures. However, CO₂ may also be isotopically similar to background readings such as CO₂ from a volcanic source with $\delta^{13}\text{C}$ -4 to -7‰ (Thasher and Fleet, 1995) versus atmospheric CO₂ of $\delta^{13}\text{C}$ -7‰ (Hoefs, 2009). Even though some carbon dioxide may have initial isotopically distinct signatures, over time this may evolve due to known mineral reactions in the subsurface. This has been observed at the Encana Weyburn Project in Saskatchewan, Canada (Shevalier et al., 2004; 2013) and also at the Frio Brine I experiment (Kharaka et al., 2006) and has implications for longer term monitoring of $\delta^{13}\text{C}$ for CO₂ as a tracer.

The Waarre C Formation in the Naylor gas field contains about 1 mol% CO₂ with a carbon isotopic composition of $\delta^{13}\text{C}$ -11.0‰ VPDB (Boreham et al., 2011). The CO₂-rich gas from Buttress is from an igneous source with $\delta^{13}\text{C}$ -6.7‰ (Boreham et al., 2011). Otway Basin natural gases with low CO₂ contents (< 5%) can show large carbon isotopic variations (Watson et al., 2004; Stalker et al., 2009a). In terms of assurance, as the regional variation in abundance and carbon isotopes of CO₂ is so varied, it was determined that tracers could be added to verify the presence of Buttress CO₂ in the subsurface if leakage were to occur and would contribute to the wider assurance program.

Tracers have been used at both Frio Brine Projects (I and II) to successfully determine breakthrough times, demonstrate the presence of the injected CO₂ and provide evidence of tracer partitioning as they migrated 30 m horizontally along the injection reservoir. Tracers used included perfluorocarbons, krypton and perdeuterated methane (CD₄). A U-tube sampling system was installed down hole in the monitoring well to allow samples to be returned to surface at reservoir pressure (Freifeld et al., 2005).

The semi-automated system was capable of acquiring subsamples of fluid at an approximately hourly frequency allowing for gas characterisation and tracer quantification. This gave rapid and certain identification of breakthrough at the monitoring well of injected CO₂ and an accurate transit time to compare with earlier model predictions. The follow-up Frio II experiment in October of 2006 allowed for more complex experimentation and included a trial of other tracers. This included an opportunity for the CO₂CRC to test the concept of using an isotopically labelled tracer, perdeuterated methane (CD₄) Boreham et al., (2007).

Perfluorocarbon tracers have been used at the In Salah capture and storage project in Algeria (Ringrose et al., 2009). This project, operational since 2004, has removed the 5–10% naturally occurring CO₂ content from the hydrocarbon gas fields in the area to meet sales export targets. Rather than venting, the CO₂ has been injected down dip of the gas field. Breakthrough of re-injected CO₂ has been detected at one of the monitoring wells (KB-5); following this observation, on 1st June 2007 perfluorocarbon tracers were added to each of three injector wells. The tracers injected at well KB-502 were subsequently detected at well KB-5 in March of 2008 confirming that the injected CO₂ was indeed the reason for the observed breakthrough at KB-5 and the likely migration pathway.

The US Department of Energy funded (DoE) South East Regional Carbon Sequestration Partnership carbon storage project at Cranfield, Mississippi has also applied tracers. A mix of krypton, xenon, perfluorocarbons and sulphur hexafluoride have been used to evaluate water-rock-CO₂ reactions in place and to obtain more detailed information about fluid migration rates and pathways from injector to monitoring wells in this depleted hydrocarbon reservoir Hovorka et al. (2011). Perfluorocarbon tracers have also been used successfully for assurance monitoring at the West Pearl Queen site in New Mexico (Wells et al., 2007). Based on their work it is possible to calculate likely injection volumes for PFCs to be added at a commercial site, which might be of the order of 25,000L for a 1 million tonne CO₂ injection.

The outcomes of the Weyburn Project where the ongoing use of CO₂ as a long term stable isotopic tracer was questioned, and the experience garnered at the Frio Brine Projects gave confidence in the use of chemical and isotopic tracers at Otway as a means of measuring, monitoring and verifying the presence of injected CO₂. As well as giving a unique “fingerprint” to the stored gas, the additional information gained

increases our understanding of the behaviour of CO₂ during its transit and storage in the subsurface via the partitioning behaviour of these different chemicals.

In the case of the CO₂CRC Stage 1 Project, tracers and other measurements from the reservoir were used to determine breakthrough or first arrival of fluids at the monitoring well. It was specifically stated in Boreham et al., (2011) that breakthrough was defined by “the first instance of the positive detection of added tracers” although other changes (pH, CO₂ concentration and carbon isotopes of CO₂) added weight to the identification of breakthrough.

2. Materials and Methods

2.1 Tracers

After an extensive review (Stalker et al., 2006; Stalker et al., 2009a) three tracers were selected for the primary batch to track the injection plume; sulphur hexafluoride (SF₆), krypton (Kr) and fully deuterated methane (CD₄). In brief, SF₆ was used because of its successful application in a number of different studies including gas leakage, groundwater monitoring and ocean mixing (Tingey et al., 2000 and references therein) as well as its previous application at the Frio Brine Projects (Freifeld et al., 2005). SF₆ was easily sourced in appropriate volumes for a reasonable cost at the time (early 2008), and can be analysed by relatively inexpensive methods at high resolution.

Krypton was used in the Frio Brine experiments successfully. It was expected that it would act conservatively and as “CO₂ becomes a gas, so also do the noble gas tracers” as stated by Nimz and Hudson, (2005). Noble gases in general are chemically inert, environmentally safe, persistent and stable in the environment (Nimz and Hudson, 2005). Relative losses of CO₂ may occur during transportation in the subsurface given it dissolves considerably into water, whereas krypton (or other noble gases) will do so to a far lower extent. Cost, availability and volume of noble gas used was a major consideration as common noble gases such as argon would be inexpensive, but would require massive volumes to be injected (causing possible logistical problems) for detection above background levels.

CD₄ was chosen because there were a number of methane sources present. Free methane is present in the gas cap at the top of the Naylor reservoir structure and there

is abundant residual methane gas saturation below the post-production gas-water contact in the reservoir. In addition, the CO₂ stream injected from Buttress-1 contains 20 mol. % methane. The high volume of methane gas in this depleted reservoir pilot is one of the more unique aspects of the CO₂CRC Otway Project and presents a great opportunity to obtain additional information about the influence of the reservoir and residual gas. CD₄ is not a natural product, but would behave very similarly to the methane present. A total of 2000L CD₄ was supplied by Novachem Pty Ltd at a cost of approx \$18,000 USD (in 2007) to be injected as part of the program.

A second set of tracers were added to the injection gas half way through the injection program. The second set included SF₆ and R-134a (1,1,1,2-tetrafluoroethane), but the results of that test are not reported here.

This paper will focus on the methods developed and the evaluation of the samples collected at Naylor 1 from pre-injection to arrival of the CO₂-rich supercritical plume at the deepest U-tube (U-tube 3) demonstrating the arrival of injected gas a number of depth intervals at the monitoring well. There is work underway and recently completed elsewhere that attempts to integrate the observations with new modelling approaches using recently acquired partitioning coefficient data described in part in Myers et al., (2014). The results of the first batch of tracers added illustrate the effective way in which the tracers complement the other data sets acquired in this small demonstration scale project.

2.2 Volumes added

The volumes of tracers used in the first pulse added to the injected gases are listed in Table 1. The amounts were based on the assumption that a maximum of 100,000 tonnes of gas would be injected at CRC-1 during up to a 24 month period. These volumes were based on the reservoir model at that time for a 30% residual methane gas saturation, average reservoir porosity of 15% and downhole pressure of 20.7 MPa (3000 psi), a 15 m radius of saturation around the injection well bore and a transit distance of 300m between injector and monitoring well. Multipliers were added to allow for the observation of tracers beyond the reservoir in atmospheric, soil-gas and groundwater monitoring, which required larger volumes of tracer to be added in order for them to be seen above background near-surface levels. No tracers were detected in

any samples taken during or post-injection in the atmospheric, soil gas or groundwater samples.

2.3 Tracer injection method – the slip-stream loop

In order to facilitate the injection of tracers with the gas stream from Buttress-1, a slip-stream injector was designed and built (Figure 2). This worked on a similar principle to a sample loop. The design allowed for the attachment of G-size cylinders of gaseous tracer. During injection of the supercritical mix of carbon dioxide and methane, the gas is directed around the tracer gas inlet. This area can be isolated by a series of valves before venting the contents of the isolated area to atmosphere. After closing this area, the tracer cylinder is then opened to the depressurised section of the pipeline (a 50mm x 5m zone) allowing tracer to pressure equilibrate between the G-size cylinder and the depressurised section or slip-stream. The tracer cylinder is then closed prior to the reopening of valves to allow the CO₂-rich gas to flow through that section of the pipeline. Once the pressure has built up to the standard injection pressure (10.3 MPa or 1500 psi) that entire batch of tracer is swept down-hole quickly and efficiently. At least 10 volumes of CO₂-rich gas was flowed through the slip-stream section during each cycle of tracer addition, prior to repeating the depressurisation step, to reduce the likelihood of the presence of tracers being released from the slip-stream and contaminating the near-site areas. The process was repeated until the all gas in the G-size cylinder was effectively used.

As an example of the efficiency of the process, Figure 3 shows the number of vent and fill cycles required to empty one G-size cylinder of each tracer. Cycle zero is the original starting pressure of the G-size cylinder. By the final cycle, < 350 kPa (< 50 psi) of gas remained in each cylinder, having delivered approximately half the contents of the cylinder during each vent/fill cycle. Consequently this system was able to utilize virtually all of the tracer chemicals contained within each cylinder, maximizing the efficient delivery of tracer and providing confidence in the volume of tracer added. The three tracers in the first batch were added over a ~30 hour period which represents a “pulse” in the overall injection program timescale.

2.4 Tracer injection timing

Various tracer injection scenarios were simulated to determine the optimal time for the introduction of the tracers; an early injection could mean that the tracer becomes

the saturating solution around the injection borehole and a late injection would negate the purpose of adding the tracers to confirm breakthrough. Based on the volume of tracers to be injected, reservoir simulations were used to model the optimum timing of injection (Stalker et al., 2009b). The simulation was based on a 3D geological model of the Naylor field using wireline log data and seismic data, with a 20m lateral grid spacing and 1m vertical grid spacing. This was matched to the pressure data during original gas production, and the depth of the post-production gas-water contact, by adjusting the aquifer response. An assumed constant injection rate of 1.55 kg/s (= 134 tonnes/day) was used, with the tracer being added in a short pulse over 6 hours. Delays of 0, 1, 2 and 4 weeks were simulated, with each week corresponding to 940 tonnes of injection, and the tracer concentrations at the location of the Naylor U-tube sampling depths was examined. Injection after 1 week (based on injection rate assumptions) was preferred, as it gave a larger peak concentration of tracer at the U-tubes in the shortest period of time. Thus, a decision was made that tracers would be introduced after 1,000 tonnes of gas injected, which was reached 17 days after the start of CO₂ injection.

Tracer injection commenced with the introduction of a G-size cylinder of CD₄ on the 4th April 2008 (1000 tonnes of gas had been injected 17 days after commencing) with the first tracer injection cycle between 09:10 and 09:16 am. After 6 vent/fill cycles with the slip-stream injector, all the CD₄ was injected from that first cylinder by 10:40am. During this time, the injection gas flow rate averaged 121.7 tonnes/day. A G-size cylinder of SF₆ followed the CD₄, with four cycles of injection taking place over 1 hour and 11 minutes, with flow averaging 126.5 tonnes/day. Three G-size cylinders followed containing Kr, then SF₆ and a final Kr cylinder were injected on that same day, completing injection by 17:20. The final cylinder of Kr and four more cylinders of SF₆ were added on the 5th April, between 08:37 and 13.48 to complete the tracer injection. The decision to put all tracer cylinders in relatively quickly was to maximise the concentration of tracer as a single “slug” to increase the likelihood of seeing the tracer arrive at the Naylor-1 monitoring well.

2.5 Sample recovery

A purpose built bottom hole assembly (BHA) containing a number of devices including three U-tube samplers was installed in Naylor-1 as a part of the monitoring and verification program to obtain samples that retain their reservoir pressure thus

minimising changes to formation water chemistry (Freifeld et al., 2005; Boreham et al., 2011). A single packer located at 2022 mRT (metres deep below the rotary table) was used to isolate the Waarre C formation from the overlying successions. The three U-tubes were carefully located to obtain maximum information about the role of the methane gas cap in a depleted gas reservoir being used to store carbon dioxide as well as the behaviour of the plume in the underlying water leg (see Figure 4). The uppermost U-tube 1 was placed at 2028.8 - 2029.4m RT within the methane gas cap. U-tube 2 was placed at 2041.8 - 2042.4m RT just below the post-production gas-water-contact (GWC) calculated to be at 2039.5m RT. The deepest, U-tube 3, was placed a further 5 m deeper at 2046.3 - 2046.9m RT.

The mechanism and methodology of sampling fluid from the U-tubes varies depending on whether the fluid is gas or liquid. As U-tube 1 is completed within the methane gas cap, it has a wellhead pressure of ~13.8 MPa (2000 psi), or ~16.9 MPa (2466 psi) bottom hole pressure (BHP) and a hydrostatic gas gradient of 1.6 kPa/m (0.23 psi/m). The gas can be sampled from the gas cap directly since the formation pressure and buoyancy allows it to flow to surface freely. Formation fluids from U-tubes 2 and 3 are denser than the methane and formation pressure is sub-artesian. As a result the formation fluids do not flow to surface and have to be recovered using a high pressure nitrogen system where a 15-pack of G-size nitrogen cylinders feed a Bauer Compressor to boost pressure to 31.0 MPa (4500 psi). The check valve in the base of the downhole U-tube system (Freifeld et al., 2005; Boreham et al., 2011) allows the 1/4" stainless steel tubing to fill with local formation fluid via the well perforations. The high pressure nitrogen is applied to the supply side of the U-tube closing the downhole check valve (internal pressure now higher than formation pressure) and lifting the formation water to surface while maintaining the higher pressure of the sample. A purpose-built field laboratory allows for various forms of sampling (free gas, dissolved gas and liquids). Sample vessels include 150mL high pressure stainless steel cylinders and low pressure Isotube[®] subsamples. Gas samples were also collected from depressurisation of a 13L volume of formation fluid (Boreham et al., 2011). These are referred to in the tabulated results as HP=high pressure in stainless cylinders; HP-I = high pressure in isotube; LP-I = low pressure in isotube; H = headspace from high pressure water sample.

As the main plume of CO₂/CH₄ approached U-tube 2 then 3, the sampling procedure was changed once the gas reached sufficient pressures in the reservoir to allow for self-lift. Nitrogen was no longer used to lift the gas, as it could rise independently.

2.6 Sample analysis

Gas samples collected from all three U-tubes were analysed for molecular and carbon isotopic composition at Geoscience Australia (GA) before being sent to CSIRO for tracer analysis. While some results of the CO₂ concentrations from GA are reported here for comparative purposes, the detailed gas geochemistry results are given in Boreham et al. (2011).

The main instrumentation used to analyse for tracers was a Hewlett Packard 5890 II gas chromatograph (GC) interfaced to a VG AutoSpecQ Ultima mass spectrometer (MS). The GC column used was a PLOT fused silica column (50 m x 0.32 mm i.d.) coated with 5A molecular sieve. The head pressure of the column was set up to 172 kPa (25 psi) with a split flow of 23 mL/min. The injector temperature was set to 250°C. The oven temperature programs were as follows: CD₄ isothermal at 40°C (one run), SF₆ isothermal at 40°C (one run) while Kr and Xe (the latter an indicator of air contamination levels) were analysed for simultaneously on an isothermal 250°C run.

Different single ion monitoring (SIM) programs were written to optimise the analysis and quantitation of the three tracers and xenon. The diagnostic mass to charge (m/z) ratios used are as follows: CD₄ m/z = 20.0564, SF₆ m/z = 126.9641, Kr m/z = 83.9115 and Xe m/z = 131.9041. The mass spectrometer was tuned to 1300 resolution (electron energy 70eV; electron multiplier 250 V; filament current 200 µA; source temperature 250°C). The overall sensitivity allowed for the GCMS in SIM mode to detect sub ppb levels of CD₄, and similar for the krypton if the sample is air-free (Boreham et al., 2007). This particular GCMS method requires a specialised sample injection port to minimise atmospheric contamination. Frequent use of blanks, column burn-offs, calibrations and replicates were conducted to reduce analytical error.

SF₆ was initially analysed by GC-ECD (electron capture detector) to obtain some preliminary results and to screen for the arrival of injected CO₂ and first evidence of tracer in the subsurface. At CSIRO's Division of Land and Water a 5890 Agilent Gas Chromatograph (GC) with ECD interfaced to a custom-built sample inlet is designed

to measure the presence of low concentrations of SF₆ in ground waters (Cook et al, 2006). The equipment allows different volumes to be injected by way of different sample loop sizes and dilution steps. A pre-column is used to clean and dry the samples using magnesium perchlorate before the sample is sent to a 5A molecular sieve column. Compounds that are not of interest are backflushed off the column and vented, leaving SF₆ to be measured. Detection limits are believed to be comparable with similar equipment described in Clark et al. (2004) of as low as 0.03 picomoles/cm³. An isothermal oven temperature of 60°C is used, with the detector set at 250°C.

Results for both the GCMS and GC-ECD methods are reported here. In each case, certified standards were used to accurately quantify the presence of the three tracers and xenon, and determine blanks and replicates for each so that baseline could be established and compared with the arrival of each of the tracers.

3. Results and Discussion

The results presented here indicate a low pre-injection baseline concentration of CO₂ followed by rapid increases of CO₂ and tracers at each U-tube, with some differences in arrival time and relative concentrations. All the injected compounds continued to accumulate over time during injection. They are, however, not directly comparable with typical tracer breakthrough curves, such as that reported by Freifeld et al. (2005). This is due to the nature of the geological structure being used to contain the sequestered gas. Rather than passing by a monitoring point, as was the case for both Frio Brine I and II, the CO₂/CH₄ mix is accumulating in the structure and as a consequence, the results show a steady accumulation/increase in concentration of CO₂ and tracers (Figure 5).

3.1 Rapid Analysis of SF₆ by GC-ECD

In order to obtain some early data and while more detailed analytical method development on the GCMS was underway, a sub-set of samples were analysed by GC-ECD at CSIRO Land & Water, Adelaide. Results are presented in Table 2, and shown in Figure 4 for each of the three U-tubes.

U-tube 2 contains the greatest amount of SF₆ (Table 2 and Figure 6). The result shows that breakthrough of this tracer has certainly occurred by the end of July 2008, or about 135 days after the start of injection (Figure 6 inset). Generally before the 17th

July, U-tube 2 shows values below detection limit or very low values (with one exception). After 121 days all values are well above the baseline values. The highest amount of SF₆ in the GC-ECD data set occurred in the sample from September 11th, 2008, i.e., the point where U-tube 2 converted to fully self-lifting and not requiring N₂-assisted lifting thereafter.

This method produced mixed results. Clearly there appears to be significant noise in the GC-ECD dataset, and this impacts somewhat on the quality of the data. The standard deviation of the results from the GC-ECD (Table 2) separate the data into two groups; samples with < 11 picomoles/cm³ tend to have very low standard deviations (commonly less than ± 0.47), while those with > 11 picomoles/cm³ tend to have far larger standard deviations. The detection limit of this instrument is such that this equipment is ideal for baseline surveys of soil gas, groundwaters or even pre-injection baseline samples which contain little or no SF₆. However, even with the maximum possible dilution of samples on this equipment, the samples collected by U-tube soon after breakthrough resulted in overloading the ECD. Thus, values greater than 11 picomoles/cm³ are regarded as semi-quantitative at best (Table 2). However the instrument did give positive results for SF₆ and demonstrated its arrival at U-tube 2 after 101 and before 121 days of injection. This method was able to provide us with a rapid validation that SF₆ had arrived and could be compared with other results for the first presence of CO₂ (Figure 7).

3.2 Detailed quantitative analysis by GC-MS

3.2.1 Baseline, blanks, standards and data manipulation

It is important to define here in the context of the data interpretation what indeed constitutes the baseline data, the “noise” in blanks and the types of standards used to quantitate the data for the tracer analyses (Table 3). All results presented here have also been corrected to remove any presence of nitrogen and are reported as “nitrogen-free” in the tables and figures (Boreham et al, 2011).

3.2.1.1 Standards and Blanks

During the GC-MS analysis of all the samples (the samples having been randomised prior to analysis) a series of standards, duplicates and blanks were analysed and reported (Table 3). The range in concentrations of the unknown samples prior to

analysis was potentially quite large and could have no tracer present (baseline or blanks) or quite high levels (i.e. maximum values for samples could reach the ppm range).

A standard containing 10.5 ppm methane, 10.4 ppm SF₆, 10.7 ppm Kr, 10.4 ppm Xe (all by vol/vol) were mixed in a balance of helium for calibration and quantitation purposes. As the standard concentration was several orders of magnitude higher in concentration of tracer relative to the field samples, a true understanding of the concentration level of the blanks was important. Blanks run during CD₄ analysis gave average values of 0.00017 ppm with standard deviations of 0.00027 ppm. Kr blanks averaged 0.03 ± 0.01 ppm and SF₆ gave results of 0.005 ± 0.006 ppm. Thus values below these blanks are regarded as indicating that tracer is not present.

The system blanks were from a stainless steel cylinder filled via a vacuum manifold with UHP grade helium. Helium is the carrier gas used for the GCMS and should contain no tracer.

3.2.1.2 Baseline

Only a few samples were obtained prior to the start of injection and prior to the first dissolved gas appearing at each U-tube. Extensive sampling was hampered by operational issues, in particular waxes plugging the U-tube lines, with U-tube 1 being particularly problematic (Boreham et al., 2008; 2011). The cause and mitigation strategy to unblock the U-tubes is discussed in detail in Boreham et al, (2011) but required flushing with solvents to remove these waxes. This limited the number of “baseline” samples being taken.

Results for the pre-injection and baseline samples from each U-tube suggest only very low concentrations of tracers in the U-tubes (Table 3). U-tubes 1 and 2 only had low levels of Kr (potentially some contamination by air during analysis). U-tube 3 showed low concentrations of all three tracers. The fact that CD₄ was seen at all in the subsurface suggested that there were some initial problems with the analytical method and so further work was done to establish proper blanks, duplicates and additional modifications to the method to eliminate air and other potential causes of contamination (Table 3).

For CD₄ and SF₆ the expectation was that the baseline values from the subsurface would be at or near zero. CD₄, as mentioned, is not a natural product therefore would

not be found elsewhere. SF₆ may be found in shallow groundwaters that have recently been recharged by precipitation, but it is not anticipated to be seen in the deeper subsurface.

Kr may be present in the deeper subsurface to varying degrees. This may be as low as 1 ppb vol/vol (based on an average concentration in a series of mantle rocks reported in Ozima and Podosek (2002) and accounting for the difference in density of the sandstone of the Waarre C and a 10% porosity estimate). However, the CO₂ rich gases in the Otway area, for example at Boggy Creek, are enriched in helium concentration and with helium isotope signatures indicating that the gases have a significant mantle contribution (Watson et al., 2004), which could mean much higher levels of Kr present in the deeper subsurface. However, the absence of mantle-derived CO₂ in Naylor-1 should mean that baseline amounts of Kr remain low, but with the Buttress-1 gas being added, may contain some indigenous Kr over and above that added as a tracer.

The few samples taken to represent baseline from each of the U-tubes show some values above this “null” expected value and are above the values measured for blanks. While the presence of Kr can be reasonably expected (air contamination at the various sample acquisition and analysis steps, or from the mantle-derived CO₂ contribution) the presence of SF₆ and CD₄ in the U-tube 3 samples as U-tube 2 was exhibiting first evidence of breakthrough was initially unexpected.

Ongoing experience in analysing for and interpreting these tracers in this multi-level U-tube configuration, ground water and soil gas samples as a part of the assurance monitoring strategy has alerted the laboratory to some difficulties associated with analysing enriched samples interspersed with samples containing no tracers (samples having been randomised prior to analysis). One of the main conclusions was to separate the assurance (essentially tracer-free) samples, and those anticipated to have near null values from the enriched U-tube samples and have them analysed separately to avoid the appearance of “memory effects”. Memory effects or carryover, is a problem resulting from efforts to perform quantitative analyses when the unknown sample values have a wide range in concentration. It becomes particularly difficult in the case of measuring trace amounts of material in our experience. The use of blank analyses gave greater confidence in the overall data set (Table 3). The development of a refined inlet port on the GCMS has reduced these effects markedly such that the

team is confident they can differentiate between baseline values for the three tracers (in conjunction with the other geochemical data; Figure 7) to define breakthrough as discussed below.

The effects of wellbore mixing were also investigated as a part of the overall project, as this process could be perceived to have had an influence on the relative abundances of the tracers and overall gas chemistry in some samples, and hence on the arrival times of the tracers. The potential for wellbore mixing relates to the total volume below the packer isolated interval and the volume of fluid extracted per U-tube sample which are similar. The general lack of wellbore mixing at critical times is influenced by the relative densities of the fluids adjacent to the U-tube samplers as the supercritical CO₂ arrives at the wellbore and fills down. The effect tends to be at its greatest when compositional differences between the U-tubes are rapidly changing (e.g. at breakthrough or first time of self-lifting), however this is not an ongoing process that affects results as discussed in Boreham et al. (2011).

3.2.1.3 Data Processing

Both results reported for the bulk gas geochemistry (Boreham et al., 2011) and here have been corrected to remove the nitrogen contents of the samples. This has been conducted due to the use of nitrogen during the sampling process for the U-tubes and allows for all sample types to be compared. As shown by Boreham et al. (2011) the ratio of N₂/CH₄ prior to the self-lifting of U-tube 2 was on average 0.84 but following self-lifting dropped to 0.05 indicating the low abundance of N₂ in the subsurface fluids at Buttress and Naylor.

The distribution of the three tracers over time in each U-tube are compared in Figures 8a, b and c against the measured CO₂ concentration (%) from samples taken prior to injection (i.e. -47 days) to 303 days after the start of injection. The raw data from the GC-MS analyses together with the nitrogen-corrected data are presented in Table 4.

A few other samples were found to be contaminated by the presence of condensate fluids. This effect was particular to U-tube 1 sitting in the overlying gas cap. The methane-rich gas is able to dissolve a range of longer chain n-alkanes at depth and pressure, however as the temperature of the sample is reduced at the surface, these waxy hydrocarbon molecules come out of solution and were found to cause problems during injection into the GCMS (Boreham et al., 2008). These are the same waxy

compounds that led to the plugging of the U-tube lines at depth and called for the design of a clean-out procedure and design of additional equipment (for further details see Boreham et al., 2011).

The tracer data points affected by this wax contamination were removed (Table 4). However, the presence of waxy compounds had no impact on the bulk gas geochemistry composition; therefore the CO₂ data for these points remain. Further presentations of the data include comparison of the same tracer in the three U-tubes (Figure 9a, b & c) as well as by ratio of tracer concentrations (Figure 10a and b).

3.2.2 Tracers by U-tube

3.2.2.1 Composition at U-tube 2

Placement of U-tube 2 just below the GWC was designed to give the first indication of tracer and CO₂ transit to the Naylor-1 monitoring well and information on the behaviour of the gas cap at this point. For example, how would the methane and carbon dioxide gases mix (dynamically or diffusively), or alter the geometry of the gas cap and would efficient sweep of residual methane add to that gas cap further affecting its volume or geometry? The additional placement of U-tube 3 would allow for potential determination of storage efficiency calculations to be made (Underschultz et al., 2011) and the movement of tracers and longer term distribution of the gas over time as the structure fills with up with gas.

SF₆ data from U-tube 2 (Table 4b) is consistently below the limit of detection before the sample taken on the 121st day. But from the 121st day after injection, an increase in SF₆ occurs, reaching 0.019 ppm with the amount of SF₆ rapidly increasing in subsequent U-tube 2 samples as migrating fluids accumulate in the area around U-tube 2 (Figure 8b). Krypton data patterns behave in a similar manner with the early samples up to day 100 averaging 0.41 ppm krypton. This is orders of magnitude less than in air and the system blanks, indicating that if the sampling and analytical protocols are carefully adhered to, then high quality samples with minimal air contamination may be collected. Beyond the first 100 days, there is a sharp rise to 1.6 ppm krypton on the 121st day, followed by a decline to values somewhat higher than the first 100 day baseline values. The CD₄ measurements tend to confirm the timing of breakthrough. Before the 121st day there is no evidence of CD₄ in U-tube 2. On the 121st day after injection started, the amount of CD₄ rises to 0.01 ppm, well above

system blanks and continues to rise as tracer accumulates with CO₂/CH₄ in the Waarre C formation.

Thus all three tracers indicate that initial breakthrough arrived at U-tube 2 prior to the 121st day i.e., at some point between the 27th June (day 101) and 17th July, 2008 and after injecting 10,000 to 12,700 tonnes CO₂/CH₄. The reason for the long gap in sampling frequency around this time was due to operational issues, including waxing of the U-tube lines preventing sampling (Boreham et al., 2008; Boreham et al., 2011).

Saturation of CO₂ or presence of an established supercritical plume at U-tube 2 on day 177, was much easier to determine than the far earlier (days 101-121) breakthrough of dissolved injected gas, as the supercritical plume arrival affected the operational sampling of fluids in the U-tube system. Samples up to this point had been retrieved by “lifting” with high pressure nitrogen (as described in detail in Boreham et al., 2011), however the arrival of the established supercritical plume resulted in sufficient changes in fluid density to allow “self-lifting” of the fluid at U-tube 2 to the surface unaided. Self-lifting occurred on the 11th September, 2008, after 177 days of injection and 21,117 tonnes gas were injected. This was 56 days after the first arrival of the front of dissolved CO₂ at U-tube 2. The concentration of CO₂ at this first self-lift of U-tube 2 at 177 days was 68.35%. This was the highest relative concentration of CO₂ observed in the U-tube 2 samples in the period presented (i.e., to 303 days after injection, or up to 15th January, 2009). This concentration of CO₂ approaches but does not match the Buttress-1 feedstock of approx. 75 mol% CO₂ (Table 4).

The tracer data (Figure 8b) also show maxima like that of the CO₂ concentration, but not at the same point in time as the CO₂. Rather than peaking with the CO₂ after 177 days, both SF₆ and krypton have maxima at 163 days after injection, or a full two weeks prior to CO₂ saturation and the CO₂ maximum. In contrast, the CD₄ does not show a maximum until much later, on the 268th day after injection, or the 11th December, 2008. The maxima of different compounds at different times suggest that the partitioning behaviour of the three tracers and the CO₂ are different over the 300m journey from injector to monitoring well. At the time of injection, there were no data on the partitioning coefficients between the tracers used and supercritical CO₂ (or with 21% CH₄ concentration in that CO₂). Subsequent work by Myers et al (2014) has measured the partition coefficients at the temperatures, pressures and CH₄ concentrations measured in the Waarre C formation in Naylor-1 and suggest that the

impact of the presence of CH₄ is extensive on the partitioning coefficients. For example at 83°C (the reservoir temperature where the U-tubes are located) the K_c/w on a mole fraction basis for Kr in pure water and supercritical CO₂ is 23.40 but in a supercritical mix of 80% CO₂ and 20% CH₄ the K_c/w is 58.87. The differences are quite marked in the other tracers tested in the presence and absence of additional CH₄ (Myers et al, 2014). But, the sample timing used at this experiment in Otway was not anticipated to observe relative arrival rates of each of the injectants, but clearly some patterns have been observed that could be used to evaluate the performance of the tracers.

3.2.2.2 Composition at U-tube 3

Tracer results for the deepest sampling point, U-tube 3, broadly show a similar pattern of evolution as for U-tube 2. Both U-tubes were placed in the water leg during deployment, though U-tube 3 is a further 5 m deeper than U-tube 2. Analysis of samples collected from U-tube 3 shows SF₆ reached above baseline values between days 212 and 226. The Kr and CD₄ results follow suit, however the three tracers could be seen to arrive slightly ahead of the dissolved CO₂ at U-tube 3. This may be a possible function of wellbore mixing (Boreham et al., 2011 and throughout this paper) although U-tube 2 results suggest this is a feature of the partitioning as mentioned in the previous paragraph.

The increased depth away from the GWC for U-tube 3 results in both longer transit times for the dissolved front (tracers arrived by the 30/10/2008 or after 226 days) and the supercritical plume is only slowly established over a number of weeks, beginning some time in late October/mid-November, 2008 and operationally self-lifting continuously from the 15th January, 2009 after 303 days. Thus, the change from the dissolved phase to supercritical was almost twice as long as for U-tube 2. The combination of the slower change to self-lifting and differences in the migration pathway of the supercritical plume at U-tube 3 relative to U-tube 2 has probably contributed to the greater variability in the quantitative measurements for all three tracers and the CO₂ (Figure 8c) and continues in the data set beyond 303 days (Boreham et al., 2011). Tracers reached their maxima in this data set on day 268 for SF₆ (3.21 ppm) and day 275 for CD₄ (0.25 ppm). Kr maximised earlier, on day 184 (5.83 ppm) however this coincides with changes in U-tube 2 (i.e., only 1 week after U-tube 2 self-lifts) that may be reflected in the composition of both U-tubes 1 and 3 at

this time where rapid changes in fluid densities within the wellbore may have resulted in some mixing effects. Similar to U-tube 2, the differences in the concentration maxima for the different tracers also suggest that there is differential partitioning during the transit between the injector and producer wells.

3.2.2.3 Composition at U-tube 1

Tracers and CO₂ were all encountered in the overlying methane gas-cap over time. The CO₂ concentrations were initially influenced by wellbore mixing (e.g. days 156 and 184; Boreham et al., 2011), but by day 233 there was clear presence of CO₂ above baseline. While there is a degree of variability in the tracer concentrations in U-tube 1 prior to this time, the establishment of increased concentrations of all three tracers is notable from day 233 onwards confirming the arrival of CO₂ labelled with tracer. As each of the plots in Figure 8a have the same scales it is easy to see that the amounts of CO₂ and tracer are initially far lower in U-tube 1 than in the underlying U-tube 2 and 3 samples. This indicates that, as mentioned previously, although some degree of wellbore mixing of the fluids occurs during sample acquisition, this tends to occur at specific points in time when major changes are taking place. As the fluids begin to stabilise towards 303 days and the filling of the reservoir down to the deepest U-tube takes place, there is clear evidence that the amount of CO₂ remains far lower in the overlying gas cap and that volume of tracers at each location remain different at each point. The tracers tend to be reaching their maximum in U-tube 1 by the end of the period displayed currently (Figure 8a), showing that there is indeed significant stratification between U-tube 1 and the two deeper U-tube inlets (and by inference differences in density of the fluids; Boreham et al., 2011) and indicate that there has been two discrete pathways that the injected fluids have travelled along towards the top of the Naylor structure to result in these different compositions (Underschultz et al., 2011). Separate modelling studies suggest that the geological model has as strong impact on matching the observed data (Ennis-King et al., 2011). The model investigated a number of scenarios and concluded that heterogeneity of the reservoir interval was highly influential, in particular how a shale break near the gas-water contact controlled not only filling with injected CO₂ but the depletion of the natural gas reservoir prior to injection (Ennis-King et al., 2011; Figure 4 at 2037m MD).

3.2.3. Results by Tracer Type

Displaying the tracer data by tracer type (see Figure 9) instead of specific U-tube (Figure 8) gives a different perspective on the evolution of the fluids. The plot of a single tracer compound in each U-tube over time is compared against the total amount of gas injected for the day of sampling. By 303 days, a total of 38,113 tonnes of Buttress gas has been injected, but not arrived at Naylor-1.

SF₆

The plots of SF₆ data shows more clearly the arrival of the first dissolved front than the supercritical CO₂/CH₄ mix in U-tube 2 ahead of the other U-tubes. Figure 9a also illustrates more clearly the effects of wellbore mixing, where the response of U-tube 1 on day 154 is clearly influenced by the rapid rise in concentration in U-tube 2 as the supercritical plume first arrives. After the arrival of the maximum amount of SF₆ on day 163, ahead of self-lifting in U-tube 2 on day 177, the amount of SF₆ has declined by about 200 days before increasing in concentration again and stabilising. By contrast, U-tubes 1 and 3 while showing some differences, generally show increases in concentration at 300 days to a maximum of 5.23 ppm for U-tube 1 and a lower concentration of approximately 3 ppm for U-tube 3. U-tube 3 shows a marked difference compared to U-tube 1 on days 226 and 233 (mirroring highs for U-tube 2); while this could be attributed to wellbore mixing it is unlikely as the CO₂ concentration and tracer concentrations for U-tube 2 are not rapidly changing.

Kr

The Kr data (Figure 9b) is far more influenced by higher background or baseline values than both SF₆ (Figure 9a) or CD₄ (Figure 9c). Baseline values clearly above the zero value are observed prior to the 121st day where first evidence of breakthrough is seen. The baseline values for U-tube 1 are lower than for either U-tube 2 or U-tube 3 and could be attributed in part to the fact that gas-lifting was never required to access fluids from U-tube 1 in the gas cap zone. Kr values in U-tube 2 rise rapidly between the first arrival of CO₂ and the arrival of the supercritical plume on day 177, though dropping (as seen in the SF₆ data at the same point in time) before recovering and becoming fairly stable from day 198 to 303. The Kr data for U-tubes 1 and 3 are noisier once the presence of the tracer has become established and concentrations in U-tube 1 reach those of U-tube 2 by day 279. Concentrations of Kr in U-tube 3 remain lower than the other two U-tubes at that time, again indicating that in general

wellbore mixing is only present with the most dramatic events/changes of fluid chemistry.

CD₄

The CD₄ results are an order of magnitude less than for SF₆ and Kr (Figure 9c) which is a reasonable reflection of the much reduced volumes of CD₄ added initially. In U-tube 2, rather than a large spike in concentration from 121 to 177 days (i.e. the rapid rise in SF₆ and Kr upon the arrival of supercritical CO₂/CH₄), the amount of CD₄ slowly increases and reaches a maximum on day 268. The amount of CD₄ in U-tube 1 is again higher than for U-tube 3, mimicking the relative proportions seen in the Kr and SF₆ data at this point in time (i.e. the lead up to U-tube 3 becoming self-lifting after 303 days of injection). This quite different pattern in the evolution of concentration of CD₄ in the three sets of U-tube samples certainly illustrates the differences in chemical behaviour compared to SF₆ and Kr.

Ratios

As the three tracers chosen have quite different behaviours, examining the ratios of the different tracer concentrations illustrates differences in the migration pathways and interactions for these tracer between the CRC-1 injector well and the Naylor-1 monitoring well. Figure 10a shows the ratio of SF₆/Kr. As approx. 50,000L SF₆ and 20,000L Kr were injected, to give a ratio of 5:2, this ratio has been added to the figure. The large spikes around days 157 and 184 for U-tube 1 are again regarded as products of wellbore mixing and not representative of the overall distribution of SF₆ and Kr at that time. Once the tracers arrive in U-tube 1 however, the ratio of SF₆/Kr tends to rise until U-tube 3 self-lifts and is then higher than the ratio for U-tubes 2 and 3.

Interestingly, comparing U-tubes 2 and 3, though delayed in time by over 100 days in demonstrating first evidence of injected gas, and 126 days between U-tube 2 and U-tube 3 for self-lifting, the actual evolution of the SF₆/Kr ratios for the samples from each U-tube are remarkably similar both in the rate of increase and stabilised values up to 303 days. However, at no point within the first 303 days does the ratio of SF₆/Kr reach the original ratio of compounds added, indicating a general depletion in the abundance of SF₆ relative to Kr. Work is currently being finalised on measuring the partition coefficients for all CO₂CRC Otway tracers used in supercritical CO₂ and

water at a range of reservoir depths and temperatures that are reflective of the site (Myers et al., 2014).

Comparing the SF_6/Kr (Figure 10a) and SF_6/CD_4 (Figure 10b) ratios for each U-tube the depletion in SF_6 relative to Kr is in contrast with the general enrichment of CD_4 relative to SF_6 seen in U-tube 1 (with some deviation over time). Though there are large variations in values, U-tube 2 shows an initial enrichment but is followed by a general decline in relative CD_4 concentration. For U-tube 3, the change in SF_6/CD_4 ratio is delayed, only increasing after 226 days. This ratio may reduce with time in U-tube 1 as the later arrival of CD_4 may reverse this trend. However the low concentrations of CD_4 mean that any analytical uncertainty might have an exaggerated impact on the ratio presented and should be treated with caution.

In U-tubes 2 and 3, enrichment in SF_6 is diminished. This effect may be due in part to the quite different chemical properties of CD_4 relative to SF_6 and Kr, and the large presence of hydrocarbons with which it might interact during its migration in the methane-rich formation waters, the methane gas-cap and methane in the injected gas itself. Based on the data presented in Myers et al, (2014) the addition of methane to the supercritical CO_2 has a marked impact on the tracer partitioning that could be further exaggerated by the additional hydrocarbons present in the Naylor field.

The ratio data confirms the later arrival of the plume deeper in the structure as the plume fills down from the GWC. The distinct differences in the ratios for each of the U-tubes especially in the period where U-tube 3 commences transition to self-lift (starting anywhere from 226-247 days) to complete self lifting by day 303 illustrates lack of wellbore mixing once the plume has become established at the deepest sampling point.

3.3 Breakthrough

Breakthrough is “defined here as the first instance of the positive detection of added tracers” (Boreham et al., 2011) and may include the CO_2 itself if baseline is sufficiently defined. In Section 3.2.2.1 the data is interpreted to observe breakthrough at U-tube 2 between 101 and 121 days after injection of between 10,000 and 12,700 tonnes of gas, but only 104 days after tracer injection. Modelling designed to locate the CRC-1 well suggested that the transit time could be as short as 4 or up to 8-9 months (Underschultz et al., 2011). The arrival of CO_2 at U-tube 2 after almost 4

months is at the early end of the predictions, though this may be tempered by differences in the value assigned in the model to allow for the cells to be converted from formation water-rich to showing a threshold percentage of dissolved CO₂ (Ennis-King et al, 2011).

The tracer data supports and is supported by the other geochemical information collected from the U-tube samples. In U-tube 2, a summary of much of the analytical information shows that breakthrough has occurred (Figure 7) using other incidental data. The change in CO₂ % is subtle but present too at the time the tracer data suggest for breakthrough, and the $\delta^{13}\text{C}$ CO₂ shows more clearly the arrival of the allochthonous CO₂ in that time period. Additional sources of information from the field sample acquisition system adds further support to both the first breakthrough of dissolved CO₂ and the transition towards U-tube 2 self-lifting. The timing of this operational event indicated the arrival of the plume at each U-tube and therefore at different depths. This information has been used to monitor and verify filling behaviour (Underschultz et al., 2011). Electrical conductivity (EC) and pH probes were fixed in-line with the U-tube sampling equipment. The EC values average 28.3 mS/cm over the four pre-breakthrough samples and remain stable until day 142 before sharply declining to only 9.1 mS/cm on the 156th day. Data from the pH meter reduced from an average of 6.2 prior to 121 days and dropped to 4.7 before water ceased to be collected. The strain gauges used to weigh the large external sampling reservoirs on the outside of the sea container sampling system show the rapid replacement of formation water fluids by supercritical gas. Prior to 163 days, the gauge showed an average of 13.1kg, which only dropped to 10.3kg on day 163 (i.e. one sample cycle) prior to conversion to self-lift. The data are summarised in Figure 7 by normalising the data for all but the stable carbon isotope data (right hand Y-axis) to show these changes happening concurrently. Use of all these field tools all aided in the observation and confirmation of the transition from mainly formation water to the arrival of the supercritical plume/downward migration of the GWC while more detailed laboratory analyses were being carried out.

The behaviour of the pH, EC and strain gauges for U-tube 3 showed a much slower transition to self-lift and mimicked the more convoluted pattern of tracer and CO₂ movement shown in the tracer data. The U-tube 3 data from the field equipment (not shown) confirm the likely combination of migration fingering of fluids both laterally

and vertically as they are emplaced in the area around the U-tube 3 wellbore area; laterally from the migration from the injection point up dip from CRC-1 and vertically in the sense of filling down from the upper zones past U-tube 2 then deeper to U-tube 3. The results also imply evidence for the collection of pockets of methane and wet hydrocarbons left behind after commercial scale methane production as residual gas is mobilized by the presence of CO₂.

3.4 Tracer Partitioning and Sorption

The results from U-tube 2, located just below the GWC, show a straightforward story of the arrival of a dissolved front of injected gas and tracers, before a rapid rise in gas concentration and the self-lifting of the supercritical plume. The tracers were added some 17 days, or after about 1000 tonnes gas had already been injected but the sampling intervals at the point of breakthrough were too coarse to see any significant offset between the arrival of any CO₂ versus the tracers. This was partly due to operational difficulties described in detail in Boreham et al., (2011) but it should be noted that the sample resolution was never intended to be of high enough resolution to resolve relative arrival rates. However, it is interesting to note that both SF₆ and Kr reach maxima in concentration a full 2 weeks prior to the CO₂ reaching maximum concentrations for the period shown (Figure 8a & b).

Evidence for the partitioning of tracers (SF₆ and Kr in particular) have previously been suggested at the Frio Brine I experiment where slight differences in the transit times for perfluorocarbon tracers versus Kr and SF₆ were seen. However, the short transit (30m distance over 50.9 hr from first injection to breakthrough) made it difficult to differentiate the partitioning specifically (Freifeld et al., 2005). While the far longer (300m and 4 months) transit at Otway Stage 1 should have allowed for this partitioning behaviour to be better observed, the coarse sampling and operational difficulties have not allowed for that level of interpretation to occur.

The partitioning behaviour of the tracers tends to be formally characterised with Henry's coefficients (air/water partition coefficients) and octanol/water partition coefficients (shown in Table 1) and had not been constrained by laboratory experiments using supercritical CO₂/water or, in the case at Otway, CO₂/CH₄ and water, though this is currently being resolved (Myers et al., 2014). Only limited data on mainly organic compounds are available currently for partition coefficients

between supercritical CO₂ and water (Timko et al, 2004; and see review in Myers et al, 2014 and references therein). But empirical correlations between supercritical CO₂/water partition coefficients and octanol/water coefficients have been drawn for organic compounds and were generally found to be “extremely poor” (Timko et al, 2004). However, as seen in Figure 8a, the amount of SF₆ is depleted relative to the abundance of krypton in the samples collected up to 303 days. SF₆ is understood to have only slight aqueous solubility (approx. 35mg/L) relative to krypton with a solubility of 234 mg/L (values at 25°C and 1 atm or 101 kPa; from Vulava et al., 2002 and references therein). The ratio of SF₆/Kr show very similar evolutions as the fluids begin to arrive at U-tube 2 and U-tube 3 as the zones sampled by them transition to self-lifting. Thus their exposure to formation water in terms of volumes and levels of interaction seems to have been similar for U-tubes 2 and 3, resulting in the very similar ratios of SF₆/Kr arriving at the deeper U-tubes as the supercritical plume arrives. The presence of significant amounts of injected CO₂ and tracers in samples from the U-tube 1 gas cap had been initially unexpected to occur to such an extent and so early and suggests a different pathway utilised by the injected gas and tracers (Ennis-King et al., 2011; Underschultz et al., 2011). The generally higher SF₆/Kr ratio may indicate lower availability of formation waters and greater propensity of the SF₆ to partition into the gas cap. This effect may also be related to the presence of other hydrocarbons (condensates and waxes) that may retard the SF₆ or even hold it in solution.

Observations made by Vulava et al. (2002) on testing dissolved gases in hydrogeological experiments have shown that while SF₆ and Kr behaved conservatively in saturated column experiments the lower solubility of SF₆ was a factor in retarding this tracer in unsaturated conditions. Both tracers will tend to partition into gas-filled void spaces (abundant in the Waarre C injection formation owing to the residual methane saturation and addition of sequestered gas). This may partially explain the behaviour of the SF₆/Kr ratio, but differences may be further exaggerated by the potential for either of these species to be retarded via sorption or interaction with other media. In the laboratory during sample analysis, SF₆ was noted to adhere readily to rubber and plastics, and therefore could have the potential to be adsorbed by organic matter in the subsurface during migration. This possibility was raised also by Vulava et al. (2002) where diffusion of SF₆ into Teflon end pieces of

the experimental column was suggested. SF₆ is not expected to adhere to clean sands (Wilson and Mackay, 1996) nor did a sand column experiment with 2.5% organic matter present appear to result in any retardation effects. However, in octanol-water partitioning coefficient measurements (Wilson and Mackay, 1996) suggested that SF₆ is more likely to partition into liquid organic phases, which is present in the form of condensates and waxes in the gas cap and residual gases of the Naylor-1 Waarre C formation used in the Otway Stage 1 test

The behaviour of SF₆ and Kr observed up to 303 days at U-tubes 2 and 3 therefore suggest similar pathways of migration from the injector well (CRC-1) to the Naylor-1 monitoring well. U-tubes 2 and 3 appear to show similar sharp breakthrough and accumulation of the tracers. Thus it can be assumed that the porosity, permeability, mineralogy and exposure to unsaturated pore space, organic liquids or other parameters that could impact on the arrival of either tracer have been quite similar, but not the same as for U-tube 1. As absolute amounts of the tracers have not begun to tail as with conventional breakthrough curves, little can be concluded about any observed tailing while the tracers continue to accumulate with the injected gas in this structural trap.

4. Conclusions

Analytical results from U-tube samples have been evaluated from baseline until the supercritical plume has arrived at the deepest U-tube (U-tube 3). The results show the evolution of fluids from their static post-methane production in Naylor-1 (before injection commenced) to the point at which the U-tubes can no longer sample formation waters due to their replacement by a mixture of supercritical CO₂ and CH₄. The tracer results were used to confirm that breakthrough (i.e., the first evidence of tracers) had indeed occurred. While breakthrough could have been difficult to determine from one set of data in isolation, a combination of gas geochemistry, tracer analysis and the physical observations of pH, change in strain gauge weight and drop in electrical conductivity all demonstrate the clear first arrival of the injected gas (in a dissolved state) by the time a sample is taken on the 121st day after injection commenced at the Otway site. This occurred at U-tube 2 which is located just below the post-production GWC. It took a further 56 days for U-tube 2 to convert to “self-lifting” so that only supercritical gas was collected. After another 126 days, U-tube 3 had completed a far slower transition to self-lifting. As discussed in Underschultz et

al. (2011) an understanding of the structure of Naylor and the rate of injection has contributed towards an improved understanding of gas storage capacity in a depleted gas reservoir.

Somewhat unexpectedly from that predicted by early numerical simulations, U-tube 1 samples showed the presence of injected gas and tracers sooner than anticipated and in higher concentrations. This is not simply caused by wellbore mixing during sampling but a consequence of a different pathway of migration of the fluids and can be accounted for current geological models (Ennis-King et al., 2011; Underschultz et al., 2011).

The presence of the tracers in samples collected by the U-tubes confirms the arrival of the injected gas at the different locations in the wellbore. Their relative abundances (i.e., partitioning) also show that for U-tubes 2 and 3, their pathway to the structure was similar, to the extent of the amount of formation water versus residual gas passed during migration. U-tube 1 again shows differences to the other two U-tubes, which is unsurprising given that this U-tube is located in the free-gas cap. SF_6 appeared to perform best at U-tube 2 with respect to identifying breakthrough. Kr was more difficult to determine breakthrough with due to its significantly higher background levels both in air and with the potential for Kr to coexist with the gas used at Buttress-1 for the test. It is more difficult to evaluate the performance of CD_4 due to the lower concentrations initially injected so it is difficult to clearly determine whether it performed better in the U-tube 1 sampled interval that was already CH_4 rich. The ratios of different tracers indicates that there has been partitioning into the residual gas present and that the CH_4 in Naylor has influenced the behaviour of the tracers and contributed to significant partitioning. Ongoing sampling and analysis (still continuing in December 2014) will give further information on the behaviour of the tracers, the injected gases and the effect of the residual and free methane in this pilot study at Otway.

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Figure legends

Figure 1. Location map of site.

Figure 2. Schematic of the slip-stream inlet for tracer injection.

Figure 3. Tracer injection efficiency showing drop in pressure with every cycle of addition into the slip-stream injector.

Figure 4. Location of U-tubes in the Naylor-1 monitoring well, illustrating location of additional bottom-hole-assembly tools and the geology of the Waarre C formation.

Figure 5. GC-ECD of SF₆ results for all three U-tubes.

Figure 6. U-tube tracer results (a) U-tube 1 (b) U-tube 2 (c) U-tube 3 relative to the mole % CO₂ measured.

Figure 7. Tracers for all U-tubes (a) SF₆ (b) Kr (c) CD₄ relative to total gas injected.

Figure 8. Ratio of (a) SF₆/Kr for each U-tube, with the line at 2.5 showing the original ratio added (by volume) and (b) SF₆/CD₄ for each U-tube with the line at 25 showing the original ratio added (by volume).

Figure 9. Field data compared with laboratory results demonstrating early warning indicators of arrival of supercritical plume confirming evidence for breakthrough (vertical line at 121 days) and supercritical CO₂ arrival (177 days) at U-tube 2 in the monitoring well.

Table 1. Properties and volumes of tracers injected in the first pulse at Otway in April, 2008 compared with the main gases injected.

Footnotes to Table 1.

[1] Boreham et al., 2008

[2] Mroz et al., 1989

[3] Nimz and Hudson, 2005

[4] IPCS Inchem MSDS (<http://www.inchem.org>)

[5] CRC Handbook of Chemistry and Physics David R. Lide, 71st Ed. 1990-1991

[6] log Po/w = n-octanol/water

[7] Sander (1999)

[8] Vulava et al., (2002) and references therein

1090

1091 Table 2. SF₆ analysis by GC-ECD giving semi-quantitative results for U-tube
1092 analyses.

1093 Footnote – BDL = below detection limit.

1094 *Results were measured in picomoles/cm³. Some were replicates that were averaged.
1095 However, as noted in the text, the samples were soon too rich and far higher than the
1096 highest calibrant gas used (i.e., results above 11 picomoles/cm³), and can therefore
1097 only be regarded as semi-quantitative.

1098

1099 Table 3. Blanks and baseline values for each U-tube and each tracer during GC-MS
1100 analysis.

1101 Footnotes

1102 n.d. = below limit of detection.

1103 n = x; x is the total number of samples averaged.

1104

1105 Table 4a. U-tube 1 results for tracers and CO₂ on a nitrogen and air-free basis (naf).

1106 Table 4b. U-tube 2 results for tracers and CO₂ on a nitrogen and air-free basis (naf).

1107 Table 4c. U-tube 3 results for tracers and CO₂ on a nitrogen and air-free basis (naf).

1108 Footnotes

1109 a Date_Sample_Time = d/m/y_U-tube and sample type_hhmin. HP=high pressure;
1110 HP-I = high pressure to isotube; LP-I = low pressure in isotube; H = headspace from
1111 high pressure water sample.

1112 b Observed tracer concentrations below 0.0002 ppb, 0.03 ppb and 0.005 ppb for CD₄,
1113 Kr and SF₆, respectively are set to 0.

1114 * naf = nitrogen and air free.

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Figures

Figure 1.

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Figure 2. Slip-stream design for injecting tracers at CO2CRC Otway Project Stage 1 at the CRC-1 wellhead (modified from Stalker et al., 2009b).

Figure 3. Tracer injection efficiency showing drop in pressure with every cycle of addition into the slip-stream injector.

Figure 4. Location of U-tubes in the Naylor-1 monitoring well, illustrating location of additional bottom-hole-assembly tools and the geology of the Waarre C formation.

1151 Figure 5. Cross section of the area to show the structure of the depleted hydrocarbon
 1152 gas reservoir (after Boreham et al., 2011).

Figure 6. GC-ECD of SF₆ results for all three U-tubes.

Figure 7. Field data compared with laboratory results demonstrating early warning indicators of arrival of supercritical plume confirming evidence for breakthrough (vertical line at 121 days) and supercritical CO₂ arrival (177 days) at U-tube 2 in the monitoring well.

Figure 8. U-tube tracer results (a) U-tube 1 (b) U-tube 2 (c) U-tube 3 relative to the mole % CO₂ measured.

(a)

(b)

1183 (c)

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1186 Figure 9. Tracers for all U-tubes (a) SF_6 (b) Kr (c) CD_4 relative to total gas injected.

1187 (a)

1188 (b)

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1192 (c)

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Figure 10. Ratio of (a) SF_6/Kr for each U-tube, with the line at 2.5 showing the original ratio added (by volume) and (b) SF_6/CD_4 for each U-tube with the line at 25 showing the original ratio added (by volume).

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Tables

1213 Table 1. Properties and volumes of tracers injected in the first pulse at Otway in April, 2008
1214 compared with the main gases injected.

Tracer	Atmospheric concentration	Tracer added at Otway Project (L)	Partitioning coefficient (ctanol/water partition coefficient as $\log P_{ow}$)	Relative vapour density	Solubility in water	Henry's Law constant M/atm ^[6]	Henry's Law constant dimensionless
CD ₄	1.3E-16 ^[1]	2,000	cf CH ₄	cf CH ₄	cf CH ₄	-	
SF ₆	1.01E-11 ^[2]	~50,000	1.68 ^[4]	1.329 kg/L (solid); 6.164 g/L (gas)	nil	2.4 x 10 ⁻⁴	170.4 ^[7]
Kr	1.14 ppmv ^[3]	20,000	1.2 ^[4]	3.749 g/L (0°C/100 kPa) ^[5]	nil	2.4 to 2.5 x 10 ⁻³	18.0 ^[7]
(CO ₂)	383 ppmv ^[3]		0.83 ^[4]	1.6 kg/L (solid); 1.98 g/L (gas) ^[5]	88 mL/100 mL (20°C) ^[4]	3.1 to 4.5 x 10 ⁻²	1.2 ^[7]
(CH ₄)	1.745 ppmv ^[3]		1.09 ^[4]	0.717 kg/m ³ (gas) ^[5]	3.3 mL/100 mL (20°C) ^[4]	1.3 x 10 ⁻³ to 9.7 x 10 ⁻⁴	

[1] Boreham et al., 2008

[2] Mroz et al., 1989

[3] Nimz and Hudson, 2005

[4] IPCS Inchem MSDS (<http://www.inchem.org>)

[5] CRC Handbook of Chemistry and Physics David R. Lide, 71st Ed. 1990-1991

[6] Sander (1999)

[7] Vulava et al., (2002) and references therein

1226 Table 2. SF₆ analysis by GC-ECD giving semi-quantitative results for U-tube
1227 analyses.

Sample ID	Date_sample_time	Days after start of injection	Results*	Standard deviation
U1				
20089099	290508_U1HP-I_1240	72	0.001	0.001
20089124	270608_U1HP-I_1036	101	0.46	0.02
20089137	170708_U1HP-I_1508	121	0.18	0.005
20089149	070808_U1LP-I_1605	142	0.10	0.07
20089159	220808_U1HP-I_1023	157	58.46	11.9
20089175	040908_U1HP-I_1554	170	0.12	0.001
20089184	110908_U1HP-I_1421	177	0.16	0.02
20089189	180908_U1HP-I_1152	184	11.99	0.47
20089194	250908_U1HP-I_1202	191	0.39	0.02
20089202	021008_U1LP-I_1344	198	0.53	0.04
20089208	091008_U1LP-I_1251	205	1.10	0.07
20089214	161008_U1LP-I_1353	212	1.87	0.07
20089226	301008_U1HP-I_1339	226	0.36	0.01
20089232	061108_U1HP-I_1521	233	9.99	0.24
U2				
20089013	310108_U2_LP-I_1700	-47	BDL	-
20089101	250508_U2LP-I_1517	68	0.13	0.15
20089117	110608_U2LP-I_1625	85	0.01	0.000
20089125	260608_U2LP-I_1350	100	BDL	-
20089138	170708_U2LP-I_1206	121	0.12	0.000
20089143	310708_U2LP-I_1253	135	0.53	0.001
20089150	070808_U2LP-I_1243	142	0.79	0.01
20089160	220808_U2LP-I_1421	157	11.38	3.93
20089170	280808_U2-I_1305	163	121.01	14.63
20089176	040908_U2LP-I_1330	170	53.98	8.96
20089185	110809_U2HP-I_1235	177	145.64	3.16
20089191	180908_U2HP-I_1056	184	67.46	73.4
20089195	250908_U2HP-I_1100	191	66.08	23.4
20089203	021008_U2LP-I_1246	198	110.34	9.14
20089215	161008_U2LP-I_1254	212	50.49	26.9
20089222	231008_U2HP-I_1223	219	47.23	0.08
20089227	301008_U2HP-I_1237	226	60.23	28.2
20089233	061108_U2HP-I_1141	233	85.77	30.9
U3				
20089014	310108_U3_LP-I_1343	-47	BDL	-
20089119	110608_U3LP-I_1355	85	0.01	0.000
20089127	260608_U3LP-I_1121	100	BDL	-
20089140	170708_U3LP-I_1015	121	0.61	0.01
20089144	310708_U3LP-I_1048	135	0.38	0.01
20089152	070808_U3LP-I_1108	142	0.04	0.09
20089162	210808_U3LP-I_1236	156	0.03	0.02
20089171	280808_U3-I_1013	163	0.61	0.06
20089177	040908_U3LP-I_1048	170	0.57	0.03
20089186	110908_U3LP-I_1025	177	0.43	0.03
20089192	180908_U3LP-I_0946	184	0.11	0.02
20089196	250908_U3LP-I_0947	191	0.34	0.04
20089204	021008_U3LP-I_1111	198	0.14	0.04
20089210	091008_U3LP-I_1031	205	0.30	0.001
20089216	161008_U3LP-I_1119	212	0.29	0.004
20089223	231008_U3LP-I_1103	219	2.16	0.16
20089228	301008_U3LP-I_1123	226	46.75	7.40
20089234	061108_U3LP-I_1015	233	45.39	8.63

1228 Footnote – BDL = below detection limit.

1229 *Results were measured in picomoles/cm³. Some were replicates that were averaged.

1230 However, as noted in the text, the samples were soon too rich and far higher than the

1231 highest calibrant gas used (i.e., results above 11 picomoles/cm³), and can therefore
1232 only be regarded as semi-quantitative.
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1238 Table 3. Blanks and baseline values for each U-tube and each tracer during GC-MS
1239 analysis (ppm).

	Blank	Baseline U1	Vessel	Baseline U2	Vessel	Baseline U3	Vessel
SF ₆	0.005 ⁿ⁼¹²	n.d	HP or HP- 1	n.d	LP	0.01 ⁿ⁼³	LP
	± 0.006					± 0.01	
Kr	0.03 ⁿ⁼²¹	0.161 ⁿ⁼³	HP or HP- 1	0.41 ⁿ⁼³	LP	0.59 ⁿ⁼³	LP
	± 0.01	± 0.005		± 0.09		± 0.30	
CD ₄	0.00017 ⁿ⁼⁵	n.d.	HP or HP- 1	n.d	LP	0.003 ⁿ⁼²	LP
	± 0.00027					± 0.004	

1240 n.d. = below limit of detection.

1241 n = x; x is the total number of samples averaged.

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1251 Table 4a. U-tube 1 results for tracers and CO₂ on a nitrogen free basis (naf).

Date_Sample_Time ^a	Days	SF ₆ naf ^{b*}	Kr naf ^{b*}	CD ₄ naf ^{b*}	SF ₆ /Kr	SF ₆ /CD ₄	CO ₂ naf [*]
		ppm	ppm	ppm			mol%
010108_U1HP	-77	0.00	0.16	0.00	0.00	2.59	1.17
010108_U1HP	-77						1.04
300108_U1HP_1845	-48						1.12
300108_U1HP-I_1845	-48	0.00	0.16	0.00	0.00	0.00	1.30
290508_U1HP-I_1240	72	0.00	0.17	0.00	0.00		1.59
120608_U1HP-I_1505	86						1.34
170708_U1HP_1508	121	0.02	0.20	0.00	0.09	37.11	1.28
170708_U1HP-I_1508	121	0.01	0.16	0.00	0.04	8.70	1.53
070808_U1HP_1549	142						1.54
070808_U1HP-I_1549	142						1.62
070808_U1LP-I_1605	142	0.01	0.18	0.00	0.05	18.37	1.27
220808_U1HP-I_1023	157	3.10	1.76	0.09	1.77	36.39	16.01
040908_U1HP_1554	170	0.00	0.10	0.00	0.04	8.35	1.24
040908_U1HP-I_1554	170	0.02	0.11	0.00	0.15	34.71	1.94
110908_U1HP_1421	177	0.00	0.11	0.00	0.03	8.41	1.81
110908_U1HP-I_1421	177	0.01	0.12	0.00	0.12	33.10	1.27
180908_U1HP_1152	184	0.64		0.04		16.38	12.98
180908_U1HP-I_1152	184	0.65	0.56	0.03	1.16	18.83	14.28
250908_U1HP-I_1202	191	0.02	0.12	0.00	0.20	30.15	1.45
250908_U1HP_1202	191	0.08	0.42	0.00	0.19	21.68	1.45
021008_U1HP_1344	198	0.03	0.42	0.00	0.06	19.30	1.68
021008_U1LP-I_1344	198	0.02	0.13	0.00	0.13	14.49	1.62
091008_U1HP_1251	205	0.09	1.37	0.00	0.06	30.45	1.38
091008_U1LP-I_1251	205	0.02	0.15	0.00	0.11	29.86	1.24
161008_U1HP_1353	212	0.09	0.28	0.00	0.30	20.95	2.57
161008_U1LP-I_1353	212	0.10	0.16	0.00	0.59	19.21	2.18
231008_U1HP_1341	219	0.12	0.25	0.01	0.48	22.54	1.39
231008_U1HP-I_1341	219						1.41
301008_U1HP-I_1339	226	0.02	0.11	0.00	0.21	28.84	1.53
061108_U1HP_1521	233						6.08
061108_U1HP-I_1521	233	0.51	0.46	0.02	1.12	21.79	8.60
131108_U1HP_1211	240						4.70
131108_U1LP-I_1211	240	0.29		0.01		38.54	2.86
201108_U1HP_1335	247						16.73
201108_U1HP-I_1335	247	0.89	0.97	0.02	0.92	36.88	13.75
271108_U1HP_1424	254						18.19
271108_U1HP-I_1424	254	1.78	1.09	0.07	1.63	25.42	16.18
041208_U1HP_1325	261						23.49
041208_U1HP-I_1325	261	4.34	2.29	0.11	1.89	40.60	23.28
111208_U1HP_1016	268						19.60
111208_U1HP-I_1016	268	1.53	0.81		1.89		17.88
181208_U1HP_1250	275						18.46
181208_U1HP-I_1250	275	3.83	1.93	0.11	1.99	35.69	18.09
221208_U1HP_1200	279						16.85
221208_U1HP-I_1200	279	4.77	2.31	0.23	2.07	20.93	16.55
050109_U1HP_1338	293						23.62
050109_U1HP-I_1338	293	4.10	3.23	0.30	1.27	13.85	22.91
150109_U1HP_1108	303						19.34
150109_U1HP-I_1108	303	5.23	2.59	0.20	2.02	26.73	18.49

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1265 Table 4b. U-tube 2 results for tracers and CO₂ on a nitrogen free basis (naf).

Date_Sample_Time ^a	Days	SF ₆ naf ^{b*}	Kr naf ^{b*}	CD ₄ naf ^{b*}	SF ₆ /Kr	SF ₆ /CD ₄	CO ₂ naf [*]
		ppm	ppm	ppm			mol%
250508_U2LP-I_1517	68	0.00	0.50	0.00	0.00		7.62
110608_U2LP-I_1625	85	0.00	0.32	0.00	0.00		7.42
260608_U2LP-I_1350	100	0.00	0.41	0.00	0.00		7.48
170708_U2LP-I_1206	121	0.02	1.57	0.01	0.01	2.15	8.84
310708_U2LP-I_1253	135	0.03	0.61	0.01	0.06	2.31	11.49
070808_U2LP-I_1243	142	0.03	0.55	0.01	0.05	3.39	13.68
210808_U2LP-I_1421	156	0.72	1.37	0.05	0.52	13.09	39.89
280808_U2LP-I_1305	163	6.61	4.54	0.01	1.46	479.21	44.33
040908_U2LP-I_1330	170	4.90	3.92	0.18	1.25	27.44	56.69
110908_U2HP_1235	177	4.06	3.52	0.17	1.15	23.52	44.42
110908_U2HP-I_1235	177	4.05	3.38	0.12	1.20	35.19	69.29
180908_U2HP_1056	184	2.72	2.81	0.11	0.97	23.92	53.46
180908_U2HP-I_1056	184	3.02	2.86	0.17	1.06	18.20	55.50
250908_U2HP-I_1100	191	2.29	1.78	0.08	1.29	30.10	54.25
250908_U2HP_1100	191	3.02					54.31
021008_U2HP_1246	198	3.50	2.50	0.27	1.40	13.12	52.19
021008_U2LP-I_1246	198	4.77	3.22	0.20	1.48	24.07	52.67
091008_U2HP_1201	205	3.22	2.26	0.21	1.43	15.12	58.54
091008_U2LP-I_1201	205						46.30
161008_U2HP_1255	212	3.65	3.22	0.29	1.13	12.66	57.59
161008_U2LP-I_1254	212	3.87	2.90	0.20	1.33	19.32	51.13
231008_U2HP_1223	219	3.57	2.43	0.30	1.47	11.72	58.20
231008_U2HP-I_1223	219	3.99	2.97	0.17	1.34	23.55	52.85
301008_U2HP_1237	226	4.25	2.66	0.40	1.60	10.69	58.24
301008_U2HP-I_1237	226	4.43	3.07	0.20	1.44	22.55	56.05
061108_U2HP_1141	233						60.24
061108_U2HP-I_1141	233	4.48	3.08	0.45	1.45	9.96	60.49
131108_U2HP_1117	240						60.05
131108-U2LP-I-1117	240	3.90	2.74	0.35	1.43	11.24	55.12
201108_U2HP_1259	247						62.47
201108_U2HP-I_1259	247	3.70	2.78	0.22	1.33	16.78	51.21
271108_U2HP_1116	254						56.89
271108_U2HP-I_1116	254	3.65	2.64	0.22	1.38	16.45	52.62
041208_U2HP_1244	261						56.11
041208_U2HP-I_1244	261	4.34	2.70	0.43	1.61	10.01	53.68
111208_U2HP_0943	268						56.38
111208_U2HP-I_0943	268	4.52	3.37	0.57	1.34	7.97	49.44
181208_U2HP_1212	275						58.43
181208_U2HP-I_1212	275	4.02	2.76	0.24	1.45	16.52	50.79
221208_U2HP_1116	279						54.40
221208_U2HP-I_1116	279	3.91	2.53	0.31	1.55	12.63	52.34
050109_U2HP_1117	293						53.23
050109_U2HP-I_1117	293	4.13	3.22	0.44	1.28	9.40	48.27
150109_U2HP_1028	303						54.95
150109_U2HP-I_1028	303	3.85	2.58	0.19	1.49	20.20	49.41

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1281 Table 4c. U-tube 3 results for tracers and CO₂ on a nitrogen free basis (naf).

Date_Sample_Time ^a	Days	SF ₆ naf ^{b*}	Kr naf ^{b*}	CD ₄ naf ^{b*}	SF ₆ /Kr	SF ₆ /CD ₄	CO ₂ naf [*]
		ppm	ppm	ppm			mol%
250508_U3LP-I_1820	68	0.00	0.53	0.01	0.01	0.66	6.91
110608_U3LP-I_1355	85	0.01	0.92	0.00	0.02		6.41
260608_U3LP-I_1121	100	0.01	0.33		0.04		7.76
170708_U3LP-I_1015	121	0.09	0.71	0.00	0.13	56.98	11.80
310708_U3LP-I_1048	135	0.03	0.58		0.05		9.50
280808_U3LP-I_1013	163	0.02	0.64	0.02	0.04	0.95	23.43
040908_U3LP-I_1048	170	0.06	0.83	0.01	0.08	4.20	22.45
110908_U3LP-I_1025	177	0.03	1.13	0.03	0.02	0.84	23.61
180908_U3LP-I_0946	184	0.01	5.83	0.01	0.00	1.92	12.84
250908_U3LP-I_0947	191	0.02	0.60	0.01	0.03	1.55	20.06
021008_U3LP-I_1111	198	0.03	0.75	0.02	0.04	1.24	29.77
091008_U3LP-I_1031	205	0.02	0.58	0.01	0.03	1.42	29.00
161008_U3LP-I_1119	212	0.03	0.58	0.02	0.05	1.41	26.05
301008_U3LP-I_1123	226	2.30	1.99	0.13	1.15	17.21	38.23
061108_U3LP-I_1015	233	1.93	1.44	0.10	1.34	18.75	47.03
131108_U3LP-I_1003	240	0.06	0.36	0.02	0.17	3.03	27.48
201108_U3LP-I_1144	247	1.61	1.50	0.07	1.07	23.12	53.64
271108_U3LP-I_1009	254	2.11	1.65	0.09	1.27	23.28	53.58
111208_U3HP_1054	268						47.46
111208_U3LP-I_1151	268	0.92	0.91	0.04	1.01	20.49	53.69
121208_U3LP-I_1116	269	3.21	2.69	0.13	1.19	24.12	54.58
121208_U3LP-I_1306	269	2.63	1.99	0.14	1.32	18.99	55.01
181208_U3HP_1129	275	3.09	2.14	0.25	1.44	12.40	52.79
181208_U3HP-I_1129	275						53.21
221208_U3HP_1033	279						58.93
221208_U3HP-I_1033	279	1.42	1.13	0.08	1.26	18.61	57.79
050109_U3HP_1210	293						56.44
50109_U3LP-I_1221	293	2.99	1.82	0.11	1.64	25.96	55.99

1282 a Date_Sample_Time = d/m/y_U-tube and sample type_hhmin. HP=high pressure;
1283 HP-I = high pressure to isotube; LP-I = low pressure in isotube; H = headspace from
1284 high pressure water sample.
1285 b Observed tracer concentrations below 0.0002 ppb, 0.03 ppb and 0.005 ppb for CD₄,
1286 Kr and SF₆, respectively are set to 0.
1287 * naf = nitrogen and air free.

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