Groundwater and geological storage of carbon dioxide

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Introduction

The geological storage of carbon dioxide (CO\textsubscript{2}) is the process whereby CO\textsubscript{2} captured from power plants or other industrial facilities is transported to a suitable location and then injected under pressure into a deep geological reservoir formation, where it remains permanently trapped and prevented from entering the atmosphere.

The processes by which captured CO\textsubscript{2} is retained in the subsurface are generally those that have trapped oil, gas and naturally generated CO\textsubscript{2} for millions of years. The geological formations that can be utilised for this trapping have the same characteristics as those that are able to act as reservoir rocks for petroleum. They have high porosity and permeability and have an overlying sealing formation, which will prevent the trapped fluids from migrating out of the storage reservoir and possibly escaping to the surface. In addition, because of the phase behaviour of CO\textsubscript{2}, efficient storage requires that they are stored at depths greater than 800 metres below the surface, where CO\textsubscript{2} density is greatly increased.

Unlike oil and gas, which rely primarily on a three dimensional structural trap to prevent them from ultimately rising to the surface, there are additional trapping mechanisms for CO\textsubscript{2}. As CO\textsubscript{2} migrates away from the injection well, some of the gas will remain residually trapped in the pores due to capillary forces. On longer time scales, CO\textsubscript{2} will dissolve into the formation water and may potentially react with primary minerals, leading to mineral trapping. Dissolution trapping of CO\textsubscript{2} into aquifers is often termed deep saline aquifer storage due to the high salinities typically encountered at depth.

Onshore geological storage in Australia

A recent nationwide review by Geoscience Australia and State Geological Surveys, as part of the Carbon Storage Taskforce, rated the suitability of geological basins across Australia for geological storage of CO\textsubscript{2}. The most geologically suitable basins are the offshore Gippsland and North Perth basins but several onshore basins also rate highly. These include the Eromanga, Cooper, Bowen, Galilee, Surat, Canning and Otway basins (Carbon Storage Taskforce, 2009). The Victorian Government has recently released areas for greenhouse gas storage exploration in the onshore Gippsland Basin and the Queensland Government in the Galilee, Bowen and Surat basins (Figure 1). The aquifers within these basins provide groundwater for human consumption, agriculture, mining, recreation and groundwater dependent ecosystems. The Surat Basin also contains oil and conventional gas accumulations that are being exploited by the onshore petroleum industry as well as coal seam gas production. Characterising groundwater chemistry and the connectivity between aquifers in the context of its current use is essential to determine whether prospective aquifers could be used for geological storage of CO\textsubscript{2} without compromising other activities.
Figure 1. Onshore areas released for greenhouse gas (GHG) storage exploration in central Queensland and onshore and offshore GHG storage exploration areas in the Gippsland, Victoria.

Risks to groundwater
The risk of groundwater contamination from the potential migration of CO$_2$ is a significant concern to the public (Ashworth et al., 2010). Compromised wells or leaky faults could potentially provide a conduit for CO$_2$ migration out of the storage reservoir to shallower aquifers (Nordbotten et al., 2009). Laboratory studies have demonstrated that reaction between CO$_2$ and caprock material can lead to mobilisation of heavy metals such as nickel, arsenic and lead (Carroll et al., 2010). Other concerns are the migration of higher salinity water to fresher aquifers (in and outside the storage area), solubilisation of trace organics if present, and migration of species potentially problematic for agriculture (boron and bromide) and water treatment plants (increased silica).

While the present number of onshore CO$_2$ storage sites is small, there have been no reported cases of CO$_2$ migration out of a reservoir or groundwater contamination. This includes groundwater monitoring at Otway (Australia), Weyburn (Canada), Frio (USA), Ketzin (Germany) and Nagoaka (Japan). Detailed groundwater investigations at the CO2CRC Otway Project’s geological storage site located in south-western Victoria provide an insight into changes in water chemistry that could occur if CO$_2$ migration did occur and the challenges of observing such a leak given natural variations in hydrogeochemical properties.

CO2CRC Otway Project case study
The CO2CRC Otway Project revolves around 3 wells: the Buttress-1 supply well delivering a ~80:20 CO$_2$:CH$_4$ mixed gas, the CRC-1 injection well into the Waarre Formation sandstone reservoir at a depth of ~2 km, and the Naylor-1 observation well located 300 m up-dip of the injection well. At the completion of injection at the end of August 2009, just over 65,000
tonnes of the CO₂-rich gas was injected over a period of 17 months. The Naylor-1 observation well accesses a depleted natural gas field from which fluid samples are routinely taken at formation pressure using a triple U-tube assembly (Boreham et al., in press). The middle U-tube and closest to the pre-injection gas-water contact (GWC) is situated just 2.3 m below the GWC. Over a period of 170 days post-injection and the cumulative injection of 20,000 tonnes of CO₂-rich gas, formation waters were sampled and their water and exsolved gas chemistry analysed (Figure 2). Subsequently, only free gas is still being recovered from this U-tube as the GWC continues its downward movement with filling of the Naylor structural trap (Boreham et al., in press). The critical point was the breakthrough of injected CO₂-rich fluid at Naylor-1, initially as a dissolved CO₂ front between 100 and 121 days where exsolved CO₂ showed a slight increase in mol% and an enrichment in $^{13}$C, followed by a rapid rise in mol% CO₂ and a $\delta^{13}$C CO₂ indistinguishable from the injected CO₂ (Figure 2). Over this time, the pH dropped from an average of 6.1 to an average of 5.1 prior to gas lift. However, little change was seen in electrical conductivity (Figure 2) or either the alkalinity or cation concentrations during subsequent analysis off site (Kirste et al., 2009). Geochemical modelling indicated that the pH appeared to be buffered by CO₂-calcite equilibrium both before and after the arrival of the CO₂-rich plume. This implies no significant contact between the aqueous phase and the CO₂ in the pore space of the reservoir. Kirste et al. (2009) concluded that the inorganic geochemistry is consistent with the CO₂ migrating as an immiscible phase with respect to both the methane gas cap and the formation water. This may, in part, explain why breakthrough of the CO₂-rich plume at Naylor-1 is at the forefront of the time constraints imposed by fluid flow models (Underschultz et al., in press).

Figure 2. Evolution of dissolved gas and water chemistry in the Waarre Sandstone (storage reservoir) at the CO2CRC Otway Project upon contact with supercritical carbon dioxide. Samples were taken from a depth of 2042 m using a U-tube.
Groundwater in the CO2CRC Otway Project is monitored in two aquifers: the shallow (0-100 m), unconfined to semi-confined Port Campbell Limestone (PCL), used locally by the dairy industry and for domestic purposes, and the deeper (800+ m), confined, Dilwyn Formation (DF) aquifer, a high quality water resource earmarked for potential development in the future. Twenty one bores in the PCL and three in the DF aquifers have been monitored biannually since June 2006 within a 10 km radius of the CO2 injection bore. Groundwater composition in the PCL aquifer is relatively homogenous, being fresh (EC 801-3900 µS/cm), near-neutral (pH 6.6-7.5) and dominated by Ca2+ to Na+ for cations, and by Cl- to HCO3- for anions. The DF groundwater is fresher (EC 527-1473 µS/cm), more alkaline (pH 7.4-9.4) and more variable in composition with cations dominated by Na+, and anions dominated by Cl- to HCO3-. Most groundwater components are stable with time, although in some bores some parameters fluctuate with season (e.g. temperature, Total Fe, Fe2+). Figure 3 shows the typically higher pH in the DF groundwater compared to the circum-neutral groundwater in the PCL. A few bores show a seasonal behaviour, such as for Fe concentration at Station N (total depth 18 m), but overall most time-series are fairly flat. No effect that can be related to the injection of CO2 is observed.

Data gaps and future challenges
Current data gaps include poor hydrogeochemical data coverage for the deeper aquifers and particularly limited data on trace metals and organics. Heavy metals such as nickel, lead and especially arsenic have not been routinely monitored in the past. In the Great Artesian Basin, for example, accurate field measurements of pH and redox for aquifers below the Cadna-owie/Hooray system are uncommon. Measurements of trace organics (e.g. BTEX) associated with groundwater near petroleum fields within the GAB are very uncommon yet these contaminants could be mobilised on contact with high CO2. Obtaining an accurate background of groundwater chemistry over potential storage areas is a priority for the Queensland Government.

One of the major differences between areas for geological storage in Australia and that typically encountered in North America and Europe is the different groundwater salinity profile with depth. At the Weyburn field in the US, CO2 storage is in hypersaline formations whereas only the shallowest aquifers above the storage field are of drinking water quality or used for agriculture. In the Great Artesian Basin, this scenario is to some degree reversed. The
upper Walumbilla Formation/Rolling Downs Group is of relatively poor quality and it is the
deeper Cadna-owie/Hooray aquifers that are primarily used for agriculture and town water
supplies. Target CO$_2$ storage formations in the deeper Precipice and Clematis sandstones have
groundwater salinities tending from fresh to brackish (Hodgkinson et al, 2010a). This presents
a challenge for geological storage of CO$_2$ in these formations. Where in Weyburn only
petroleum wells tap into the deeper hypersaline formations, in Australia petroleum and
agricultural bores tap into the equivalent deep brackish formations in the Great Artesian
Basin. Agricultural bores are typically open wells to the surface. While there are only a
handful of agricultural bores that tap into the Precipice Sandstone in the deepest parts of the
Surat Basin, there are a considerable number of sub-artesian bores in the shallower up-dip
parts of the formation. More problematic are the agricultural wells that use groundwater from
the overlying Hutton aquifer if connectivity between the two aquifer systems were
established.

While the risk of increased salinity in overlying aquifers in the GAB from CO$_2$ migration out
of the storage reservoir is negligible, there is a risk of CO$_2$-laden water intersecting bores
currently used for agriculture if migration out of a reservoir did occur. Evaluating such
projects will require balancing the risks of the possibility of such a migration event occurring
and any subsequent impact of that event on groundwater quality. Seal integrity of overlying
geological units is critical for the success of a geological storage project and the permanent
storage of carbon dioxide (Hodgkinson et al, 2010b). Further integration of new data and
information between researches, industry, governments and the public should enable a future
for CO$_2$ storage without affecting overlying groundwater resources.

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