



Record 2020/43 | eCat 135936

Exploring for the Future—Groundwater hydrochemistry data release

East Kimberley project, Northern Territory

J. M. Trihey and C. Harris-Pascal

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GEOSCIENCE AUSTRALIA
RECORD 2020/43

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Department of Industry, Science, Energy and Resources

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ISSN 2201-702X (PDF)

ISBN 978-1-922446-12-1 (PDF)

eCat 135936

Bibliographic reference: Trihey, J. M & Harris-Pascal, C. 2020. *Exploring for the Future—groundwater hydrochemistry data release: East Kimberley project, Northern Territory*. Record 2020/43. Geoscience Australia, Canberra. <http://dx.doi.org/10.11636/Record.2020.043>

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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)
EK	East Kimberley
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
ND	No Data
ORC-	Octopole Reaction Cell Inductively-Coupled Plasma-Mass Spectrometry
ICPMS	
pH	Negative log of active hydrogen concentration; acid-base character of water
RN	Registered Number of a 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 East Kimberley project conducted as part of the Exploring for the Future (EFTF) Program, an Australian Government funded geoscience data and information acquisition program. The program focusses on better understanding the potential mineral, energy and groundwater resources in northern Australia.

This data release records the groundwater and surface water sample collection methods, and hydrochemistry and isotope data from monitoring bores in the East Kimberley project, Northern Territory (NT). The East Kimberley project incorporates the area around the Keep River Plains near the western border of the NT.

The sampling methods, quality assurance/quality control procedures, analytical methods and results are included in this report.

Hydrochemistry data were collected from existing and newly drilled bores in the Keep River Plains 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.

The East Kimberley region has been identified as a potential area for new irrigated agriculture development and to support water supply for communities in the region (O'Boy et al. 2001; Bennet 2018). The East Kimberley groundwater sampling program was designed to collect targeted groundwater chemistry samples to improve our understanding of water-rock interactions and groundwater dynamics in the region, with the ultimate aim of assessing the potential for an expansion of irrigated agriculture. The Cenozoic and Permo-Carboniferous aquifers of the East Kimberley study area currently support domestic and stock water. The aquifers also contribute baseflow to streams and creeks and may support significant groundwater-dependent ecosystems. Demand for water in the area is likely to grow if agricultural development expands in the region.

This report provides a summary of the hydrochemistry data collected in the East Kimberley region. The data presented here targeted existing and newly drilled groundwater monitoring bores, and surface water sites in the Keep River, Oakes Creek, and Sandy Creek. Geoscience Australia and the Northern Territory Department of Environment and Natural Resources collected 51 groundwater and surface water samples in the Northern Territory over the 2017, 2018 and 2019 dry seasons. These samples were analysed for field parameters, major ions, trace metals, and a selection of isotopic systems. Sample locations are shown in Figure 1.1.

This document contains the results of groundwater sample analysis and is one of a number of data release and interpretation reports for EFTF in northern Australia. All data, information and images are

available through the GA website. (<http://pid.geoscience.gov.au/dataset/ga/135936>) and EFTF portal (<https://portal.ga.gov.au/>).

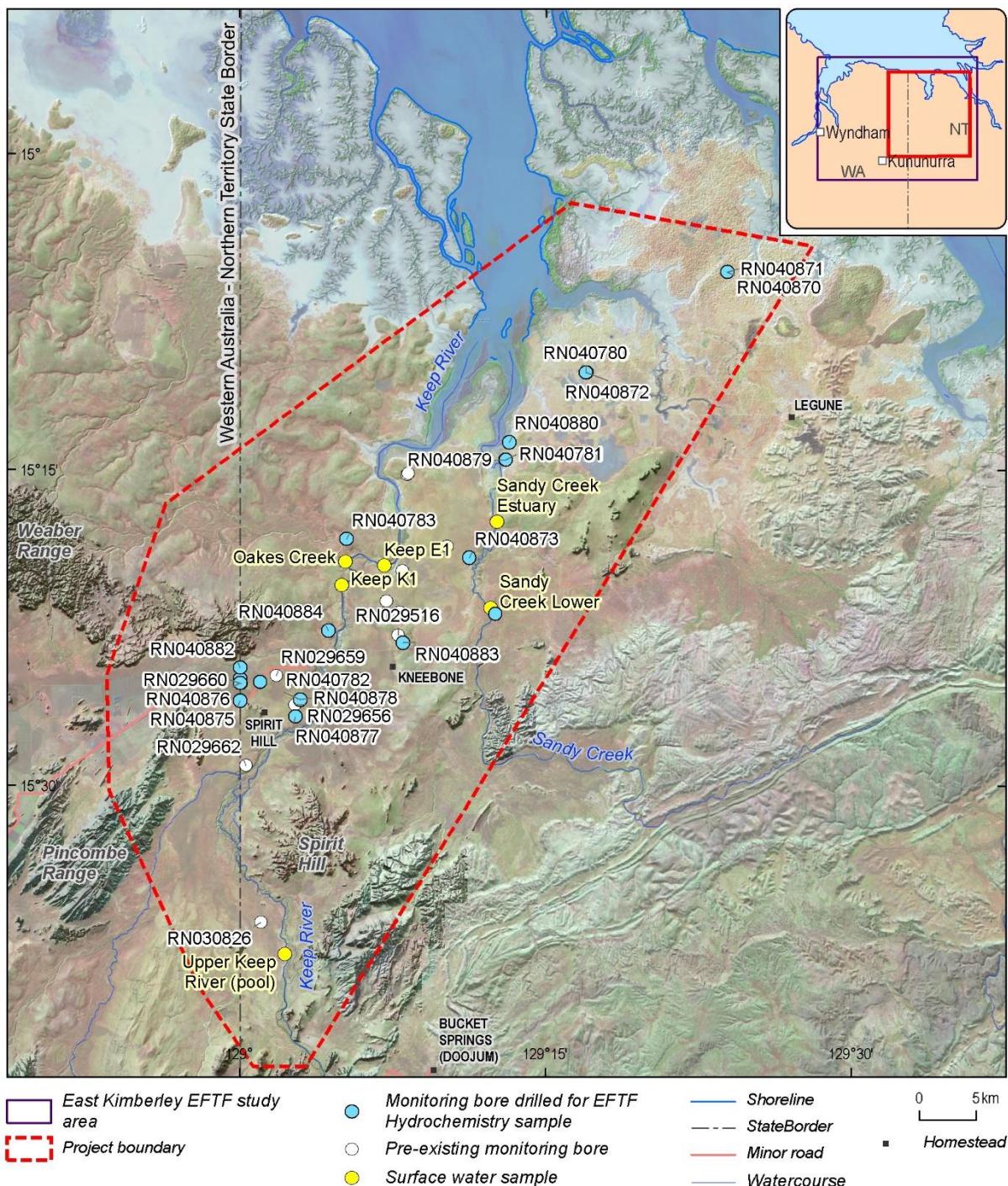


Figure 1.1 Map of the Keep River Plains showing surface water sample sites, and existing and newly-drilled groundwater monitoring bores. Bores at which hydrochemical samples were collected are labelled with the bore RN.

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 established 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. A small number of samples were collected using the bore purging method where bores were not equipped and when a low-flow pump was not available. The bore purging method also removes stagnant water within the bore prior to sample collection. Artesian bores were also sampled in the East Kimberley project area. In all instances, field parameters were monitored to confirm the sample was representative of the targeted aquifer. The four 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 (see Section 2.1) 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 deeper groundwater samples. The maximum depth of the Bennett pump is 110 m, so samples that were deeper than this were collected using a ‘drop tube’ that attached to the Bennett pump. The drop tube is a rod-like intake screen unit with low density polyethylene (LDPE) tubing attached. Weights are attached at the bottom part of a length of tubing and lowered down the bore. The weights are necessary to counter the buoyancy created by the LDPE tubing. More detail on the drop tube set-up can be found in Sundaram et al. (2009). This set up enabled samples to be collected from a maximum of 400 m depth.

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.

2.1.3 Artesian bores

Two artesian bores were sampled in the East Kimberley project area. One of these (RN040780) is equipped with head works and an outlet that can be opened or closed. The other (RN040870) does not have head works, but is constructed with a tall (~1.5 m) casing stickup to prevent water overflow of water from the monitoring bore. To collect a representative sample from RN040780 the head works valve was opened water passed through a flow cell to monitor field parameters until they were considered stable. Monitoring bore RN040870 was sampled in accordance with the low flow sampling method described above.

2.2 Collecting a representative surface water sample

Representative surface water samples were collected using an SS Mega Monsoon™ pump or a 12 volt submersible Amazon 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. For parts of the dry season some streams in the East Kimberley area do not flow at all and surface water upstream of estuarine areas is restricted to pools or water holes in the stream bed. These pools were sampled at the Upper Keep River Pool and Sandy Creek Lower surface water sample sites.

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 FLT™ multi-parameter meter: pH, electrical conductivity (EC), temperature, dissolved oxygen (DO) and oxidation-reduction (redox) potential (ORP). Pumped or flowing artesian 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 µS/cm and the second for higher salinity water samples, with a range of 0–19 900 µS/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 µS/cm; the higher salinity calibration solution was a 0.1 molar KCl solution with a conductivity of 12 880 µS/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 milligrams per litre 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 was titrated to a light yellow end point and alkalinity appropriately calculated. Field alkalinity is reported in mg/L as bicarbonate (HCO_3^-) and total alkalinity as calcium carbonate (CaCO_3).

3.6 Dissolved iron and hydrogen sulfide

Ions that are important for understanding oxidation and reduction processes such as ferrous iron (Fe^{2+}) and sulfide (S^{2-}) 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 comprehensive 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 (Table 4.1, Appendix A). 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 below 25°C
Anions	125 mL HDPE bottle	Filter through 0.45 µm membrane filter	Store below 4°C
Stable isotopes of water: Deuterium (^2H) and Oxygen (^{18}O)	15 mL vacutainers	No air bubbles	Store below 25°C
Radiocarbon (^{14}C) and $\delta^{13}\text{C}$	500 mL HDPE bottle	None	Store below 25°C
Chlorofluorocarbons (CFCs)	2 × 125 mL glass bottles with aluminium foil caps	Collected under water, no air bubbles, tape lid	Store below 25°C
Strontium	500mL HDPE bottle	Filter through 0.45 µm membrane filter	Acidify to pH≤2 with ultrapure nitric acid. Store at below 25°C
Tritium	1L HDPE bottle	None	Store below 25°C
Stable Isotopes of Sulphate ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$)	500+ mL HDPE bottle	Filter through 0.45 µm membrane filter	Add 1-2 mL of acid (2N HCl), shake and let react, then precipitate sulphate by addition of 10 g BaCl
Noble gases	Copper tube	Collected with positive pressure in copper tube. Ends of tube sealed by crimping.	Store below 25°C
Sulphur hexafluoride (SF ₆)	1000 mL Amber glass bottle *	Overflow sample bottle several time, ensure no air bubbles, tape lid to bottle.	Store below 25°C

*provided by GNS Science in New Zealand

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 procedures (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).
- Field duplicates (two groundwater samples collected in sequence at the bore) were collected and analysed ‘blind’ together with the unknown samples.
- Laboratory duplicates were split in the laboratory and analysed ‘blind’ together with the unknown samples.
- Commercial analytical standards with known ionic concentrations were analysed ‘blind’ together with the unknown samples where possible.
- The commercial laboratories used a combination of certified reference materials, internal standards and blanks/spikes to quantify uncertainty.

To assess sample suitability for analysis, several quality control 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:

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

where $\sum meq_{cations}$ is the sum of the major cation activities ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$) in units of milli-equivalents per litre, and $\sum meq_{anions}$ is the sum of the major anion activities ($Cl^- + total alkalinity + SO_4^{2-}$) in units of milliequivalents per litre. CBE results are shown in Table B.3. The CBE of East Kimberley groundwater and surface water samples largely falls within $\pm 5\%$, with 24 samples exceeding this threshold and nine samples exceeding a CBE of $\pm 10\%$ (Figure 5.1).

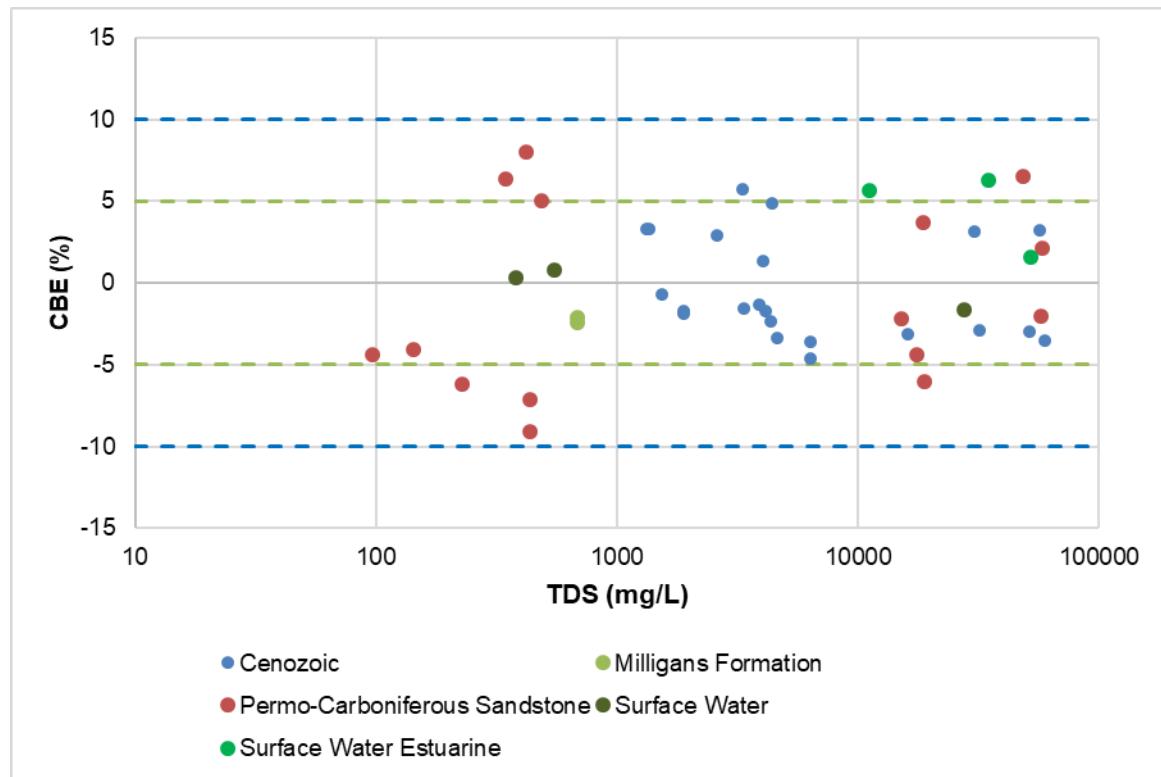


Figure 5.1 Charge Balance Error (CBE) for all samples, symbolised based on aquifer or surface water site. CBE is generally higher when Total Dissolved Solids (TDS) concentration is low.

Field and laboratory duplicates were used to assess sampling, preparation, and analytical errors. Relative percent difference was calculated using Equation 2:

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

Where Sample 1 and Sample 2 represent the two samples that are being compared. RPD results are given in Appendix D. Overall, the data were found to be within $\pm 10\%$ CBE. RPD values for lab duplicates (Appendix D) were within 5%, with the exception of 16 samples. In this data release, raw data has been used and results have not been corrected based on blank and duplicate performance.

Field duplicates performed well for the analysis of the stable isotopes of water ($\delta^{18}O$ and δ^2H). This was assessed by reviewing the absolute difference between field duplicates. Other isotopes were reported against internal laboratory standards as part of standard reporting. Results are shown in Appendix D.

Additional quality control measures were applied to results of CFC analysis. The detection limit for CFCs in groundwater is extremely low which introduces complications for groundwater recharged

prior to the 1940s, which may have experienced low levels of contamination of CFCs from interaction with the atmosphere or from sampling equipment during sample collection. In water recharged prior to the 1940s, contamination resulting in even a few pg/kg of CFC could result in an apparent groundwater age of several decades, where the reality may be several centuries or millennia. Such false positives have the potential to cause significant problems in water management as allocations made on the assumption of substantial modern recharge to a groundwater system, where the reality is little or no modern recharge, will clearly result in over-allocation of the resource leading to lowering of water tables, reduced access, and poor environmental outcomes.

To avoid false positives in the presentation of CFC data a number of quality control measures were included in sampling strategy and data interpretation. These were:

1. Duplicate samples were collected and analysed for all sample locations. Any duplicate pairs which varied by more than twice the standard error (SE) are not presented.
2. As part of the EFTF program, CFC concentrations were analysed in a sample from a monitoring bore with a deep (> 90 mbgl) screen and artesian groundwater pressures (RN040870). Groundwater from this bore is assumed to contain no CFCs. It is used as a blank sample for comparison with other results. Analysis of samples collected from RN040870 returned CFC concentrations of 0.014 and 0.17 pmol/kg for CFC-11 and CFC-12 respectively, indicating low levels of contamination in the sampling or analysis procedure. CFC-113 was not detected in samples from RN040870. To minimise the potential for false positives in CFC data, the maximum values of CFC-11 and CFC-12 measured in samples from RN040870 were subtracted from all other results. Following this procedure, any samples returning CFC concentrations within twice the reported standard error (SE) of the detection limit (assumed to be 0.02 pmol/kg) were then assumed to have negligible concentrations of CFCs.

Following these QC procedures only four samples showed measurable CFC concentrations.

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.

6.1 Field parameters

6.1.1 Groundwater

Groundwater across the East Kimberley study area range from very fresh to hyper-saline, with a measured EC range of 20.37 µS/cm to 93 843 µS/cm and a median of 6 120 µS/cm (Table B.2, Figure 6.1). The pH of waters were mostly neutral to slightly acidic and ranged from 4.91 to 8.98. Temperatures of the groundwater sources ranged from 17.4 °C to 36.1 °C. The ORP of groundwater samples ranges from -269 mV to +190 mV with a median of -56 mV. Concentration of DO had an average of 1.02 mg/L, with a range from 0 mg/L¹ to 6.58 mg/L. The range of ORP and DO data indicates a combination of reducing and oxidising conditions. At some sites a S₂- concentration was measured and ranged from 0 µg/L to 621 µg/L. Fe²⁺ concentrations ranged from 0 mg/L to 2.78 mg/L. Total alkalinity ranged from 6 mg/L to 759 mg/L.

6.1.2 Surface Water

Surface Water across the East Kimberley study area range from very fresh to hypersaline with a measured EC range of 502 uS/cm to 76 700 µS/cm, and a median of 18015 µS/cm (**Error! Hyperlink reference not valid.**). The pH of surface waters were mostly neutral and ranged from 7.8 to 8.5. Temperatures of the surface water sources ranged from 17.4 °C to 31.7 °C. The ORP of surface water samples ranged from +74 mV to +147 mV indicating oxidising conditions. Concentration of DO showed an average of 4.5 mg/L, with a range from 1.28 mg/L to 6.58 mg/L. These data indicate oxidising conditions.

¹ Due to the sensitivity of the equipment, some DO readings came out as negative values. These have been reassigned a value of zero.

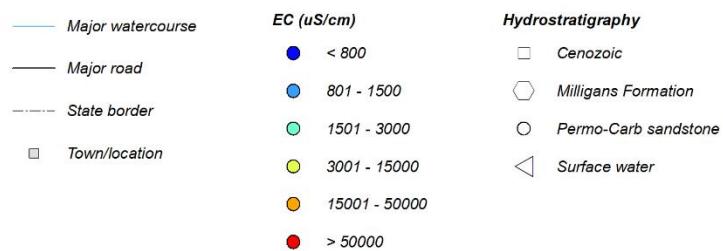
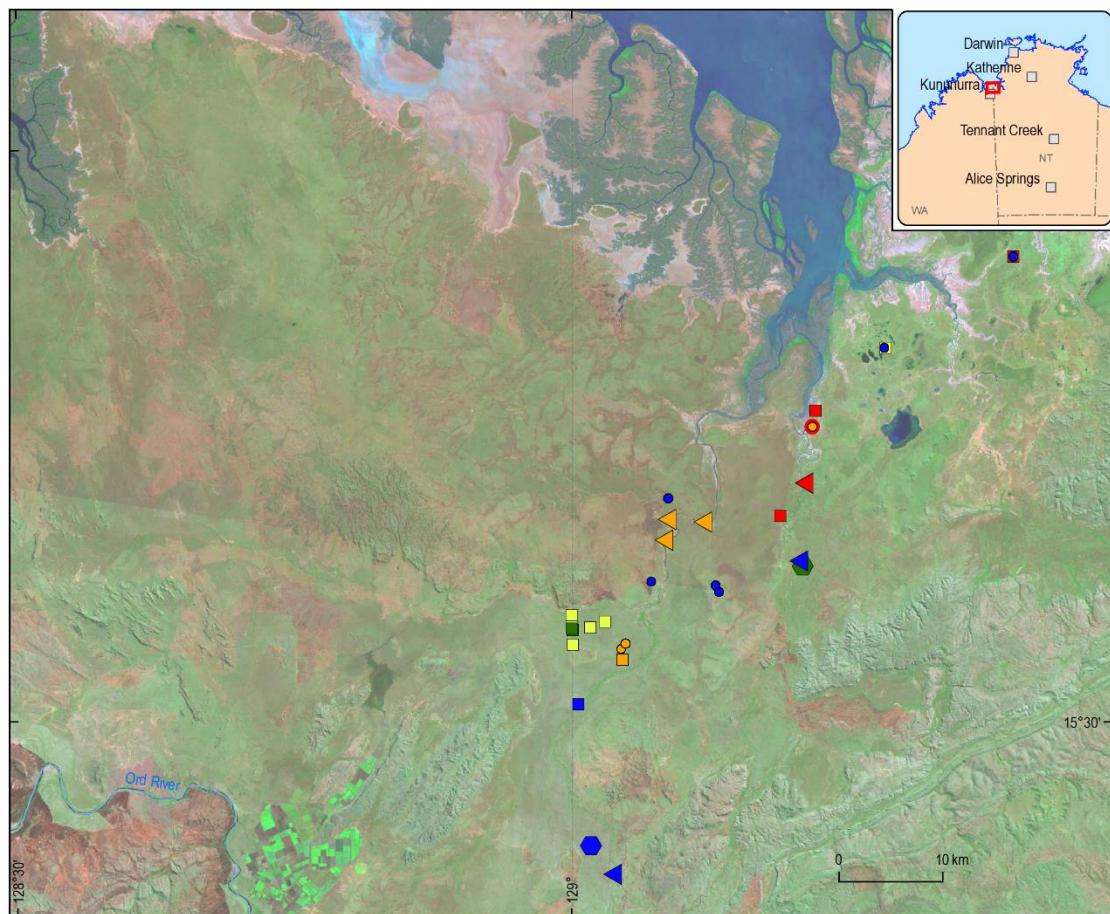


Figure 6.1 Spatial distribution of electrical conductivity (EC) in the East Kimberley project area.

6.2 Major Ions

Major ion data are shown using a Piper diagram (Piper, 1944) in Figure 6.2, where sample position on a Piper diagram is plotted spatially using the colour scheme of Peeters (2014). Waters are largely dominated by Na-Cl type, but range to the areas of Na-HCO₃ and Ca-HCO₃ types. Total Dissolved Solids (TDS) was calculated by summing major ion concentrations (Ca²⁺, Mg²⁺, Na⁺, K⁺, total alkalinity, Cl⁻, SO₄²⁻, F⁻, Si). The TDS range of groundwater samples was 69 to 59 898 mg/L, and 382 to 52 391 mg/L for surface water samples.

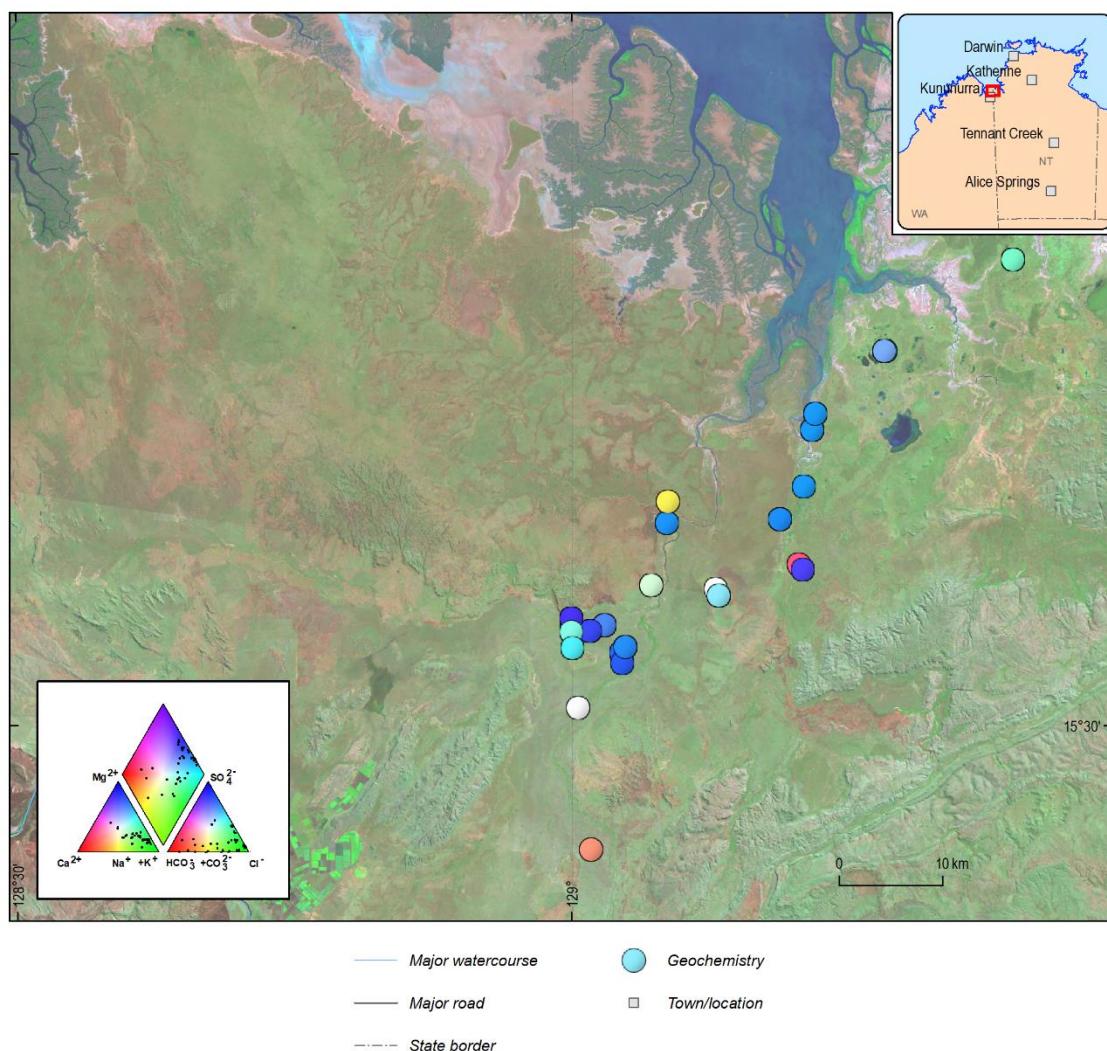


Figure 6.2 Major ion chemistry for the East Kimberley area. The colour of each point represents the sample position on the central diamond of a Piper diagram using the colour scheme of Peeters (2014).

6.3 Minor and trace elements

Minor and trace metal concentrations for all samples are shown in

Figure 6.3 through

Figure 6.8. Each of these figures shows data that were collected in a specific year using octopole reaction cell inductively-coupled plasma mass spectrometry (ORC-ICPMS) for either fresh or saline water, with the limit of detection for each analyte shown. The limit of detection differs for each year and between the two TDS categories, leading to the need for multiple plots. Where results were below detection a value of 0.00001 was assigned to allow an easy visualisation of where trace elements were detected.

Trace element results show that for most samples and elements the concentrations are below the detection limit. Spikes above the detection limit common to most samples are: Al, Ba, B, Br, Co, Cu, Fe, Li, Mn, Ni, Sr, U, V, and Zn.

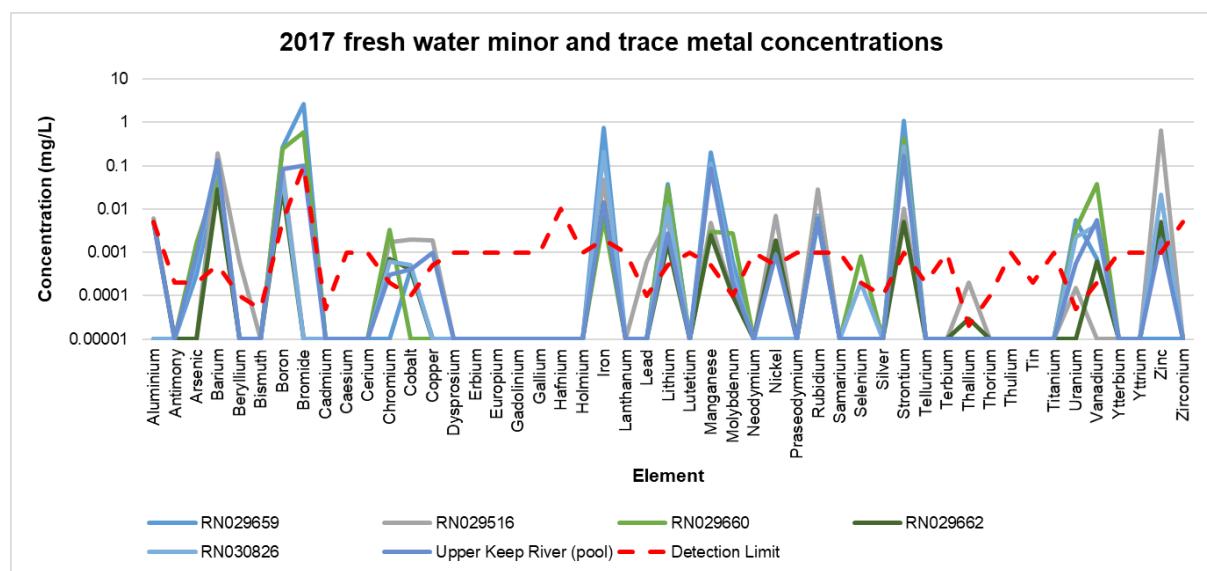


Figure 6.3 Minor and trace element compositions for 2017 East Kimberley samples measured using fresh water ORC-ICPMS.

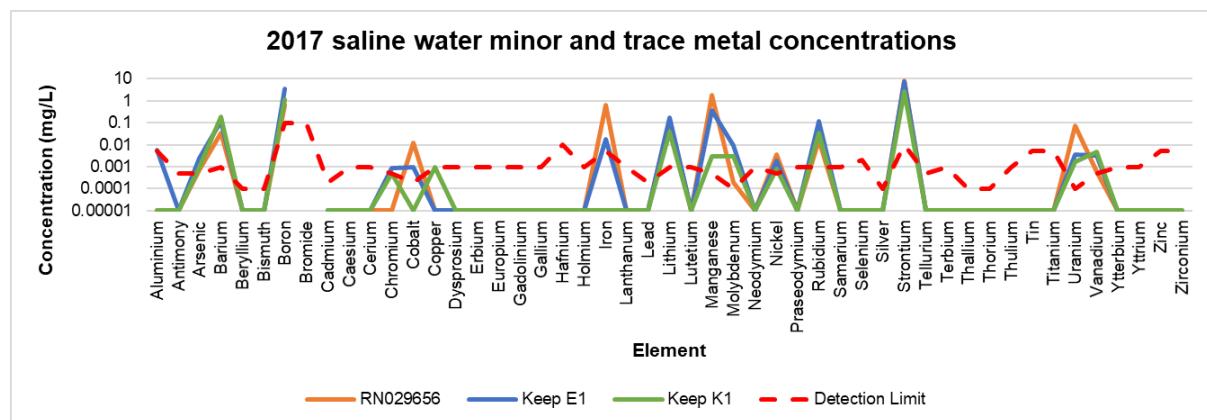


Figure 6.4 Minor and trace element compositions for 2017 East Kimberley samples measured using saline water ORC-ICPMS.

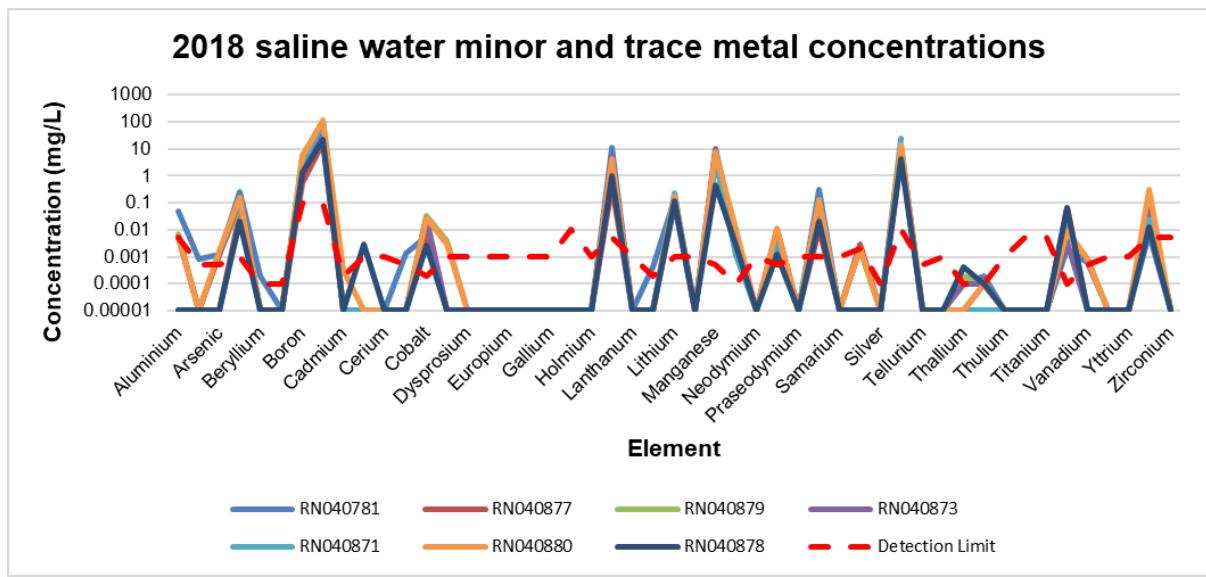


Figure 6.5 Minor and trace element compositions for 2018 East Kimberley samples measured using fresh water ORC-ICPMS.

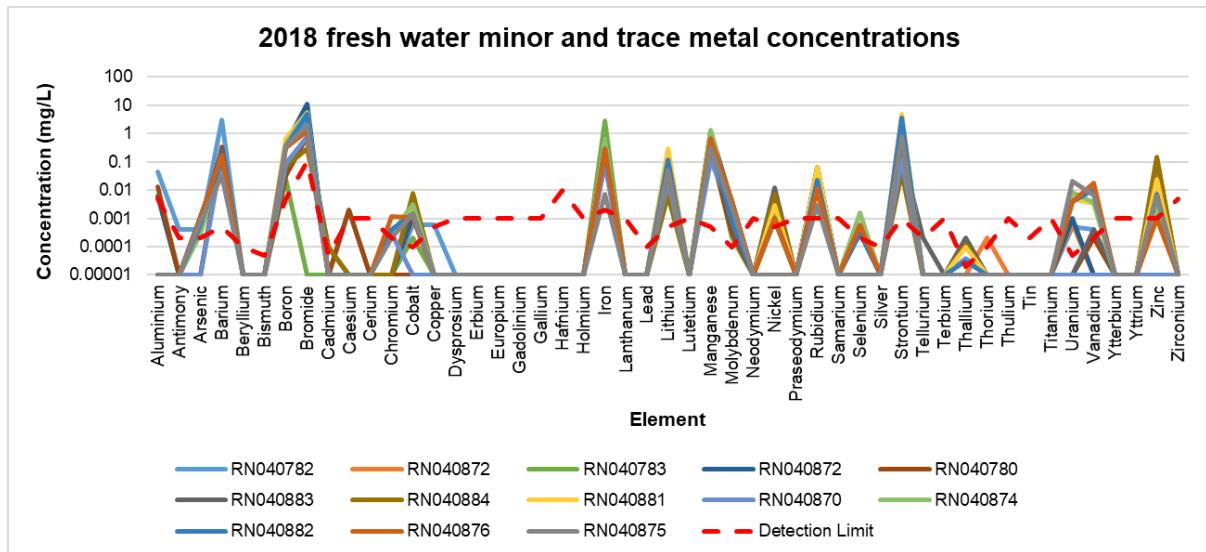


Figure 6.6 Minor and trace element compositions for 2018 East Kimberley samples measured using saline water ORC-ICPMS.

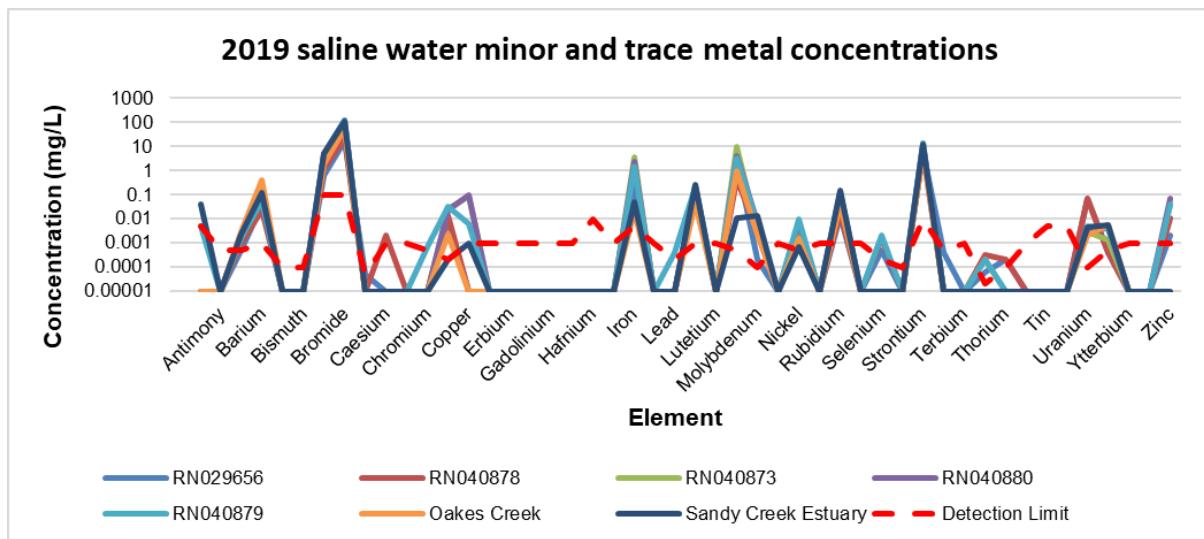


Figure 6.7 Minor and trace element compositions for 2019 East Kimberley samples measured using fresh water ORC-ICPMS.

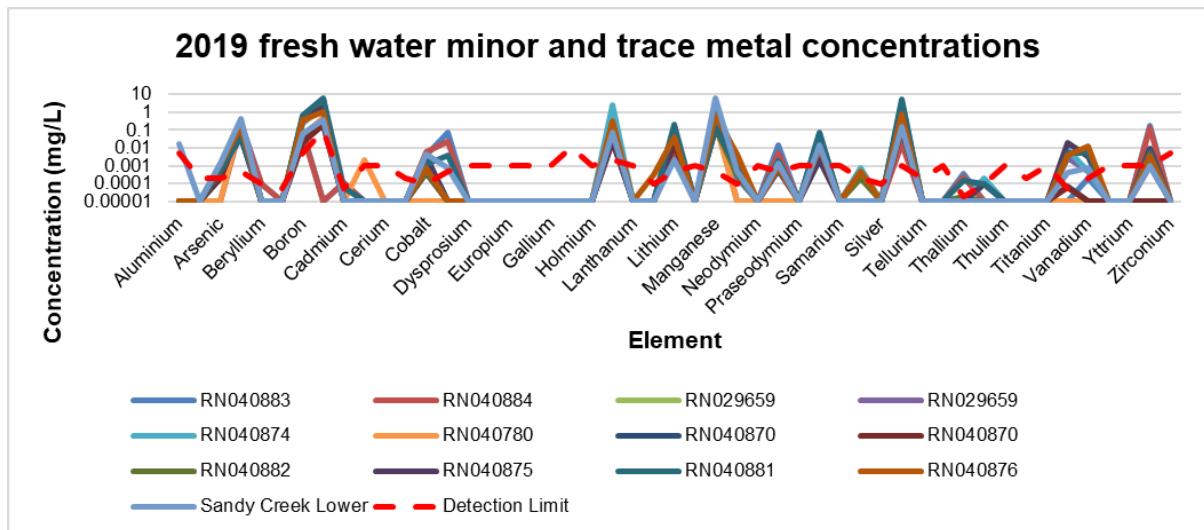


Figure 6.8 Minor and trace element compositions for 2017 East Kimberley samples measured using fresh water ORC-ICPMS.

6.4 Stable Isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

Stable isotopes of water are reported relative to the Vienna Standard Mean Ocean Water 2 (VSMOW2) (IAEA, 2017) as $\delta^{18}\text{O}$, $\delta^2\text{H}$, plotted with the Darwin Local Meteoric Water Line (Hollins et al., 2018) and Global Meteoric Water Line (Craig, 1961) (Figure 6.9).

East Kimberley Stable Isotopes

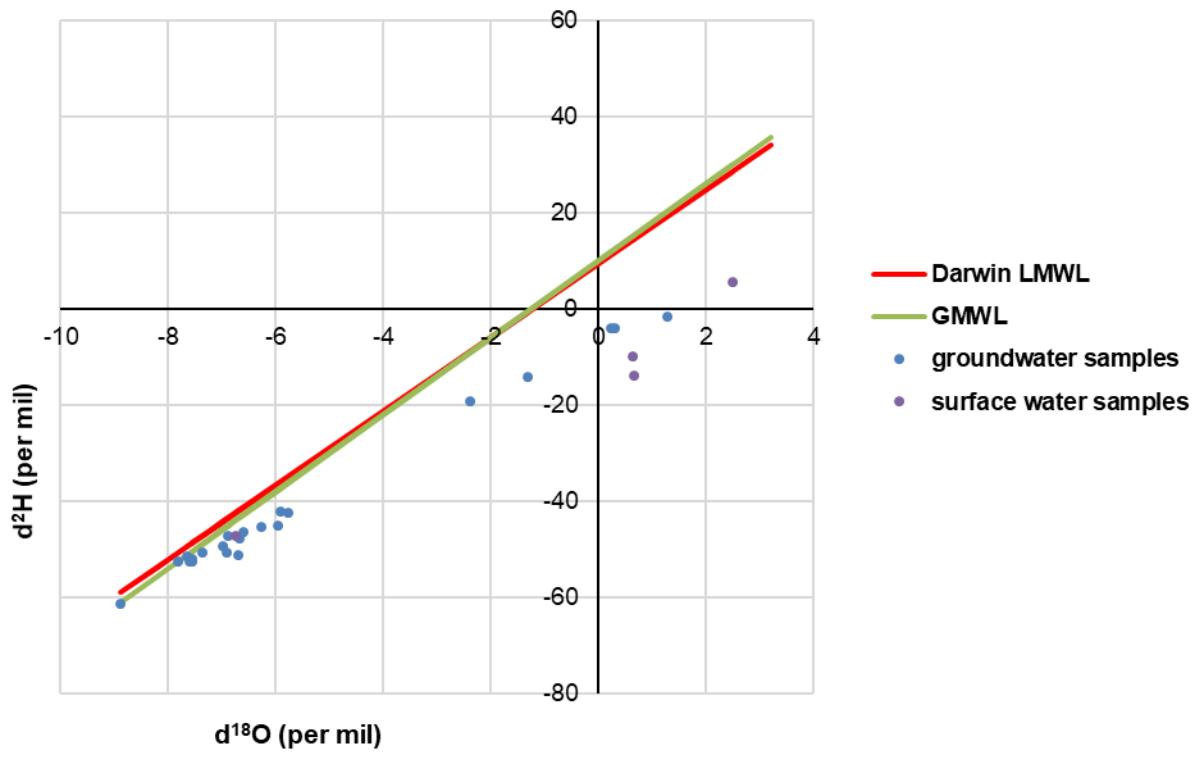


Figure 6.9 Oxygen ($\delta^{18\text{O}}$) and $\delta^{2\text{H}}$ plotted with the Darwin Local Meteoric Water Line (red) and the Global Meteoric Water Line (green).

6.5 Strontium Isotopes

The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ in dissolved Sr^{2+} from groundwater and surface water samples is shown in Figure 6.10 and Appendix B; Table B.5.

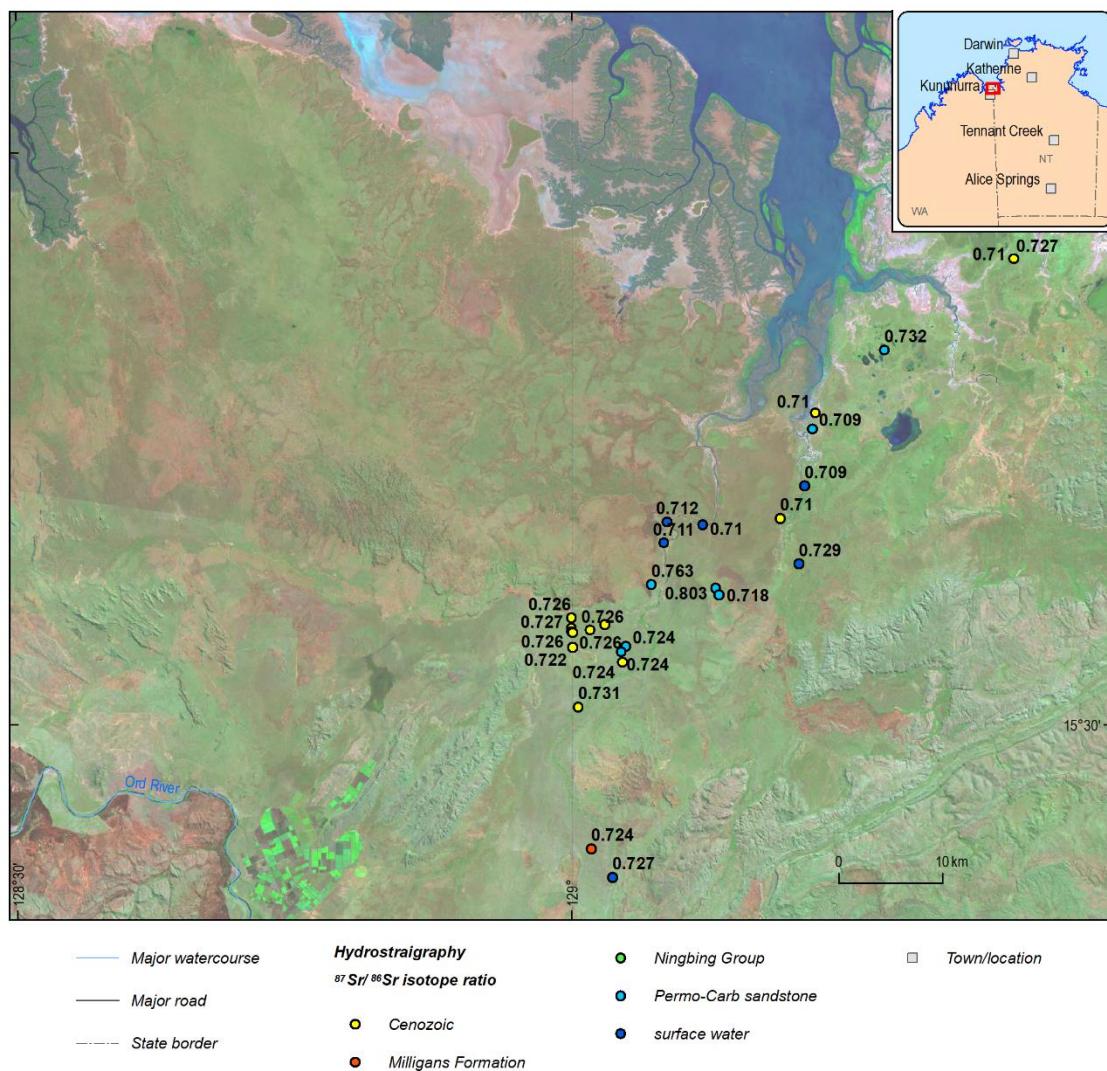


Figure 6.10 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of water samples in the East Kimberley region.

6.6 Radiocarbon (Carbon-14)

Radiocarbon results are reported as percent modern carbon (pmc) and are displayed in Figure 6.11 and Appendix B. Groundwater samples contain 3.45 – 107.51 pmc. $\delta^{13}\text{C}$ data collected with ^{14}C data are also available in Appendix B and are reported relative to the Peedee Belemnite standard reference material (Coplen, 1994).

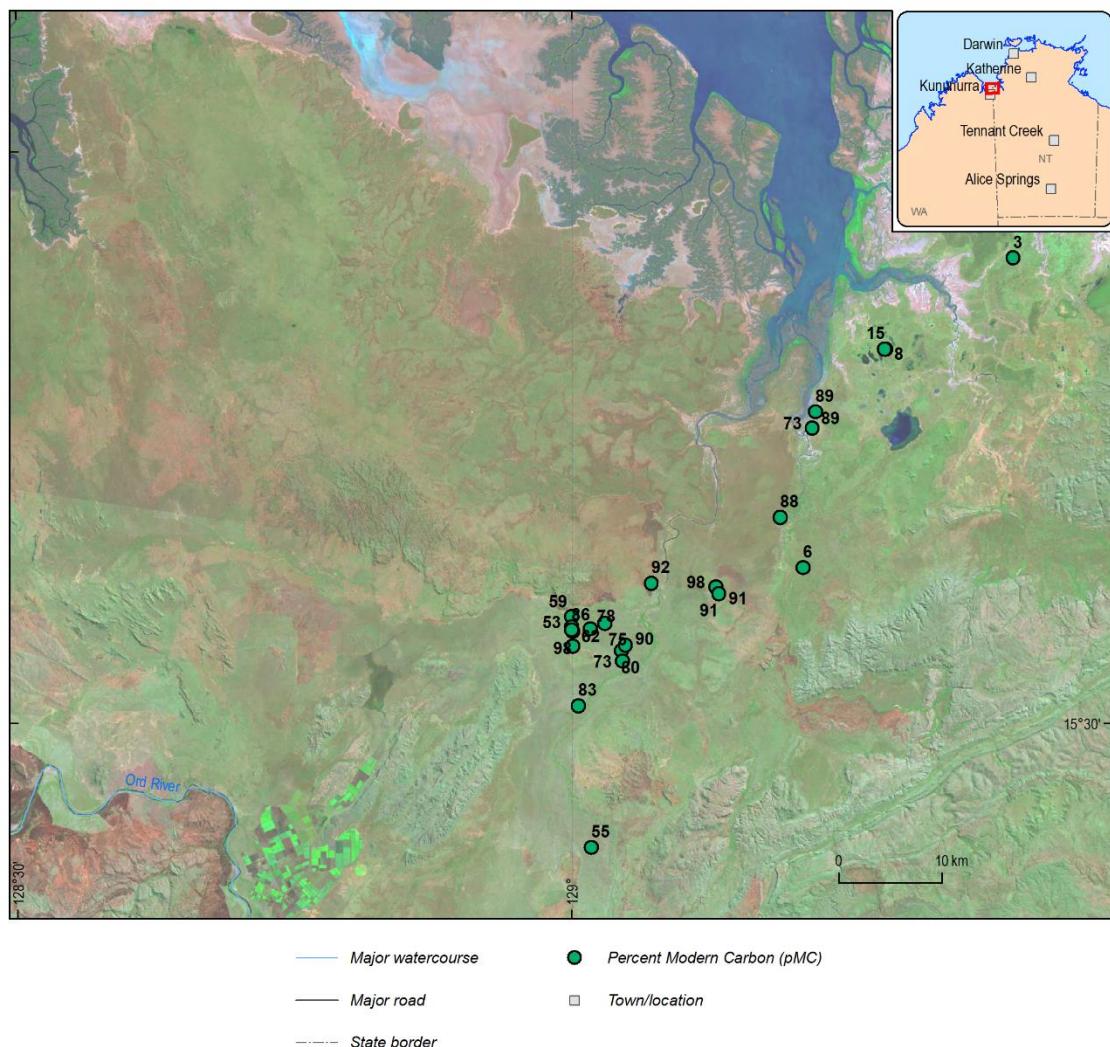


Figure 6.11 Distribution of groundwater samples showing percent modern carbon.

6.7 Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6)

CFC and SF_6 results are reported as the concentration of CFC-11, CFC-12, CFC-113, and SF_6 in groundwater and are shown in Appendix B, Table B.6.

Acknowledgements

Geoscience Australia's groundwater expertise is complemented by strong collaboration with State and Territory government, academia, landholders and traditional owners. The East Kimberley project would particularly like to acknowledge and pay respects to 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. In the East Kimberley area this included the Spirit Hills, and Legune pastoral stations.

The Exploring for the Future East Kimberley Project was funded by the Australian Government as administered by Geoscience Australia with in-kind support from the Northern Territory Department of Environment and Natural Resources (DENR), and Western Australia Department of Agriculture and Food (DAFWA). Thanks go to Dr Michael Short, Steve Tickell and Des Yin Foo from DENR, and Richard George and Don Bennett from DAFWA. The project also wishes to thank the Northern Land Council and the Aboriginal Areas Protection Authority.

Geoscience Australia staff who have contributed to the EFTF program are numerous and we would like to thank them all for their valuable and helpful contributions. The authors would like to acknowledge and thank the field crews including Dr Jessica Northey, Anna Haiblen, Dr Andrew McPherson, Neil Symington, and Ray deGraaf for collecting the data used and described herein. We'd also like to thank John Vizy for GIS support and gratefully acknowledge support from Saskia Becher, Jacob Sohn, Junhong Chen and Wendy van Tol.

Sincere thanks go to Eamon Lai, Dr Stephen Hostetler, Dr Donna Cathro and Dr Baskaran Sundaram for their constructive and helpful review comments.

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Appendix A Laboratory Analysis

Analytical methods are outlined in Table A.1. Duplicates (field and laboratory) were used to assess results and cross-laboratory analyses to facilitate comparison of different instruments for data integration.

Table A.1 Analytical methods.

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 (IC)
Dissolved Si	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 ($\delta^{18}\text{O}$ and $\delta^2\text{H}$)	Australian Nuclear Science and Technology Organisation (ANSTO)	Finnigan MAT 252 mass spectrometer
$^{87}\text{Sr}/^{86}\text{Sr}$ for dissolved Sr.	Research School of Earth Sciences, Australian National University	Dissolved Sr was isolated from other elements through an ion exchange chromatograph, and analysed with a thermal ionisation mass spectrometer.
Chlorofluorocarbons (CFCs) and SF ₆	GNS Science, New Zealand, University of Utah Noble Gas Lab	Gas chromatography with electron capture detection
^{14}C , $\delta^{13}\text{C}$, ^3H ,	ANSTO	Accelerator mass spectrometry ^{^A}

^AD. 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 East Kimberley project are presented in Table B.1 to Table B.7

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	Hydrostratigraphic unit	Screened interval (mbgl)	Depth of pump (mbgl)	Sample collection method^
2019161001	20/07/2019	635738	RN040883	-15.387	129.133	Permo-Carb sandstone	39-45	42	Low flow
2019161002	21/07/2019	635737	RN040884	-15.378	129.072	Permo-Carb sandstone	29-35	32	Low flow
2019161003	21/07/2019	626980	RN029659	-15.413	129.03	Cenozoic	33-37.1	35	Low flow
2019161004	21/07/2019	626980	RN029659	-15.413	129.03	Cenozoic	33-37.1	35	Low flow
2019161005	22/07/2019	635733	RN040874	-15.418	129.017	Cenozoic	18-24	20	Low flow
2019161006	24/07/2019	635744	RN040780	-15.173	129.282	Permo-Carb sandstone	131.39-137.39	Artesian bore	Low flow
2019161007	24/07/2019	635746	RN040870	-15.093	129.398	Permo-Carb sandstone	85-91	85	Low flow
2019161008	25/07/2019	635746	RN040870	-15.093	129.398	Permo-Carb sandstone	85-91	85	Low flow
2019161009	25/07/2019	626989	RN029656	-15.437	129.045	Permo-Carb sandstone	25-29	26	Low flow
2019161010	26/07/2019	626989	RN029656	-15.437	129.045	Permo-Carb sandstone	25-29	26	Low flow
2019161011	26/07/2019	635735	RN040878	-15.432	129.049	Permo-Carb sandstone	36-42	39	Low flow

Sample number	Sample date	Sample ID (GA Oracle database)	Bore ID	GDA 94 Latitude	GDA 94 Longitude	Hydrostratigraphic unit	Screened interval (mbgl)	Depth of pump (mbgl)	Sample collection method^
2019161012	26/07/2019	635740	RN040882	-15.407	129	Cenozoic	17-23	20	Low flow
2019161013	26/07/2019	635740	RN040882	-15.407	129	Cenozoic	17-23	20	Low flow
2019161014	29/07/2019	635742	RN040875	-15.433	129.001	Cenozoic	29-35	32	Low flow
2019161016	30/07/2019	635728	RN040873	-15.32	129.188	Cenozoic	31-37	34	Low flow
2019161017	31/07/2018	635730	RN040880	-15.228	129.22	Cenozoic	16-22	19	Low flow
2019161018	31/07/2019	635739	RN040881	-15.416	129	Cenozoic	29-35	32	Low flow
2019161019	1/08/2019	635741	RN040876	-15.419	129	Cenozoic	20-26	23	Low flow
2019161020	20/07/2019	635729	RN040879	-15.242	129.217	Permo-Carb sandstone	25-31	28	Low flow
20171610001	18/08/2017	626980	RN029659	-15.413	129.03	Cenozoic	33.2-33.6	35	Low flow
20171610003	20/08/2017	626982	RN029516	-15.381	129.13	Permo-Carb sandstone	43.5-55.5	Equipped	Low flow
20171610007	24/08/2017	626986	RN029660	-15.42	129.001	Cenozoic	19.9-23.9	21.5	Low flow
20171610010	26/08/2017	626989	RN029656	-15.437	129.045	Permo-Carb sandstone	25.5-29.5	26	Low flow
20171610016	30/09/2017	626991	RN029662	-15.485	129.006	Cenozoic	15.5-18.8	15.5	Low flow
20171610017	01/10/2017	626992	RN030826	-15.609	129.018	Milligans Formation	24.55-30.55	27	Low flow
20171610018	01/10/2017	626992	RN030826	-15.609	129.018	Milligans Formation	24.55-30.55	27	Low flow
20181610001	13/10/2018	635732	RN040782	-15.364	129.209	Milligans Formation	85.8-91.8	39	Low flow
20181610005	16/10/2018	635921	RN040781	-15.242	129.217	Permo-Carb sandstone	120-126	124	Low flow
20181610007	08/11/2018	635734	RN040877	-15.446	129.046	Cenozoic	29-35	32	Low flow

Sample number	Sample date	Sample ID (GA Oracle database)	Bore ID	GDA 94 Latitude	GDA 94 Longitude	Hydrostratigraphic unit	Screened interval (mbgl)	Depth of pump (mbgl)	Sample collection method^
20181610008	09/11/2018	635736	RN040783	-15.305	129.087	Permo-Carb sandstone	124-130	92.5	Low flow
20181610009	10/11/2018	635743	RN040872	-15.173	129.283	Cenozoic	24-30	27	Low flow
20181610010	10/11/2018	635744	RN040780	-15.173	129.282	Permo-Carb sandstone	131.39-137.39	Artesian bore	Low flow
20181610011	10/11/2018	635729	RN040879	-15.242	129.217	Permo-Carb sandstone	25-31	28	Low flow
20181610012	11/11/2018	635728	RN040873	-15.32	129.188	Cenozoic	31-37	34	Low flow
20181610013	11/11/2018	635738	RN040883	-15.387	129.133	Permo-Carb sandstone	39-45	42	Low flow
20181610014	11/11/2018	635737	RN040884	-15.378	129.072	Permo-Carb sandstone	29-35	34	Low flow
20181610020	14/11/2018	635745	RN040871	-15.093	129.398	Cenozoic	41-47	44	Low flow
20181610021	14/11/2018	635730	RN040880	-15.228	129.22	Cenozoic	16-21	18.5	Low flow
20181610022	14/11/2018	635739	RN040881	-15.416	129	Cenozoic	29-35	32	Low flow
20181610023	29/11/2018	635746	RN040870	-15.093	129.398	Permo-Carb sandstone	85-91	40	Purging
20181610024	30/11/2018	635733	RN040874	-15.418	129.017	Cenozoic	18-24	21	Purging
20181610025	30/11/2018	635735	RN040878	-15.432	129.049	Permo-Carb sandstone	36-42	40	Purging
20181610026	30/11/2018	635740	RN040882	-15.407	129	Cenozoic	17-23	21	Purging
20181610027	30/11/2018	635741	RN040876	-15.419	129	Cenozoic	20-26	21	Purging
20181610028	30/11/2018	635742	RN040875	-15.433	129.001	Cenozoic	29-35	30	Purging

Table B.2. Field parameters.

Bore ID	pH	EC ($\mu\text{S}/\text{cm}$)	DO (mg/L)	ORP (mV)	Temperature (°C)	S^{2-} concentration ($\mu\text{g}/\text{L}$)	Fe^{2+} concentration (mg/L)	Total Alkalinity (HCO_3^- equivalent) (mg/L)
RN040883	4.91	230	1.45	143	28.8	6	0.32	32
RN040884	4.96	84	2.05	147	26.3	12	0.28	47
RN029659	7.4	3580	0.1	-156	19.1	12	0.42	339
RN040874	7.02	8170	0.27	-128	25.7	10	2.69	378
RN040780	7.58	530	0	-214	23.5	133	0.07	52
RN040870	7.16	587	0	-171	25.1	13	0.02	201
RN029656	6.65	20720	0.16	-74	28.2	14	0.4	421
RN040878	6.71	25800	0.05	-96	23.8	10	2.31	760
RN040882	6.81	6660	0.22	-56	26.6	10	0.31	329
RN040875	6.95	4378	0.06	-42	22	6	0.04	732
RN040873	6.58	49100	0.18	-81	28	6	OVR	268
RN040880	6.71	81000	0.1	-76	25	8	2.51	397
RN040881	6.6	7330	0.2	3	26.7	7	0.16	395
RN040876	7.11	2113	0.63	-87	26.8	13	0.08	552
RN040879	6.52	59000	0.23	-39	25.7	5	1.85	421
RN029659	7.2	4267	0.3	-169	31.6	N/A	0.16	332
RN029516	4.9	105.2	2.25	174	31.7	N/A	N/A	13
RN029660	7.3	1550	3.45	-66	28.1	N/A	N/A	552
RN029656	6.5	25420	0.15	-60	28	N/A	0.21	570

Bore ID	pH	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)
RN029662	5.5	59	4.47	190	27.7	N/A	0.26	22
RN030826	7.2	767	0.1	-116	27.7	N/A	0.35	382
RN040782	7.08	1015	0.81	-55	32.7	139	0.57	182
RN040781	6.32	26440	0	-205	33.7	621	1.36	258
RN040877	6.79	24966	0.07	4	31.6	16	0.5	425
RN040783	6.51	20.37	0	-269	34.9	201	2.78	138
RN040872	7.39	9859	0.01	-148	33.6	15	0.49	163
RN040780	7.51	695	1.27	-200	34.4	114	0.17	104
RN040879	6.57	77200	0.03	-9	28	0	OVR	342
RN040873	6.78	50207	0.07	-98	32.9	17	OVR	174
RN040883	6.18	412	0.67	8	36.1	36	0.63	71
RN040884	6.98	119	0.5	76	34.5	23	1.56	27
RN040871	6.52	66100	0.18	-33	n/a	29	2.46	464
RN040880	6.81	75800	0.13	-106	34.8	7	OVR	303
RN040881	6.83	4690	0.15	-14	32.4	40	0.14	293
RN040870	8.98	478	0.03	N/A	30.9	N/A	N/A	101
RN040874	7.91	6300	0.05	N/A	30.19	N/A	N/A	328
RN040878	7.69	102.3	0.06	N/A	30.81	N/A	N/A	603

Bore ID	pH	EC ($\mu\text{S}/\text{cm}$)	DO (mg/L)	ORP (mV)	Temperature (°C)	S^{2-} concentration ($\mu\text{g}/\text{L}$)	Fe^{2+} concentration (mg/L)	Total Alkalinity (HCO_3^- equivalent) (mg/L)
RN040882	7.85	5941.205374	0.17	N/A	31.97	N/A	N/A	264
RN040876	8.39	1880.872056	2.37	N/A	30.24	N/A	N/A	397
RN040875	8.14	4905.724507	0.11	N/A	31	N/A	N/A	588

*OVR = Readings above the range of analytical method

[^]N/A = not analysed, BDL = Below detection limit, OVR = Over measuring range

Table B.3 Major ion concentrations.

Bore ID	HCO_3^-	Cl^-	SO_4^{2-}	Br^-	F^-	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	%
RN040883	32	39.4	2.62	0.176	0.016	4	4	13	18	31	144	-4.09
RN040884	47	13.9	0.398	0.049	0.024	1	2	6	4	13.1	87	-33.92
RN029659	339	735	204	1.56	0.1	84	97	399	9	20.3	1887	-1.74
RN040874	378	1920	635	4.02	0.25	268	231	879	19	24.6	4355	-2.31
RN040780	52	188	9.55	0.489	0.076	41	11	94	17	8.2	421	8.02
RN040870	201	106	1.33	<0.500	0.25	19	5	90	8	6.49	437	-7.09
RN029656	421	5380	4350	11.5	0.5	630	645	3670	10	16.1	15123	-2.17
RN040878	760	7590	4490	10.8	0.5	509	636	4860	10	26.7	18882	-5.99
RN040882	329	1750	576	3.46	0.5	462	176	726	13	33.8	4067	1.38
RN040875	732	570	874	1.48	0.5	75	90	966	4	22.3	3334	5.74
RN040873	268	16000	2720	39.6	0.5	711	1220	9360	273	14	30567	3.18

Bore ID	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Br ⁻	F ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Si	TDS	CBE
RN040880	397	30300	4760	83.8	0.5	818	2230	18200	587	13.7	57306	3.21
RN040881	395	1920	494	4.22	0.578	354	205	1000	35	23.3	4426	4.87
RN040876	552	369	131	0.514	0.64	46	47	360	10	25.4	1541	-0.65
RN040879	421	31400	4430	83.8	0.5	814	2230	18300	580	7.68	58183	2.17
RN029659	332	1020	340	2.22	0.11	116	125	631	10	40.3	2617	2.36
RN029516	13	22	0	0.084	0.02	<1	2	10	7	42.4	97	N/A
RN029660	552	239	77	0.511	1.05	31	30	332	8	57.1	1327	3.23
RN029656	570	6270	5370	13.8	0.15	770	892	4810	12	41	18748	2.54
RN029662	22	6	3	0.023	0.03	<1	2	6	2	28.3	69	-10.93
RN030826	382	28	72	0.078	0.22	54	35	55	8	52.8	687	-2.87
RN040782	182	864	49.2	2.26	0.689	170	83	297	28	8.32	1682	0.87
RN040781	258	25300	3670	101	<1	817	1920	16100	446	11.3	48521	6.50
RN040877	425	5700	4780	12.1	<1	720	736	3690	13	22.4	16085	-3.12
RN040783	138	13.3	0.958	0.045	0.115	13	7	17.000	15	23.1	227	-6.20
RN040872	163	3580	331	8.75	0.332	92	143	1960	65	11.9	6346	-3.61
RN040780	104	191	5.83	0.515	0.065	43	12	101	18	8.79	484	5.03
RN040879	342	32700	4120	105	<1	790	2110	17300	544	8.25	57913	-2.00
RN040873	174	18200	2370	52	<1	664	1200	9160	274	13.9	32055	-2.85
RN040883	71	67.2	8.7	0.225	0.045	10	10	61	22	26.1	276	16.50
RN040884	27	15.6	0.84	0.055	0.031	5	4	16	4	13.7	86	20.88
RN040871	464	29300	3460	88.4	<1	716	1480	15900	341	18.5	51679	-3.00
RN040880	303	34300	4210	107	<1	797	2120	17600	558	10.7	59898	-3.49

Bore ID	HCO_3^-	Cl^-	SO_4^{2-}	Br^-	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Si	TDS	CBE
RN040881	293	2140	652	4.55	<0.5	357	186	930	33	22.5	4613	-3.39
RN040870	101	113	0.817	0.298	0.077	19	5	91	8	6.28	344	6.37
RN040874	328	1880	561	3.98	<0.5	273	217	840	20	25.8	4144	-1.67
RN040878	603	7240	3920	15.4	<1	484	609	4630	10	27.2	17522	-4.37
RN040882	264	1770	546	3.81	<1	443	166	655	14	32.7	3890	-1.35
RN040876	397	384	116	<1	<1	49	44	344	10	25.3	1368	3.33
RN040875	588	620	1080	1.53	<1	76	83	893	4	23.8	3367	-1.53

Table B.4 Stable Isotopes of water results.

Bore ID	$\delta^2\text{H} (\text{\textperthousand})$	$\delta^{18}\text{O} (\text{\textperthousand})$
RN040883	-46.4	-6.71
RN040884	-46.2	-6.95
RN029659	-54	-7.57
RN040874	-49.4	-6.96
RN040780	-51.8	-7.64
RN040870	-51.7	-7.62
RN029656	-54.5	-7.62
RN040878	-42.4	-5.96
RN040882	-49.5	-7.13
RN040875	-52.7	-7.66
RN040873	-2.2	0.97

Bore ID	$\delta^{2\text{H}} (\text{\textperthousand})$	$\delta^{18\text{O}} (\text{\textperthousand})$
RN040880	-5.8	-0.33
RN040881	-49	-7.08
RN040876	-53	-7.77
RN040879	-3.4	0
RN029659	-51.0	-6.68
RN029516	-47.5	-6.68
RN029660	-50.6	-6.90
RN029656	-45.1	-5.96
RN029662	-47.5	-7.00
RN030826	-52.0	-7.55
RN040782	-47.0	-6.75
RN040781	-14.1	-1.32
RN040877	-42.4	-5.77
RN040783	-47.2	-6.87
RN040872	-45.2	-6.27
RN040780	-50.5	-7.36
RN040879	-4.1	0.23
RN040873	-1.6	1.29
RN040883	-44.6	-6.41
RN040884	-44.0	-6.60
RN040871	-19.3	-2.37
RN040880	-4.0	0.31

Bore ID	$\delta^{2\text{H}} (\text{\textperthousand})$	$\delta^{18\text{O}} (\text{\textperthousand})$
RN040881	-47.7	-6.67
RN040870	-51.5	-7.64
RN040874	-49.3	-6.99
RN040878	-41.9	-5.91
RN040882	-52.4	-7.80
RN040876	-61.3	-8.89
RN040875	-52.4	-7.59

Table B.5 Sr Isotope Results.

Bore ID	$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio
RN040884	0.762703
RN040874	0.725850
RN040780	0.732271
RN040870	0.727403
RN040870	0.727413
RN040878	0.724232
RN040882	0.726408
RN040875	0.722382
RN040881	0.726487
RN040876	0.726393

Bore ID	$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio
RN029659	0.72420
RN029663	0.72661
RN029516	0.80312
RN029660	0.72639
RN029656	0.72366
RN029662	0.73062
RN030826	0.72404
RN030826	0.72404
RN040877	0.72374
RN040879	0.70941
RN040873	0.71029
RN040883	0.71754
RN040871	0.71025
RN040880	0.70948

Table B.6 CFC and SF₆ results.

Sample number	Bore ID	Sample date	Lab used for analysis	CFC-11 (pmoles/kg)	CFC-12 (pmoles/kg)	CFC-113 (pmoles/kg)	Measured conc SF ₆ (fmol/kg)
2019161007	RN040870	24/07/2019	Utah	0.014	0.15	ND*	N/A
2019161007	RN040870	24/07/2019	Utah	0.011	0.17	ND	N/A
2019161015	RN040870	24/07/2019	GNS	0.01	0.05	ND	N/A
2019161015	RN040870	24/07/2019	GNS	0.00	0.05	ND	N/A
2019161008	RN040870	24/07/2019	GNS	0.01	0.02	ND	N/A
2019161008	RN040870	24/07/2019	GNS	0	0	ND	N/A
2019161001	RN040883	19/07/2019	Utah	0.171499	0.228049	ND	N/A
2019161001	RN040883	19/07/2019	Utah	0.109193	0.188508	ND	N/A
2019161002	RN040884	20/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161002	RN040884	20/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161003	RN029659	21/07/2019	Utah	< 0.014	< 0.17	ND	4.43
2019161003	RN029659	21/07/2019	Utah	< 0.014	< 0.17	ND	
2019161005	RN040874	21/07/2019	Utah	0.113205	0.205687	ND	N/A
2019161005	RN040874	21/07/2019	Utah	0.165043	0.205292	ND	N/A
2019161009	RN029656	25/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161009	RN029656	25/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161011	RN040878	26/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161011	RN040878	26/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161012	RN040882	26/07/2019	Utah	< 0.014	< 0.17	ND	2.93

Sample number	Bore ID	Sample date	Lab used for analysis	CFC-11 (pmoles/kg)	CFC-12 (pmoles/kg)	CFC-113 (pmoles/kg)	Measured conc SF ₆ (fmol/kg)
2019161012	RN040882	26/07/2019	Utah	< 0.014	< 0.17	ND	
2019161014	RN040875	27/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161014	RN040875	27/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161016	RN040873	29/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161016	RN040873	29/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161017	RN040880	30/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161017	RN040880	30/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161018	RN040881	31/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161018	RN040881	31/07/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161019	RN040876	31/07/2019	Utah	1.186014	1.123218	0.072489	N/A
2019161019	RN040876	31/07/2019	Utah	1.238754	1.462859	0.069916	N/A
2019161020	RN040879	1/08/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161020	RN040879	1/08/2019	Utah	< 0.014	< 0.17	ND	N/A
2019161004	RN029659	21/07/2019	GNS	< 0.014	< 0.17	ND	N/A
2019161004	RN029659	21/07/2019	GNS	< 0.014	< 0.17	ND	N/A
2019161010	RN029656	25/07/2019	GNS	< 0.014	< 0.17	ND	N/A
2019161010	RN029656	25/07/2019	GNS	< 0.014	< 0.17	ND	N/A
2019161013	RN040882	26/07/2019	GNS	0.17	0.11	ND	N/A
2019161013	RN040882	26/07/2019	GNS	0.18	0.11	ND	N/A

*ND = Not detected

Table B.7 Radiocarbon data.

Sample number	Bore ID	$\delta^{13}\text{C}$ (‰)	$\delta^{13}\text{C}$ error (+/- ‰)	^{14}C as Percent Modern Carbon	^{14}C error (+/-)
2019161001	RN040883	-17.4	0.3	90.94	0.3
2019161002	RN040884	-17.4	0.1	91.68	0.32
2019161005	RN040874	-11.9	0.1	77.93	0.23
2019161012	RN040882	-10.5	0.3	58.96	0.22
2019161014	RN040875	-12.1	0.1	61.63	0.21
2019161016	RN040873	-9.4	0.2	88.23	0.3
2019161017	RN040880	-5.9	0.4	88.64	0.23
2019161018	RN040881	-10.1	0.1	53.26	0.19
2019161020	RN040879	-7.6	0.1	88.56	0.24
20171610001	RN029659	-12.5	0.1	74.55	0.16
20171610003	RN029516	-12.4	0.1	98.05	0.25
20171610007	RN029660	-12.8	0.1	97.9	0.24
20171610010	RN029656	-10.2	0.1	79.56	0.17
20171610016	RN029662	-14.1	0.1	82.99	0.27
20171610017	RN030826	-10.9	0.1	55.39	0.14
20171610018	RN030826	-10.9	0.1	54.78	0.14
20181610001	RN040782	-8.9	0.2	5.7	0.05
20181610005	RN040781	-8.7	0.1	73.07	0.18
20181610007	RN040877	-12	0.1	73.22	0.23
20181610009	RN040872	-12.2	0.1	14.65	0.09
20181610010	RN040780	-13.2	0.1	7.54	0.06
20181610013	RN040883	-13.8	0.1	91.1	0.22

Sample number	Bore ID	$\delta^{13}\text{C}$ (‰)	$\delta^{13}\text{C}$ error (+/- ‰)	^{14}C as Percent Modern Carbon	^{14}C error (+/-)
20181610023	RN040870	-12.6	0.2	3.45	0.04
20181610025	RN040878	-12.9	0.2	89.81	0.23
20181610027	RN040876	-11.1	0.2	86.13	0.22

Appendix C Surface Water hydrochemistry Data

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

Sample number	Date collected	eno	Site name	Latitude	Longitude	pH	EC (µS/cm)	DO (mg/L)	ORP (mV)	Temperature (°C)	Total Alkalinity (mg/L) (HCO ₃ equivalent)	S ²⁻ (µg/L)	Fe ²⁺ (mg/L)
20191620 01	23/07/2019	644657	Oakes Creek	-15.323426	129.086377	8.47	15930	5.47	147	20.4	214	0	0.36
20191620 02	27/07/2019	644658	Sandy Creek Lower*	-15.359732	129.204959	8.08	502	1.28	77	17.4	226	0	0.51
20191620 03	27/07/2019	644658	Sandy Creek Estuary	-15.291638	129.209903	8.17	76700	3.05	96	23	229	0	0.14
20171620 003	28/09/2017	627057	Upper Keep River (pool)*	15.63388889	129.0369444	8.2	730	3.75	74	27.1	259	N/A	N/A
20171620 008	3/10/2017	627050	Keep E1	15.32583333	129.1183333	7.8	43600	4.76	124	31.7	249	N/A	N/A
20171620 009	3/10/2017	627051	Keep K1	15.34166667	129.0833333	8.5	20100	6.58	90	28.9	269	N/A	N/A

*Samples collected from dry season pools/waterholes, not from flowing streams.

Table C.2 Major ion concentrations of surface water.

Sample location	HCO_3^-	Cl^-	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	%
Oakes Creek	214	15800	1740	1.98	26.3	438	1070	8210	200	2.16	27676	-1.63
Sandy Creek Lower	226	42.2	7.02	1.66	<1.00	39	26	10	22	8.07	382	0.37
Sandy Creek Estuary	229	28700	3790	0.5	49.5	722	1980	16400	567	2.28	52391	1.61
Upper Keep River (pool)	259	57	65	0.16	0.088	50	30	50	7	30.9	548	0.84
Keep E1	249	18300	2500	0.54	50.9	463	1490	11400	345	11.7	34810	6.32
Keep K1	269	5750	778	0.23	15.2	173	453	3580	132	5.2	11155	5.67

Table C.3 Isotope results of surface water.

Sample number	$\delta^{2\text{H}} (\text{\textperthousand})$	$\delta^{18\text{O}} (\text{\textperthousand})$
Oakes Creek	35.3	10.7
Sandy Creek Lower	16.8	5.76
Sandy Creek Estuary	31.2	6.6
Upper Keep River (pool)	-13.9	0.66
Keep E1	5.5	2.50
Keep K1	-9.9	0.64

Duplicates of the stable isotopes were taken by ANSTO and are shown in Appendix D.

Table C.4 Sr isotope results of surface water.

Sample number	$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio
Oakes Creek	0.711537
Sandy Creek Lower	0.729030
Sandy Creek Estuary	0.709271
Upper Keep River (pool)	0.72726
Keep E1	0.70946
Keep K1	0.71087

Appendix D Quality Control Data

D.1 Laboratory Duplicates

Laboratory duplicate results are shown in Table D.1 and Table D.2.

Table D.1 Laboratory duplicate results for anions.

Sample number		Br^-	F^-	Cl^-	SO_4^{2-}	Si
20181610001	Original (mg/L)	2.26	0.689	864	49.2	N/A
	Duplicate (mg/L)	2.25	0.488	864	43.2	N/A

Sample number		Br ⁻	F ⁻	Cl ⁻	SO ₄ ²⁻	Si
	RPD	0.44	34.15	0.00	12.99	N/A
20181610020	Original (mg/L)	88.4	<1.00	29300	3460	18.5
	Duplicate (mg/L)	83.6	<1.00	29300	3420	18.5
	RPD	5.58	-	0.0	1.16	0.0
20181610029	Original (mg/L)	N/A	N/A	N/A	N/A	424
	Duplicate (mg/L)	N/A	N/A	N/A	N/A	440
	RPD	N/A	N/A	N/A	N/A	3.70
2019161001	Original (mg/L)	0.176	0.016	39.4	2.62	31
	Duplicate (mg/L)	0.175	0.016	39.4	2.6	31.4
	RPD	0.57	0.0	0.0	0.77	1.28
2019161008	Original (mg/L)	0.278	0.099	110	0.691	N/A
	Duplicate (mg/L)	0.275	0.087	108	0.685	N/A
	RPD	1.08	12.9	1.83	0.87	N/A
2019162001	Original (mg/L)	26.3	1.98	15800	1740	N/A
	Duplicate (mg/L)	30	<1.00	17100	1800	N/A
	RPD	13.14	-	7.90	3.39	N/A
2019161014	Original (mg/L)	N/A	N/A	N/A	N/A	22.3
	Duplicate (mg/L)	N/A	N/A	N/A	N/A	22.4
	RPD	N/A	N/A	N/A	N/A	0.45
2019392001	Original (mg/L)	N/A	N/A	N/A	N/A	7.87
	Duplicate (mg/L)	N/A	N/A	N/A	N/A	7.71
	RPD	N/A	N/A	N/A	N/A	2.05

Sample number		Br ⁻	F ⁻	Cl ⁻	SO ₄ ²⁻	Si
2019161016	Original (mg/L)	N/A	N/A	N/A	N/A	14
	Duplicate (mg/L)	N/A	N/A	N/A	N/A	13.6
	RPD	N/A	N/A	N/A	N/A	2.90
20171610010	Original (mg/L)	13.8	0.154	6270	5370	N/A
	Duplicate (mg/L)	13.9	0.154	6340	5420	N/A
	RPD	0.72	0.00	1.11	0.93	N/A

Table D.2 Laboratory duplicate results for cations.

Sample number		Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
20181610001	Original (mg/L)	170	83	297	28
	Duplicate (mg/L)	164	82	292	27
	RPD	3.59	1.21	1.70	3.64
20181610020	Original (mg/L)	716	1480	15900	341
	Duplicate (mg/L)	725	1460	15800	344
	RPD	1.25	1.36	0.63	0.88
2019161002	Original (mg/L)	1	2	6	4
	Duplicate (mg/L)	1	2	6	4
	RPD	0.0	0.0	0.0	0.0
2019161012	Original (mg/L)	462	176	726	13
	Duplicate (mg/L)	454	178	736	13

	Sample number	Ca^{2+}	Mg^{2+}	Na^+	K^+
	RPD	1.75	1.13	1.37	0.0
2019392002	Original (mg/L)	38	27	2	<1
	Duplicate (mg/L)	38	27	2	<1
	RPD	0.0	0.0	0.0	-
2019161008	Original (mg/L)	18	4	88	8
	Duplicate (mg/L)	18	4	86	8
	RPD	0.0	0.0	2.30	0.0
20171610001	Original (mg/L)	116	125	631	10
	Duplicate (mg/L)	114	126	635	10
	RPD	1.74	0.80	0.63	0.0

D.2 Field Duplicates

RPD values are calculated for all duplicate samples in Table D.3 and Table D.4.

*RPD = Relative percent difference

Table D.3 RPD values for duplicate major ion samples.

RN		Sample Number	Cl ⁻	SO ₄ ²⁻	Br ⁻	F ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Si
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
RN029659	Original (mg/L)	2019161003	735	204	1.56	0.1	84	97	399	9	20.3
	Duplicate (mg/L)	2019161004	734	205	1.56	0.1	85	97	396	9	20.6
	RPD		0.14	0.49	0.00	0.00	1.18	0.00	0.75	0.00	1.47
RN040870	Original (mg/L)	2019161007	106	1.33	<0.500	0.25	19	5	90	8	6.49
	Duplicate (mg/L)	2019161008	110	0.691	0.278	0.099	19	5	87	8	6.52
	RPD		3.70	63.24	-	86.53	0.00	0.00	3.39	0.00	0.46
RN030826	Original (mg/L)	20171610017	28	72	0.078	0.22	54	35	55	8	52.8
	Duplicate (mg/L)	20171610018	28	72	0.078	0.22	55	35	55	8	53
	RPD		0.00	0.00	0.00	0.00	1.83	0.00	0.00	0.00	0.38

Table D.4 RPD value for stable isotopic data.

RN or Field Site		Sample Number	$\delta^2\text{H} (\text{\textperthousand})$	$\delta^{18}\text{O} (\text{\textperthousand})$
RN030826	Original	20171610017	-52.0	-7.55
	Duplicate	20171610018	-52.4	-7.54
	RPD		0.77	0.13
RN040883	Original	2019161001	-46.4	-6.71
	Duplicate	2019161001 - 2	-46.4	-6.71
	RPD		0.00	0.00
RN040884	Original	2019161002	-46.2	-6.95
	Duplicate	2019161002 - 2	-45.3	-6.87
	RPD		1.97	1.16
RN029659	Original	2019161003	-54	-7.57
	Duplicate	2019161003 - 2	-53.4	-7.52
	RPD		1.12	0.66
RN029659	Original	2019161004	-53.9	-7.55
	Duplicate	2019161004 - 2	-53.9	-7.55
	RPD		0.00	0.00
RN040874	Original	2019161005	-49.4	-6.96
	Duplicate	2019161005 - 2	-49.4	-6.96
	RPD		0.00	0.00
RN040780	Original	2019161006	-51.8	-7.64

RN or Field Site	Sample Number	$\delta^{2\text{H}} (\text{\textperthousand})$	$\delta^{18\text{O}} (\text{\textperthousand})$	
RN040870	Duplicate	2019161006 - 2	-51.5	-7.56
	RPD		0.58	1.05
	Original	2019161007	-51.7	-7.62
RN040870	Duplicate	2019161007 - 2	-51.4	-7.62
	RPD		0.58	0.00
	Original	2019161008	-51.7	-7.62
RN040870	Duplicate	2019161008 - 2	-51.7	-7.62
	RPD		0.00	0.00
	Original	2019161009	-54.5	-7.62
RN029656	Duplicate	2019161009 - 2	-54.3	-7.59
	RPD		0.37	0.39
	Original	2019161011	-42.4	-5.96
RN040878	Duplicate	2019161011 - 2	-42.4	-5.96
	RPD		0.00	0.00
	Original	2019161012	-49.5	-7.13
RN040882	Duplicate	2019161012 - 2	-49.5	-7.13
	RPD		0.00	0.00
	Original	2019161014	-52.7	-7.66
RN040875	Duplicate	2019161014 - 2	-52.5	-7.64
	RPD		0.38	0.26
	Original	2019161016	-2.2	0.97
RN040873	Duplicate	2019161016 - 2	-2.2	0.97

RN or Field Site	Sample Number	$\delta^{2\text{H}} (\text{\textperthousand})$	$\delta^{18\text{O}} (\text{\textperthousand})$
	RPD	0.00	0.00
RN040880	Original	2019161017	-5.8
	Duplicate	2019161017 - 2	-4.6
	RPD		23.08
RN040881	Original	2019161018	-49
	Duplicate	2019161018 - 2	-49
	RPD		0.00
RN040876	Original	2019161019	-53
	Duplicate	2019161019 - 2	-53
	RPD		0.00
RN040879	Original	2019161020	-3.4
	Duplicate	2019161020 - 2	-1.1
	RPD		102.22
Oakes Creek	Original	2019162001	35.3
	Duplicate	2019162001 - 2	35.4
	RPD		0.28
Sandy Creek Lower	Original	2019162002	16.8
	Duplicate	2019162002 - 2	16.8
	RPD		0.00
Sandy Creek Estuary	Original	2019162003	31.2
	Duplicate	2019162003 - 2	32.1
	RPD		2.84
			0.76

