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Exploring for the Future—Groundwater hydrochemistry data release

Daly River project, Northern Territory

J. M. Trihey, E. S. B. McGrath-Cohen and A. M. Haiblen

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GEOSCIENCE AUSTRALIA RECORD 2020/46

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Department of Industry, Science, Energy and Resources

Minister for Resources, Water and Northern Australia: The Hon Keith Pitt MP

Secretary: Mr David Fredericks PSM

Geoscience Australia

Chief Executive Officer: Dr James Johnson

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Geoscience Australia acknowledges the traditional custodians of the country where this work was undertaken. We also acknowledge the support provided by individuals and communities to access the country, especially in remote and rural Australia.



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List of Abbreviations

BDL Below Detection Limit
CFC Chlorofluorocarbon
DO Dissolved Oxygen
EC Electrical Conductivity

EFTF Exploring for the Future (an Australian Government program; http://www.ga.gov.au/eftf)

ORP Reduction-oxidation potential
HDPE High-Density Polyethylene
IC Ion Chromatography

ICP-AES Inductively-Coupled Plasma - Atomic Emission Spectrometry

ICP-MS Inductively-Coupled Plasma - Mass Spectrometry

N/A Not Available

pH Negative log of active hydrogen concentration; acid-base character of water

RN Registered Number of a groundwater monitoring bore

RPD Relative Percent Difference
TDS Total Dissolved Solids

Note: Chemical symbols as per the Periodic Table of Elements (e.g. https://iupac.org/what-we-do/periodic-table-of-elements/)

Executive Summary

This report presents a summary of the groundwater and surface water hydrochemistry data release from the Daly River project conducted as part of the Exploring for the Future (EFTF) program, an Australian Government funded geoscience data and information acquisition program. The program focused on better understanding the potential mineral, energy and groundwater resources in northern Australia.

This data release records the groundwater sample collection methods and hydrochemistry and isotope data from monitoring bores in the Daly River project area, Northern Territory (NT). The Daly River project is a collaborative study between Geoscience Australia and the NT Government.

The sampling methods, quality assurance/quality control procedures, analytical methods and results are included in this report. Hydrochemistry and isotope data were collected from existing bores in the Daly River area and are available for download from http://pid.geoscience.gov.au/dataset/ga/100521.

1 Introduction

The Australian Government's Exploring for the Future (EFTF) Program received \$225.5 million over eight years starting in 2016. The Program's objective over the four years from 2016-2020 was to provide a holistic picture of the potential mineral, energy and groundwater resources in northern Australia. The program has delivered new geoscience data, knowledge and decision support tools to support increased industry investment and sustainable economic development across the north. Further detail is available at (http://www.ga.gov.au/eftf).

Groundwater is a critical resource that accounts for most water used across northern Australia. The groundwater component of the EFTF program focused on addressing groundwater resource knowledge gaps, to support future opportunities for economic development via irrigated agriculture, extractive industries and increased security of community water supplies. Through collaboration with State and Territory partners, the program undertook targeted regional investigations of groundwater systems and assessments of groundwater potential more broadly across the region.

The program's activities, implemented by Geoscience Australia, involved application of innovative geoscience tools to collect, integrate and analyse a range of data. It includes geological and hydrogeological data, airborne and ground-based geophysical and hydrogeochemical surveys, remote sensing data as well as stratigraphic drilling. The new data and improved understanding of groundwater systems helps inform decision making about groundwater use to protect environmental and cultural assets. These outcomes strengthen investor confidence in resources and agricultural projects by de-risking groundwater in northern Australia.

As part of the EFTF groundwater program, groundwater and surface water were collected for a suite of hydrochemistry and isotopes. Collection of hydrochemistry data allows for a greater understanding of groundwater quality, age, flow dynamics, recharge processes, inter-aquifer connectivity and interactions with surface water systems.

Groundwater is the primary source of water for forestry, agriculture, and drinking water supply in the Daly River region. Groundwater also provides baseflow to the Daly River during the dry season and is critical for sustaining environmental and cultural water requirements and tourism. Groundwater is predominantly extracted from the Cambrian Tindall Limestone and Oolloo Dolostone aquifers. Water allocation plans govern groundwater use in the Daly River region, and demand for water in the area is likely to grow with development. Sustainable groundwater management relies on detailed characterisation for the groundwater system. The Daly River groundwater sampling program was designed to collect targeted groundwater chemistry samples to improve our understanding of groundwater dynamics in the region.

This report provides a summary of groundwater chemistry data collected in the Daly River region for EFTF. The data presented here targeted existing groundwater monitoring bores. Geoscience Australia collected 16 groundwater and two surface water samples during the 2018 dry season. These samples were analysed for field parameters and a number of laboratory analytes.

This data release is one of many data releases and interpretation reports for EFTF in northern Australia. All data, information, and images are available through the Geoscience Australia website (http://pid.geoscience.gov.au/dataset/ga/100521) and EFTF portal (https://portal.ga.gov.au/).

2 Sample collection methods

Hydrochemistry and isotope samples were largely collected by Geoscience Australia staff, with additional sampling undertaken by staff from the Northern Territory Department of Environment and Natural Resources.

2.1 Collecting a representative groundwater sample

For all groundwater EFTF projects, groundwater sampling was conducted in accordance with sampling guidelines (Sundaram et al., 2009). Representative groundwater samples were collected primarily using the low-flow sampling method or from bores that were equipped with pumps. The low flow method is designed to leave the stagnant water within the bore undisturbed, whilst obtaining a representative sample directly from the aquifer. At equipped bores samples were collected after sufficient pumping had occurred for field parameters (see Section 3) to stabilise. This process ensures that stagnant water in the bore was removed and the sample attained was representative of the targeted aquifer. The sampling methods are described in further detail below.

2.1.1 Low flow method

This method uses specifically designed low-flow sample pumps that can extract water from the bore at low volumes, typically 0.5–2.0 L/min. The principle behind this method is to extract groundwater through the bore screen no faster than it flows out of the formation, without disturbing the stagnant water column. This is achieved by pumping at a rate which results in minimal drawdown of the water level within the bore. The method has the added benefits of minimising the entrainment of sediment within the sample and reducing the time required for sampling compared with traditional bore purging methods that require a minimum of three casing volumes to be pumped from the bore before a representative sample can be obtained (Sundaram et al., 2009).

Geoscience Australia used an SS Mega-Monsoon™ pump to collect groundwater samples from less than ~40 m depth and a Bennett™ submersible double piston pump to collect groundwater samples >40 m.

To collect a representative groundwater sample, the pump was lowered to the middle of the slotted interval. The pumping rate was set to a speed consistent with low-flow sampling (0.5–2 L/min) and the groundwater level was monitored before, during and after pumping to ensure the pumping did not induce groundwater drawdown.

2.1.2 Equipped bores

A number of samples were collected from bores that were equipped with a solar or diesel generator powered pump. In some instances the pumps were running at the time of sampling so there was no need to purge the bore. When equipped bores were not flowing, the equipped pump was started and groundwater flow was monitored until approximately three well casings worth of water had been removed, based on bore construction information and measured flow rates. This is to ensure all stagnant water contained within the bore casing has been removed and the sample is representative of the targeted aquifer.

2.2 Collecting a representative surface water sample

Representative surface water samples were collected using an SS Mega Monsoon™ pump powered by a car battery. The pump was placed as close as possible to the middle of the stream and samples were collected from areas of flowing surface water where possible.

3 Measuring field parameters

Field parameters were monitored to ensure stabilisation prior to sampling, and because some groundwater parameters can change rapidly. The following parameters were measured in the field using a TPS-90 FLTTM multi-parameter meter: pH, electrical conductivity (EC), temperature, dissolved oxygen (DO) and oxidation-reduction (redox) potential (ORP). Pumped groundwater was run through an in-line flow-cell to facilitate monitoring of field parameters with minimal contact with the atmosphere. Measurements were recorded approximately every five minutes until all parameters had stabilised. For surface water samples the same multi-parameter unit was used and temperature, pH and EC were recorded.

3.1 pH

A TPS pH sensor was used to measure pH and adjusts the reading according to the temperature of the water. A two or three-point calibration was undertaken daily using buffer solutions at pH 4.01, 7.00 and 10.01, ensuring that the measured value was within ± 0.1 pH units of the calibration standard used.

The pH electrode was rinsed well with deionised water prior to monitoring, blotted dry using Kimwipes and placed in the flow cell. The pH of groundwater was considered stable when it was within ±0.05 pH units over three consecutive five-minute intervals. Once all field parameters had stabilised and been recorded, the pH sensor was rinsed thoroughly with deionised water, blotted dry and placed in a wetting cap that contained a few drops of deionised water for storage.

3.2 Electrical Conductivity

Electrical conductivity (EC) is an indirect measure of water salinity and one of the most common and convenient methods used to test water quality. Electrical conductivity is significantly affected by temperature, so the TPS-90 FLT automatically normalises the EC to 25°C. Two probes were used in the field, one that had a range of 0–1990 μ S/cm and the second for higher salinity water samples, with a range of 0–19 900 μ S/cm. Temperature readings were also taken from the EC probe.

The EC meter uses a single-point calibration and was generally calibrated daily. Sometimes the EC meter was recalibrated during monitoring of field parameters to ensure the most appropriate calibration solution was used for the salinity of the water being sampled. The lower salinity calibration solution was a 0.01 molar KCl solution with a conductivity of 1413 μ S/cm; the higher salinity calibration solution was a 0.1 molar KCl solution with a conductivity of 12 880 μ S/cm. The electrodes were rinsed thoroughly with deionised water before and after calibration.

Prior to monitoring, the EC electrode was rinsed well with deionised water, blotted dry using Kimwipes and placed in the flow cell. The EC of groundwater was considered stable when it was within 3% over three consecutive five-minute intervals. Once all field parameters had stabilised and been recorded, the EC sensor was rinsed thoroughly with deionised water and blotted dry for storage.

3.3 Dissolved oxygen

A YSI-5739 dissolved oxygen (DO) probe was used to measure the quantity of dissolved oxygen present in water. The sensor measures DO concentration in milligrams per litre or percentage saturation, however we preferentially collected percent saturation values.

The DO probe was generally calibrated daily using a zero-oxygen solution and air calibration. The membrane was checked for air bubbles regularly and replaced as needed.

The DO probe was rinsed well with deionised water prior to monitoring and placed in the flow cell. The DO of groundwater was considered stable when measurements were within 3% over three consecutive five-minute intervals. Once all field parameters had stabilised the DO probe was removed, thoroughly rinsed and placed inside a protective sleeve with a wet sponge for storage to prevent the probe from drying out.

3.4 Oxidation-reduction potential (ORP)

Oxidation-reduction potential (ORP) is a measure of the oxidising/reducing capacity of groundwater. ORP is measured in units of millivolts (mV) relative to the Ag/AgCl electrode.

The TPS ORP sensor used is factory calibrated and there is no user-calibration facility available. Prior to use, the ORP sensor was rinsed with deionised water, blotted dry using Kimwipes and placed in the flow cell. The ORP of groundwater was considered stable when it was within 3% over three consecutive five minute intervals. Once all field parameters had stabilised the ORP probe was removed, thoroughly rinsed with deionised water and placed inside a protective cap for storage.

3.5 Alkalinity

A Hach digital titrator kit was used for determining alkalinity in the field for both surface water and groundwater samples. This enables accurate titrations rated at $\pm 1\%$. The alkalinity titration was ideally undertaken on a sample volume of 25 mL, however sample volumes ranging from 10-50 mL were used. Alkalinity of the majority of samples was determined by titrating with sulfuric acid with a normality of either 0.16 or 1.6, depending on the expected alkalinity concentration. If the pH of the sample was greater than eight, a phenolphthalein indicator powder pillow was added and if the solution turned pink, the sample was titrated to a colourless end point and the amount of acid used recorded. The sample was next titrated using a bromocresol green-methyl red indicator powder pillow to a light pink (pH 4.5) end point and the amount of acid used recorded. Where the pH of the sample was lower than eight, the sample was only titrated using a bromocresol green-methyl red indicator powder pillow to a light pink end point and the amount of acid used was recorded. In some cases, a methyl orange indicator was used and the samples were titrated to a light yellow end point and alkalinity appropriately calculated. Field alkalinity is reported in mg/L as bicarbonate (HCO3 $^-$) and total alkalinity as calcium carbonate (CaCO3).

3.6 Dissolved iron and hydrogen sulfide

lons that are important for understanding oxidation and reduction processes such as ferrous iron (Fe2+) and sulfide (S2-) were measured in the field using a Hach DR1900 portable spectrophotometer. The spectrophotometer was laboratory calibrated when required. These ions need to be measured in the field rather than in a laboratory at a later time as they can be oxidised when exposed to the atmosphere. Ferrous iron concentration was determined on a 10 mL sample using a Hach 1, 10-phenanthroline powder pillow at a wavelength of 510 nm (Hach method 8146). The concentration of sulfide was also determined on a 10 mL sample using the Hach method 8131 (methyl blue method) at a wavelength of 665 nm.

4 Hydrochemical and isotope sampling

When it was determined that the field parameters had stabilised, the flow cell containing the probes was by-passed allowing samples to be collected directly from the pump outlet. Samples were collected and preserved at each site for a suite of hydrochemical analyses as listed in Table 4.1 and shown in Appendix B. Sample preparation was completed in line with established guidelines (Sundaram et al., 2009) and adapted to individual lab requirements where needed. Samples that did not require filtration (see Table 4.1) were collected directly from the LDPE tubing. For samples requiring filtration (see Table 4.1), a single-use 0.45µm Waterra inline filter was attached to the pump tubing from which samples were collected. Where necessary, various preservation methods were applied as shown in Table 4.1.

Groundwater samples were collected and preserved at each site for a number of hydrochemical analytes (Figure 4.1; Table 4.1). Sampling requirements for each analyte are listed in Table 4.1.



Figure 4.1 Groundwater sample collection.

Table 4.1 Groundwater sampling requirements.

Analyte	Container	Preparation	Preservation
Cations and trace metals	125 mL HDPE bottle	Filter through 0.45 µm membrane filter	Acidify to pH≤2 with ultrapure nitric acid. Store at <25°C
Anions	125 mL HDPE bottle	Filter through 0.45 µm membrane filter	Store at <4°C
Stable isotopes of water: Deuterium (δ^2 H) and oxygen (δ^{18} O)	15 mL vacutainer	None	Store at <25°C
Radiocarbon (14C) and δ^{13} C	500 mL HDPE bottle	None	Store at <4°C
Noble gases and isotopes of helium (³ He, ⁴ He, Helium, Neon, Argon, Krypton, Xenon)	Two copper tubes with crimped ends	Sample flushed through line, ensure no air bubbles and apply back pressure to sample.	Stored so that copper tubes did not bend.

5 Quality assurance and quality control

The collection of high-quality, representative groundwater samples requires a range of quality assurance and quality control measures to ensure field and laboratory results are reliable and consistent.

5.1 Quality assurance

Prior to fieldwork, a sampling plan was developed identifying which bores to sample, what equipment to use and which personnel would undertake the work. Standard operating produces (SOPs) were developed for all aspects of the sampling program to ensure samples were collected in a consistent and rigorous manner for all fieldwork. SOPs were also written for sampling equipment including for the pumps and monitoring equipment that were used. Personnel undertaking sampling were given appropriate training in sample collection and handling procedures prior to, and during fieldwork. All chemicals required for sample preservation were handled according to the material safety data sheets (MSDS) and field staff were trained in chemical handling.

5.2 Quality control

Quality control measures during fieldwork included:

- Sampling and sample preparation was conducted with the staff wearing powder-free nitrile gloves.
- Triple rinsing of all equipment and containers was carried out using the water to be sampled (i.e. filtered or not, as applicable for the sample).
- Laboratory duplicates were split in the laboratory and analysed 'blind' together with the unknown samples.

To assess the suitability of analytes for subsequent analysis, several quality assurance measures were applied, including assessing:

- Charge balance error (CBE) for each sampling location.
- Relative percent difference (RPD) between laboratory duplicates.

The percent CBE was calculated for all samples using Equation 1:

$$CBE(\%) = 100 \times \left(\frac{\sum meq_{cations} - \sum meq_{anions}}{\sum meq_{cations} + \sum meq_{anions}}\right)$$
(1)

where \sum meqcations is the sum of the major cation activities (Na⁺ + K⁺ + Ca²⁺ + Mg²⁺) in units of milliequivalents per litre (meq/L), and \sum meqanions is the sum of the major anion activities (Cl- + total alkalinity + SO42-) in units of meq/L. Results for CBE are shown in Appendix D. All but four of the Daly River groundwater samples have a CBE between ±5% (Figure 5.1). Of the four that are outside that range, only one exceeds ±10% CBE. Of the two Daly River surface water samples, one has a CBE that is within ±5% and the other is within ±10% CBE

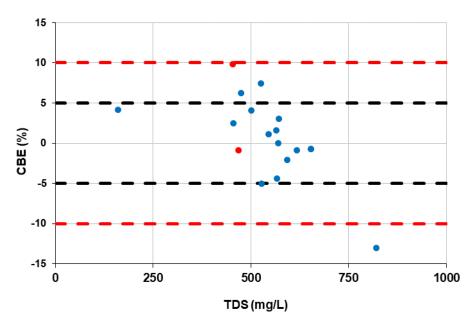


Figure 5.1 Charge Balance Error (CBE) for groundwater samples (blue dots) and surface water samples (red dots). The black dashed line indicates 5% CBE and the red dashed line indicates 10% CBE.

Laboratory duplicates were used to assess sampling, preparation and analytical errors. RPD was calculated using Equation 2:

$$RPD(\%) = 100 \times \frac{|Sample \ 1 - Sample \ 2|}{\frac{(Sample \ 1 + Sample \ 2)}{2}}$$
(2)

Where Sample 1 and Sample 2 represent the two samples that are being compared. All RPD values are displayed in Appendix D. Original data are reported as received from laboratories. Results have not been corrected based on blank and duplicate performance.

6 Results

Laboratory analytical methods are presented in Appendix A. Groundwater sampling results are presented in full in Appendix B with surface water sampling results presented in full in Appendix C. Pump depth is unknown for several samples (Table B.1). Results for these samples should be treated with caution.

6.1 Field parameters

Groundwater (Appendix B Table B.2) and surface water (Appendix C; Table C.1) samples from the Daly River area exhibit similar compositions. EC ranges from 195 μ S/cm to 786 μ S/cm (Figure 6.1) and pH ranges from 6.03 to 7.93. The ORP of groundwater and surface water samples is positive for all but one sample, ranging from 12 mV to 134 mV with the exception being -133 mV. This means that the samples are predominantly oxidising. Concentration of DO ranges between 0 mg/L and 5.16 mg/L in the groundwater samples. S²⁻ concentration range between 6 μ g/L and 34 μ g/L and Fe²⁺ concentrations are between 0.01 mg/L and 0.38 mg/L for groundwater samples. Total Alkalinity ranges from 98 mg/L to 665 mg/L for groundwater samples and is 305 mg/L and 326 mg/L for surface water samples.

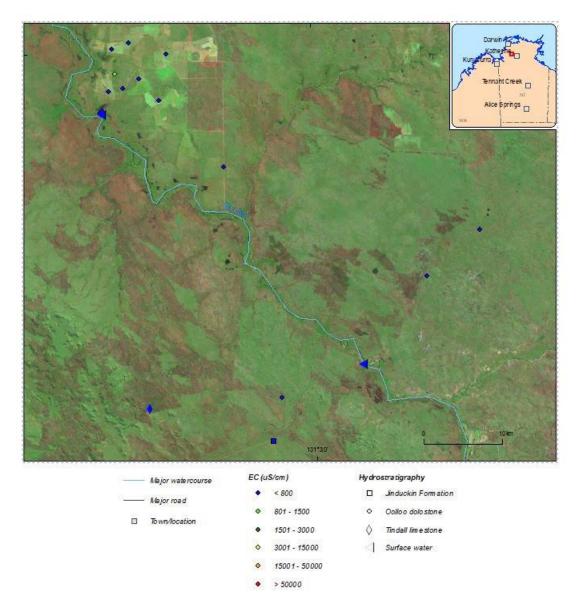


Figure 6.1 Electrical conductivity (EC) of groundwater and surface water samples collected in the Daly River project area.

6.2 Major lons

Major ion data are displayed in Appendix B; Table B.3 and Appendix C; Table C.2. Major ion data are classified using a Piper diagram (Piper, 1944) and sample position on a Piper diagram is plotted spatially using the colour scheme of Peeters (2014; Figure 6.2). All samples contain Mg-Ca-HCO₃ type water.

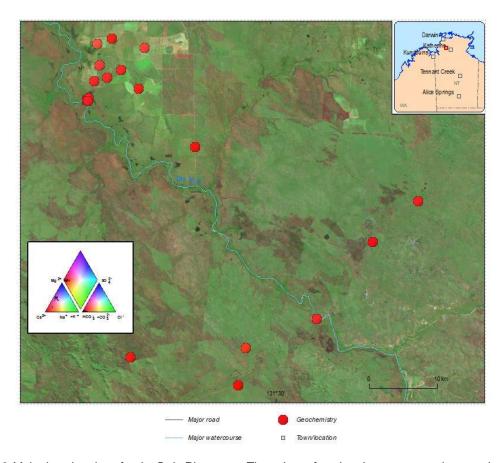


Figure 6.2 Major ion chemistry for the Daly River area. The colour of each point represents the sample position on the central diamond of a Piper diagram (inset) using the colour scheme of Peeters (2014).

6.3 Minor and trace elements

Minor and trace element concentrations for all samples are shown in Figure 6.3. Most minor and trace elements in the groundwater and surface water samples are below the detection limit of analysis. Exceptions are Ba, Cu, Li, Mn, Rb, Sr, Zn, B, and Fe, however, these only appeared in concentrations <1 mg/L.

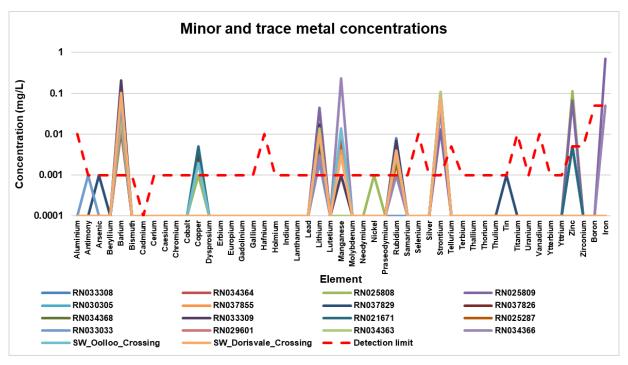


Figure 6.3 Minor and trace element compositions for Daly River samples. Where elemental concentrations are below the detection limit a value of 0.00001 is assigned for plotting here.

6.4 Stable Isotopes of water (δ 18O, δ 2H)

Stable isotopes of water are reported as $\delta^{18}O$ and $\delta^{2}H$ in ‰ relative to Vienna Standard Mean Ocean Water 2 (VSMOW2; IAEA, 2017). Result are plotted with the Darwin Local Meteoric Water Line (Hollins et al., 2018) and Global Meteoric Water Line (Craig, 1961; Figure 6.4Figure 6.5). The majority of samples sit on the meteoric water lines. A few samples sit to the right of the meteoric water lines indicating an evaporative trend. Stable isotope results are shown in Appendix B, Table B.4.

Daly River Stable Isotopes 0 -8 -3 -10 -20 -30 δ²H (permille) -40 -50 Daly River -60 SW Darwin LMWL -70 Daly River Trendline - GMWL -80 δ18O (permille)

Figure 6.4 Stable isotopes of water (δ^{18} O and δ^{2} H in %VSMOW2) plotted with the Darwin Local Meteoric Water Line (red) and the Global Meteoric Water Line (black). A linear best fit line (blue) is calculated for all groundwater samples (blue dots). Surface water samples are shown using red dots.

6.5 Radiocarbon (Carbon-14)

Radiocarbon results are reported as percent modern carbon (pMC), displayed in Figure 6.5 and Appendix B; Table B.5. Groundwater samples contain 67.22% to 92.00% modern carbon. δ^{13} C data collected with 14 C data is also available in Appendix B and is reported relative to the Peedee Belemnite standard reference material (Coplen, 1994).



Figure 6.5 Distribution of samples analysed for radiocarbon content showing pMC values.

6.6 Noble Gases

Noble gas results can be found in Appendix B; Table B.6.

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Geoscience Australia's groundwater expertise is complemented by collaboration with State and Territory government, academia, landholders and traditional owners. We would particularly like to acknowledge and pay respects to the traditional custodians of the country where this work was undertaken.

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References

- Coplen, T.B., 1994. Report of stable hydrogen, carbon, and oxygen isotopic abundances. Pure Appli. Chem, 66, 273-276, https://nucleus.iaea.org/rpst/Documents/tecdoc_0825.pdf
- Craig, H., 1961. Isotopic variations in meteoric waters. Science, 133, 1702-1703.
- Hollins S.E., Hughes C.E., Crawford J., Cendón D.I. & Meredith K.T., 2018. Rainfall isotope variations over the Austrailian continent implications for hydrology and isoscape applications. Science of the Total Environment, 645, 630-645, https://doi.org/10.1016/j.scitotenv.2018.07.082
- International Atomic Energy Agency (IAEA), 2017. Reference Sheet for International Measurement Standards VSMOW2 Vienna Standard Mean Ocean Water 2, water and SLAP2 Standard Light Antarctic Precipitation 2, water. International Atomic Energy Agency, https://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf
- Peeters, L., 2014. A background colour scheme for Piper plots to spatially visualize hydrochemical patterns. Groundwater, 52, 2–6.
- Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water-analyses. Transactions-American Geophysical Union, 25, 914–923.
- Sundaram, B., Feitz, A., Caritat, P. de, Plazinska, A., Brodie, R., Coram, J. & Ransley, T., 2009. Groundwater Sampling and Analysis A Field Guide. Record 2009/27. Geoscience Australia, Canberra, 95 pp.

Appendices

Appendix A Laboratory Analysis

Sample analysis details are outlined in Table A.1. Laboratory duplicates were used to assess results.

Table A.1 Summary of sample analysis details for samples collected in the Daly River project area.

Analyte	Laboratory	Analysis method
Major cation concentrations (Na+, K+, Ca ²⁺ , Mg ²⁺)	Australian Laboratory Services Global (ALS), Sydney	Inductively-coupled plasma optical emission spectrometry (ICP-AES)
Major anion concentrations (Br, Cl-, F-, SO_4^{2-})	ALS Sydney	Ion chromatography
Dissolved silica	ALS Sydney	Inductively-coupled plasma atomic emission spectrometry (ICP-AES).
Minor and trace elements	ALS Sydney	Inductively-coupled plasma mass spectrometry (ICP-MS)
Stable isotopes of water: Deuterium ($\delta^2 H$) and oxygen ($\delta^{18} O$)	Australian Nuclear Science and Technology Organisation (ANSTO)	Finnigan MAT 252 mass spectrometer
Radiocarbon (14 C) and carbon isotopic composition (δ^{13} C)	ANSTO	Accelerator mass spectrometry^
Noble gasses	University of Utah Noble Gas Lab	Gas chromatography with mass spectrometer

[^]D. Fink, M. Hotchkis, Q. Hua, G. Jacobsen, A. M. Smith, U. Zoppi, D. Child, C. Mifsud, H. van der Gaast, A. Williams and M. Williams (2004) The ANTARES AMS facility at ANSTO, NIM B 223-224, 109-115.

Appendix B Groundwater sample collection details and hydrochemistry data

Results from field and laboratory analysis of groundwater samples in the Daly River project are presented in the tables below.

Table B.1 Groundwater sampling locations and sample collection methods.

Sample number	Sample date	eno (GA Oracle Database)	Bore ID	GDA 94 Latitude	GDA 94 Longitude	Stratigraphic unit	Screened interval (mbgl)	Depth of pump (mbgl)	Sample collection method^
20183910011	16/08/2018	641132	RN021671	-14.0306	131.2965	Oolloo dolostone	44.6-51	unknown	EP
20183910012	16/08/2018	641130	RN025287	-14.0556	131.3197	Oolloo dolostone	46-76	unknown	EP
20183910003	10/08/2018	641122	RN025808	-14.4108	131.3031	Tindall Limestone	36-42	unknown	EP
20183910004	10/08/2018	641123	RN025809	-14.4005	131.4596	Oolloo dolostone	48-54	unknown	EP
20183910014	17/08/2018	641135	RN029601	-13.9953	131.2651	Oolloo dolostone	21-23.5	unknown	EP
20183910005	10/08/2018	641131	RN030305	-14.4498	131.4484	Jinduckin Formation	26-30	unknown	EP
20183910013	16/08/2018	636287	RN033033	-14.1338	131.395	Oolloo dolostone	30-36,48-54,78-84	not recorded	MM
20183910001	8/08/2018	636257	RN033308	-14.2626	131.6338	Oolloo dolostone	61-97	80	BP
20183910010	15/08/2018	641111	RN033309	-14.2099	131.6963	Oolloo dolostone	unknown	49.5	BP
20183910015	17/08/2018	641112	RN034363	-14.002	131.3292	Oolloo dolostone	31.5-37.5	34.5	BP
20183910002	9/08/2018	636256	RN034364	-14.0693	131.2499	Oolloo dolostone	13-19	31	MM
20183910016	18/08/2018	641113	RN034366	-14.0669	131.2522	Oolloo dolostone	24.5-37	30.75	MM
20183910009	14/08/2018	641114	RN034368	-14.0409	131.2777	Oolloo dolostone	22.3-28.3	25.3	MM (BP for noble gases)

Sample number	Sample date	eno (GA Oracle Database)	Bore ID	GDA 94 Latitude	GDA 94 Longitude	Stratigraphic unit	Screened interval (mbgl)	Depth of pump (mbgl)	Sample collection method^
20183910008	14/08/2018	641128	RN037826	-14.0448	131.2601	Oolloo dolostone	44.45-48.55,49-66.93, 72.90-78.86, 84.74-90.73, 96.6-98.65	unknown	EP
20183910007	14/08/2018	641129	RN037829	-14.024	131.2678	Oolloo dolostone	48.495-54.47, 54.87-60.92, 61.32-67.37,73.36-81.41, 87.36-99.235	unknown	EP
20183910006	12/08/2018	641115	RN037855	-13.9888	131.2851	Oolloo dolostone	54-132	63	BP

[^]EP = Existing Pump, MM = Stainless Steel Mega Monsoon Pump, and BP = Bennett Pump

Table B.2 Field Parameters.

Bore ID	рН	EC (μS/cm)	DO (mg/L)	ORP (mV)	Temperature (°C)	S ²⁻ concentration (µg/L)	Fe ²⁺ concentration (mg/L)	Total Alkalinity (HCO ₃ · equivalent) (mg/L)
RN021671	6.93	572	5.16	134	31	12	0.01	318
RN025287	6.81	646	4.19	124	30.6	9	0.02	437
RN025808	6.68	632	0.39	18	29.5	25	0.03	366
RN025809	6.03	195	0	12	29.4	BDL^	BDL^	97.6
RN029601	6.9	644	2.87	98	30.7	11	0.02	386
RN030305	6.57	761	0	59	29.6	11	0.03	665
RN033033	7.05	722	0.81	65	32	13	0.04	486
RN033308	7.12	643	2.48	108	33.9	7	0.01	334
RN033309	6.31	719	1.45	109	36	6	0.38	378
RN034363	6.71	755	1.76	117	30.9	11	0.02	444
RN034364	6.66	699	0.4	62	31.6	9	0.03	406
RN034366	7.06	720	0.1	-133	29.9	34	0.19	447
RN034368	6.34	786	3.08	115	32.5	12	0.01	386
RN037826	6.37	784	3.71	118	30.5	10	0.01	359
RN037829	6.36	822	3.36	102	31.9	10	0.01	376
RN037855	7.03	644	3.1	21	31.4	9	0.05	422

[^]Below detection limit

Table B.3 Major ion concentrations.

Bore ID	HCO₃⁻	Cl-	SO ₄ ² -	Br ⁻	F	Ca2+	Mg ²⁺	Na ⁺	K ⁺	Si	TDS^	СВЕ
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	%
RN021671	318	17.6	2.03	0.025	0.325	52	34	14	2	16	455	2.516
RN025287	437	16	1.76	0.025	0.173	62	44	14	1	17.3	593	-2.051
RN025808	366	5.52	3.68	0.025	0.331	58	42	7	5	12.5	500	4.091
RN025809	97.6	3.77	0.05	0.018	0.024	26	4	5	0.5	22.4	160	4.158
RN029601	386	35.4	8.42	0.025	0.696	55	34	30	2	15.8	567	-4.379
RN030305	665	2.37	0.578	0.025	0.268	71	56	6	2	16.8	820	-13.001
RN033033	486	8.54	1.33	0.025	0.202	68	52	10	0.5	26.6	653	-0.728
RN033308	334	4.58	11.4	0.025	0.184	62	40	4	3	14.5	474	6.244
RN033309	378	10.6	17.6	0.025	0.798	64	31	8	5	12.1	527	-5.068
RN034363	444	34.2	10.8	0.025	0.638	71	42	30	3	17.1	653	-0.724
RN034364	406	18.1	3.41	0.052	0.132	70	43	9	2	12.7	564	1.602
RN034366	447	22.1	4.84	0.068	0.093	75	44	12	1	11.8	618	-0.865
RN034368	386	19.8	3.71	0.025	0.321	56	37	16	2	15.3	545	1.087
RN037826	359	19.3	5.06	0.025	0.267	62	39	17	2	14.5	526	7.418
RN037829	376	35.4	7.72	0.025	0.335	60	38	25	3	14.9	572	3.025
RN037855	422	9.79	2.26	0.025	0.4	62	43	13	1	14.8	570	0.007

[^]Total dissolved solids (TDS) was calculated by summing all ion concentrations measured.

Table B.4 Stable isotopic results.

Bore ID	δ2H (‰)	δ18Ο (‰)
RN021671	-48.6601	-7.3596
RN025287	-47.8690	-7.2301
RN025808	-47.4209	-7.1897
RN025809	-47.1406	-7.0499
RN029601	-47.6918	-7.2000
RN030305	-44.6417	-6.7859
RN033033	-50.9435	-7.545
RN033308	-48.3868	-7.2982
RN033309	-47.5590	-7.2099
RN034363	-45.8713	-6.9456
RN034364	-40.2003	-5.6173
RN034366	-43.2527	-6.4974
RN034368	-47.8647	-7.3106
RN037826	-47.4690	-7.2427
RN037829	-46.7500	-7.0609
RN037855	-47.8832	-7.1929

Table B.5 Radiocarbon results.

Sample number	Bore ID	δ 13C (‰)	δ13C error (± ‰)	14C as Percent Modern Carbon	14C error (±)
20183910001	RN033308	-11.5	0.2	67.22	0.25
20183910002	RN034364	-12.5	0.1	83.34	0.29
20183910003	RN025808	-11.5	0.2	79.54	0.19
20183910004	RN025809	-11.8	0.1	92.00	0.25
20183910006	RN037855	-12.2	0.4	89.94	0.23
20183910009	RN034368	-12.5	0.2	76.75	0.2
20183910011	RN021671	-12.5	0.1	72.89	0.18
20183910014	RN029601	-11.6	0.1	78.6	0.21
20183910016	RN034366	-12.6	0.1	83.05	0.21

Table B.6 Noble Gas results.

Bore ID	3Не	4He	R/Ra	Helium Total	Neon Total	Argon Total	Krypton Total	Xenon Total		
		ccSTP/g								
RN025287	8.66E-14	6.68E-08	0.94	6.68E-08	2.49E-07	3.17E-04	5.61E-08	7.28E-09		
RN025808	8.12E-14	6.85E-08	0.86	6.85E-08	2.08E-07	2.98E-04	6.13E-08	7.71E-09		
RN025809	1.59E-13	1.15E-07	0.99	1.15E-07	4.82E-07	4.66E-04	8.16E-08	8.28E-09		
RN030305	7.70E-14	2.61E-07	0.21	2.61E-07	2.30E-07	2.48E-04	5.10E-08	5.64E-09		
RN033308	8.85E-14	8.67E-08	0.74	8.67E-08	2.44E-07	3.05E-04	6.24E-08	7.13E-09		
RN034363	8.68E-14	7.39E-08	0.85	7.39E-08	2.62E-07	3.27E-04	5.94E-08	7.13E-09		
RN034364	1.41E-13	4.98E-06	0.02	4.98E-06	2.01E-07	2.73E-04	6.33E-08	7.66E-09		
RN034368	6.70E-14	6.37E-08	0.76	6.37E-08	1.80E-07	2.54E-04	5.59E-08	7.12E-09		

Appendix C Surface water hydrochemistry data

Results from field and laboratory analysis of surface water samples in the Daly River project are presented in the tables below.

Table C.1 Surface water sampling locations and field parameters.

Sample number	Date collected	eno (GA Oracle Database)	Site name	GDA 94 Latitude	GDA 94 Longitude	рН	EC (μS/cm)	DO (mg/L)	ORP (mV)	Temperature (°C)	Total Alkalinity (HCO₃˙ equivalent) (mg/L)
20183910001SW	9/08/2018	644619	SW_Oolloo_Crossing	-14.0708	131.2512	7.84	612	5.75	80	24.7	305
20183910002SW	10/08/2018	644620	SW_Dorisvale_Cross	-14.3633	131.5564	7.93	577	N/A	N/A	24.1	326

Table C.2 Major ion concentrations for surface water.

Sample number	HCO₃⁻	CI ⁻	SO ₄ ²⁻	F*	Br ⁻	Ca ²⁺	Mg ²⁺	Na⁺	K ⁺	Si	TDS^	CBE
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	%
20183910001SW	305	10.7	11	0.176	0.033	59	40	10	3	14.7	454	-0.85
20183910002SW	326	13.3	14.4	0.177	0.044	45	37	13	3	15.1	468	9.83

[^]Total dissolved solids (TDS) was calculated by summing all ion concentrations measured.

Table C.3 Stable isotopic results of surface water.

Sample number	δ²H (‰)	δ ¹⁸ Ο (‰)
20183910001SW	-45.6428	-6.547
20183910002SW	-46.4931	-6.4643

Appendix D Quality control data

Laboratory duplicates come from analysis of all Northern Stuart Corridor (Howard East and Daly River project) samples as they were analysed in one batch.

Table D.1 Laboratory duplicate results for anions.

Project	Sample number		Br ⁻	F°	CI ⁻	SO ₄ ²⁻	Si
		Original (mg/L)	<0.050	0.184	4.58	11.4	14.5
Daly River	20183910001	Duplicate (mg/L)	<0.050	0.181	4.7	11.7	14.4
		RPD	-	1.64	2.59	2.60	0.69
		Original (mg/L)	<0.050	0.325	17.6	2.03	N/A
Daly River	20183910011	Duplicate (mg/L)	<0.050	0.358	17.9	2.11	N/A
		RPD	-	9.66	1.69	3.86	N/A
		Original (mg/L)	N/A	N/A	N/A	N/A	17.3
Daly River	20183910012	Duplicate (mg/L)	N/A	N/A	N/A	N/A	17.4
		RPD	N/A	N/A	N/A	N/A	0.58
		Original (mg/L)	34.2	<0.500	12700	1560	7.61
Howard East	20183920005	Duplicate (mg/L)	34.3	<0.500	12600	1600	7.12
		RPD	0.29	-	0.79	2.53	6.65

Table D.2 Laboratory duplicate results for cations.

Project	Sample	number	Ca ²⁺	Mg²+	Na⁺	K ⁺
		Original (mg/L)	62	40	4	3
Daly River	20183910001	Duplicate (mg/L)	62	39	4	3
		RPD	0.00	2.53	0.00	0.00
		Original (mg/L)	52	34	14	2
Daly River	20183910011	Duplicate (mg/L)	53	34	14	2
		RPD	1.90	0.00	0.00	0.00
		Original (mg/L)	62	43	14	1
Daly River	20183910006	Duplicate (mg/L)	61	41	13	1
		RPD	1.63	4.76	7.41	0.00
		Original (mg/L)	491	795	5800	37
Howard East	20183920005	Duplicate (mg/L)	478	750	5430	35
		RPD	2.68	5.83	6.59	5.56
	2019392002	Original (mg/L)	38	27	2	<1
Howard East	2013032002	Duplicate (mg/L)	38	27	2	<1
		RPD	0.0	0.0	0.0	-