Comparing different sampling methods of greenhouse gas stable isotopes in groundwater and coal seam gas production waters

Julie K. Pearce[1,2,*], Kim Baublys[2], Harald Hofmann[2,3]

[1] Gas and Energy Transition Research Centre, University of Queensland [2] School of the Environment, University of Queensland
[3] Commonwealth Scientific and Industrial Research Organisation (CSIRO), Brisbane, QLD 4102, Australia (current address)
Author for correspondence: j.pearce2@uq.edu.au

Introduction

- Methane and carbon dioxide are ubiquitous in aquifers, gaining increased attention through global warming. The stable carbon and hydrogen isotopes of methane and carbon dioxide, $\delta^{13}C\text{-}CH_4$, $\delta^{13}C\text{-}CO_2$ and $\delta^{2}H\text{-}CH_4$, inform on the sources of gas and if the origin is thermogenic / different biogenic (microbial) processes. Also used in monitoring in a range of natural and industrial settings, e.g., CO_2 geological storage (Hofmann et al., 2024).
- Pumping of groundwater to the surface results in depressurisation and gas effervescence, the sampling method (i.e. if the sample contacts atmosphere) is known to affect measured gas concentrations (Pearce et al., 2022); however, the effect of sample collection on the stable isotopes remains unresolved.
- Gas stable isotopes can be collected in the field in a range of sample containers. Different containers may be selected based on the field sampling environment, person who is sampling, laboratory preferences, cost etc.
- Does the sampling container affect the stable isotope ratio results?
- The study region, the Surat Basin, QLD, is part of the Great Artesian Basin (GAB), and hosts various industries that extract groundwater including for coal seam gas (CSG), feedlots, town water supply and agriculture.

Figure 3: Left: CSG wells, and various aquifer monitoring bores including private landholders, and on CSG and mine tenements. Above: examples of town water supply bores sampled, both those in use and pre use.

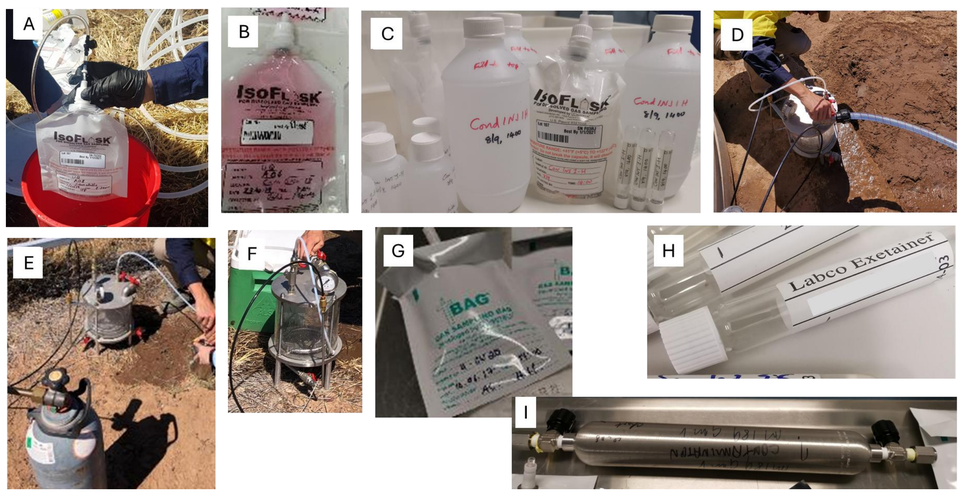


Figure 4: A –C) Isoflask, D-F) Terra sana Gas Water separator. G) Gas bag. H) Exetainer vial. I) Stainless steel gas cylinder. Note a few samples were also compared from serum vials.

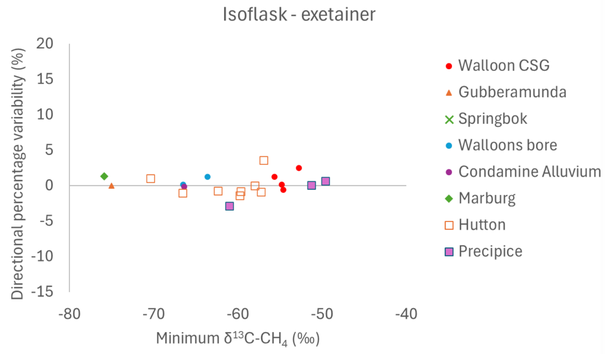


Figure 6: Percentage variability between $\delta^{13}C\text{-}CH_4$ in pairs of samples collected in Isoflasks vs exetainer vials. See Pearce et al., 2025 for other container comparisons, and $\delta^{2}H\text{-}CH_4$ and $\delta^{13}C\text{-}CO_2$.

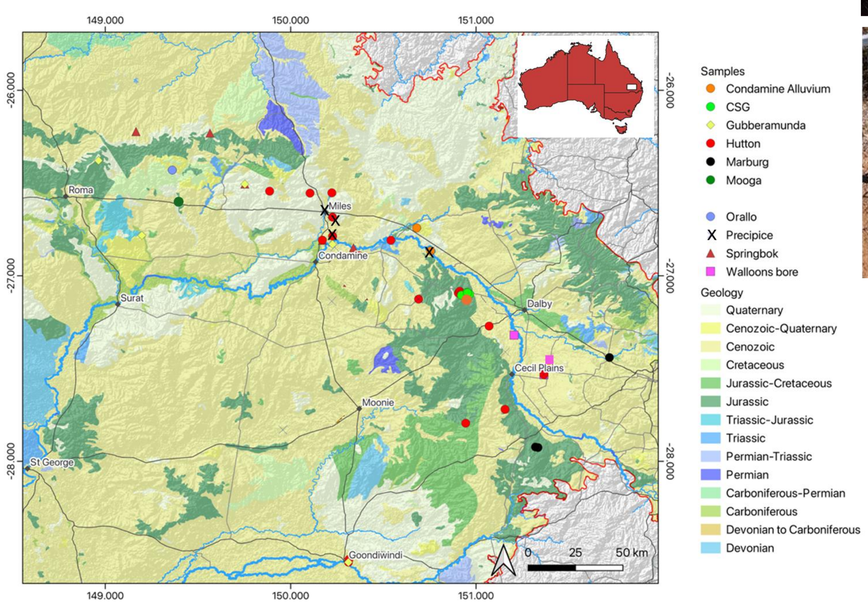


Figure 1: Map of the aquifer water bores and CSG wells sampled in the Surat Basin (and Clarence-Moreton Basin). Note many were nested bores.

Results

- Samples had a wide range of methane concentrations, 0.003 to 2100 mg/L dissolved methane measured in Isoflasks, and 0.005 to 90 mol% methane reported in the headspace. Dissolved methane concentrations measured from vials (ALS) were much lower at 0.001 to 36.8 mg/L.
- Stable isotope signatures of sample pairs from exetainer vials and Isoflasks were compared and generally had excellent low directional percentage variabilities (Fig. 5,6).
- A subset of sample pairs from other containers were also compared with consistent stable isotope signatures generally measured. For more details see (Pearce et al., 2025).
- This brings confidence for using different sample containers for different field conditions and situations.

Methods

- Groundwater and dissolved gas samples collected from a wide variety of water bores and CSG wells. Including monitoring bores pumped via low flow methods or landholder and town water supply bores with existing infrastructure (Fig 1,2,3). Bore screen depths range from 18 to 2474 m.
- Dissolved gases in production waters and aquifer groundwaters collected in exetainer vials and Isoflask containers (Fig 4).
- Subset of CSG gases collected in cylinders; or gas stripped from aquifer groundwater and collected in gas bags.
- Replicate sample pairs, and in a few cases triplicate or quadruplicate samples were collected at a range of bores.
- Stable isotopes of methane and CO_2 were measured at The University of Queensland's Stable Isotope Geochemistry Laboratory (UQ SIGL).
- Gas concentrations (Stratum and ALS) and a range of isotopes and parameters not mentioned here were also measured (Pearce et al., 2024).

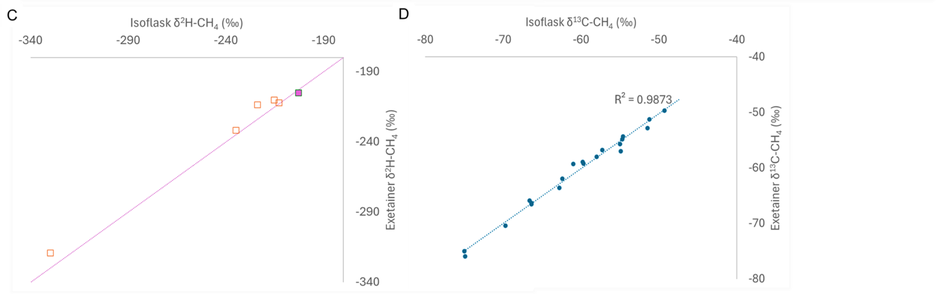


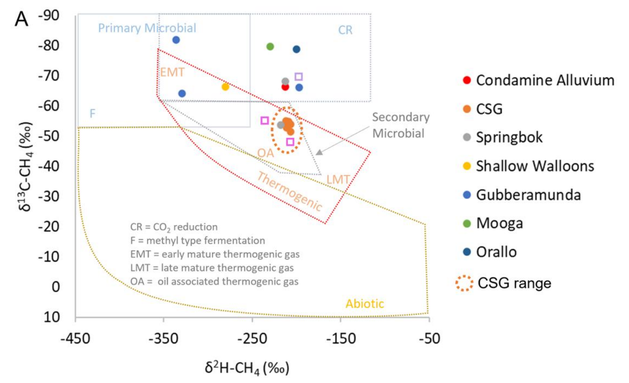
Figure 5: Isoflask vs Exetainer collected samples from the different formations A) $\delta^{13}C\text{-}CH_4$ B) $\delta^{2}H\text{-}CH_4$ and C) $\delta^{13}C\text{-}CO_2$. D) showing R^2 in A. Data for different sample containers are shown in (Pearce et al., 2025).

Conclusions and sampling considerations

- Different sample containers, e.g. exetainer vials or Isoflasks, can be used with comparable stable isotope results. This is favourable as different field sampling conditions favour different sample containers. E.g., private landholder bores can have outlets not suitable to connect air-tight connections, necessitating the filling of a vial container. Sampling of springs or culturally significant groundwaters may also necessitate simple non-intrusive sample collection methods. Vials are also simpler to use for citizen science or industry collection, and partially reusable.
- A closed method, connecting the Isoflask container directly to the bore headworks, or a gas stripper can result in a larger volume or concentration of sampled gas that improves the chances that the analysis lab can detect all three stable isotopes above detection. Dry or stripped gases also have higher stability and can be preferable for GC injection. However, gas strippers can be cumbersome to use in the field. Isoflasks contain a biocide and do not need refrigeration (usually vials do), preferable for regional field trips in hot climates, however they are more expensive.

Suggested future work

- Compare stable isotope signatures and methane concentrations from other containers such as copper tubes, or specialised downhole sampling devices (e.g. Banks et al., 2017).
- Compare different methods to measure isotope signatures of gas emissions to the atmosphere from bores and springs.



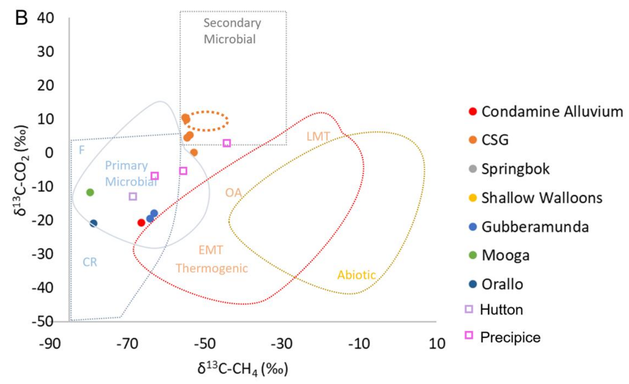


Figure 7: Example of stable isotopes of methane and CO_2 in selected samples of GAB aquifer bores and CSG (Pearce et al., 2022). CSG are from secondary microbial CO_2 reduction. The majority of aquifer gases shown are primary microbial or fermentation processes. Regions from the revised diagrams of Milkov and Etiope (2018). The dashed orange circle shows the range of CSG previously reported from QLD Walloon Coal Measures (Baublys et al., 2015; Owen et al., 2016; Hamilton et al., 2014).

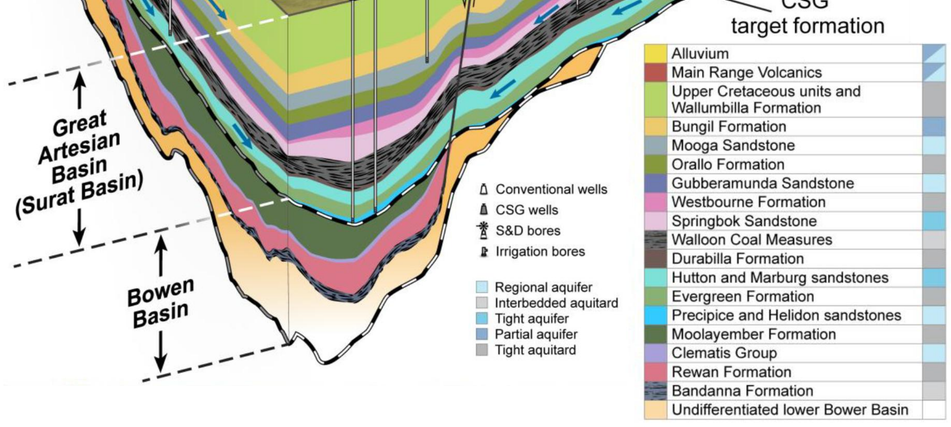


Figure 2: Aquifers of the Great Artesian Basin (GAB) in the Surat Basin. GAB aquifers overlie and underlie the Walloon Coal Measures, where production water and coal seam gas is extracted (modified after OGIA 2021).

References

Hofmann, H., Pearce, J.K., Hayes, P., Golding, S.D., Hall, N., Baublys, K.A., Raiber, M., Suckow, A., 2024. Multi-tracer approach to constrain groundwater flow and geochemical baseline assessments for CO_2 sequestration in deep sedimentary basins. International Journal of Coal Geology 282, 104438.

Pearce et al., 2022. Methane in aquifers and alluvium overlying a coal seam gas region: Gas concentrations and isotopic differentiation, Science of the Total Environment https://doi.org/10.1016/j.scitotenv.2022.160639

Pearce, J.K., Hofmann, H., Baublys, K., Cendón, D.I., Golding, S.D., Herbert, S.J., Bhebhe, Z., Nguyen, A., Hayes, P., 2024. Geochemical tracers associated with methane in aquifers overlying a coal seam gas reservoir. International Journal of Coal Geology 289, 104535.

Pearce, J.K., Baublys, K., Hofmann, H., 2025. Comparing greenhouse gas stable isotopes from different sampling methods: Aquifer groundwater and coal seam gas production waters. Appl. Geochem. 190, 106482.

J.Pearce2@uq.edu.au
Julie Pearce
uq.edu.au

Gas and Energy Transition Research Centre

Acknowledgements

Terra Sana consultants are thanked for the use of their gas water separator.
ANLEC R&D provided funding for this project.
This research has been conducted with the support of the Centre's industry members – APLNG, Arrow Energy, and Santos.
Various landholders, feedlots, regional council's (town water supplies) and industries are thanked for access and assistance.

Now published: Pearce, Julie K., Baublys, Kim, and Hofmann, Harald (2025). Comparing greenhouse gas stable isotopes from different sampling methods: Aquifer groundwater and coal seam gas production waters. Applied Geochemistry 190 106482 1-10.

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA
CREATE CHANGE