

# Monitoring geochemical and isotopic characteristics of groundwater in aquifers of the Beetaloo Sub-basin, NT

## Some results of 2017 and 2018 fieldwork

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# 1. Data sources

This presentation presents some results from the groundwater sampling work done by CSIRO Energy and CSIRO Land and Water in:

2017 funded by CSIRO Energy, Origin and Santos – 2 reports EP182563 and EP 186868, in 2018

2018 funded by GISERA as project W16. Geochemistry results were presented in report EP193161, June 2019

Further results are awaited for noble gas analyses and stable isotope results from the 2018 sampling program. Stable isotope data have been received at end July 2019 from Geological and Nuclear Sciences (GNS), New Zealand. Analysis is in progress for these data.

## 2. Acknowledgements

These two projects were done jointly between CSIRO Energy and CSIRO Land and Water. Planning and fieldwork were greatly assisted by staff in Origin, Pangaea and Santos.

The fieldwork in 2017 was led by Praveen Rachakonda and in 2018 by Alf Larcher.

For assistance with the fieldwork, we gratefully acknowledge Dave Armstrong on behalf of Pangaea Resources, Robert Wear on behalf of Origin Energy and Simon Fulton and Peter Evans on behalf of Santos who provided logistical and field support for the CSIRO field researchers. We also acknowledge the NT Department of Primary Industry and Resources for help with organisation and guidance for the survey

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# 3. Project objectives

GISERA project W16 in 2018/19 has four objectives for better understanding groundwater characteristics of the important aquifers in the Beetaloo Sub-basin.

1. Extend baseline groundwater characterization of important aquifers of the Beetaloo Sub-basin.
2. Identify groundwater velocity, recharge rate and source of recharge of the Cambrian Limestone Aquifer, using studies of naturally occurring tracers.
3. Undertake background measurement of dissolved methane and methane isotopes, Total Recoverable Hydrocarbons ( $C_6 - C_{40}$ ), Phenols, Polycyclic Aromatic Hydrocarbons (PAH) and benzene, toluene, ethylbenzene, xylenes and naphthalene (BTEXN) in water from these aquifers. This includes 41 hydrocarbon compounds.
4. Alpha and beta radiation measurements which are related to Uranium and Thorium and their decay series. Note that Uranium was also measured geochemically in this project.

This project builds on learning from the 2017 project.

## 4. Environmental tracer study

Major ions, strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and the stable isotopic ratios of the water molecule ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) are the most widely used tracers to identify the origin of groundwater. These are all naturally-occurring compounds that vary in composition in the environment because of climatic and geological factors.

Tritium ( $^3\text{H}$ ), sulfur hexafluoride ( $\text{SF}_6$ ), chlorofluorocarbons (CFCs), carbon-14 ( $^{14}\text{C}$ ) and helium ( $^4\text{He}$ ) are common tracers to identify the presence of either 'young' (>50 years;  $^3\text{H}$ , CFCs, and  $\text{SF}_6$ ), 'old' ( $^{14}\text{C}$ ; 1000 – 10,000 years), or 'very old' (>20,000 years and no age limit;  $^4\text{He}$ ) groundwater. These can be used as age-dating tools because their concentrations vary in a predictable fashion over time in the environment.

Variations in noble gas concentrations (neon, argon, krypton and xenon) in groundwater can be used to infer recharge processes, either via the inference of recharge temperature or its 'excess air' content (a measure of gradual vs. rapid rising water tables during recharge events).

## 5. What was measured at each bore ?

Water level (m AHD)

Temperature (°C)

Conductivity in mS/cm

pH

Redox potential (Eh)

Dissolved oxygen (mg/L and %DO)

Bicarbonate ( $\text{HCO}_3^-$ ) as alkalinity

# 6. Water quality parameters analysed

Parameters	Typical Limit of Detection
Inorganics: Alkalinity (Total) as $\text{CaCO}_3$ , bromide, calcium (total and dissolved), chloride, fluoride, magnesium (total and dissolved), nitrate (as n), phosphate, potassium (total and dissolved), sodium (total and dissolved), sulphate as $\text{SO}_4$	0.01 - 1 mg/L
Metals (Total and Dissolved): aluminium, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, mercury, nickel, selenium, strontium, tin, uranium, vanadium, zinc	0.005 – 0.5 $\mu\text{g/L}$
Benzene, Toluene, Ethylbenzene, Xylenes and Naphthalene (BTEXN)	1 – 2 $\mu\text{g/L}$
Total Recoverable Hydrocarbons (TRH) : fractions of $\text{C}_6$ – $\text{C}_{10}$ , $\text{C}_{10}$ – $\text{C}_{16}$ , $\text{C}_{16}$ – $\text{C}_{34}$ , $\text{C}_{29}$ – $\text{C}_{36}$ , $\text{C}_{34}$ – $\text{C}_{40}$	100 $\mu\text{g/L}$
Phenols : 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,6-dichlorophenol, 2-chlorophenol, 2-methylphenol, 2-nitrophenol, 3-&4-methylphenol, 4-chloro-3-methylphenol, Pentachlorophenol, Phenol	0.5 – 2.0 $\mu\text{g/L}$
Polycyclic Aromatic Hydrocarbons (PAH) : Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(a)pyrene TEQ (zero), Benzo(b&j)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d) pyrene, Naphthalene, Phenanthrene, Pyrene	0.5 – 2.0 $\mu\text{g/L}$
Dissolved methane and isotopes Alpha and beta radiation measurements	8-20 $\mu\text{g/L}$



# Geochemical analyses

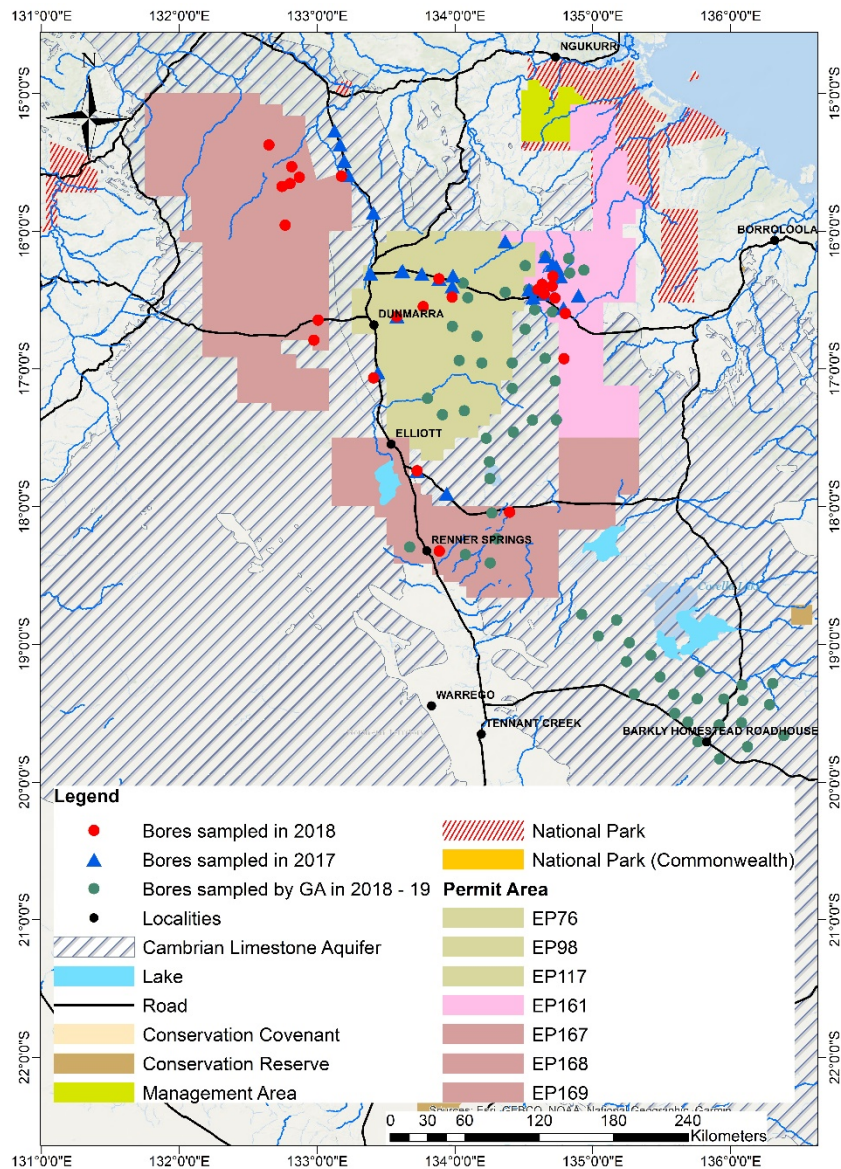
Geochemical analyses are shown in spreadsheets included in:

Groundwater Baseline assessment of Beetaloo Sub-basin, Northern Territory. CSIRO Report EP 182563, September 2018

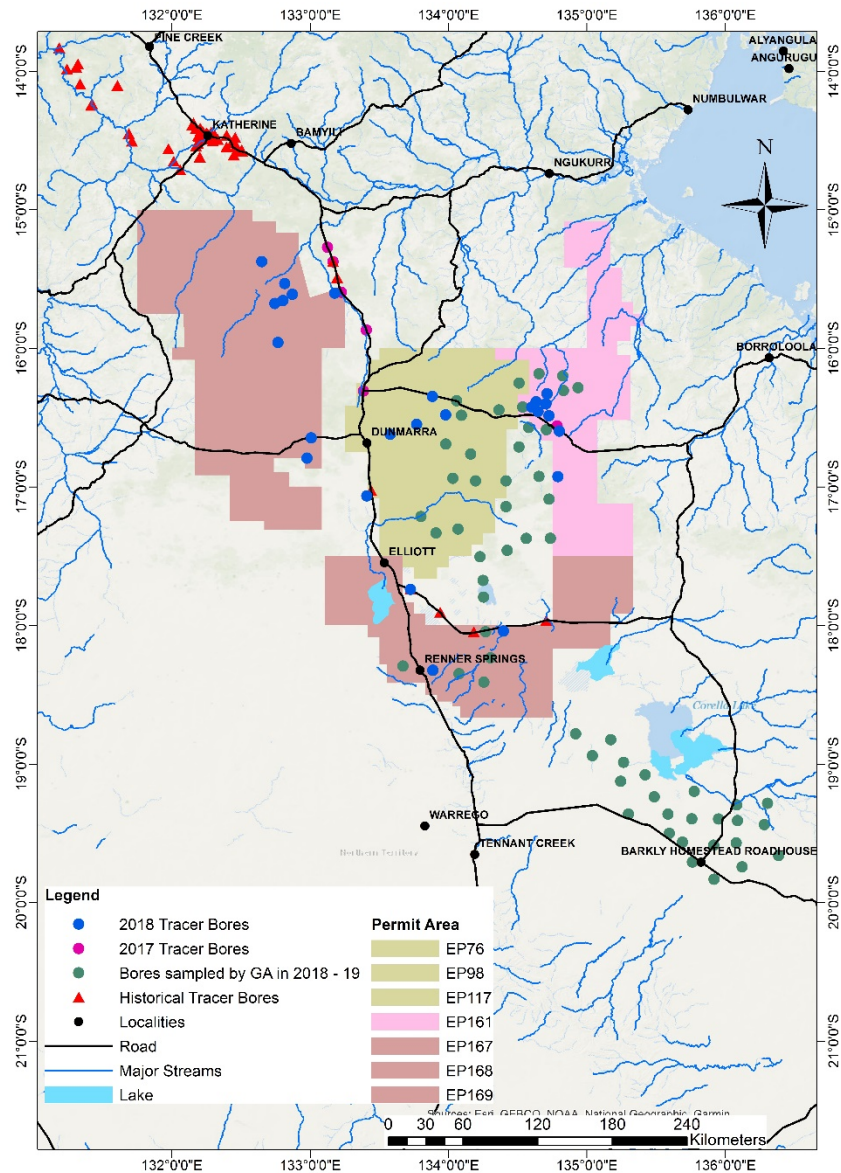
Baseline assessment of groundwater characteristics of the Beetaloo Sub-basin, NT – Geochemistry analysis. CSIRO report EP193161, June 2019

# 7. Maps – sample sites and geochemistry

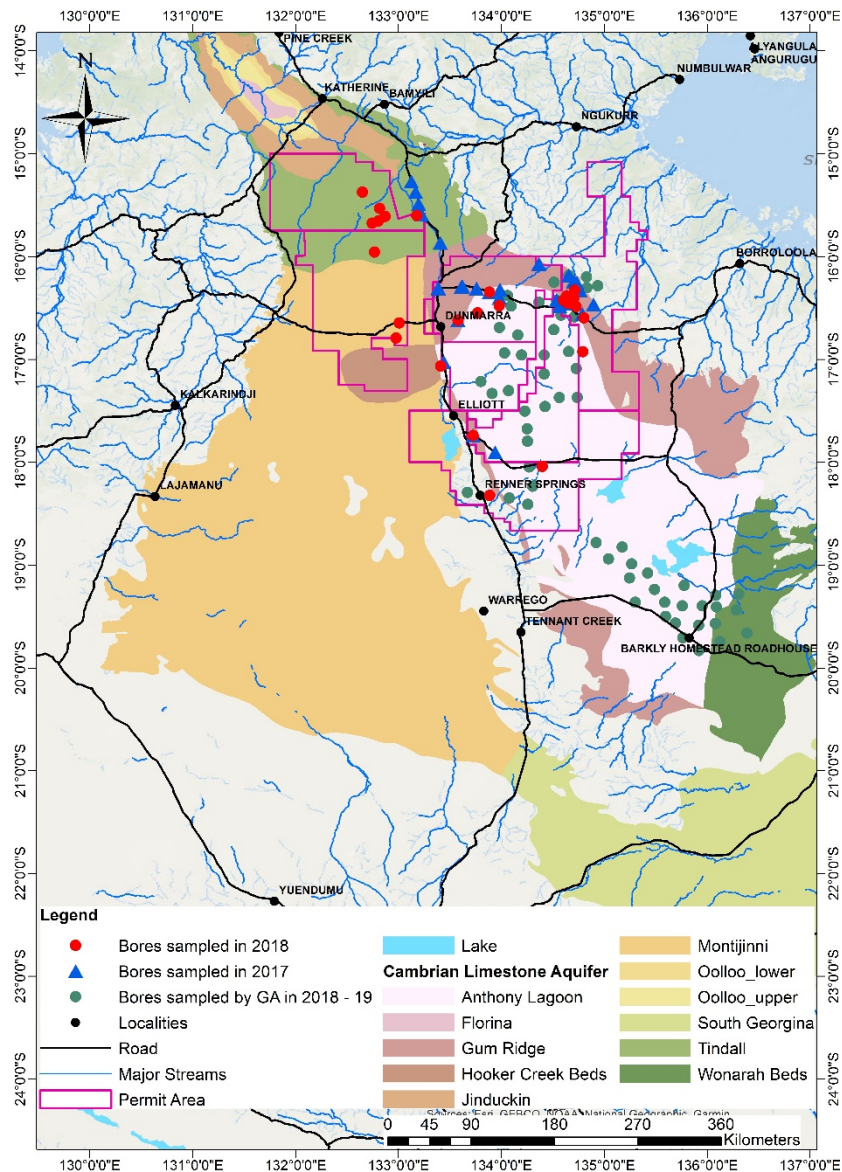
# Location map showing bores sampled for geochemistry in 2017 (25) and 2018 (25)



# Location map showing bores sampled for tracers in 2017 (8) and 2018 (25)

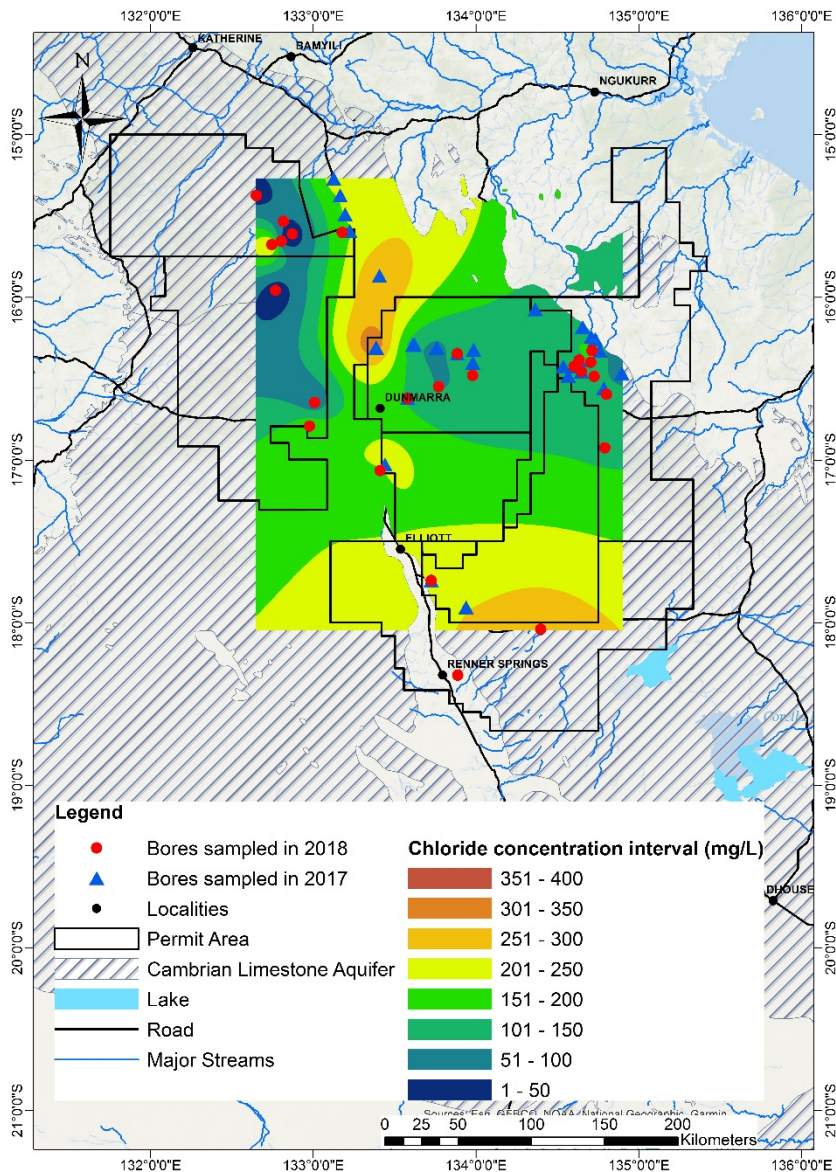


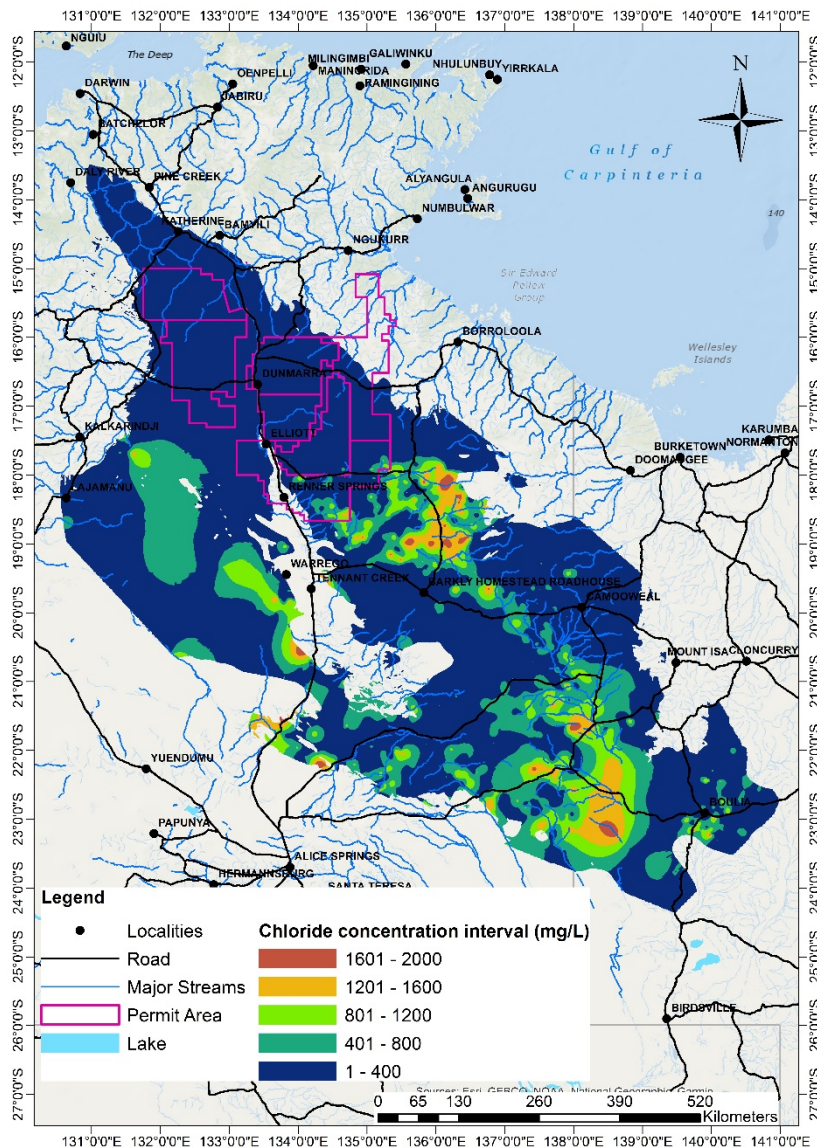




## Formations sampled

## Chloride concentrations from CSIRO/GISERA sampling in 2017 and 2018



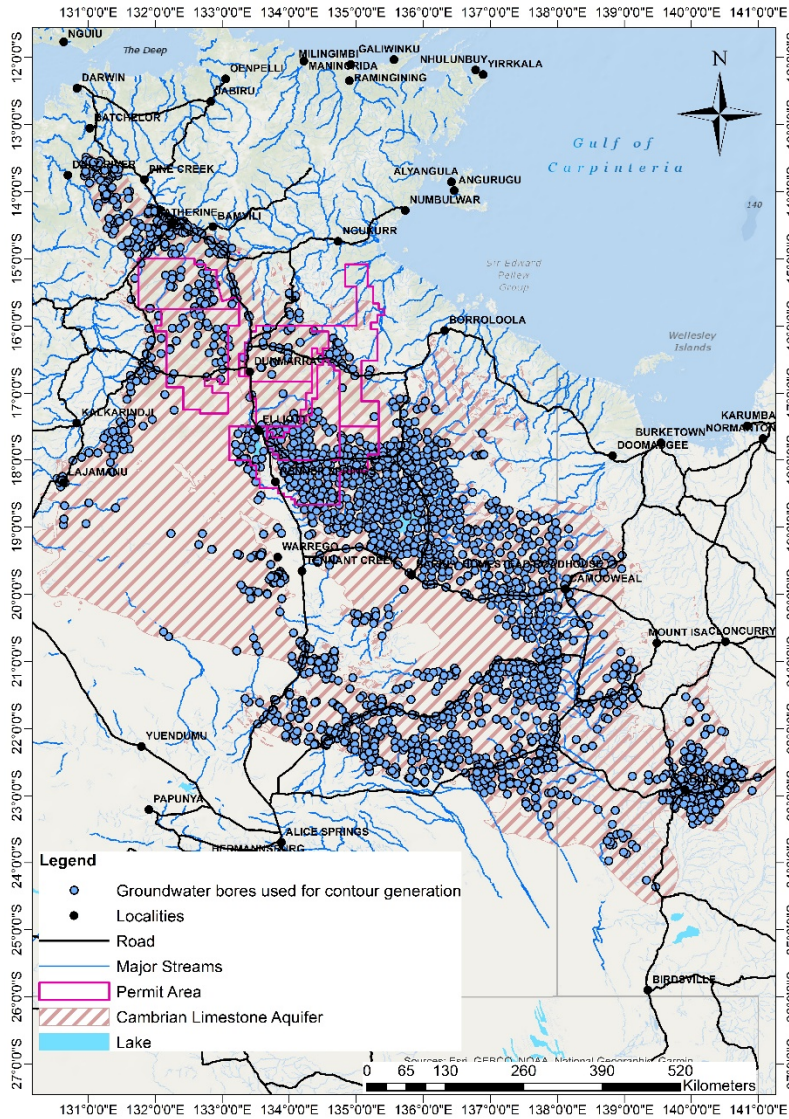


# Chloride concentrations across Cambrian Limestone Aquifer

note: different colour table from previous slide

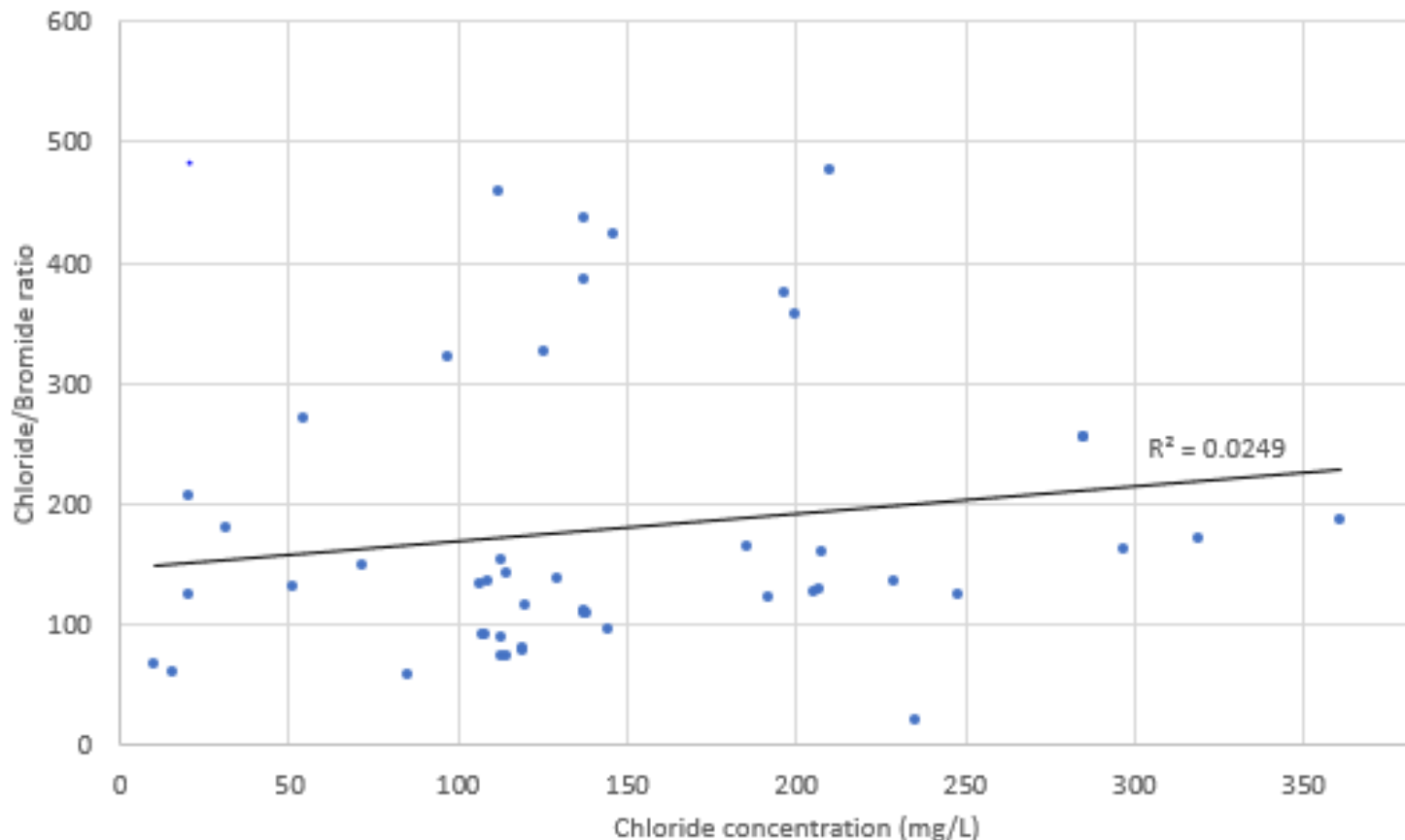


## Data points used in previous map





# Chloride/Bromide ratios for 2017 and 2018 surveys



Average Chloride/Bromide ratio for these data is 180. 100 – 200 is typical for shallow groundwater sources. Ratio for rainfall is 50 – 150. Ratio for deeper sources 1000 – 10000. Ref Davis et al (1998)

# 8. Key results from geochemistry (1)

## Groundwater quality

Based on the 2015-18 groundwater monitoring results, groundwater in the permit areas is suitable for irrigation and livestock purposes

## Salinity

The conductivity of groundwater in the Cambrian Limestone Aquifer shows water is of poor to good water quality with the average EC value for most of the bores less than the acceptable upper limit for potable water of 1875  $\mu\text{S}/\text{cm}$ .

## Metals

Most of the groundwater sample metal concentrations were below the ANZECC (2000) and Australian Drinking Water Guidelines (NHMRC, 2017) values.

## Methane

During the October – November 2018 monitoring program, groundwater sample dissolved methane concentrations were less 10 mg/l. Stable carbon isotopic compositional range of methane were detected in two groundwater wells (RN031397 and RN038179) and observed methane is due to sub-surface microbial activities (Coleman et al., 1993).

# Key results from geochemistry (2)

## **Phenolic and hydrocarbon compounds**

Phenolic and hydrocarbon compounds were not detected during the October – November 2018 sampling program

## **BTEXN**

BTEXN compounds were not detected during the October – November 2018 sampling period.

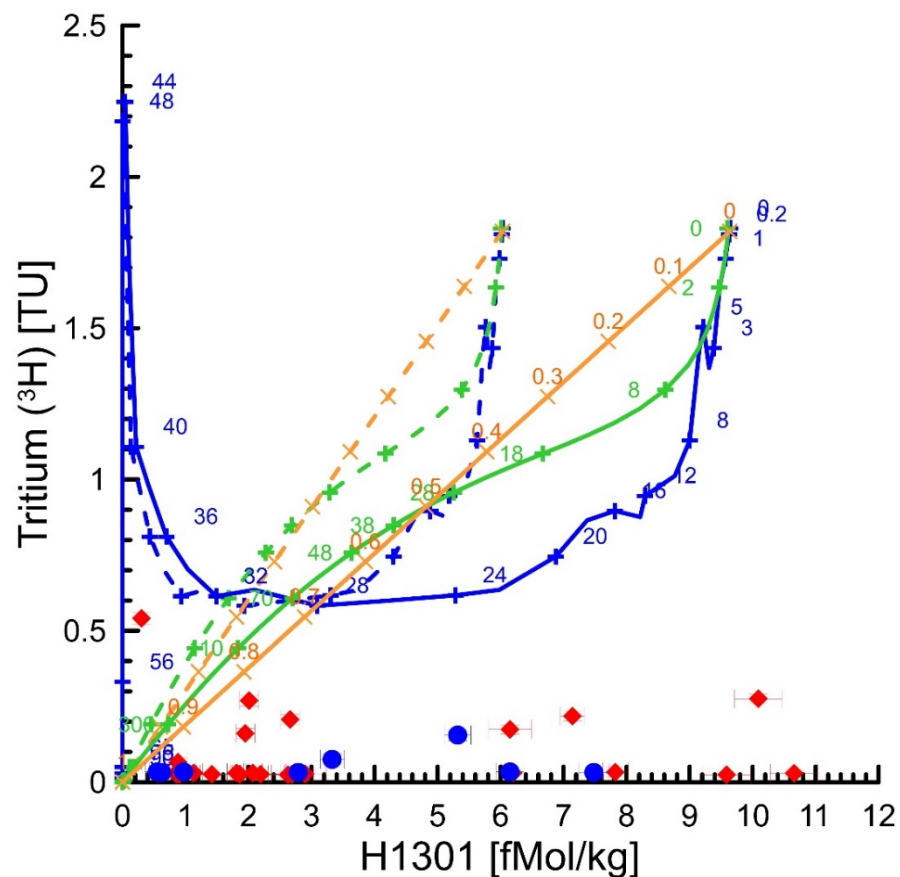
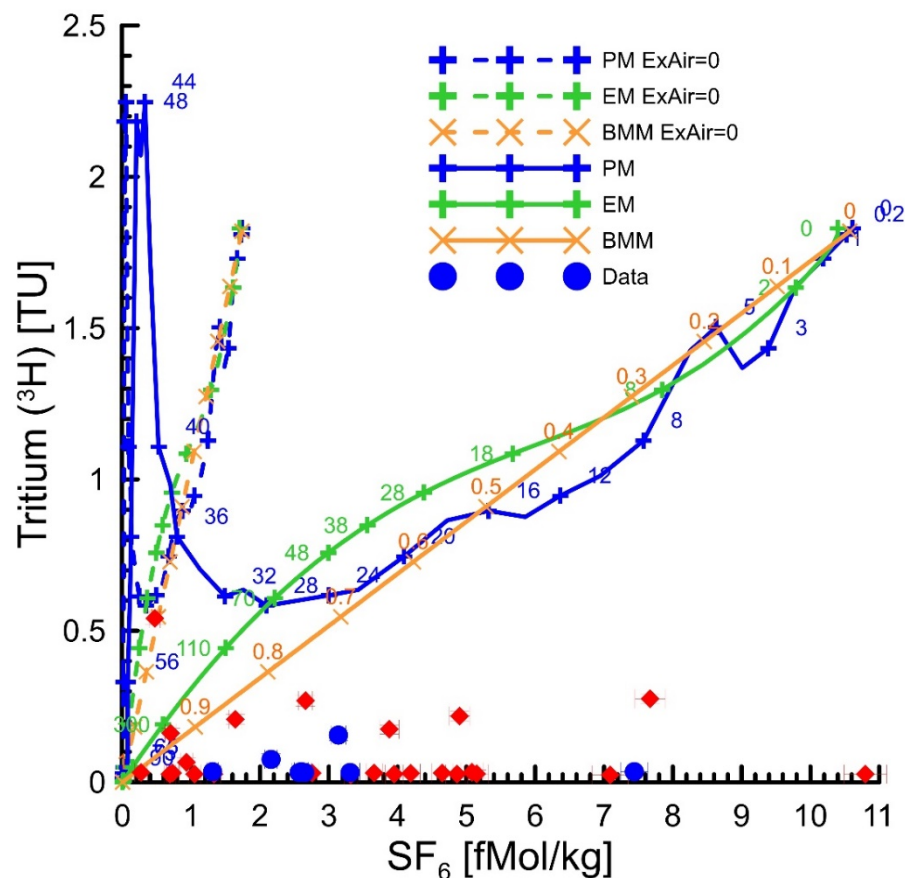
## **Alpha and Beta Activity**

During the October – November 2018 sampling program, three groundwater bores: RN037654, RN038580 and RN039080 have exceeded the WHO (2017) initial gross alpha screening level (less than 0.5 Bq/l) for drinking water quality and would require that the concentrations of individual radionuclides be measured and compared with the radionuclide specific guidance levels, taking local circumstances (e.g. geology, hydrogeology) into account.

# 9. Plots and maps from tracer studies

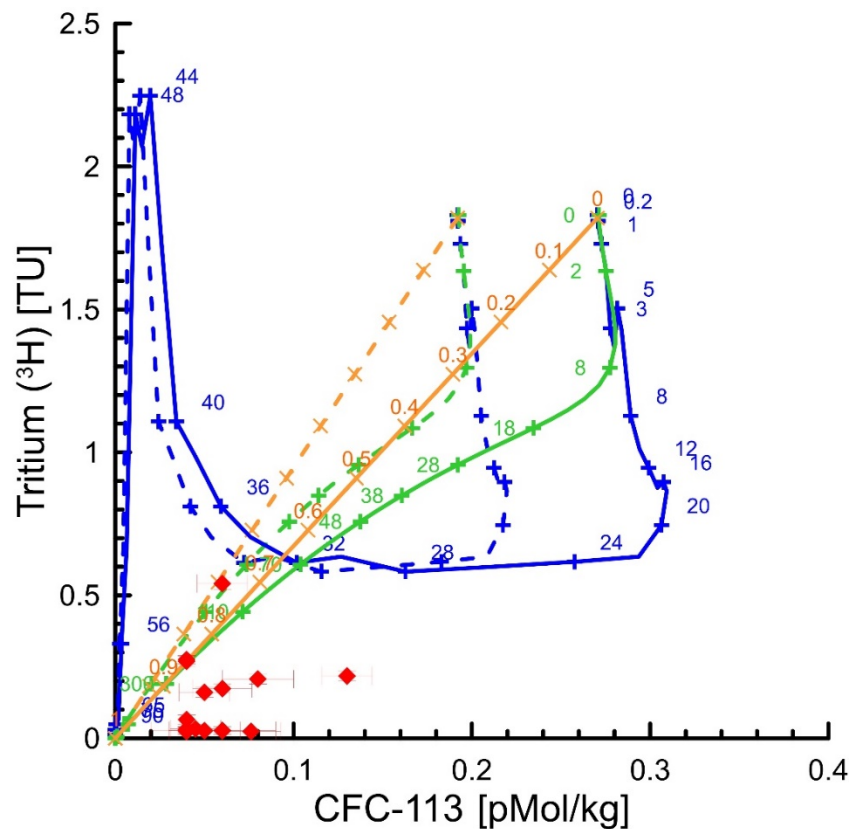
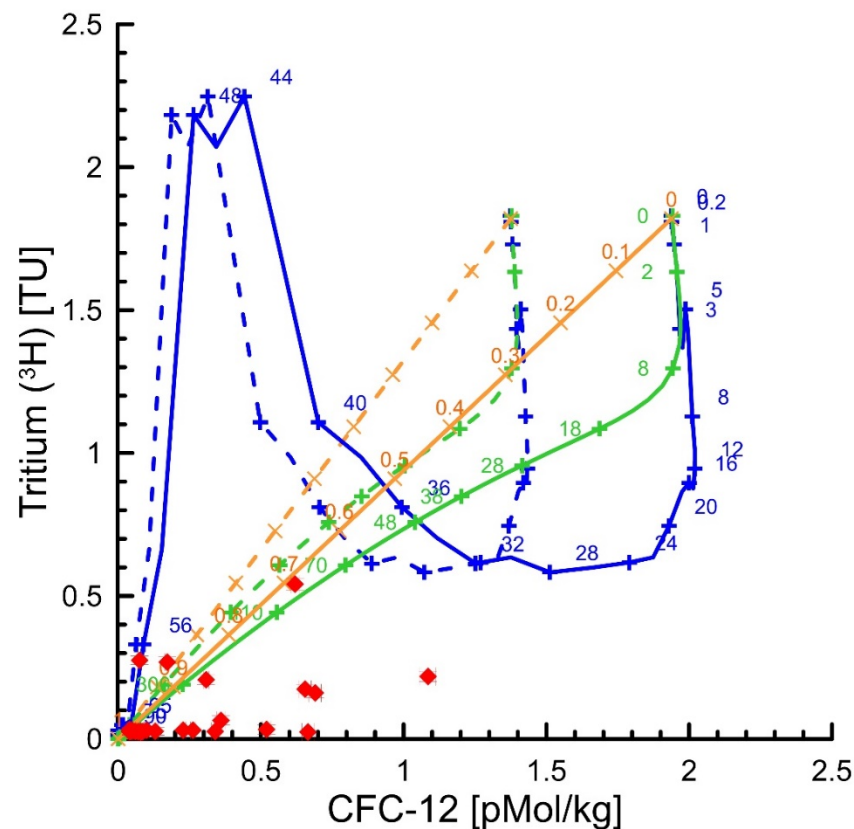
## Tritium & CFCs

Gas tracers  $\text{SF}_6$  and  $\text{H1301}$  are even above modern values for some samples, And can be explained only by very large amounts of Excess Air (a surplus of dissolved gas bubbles) of 25 cc/kg.



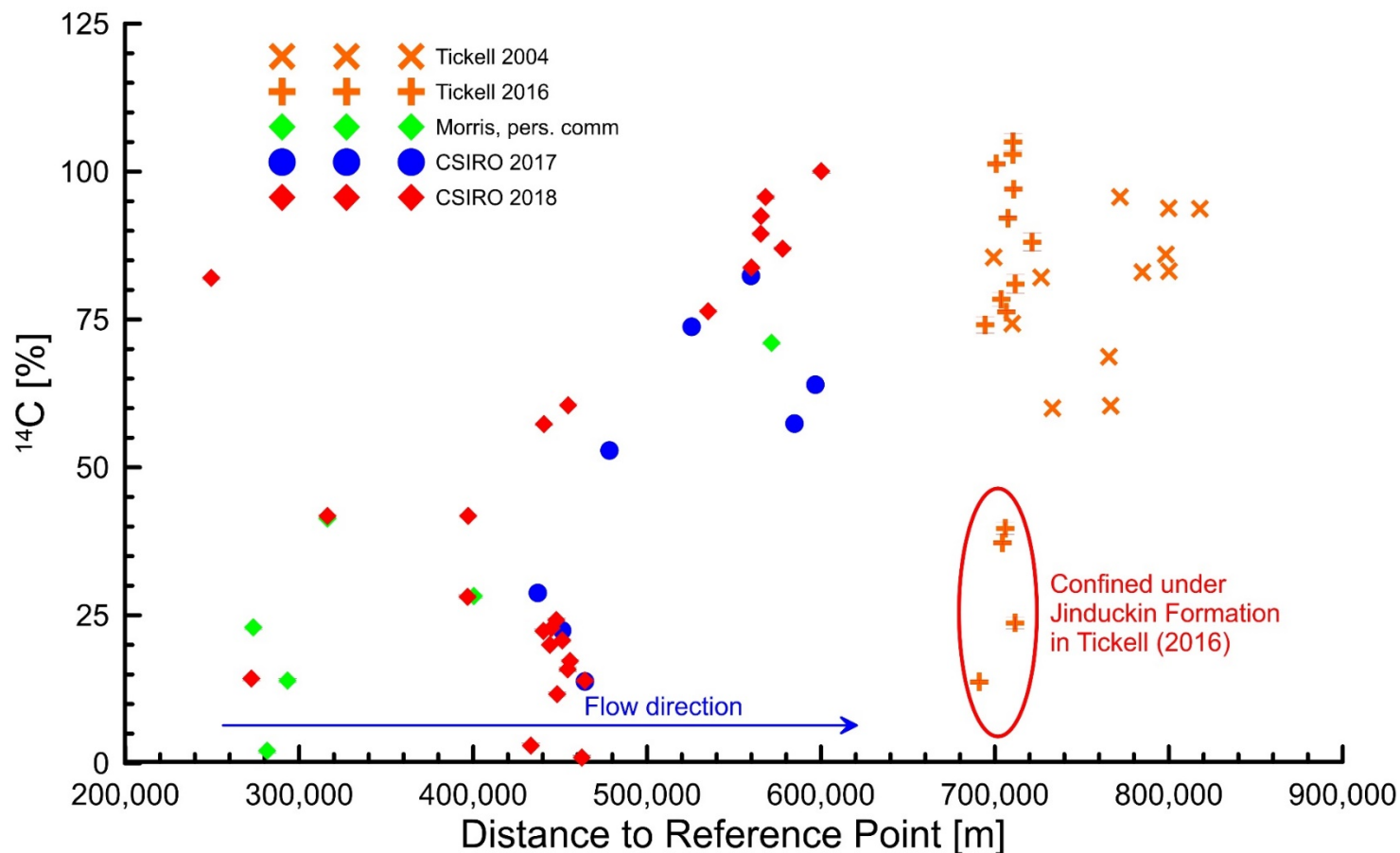
## Tritium & CFCs

Tritium is very low, gas tracers (CFCs) are detectable and in the “forbidden space” below the model lines. Somehow “young” gas is getting into the water (CFCs) but avoiding the young water (tritium).



# Radiocarbon

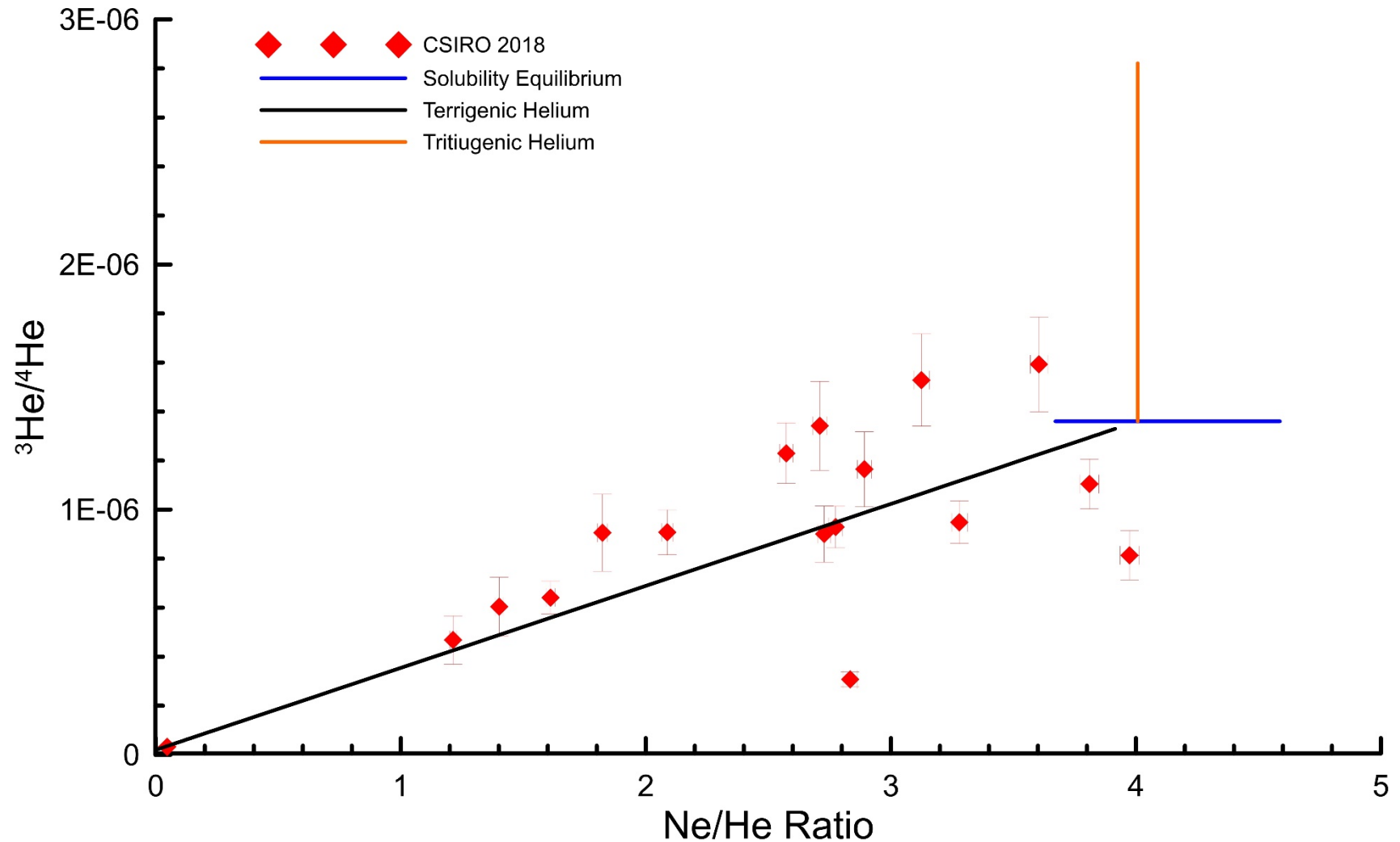
Radiocarbon (not radiocarbon age!!!) increases with flow distance.  
The water gets “younger” on the flow.



Reference point is 20.5 deg S, 134.5 deg E

# Helium

The second round of samples in 2018 gave many more samples with detectable helium than before. All seem to be radiogenic (no indication of mantle helium or volcanic origin).



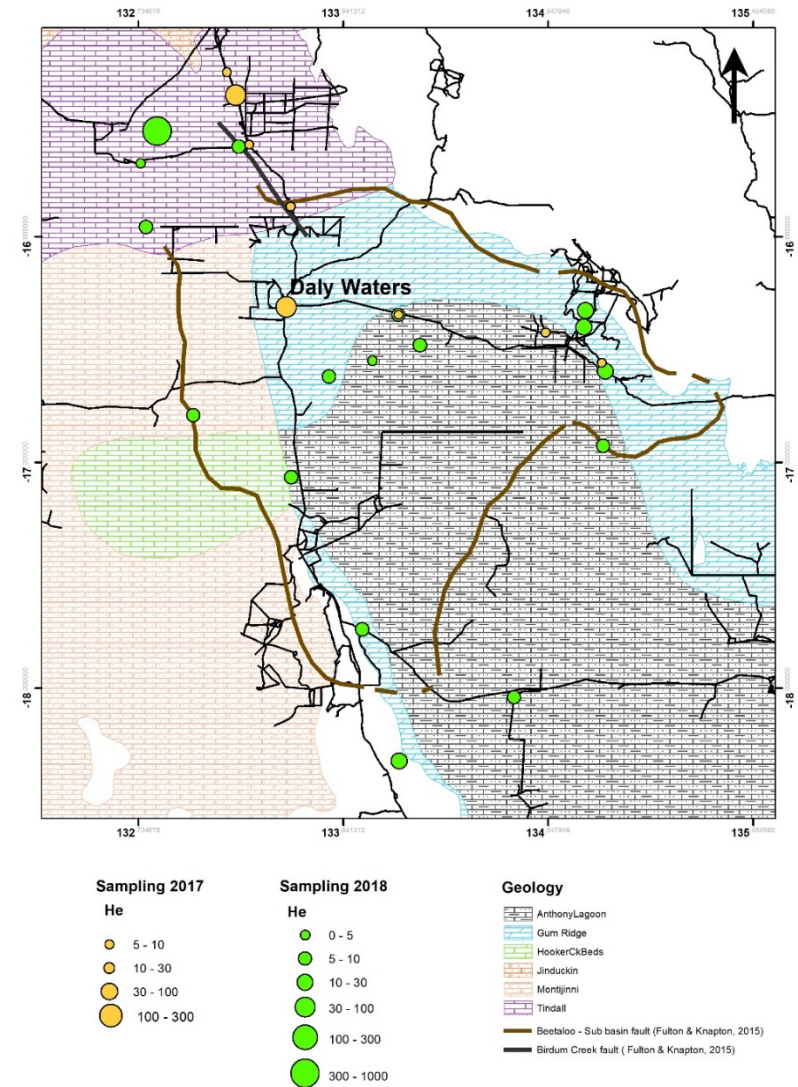
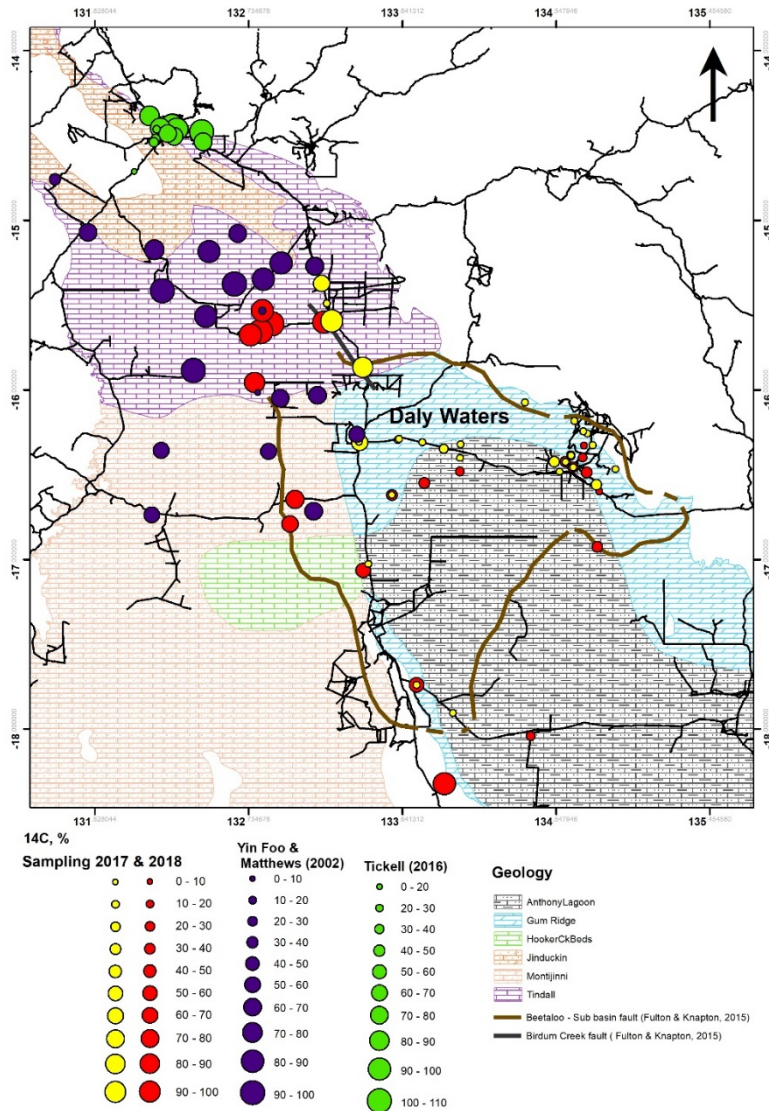


# Radiocarbon

# &

# Helium on the Map.

Data exchange with Geoscience Australia highly desirable (Energy for the future program)





# 10. Key results from tracer work

In the 2017 survey, eight wells were sampled along a north – south transect spanning approximately 300 km from Daly Waters to Larrimah. In the 2018 survey, another 25 samples were taken, also in the WISO basin and more spread in the area.

- The key finding is that the aquifer is likely recharged via point-recharge associated with sinkholes creating recharge rates that vary significantly in time and space.
- Tracers generally did not follow a traditional pattern for groundwater getting ‘older’ along a groundwater flow-path. For example,  $^{14}\text{C}$  activity increased along the flow-path, whereas the opposite pattern would have been expected with decreasing  $^{14}\text{C}$  activity as groundwater residence time increases in the direction of the discharge area.
- CFCs, halon-1301 and  $\text{SF}_6$  (gases) were present at above background concentrations, indicating a ‘modern’ source of water everywhere in the aquifer.
- Tritium in contrast was found only in a few bores, indicating that the water molecule itself only in some spots contains recharge after 1960.
- The noble gas content indicated an environment with large temporal variations in the water table (excess air)
- Helium was found at above background concentration in several wells, representing an input of “old” groundwater from underlying geological formations.

FOR FURTHER DETAIL SEE CSIRO REPORT EP 186868, Suckow et al, July 2018 and another report in preparation (September 2019)

# Comments on the tracer results

Present model hypothesis to explain the unusual tracer patterns:

- The study area represents a climate and vegetation gradient, where the recharge rate to the aquifer varies systematically, increasing from south to north;
- Some of the wells sampled had large screens or were open boreholes, thus integrating groundwater over a large vertical cross-section of the CLA and complicating the interpretation of tracer patterns;
- The CLA is karstic, implying a potential for point recharge and faster preferential groundwater flow, which complicates the flow system characterisation;
- Tracer results can be explained by local recharge (sinkholes?) supplying young water (tritium) only locally, but groundwater level fluctuation over the whole area, “pumping” the young gas tracers (CFCs, SF<sub>6</sub>, H1301) into the groundwater.
- Significant faulting occurs at the edges of the Beetaloo Sub-Basin; these geological structures may provide conduits for groundwater discharge from deeper geological formations (discernible as helium signal).
- Quantifying how much water is coming from deeper formations requires isotopic characterisation – e.g helium concentrations in the Jamison Sandstone and Moroak Sandstone formations
- Radiocarbon can be explained for all samples from the CLA as a two-component mixture between an “old” water with only 2% in <sup>14</sup>C and modern recharge with >100% in <sup>14</sup>C. This mixing relationship also explains the results for <sup>13</sup>C, TDIC, Cl, Na, Mg and Ca.

# 11. References

ANZECC (2000) Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), October 2000, Australian and New Zealand Guidelines for Fresh and Marine Water Quality

Coleman DD, Liu CL, Hackley KC and Benson LJ (1993) Identification of Landfill Methane Using Carbon and Hydrogen Isotope Analysis. Proceedings of 16th International Madison Waste Conference, Municipal & Industrial Waste, Department of Engineering Professional Development, University of Wisconsin Madison, Madison, 22-23 September 1993, 303-314.

Davis SN, Whittemore DO and Fabryka-Martin J (1998) Uses of Chloride/Bromide Ratios in Studies of Potable Water, Groundwater, 36 (2), 338- 350.

NHMRC (2017) Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy.

WHO (2017) Guidelines for drinking-water quality: fourth edition incorporating the first addendum, World Health Organization, Geneva

# Thank you

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