

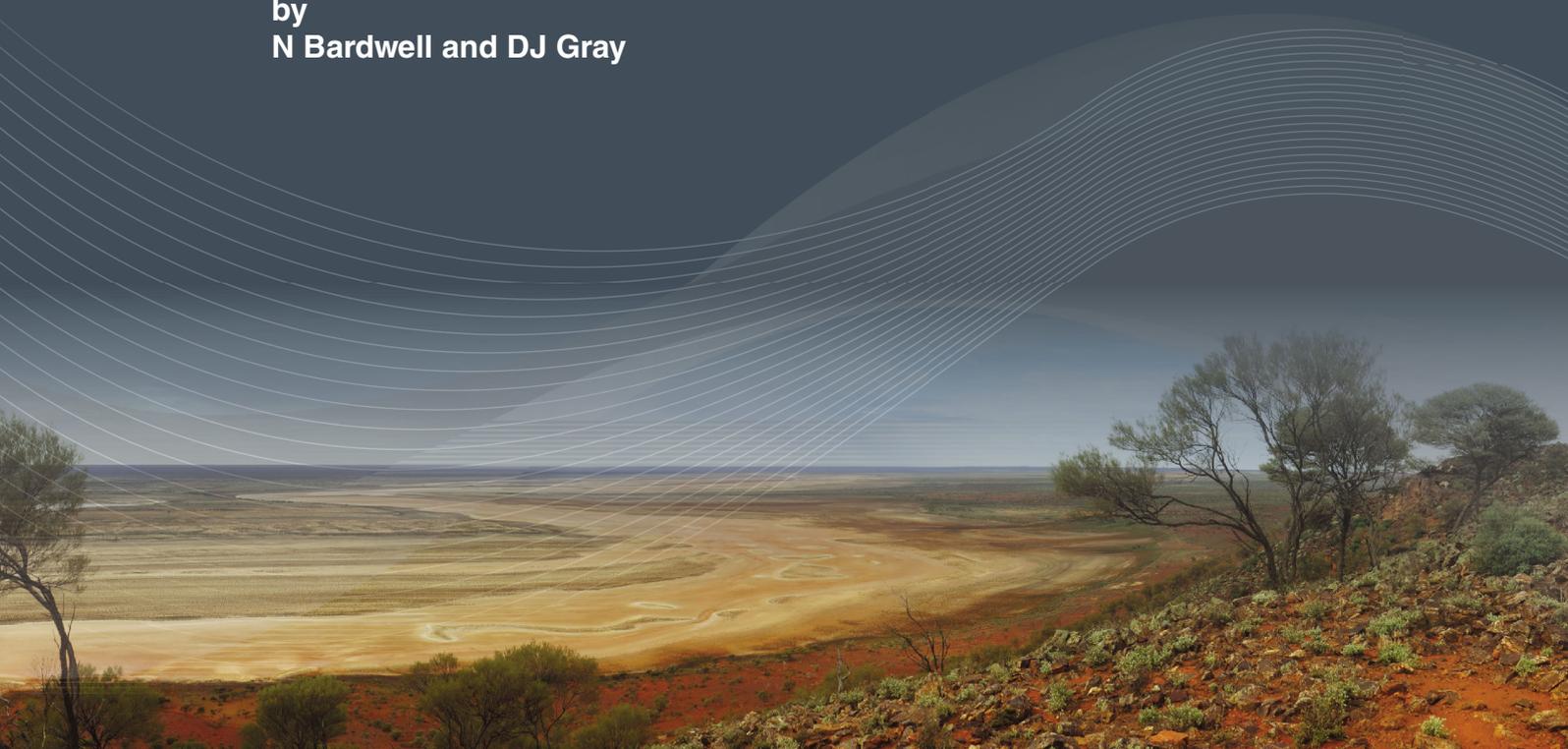


Government of **Western Australia**
Department of **Mines and Petroleum**

RECORD 2016/7

HYDROGEOCHEMISTRY OF WESTERN AUSTRALIA DATA RELEASE: ACCOMPANYING NOTES

by
N Bardwell and DJ Gray



Geological Survey of
Western Australia





Government of **Western Australia**
Department of **Mines and Petroleum**

Record 2016/7

HYDROGEOCHEMISTRY OF WESTERN AUSTRALIA DATA RELEASE: ACCOMPANYING NOTES

by
N Bardwell and DJ Gray

Perth 2016



**Geological Survey of
Western Australia**

MINISTER FOR MINES AND PETROLEUM
Hon. Sean K L'Estrange MLA

DIRECTOR GENERAL, DEPARTMENT OF MINES AND PETROLEUM
Richard Sellers

EXECUTIVE DIRECTOR, GEOLOGICAL SURVEY OF WESTERN AUSTRALIA
Rick Rogerson

REFERENCE

The recommended reference for this publication is:

Bardwell, N and Gray, DJ 2016, Hydrogeochemistry of Western Australia, Data release: accompanying notes: Geological Survey of Western Australia, Record 2016/7, 40p.

National Library of Australia Card Number and ISBN 978-1-74168-688-3

About this publication

This Record presents the notes to accompany data provided to CSIRO from the Department of Water, which forms part of a national hydrogeochemistry program. GSWA is releasing the report as part of its Record Series to ensure that the data are understood by the wider community. The scientific content of the Record, and the drafting of figures, has been the responsibility of CSIRO. No editing has been undertaken by GSWA.

Grid references in this publication refer to the Geocentric Datum of Australia 1994 (GDA94). Locations mentioned in the text are referenced using Map Grid Australia (MGA) coordinates, Zone 50. All locations are quoted to at least the nearest 100 m.

Disclaimer

This product was produced using information from various sources. The Department of Mines and Petroleum (DMP) and the State cannot guarantee the accuracy, currency or completeness of the information. DMP and the State accept no responsibility and disclaim all liability for any loss, damage or costs incurred as a result of any use of or reliance whether wholly or in part upon the information provided in this publication or incorporated into it by reference.

Published 2016 by Geological Survey of Western Australia

This Record is published in digital format (PDF) and is available online at <www.dmp.wa.gov.au/GSWApublications>.

Further details of geological products and maps produced by the Geological Survey of Western Australia are available from:

Information Centre
Department of Mines and Petroleum
100 Plain Street
EAST PERTH WESTERN AUSTRALIA 6004
Telephone: +61 8 9222 3459 Facsimile: +61 8 9222 3444
www.dmp.wa.gov.au/GSWApublications

Cover image: Elongate salt lake on the Yilgarn Craton — part of the Moore–Monger paleovalley — here viewed from the top of Wownaminya Hill, 20 km southeast of Yalgoo, Murchison Goldfields. Photograph taken by I Zibra for the Geological Survey of Western Australia



Hydrogeochemistry of Western Australia

Data Release: Accompanying Notes

Nicole Bardwell and David J. Gray

EP156404

December 2015

Citation

Gray, David J. and Bardwell, Nicole (2015). Hydrogeochemistry of Western Australia: Data Release: Accompanying Notes. CSIRO, Australia. EP156404 37p

Copyright and disclaimer

© 2015 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

Important disclaimer

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

Contents

1	Introduction	1
2	Data QA/QC Workflow	1
2.1	General Conversions	1
2.2	Conductivity	2
2.3	Alkalinity and pH (Figure 2).....	2
2.4	Al and pH.....	3
2.5	Salinity and Major Ions	3
2.6	Nitrogen and Organic Carbon	5
2.7	Minors	5
2.8	Base Metals and Trace Elements	7
2.9	Isotopes.....	8
3	Element and Exploration Indices	11
3.1	Ion Ratios	11
3.2	Ion Excess or Deficit	12
4	Solution Modelling	13
4.1	Activity Plots	13
4.2	Mineral Saturation Indices.....	14
5	Some Results	16
6	Conclusion	32
	References	33

Table of Figures

Figure 1: Positions of WA groundwaters	1
Figure 2: Initial HCO ₃ vs. pH, and results following QA/QC correction of the WA groundwater data	2
Figure 3: Initial Al vs. pH, and results following QA/QC correction of the WA groundwater data	3
Figure 4: Initial SO ₄ vs. Cl, and results following QA/QC correction of the WA groundwater data	4
Figure 5: Initial Charge Balance vs. TDS, and results following QA/QC correction of the WA groundwater data	4
Figure 6: Initial K vs. Na, and results following QA/QC correction of the WA groundwater data	5
Figure 7: Initial Mg vs. Na, and results following QA/QC correction of the WA groundwater data	5
Figure 8: Initial F vs. TDS, and results following QA/QC correction of the WA groundwater data	6
Figure 9: Initial Br vs. Cl, and results following QA/QC correction of the WA groundwater data	6
Figure 10: Initial P vs. TDS, and results following QA/QC correction of the WA groundwater dat	6
Figure 11: Initial B vs. Na, and results following QA/QC correction of the WA groundwater data	7
Figure 12: Initial Sr vs. Ca, and results following QA/QC correction of the WA groundwater data	7
Figure 13: Initial Fe vs. pH, and results following QA/QC correction of the WA groundwater data	8
Figure 14: Initial Mn vs. pH, and results following QA/QC correction of the WA groundwater data	8
Figure 15: Initial Cu vs. pH, and results following QA/QC correction of the WA groundwater data	9
Figure 16: Initial Zn vs. pH, and results following QA/QC correction of the WA groundwater data	9
Figure 17: Initial Pb vs. pH, and results following QA/QC correction of the WA groundwater data	9
Figure 18: Initial Cr vs. pH, and results following QA/QC correction of the WA groundwater data	10
Figure 19: Initial U vs. pH, and results following QA/QC correction of the WA groundwater data	10
Figure 20: Initial ² H vs. ¹⁸ O, and results following QA/QC correction of the WA groundwater data	10
Figure 21: Dissolved Ca vs. Na for WA groundwaters, coloured by the CaNaSW range	12
Figure 22: Dissolved Ca vs. Na for WA groundwaters, coloured by the CaNaDSW range	13
Figure 23: Modelled Eh-pH plot of Fe speciation overlain with Eh:pH data for WA groundwater	14
Figure 24: Modelled Eh-pH plot of Fe speciation (crystalline Fe oxides not involved) overlain with Eh:pH data for WA groundwater	14
Figure 25: Gypsum Saturation Index (SI) vs. TDS for WA groundwaters	15
Figure 26: Calcite Saturation Index (SI) vs. pH for WA groundwaters	15
Figure 27: Groundwater pH vs. TDS for the Western Australian groundwater dat	16
Figure 28: TDS distribution across Australia and in Western Australia	18
Figure 29: Groundwater pH distribution across Australia and in Western Australia	19
Figure 30: Groundwater Mg:Na Ion Ratio (MgNaSW) distribution across Australia and in Western Australia	20
Figure 31: Groundwater Ca:Na Ion Ratio (CgNaSW) distribution across Australia and in Western Australia	21
Figure 32: Groundwater Ca:Na Ion Difference (CaNaDSW) distribution across Australia and in Western Australia	22
Figure 33: Groundwater K:Na Ion Ratio (KNaSW) distribution across Australia and in Western Australia	23
Figure 34: Groundwater K:Na Ion Difference (KaNaDSW) distribution across Australia and in Western Australia	24
Figure 35: Groundwater Br:Cl Ion Ratio (BrClSW) distribution across Australia and in Western Australia	25
Figure 36: Groundwater SO ₄ :Cl Ion Ratio (SO ₄ ClSW) distribution across Australia and in Western Australia	26
Figure 37: Groundwater gypsum saturation distribution across Australia and in Western Australia	27
Figure 38: Groundwater celestine saturation distribution across Australia and in Western Australia	28
Figure 39: Groundwater F concentration distribution across Australia and in Western Australia	29
Figure 40: Groundwater U concentration distribution across Australia and in Western Australia	30
Figure 41: Groundwater Mo concentration distribution across Australia and in Western Australia	31

1 Introduction

This is the accompanying notes to the revised groundwater data from the Government of Western Australia (WA). Data was supplied by Lindsay Preece and Robert Lavis from Water Information Management at the Department of Water, Western Australia. If users need original files, they can contact the authors to obtain a new copy. By combining data into one file, with consistent detection limits, correcting for analytical differences, and comparing with recent data, these data should now be readily usable and “seamlessly” comparable. This data release is part of the “Continental Scale Hydrogeochemistry” initiative (Figure 1).

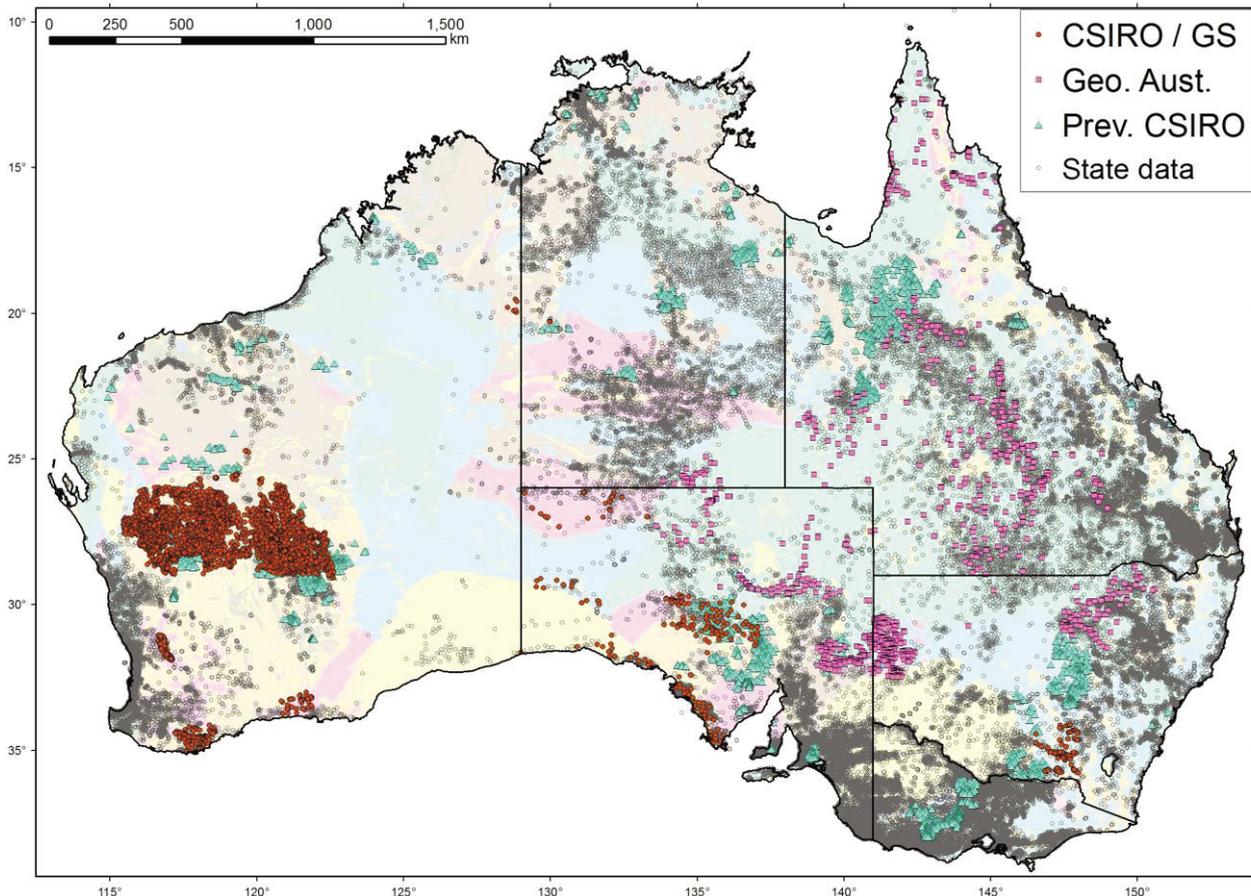


Figure 1: Positions of WA groundwaters (grey circles within WA), along with sampling by CSIRO and Geological Surveys (Forbes et al., 2013; Giblin, 2001; Gray, 2015; Gray et al. 2012, 2014, 2015, 2016a,b), Geoscience Australia Curnamona sampling (de Caritat et al., 2005), Geoscience Australia Great Artesian Basin sampling (Radke et al., 2000), and other State samples (Bardwell and Gray, 2015a,b; Gray and Bardwell, 2015a,b,2016).

2 Data QA/QC Workflow

2.1 General Conversions

The object of this was to produce a single, robust groundwater dataset for WA that could be combined with other datasets across Australia. When the same data were expressed in different ways (e.g. Oxidised N and NO₃ N) columns were combined. A common issue with minor and trace elements was mis-assigned units (supposedly as mg/L in the database but more likely µg/L, which would result in values 1000x too high if not corrected or deleted). These were either divided by 1000 when this was unambiguous, or deleted when the issue could not be resolved. Groups of specific analyses with high detection limits were removed.

In some cases, field, isotope and chemical data for the same sample appeared to be separated as different samples. These were recombined. All ">" values, were removed and "<" was converted to "-". Data columns with very few values (generally < 12) were discarded. Note that these modifications are only a minor component of the dataset. The deletions represent the removal of a minor proportion of apparently erroneous data that could not be verified.

2.2 Conductivity

The database received contained two columns with conductivity data. All conductivity (field) data was removed due to the ambiguity of the units used. Conductivity (lab) data, in $\mu\text{S}/\text{cm}$, with values below 100 and above 300,000 were deleted as they were below detection limits and erroneous, respectively. The remaining conductivity data was used to calculate total dissolved solids (Section 2.5) for a number of samples and then removed from the final database. For numerous samples there were duplicate lines that contained different data. In these cases, the duplicate line with additional elemental data was maintained, and duplicates containing salinity and/or Cl data only, with no additional chemical data, were deleted.

2.3 Alkalinity and pH (Figure 2)

Alkalinity was measured in varying ways: e.g., as HCO_3^- , CO_3^{2-} and CaCO_3 equivalencies. All data was recalculated as HCO_3^- equivalency and combined (Figure 2). Any pH values below 1.8 and above 12.9 were deleted as these were suspected to be erroneous.

The pH and HCO_3^- data were verified, based on an understanding of HCO_3^- speciation vs pH. Very high (> 1,000 mg/L) HCO_3^- values were checked, when the particular sample calculated to have poor electrical balance (Section 2.5), or other sample duplicates had HCO_3^- values more than 10x lower, the particular HCO_3^- value was deleted (Figure 2).

Other HCO_3^- and pH were cross-checked, according to:

If $\text{pH} < 4.5$ and $\text{HCO}_3^- > 5$ and $< 25 \rightarrow$ change HCO_3^- to 0;

If $\text{pH} < 4.5$ and $\text{HCO}_3^- > 25 \rightarrow$ remove both pH and HCO_3^- ;

If $\text{pH} < 5$ and $\text{HCO}_3^- > 50$ and $\text{Al} > 5 \rightarrow$ remove HCO_3^- ;

If $\text{pH} < 5$ and $\text{HCO}_3^- > 10 \rightarrow$ remove both pH and HCO_3^- ;

If $\text{pH} > 7$ and $\text{HCO}_3^- > 0$ and $< 5 \rightarrow$ remove HCO_3^- .

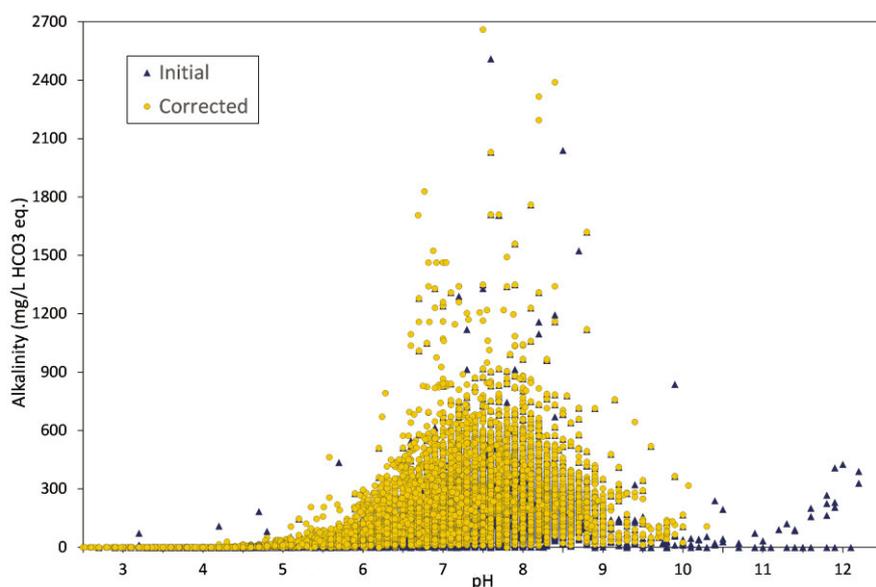


Figure 2: Initial HCO_3^- vs. pH, and results following QA/QC correction of the WA groundwater data

2.4 Al and pH

Anomalous Al data (> 1 mg/L for pH > 6) were deleted (Figure 3). These may be incorrect units of measure of µg/L data assigned as mg/L in the database.

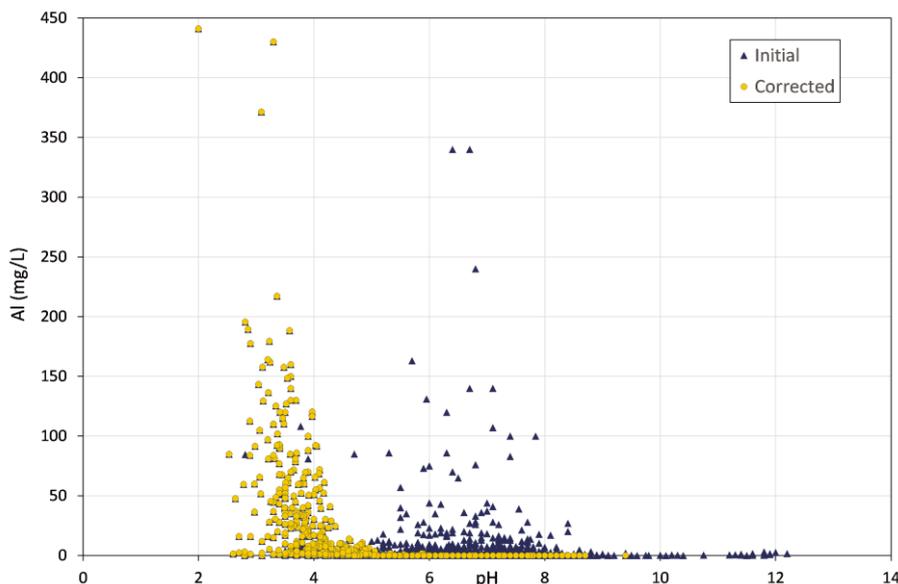


Figure 3: Initial Al vs. pH, and results following QA/QC correction of the WA groundwater data. Single erroneous initial data with Al = 750 mg/L not shown.

2.5 Salinity and Major Ions

Based on charge balance calculations (see below), and checking with plotting against Cl, SO₄ -S appeared to actually be SO₄, and S and S²⁻ appeared to be SO₄ - S. These were corrected and SO₄ was calculated for each sample on this basis. Salinity is measured as total dissolved solids (TDS; commonly in mg/L), and would generally be determined as the sum of all major ions (i.e., first formula below). However, much of the data had missing major element values. To deal with this, and obtain the most accurate TDS value possible, salinity was determined, in order (and with the proportion of samples calculated in brackets), according to:

TDS = Na + K + Mg + Ca + Cl + SO ₄ + 0.49*HCO ₃ (all data present)	(15.0%)
TDS = (Cl + SO ₄ + 0.49*HCO ₃) / 0.64	(0.6%)
TDS = (Na + K + Mg + Ca) / 0.37	(0.9%)
TDS = (Cl + 50) / 0.57	(23.5%)
TDS = (Na + 50) / 0.325	(0.1%)
TDS = TDS value from original database	(3.5%)
TDS = Cond / 1.45	(45.6%)
TDS not calculated	(10.8%)

Charge balance was calculated, according to:

$$\frac{(Na/22.99 + K/39.1 + Mg/12.15 + Ca/20.04) - (Cl/35.45 + SO_4/48.03 + HCO_3/61.02)}{(Na/22.99 + K/39.1 + Mg/12.15 + Ca/20.04) + (Cl/35.45 + SO_4/48.03 + HCO_3/61.02)}$$

This calculated balance was plotted vs TDS (Figure 5). The charge balance is expected to be zero, and the calculated balance should be between -0.05 and 0.05, except for very fresh waters for which other phases not used in the calculation can affect the calculated balance. All anomalous points were checked in the database. Where erroneous balance could be readily explained by a transposition error (e.g., Na 10x to high due to decimal point being typed into the database incorrectly), the specific value was removed. Where the reason for erroneous balance could not be readily revealed, the data line was deleted. All the major elements had only a minor number of corrections or data deletions required (e.g. Figures 4 – 7).

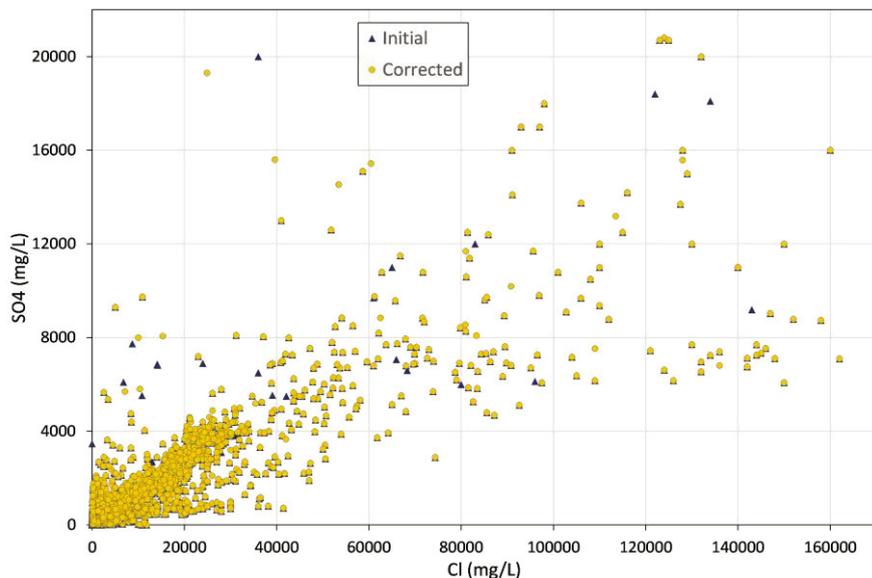


Figure 4: Initial SO₄ vs. Cl, and results following QA/QC correction of the WA groundwater data.

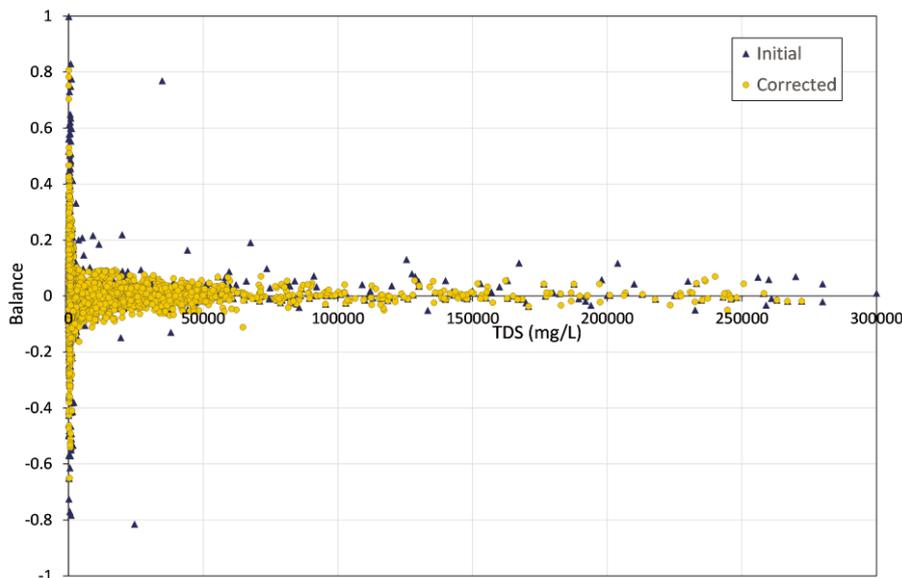


Figure 5: Initial Charge Balance vs. TDS, and results following QA/QC correction of the WA groundwater data

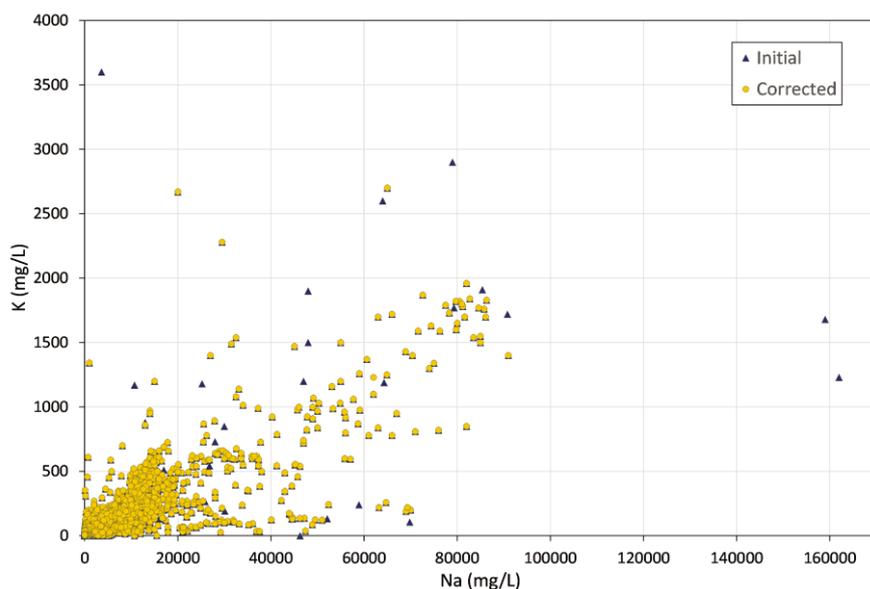


Figure 6: Initial K vs. Na, and results following QA/QC correction of the WA groundwater data.

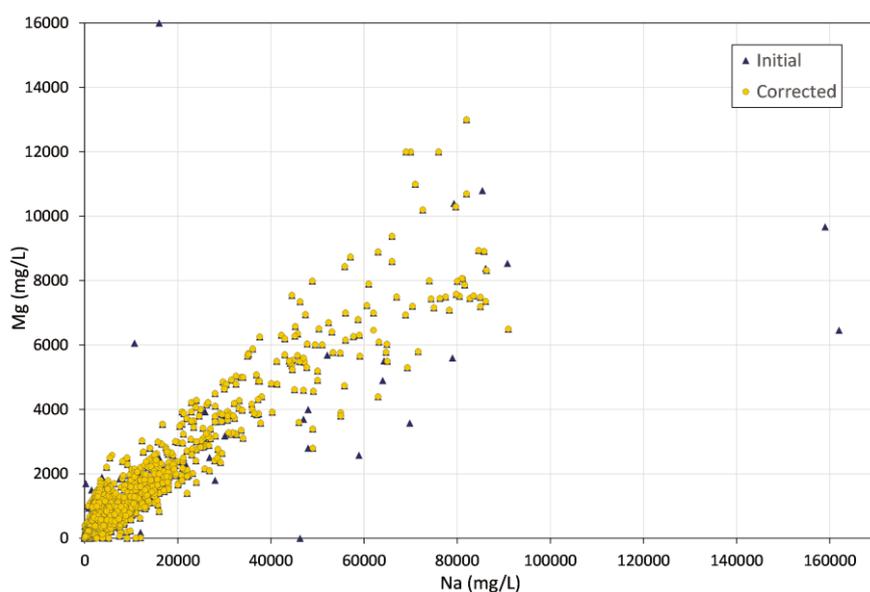


Figure 7: Initial Mg vs. Na, and results following QA/QC correction of the WA groundwater data.

2.6 Nitrogen and Organic Carbon

Nitrogen data was as varying types. Oxidised N and NO_3 values that were either exactly 10 or < 10 were deleted, and the two columns combined as NO_3 . When the NO_3 , N(org) and N (tot) values were greater than the TDS value, the samples were removed (8 samples). NO_3 was calculated by subtraction of N (org) from N (tot) for 7 samples. For dissolved organic carbon (DOC), values greater than 190 in the Perth region were deleted, as were all values below detection for particular sample batches (i.e. < 20 , < 10 , < 5 , < 3 , < 2).

2.7 Minors

SiO_2 values were recalculated as Si and combined with Si data (both datasets had very similar data distributions). Values greater than 62 mg/L Si were deleted: such concentrations are above amorphous silica solubility, and may be erroneous. Dissolved F analyses may have larger errors in saline samples: therefore F data was deleted when Cl was greater than 40,000 mg/L (Figure 8). Anomalous Br values were deleted as were values below the detection limit of 0.2 mg/L for particular sample batches (Figure 9). Dissolved P was reported in a number of forms. The PO_4 column was deleted as it was unclear if it was PO_4 or $\text{PO}_4\text{-P}$ (Figure 10). A number of PO_4 (tot) values were removed due to the different detection limits used.

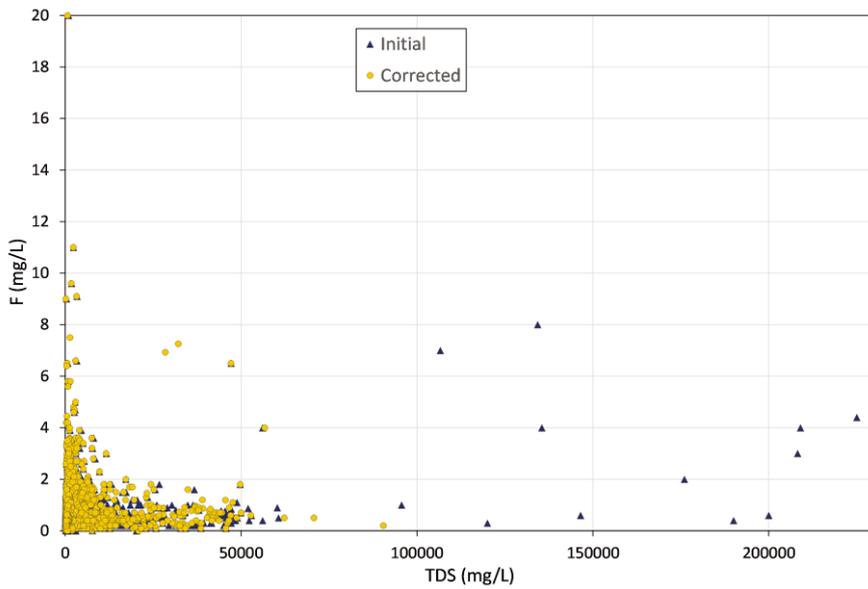


Figure 8: Initial F vs. TDS, and results following QA/QC correction of the WA groundwater data. Other erroneous initial data with F = 125 and 1944 mg/L not shown.

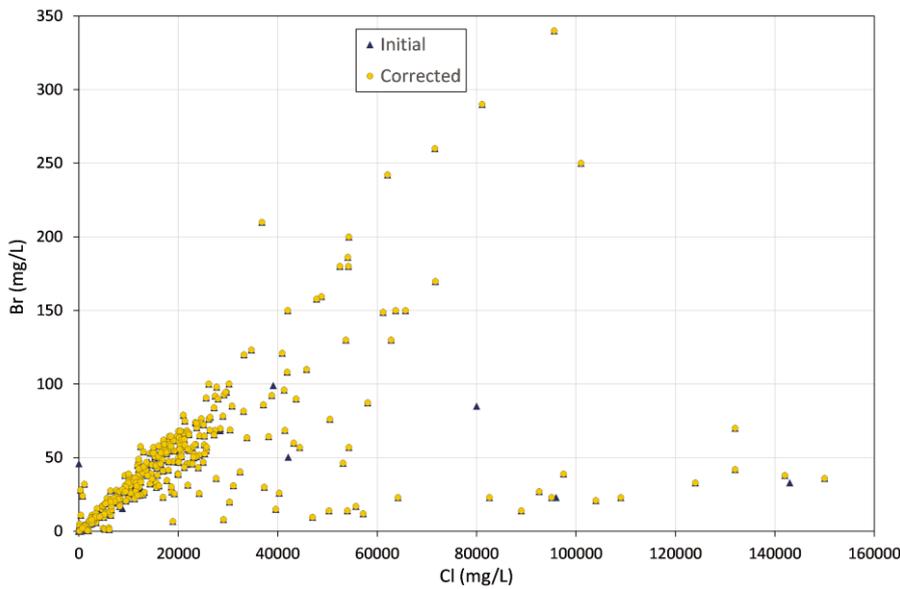


Figure 9: Initial Br vs. Cl, and results following QA/QC correction of the WA groundwater data.

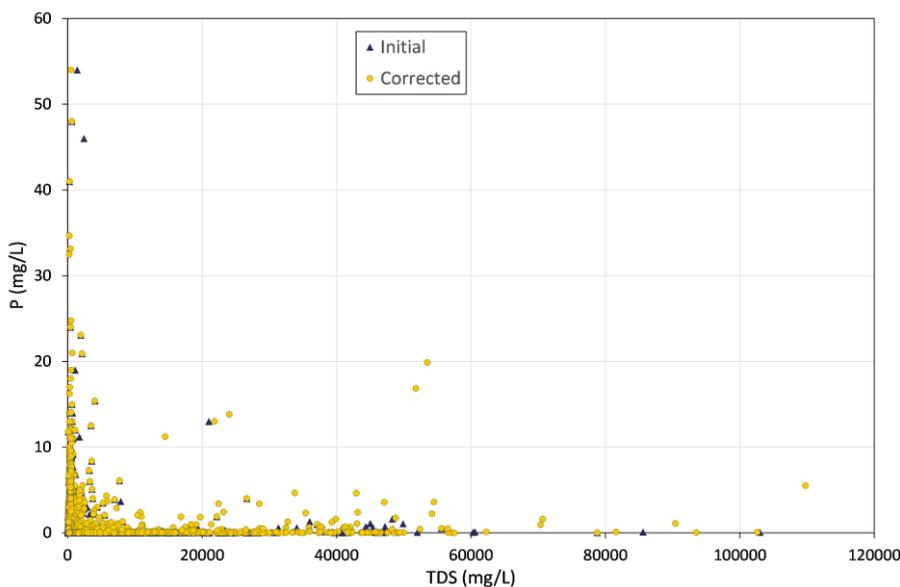


Figure 10: Initial P vs. TDS, and results following QA/QC correction of the WA groundwater data. Other erroneous initial data with TDS 225000 – 300000 mg/L not shown

A group of B analyses that were very high (> 13 mg/L), integer values, and represented greater B:Na ratios than other samples (Figure 11), may be incorrect units of measure of $\mu\text{g/L}$ data assigned as mg/L in the database, and were deleted. Other B values were deleted when in multiples of 5 and associated with Si or Al also in multiples of 5 in the same sample. Batches of Sr analyses at high detection limits were deleted (i.e. 10mg/L 5mg/L, 1mg/L associated with <10mg/L, <5mg/L and <1mg/L respectively) (Figure 12).

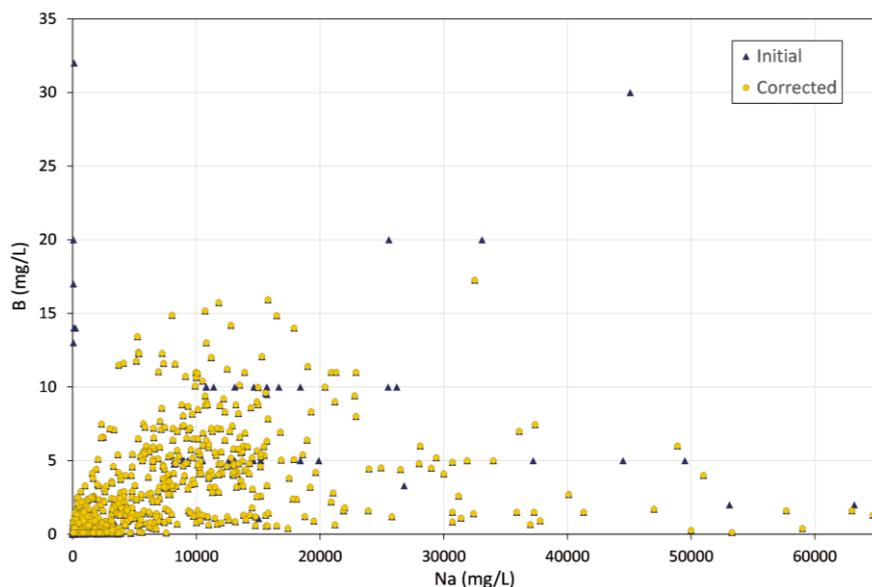


Figure 11: Initial B vs. Na, and results following QA/QC correction of the WA groundwater data.

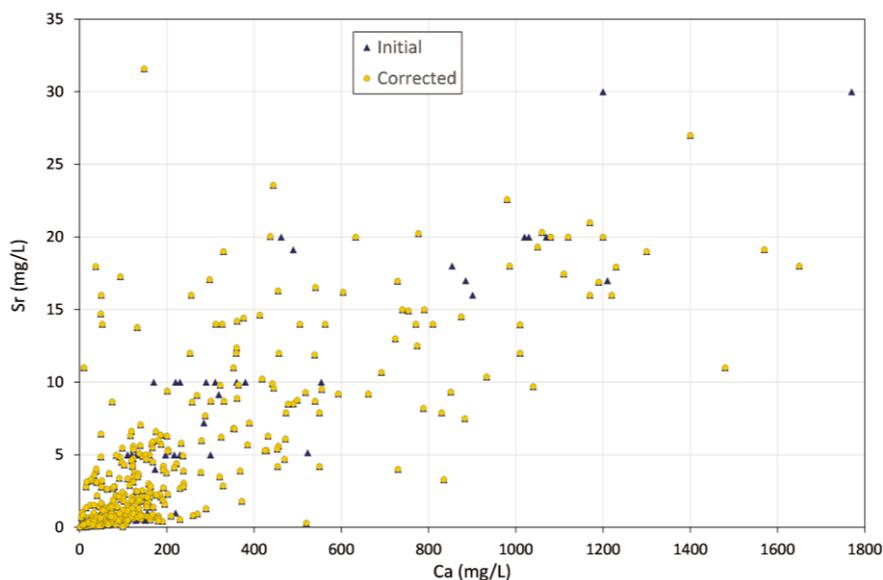


Figure 12: Initial Sr vs. Ca, and results following QA/QC correction of the WA groundwater data.

2.8 Base Metals and Trace Elements

When no Fe value existed, Fe (II) or Fe (III) values were used, and all data was combined into one column. All Fe analyses with a detection limit below 0.1 were deleted, as were two erroneously high values of 740 and 3700 mg/L (Figure 13). All Mn values below the detection limit of 0.05 mg/L were removed, as were erroneous analyses at high pH (Figure 14).

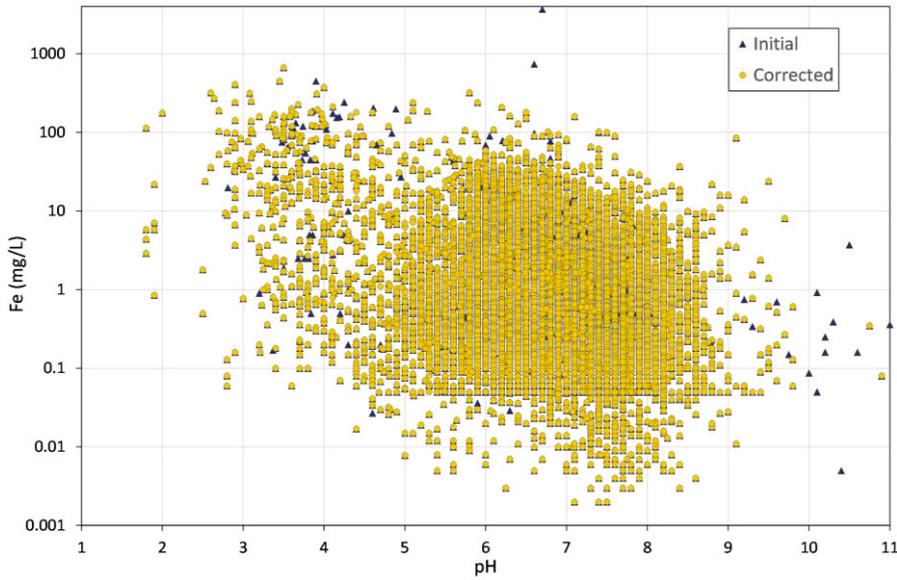


Figure 13: Initial Fe vs. pH, and results following QA/QC correction of the WA groundwater data.

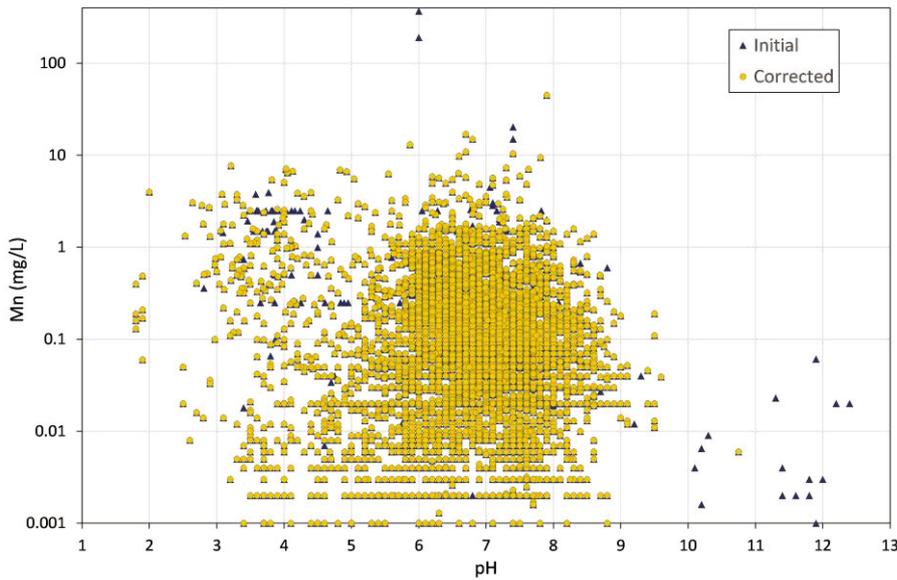


Figure 14: Initial Mn vs. pH, and results following QA/QC correction of the WA groundwater data.

All other base metal and trace element data were examined and erroneous data and values with a range of detection limits were deleted. This was done for Cu (Figure 15), Zn (Figure 16), Pb (Figure 17) and U (Figure 19), and other trace elements. In some cases, values were removed when they appeared to have incorrect units (ie. mg/L when likely $\mu\text{g/L}$), although this affected relatively few samples. Anomalously high Cr values around the Perth area and Cr values correlated with high pH were removed (Figure 18).

2.9 Isotopes

Water isotopes (^2H and ^{18}O) data not associated with other geochemical data were deleted and where values were clearly transposed, they were swapped (Figure 20).

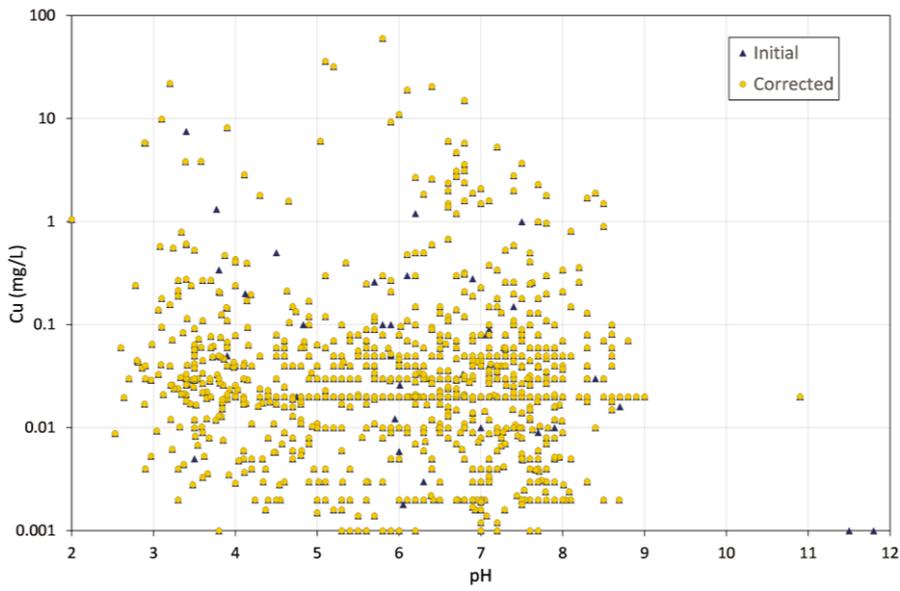


Figure 15: Initial Cu vs. pH, and results following QA/QC correction of the WA groundwater data.

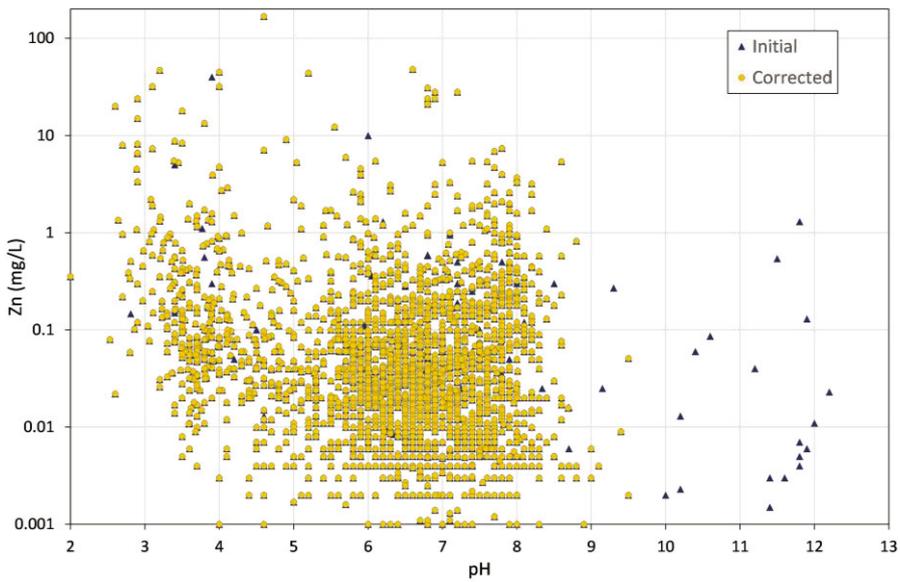


Figure 16: Initial Zn vs. pH, and results following QA/QC correction of the WA groundwater data.

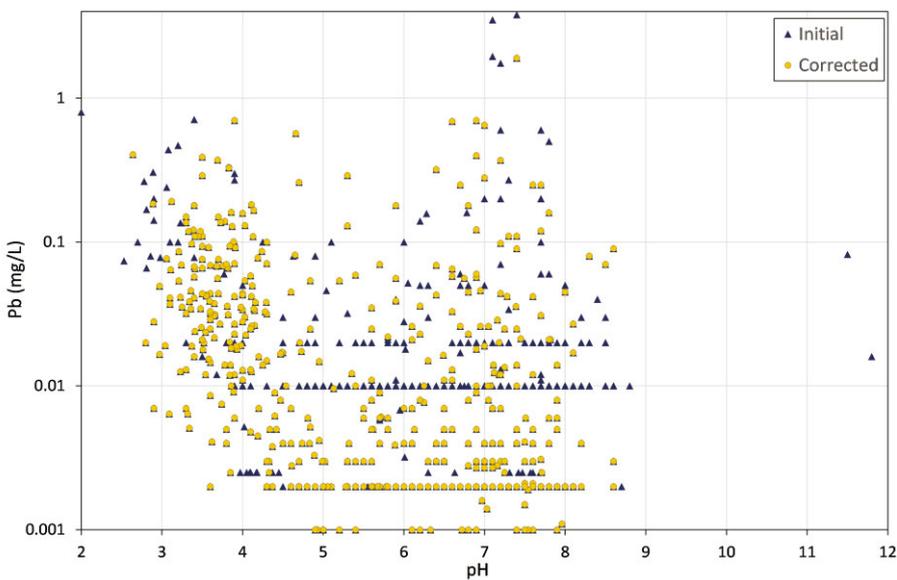


Figure 17: Initial Pb vs. pH, and results following QA/QC correction of the WA groundwater data.

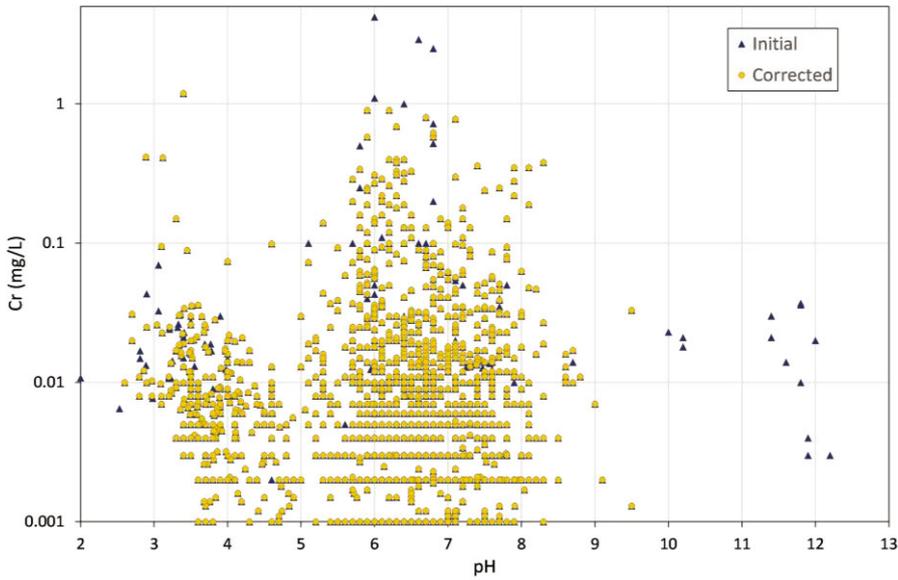


Figure 18: Initial Cr vs. pH, and results following QA/QC correction of the WA groundwater data.

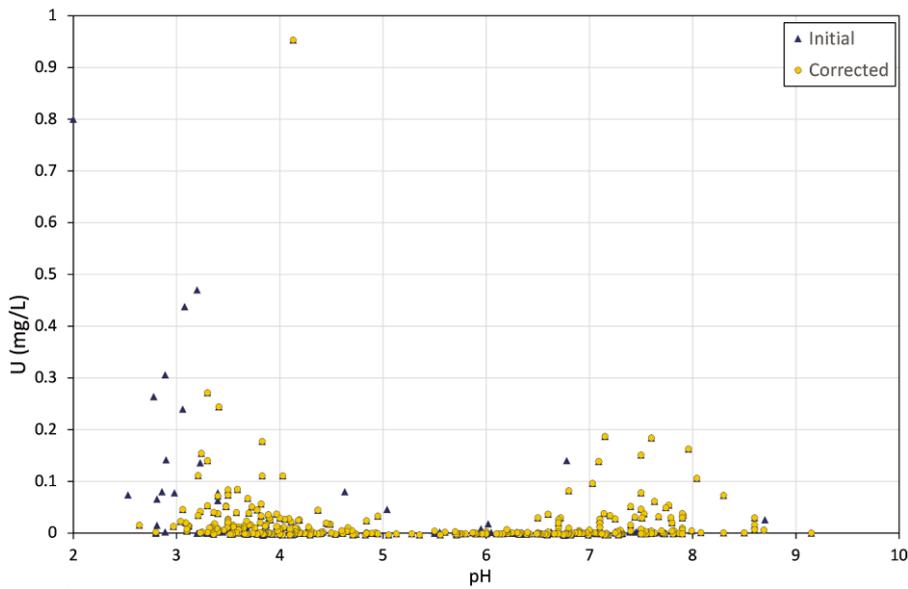


Figure 19: Initial U vs. pH, and results following QA/QC correction of the WA groundwater data.

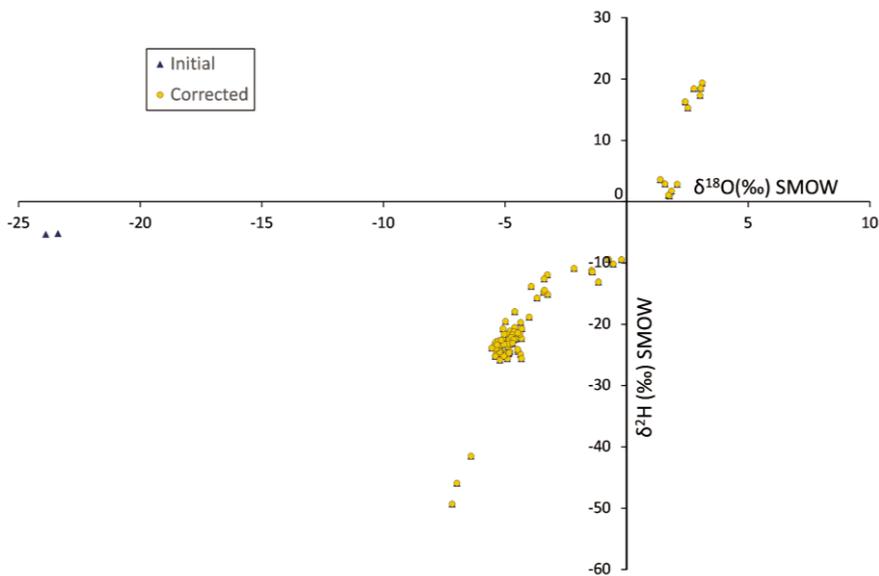


Figure 20: Initial ^2H vs. ^{18}O , and results following QA/QC correction of the WA groundwater data.

3 Element Indices

3.1 Ion Ratios

Using element ratios (compared to Cl or Na), some samples were observed to be in excess or deficit relative to the ion ratio observed for sea water. The distance away from the sea water dilution/evaporation trend line was determined, and provided a numerical measurement of the excess or depletion. For example, this was done for K, Mg, Ca (Figure 21) and B with respect to Na, Mg and Sr with respect to Ca, and SO₄ and Br with respect to Cl. At close scales (Gray and Noble, 2006), sulfate excess was particularly important for evaluating changes related to weathering sulfide ore bodies in shallow groundwater. At broader sampling (> km spacing), sulfate excess is subdued and more related to faults and other geological structures (Gray et al., 2014).

The other major element indices are strongly controlled by lithology and hydrothermal alteration. For example, Sr relative to Ca is useful in distinguishing basic and acid lithologies (Gray et al., 2016a). The derived formulas are listed below (all in mg/L). Note that the ratio used in each equation is the relevant ratio between the two elements in sea water. Two different equations are used for each ratio calculation; the variant for lower salinity (e.g., Na < 500 mg/L for KNaSW etc.) is derived so as to minimise issue for errors at low value of the denominator). Figure 21 provides a visible example of the variation in the relevant ratio.

$$\begin{aligned} \mathbf{KNaSW} &= [2 \times (\text{K} - 0.0363 \times \text{Na})] / [0.0363 \times (\text{Na} + 500)] \quad \dots \text{Na} < 500 \text{ mg/L} \\ &= [\text{K} - 0.0363 \times \text{Na}] / [0.0363 \times \text{Na}] \quad \dots \text{Na} \geq 500 \text{ mg/L} \\ \\ \mathbf{MgNaSW} &= [2 \times (\text{Mg} - 0.1194 \times \text{Na})] / [0.1194 \times (\text{Na} + 500)] \quad \dots \text{Na} < 500 \text{ mg/L} \\ &= [\text{Mg} - 0.1194 \times \text{Na}] / [0.1194 \times \text{Na}] \quad \dots \text{Na} \geq 500 \text{ mg/L} \\ \\ \mathbf{CaNaSW} &= [2 \times (\text{Ca} - 0.0381 \times \text{Na})] / [0.0381 \times (\text{Na} + 500)] \quad \dots \text{Na} < 500 \text{ mg/L} \\ &= [\text{Ca} - 0.0381 \times \text{Na}] / [0.0381 \times \text{Na}] \quad \dots \text{Na} \geq 500 \text{ mg/L} \\ \\ \mathbf{BNaSW} &= [\text{B} - 2 \times \text{Na} / 2400] / [(\text{Na} + 500) / 2400] \quad \dots \text{Na} < 500 \text{ mg/L} \\ &= [\text{Ca} - \text{Na} / 2400] / [\text{Na} / 2400] \quad \dots \text{Na} \geq 500 \text{ mg/L} \\ \\ \mathbf{MgCaSW} &= [2 \times (\text{Mg} - 3.14 \times \text{Ca})] / [3.14 \times (\text{Ca} + 20)] \quad \dots \text{Ca} < 20 \text{ mg/L} \\ &= [\text{Mg} - 3.14 \times \text{Ca}] / [3.14 \times \text{Ca}] \quad \dots \text{Ca} \geq 20 \text{ mg/L} \\ \\ \mathbf{SrCaSW} &= [2 \times (\text{Sr} - 0.0195 \times \text{Ca})] / [0.0195 \times (\text{Ca} + 20)] \quad \dots \text{Ca} < 20 \text{ mg/L} \\ &= [\text{Sr} - 0.0195 \times \text{Ca}] / [0.0195 \times \text{Ca}] \quad \dots \text{Ca} \geq 20 \text{ mg/L} \\ \\ \mathbf{SO_4ClSW} &= [2 \times (\text{SO}_4 - 0.1396 \times \text{Cl})] / [0.1396 \times (\text{Cl} + 500)] \quad \dots \text{Cl} < 500 \text{ mg/L} \\ &= [\text{SO}_4 - 0.1396 \times \text{Cl}] / [0.1396 \times \text{Cl}] \quad \dots \text{Cl} \geq 500 \text{ mg/L} \\ \\ \mathbf{BrClSW} &= [2 \times (\text{Br} - 0.00345 \times \text{Cl})] / [0.00345 \times (\text{Cl} + 500)] \quad \dots \text{Cl} < 500 \text{ mg/L} \\ &= [\text{Br} - 0.00345 \times \text{Cl}] / [0.00345 \times \text{Cl}] \quad \dots \text{Cl} \geq 500 \text{ mg/L} \end{aligned}$$

The different calculation methods for lower ion concentrations are so as to minimise skewing data due to analytical errors close to detection limits. At higher concentrations these become a ratio difference:

e.g., for Na > 500 mg/L

- CaNaSW = 12 means the Ca/Na sample ratio is 13 x sea water
- CaNaSW = 6 means the Ca/Na sample ratio is 7 x sea water
- CaNaSW = 2.5 means the Ca/Na sample ratio is 3.5 x sea water
- CaNaSW = 1 means the Ca/Na sample ratio is 2 x sea water
- CaNaSW = 0.3 means the Ca/Na sample ratio is 1.3 x sea water
- CaNaSW = 0 means the Ca/Na sample ratio is at the sea water value
- CaNaSW = -0.1 means the Ca/Na sample ratio is 0.9 x sea water
- CaNaSW = -0.4 means the Ca/Na sample ratio is 0.6 x sea water
- CaNaSW = -0.8 means the Ca/Na sample ratio is 0.2 x sea water

This is demonstrated for Ca:Na in Figure 21.

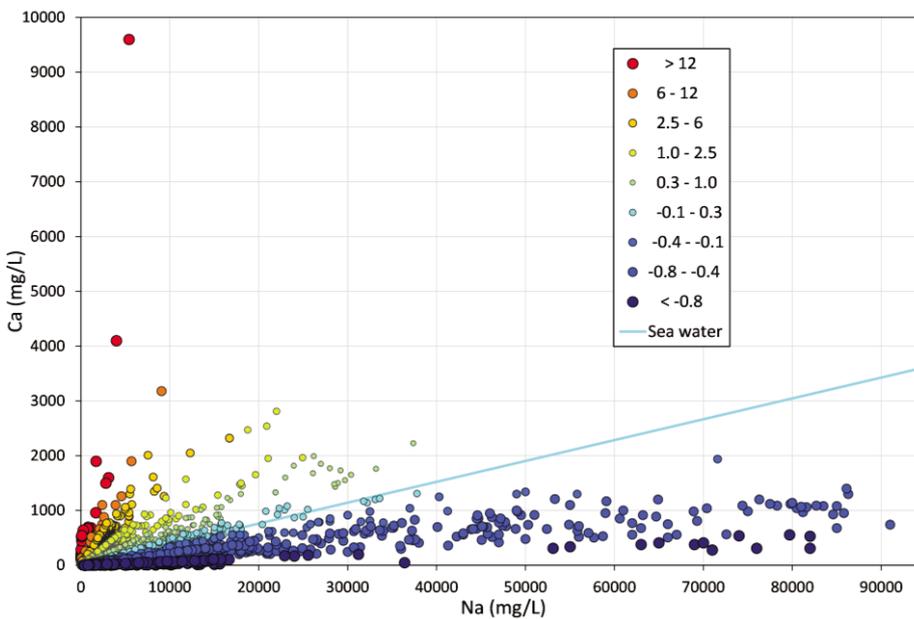


Figure 21: Dissolved Ca vs. Na for WA groundwaters, coloured by the CaNaSW range.

3.2 Ion Excess or Deficit

Absolute differences in ion concentration relative to the sea water line (e.g., Figure 22), were calculated. In order to remove erroneous values in saline samples due to analytical error, only deviations greater than 10% from the sea water line gave non-zero values:

$$\begin{aligned}
 \mathbf{KNaDSW} &= K - (0.0399 \times Na) && \dots \text{KNaSW} > 0.1 \\
 &= 0 && \dots -0.1 \leq \text{KNaSW} \leq 0.1 \\
 &= K - (0.0327 \times Na) && \dots \text{KNaSW} < -0.1 \\
 \\
 \mathbf{MgNaDSW} &= Mg - (0.1314 \times Na) && \dots \text{MgNaSW} > 0.1 \\
 &= 0 && \dots -0.1 \leq \text{MgNaSW} \leq 0.1 \\
 &= Mg - (0.1075 \times Na) && \dots \text{MgNaSW} < -0.1 \\
 \\
 \mathbf{CaNaDSW} &= Ca - (0.0419 \times Na) && \dots \text{CaNaSW} > 0.1 \\
 &= 0 && \dots -0.1 \leq \text{CaNaSW} \leq 0.1 \\
 &= Ca - (0.0343 \times Na) && \dots \text{CaNaSW} < -0.1 \\
 \\
 \mathbf{BNaDSW} &= K - (Na/2182) && \dots \text{BNaSW} > 0.1 \\
 &= 0 && \dots -0.1 \leq \text{BNaSW} \leq 0.1 \\
 &= K - (Na/2667) && \dots \text{BNaSW} < -0.1
 \end{aligned}$$

$$\begin{aligned}
 SO_4CISW &= SO_4 - (0.1536 \times Cl) && \dots SO_4CISW > 0.1 \\
 &= 0 && \dots -0.1 \leq SO_4CISW \leq 0.1 \\
 &= SO_4 - (0.1256 \times Cl) && \dots SO_4CISW < -0.1 \\
 \\
 BrCISW &= Br - (0.0038 \times Cl) && \dots BrCISW > 0.1 \\
 &= 0 && \dots -0.1 \leq BrCISW \leq 0.1 \\
 &= Br - (0.00311 \times Cl) && \dots BrCISW < -0.1
 \end{aligned}$$

Comparing the Ca:Na difference (Figure 22) with the ion ratio parameter differentiation (Figure 21) indicates how the ion ratio and ion difference parameters differentiate the data in different manners.

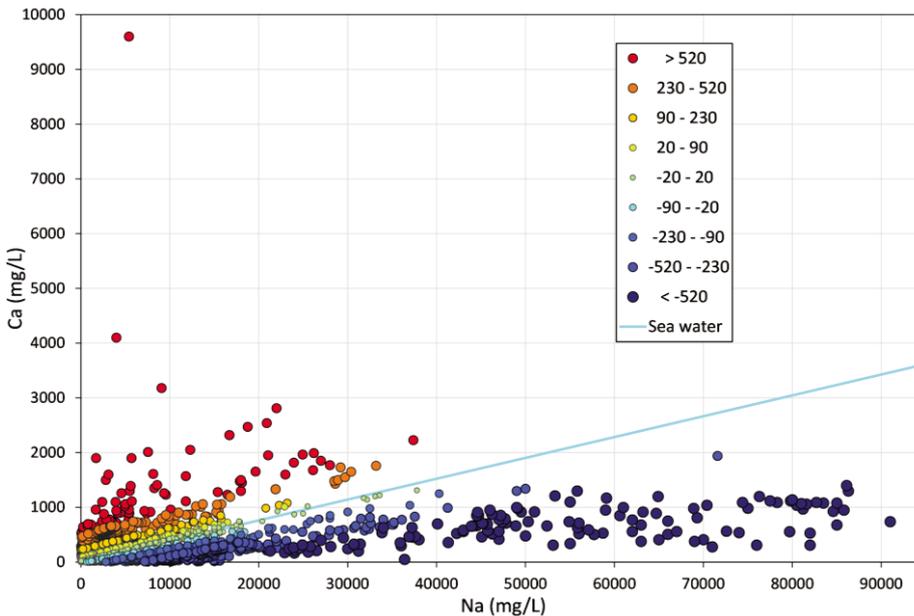


Figure 22: Dissolved Ca vs. Na for WA groundwaters, coloured by the CaNaDSW range.

4 Solution Modelling

4.1 Activity Plots

Plotting the Eh/pH data for WA groundwaters on the crystalline Fe mineral stability plot (Figure 23; derived using The Geochemist's Workbench®), indicates that many WA groundwaters are within the stability field for hematite (Fe_2O_3), with a significant component (generally along the west coastal plain) sufficiently reduced to sit in the pyrite (FeS_2) stability field. Additionally a component of the acid (down to pH 3) groundwaters are in the blue region of Figure 23, indicating that hematite, pyrite and other Fe minerals will be soluble. However, groundwater Fe concentrations are commonly much higher than expected for crystalline Fe oxide solubility waters, and are commonly in equilibrium with amorphous forms of Fe (Schwab and Lindsay, 1983) such as ferrihydrite [$Fe(OH)_3 \cdot xH_2O$] or $Fe_3(OH)_8$. With crystalline Fe oxides removed from the modelling (Figure 24), the more oxidised groundwaters sit within the amorphous $Fe(OH)_3$ stability field, with acid waters in the stability zone for soluble Fe^{2+} . Such modelling for Fe, and for other elements such as Mn and other base metals, and oxy anions such as Mo, As, and Sb can assist in understanding element mobilities.

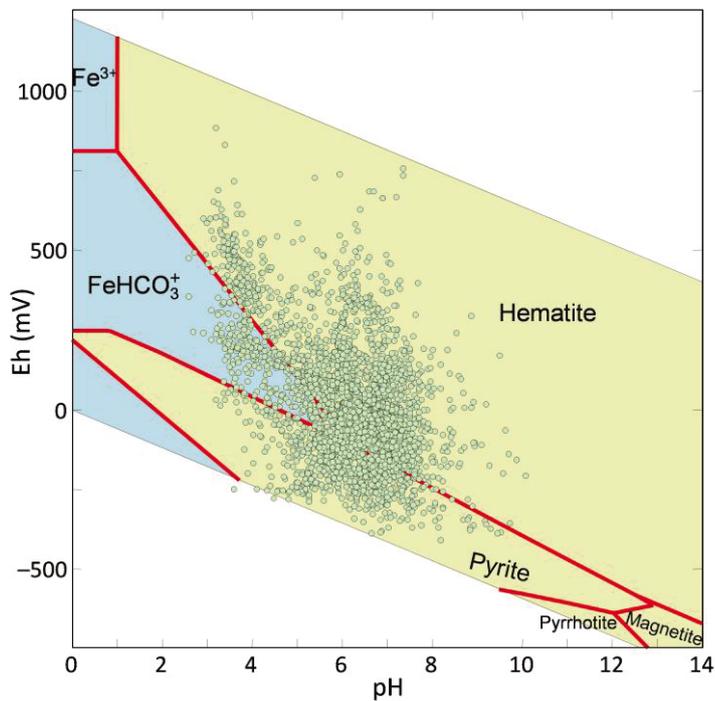


Figure 23: Modelled Eh-pH plot of Fe speciation overlain with Eh:pH data for WA groundwaters. Blue zones denote where Fe is soluble and yellow zones where Fe will precipitate as the mineral shown. Solution activities used in the modelling are 10^{-4} M Fe, 0.01M S, 1% CO_2 fugacity, 25°C/1.013 bars. (Geochemists Workbench[®], thermo.dat database).

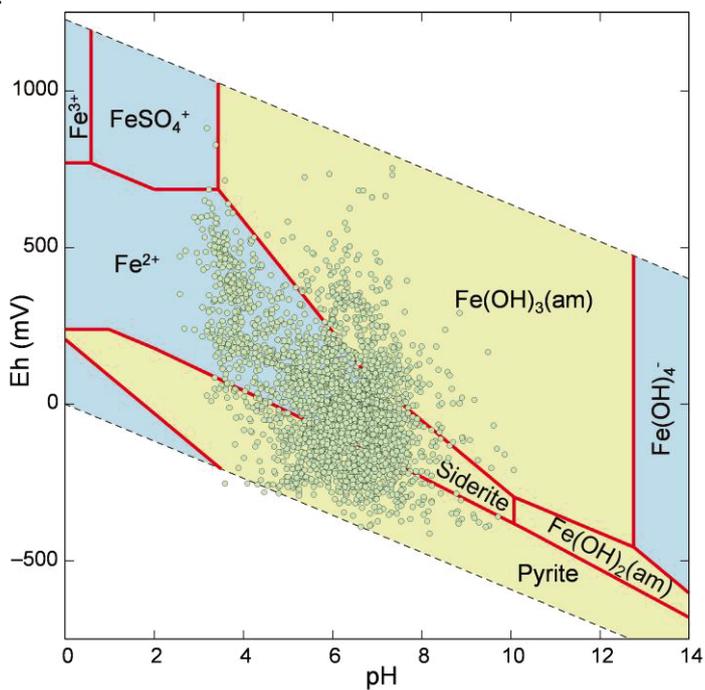


Figure 24: Modelled Eh-pH plot of Fe speciation (crystalline Fe oxides not involved) overlain with Eh:pH data for WA groundwaters. Blue zones denote where Fe is soluble and yellow zones where Fe will precipitate as the mineral shown. Solution activities used in the modelling are 10^{-4} M Fe, 0.01M S, 1% CO_2 fugacity, hematite, goethite, magnetite, FeO, and troilite suppressed, 25°C/1.013 bars. (Geochemists Workbench[®], thermo.dat database).

4.2 Mineral Saturation Indices

Solution chemical speciation and degree of mineral saturation were computed from the solution compositions using the program PHREEQE (Parkhurst et al., 1980). Saturation indices (SI) for each water sample were calculated for various minerals. If the SI for a mineral is within the zero range the water is in equilibrium with that mineral, under the conditions specified. The zero range is estimated for every mineral based on stoichiometry, thermodynamic accuracy and analytical issues; generally ranging from -0.2 to 0.2 for major element minerals such as gypsum (Figure 25) to -1 to 1 for minor element minerals. Where the SI is below the zero range, the solution is under-saturated with respect to that mineral, so that, if present, the

phase may dissolve. If the SI is greater than zero the solution is over-saturated with respect to this mineral, which could potentially precipitate from solution.

Note that SI determinations only specify possible reactions, and kinetic constraints may rule out reactions that are thermodynamically allowed. Thus, for example, waters are commonly close to equilibrium with respect to carbonate minerals such as calcite (Figure 26), but may become dolomite over-saturated, due to the slow rate of precipitation of this mineral (Drever, 1982). However, this method provides some understanding of solution processes at a site and adds value in determining whether the spatial distribution of an element is correlated with geological phenomena such as lithology or mineralisation, or whether solubility is related to weathering or environmental effects. For example, if Ca distribution is controlled by equilibrium with gypsum in particular samples (Figure 25), then the spatial distribution of dissolved Ca will reflect SO_4 concentration alone and have no direct exploration significance.

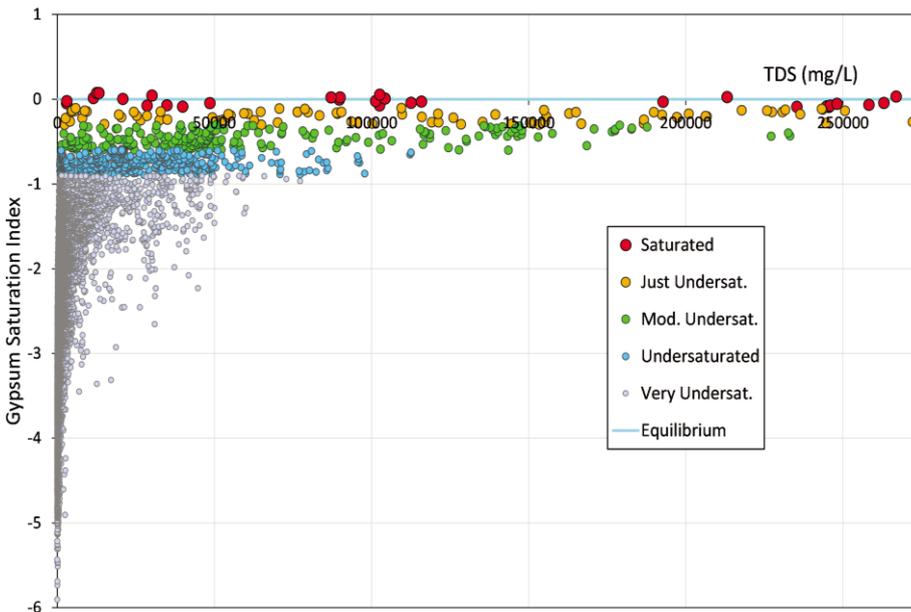


Figure 25: Gypsum Saturation Index (SI) vs. TDS for WA groundwaters, coloured by the defined saturation level.

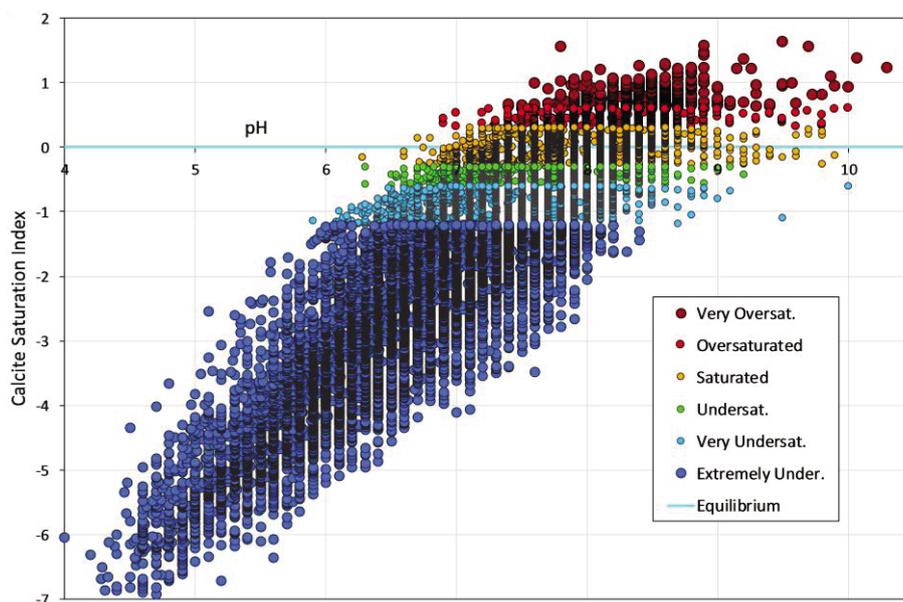


Figure 26: Calcite Saturation Index (SI) vs. pH for WA groundwaters, coloured by the defined saturation level.

5 Some Results

The Western Australian database is included in the attached CD.

This section shows some potential uses of the WA groundwater database for regional analysis, often in conjunction with other data (Figure 1). This is not meant to be exhaustive, but to generally give a flavour of the utility of this dataset. It is expected that further research will be conducted on optimising this data for geological mapping, prospectivity analysis, environmental baselines and other uses.

The geology of Western Australia encompasses the two main Pilbara and Yilgarn Archaean Cratons, various Proterozoic systems including the Kimberley, Capricorn and Albany-Fraser Orogens, as well as the western parts of the Arunta and Musgraves. The east of the state is dominated by Basin systems, including the Canning and Officer Basins and the Eucla Basin to the SE. The coastal plain in the SW has extensive groundwater data, due to human usage requirements. Completing the groundwater map of the region should assist in further discriminating various geological regions. There has been extensive groundwater (> 3000) sampling in the northern Yilgarn by CSIRO (Figure 1; Gray, 2015; Gray et al., 2014, 2016a), which is now being extended into the Capricorn Orogen. The northern Yilgarn data and report is also included in the CD. Based on the information available, some initial observations for specific regions are given below.

Two major controlling factors in groundwater are salinity and pH (Figure 27). There is a broad saline zone across the south of Australia (Figure 28), from the southern part of WA, through the southern half of SA, and into the SW Murray Basin. In WA, this saline region is strongly correlated with low pH groundwaters (Figure 27 and Figure 29), sitting south of the EW Menzies Line, a botanical, soil, and groundwater (Gray, 2001) division of the Yilgarn Craton. In these southern acid groundwaters, base levels for the ion ratios differ from the north (e.g., Figure 30), base metals (which are highly soluble in these acid groundwaters; Gray, 2001) have much higher thresholds, and oxy-anions such as As and Mo (which have low solubility in acid groundwaters; Gray, 2001) will work poorly for prospecting using groundwater. Further delineating these processes will be critical to mapping anomalies and prospectivity mapping in these regions.

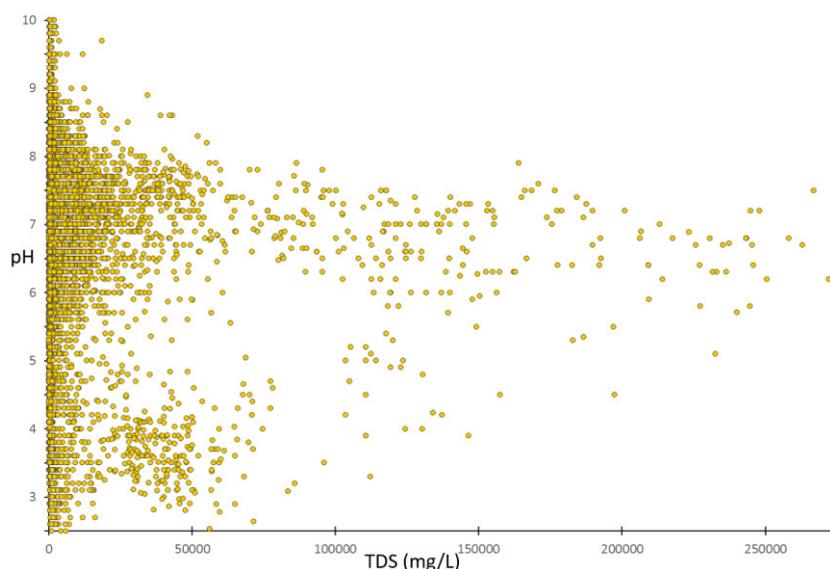


Figure 27: Groundwater pH vs. TDS for the Western Australian groundwater data. Acidic (pH < 5) groundwaters are commonly saline, though there is an additional component of circum-neutral pH saline to hyper-saline groundwaters.

Ion ratios (Section 3.1), identify deviations from the sea water line for ion pairs. At the continental scale, the Eromanga Basin is clearly identified by the low Mg:Na ratio (Figure 30), with contrasting high Mg:Na along the Great Dividing Range to the east, Flinders and Adelaidean rocks to the south and the North Australian Craton to the west. The Musgrave Complex also shows greater Mg:Na. Variation in Mg:Na is

more gradational in WA, although there is a subtle increase in Mg:Na in groundwaters from greenstones, relative to granites, in the northern Yilgarn Craton.

The CaNaSW index (Figure 31) also shows up the Eromanga Basin as a zone of low Ca:Na, although with internal differentiation. Critically, the saline groundwaters of the southern Yilgarn (Figure 28) also have low Ca:Na (Figure 31), which is indicated to be an absolute Ca depletion (based on ion difference calculations; Figure 32). Future research will be required to “remove” these surficial effects in the groundwater data for the southern Yilgarn Craton and other regions in southern Australia.

In contrast, the strongest features delineated in a continental map of the KNaSW index (Figure 33), are high K:Na groundwaters in the NE Yilgarn Craton, the Musgraves and other shield rocks of northern Australia. Using the ion excess (KNaDSW) index (Figure 34), the NE Yilgarn has a moderate enrichment in K relative to Na, suggesting a K source from rock weathering. This effect is stronger in northern Australia. The (KNaDSW) index (Figure 34) also indicates major zones of low K (relative to Na) in the southern Yilgarn Craton, central SA and the Murray Basin, correlated with regions of strong Ca depletion (Figure 32). This is postulated to reflect processes correlated with acid/saline groundwater systems, including Ca-depletion due to calcite precipitation in overlying soils, and K-depletion due to alunite and/or jarosite precipitation in the regolith (McArthur et al., 1989).

Data for dissolved Br is more limited than the major ions, with the BrClSW Index (Figure 35) indicating major variation in Br:Cl within the Eromanga Basin, moderate variation in the northern Yilgarn Craton, and high Br:Cl in the Musgraves. The SO₄ClSW Index (Figure 36) shows high SO₄:Cl across much of central Australia. For parts of this central zone where high SO₄:Cl (Figure 36) correlates with waters at or near gypsum (CaSO₄·H₂O) saturation (Figure 37), this suggests S dissolving into the groundwaters, possibly from gypsum itself, with possible other sources including oxidation of sulfides. In contrast the southern Yilgarn groundwaters are saline (Figure 28), with low SO₄:Cl (Figure 36), low Ca:Na (Figure 32), and close to gypsum saturation (Figure 37): this suggests salinization via evaporation brings waters to gypsum saturation, with loss of Ca and SO₄ as gypsum precipitates. Though there is lesser dissolved Sr data, these are consistent with similar behaviour for Sr, in terms of celestine (SrSO₄) saturation (Figure 38).

Extremely high dissolved F data are specifically observed in NW Queensland (Figure 39; duplicated in two different datasets; Bardwell and Gray, 2015a). In WA (Figure 39), Albany-Fraser rocks around Esperance show high dissolved F, and in the northern Yilgarn Craton, there is a correlation of relatively higher dissolved F with granitic rocks

Dissolved U is high in the Yilgarn Craton and in the Curnamona Basin (Figure 40; de Caritat et al., 2005), reflecting active and potential secondary U deposits in these region. Similar U contents are observed in the northern Stuart Shelf, and are of interest for exploration. Other elements such as Mo (Figure 41) are high in specific regions, such as the western Olary and sporadically across the Yilgarn Craton and the Stuart Shelf. Such data for varying elements such as As and W may become useful for lithological discrimination and detection of hydrothermal dispersion (e.g., Gray et al., 2014).

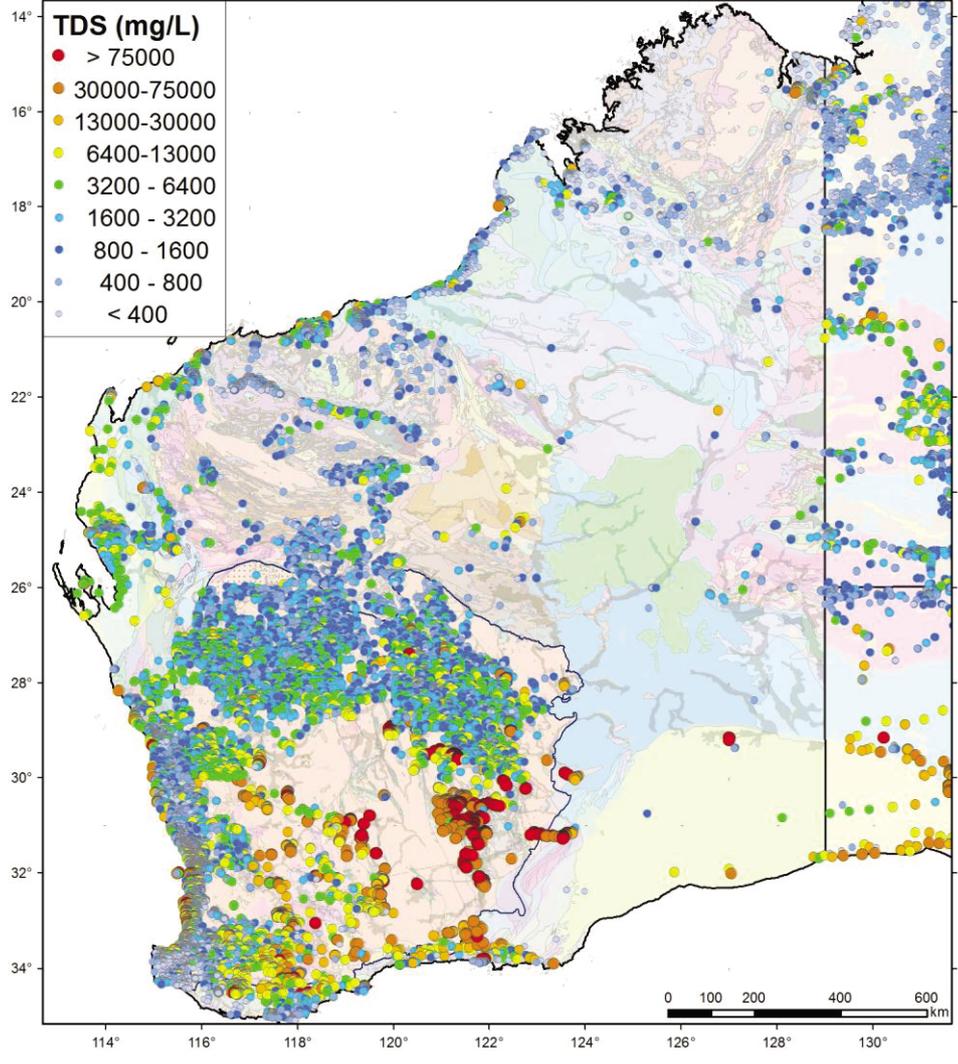
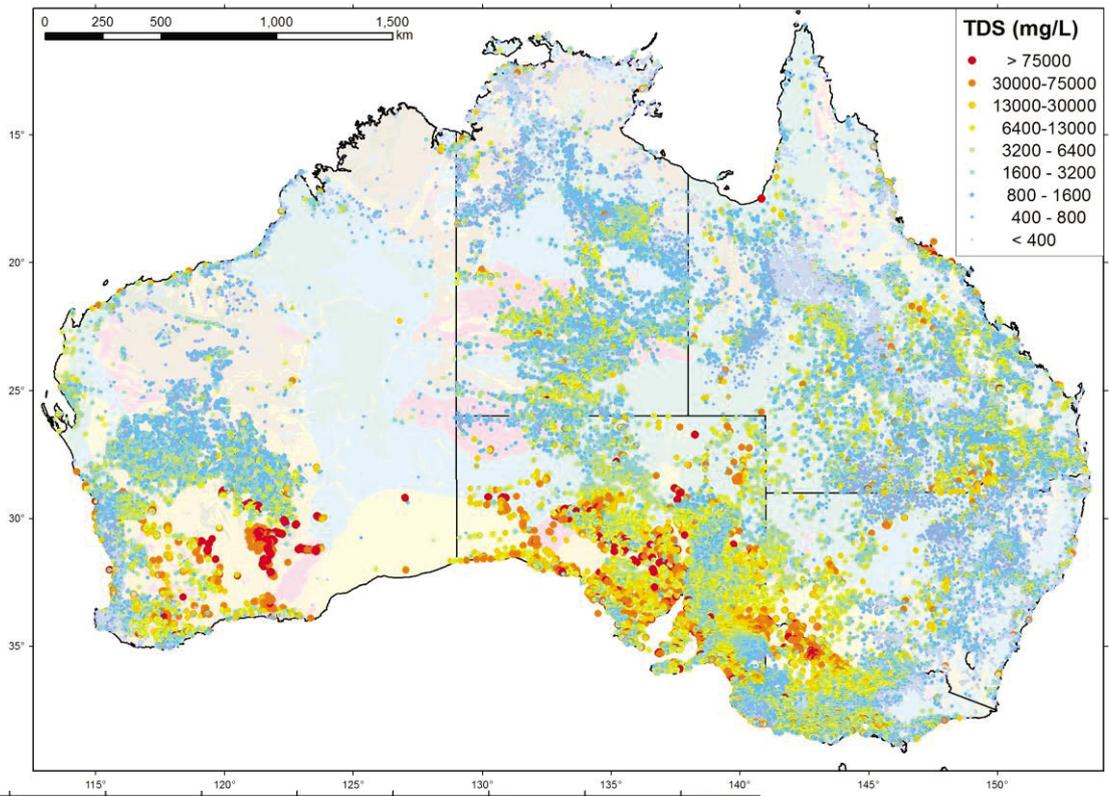


Figure 28: TDS distribution across Australia and in Western Australia.

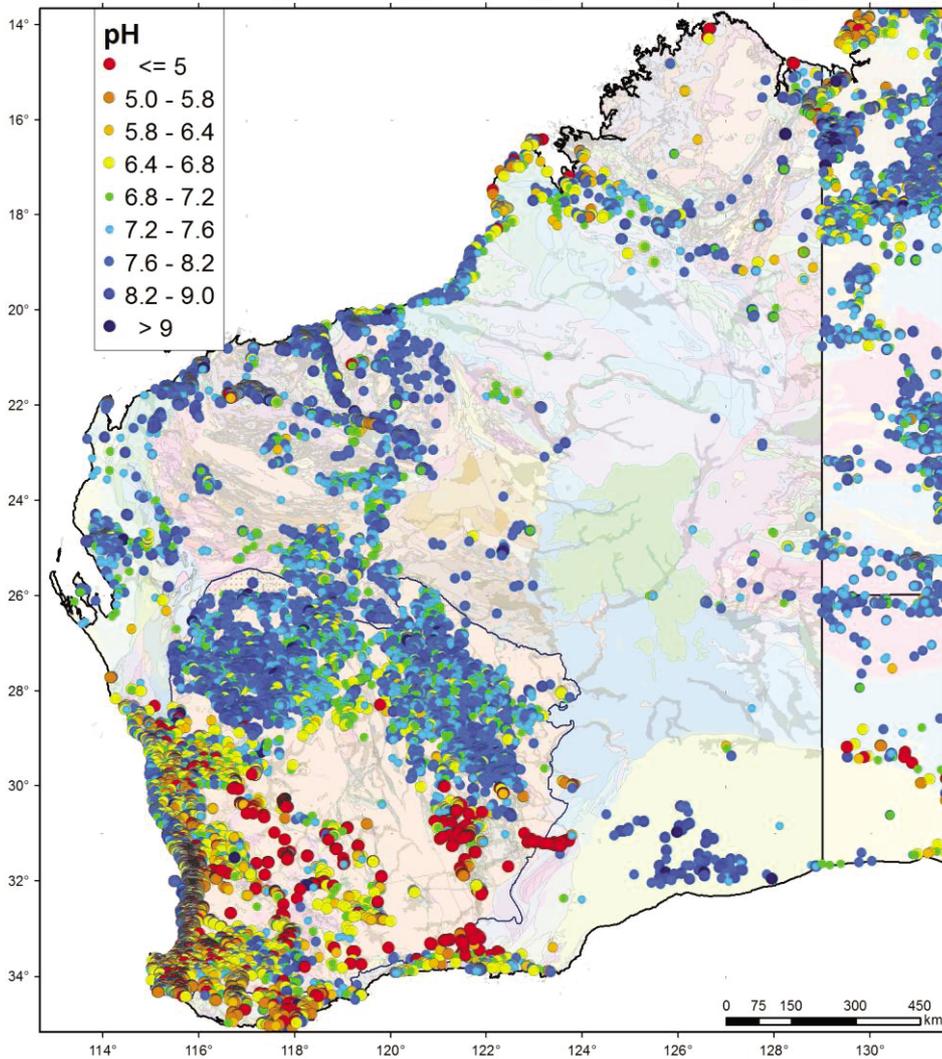
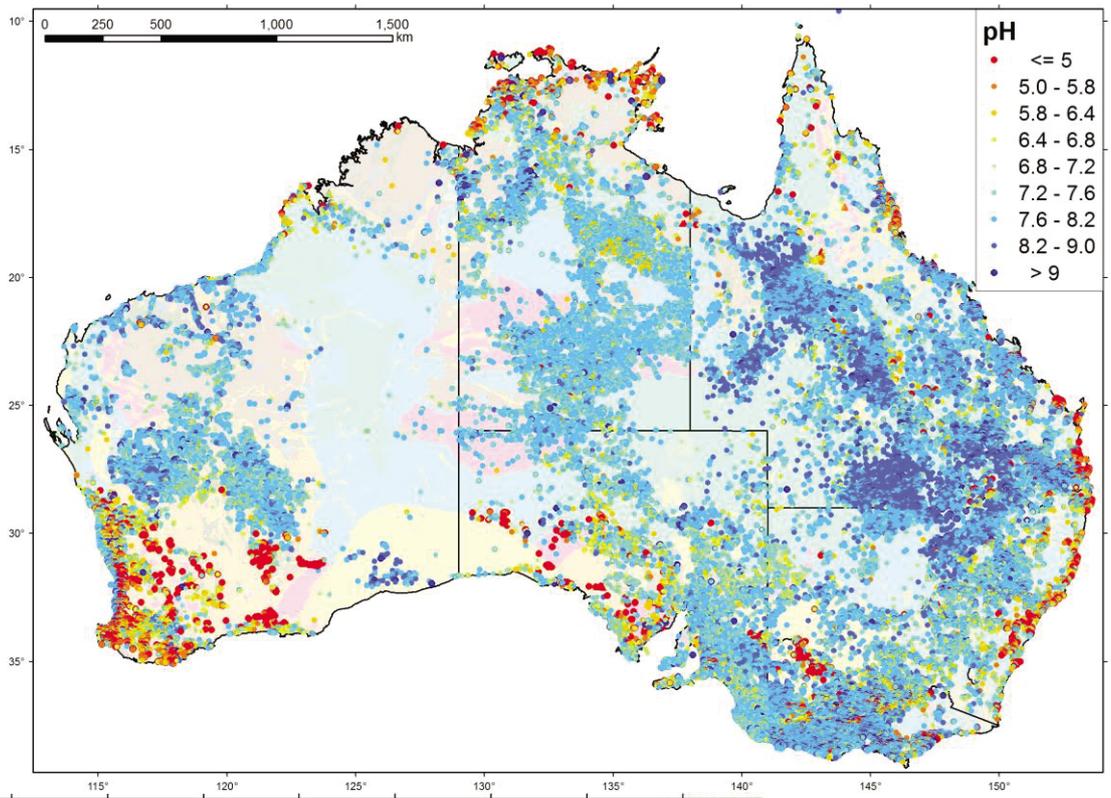


Figure 29: Groundwater pH distribution across Australia and in Western Australia.

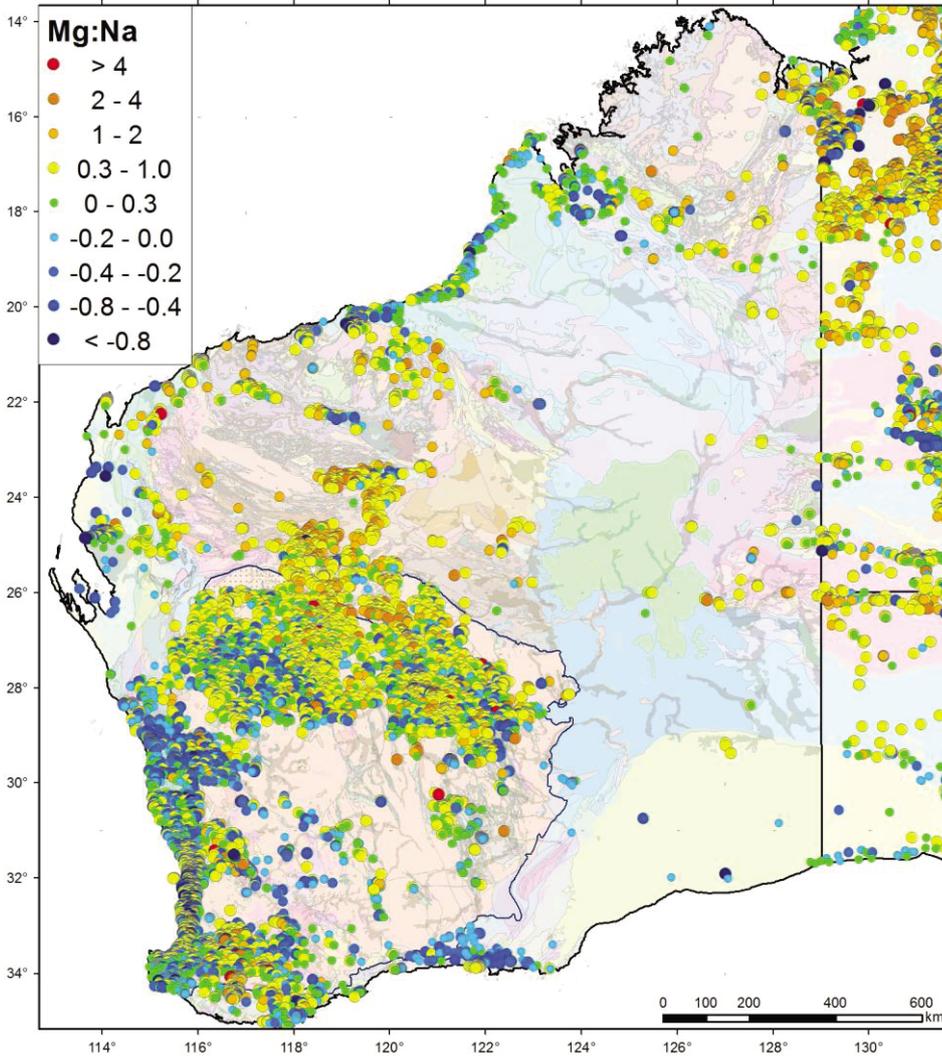
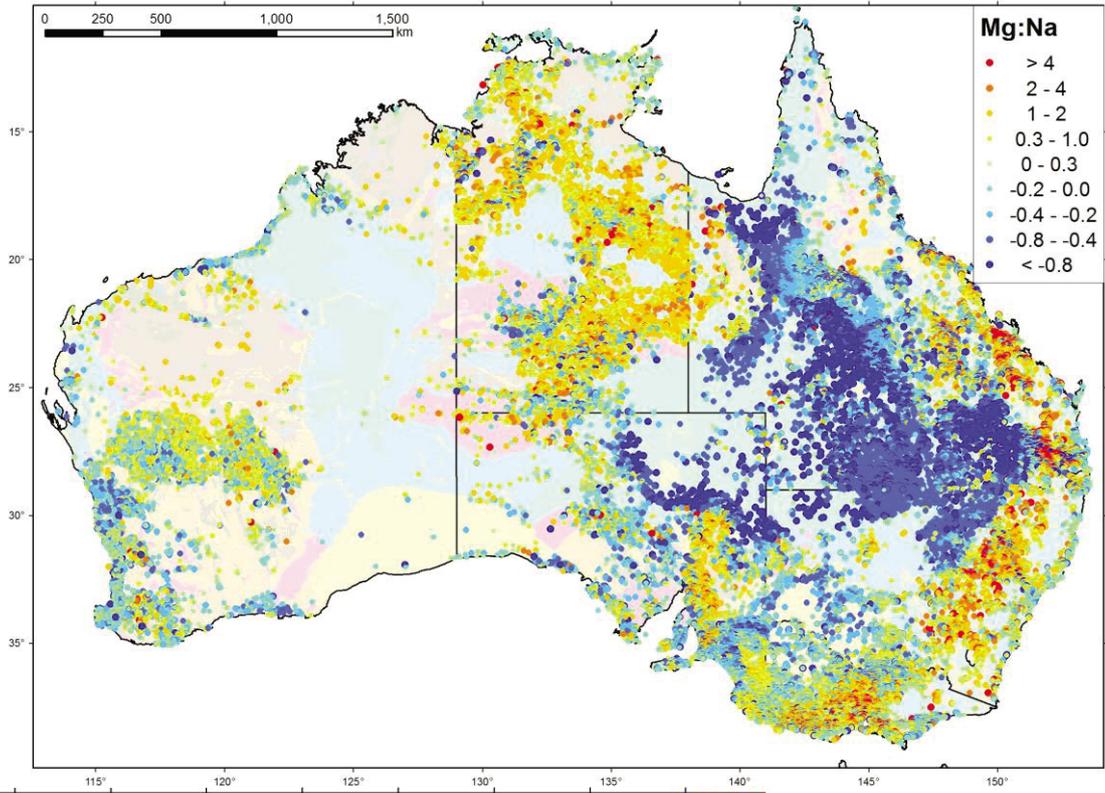


Figure 30: Groundwater Mg:Na Ion Ratio (MgNaSW) distribution across Australia and in Western Australia.

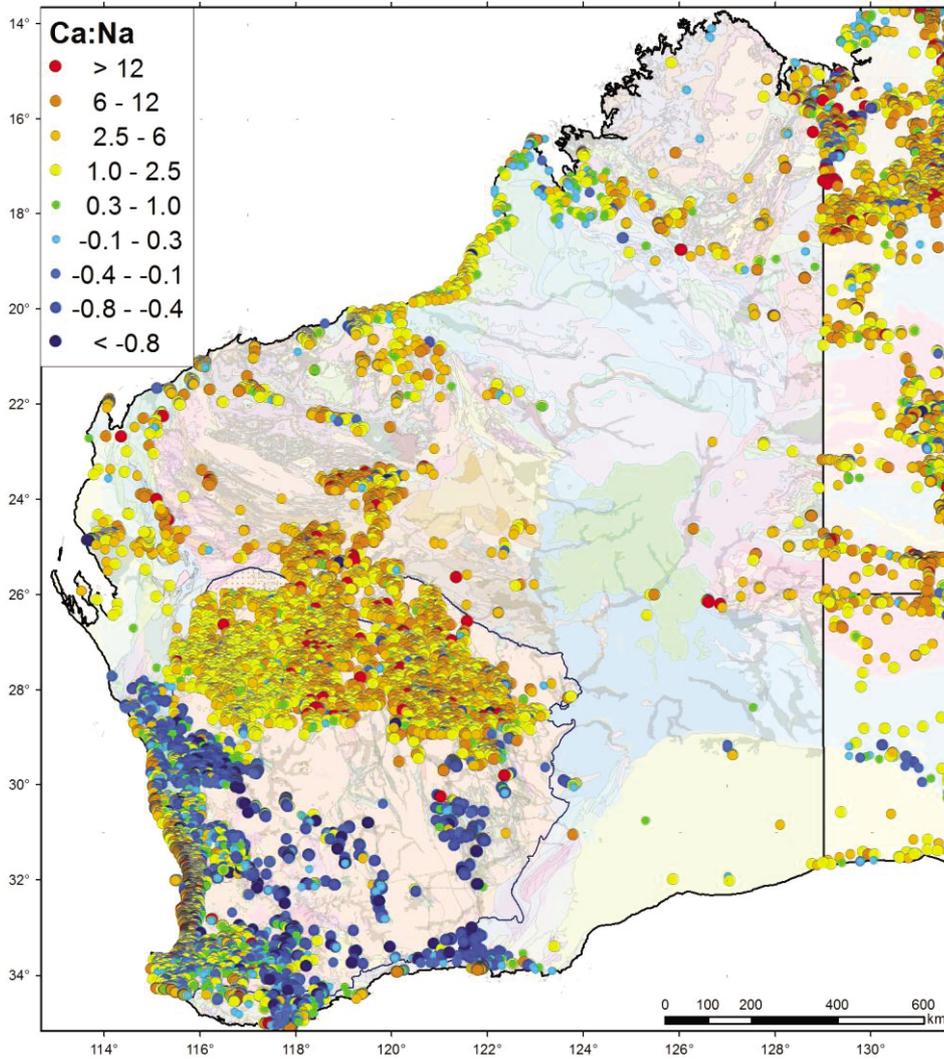
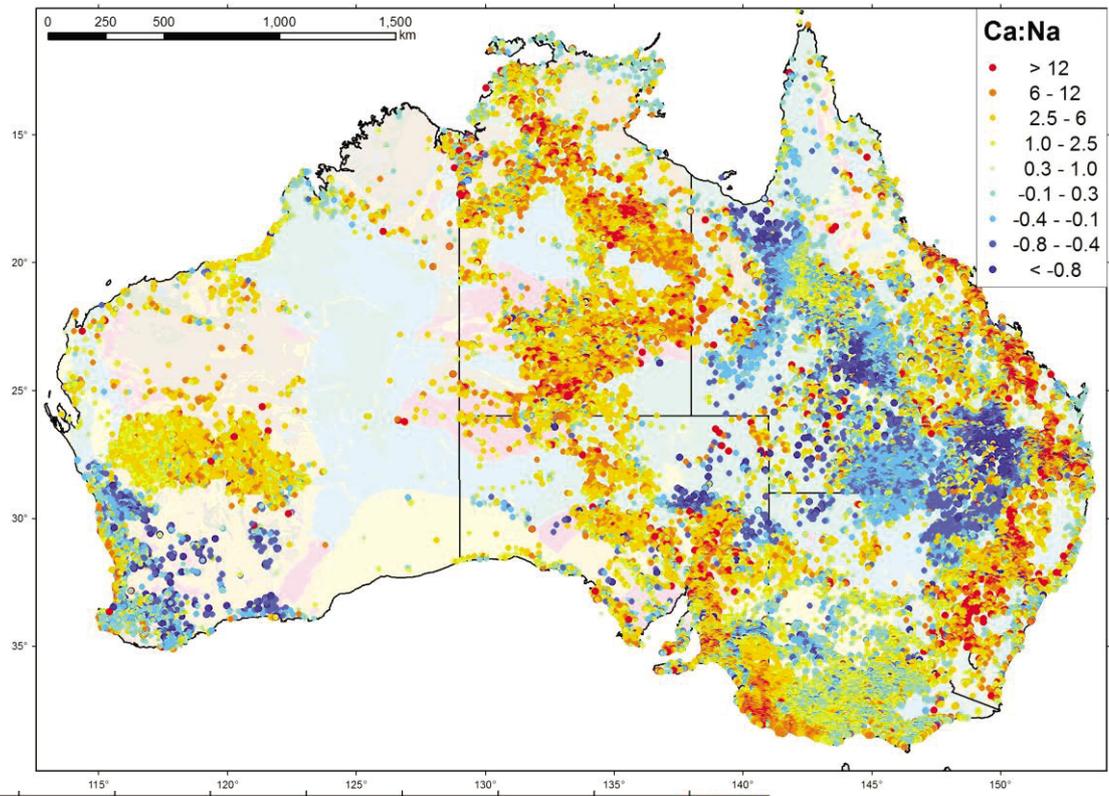


Figure 31: Groundwater Ca:Na Ion Ratio (CgNaSW) distribution across Australia and in Western Australia.

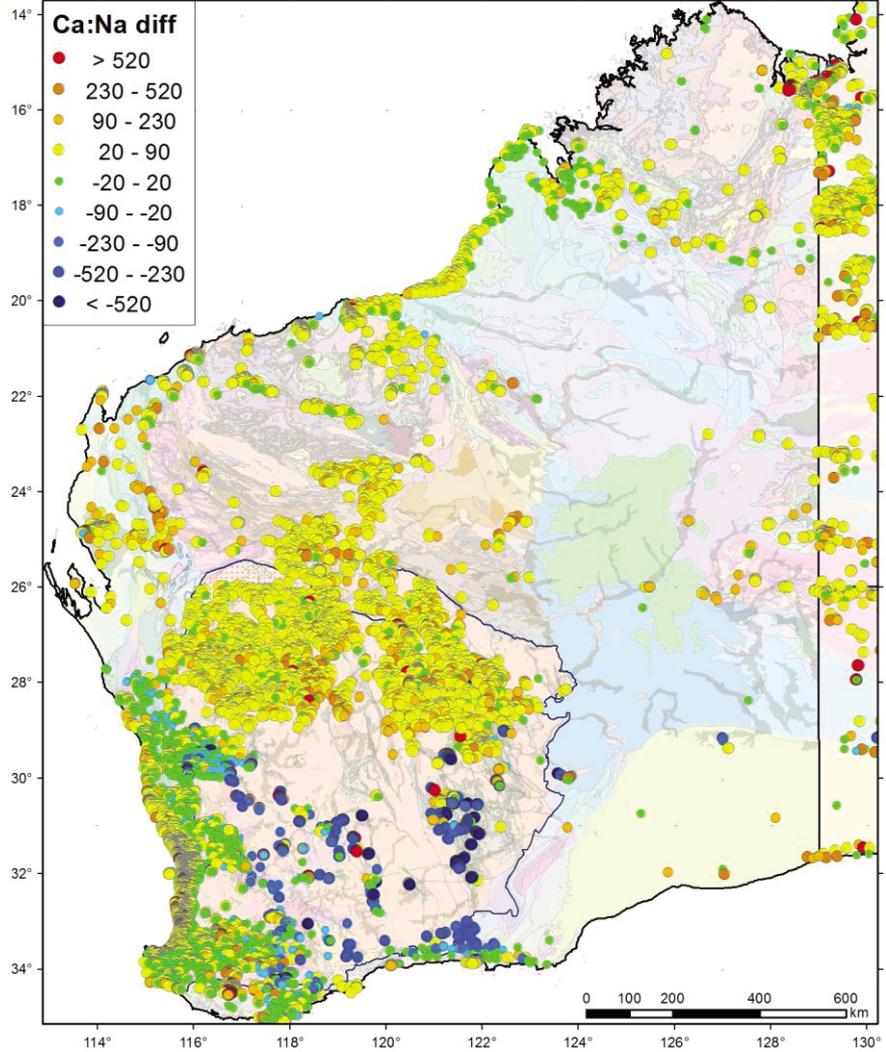
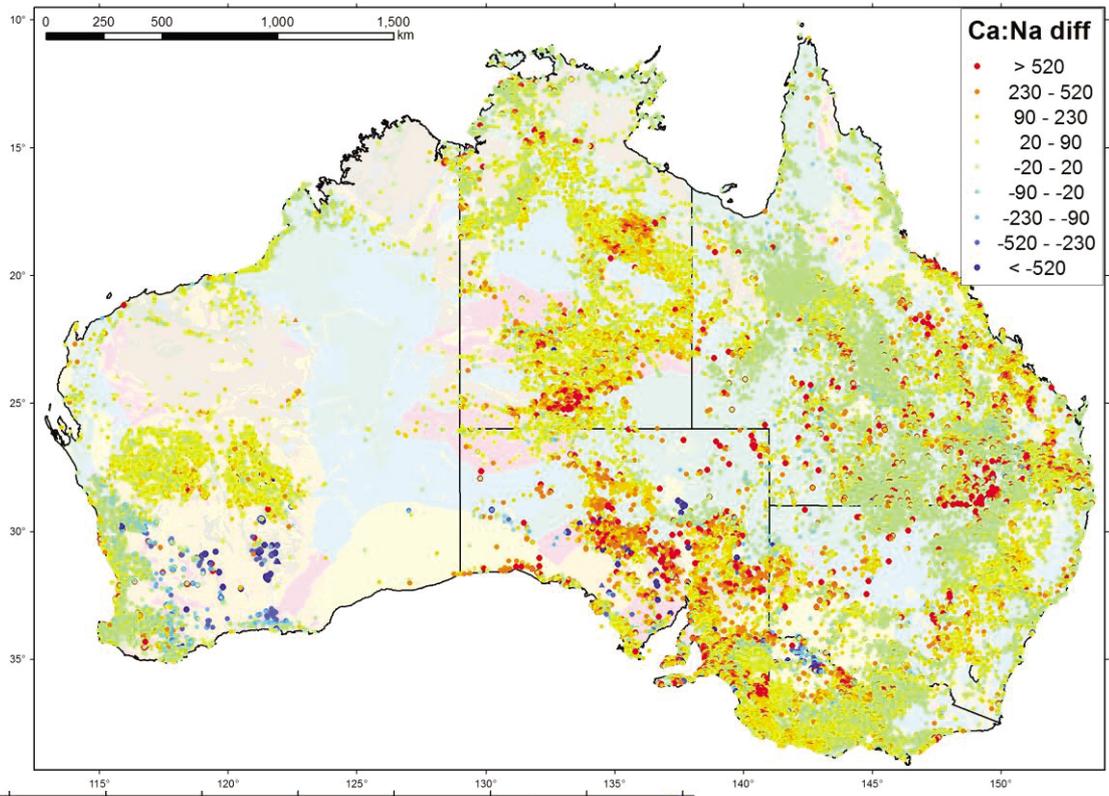


Figure 32: Groundwater Ca:Na Ion Difference (CaNaDSW) distribution across Australia and in Western Australia.

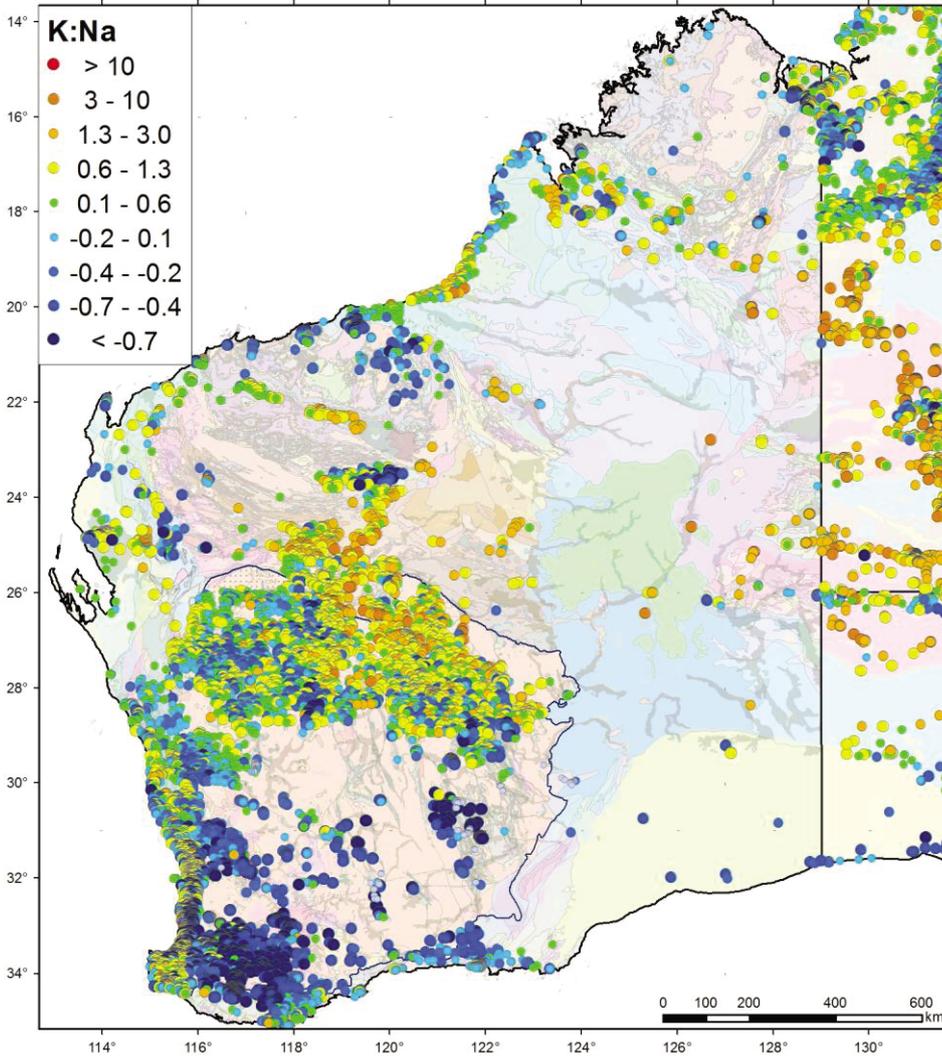
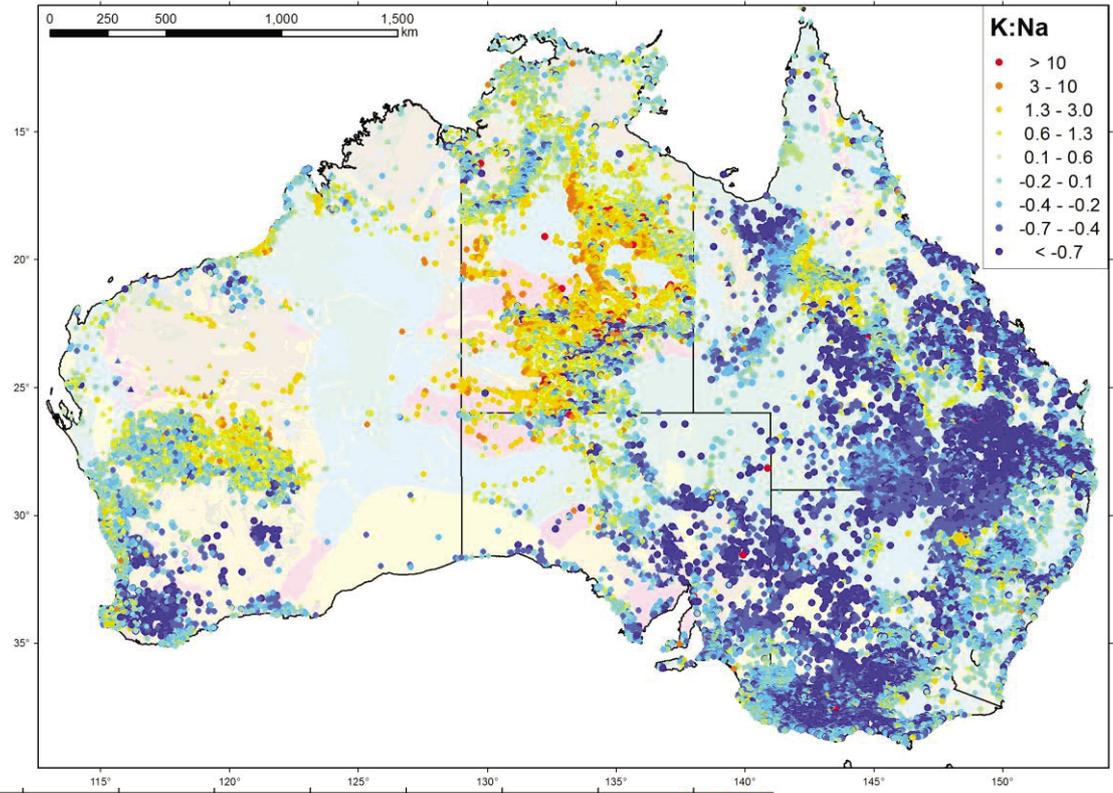


Figure 33: Groundwater K:Na Ion Ratio (KNaSW) distribution across Australia and in Western Australia.

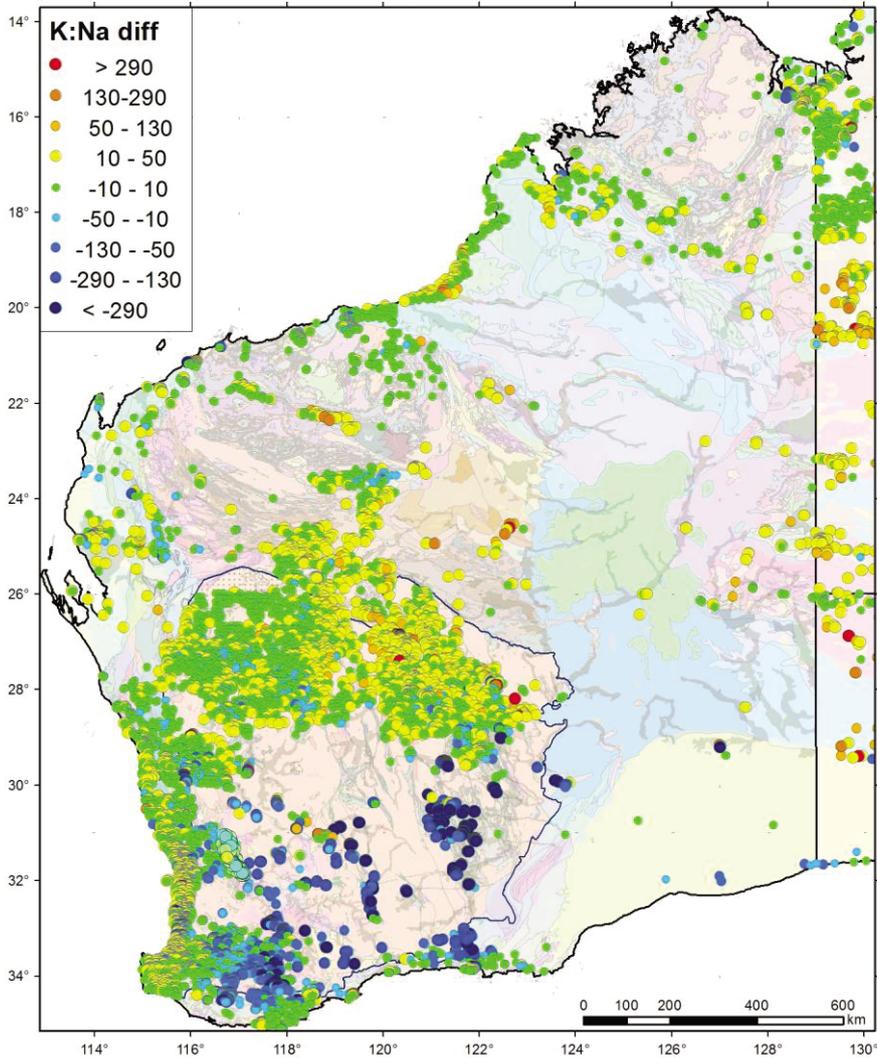
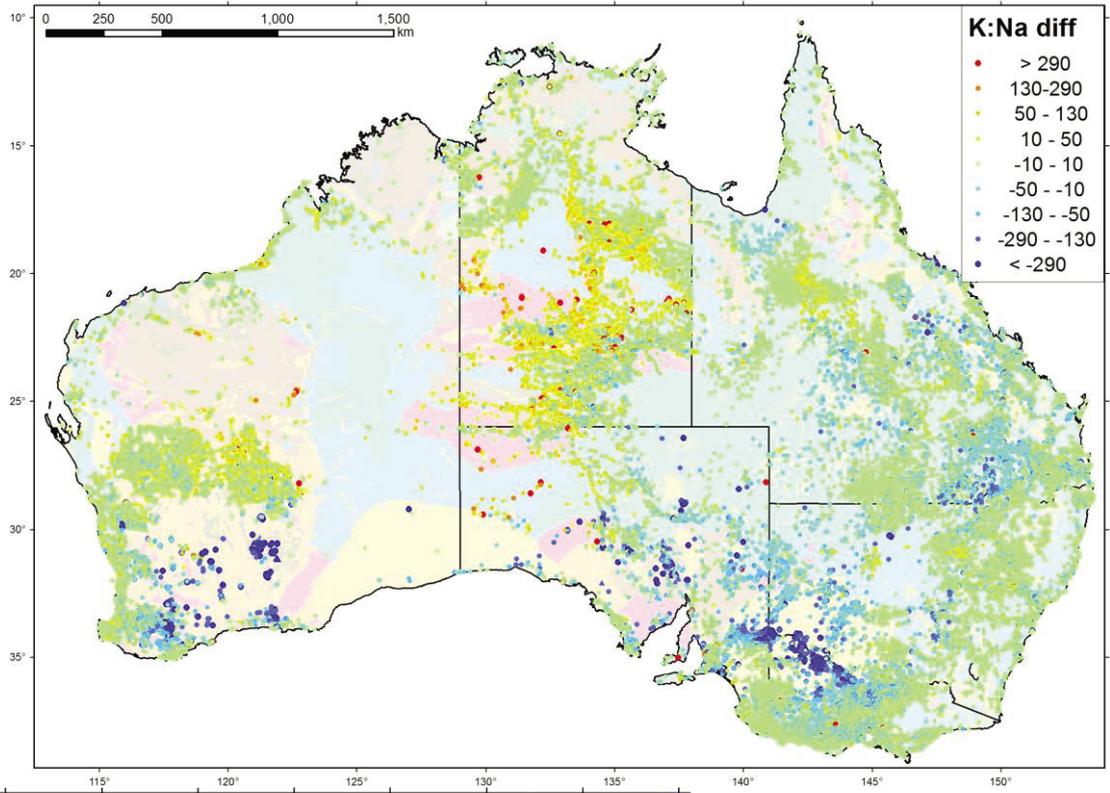


Figure 34: Groundwater K:Na Ion Difference (KaNaDSW) distribution across Australia and in Western Australia.

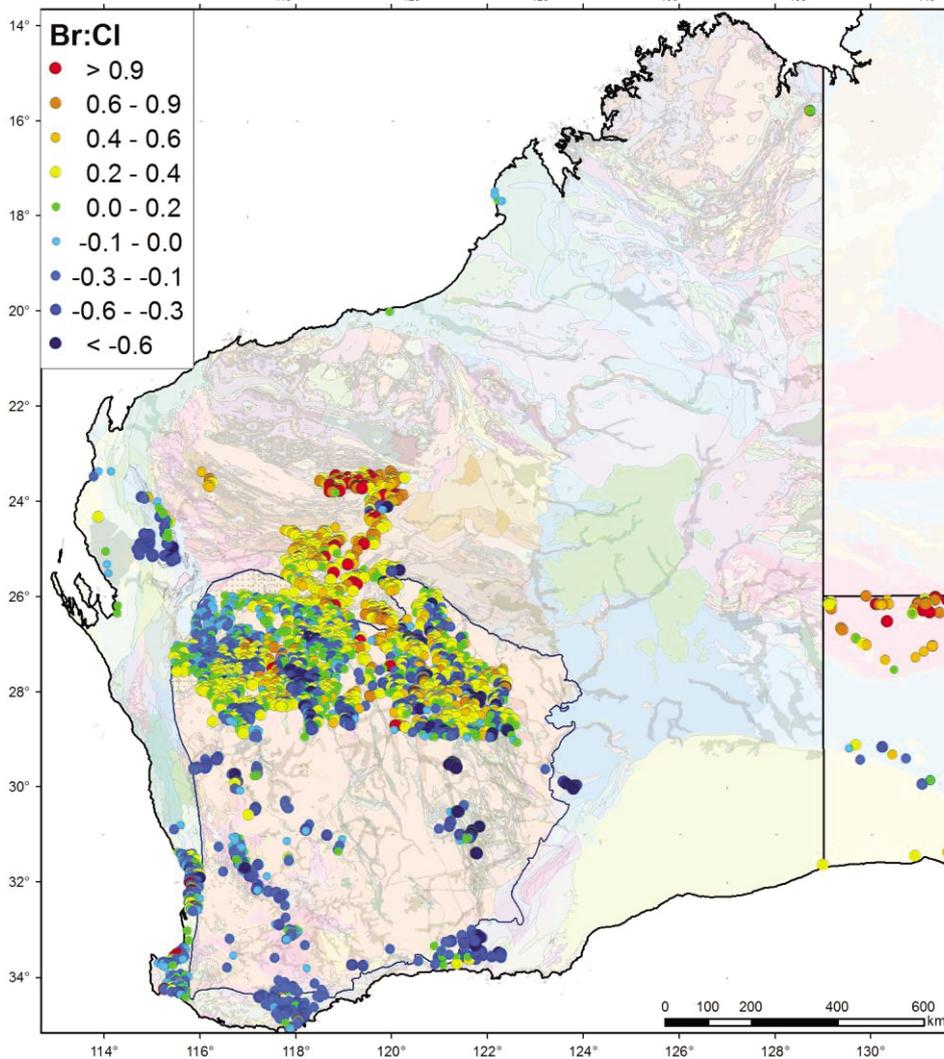
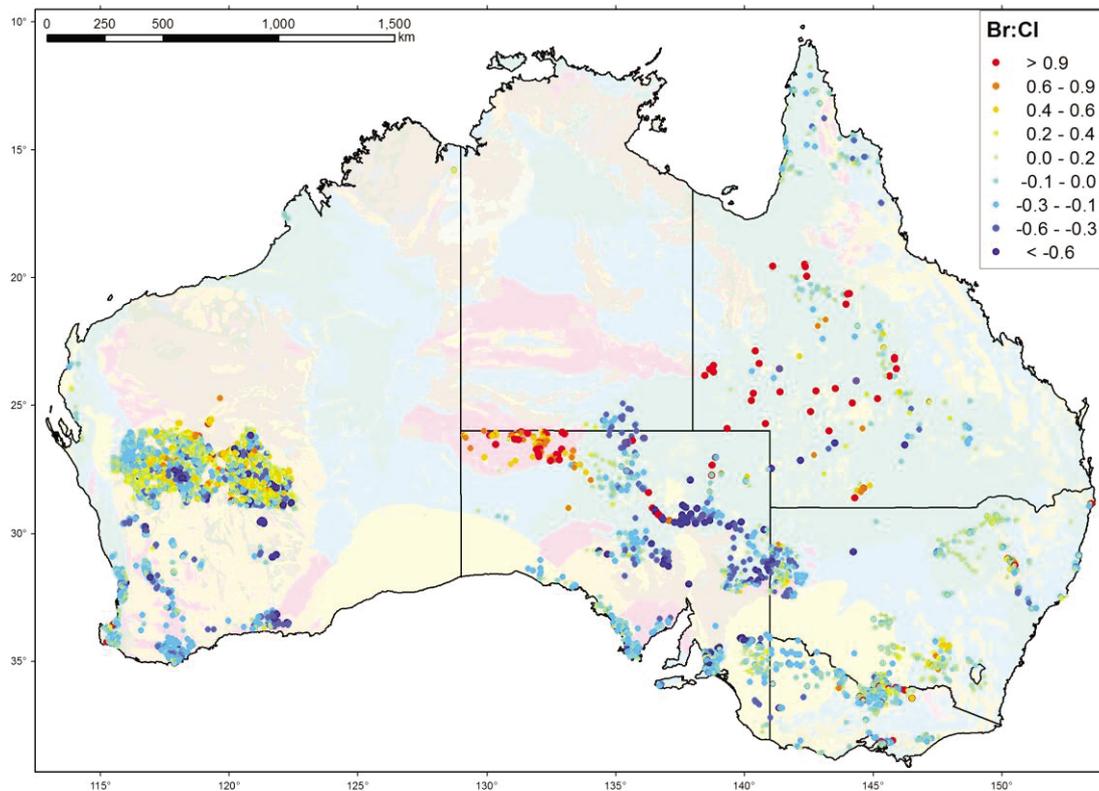


Figure 35: Groundwater Br:Cl Ion Ratio (Br:Cl_{SW}) distribution across Australia and in Western Australia.

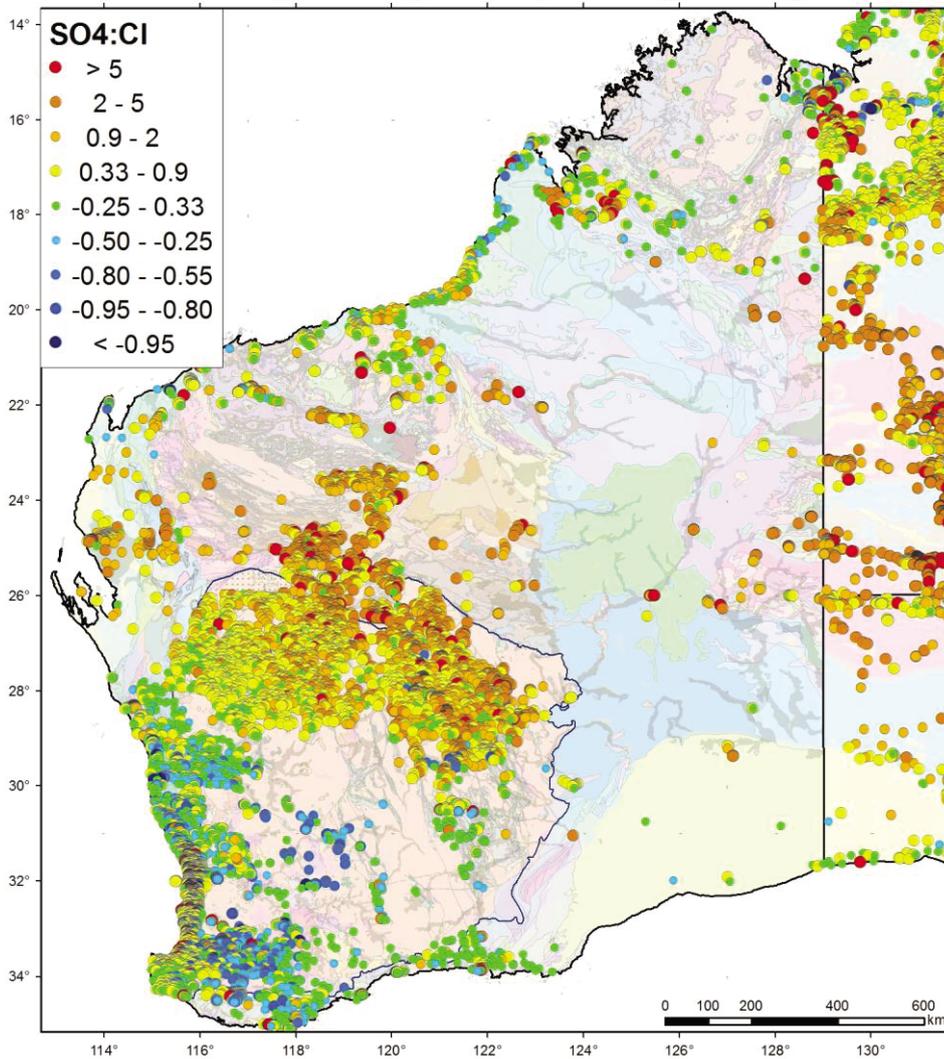
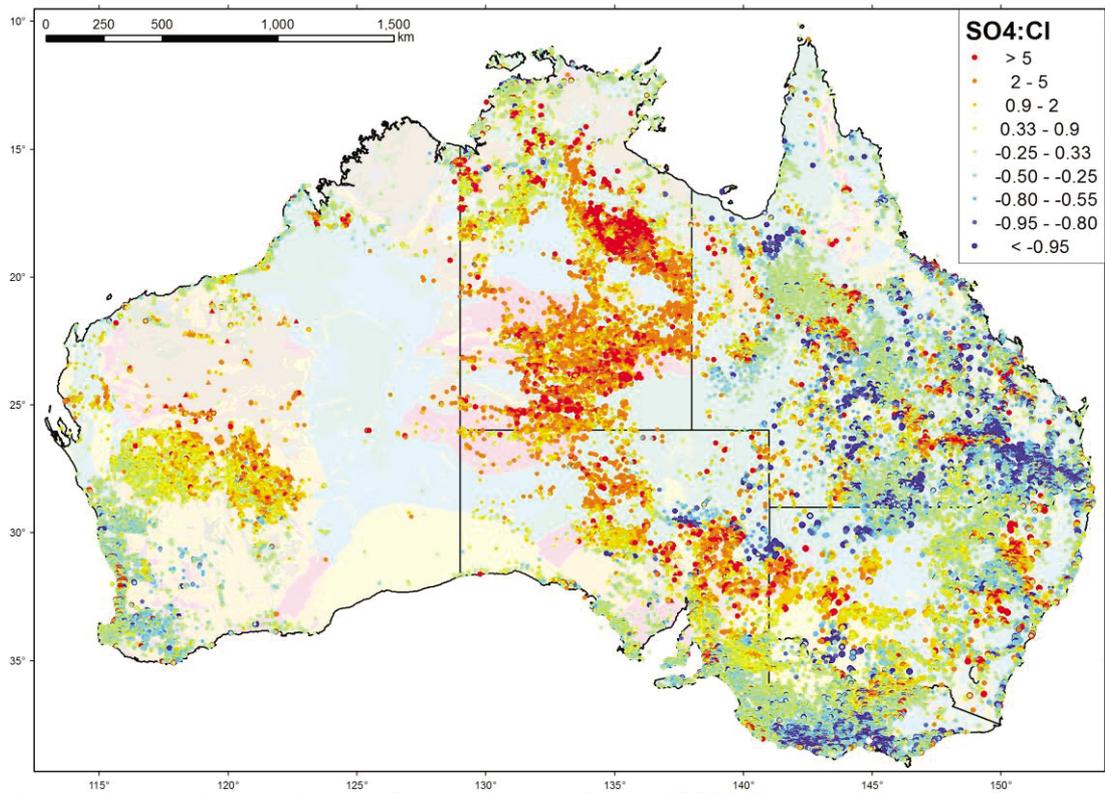


Figure 36: Groundwater $\text{SO}_4:\text{Cl}$ Ion Ratio ($\text{SO}_4:\text{Cl}_{\text{ISW}}$) distribution across Australia and in Western Australia.

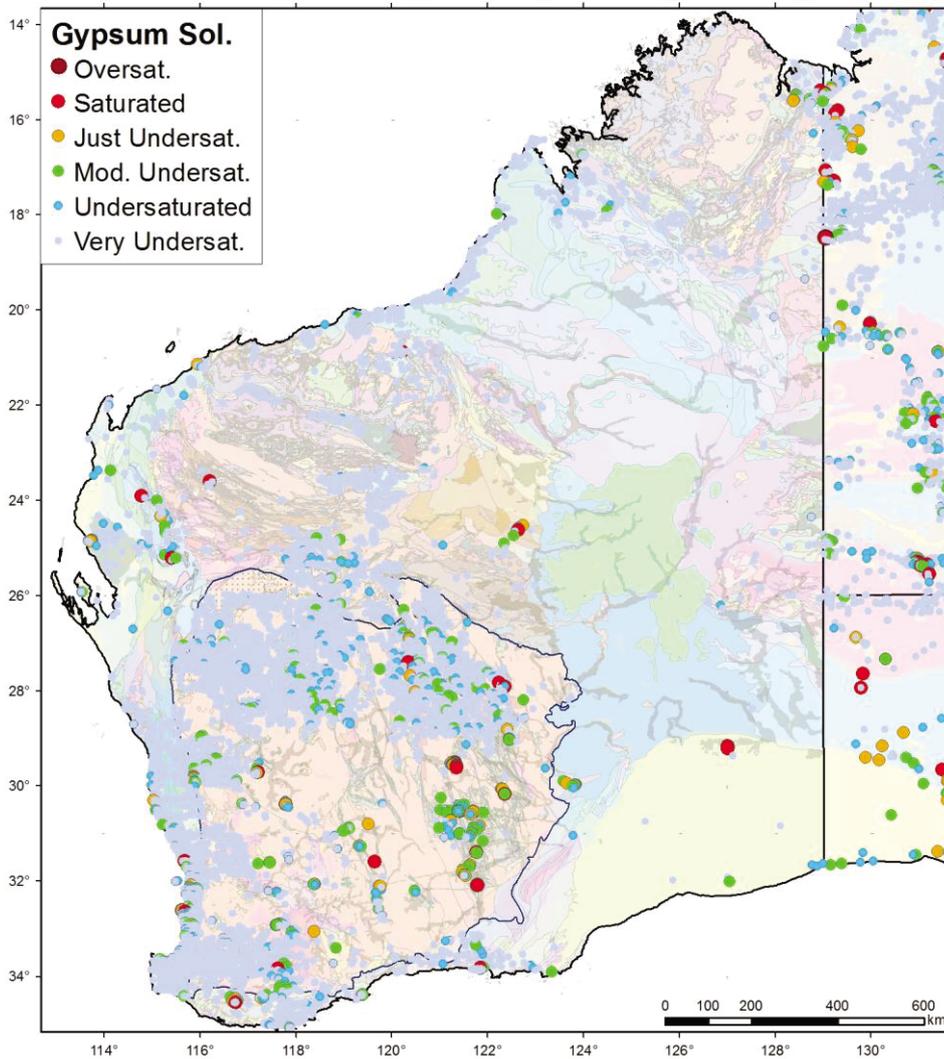
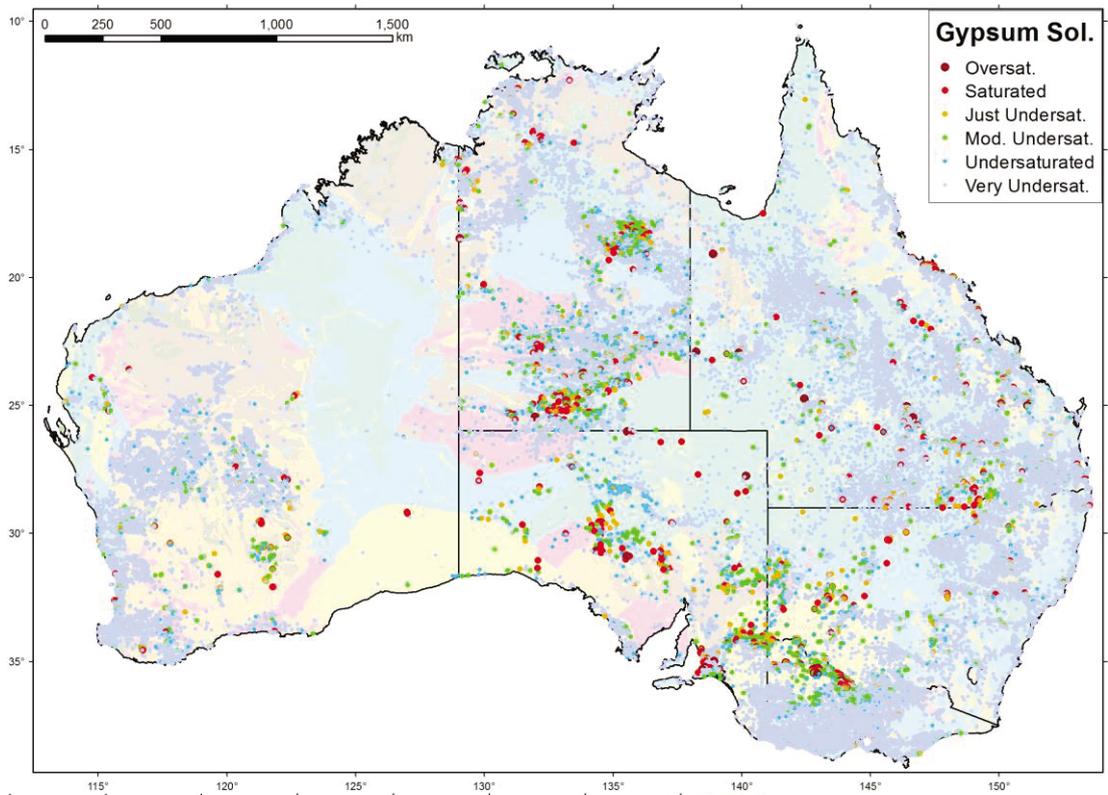


Figure 37: Groundwater gypsum saturation distribution across Australia and in Western Australia.

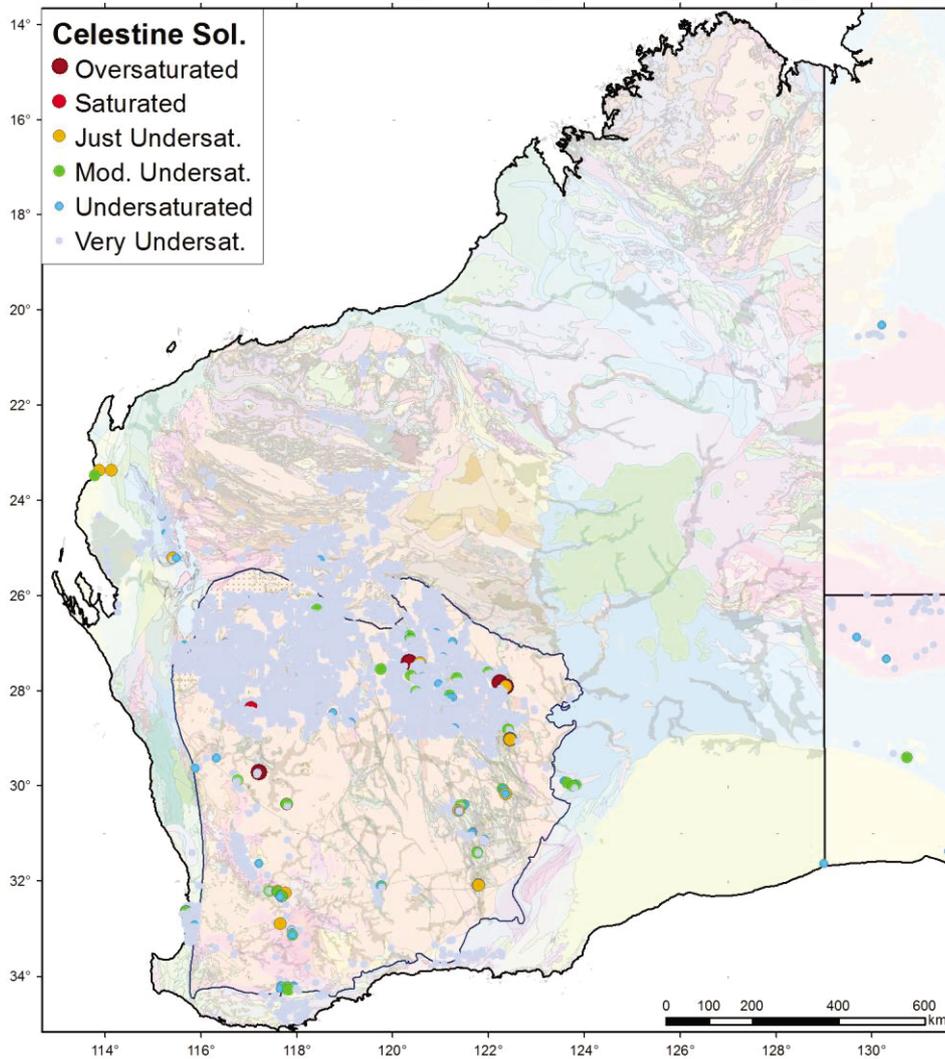
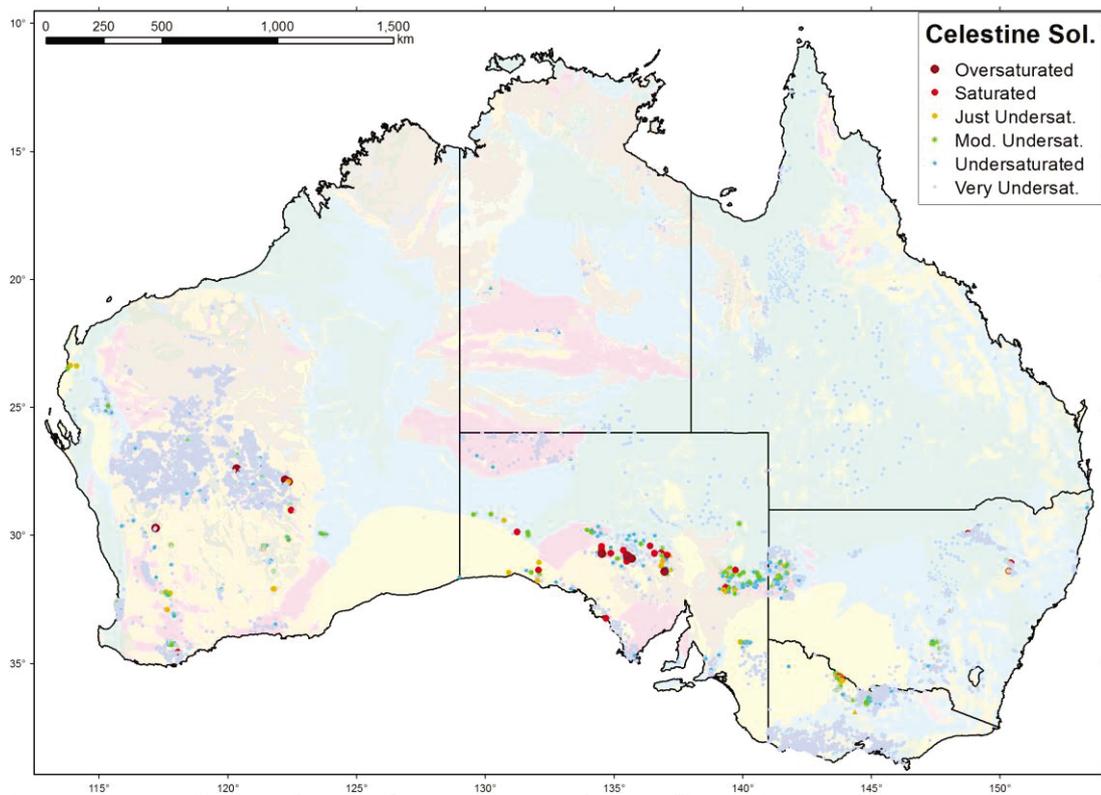


Figure 38: Groundwater celestine saturation distribution across Australia and in Western Australia.

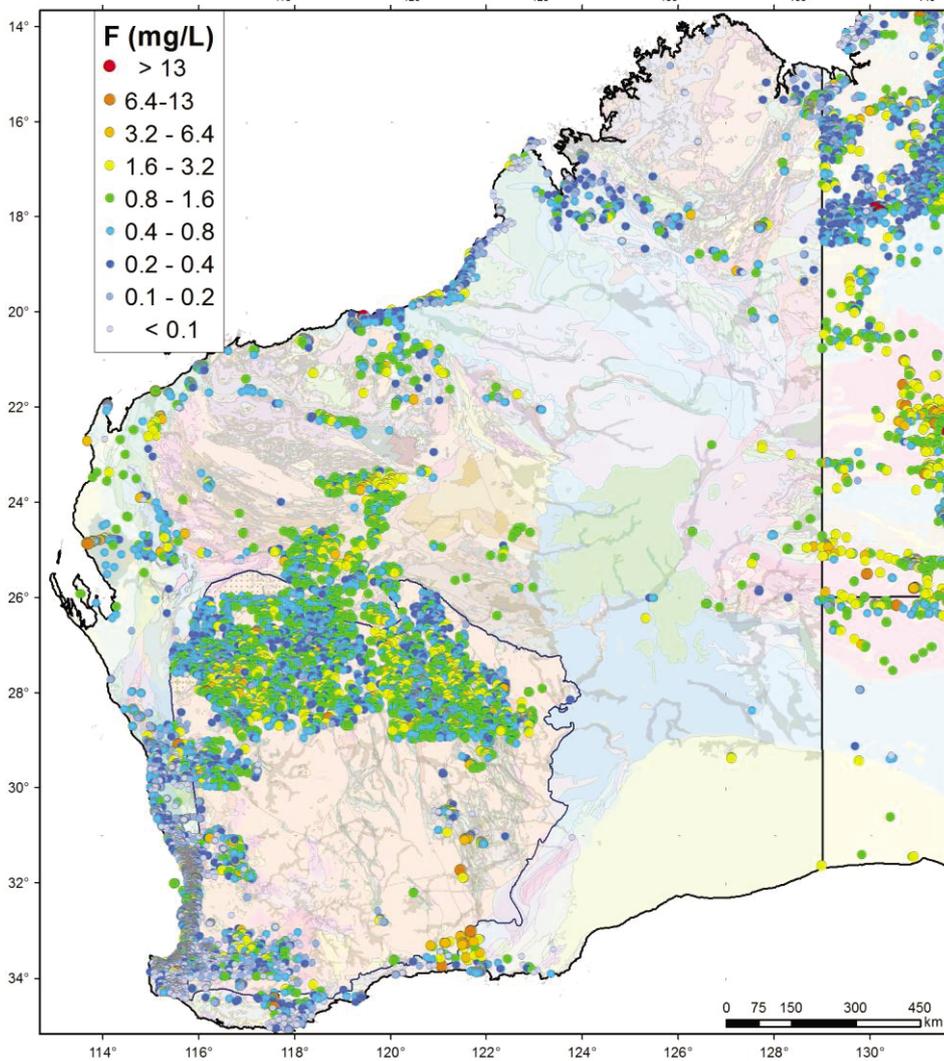
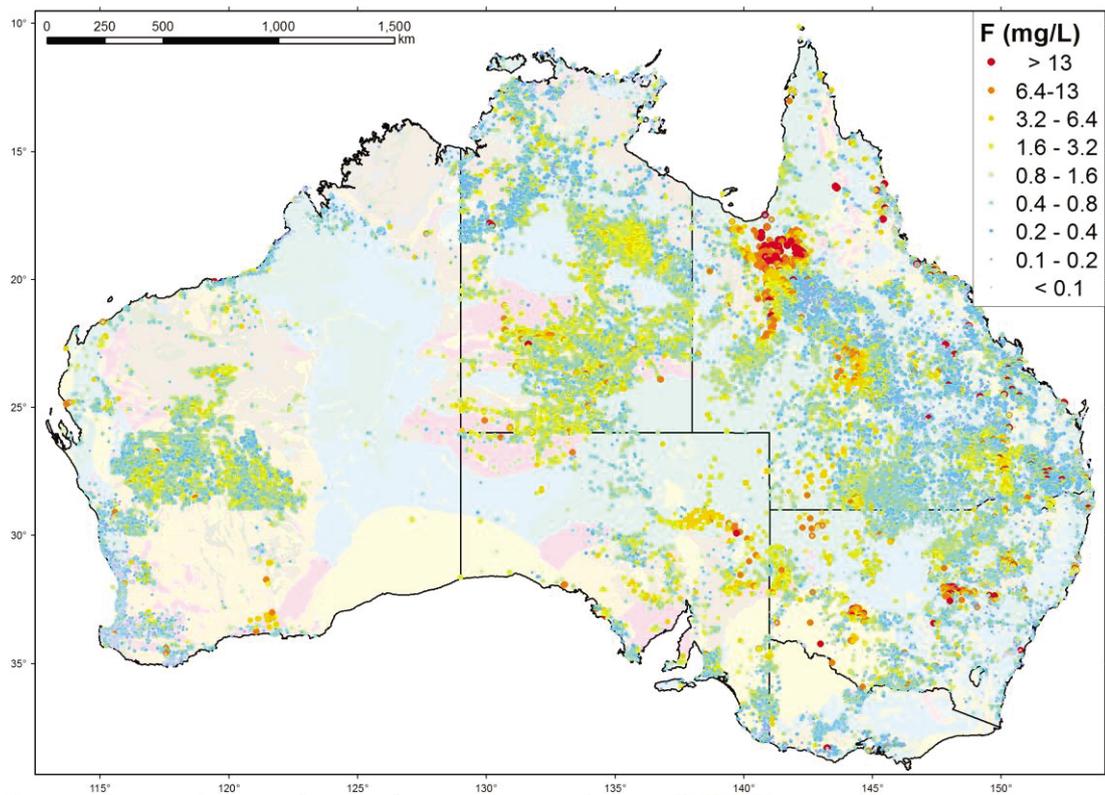


Figure 39: Groundwater F concentration distribution across Australia and in Western Australia.

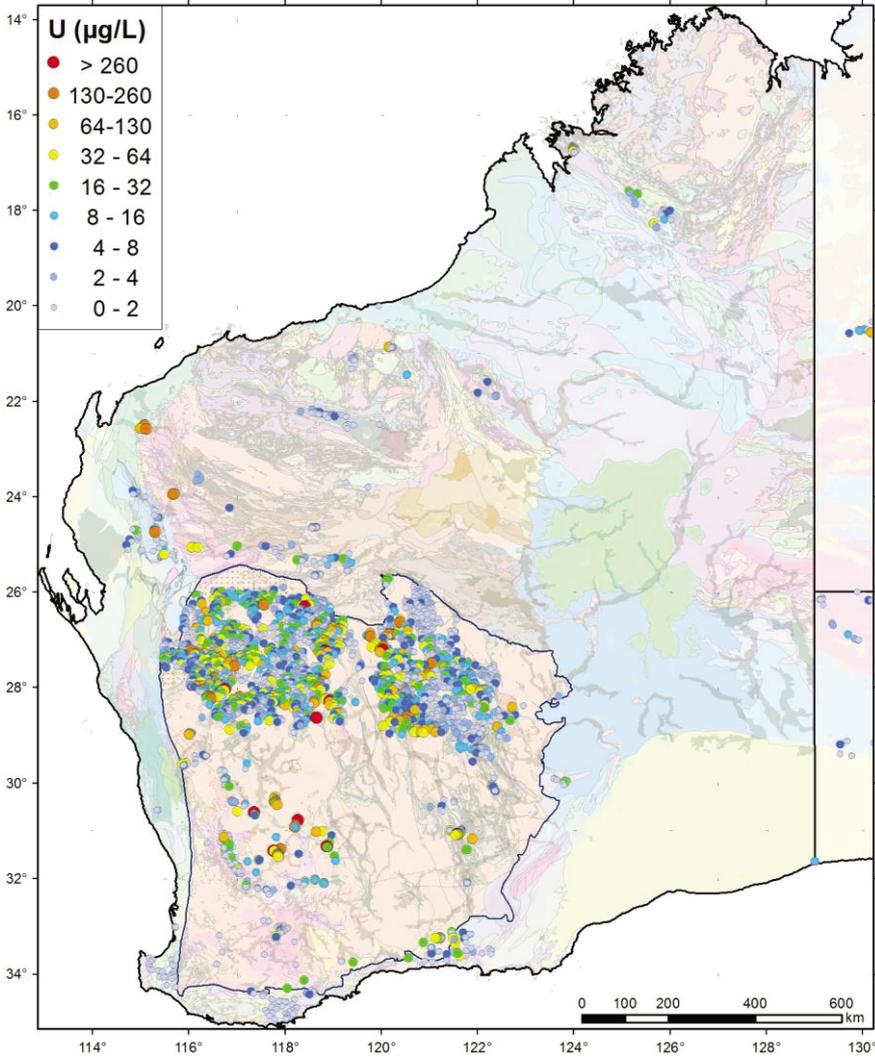
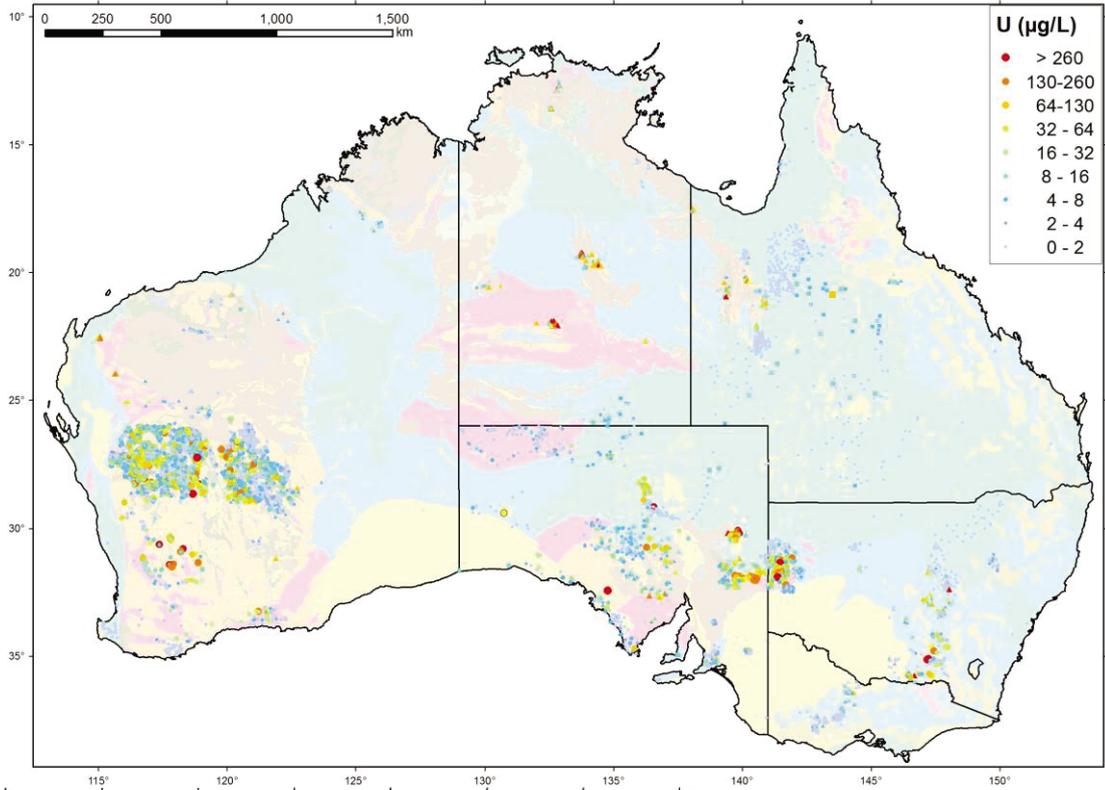


Figure 40: Groundwater U concentration distribution across Australia and in Western Australia.

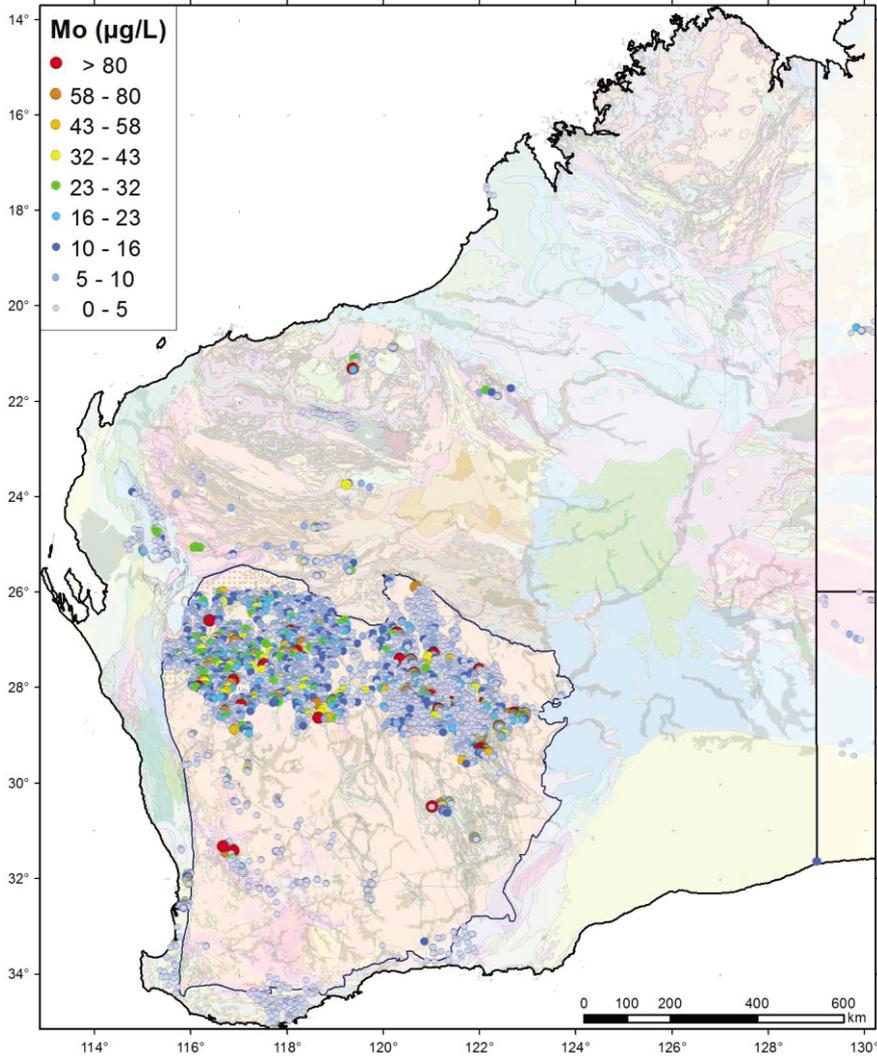
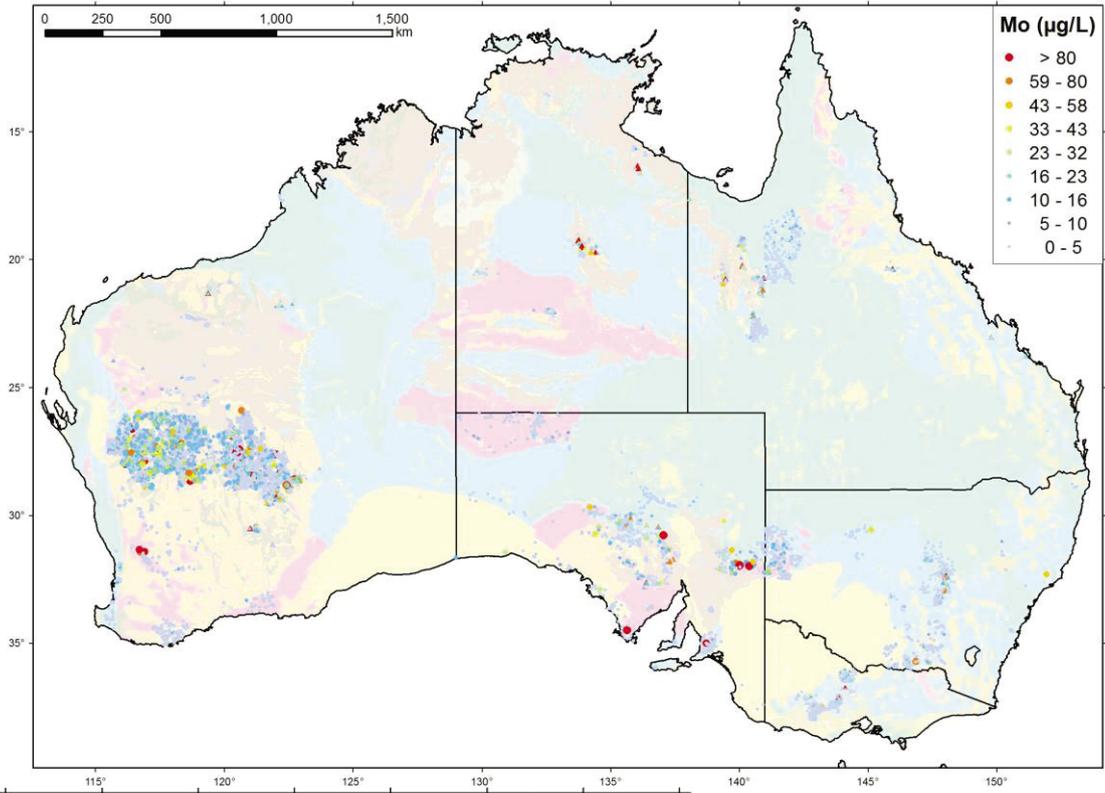


Figure 41: Groundwater Mo concentration distribution across Australia and in Western Australia.

6 Conclusion

Utilising historical data, with minimal meta-data, is not ideal for geochemical accuracy. However, given the number of samples and their potential utility, it is advantageous to extract useful data from these samples. Western Australia groundwater data sent from the Department of Water was therefore subject to a thorough QA/QC assessment. Data that did not pass the assessment was rejected. Though it cannot be assured that all erroneous data had been removed (with particular concern for trace metals with concentrations expressed in mg/L or µg/L), these have been minimised and data appears coherent, with seamless geochemical mapping across state borders.

Utilising this information, the Western Australia government data is being combined with other databases, to map the groundwater chemistry of major regions within Australia. Deriving relatively simple parameters such as ion ratios and ion excess, as well as mineral saturation indices, gives useful input into geological, geochemical and geomorphological mapping. These tools will be enhanced for specific regional studies in ongoing research as part of the “Continental Scale Hydrogeochemistry” initiative.

References

- Bardwell, N. and Gray, D.J., 2015a. Hydrogeochemistry of Queensland. Data release: Accompanying Notes. EP156406 CSIRO, Australia. 22 p.
- Bardwell, N. and Gray, D.J., 2015b. Hydrogeochemistry of Northern Territory. Data release: Accompanying Notes. EP156405 CSIRO, Australia. 21 p.
- de Caritat, P., Kirste, D., Carr, G. and McCulloch, M., 2005. Ground water in the Broken Hill region, Australia; recognising interaction with bedrock and mineralization using S, Sr and Pb isotopes. *Applied Geochemistry*: 20, 767-787.
- Drever, J.I., 1982. *The Geochemistry of Natural Waters*. Prentice-Hall, Inc., Englewood Cliffs, N.J. U.S.A. 388 p.
- Forbes, C., van der Hoek, B., Gray, D.J., Hill, S.M., Giles, D. Normington, V., Anand, R.A., Dietman, B.J., Johnson, A.K., McLennan, Reid, N., Rollison, L. Salama, W., Stoate, K. and Wolff, K., 2013. Geological and Hydrological Atlas of the Gawler Craton, South Australia. DET CRC Report Number 2013/326
- Giblin, A.M., 2001. Groundwaters: geochemical pathfinders to concealed ore deposits. A handbook of recommended procedures for sample collection, analyses and some methods of data interpretation for exploration. CSIRO Division of Exploration and Mining, 2001 70 pp.
- Gray, D.J., 2001. Hydrogeochemistry in the Yilgarn Craton. *Geochemistry: Exploration, Environment, Analysis*: 1, 253-264.
- Gray, D.J., 2015. Integrating Previous Groundwater Research by Angela Giblin, CSIRO, with modern-day Sampling: a Significant Contribution to Continental-Scale Hydrogeochemistry. Submitted to *Australian Journal of Earth Sciences*
- Gray, D.J., and Bardwell, N., 2015a. Hydrogeochemistry of South Australia. Data release: Accompanying Notes. EP156406 CSIRO, Australia. 34 p.
- Gray, D.J., and Bardwell, N., 2015b. Hydrogeochemistry of Victoria. Data release: Accompanying Notes EP158526 CSIRO, Australia. 28 p.
- Gray, D.J., and Bardwell, N., 2016. Hydrogeochemistry of New South Wales. Data release: Accompanying Notes. In preparation
- Gray, D.J. and Noble, R.R.P., 2006. Nickel hydrogeochemistry of the northeastern Yilgarn Craton, Western Australia. CRC LEME Open File Report 243R / CSIRO Exploration and Mining Report P2006/524. 133 p.
- Gray, D.J., Reid, N., Dick, S. and Flitcroft, P., 2012. Pilot Hydrogeochemical investigations in the Thomson Orogen, New South Wales. CSIRO Report EP125537, GSNSW Report GS2012/0972, Australia. 29 p.
- Gray, D.J., Reid, N. and Noble R.R.P., 2014. Improved Hydrogeochemical Exploration in the northwest Yilgarn – Adding Value to Underexplored Areas. EP143875 CSIRO, Australia. 86 p.
- Gray D.J., Reid, N., Parker, P and Hughes, K., 2015 Hydrogeochemical Investigations in the Wagga Wagga Region. CSIRO Report EP151283, GSNSW Report GS2015/0219. Australia. 49 p.
- Gray, D.J., Noble R.R.P., Reid, N., Sutton, G.J. and Pirlo, M.C., 2016a. Regional Scale Hydrogeochemical Mapping of the Northern Yilgarn Craton, Western Australia: A new Technology for Exploration in Arid Australia. *Geochemistry: Exploration, Environment, Analysis*. In press
- Gray, D.J. and others, 2016b. Hydrogeochemistry of Australia. In preparation.
- Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N., 1980. PHREEQE, a computer program for geochemical calculations. U.S. Geological Survey Water Resources Investigations 80 96, 210p.
- McArthur, J.M., Turner, J., Lyons, W.B. and Thirlwall, M.F., 1989. Salt sources and water-rock interaction on the Yilgarn Block, Australia: isotopic and major element tracers. *Applied Geochemistry* 4, 79–92.
- Radke, B.M., Ferguson, J., Cresswell, R.G., Ransley, T.R., and Habermehl, M.A., 2000. Hydrochemistry and implied hydrodynamics of the Cadnaowie – Hooray Aquifer, Great Artesian Basin, Australia. Bureau of Rural Sciences, Commonwealth of Australia, Canberra, 229pp.
- Schwab, A.P. and Lindsay, W.L., 1983. Effect of redox on the solubility and availability of iron. *Soil Science Society of America Journal*. 47, 201-5.

CONTACT US

t 1300 363 400
+61 3 9545 2176
e enquiries@csiro.au
w www.csiro.au

YOUR CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.

FOR FURTHER INFORMATION

CSIRO Mineral Resources
David J Gray
t +61 8 64368678
e david.gray@csiro.au

CSIRO Mineral Resources

Nicki Bardwell
t +61 8 93348028 / +61 8 64368593
e nicole.bardwell@csiro.au

This Record is published in digital format (PDF) and is available as a free download from the DMP website at www.dmp.wa.gov.au/GSWApublications.

Further details of geological products produced by the Geological Survey of Western Australia can be obtained by contacting:

Information Centre
Department of Mines and Petroleum
100 Plain Street
EAST PERTH WESTERN AUSTRALIA 6004
Phone: +61 8 9222 3459 Fax: +61 8 9222 3444
www.dmp.wa.gov.au/GSWApublications

