This is potentially an interesting study with important results and HESS would be a suitable place for publication. I started making detailed comments on the earlier sections (and have included them below as they may be useful) but once I got to Section 4, which represents the bulk of the scientific discussion, I came to the conclusion that the paper needed major rewriting and reorganization before it was suitable for publication. In its present form it is difficult to comprehend and I do not think it would be impactful. I have outlined some of the problems below together with suggestions.

We thank the reviewer for taking the time to review our manuscript closely. We have accepted the majority of suggestions detailed below, in particular the suggestion to reorganise the results-discussion sections. Throughout this response reviewer comments are bold whereas our responses are normal font.

The results and discussion section is poorly set out and not convincingly written. For example, take the text near the start of section 4.1 (line 343):

“There is an excess of both Na+ and HCO3- in the groundwater of the LNA (Supplementary Table 2), compared to ion ratios expected from local rainfall sources and other shallow groundwater alluvial systems in eastern Australia (Martinez et al. 2017). Their abundance defines the ubiquitous presence of Na-HCO3-type groundwater we observe throughout the study area. The Na-HCO3 ratio in GAB groundwater is generally 1:1 (ppm) (Radke et al. 2000; McLean 2003), which is reinforced by the position of the regional GAB samples in Figure 3a. The Namoi River and other regional streams have lower Na+ and HCO3- concentrations and a lower Na+/HCO3- ratio than both the historic GAB data and the deeper alluvial data collected in this study.”

This paragraph makes conclusions without explaining their basis and does not adequately describe the data (it just points the reader to tables and figures where the data are summarized / plotted). There are also several concepts mixed together (the ion excesses, the comparison of water from different reservoirs).

The results and discussion have been split now and both sections have been updated. The results section starts at line 357 and is split into major ions, water stable isotopes and isotopic tracers. The discussion section at line 438 and contains the same headings as the original paper.

The next part of this discussion (lines 351 to 362) also mixes observations with conclusions and deals with a variety of processes (mixing, evapotranspiration, and calcite saturation). There are again few details; what does “towards calcite saturation” mean (what are the saturation indices, where do you discuss them)? Why is the calcrete important (is it found at groundwater discharge points in the watershed, for example?).

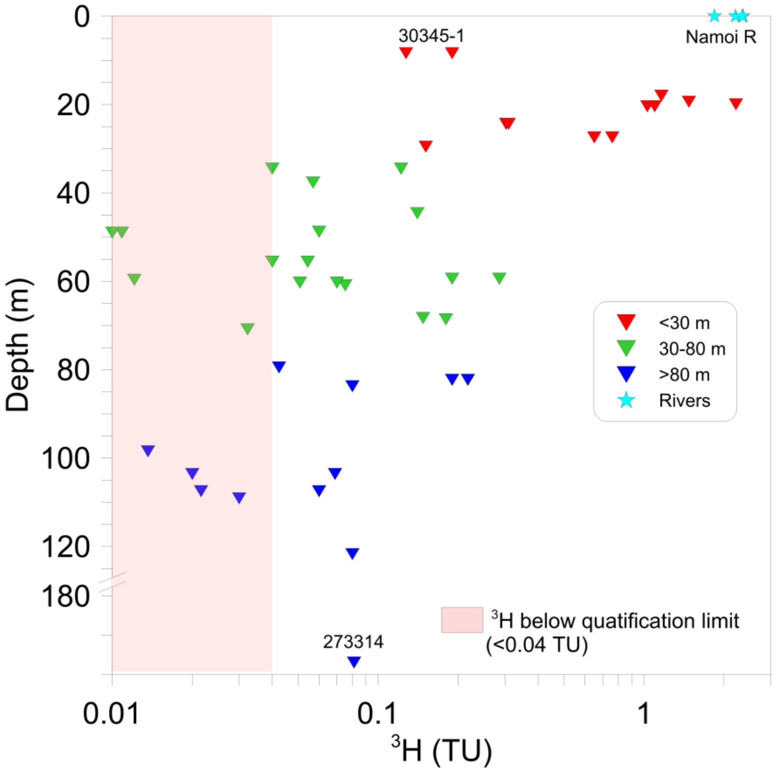
The discussion on calcrete has been deleted in the streamlining of the manuscript in our attempt to remove anything that was tangential to the primary story we are presenting.

I agree that the halogen chemistry in Fig. 4 is consistent with evaporation but you need to explain why that is so in the text (perhaps more to the point is this important for understanding recharge and mixing?).

At line 453 as part of the new discussion we state “As we assume that Cl^- is behaving conservatively (Appelo & Postma 2005) we surmise that increases in dissolved major ion concentrations concomitant with increases in Cl^- in the shallow groundwater are likely to be a result of evaporation" to explain our interpretations regarding the increases in major ion chemistry. Additionally, this comment now refers to the new Figure 3a, b, and c in the results section. Further, all parts of figure 3 are also primarily used to show mixing between the GAB and the alluvial groundwater.

Most of the other sections / paragraphs in the results and discussion are similarly hard to follow. For example, the discussion of Tritium (lines 416 to 431) includes discussion on historic Tritium concentrations with the distribution of Tritium from this study. The latter is never illustrated (the data are in a supplemental table but the spatial variation is important so should go on a map or section). The Tritium activities are not specified so sentences such as "However, despite decreasing activities, 3H remains relatively prevalent in the deeper part of the system." are very non-specific. The conclusion reached "This indicates the extent of recharge from episodic flooding and shows that surface recharge reaches the deeper LNA (down to _80 m bgs) relatively quickly (< 70 years)." then becomes impossible to assess.

3H activities are now included and described in the results section (Section 4.3 – line 417). Past data is introduced mentioned in the discussion (lines 483-488), to put our results into regional and temporal context. We have now added a plot of 3H (TU) vs depth (Figure 5 - as seen below) so that the reader can easily put into context the activity of 3H at a given depth throughout the LNA. The rest of the discussion has been edited so that any results are now in the results section and the writing cleaned up.



There has been a lot of work on determining residence times and mixing from concentrations of radioactive isotopes (including by the coauthors of this paper). Much

more could be done to firm up the conclusions, for example some of the samples on Fig. 5 seem to not have undergone extensive mixing and probably could be used to determine residence times.

It is correct that some samples in the old Figure 5 (now Figure 6 in the revised manuscript) have not undergone extensive mixing. That is firmly portrayed in the original figure 6 (now Figure 7) for the same dataset. We included residence time ranges in figure 6 (now 7) for both end-members. However, this is not a paper about complex dating corrections and decoupling of residence times in mixed samples, which we have now emphasised at lines 108-112. The emphasis is on identifying main groundwater sources within an alluvial aquifer, the use of a multi-tracer approach and to bring attention to water managers about the dangers of utilising simple hydrogeological models without incorporating any hydrochemical evidence.

In section 4.3 it is not clear whether the Chlorine-36 data are being interpreted in terms of ages or mixing. Elsewhere, you have stressed mixing but here you calculate ages. This is despite Chlorine-36 being notoriously difficult to use for anything other than broad indications of residence times due to the input function varying (in unknown ways) over time due to climate variations. The Chlorine-36 ages are presented without much scepticism or discussion.

We agree that 36Cl can be notoriously difficult to interpret and we have acknowledged this in text now (lines 87-90). However, the Pilliga Sandstone has low and fairly consistent Cl concentrations, so if there was ever a system where 36Cl could be used to say something about GAB residence times, it is this one (this has also been mentioned at the same location: lines 87-90). This is the same for the Coonamble Embayment elsewhere (eg. Mahara et al. 2007). There is an abundance of regional background information on 36Cl, which we refer to throughout the manuscript. Using similar assumptions applied to 36Cl elsewhere in the GAB, we provide some residence times (line 520), only applicable for the extreme GAB end-member. The caution and scepticism regarding “absolute ages” is incorporated in figure 6 (now Figure 7). The 36Cl section (section 5.2 – line 506) reinforces the mixing processes and only provides some residence time interpretation for the extreme end-members, similarly to what is done with 3H (see original figure 6).

Mahara, Y., Habermehl, M.A., Miyakawa, K., Shimada, J. and Mizuochi, Y. (2007) Can the 4He clock be calibrated by 36Cl for groundwater dating? Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 259, 536-546.

Calculations through Section 4 are poorly presented. For example, the discussion of mixing (lines 509-530) uses a single composition for the end-members and these is no sensitivity analysis. The results are presented without much discussion of uncertainties etc.

We have added a ‘Geochemical calculations’ section (section 3.3 – line 326) to explain our calculations in the old results and discussion. Regarding uncertainties, mixing and other processes (such as evapotranspiration and irrigation returns) can overprint the simple Cl mixing. However, the Cl mixing isn’t considered in isolation – this is where our multiple tracers come into effect. For example, samples with [Cl] < 31 mg/L, 3H activities above our detection limit (> 0.04 TU) and/or 14C > 90 pmc are considered as 100% modern (< 70 a) flood recharge (eg. 36001-1&2, 25329-1, 30345-1, 25332-1, 25327-1&2). In this case, two samples (25327-1&2) with anomalously high NO_3 concentrations could be influenced by potential irrigation returns. Conversely, samples recovered from generally deeper piezometers along the B-B' section in figure 2 have higher Cl concentration that coincide with 3H below or very close to the detection limit, 14C contents generally < 5 pmc and, most importantly, 36Cl/Cl below 58 ($x10^{-15}$) and are considered to be comprised of a higher percentage of GAB groundwater.

Section 4 is not helped by its structure. It mixes introductory material (e.g., lines 453-455), conclusions, and description. It is also not very tightly written and uses mainly qualitative descriptors rather than specific values. It is possible to mix results and discussion, but it needs skill otherwise the text becomes meandering and there is commonly not the rigor in explaining the salient features of the data before they are interpreted. The conclusions of this paper are plausible, but the way that it is written does not do them justice.

The results and discussion have now been split and the writing throughout the entire paper tightened. All the results are now explained using their specific numbers in section 4 and we have aimed to remove most of the qualitative descriptors.

Some suggestions for revamping the paper are:
1) Separate the results and discussion and make sure that you adequately describe the important pieces of the data (don't just say which diagram or figure it is contained in).

Results and discussion have been separated. The results section now describes important aspects of the data such as parameter ranges and trends (Section 4).

2) Concentrate on what is important. The aims of this study is to understand recharge and mixing, in which case some of the details of the water chemistry seem superfluous. For example, it is important to determine whether the GAB waters and local recharge have different compositions but some of the details of the processes could be omitted. The Chlorine-36 is more valuable as an indicator of mixing rather than residence time, but recharge rates estimated from Tritium are important.

The manuscript has been cleaned up substantially, primarily as a result of the restructure. Discussions on sustainability have been omitted and the geochemistry of the groundwater, and our multi-tracer approach to estimating GAB discharge made the focus. We have further included clarification of the 3H results (Figure 5 and section 5.1.1 – line 476) and detail on how we use the 36Cl data (section 3.3 – line 326, section 5.2 - 506, Figure 2).

3) In a similar vein, the paper would be improved by more hydrologic information at the expense of some of the detailed geologic information. Is the interpretation of mixing consistent with the hydraulic heads? What are the groundwater flowpaths?

The geologic information has been considerably shortened and we have added more hydrologic information such as the general groundwater flowpaths and K values (lines 180-184).

4) Include enough justification of calculations to make them convincing and some sensitivity analysis or discussion of uncertainties.

Please refer to our comments above regarding the calculations.

I am guessing that the senior author is a graduate student. The coauthors, however, are not and should have picked up on the more obvious problems with the way that this study was framed and presented.

Specific comments

Introduction

The introduction provides a general outline of the science and the reasons for carrying out the study. The first paragraph is not very clearly expressed. For example, Why specify “modern infiltration” – recharge implies modern processes

The first paragraph has been restructured and edited. “modern” has been removed

“Spatial and temporal data resolution and heterogeneity in hydrogeological properties result in considerable uncertainty when allocating recharge to each source and mapping pathways of flow” is very unclear.

At lines 53-54 this sentence has been revised to make it more comprehensible. “…mapping pathways of flow” has been removed as it wasn’t pertinent to the story (compared to allocating sources of recharge) and made the sentence laborious.

What is a “dynamic groundwater gradient”?

“Dynamic groundwater gradient” has been changed to “…change in the magnitude of groundwater gradients and direction over time…” (line 56).

The introductions to papers are important as they frame the study and hopefully persuade the reader to continue reading, so it is worth making them as clear as possible. Line 86. What do you mean by “modern/submodern”?

Submodern has been removed.

Line 89. It would be useful to explain briefly how the various isotopes help understand mixing as it might not be clear to all readers.

We have included a simple sentence at lines 77-79 to explain how various isotopes help understand mixing (“Isotopes of dissolved species can be useful for elucidating groundwater mixing provided the different sources of groundwater have distinctly different and consistent isotopic signatures”). We also refer to Bentley et al. 1986; Andrews & Fontes 1993; Love et al. 2000; Moya et al. 2016 at this location for the reader to peruse for further information.

Line 96. It would be clearer if you split this material off as your objectives get lost at the end of the discussion of the techniques (perhaps put a subheading in for emphasis).

We have made this a new paragraph so as to emphasise the objectives (lines 97-109).

Lines 98-99. This is stating a conclusion, which you should leave until later.

We have changed the end of the introduction (lines 97-109) to now state only what we did, rather than what we found and moved the conclusions to the end of the manuscript.

Study Area

This section provides a comprehensive description of the study area. Some specific comments

Lines 139-141 is difficult to follow for anyone not familiar with eastern Australian groundwater hydrology. Can you add a key map of the basins to Fig. 2?

We have simplified this text so that it is not quite so laborious on the reader and simplifies the concept we were trying to convey. We have also referred to our main GAB reference (Radke et al. 2000), which has some excellent basin maps for the readers perusal. We have not included a map in Figure 2 of this work because we did not want to oversaturate with figures and have too many geological maps in the one figure.

Lines 141-162. The description of geological framework is difficult to relate to Fig. 2 as you do not specify the age of the various units. Provide a few more details in the text.

Age of the various units has been specified in text throughout lines 141-156 now.

Section 2.1 is probably too detailed for the study. While understanding the geology of the area is important, I am not convinced that the geologic history needs to be gone through in this much detail (for example, is the rainfall variation between the Miocene and today important for this study). This section could be cut fairly substantially. What would be more useful, and which is not there, are firstly some hydraulic properties (K, porosity etc) and secondly some description of groundwater flow.

This section has been shortened considerably. There is no porosity or permeability data for the region, however we have added some K values and we explain the general direction of groundwater flow (lines 180-184).

Lines 197-201. This repeats material in the introduction and could be removed.

This section at 188-192 has been shortened, however not removed completely because it highlights the gap in the literature regarding the use of catchment water balance models together with hydrochemical data.

Line 205. The numerous Merrick references seem to be to a series of non-publically available documents. The reference to the Kelly et al., summary would seem sufficient.

The references have been eliminated and instead Merrick 2000, a PhD thesis available through the UTS library, has been used (line 196). Additionally, Kelly et al. 2007 has been included in many of these places.

Lines 208-209. Not clear what you mean by “There are equivalent solutions for all water balance models and the solution presented is often constrained by several factors.”

We agree and this sentence has been changed to “There are multiple plausible solutions for all…” (line 198).

Section 2.2.1 does not add that much useful. You state that there are a range of models but provide few details. The discussion of the models seems to reside only in unavailable

consultants' reports and then the point about not taking into account geochemistry is reiterated. This section could be shortened, especially as you do not make detailed comparisons with specific models later in the paper.

This section is core to the problem with respect to the issue of water balance modelling in the Namoi. We have removed the references to unavailable reports and replaced with a PhD thesis (Merrick 2000) but we have left the section (beginning at line 194) in the manuscript so that the 22% GAB contribution that we later use for comparison to our estimates of 70% have some basis.

Figures

Fig. 1. Define "bgs". Rather than describing what is on the two axes, just label them in the graphs. Text on the map is too small (you could make the map larger and put the Australian map in an unused corner)

Bgs has been defined. We describe the axes rather than place them on the graphs because the font is too small otherwise and the repetition of labelling the axes on every graph was taking up too much room. The map has been made larger and the map of Australia placed in an unused corner of the map.

General Comments: **This manuscript has potential to be a very interesting article and could have a big impact on our current understanding of the interactions between alluvial aquifers, regional aquifers, and surface-water systems. The topic should have broad interest to other research on alluvial aquifers and broad applicability to global alluvial groundwater systems. The combined geochemical tracer and multiple isotopic tracer approach is a potentially robust way to sort out these interactions. However, the manuscript suffers from poor organization and lack of specificity in the methods and interpretations. This prevents a recommendation to accept the article as it is currently written. Instead, the recommendation is to accept after major revisions including the organization and technical detail of the article. In addition, it was very difficult to read the manuscript due to awkward syntax and lack of focus (see Specific Comments).**

We thank the reviewer for their time in reviewing our manuscript closely. We have attempted to address all concerns below, particularly the major concern of the organisation and technical detail of the article and the syntax and focus. The manuscript has been restructured and this has made the manuscript more focused on the key messages.

The major findings/contributions of this manuscript hinge on the authors' interpretations of the isotopic and geochemical data. In general, these sections need much more clarification than is provided and in some cases, additional data mining may be necessary (although I think the latter is the smaller of the issues). For example, a considerable emphasis is placed on 3H concentrations. However, almost all of the 3H concentrations are close to background or are 3H dead. This has implications for the mixing model and it has implications for the residence time estimates. It's not unusual to find 3H dead waters which have slightly elevated 36Cl/Cl ratios. 3H, even from the bomb-pulse, is decaying faster than 36Cl even in the presence of mixing with recent recharge and sometimes 36Cl does a better job of sorting out mixing than 3H (especially for waters that are 100 years or older). However, the real strength that the authors have is the ability to sort out young and old fractions (relative terminology) using 14C pmc. In the absence of carbonate exchange and mixing in the aquifer (another topic which needs additional clarification) the 14C pmc value is very useful in sorting out these endmembers as the authors attempt to do in Figures 5 and 6. In any case, the authors need to provide additional clarification on how they sorted out the mixing processes that affect these tracers.

Regarding data mining, this manuscript and the authors' interpretations would be strengthened by providing the 3H, 14C, and 36Cl/Cl of modern precipitation. Are these data available? If so, cite them. This would enhance the mixing model which is used to determine the fractions of GAB water in the LNA. This calculation also needs additional clarification and the authors should present the equation and discuss sources/estimates of uncertainty in this calculation.

These are some interesting observations that we have endeavoured to address here and in the re-organised manuscript. Firstly, we would like to stress a couple of points specific to our data and the southern hemisphere that we will emphasise in the revised manuscript (lines 422-425). The quantification limit for 3H in our lab is 0.04 TU, so only 16 out of 50 samples are either at the detection limit or below it. This low detection limit has been driven by low 3H concentrations in the southern hemisphere. At the peak of the bomb pulse, weighted averages in Australia were around 60 TU (compared to, for example, ~ 6000 TU in Ottawa). In Australia, tritium in rainfall has been at natural background levels for some time. Values from samples in the Namoi River, collected at the time of our groundwater sampling (and provided in the dataset: ~2.3 TU) are in good agreement with rainfall data provided in Tadros et al. 2014.

Regarding 14C, whilst not generally sampled in rain or surface samples, it is almost at natural/background content, as seen in the Namoi River samples (~102 pmc; also provided in the dataset). However, shallow groundwater, recharged in recent years, still has a slight bomb pulse component in some boreholes (values of around 107 pmc).

Regarding 36Cl/Cl, no data in rainfall exist in the region to our knowledge. Namoi River samples at two different times (summer and winter 2016) have values of ~416 (x10^{-15}), while tributaries draining the igneous rock terrains have higher ratios than modern river water. However, most shallow groundwater also shows the mixing with deeper 36Cl/Cl sources and therefore has lower 36Cl/Cl ratios than modern surface waters.

We have added a 'Geochemical calculations' section to the methods (section 3.3) that details the method used for the calculations in old Section 4 (now section 5 in the rearranged manuscript). In terms of sources of uncertainty in this calculation, mixing and other processes (such as evapotranspiration and irrigation returns) can overprint the simple Cl mixing. However, we draw our interpretations from our Cl mixing results, alongside the other tracers that we used. For example, we consider samples with [Cl] < 31 mg/L, 3H activities above our detection limit and/or 14C > 90 pmc as originating from 100% modern (< 70 a) flood recharge (eg 36001-1&2, 25329-1, 30345-1. 25332-1. 25327-1&2). Samples recovered from generally deeper piezometers along the B-B' section in figure 2 show higher [Cl] that coincide with 3H below or very close to detection limits, 14C contents generally < 5 pmc and, most importantly, 36Cl/Cl below 58 (x10^{-15}).

Specific Comments:

Line 56: This paragraph lacks focus. The authors bring in agriculture and it's not clear how this is connected to the bigger issue.

This paragraph has been edited to try to bring it into focus. Agriculture is no longer mentioned here, just groundwater abstraction for irrigation, stock and domestic water supplies (lines 57-58).

Line 64: What is meant by the international export market?

This part of the introduction has been removed.

Lines 65-78: What is the focus here? Aquifers in general or alluvial aquifers?

Alluvial aquifers are the focus. This has been clarified in text at line 62.

Line 81: It's not just the half-life that is important, the tracer systematics including mixing and processes that affect their interpretations are needed.

We have acknowledged that each tracer undergoes processes specific to it that can often affect the interpretation of it and therefore these tracers can provide insights into the groundwater, but for only a given window of time and in favourable conditions (lines 80-81).

Lines 96-105: The manuscript needs a focused statement about the current knowledge gaps (this should be developed in the Introduction more succinctly) and what is new and novel about this research in addressing those gaps. The manuscript would benefit from a clear hypothesis statement or statement of science questions. This, in my opinion, would help focus the entire manuscript and the authors should return to this statement in the opening paragraph of the conclusions.

The introduction has been edited and aspects of it cut. The last paragraph (lines 97-114) has been edited to highlight that we are for the first time (to our knowledge) combining multiple geochemical tracers to assess artesian discharge to an alluvial aquifer and that we show a need to combine this with water balance models of alluvial systems. This is reiterated in the conclusions.

Lines 208-213: This sentence is difficult to understand, yet this paragraph is critical in identifying the knowledge gaps.

This sentence has been changed to "..there are multiple plausible solutions for all water balance models…" at lines 198-199

Line 237: This is a good place to re-state or reiterate what is missing by identifying the knowledge gaps and how your research addresses those gaps.

We have moved a section of the introduction to here (lines 226-230), stating that there is an over-reliance on water balance models, which are not constrained by hydrochemistry and that this study shows that the conceptual insights from geochemistry provide a new set of constraints not considered in previous hydrogeological models.

Lines 292-293: Please clarify the statement on NH4 concentrations.

A sentence has been added to clarify the statement on NH4 concentration (lines 333-335). We explain that the NH4 concentration skewed the charge balance because it was not considered in the initial calculations. This is now in section 3.3 – geochemical calculations.

Line 336: Does it make more sense to separate the Results and Discussion. This may help streamline and better organize the manuscript.

The results and discussion have now been split and the discussion streamlined.

Lines 343-362: This needs to be better organized, perhaps start with description of how GAB works hydrologically, then describe the ratios and their implications for the LNA. Suggest breaking this paragraph into 2 new, concise paragraphs.

The original lines 343-362 have been changed because of the restructure. Some of the original text is now in section 5.1, line 449, but the organisation has been changed considerably.

Lines 375-376: Be assertive here. This does suggest...rather than may suggest.

We have changed to 'This suggests…' (line 520).

Lines 376-378: Needs clarification.

This has been split up because of the split in results and discussion. Section 4.2 details the ranges of the isotopic values and that they lie on an evaporation line whereas lines 443-448 now explain the connection between evaporated surface water and shallow groundwater.

Lines 380-381: Please provide sources of F- and how that relates to the point you are making.

The source of F^- is the weathering of silicate minerals in the region (noted now at lines 460-461). This relates to our overall message because the covariation of Na and F (from the weathering of silicate minerals) show the same mixing trend in the alluvium between shallow groundwater and GAB samples that other parameters do (such as Na-HCO3).

Lines 416-431: Please clarify. Most 3H values are close to background or are dead with respect to 3H. This complicates your interpretation, but you seem to pull it back in focus with the figure. Suggest picking specific sites and describe what the data is telling you.

Please refer to our previous comments above regarding the activity of 3H in the southern hemisphere.

Lines 432-434: Prevalence of 3H?? Again, the 3H values are almost all very low or 3H dead. Consider rewording and clarifying this statement. Also, are there recent 3H values for precipitation?

"Prevalence of 3H" has been changed to "the activities of 3H above the detection limit" (line 492) so as to be more precise with our wording. Please refer to our previous comment regarding 3H activities in Aus and values for precipitation.

Line 434: 3H and 14C and not entirely consistent are they? This needs clarification. Why are they inconsistent?

Figure 5 (now Figure 6 in revised manuscript) illustrates why the 3H and 14C in the groundwater are inconsistent. Normally we would expect to see a very sharp decline in 3H activities as 14C (pmc) decreases. However, we see a mixing trend that shows that some groundwater samples still have measurable 3H despite having a 14C content of less than 50 pmc. We have clarified this in text at lines 492-503, better explaining the figure.

Lines 432-445: Please clarify and provide a more concise discussion on mixing effects.

This section (now lines 492-503) has been clarified with respect to the 3H (see above comment). It has also been shortened as a result of the streamlining of tangential information in the manuscript (mention of calcrete removed).

Line 458: What about 36Cl/Cl of modern precipitation? High 36Cl/Cl can be indicative of mixing of bomb-pulse with recent (low 36Cl/Cl) recharge. But, low 36Cl/Cl can also imply very old groundwater (your case). Can you clarify this uncertainty with modern precipitation?

Please refer to our comments above concerning 36Cl/Cl values of modern precipitation. In regards to lingering 36Cl/Cl derived from the bomb pulse: Cl has a very low residence time in the atmosphere (2 days) so most of the bomb derived 36Cl would be gone.

Line 487 (Figure 7): Please cite Phillips (2000) Chapter 10.

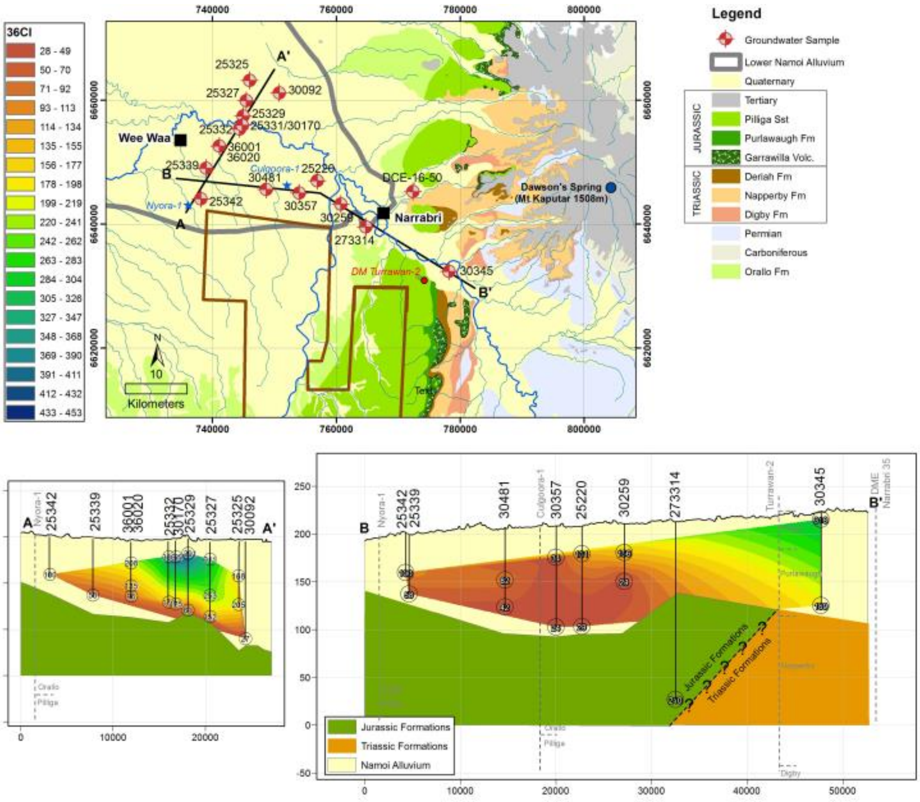
This has been cited (line 535) and added to the reference list.

Lines 510-523: Please provide the equation used to calculate the mixing proportions. Can you also provide estimates of uncertainty in these calculations? Are there other solutes or solute ratios (Cl/Br for example) which may be more suitable for these calculations? It’s not clear how this was estimated.

Mixing proportions were calculated in NetPath and were treated as a mixing problem. We have added a ‘geochemical calculations’ section to the methods that explains this (section 3.3). Please refer to our comment above regarding mixing proportions. Additionally, we believe that the Cl ion was the most appropriate because of its conservative nature (line 556) and in our study area the end member water sources have distinct Cl signatures that facilitate its use as a tracer.

Line 535: Can you provide plots showing the spatial map of appropriate chemical concentrations?

Figure 2 has now been adapted as below. We show a spatial map of the 36Cl data, which is crucial for understanding the discussion regarding GAB discharge into the alluvium at lines 433-439.



<u>General comments:</u> **The presented study is well designed and informative for regions, where different water bodies seem to exist and mix in ratios, which are unknown yet. Thematically the paper fits to HESS, although I see some points of weakness, mainly related to formulation (or omitting) of hard facts. I guess, with considerable revision, that manuscript has the potential to be of interest for a wide audience. In general, the manuscript should be shortened and particularly the geological part must be clarified for readers outside Australia. In the following, I give some specific remarks to points, where I see difficulties:**

We thank the reviewer for their time in closely reviewing our manuscript. We have aimed to address all concerns below.

Hydrographs in Figure 1 are not very informative, despite the information, that gw-tables are fluctuating. the legends of hydrographs are not explained and it becomes not obvious, why red texted hydrographs are representative for GAB contribution. Instead of showing relative depths of screen bottoms (bgs), it would be more distinctive, when depths would be given relative to msl., to explain the absolute depth.

We have now explained in the legend of Figure 1 why the 2 red text hydrographs show GAB contribution (the deeper piezometric head is higher than head from the shallower wells, indicating upward flow). We think that the hydrographs figure gives the reader a nice overview of the state of the groundwater system in the study area, in particular, areas that are affected by seasonal pumping and areas where the GAB may be contributing water. The NSW Government hydrograph data available only lists the below ground surface depth, however in the region that the hydrographs cover, there is very little elevation change (80 m change in elevation from the south-east to the north-west portions of the study area).

Hydrogeological setting The entire paragraph is very hard to understand, since local formation names are abundant and the hydrogeological context is not clear. Why are all these details necessary for the reader of the manuscript (e.g. lines 191-193)? Paleogeographic features are very difficult to understand. It would be of more importance to reduce the (doubtless interesting) geological context and focus on the formations, which are hydraulically relevant. Probably a stratigraphic table would help a lot, showing thickness, lithological composition and phreatic/confined conditions in each of the relevant formations.

The geological section has been shortened, with most of the second half (including old lines 191-193) removed. We have not included a stratigraphic table, only because the legend in Figure 2 shows a stratigraphic column by age and the cross sections in figure 2 show the depth of the different formations in the Jurassic and Triassic. However, we have cleaned the section up substantially (including removing most paleogeographic features) and have included some 36Cl data in the cross sections of Figure 2.

221 Water balance modeling for recharge That paragraph explains a series of MODFLOW attempts to define various sources for recharge. I believe, the paragraph is to long, since the basic and neccessary information are the outcoming numbers (ratios) for the different proposed sources. The authors use a unit (ML/a) which is unknown to me (Megalitres/year?)

This paragraph has undergone minor phrasing edits (eg line 198: “multiple plausible solutions” has replaced “there are numerous equivalent solutions…”); however, the bulk remains because it is core to the problem with respect to the issue of water balance modelling in the Namoi. ML/a is megalitres/year. We aimed to be consistent using “a” (annum) for year throughout the manuscript, because we referred to “ka” (kilo annum) when assessing the 36Cl residence times.

Specific comments

Line 302: what is the reason to use pmc and pMC?

We detailed both units (normalised pMC and de-normalised pmc) for completeness and to ensure our results were comparable with other study results reported only as pMC’s without having to transform units or search information relating to the type of AMS used, or how the d13CDIC was obtained. However, the text has all data consistently as pmc following best practice for reporting groundwater 14C data (Plummer & Glynn 2013). pMC results are only presented in the Supplementary Table.

Line 358: which 2 processes are meant? ET leads to enrichment of all elements, leading eventually to Cc-saturation. Na/HCO3 increases only, when calcite precipitates.

This sentence has been removed now as part of streamlining the manuscript. Additionally, at lines 456-458 (where this old sentence would have been in the restructure) we have explained why we consider an evaporative enrichment in all elements.

Line 360: I suggest to be careful in interpreting Cl/Br ratio changes in these context. Cl/Br ratio will change only, when degree of evaporation results in supersaturation of the water in respect to halite, otherwise there is no change observable. Since Cc-precipitation is discussed, it might be worthwhile to compare Ca/Mg ratios and (Ca+Mg)/HCO3 ratios? Cl/Br ratio might change due to geological reasons...

This is an omission on our part. We should have mentioned the Cl/Br ratio in the context of the Cl v Cl/Br plot. It is not the Cl/Br ratio itself, but rather the trend when plotted against Cl that provides the evidence for our claim. However, in the restructure of the manuscript the original sentence at 358 (“the evaporative enrichment is also evident in the concentrations of F, Cl and Cl/Br”) has been removed. We have instead made these data (presented in the new Figure 3) more relevant to the main groundwater mixing message that this manuscript conveys, rather than tangential processes. We had a look at Ca/Mg and (Ca+Mg)/HCO ratios but they revealed nothing additional.

line 390: delete charges. What means “closer”? compared to what?

Charges have been deleted. “Closer to seawater…” has been changed “more similar to seawater…” at line 382.

line 399-401: that sentence is not helpful, since the reader does not know which parameters you refer to. From Figs 3 and 4 it is not given, that 273314 resembles river water, it is obviously just fresh water.

This sentence has been removed as the parameters concerning the outlying sample are described in the separate results section at lines 383-399 (particularly line 397) now.

line 401 ff: from that moment it becomes highly difficult to follow: you refer to the only

sample from the Jurassic Fmt. Why is it strange to have fresh water in there? The base of the well is just above a Napperby fmt. Which indicators suggest recharge through a formation, which is even below Napperby? And which river is referred to? Why should Pilliga Sandstone contribute? The explanation lacks from facts, which give an overview about the hydraulic concept, which obviously led to the formulations. Latest here a regional W-E geological cross-section, showing Fmts. of GAB and their regional confined and phreatic conditions (piezometer heights) is urgently needed to understand the hydrogeological context of the region. In addition, it would also help, to (i) show Fmt. and (ii) add water table heights of the different aquifers in the cross-sections of Fig. 2. Situation becomes harder due to the jumping between formation names.

It is an anomaly to have such fresh water in this sample because the well screen is 207 m bgs and in the GAB Jurassic formation. All other studies that have taken samples at this depth in the GAB have had water that is more representative of the GAB, ie higher TDS. We don't have particular indicators that suggest recharge through the Digby into the Napperby, however this was our hypothesis because of the fresh water 207 m bgs, and the contact between the Namoi River and the Digby Fmt to the south of our study area.
The Namoi River is referred to. This is the only river in our study area and it is in direct contact at the surface with the Digby Fmt to the south of our specific study area. The Pilliga Sandstone should contribute because the sample is taken from the Pilliga SS. "Overlying Pilliga SS" has been changed to "Pilliga SS" to try to make that clearer (line 472).
We have changed 'This suggests' to 'We hypothesise' (line 469) because the first sentence did not necessarily suggest the second.
Figure 2 provides a cross section of the geology and piezometer height, as well as a geological map that shows the Digby Fmt outcropping to the south of the study area, where it is in contact with the Namoi River.
The formations are shown in the cross section of figure 2. Water table heights change over time due to floods and the intensive pumping in the study area. We have included the standing water level at the time of sampling in the Supplementary Information.
A paragraph at lines 467-477 now aims to describe all the above better.

line 407 ff: again, why do the authors claim for contact between that river and deeper Triassic Fmt.? According to Fig. 2: Napperby is the uppermost Triassic. Where is that river situated and why is the river the only option of fresh-water supply? Are these ideas consistent with hydraulic?

At the depth that these samples are situated at, and given the regional data for the quality of the GAB groundwater, the river is the primary source of fresh water. We claim contact between the river and deeper Triassic formations because the river contacts the deeper Digby to the east of the study site, which is consistent with the groundwater flowpaths in the region. This then is important because deeper mixing between the GAB groundwater and the water of the Namoi River is an important consideration in water balance models of the catchment. This is all clarified at lines 467-477 now.

Line 412f. : To be very critically: I don't see clear indications for that statement from Figs. 3 and 4. Major elements in samples >80 m (blue) spread over the entire range and only a few blue samples fall in the same region as GAB analyses from Radke et al. (2000). Is there a geographic link?

We interpret the spread of samples from the shallow, intermediate and deep, and the mixing between them over the entire range of Figs 3 and 4 to be indicative of the mixing occurring throughout the groundwater system. Most of the blue samples in new Figures 3 and 4 fall in the same region as GAB samples. That the deeper blue samples cluster more with the GAB samples than the red or green indicates to us that the deeper groundwater is experiencing greater mixing with the GAB in some places, which is then mixing in varying proportions with the more shallow groundwater, up until the very shallow groundwater is comprised entirely of itself at the other end of the mixing trend. We acknowledge that the blue (deep) samples are spread over a large range, this to us indicates significant mixing throughout the entire vertical groundwater profile. There is no specific geographic link that we have been able to identify.

Line 517f. : Why is not a sample chosen, which was not evaporated at all or even better, a recent rainfall sample, giving the precise input signal for Cl and 3H?

Choosing a more evaporated end-member makes our calculations even more conservative, as it ensures we aren't overestimating the GAB contribution. Rainfall and recharged shallow groundwater do not usually have the same Cl composition, generally Cl is higher in the shallow groundwater. Additionally, we chose the groundwater sample with the highest ^{3}H activity, as an indicator of recent surface infiltration.

lines 521-523: I do not understand the reason of that thought: "...to consider overall transport of Cl from shallow groundwater."

This sentence has been changed to "Thus, the use of the evaporated sample as our end-member represents a conservative approach when considering the mixing components from both the LNA and the GAB" (line 567-569) so that it is clearer.

line 532/fig. 8: Actually these percentages are calculated on Cl-mixing approach only. Within the description, "multiple geochemical tracers and major ion data" are mentioned. Which exactly were used and how does the respective results fit to the described Cl-mixing? According to that figure, it strikes, that heterogeneity of GAB contribution might be related to structural features or any other elements that provide preferential flow? Are there any tectonic lineaments or other indications, which could be responsible for the different contributions from the GAB?

Cl- only was used for this percentage based assessment of GAB contribution, but the other major tracers were used to qualitatively show GAB contribution to the alluvial groundwater. We used the multiple tracers approach to constrain GAB discharge and used the Cl ion to estimate a percentage. For example, we consider samples with [Cl] < 31 mg/L. 3H activities above our detection limit (> 0.04 TU) and/or 14C > 90 pmc to be 100% modern (< 70 a) flood recharge (for example: 36001-1&2, 25329-1, 30345-1, 25332-1, 25327-1&2). Samples that were recovered from generally deeper piezometers along the B-B' section in figure 2 show higher [Cl] that coincide with 3H below or very close to the detection limit, 14C contents generally < 5 pmc and, most importantly, 36Cl/Cl below 58 (x10^{-15}). There are no other indications that could be responsible for different contributions from the GAB.

Lines 619-621: That sentence is very vegetarian, it gives no information at all. Please prevent to use such phrases, instead of describing which reason will result in which effect.

This sentence in the conclusion has been removed.

A multi-tracer approach to constraining artesian groundwater discharge into an alluvial aquifer

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Understanding pathways of recharge to alluvial aquifers is important for maintaining sustainable access to groundwater resources. Water balance modelling is often used to proportion recharge components and guide sustainable groundwater allocations. However, it is not common practice to use hydrochemical evidence to inform and constrain these models. Here we compare geochemical versus water balance model estimates of artesian discharge into an alluvial aquifer, and demonstrate why multi-tracer geochemical analyses should be used as a critical component of water budget assessments. We selected a site in Australia where the Great Artesian Basin (GAB), the largest artesian basin in the world, discharges into the Lower Namoi Alluvium (LNA), an extensively modelled aquifer, to convey the utility of our approach. Water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) and the concentrations of Na^{+} and HCO_3^{-} suggest a continuum of mixing in the alluvial aquifer between the GAB (artesian component) and surface recharge, whilst isotopic tracers (^{3}H, ^{14}C and ^{36}Cl) indicate that the alluvial groundwater is a mixture of groundwaters with residence times of < 70 years~~a~~ using ^{3}H and ~ 900 ka using ^{36}Cl methods. In addition, Cl^{-} concentrations provide a means to calculate a percentage estimate of the artesian contribution to the alluvial groundwater. In some locations, an artesian contribution of up to 70% is evident from the geochemical analyses, a finding that contrasts previous ~~contrasting historical~~ water balance modelling estimates of 22%. Our results show that hydrochemical investigations need to be undertaken as part of developing the conceptual framework of a catchment water balance model, as they can improve our understanding of recharge pathways and better constrain artesian discharge to an alluvial aquifer.

1 Introduction

Recharge to alluvial aquifers can occur via ~~modern~~ infiltration from the land surface and/or discharge into the alluvium from surrounding geological formations and artesian groundwater resources (Costelloe et al. 2012; Schilling et al. 2016; Rawling & Newton 2016; Salameh et al. 2017). Insufficient s~~S~~patial and temporal data resolution, ~~and~~ as well as heterogeneity in hydrogeological properties can result in considerable uncertainty when allocating recharge to each source ~~and mapping pathways of flow~~ (Anderson & Woessner 1992; Beven 2009; Gardner et al. 2012). Additional uncertainties when allocating recharge to each source include change in the magnitude of groundwater gradients and directions over time ~~Most aquifer systems used in agricultural landscapes have dynamic groundwater gradients~~ due to ongoing groundwater abstraction (for irrigation, stock and domestic water supplies), and the impact that this and f~~, which adds to this uncertainty. F~~lood frequency may have~~s~~ on the extent of artesian discharge and groundwater mixing. T~~and intensive pumping from an alluvial aquifer overlying an artesian aquifer (to supply water for irrigated agriculture) can affect head gradients and cause a temporal decrease or increase in artesian discharge and increased mixing. T~~hese complexities make it challenging to accurately proportion contributions from various sources to an alluvial aquifer and to guide water allocations. ~~Balancing groundwater allocations is especially difficult when the groundwater is relied upon to sustain ecosystems, the local economy and international export markets.~~

Water balance modelling of alluvial aquifers is commonly used to quantify and proportion recharge inputs from river leakage, floodwaters, areal (diffuse recharge) and artesian sources (Anderson & Woessner 1992; Middlemis et al. 2000; Zhang et al. 2002; Dawes et al. 2004; Barnett et al. 2012; Giambastiani et al. 2012; Hocking & Kelly 2016). Historically, hydrochemical analyses are not often used to constrain catchment scale water balance modelling (Reilly and Harbaugh 2004; Barnett et al. 2012), despite~~.~~ Scanlon et al.

(2004) highlighting~~ed~~ the need to use multiple techniques (including hydrochemical insights) to increase the reliability of recharge estimates. Geochemical data can improve our understanding of recharge processes because of the potential to trace pathways of groundwater movement and water-rock interactions, whilst also providing insights on the impacts of past groundwater extractions (Martinez et al. 2017). Therefore, the integration of geochemical ~~insights~~ evidence to constrain aquifer water balance models provides a more rigorous approach for estimating and proportioning sources of recharge to groundwater resources (Raiber et al. 2015; Currell et al. 2017).

Radioactive isotopic tracers that provide insights into groundwater residence times can constrain mechanisms of recharge and detect groundwater mixing. Isotopes of dissolved species can be useful for elucidating groundwater mixing provided the different sources of groundwater have distinctly different and consistent isotopic signatures. However, each tracer has a different half-life and undergoes processes specific to it that can often affect interpretations. T~~, and t~~hus, these tracers can provide process insights but only for~~ only~~ a given window of time. Therefore, multiple tracers are needed to cover the time scales relevant for the large range required for groundwater residence times~~flow paths~~. Tritium (^{3}H) is an excellent indicator of modern recharge inputs in shallow groundwater (Robertson et al. 1989; Chen et al. 2006; Duvert et al. 2016), and provides valuable information on processes active in the past ~ 70 years. Carbon-14 (^{14}C) is used to understand processes active from modern~~/sub-modern~~ to ~ 30 ka (Clark & Fritz 1997; Cartwright et al. 2010; Cendón et al. 2014) and chlorine-36 (^{36}Cl), whilst applicable in modern groundwater (Tosaki et al. 2007), is usually reserved for the identification of much older groundwater (100 ka to 1 Ma).~~-~~ One of the challenges of using ^{36}Cl is that, in certain cases, nucleogenic production of ^{36}Cl can be significant and/or varying Cl concentrations can complicate groundwater residence time interpretations. ~~Chlorine-36 can be notoriously difficult to interpret anything other than broad~~

~~indications of residence times, ~~H~~h~~owever in regions with low and fairly consistent Cl concentrations (such as in our study area), ^{36}Cl values can provide solid indications of old groundwater residence times (Mahara et al. 2007).

These isotopes can also be used for tracer mixing ~~processes ~~calculations independent of residence time estimations (Bentley et al. 1986; Andrews & Fontes 1993; Love et al. 2000; Moya et al. 2016). Therefore, the combination of ^{3}H, ^{14}C, and ^{36}Cl dating techniques can provide hydrochemical process insights that cannot be captured by using only one isotope.

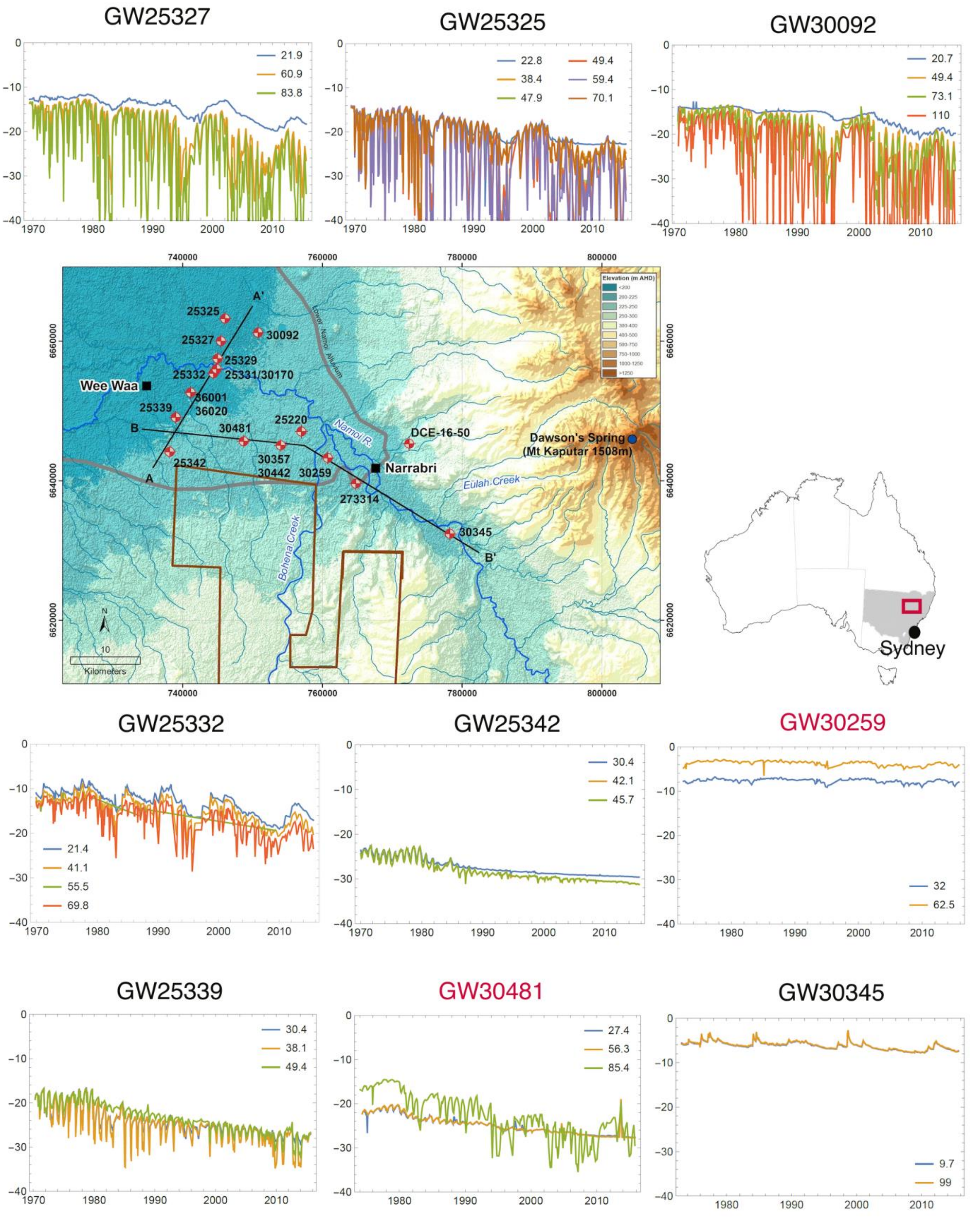
~~-~~Identification of recharge and discharge pathways, particularly from underlying artesian contributions, can be better constrained by combining traditional geochemical data with multiple dating techniques and other hydrologic analyses (Amiri et al. 2016; Rawling & Newton 2016; Schilling et al. 2016). ~~Thus~~Here,

w~~W~~e present for the first time a multi-tracer approach to constraining artesian discharge from the Great Artesian Basin (GAB) into the Lower Namoi Alluvium (LNA), north-west New South Wales (NSW), Australia (Figure 1). We use water stable isotopes and major ion data to assess the major recharge pathways ~~to ~~and occurrences of groundwater mixing in the LNA ~~show that recharge to the alluvial aquifer of the LNA is mainly by surface water recharge and artesian inflow from the GAB~~. We also use ^{3}H, ^{14}C and ^{36}Cl to show that artesian discharge from the underlying GAB to the LNA is locally much higher than is currently estimated from water balance models used to guide groundwater allocations in the region (Lower Namoi Groundwater 2008).

In this study we are not attempting to determine groundwater ages for all sampling locations, as it is very difficult to obtain meaningful ages for samples where significant mixing of old and recent groundwater has occurred. However, we do present “age” constraints for both modern and old end-members as a basis for delineating the relative ages of these end-members. Our results highlight the need to consider a multi-tracer geochemical approach when assessing artesian contributions to alluvial aquifers and constraining water balance models of alluvial systems globally.

~~This has implications for ongoing groundwater use in the region, and highlights the need to protect surface recharge zones in both alluvial and artesian portions of catchments.~~

~~The over-reliance of water balance models used to allocate groundwater resources that have not been constrained by isotopic tracer residence times or hydrochemical results is a common issue globally. This research highlights that comprehensive hydrochemical investigations improve our conceptual understanding of recharge pathways and that such investigations should be applied to all important groundwater resource assessments to enable sustainable management.~~


GW25327
21.9
60.9
83.8
GW25325
22.8
38.4
47.9
49.4
59.4
70.1
GW30092
20.7
49.4
73.1
110
0
−10
−20
−30
−40
1970
1980
1990
2000
2010
740000
760000
780000
800000
6660000
6640000
6620000
Elevation (m AHD)
<200
200-225
225-250
250-300
300-400
400-500
500-750
750-1000
1000-1250
>1250
A'
A
B
B'
25325
25327
30092
25329
25332
25331/30170
Wee Waa
36001
36020
25339
30481
25220
25342
30357
30442
30259
273314
30345
DCE-16-50
Narrabri
Namoi R.
Lower Namoi Alluvium
Eulah Creek
Bohena Creek
Dawson's Spring
(Mt Kaputar 1508m)
N
10
Kilometers
Sydney
GW25332
21.4
41.1
55.5
69.8
GW25342
30.4
42.1
45.7
GW30259
32
62.5
GW25339
30.4
38.1
49.4
GW30481
27.4
56.3
85.4
GW30345
9.7
99

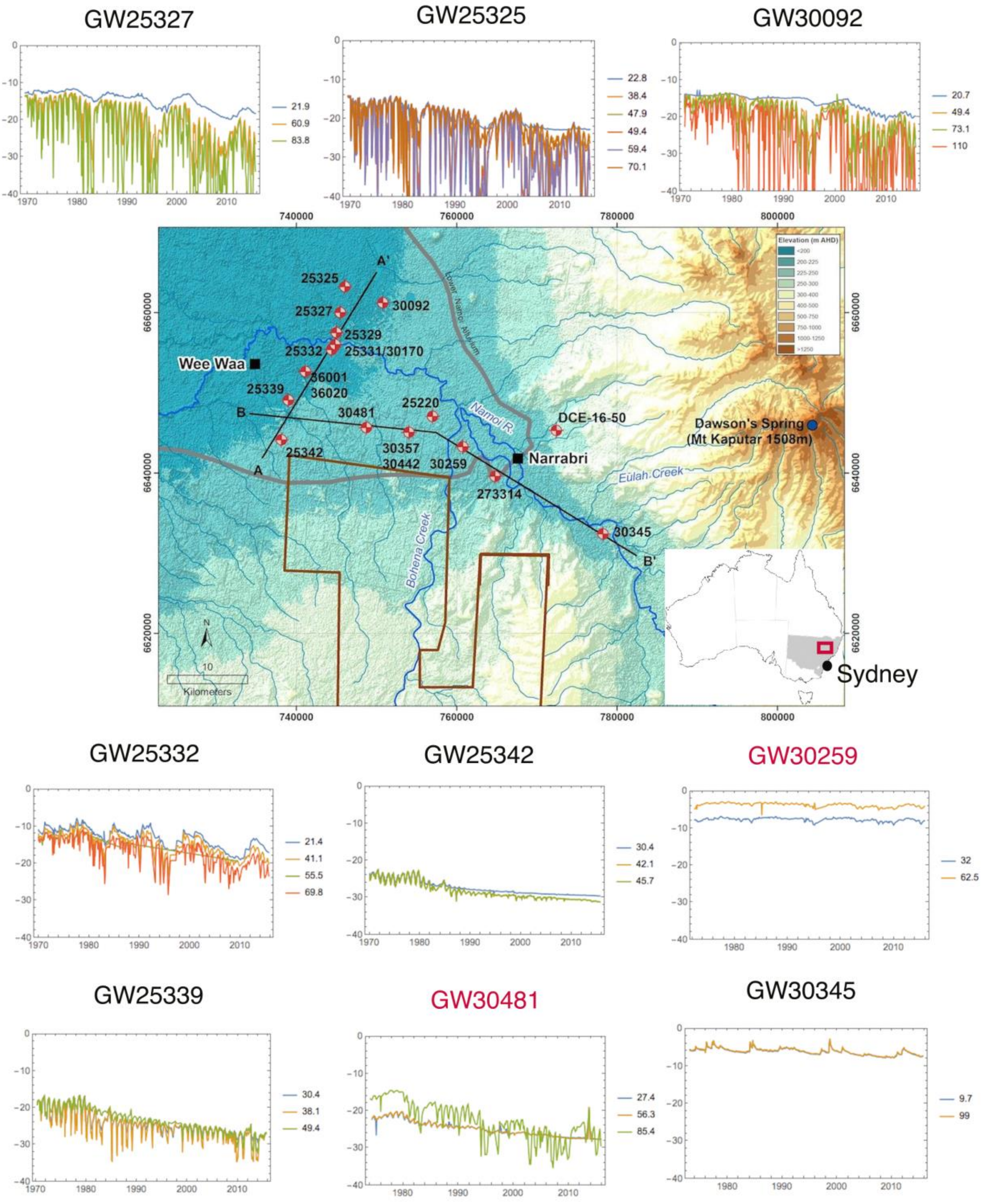


Figure 1. Map of the study area and sample locations, along with the location of the study area in Australia. Accompanying hydrographs show the groundwater level response in different piezometers throughout the study area (groundwater level data sourced from BOM 2017). The different colours in the hydrographs represent the different monitoring bores in the nested set. The bottom of the slotted

interval for each bore is shown in the key. The x-axis in each hydrograph is the year (1970-2010) and the y-axis is depth (between 0 and 40 m below ground surface (bgs)). The two locations with red text highlight areas where the hydrograph heads show clear GAB contribution, with the deeper piezometer showing a higher head than the shallow one. The remaining locations show no apparent GAB contribution to the LNA based on the hydrograph data.

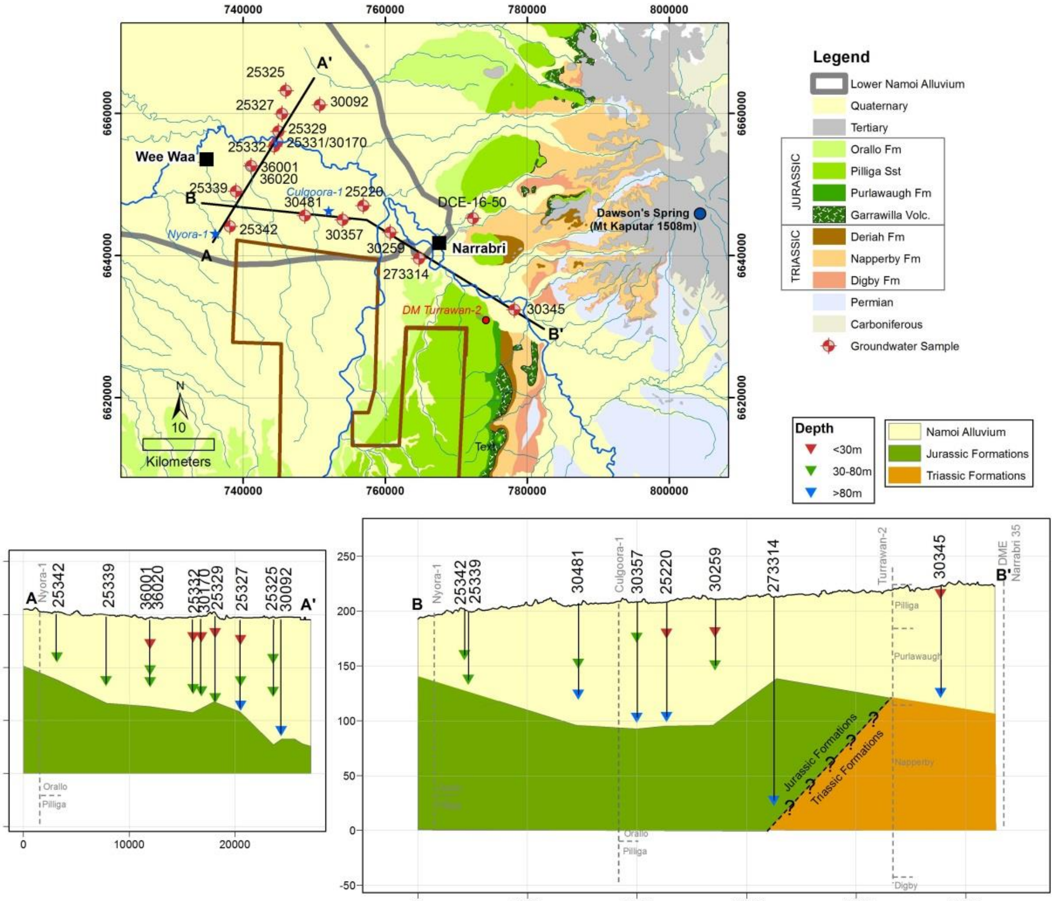
2 Study Area

The lower Namoi River catchment is located in the north-west of NSW, Australia (Figure 1). Groundwater resources in the LNA are the most intensively developed in NSW (DPI Water 2017). For this reason, there is concern regarding groundwater exploitation and threat to the long-term sustainability of the system (Lower Namoi Groundwater 2008; DPI Water 2017). Groundwater abstraction from the LNA supports a multibillion-dollar agricultural sector (focused around cotton growing established in the 1960s), supplying around 50% of water for irrigation in the region (Powell et al. 2011). ~~The first high-volume irrigation bore was installed in 1966 (Rural Forum 1967) and the use of groundwater expanded rapidly throughout the region throughout the 1960s to 1990s.~~ Peak extraction of approximately 170,000 mega litres (ML) occurred over the 1994/1995 growing season (Smithson 2009). Consistently declining groundwater levels and concern regarding the long-term sustainability of groundwater abstraction led to the implementation of a Water Sharing Plan in 2006, which systematically reduced groundwater allocations to the irrigation sector over a ten-year period. The present allocation is 86,000 ML/a (Lower Namoi Groundwater 2008).

2.1 Hydrogeological setting

The lower Namoi River catchment lies within the Murray-Darling Basin, overlying the Coonamble Embayment, which is in the south-east portion of the GAB (Radke et al. 2000). ~~The lower Namoi River catchment lies within the Murray-Darling Basin and overlies the~~

~~confined Coonamble Embayment, which is a subdivision of the Surat Basin, which in turn is a sub-basin of the GAB.~~ The southernmost portion of the LNA is underlain by Triassic formations, while northwest of monitoring bore 30345 the LNA is underlain by Jurassic formations (Figure 2). Within the region of study, the oldest outcropping bedrock formation is the early Triassic Digby Formation (lithic and quartz conglomerates, sandstones and minor finer grained sediments) (Tadros 1993). The Digby Formation outcrops in the south-east of the area and the Namoi River abuts the formation just south of B' on Figure 2. The Digby Formation is overlain by the Triassic Napperby Formation (thinly bedded claystone, siltstones and sandstone). This formation occurs at a depth of 106 m, just below the base of monitoring bore 30345 (NSW Pinneena Groundwater Database, driller logs).~~, where the paleo-Namoi river carved a path through a syncline.~~ In outcrops to the east of the study area, the Napperby Formation is overlain by the late Triassic Deriah Formation (green lithic sandstone rich in volcanic fragments and mud clasts) (Tadros 1993).~~, however this has not been identified beneath the bores used in this study.~~ The boundary between the Triassic and Jurassic lies west of monitoring bore 30345. ~~There is an unconformable boundary between the Triassic and Jurassic formations, and in some outcropping regions the Garrawilla Volcanics (alkali basalts, trachyte, hawaite, pyroclastic and subordinate sediments) is the base Jurassic formation. Overlying the Garrawilla Volcanics are the~~The early Jurassic formations important to this study are the Purlawaugh Formation (carbonaceous claystone, siltstone, sandstone and subordinate coal), ~~Jurassic~~ Pilliga Sandstone (medium to coarse quartzose sandstone~~; Tadros 1993~~) and the ~~late Jurassic~~ Orallo Formation (clayey to quartzose sandstone, subordinate siltstone and conglomerate) (Tadros 1993). The Pilliga Sandstone forms the bedrock below monitoring bores 25325 to 25342, and in the Namoi region is the primary aquifer of the GAB.


Legend
Lower Namoi Alluvium
Quaternary
Tertiary
JURASSIC
Orallo Fm
Pilliga Sst
Purlawaugh Fm
Garrawilla Volc.
TRIASSIC
Deriah Fm
Napperby Fm
Digby Fm
Permian
Carboniferous
Groundwater Sample
Depth
<30m
30-80m
>80m
Namoi Alluvium
Jurassic Formations
Triassic Formations
Wee Waa
Narrabri
Dawson's Spring (Mt Kaputar 1508m)
Culgoora-1
Nyora-1
DM Turrawan-2
DCE-16-50
Tert
A
A'
B
B'
25325
25327
30092
25329
25332
25331/30170
36001
36020
25339
30481
25220
30357
25342
30259
273314
30345
N
10
Kilometers
740000
760000
780000
800000
6620000
6640000
6660000
Nyora-1
Orallo
Pilliga
36001
36020
25332
30170
25329
25327
25325
30092
0
10000
20000
Culgoora-1
Turrawan-2
DME Narrabri 35
Pilliga
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0
-50
30000
40000
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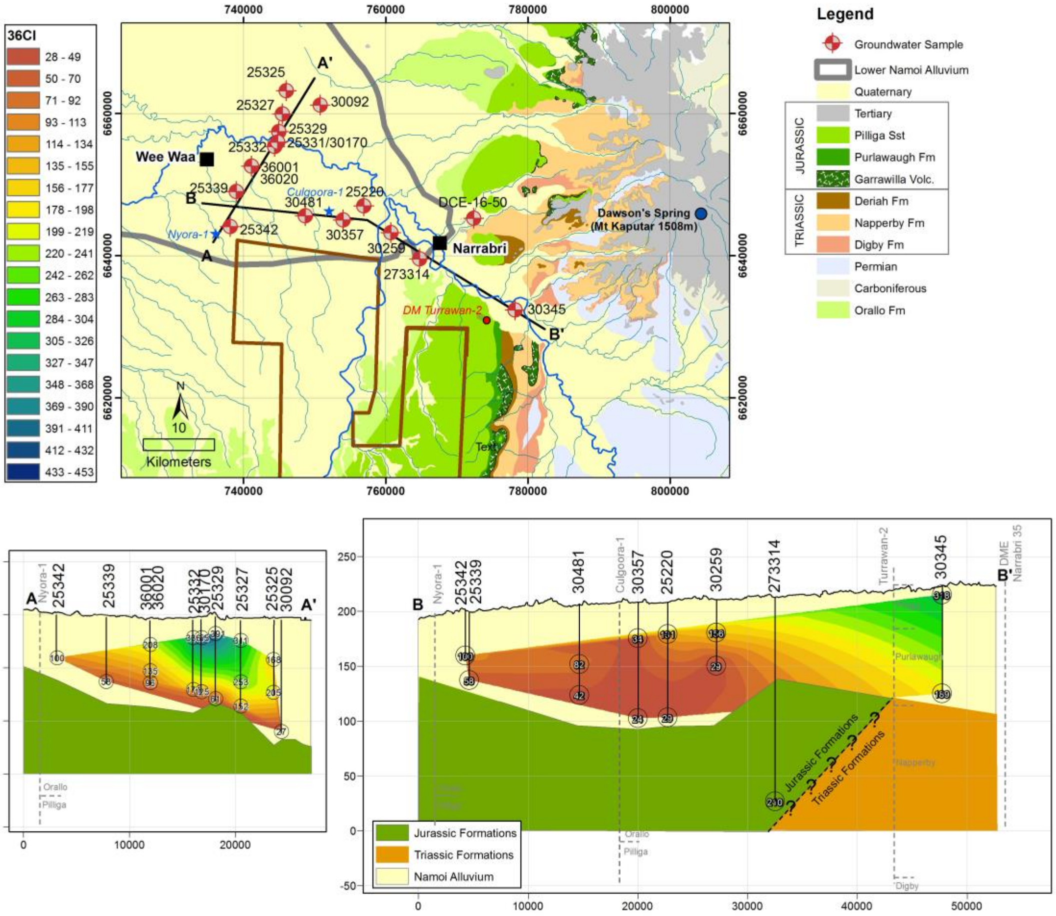


Figure 2. Two cross sections through the study area, showing the location and depth of the samples in the alluvium and their proximity to formations of the GAB. Contacts obtained from gas wells Nyora-1, Culgoora-1 and Turrawan-2, coinciding with our cross sections, are added. Their locations are displayed on the map. The chlorine-36 data interpolated using the 'natural neighbours' algorithm is shown in each cross section.

From the late Cretaceous to the mid Miocene, a palaeovalley was carved through the basement rocks (Kelly et al. 2014). Then from the mid Miocene until present, the palaeovalley was filled with reworked alluvial sediments. Groundwater abstraction in the study area is mostly from these alluvial sediments. Fluvial and aeolian interbedded clays, silts, sands and gravels form the up to ~ 140 m thick alluvial sequence of the Lower Namoi Catchment (Williams et al. 1989). Traditionally, three main non-formally defined aquifers/formations have been used to describe the LNA. The semi-confined Cubbaroo Formation overlies the bedrock in the northern palaeochannel (which passes beneath monitoring bores 25325 and 30092). This formation is up to 60 m thick. The Cubbaroo Formation is overlain by the semi-confined Gunnedah Formation, which is up to 80 m thick, and is conformably overlain by the unconfined Narrabri Formation, which is 10 to 40 m thick (Williams et al. 1989). However, ~~more~~ recent ~~research~~ studies in the Namoi Catchment suggest~~s~~ that the rigid subdivision in to the Narrabri, Gunnedah, and Cubbaroo formations ~~or aquifers based on depth (upper, middle, lower)~~ cannot easily explain the continuum in chemical evolution observed (discussed further below) and that the valley filling sequence is better characterised as a distributive fluvial system ~~or the facies distribution~~ (Kelly et al. 2014, Acworth et al. 2015).

-Groundwater drains from the Upper Namoi into the LNA via a bedrock constriction north of Narrabri and generally flows from east to west within the LNA (Barrett 2012). Hydraulic conductivity in the alluvial aquifer is highly variable (0.008-31 m/day) due to the presence of variable sand and clay (Golder Associates 2010). However, ~~generally~~ hydraulic conductivity generally increases with depth. ~~Kelly et al. (2014) argue that the sedimentary sequence is better represented as a distributive fluvial system, with high energy sedimentary gravel and sand deposits dominating at depth and low energy silt and clay deposition dominating near the ground surface. This is due to a shift from a relatively wet climate in the mid Miocene (greater than 1500 mm annual rainfall; Martin 2006) to the present drier climate in the region, which averages approximately 660 mm at Narrabri (BOM). There is also a higher proportion of gravel and sand deposits in the proximal portion of the catchment, between Narrabri and Wee Waa (the area of this study), than the distal portion of the system west of Cryon (Kelly et al. 2014). Acworth et al. (2015) showed that within the alluvial sequence there are time gaps of hundreds of thousands to millions of years in the sedimentary sequence, which is expected in meandering river sedimentary environments.~~

2.2 Current understanding of recharge and discharge processes in the Lower Namoi Alluvium

There have been numerous catchment water balance models and hydrochemical investigations ~~many investigations~~ in the study area because of the local and national economic importance of the LNA. ~~These investigations encompassed both catchment water balance models and hydrochemical investigations.~~ However, the hydrochemistry of the groundwater in the region has not been used in conjunction with water balance modelling prior to this study (~~Merrick 2001;~~ Merrick 2000; CSIRO 2007; Kelly et al. 2007).

2.2.1 Water balance modelling of recharge

To guide groundwater allocations from the LNA, a series of water budget models were developed using MODFLOW (~~Merrick 1989, 1998a, 1998b, 1998c; 1999, 2000; 2001~~Merrick 2000; summarised in Kelly et al. 2007). ~~The complete history of the development of these models is discussed in Kelly et al. (2007).~~ These models were driven by climatic, rainfall, flood and streamflow data and calibrated to groundwater head data. There are multiple plausible ~~equivalent~~ ~~numerous~~ solutions for all water balance models and the solution presented is often constrained by several factors. These constraining factors include geological insights; the modeller's experience and biases (such as, for example, the way diffuse recharge is modelled either as a percentage of rainfall (Merrick 2000~~1~~; CSIRO 2007) or as a complex evapotranspiration function (Giambastiani et al. 2012)); verification measures and pragmatic goals. One MODFLOW derived water balance model ~~presented in Merrick (2001)~~ proportioned the recharge for the water budget period 1980-1994 as following: flood and diffuse rain recharge 24,100 ML/a, stream recharge 33,700 ML/a, up gradient alluvial inflow 3,060 ML/a, and artesian (GAB) recharge 9,500 ML/a. In that model, artesian recharge was inferred to ~~primarily~~ occur in the eastern portion of the model (between Narrabri and Wee Waa), which overlaps with this study area (Figure 1). The zone between Narrabri and Wee Waa accounted for 42,700 ML/a of the total recharge to the LNA. Thus, according to the model, GAB ~~the artesian~~ discharge into the LNA in this area equated to 22%. When the LNA MODFLOW model was calibrated there was no consideration given to using hydrochemical data to constrain the calibration (Merrick 2000;~~Merrick 2001;~~ CSIRO 2007; Kelly et al. 2007).

2.2.2 *Hydrochemical estimates of recharge*

The first isotopic investigation in the area was conducted from 1968 to 1975 and partially published by Calf (1978). The author used ^{14}C and ^{3}H to assess recharge pathways to the LNA and found evidence for river recharge in the upper aquifer, and that modern groundwater penetrated the deeper parts of the LNA. Calf (1978) also found evidence for ‘leakage’ of groundwater from the GAB up into the deeper LNA, however volumetric estimates were not provided.

McLean (2003) conducted an extensive hydrochemical and isotopic characterisation of both the GAB groundwater and the alluvial groundwater in 1999-2000. This research concluded that mixing of groundwater from the GAB into the lower and middle parts of the LNA is an important process especially in the south of the catchment. This study also did not quantify the amount of mixing occurring between the two groundwater sources.

The over-reliance of water balance models used to allocate groundwater resources that have not been constrained by isotopic tracer residence times or hydrochemical results is a common issue globally. This research highlights that ~~comprehensive~~ hydrochemical investigations improve our conceptual understanding of recharge pathways and that such investigations should be applied to all important groundwater resource assessments to enable sustainable management.

3 Materials and methods

3.1 Groundwater collection

This study comprised two field campaigns, the first one from 28 January 2016 to 8 February 2016 (summer) when the aquifer was stressed by pumping for irrigation, and the second from 21 June 2016 to 30 June 2016 (winter) in the absence of abstraction for irrigation.

In summer, ~~we collected groundwater samples from~~ 28 groundwater samples were collected from NSW Department of Primary Industries Water (DPI Water) monitoring bores and a surface water sample from the Namoi River. In winter, 16 groundwater samples were collected ~~groundwater samples~~ from ~~16~~ NSW DPI Water monitoring bores and surface water samples from the Namoi River and 2 upstream tributaries (see Supplementary Table 2 for locations). The bores are screened at varying intervals, intersecting the shallow, middle and deep alluvium. Most bores were sampled with either a Grundfos (MP1 sampling pump) or Bennett compress air piston pump, with the pump placed ~ 1 m above the screen when using the Grundfos pump and a drop-tube extension adjusted to place the pump intake within the screen when using the Bennett pump. Some deep monitoring bores were sampled with a portable bladder pump using low-flow methods (Puls & Barcelona, 1996). In these bores the pump was placed approximately 10 m below standing water level, with a drop-tube cut to place the pump intake within the screen. For shallower bores (less than 50 m), a 12 V battery operated pump was used with the pump intake placed ~1 m above the screen. For all sample sites, physico-chemical parameters (pH, DO, EC) were monitored and samples collected once three well volumes had been pumped and/or the physico-chemical parameters stabilised. This was generally achieved within 1 to 3 hours after onset of pumping. Sample collection involved an in-line, 0.45 μm, high-volume filter connected to a high density polyethylene (HDPE) tube. Total alkalinity concentrations (field alkalinity) were determined in the field by acid titration using a HACH digital titrator and external pH meter control. The Fe^{2+} and HS^- concentrations were determined using a portable colorimeter (HACH DR/890).

Samples for anion and water stable isotope (δ^2H and $\delta^{18}O$) analyses were collected in 60 mL and 30 mL HDPE bottles, respectively, with no further treatment. Samples for cation analysis were collected in 60 mL HDPE bottles and acidified with ultrapure nitric acid. Samples for ^{14}C and ^3H were collected in 1 L narrow mouth HDPE bottles and 2 L HDPE bottles respectively, and were sealed with tape to avoid potential atmospheric exchange during storage. Samples for ^{36}Cl were collected in 1 L narrow mouth HDPE bottles with no further treatment. Major ion and ^{14}C samples were refrigerated at 4°C until analysed.

For both sampling campaigns, we aimed to collect samples representative of the river, the alluvium and the GAB, however we were not able to access any previously characterised GAB bores within the study area, with the only bore screened within the Pilliga Sandstone (273314) (Figure 2). To better constrain GAB groundwater characteristics, we reviewed regional information and used geochemical data from known GAB bores collected by Radke et al. (2000) and McLean (2003). These data were collected to the northwest of our study area and are used as a range (depending on availability of the original reported data) for the GAB end-member in all future plots and discussions (Supplementary Table 1).

To help in the description of results, we use shallow (< 30 m), intermediate (30 – 80 m) and deep (> 80 m) as a rough guide to the origin of the groundwater sample. The chosen depth categories are based on clusters and trends in the ^{14}C analyses. Groundwater samples from similar contemporaneous alluvial-filled valleys in other eastern Australian river valleys show a continuum of geochemical evolution that cannot be explained by separating samples into arbitrary aquifers (such as the aforementioned Narrabri, Gunnedah and Cubbaroo Formations). In such settings, proximity to modern channels and depth are the primary controls on residence time (Cendón et al. 2010; Iverach et al. 2015).

3.2 Geochemical analyses

Groundwater samples from both campaigns were analysed at ANSTO by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for cations and ion chromatography (IC) for anions. ~~The cation and anion analyses were assessed for accuracy by evaluating the charge balance error percentage (CBE%). All samples fell within the acceptable ± 5% range, except for samples 25327-1 and 36001-1, which both contained high NH_4^+ concentration that was not part of the initial ion analyses. This elevated NH_4^+ concentration skewed the CBE% so that they were initially outside the acceptable ± 5% range.~~ Samples for δ^2H and $\delta^{18}O$ were analysed using Cavity Ring-Down Spectroscopy (CRDS) on a Picarro L2130-*i* analyser. These values are reported as ‰ deviations from the international standard V-SMOW (Vienna Standard Mean Ocean Water) and results are accurate to ± 1‰ for δ^2H and ± 0.15‰ for $\delta^{18}O$.

The ^{14}C samples were processed and analysed at ANSTO using methods described in Cendón et al. (2014). The ^{14}C activities were measured by accelerator mass spectrometry (AMS) using the ANSTO 2MV tandetron accelerator, STAR (Fink et al. 2004). The ^{14}C results were reported as percent modern carbon (pmc) following groundwater ^{14}C reporting criteria (Mook & van der Plicht 1999; Plummer & Glynn 2013) with an average 1σ error of 0.21 pmc. ~~(pmc and pMC values are included in Supplementary Table 3 for completeness).~~

The ^{3}H samples were analysed at ANSTO. Water samples were distilled and electrolytically enriched prior to analysis by liquid scintillation. The ^{3}H concentrations were expressed in tritium units (TU) with a combined standard uncertainty of ± 0.03 TU and quantification limit of 0.04 TU. Tritium was measured by counting beta decay in a liquid scintillation counter (LSC). A 10 mL sample aliquot was mixed with the scintillation cocktail that releases a photon when struck by a beta particle. Photomultiplier tubes in the counter convert the photons to electrical pulses that are counted over 51 cycles for 20 minutes.

The $^{36}Cl/Cl$ and $^{36}Cl/^{37}Cl$ ratios were measured by AMS using the ANSTO 6MV SIRIUS Tandem Accelerator (Wilcken et al. 2017). Samples were processed in batches of 10, with each batch containing 1 chemistry blank. The amount of sample used was selected to yield ~ 5 mg of Cl for analysis without carrier addition. Chloride was recovered from the sample solutions by precipitation of AgCl from hot solution (Stone et al. 1996). This AgCl was re-dissolved in aqueous NH_3 (20-22 wt %, IQ grade, Seastar) to remove sulfur compounds of Ag. Owing to isobaric interference of ^{36}S with ^{36}Cl in the AMS measurements, a saturated $Ba(NO_3)_2$ solution (99.999% trace metal basis) was used to precipitate sulfur as $BaSO_4$. At least 72 h were allowed for $BaSO_4$ to settle from a cold solution (4℃) in the dark before removal of the supernatant by pipetting and filtration (0.22 Millex GS). Pure AgCl was re-precipitated by acidifying the $Ag(NH_3)_2$-Cl solution with 5M nitric acid (IQ Seastar, sub-boiled). Finally, AgCl was recovered, washed twice and dried. It was then pressed into high-purity AgBr (99% trace metal basis, Aldrich) in 6 mm diameter Cu-target holders. AgBr has a much lower sulfur content than Cu. The stable Cl isotopes ^{35}Cl and ^{37}Cl were measured with Faraday cups and ^{36}Cl events were counted with a multi-anode gas ionisation chamber. Gas (Ar) stripping (for good brightness/low ion straggling) the ions to 5+ charge state in the accelerator terminal suffices for effective ^{36}S interference separation in the ionisation chamber combined with sample-efficient and rapid analysis. Purdue PRIMELab Z93-0005 (nominally 1.20×10^{-12} $^{36}Cl/Cl$) was used for normalisation with a secondary standard (nominally 5.0×10^{-13} $^{36}Cl/Cl$ (Sharma et al. 1990)) used for monitoring. Background subtraction was done with a linear dependence between ^{36}Cl-rate and interfering ^{36}S-rate. This dependency is established by combining all the blank and test sample measurements and applied to the unknown samples during offline data analysis. This correction factor was typically less than analytical uncertainty of 3-4% bar one sample that had a correction factor of 12% with an analytical uncertainty of 6%.

3.3 Geochemical calculations

Calculations necessary to assess electrical neutrality, dissolved element speciation and saturation indices for common mineral phases were undertaken using the PHREEQC Interactive program (3.3.8) (Parkhurst & Appelo 1999) and the incorporated WATEQ4F thermodynamic database (Ball & Nordstrom 1991). The cation and anion analyses were assessed for accuracy by evaluating the charge balance error percentage (CBE%). All samples fell within the acceptable ± 5% range, except for samples 25327-1 and 36001-1, which both contained high NH_4^+ concentration that was not part of the initial ion analyses. This elevated NH_4^+ concentration skewed the CBE% so that they were initially outside the acceptable ± 5% range. The inverse geochemical modelling code NEPATH XL (Plummer et al. 1994; Parkhurst & Charlton 2008) has been used to calculate the mixing ratio between two end-members, using their Cl concentrations. The choice of end-members will influence calculated proportions. However, end-members were ~~have been~~ selected to provide ~~a~~ conservative approximations. In general, Cl concentrations in surface water and shallow groundwater in the study area are low (< 30 mg/L), while samples recovered from the Pilliga Sandstone (GAB) have higher concentrations (~ 60 mg/L). We mix a representative shallow, modern groundwater (30170-1) with an average GAB composition obtained from regional groundwater samples (McLean 2003). These two initial end-members are mixed in different proportions so that Cl concentrations in a selected final bore can be explained via inverse modelling calculations.

^{36}Cl residence times were calculated from the equations of Bentley et al. (1986), assuming no other sources or sinks besides recharge and natural decay (eqn. 1):

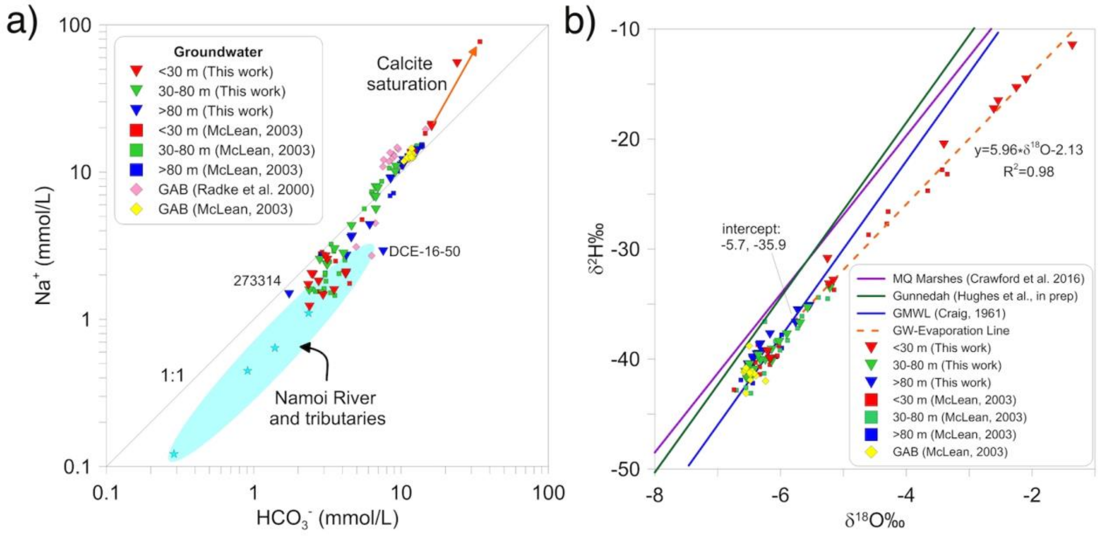
$$t = \frac{-1}{\gamma_{36}} \ln \frac{R - R_{se}}{R_0 - R_{se}} \qquad (1)$$

where R = ^{36}Cl/Cl ratio measured in the sample, R_0 = the initial ^{36}Cl/Cl ratio (meteoric water), ~~and~~ R_{se} = the ^{36}Cl/Cl ratio under secular equilibrium (in this case the ^{36}Cl/Cl ratio from the Pilliga Sandstone), and λ_{36} is the decay constant (2.303 x 10^{-6}). We used a R_0 value of 160 ($x10^{-15}$), which was an average of 10 samples compiled from studies in the Coonamble Embayment and reported in Radke et al. (2000). For R_{se} a value of 5.7 ($x10^{-15}$) was used, which is appropriate for aquifers dominated by sandstone (this secular equilibrium value can vary according to the dominant lithology). This R_{se} value has been applied to ^{36}Cl/Cl calculations elsewhere in the GAB (Moya et al. 2016).

4 Results

4.1 Major ~~and minor~~ ion chemistry

The groundwater ~~in~~of the alluvial aquifer is predominantly Na-HCO_3-type water, with concentrations ranging from 0.12~~1.1~~ mmol/L to– 54.6 mmol/L (average: 6.85 mmol/L) for Na^+ and 0.29 mmol/L to~~1.7 –~~ 24.0 mmol/L (average: 6.43 mmol/L) for HCO_3^- (Supplementary Table 2). Generally, the highest concentrations of Na^+ and HCO_3^- occur in the deeper groundwater and decrease up the vertical groundwater profile (Figure 3a). The concentration of these two ions in the groundwater of the LNA is higher than expected from local rainfall sources and other shallow groundwater alluvial systems in eastern Australia (Martinez et al. 2017). In GAB groundwater, the Na-HCO_3 molar ratio is generally 1:1 and the two ions are generally present in higher ~~more~~ concentrations~~ted~~ than in our alluvial samples (Radke et al. 2000; McLean 2003), which is evident in the position of the regional GAB samples in Figure 3a.



~~**Figure 3.** a) Na^+ vs HCO_3^- showing the mixing trend that the alluvial samples form between the Namoi River and samples from the GAB (Radke et al. 2000; McLean 2003). The shaded blue ellipse represents all river chemistry data available for the Namoi River and tributaries (this work (n=4), McLean 2003 (n=4), Mawhinney 2011 (n=79)); b) Water stable isotopes in the LNA, showing the two separate mechanisms of recharge; surface water recharge plotting along an evaporation trend line and potential inflow from the GAB clustered with regional samples from the GAB (McLean 2003).~~

Additional ions used in this study are F^-, Cl^- and the Cl/Br ratio. The concentration of F^- in the groundwater ranges from 0.002 mmol/L to 0.215 mmol/L (average: 0.028 mmol/L). Fluoride concentrations generally increase with depth and accumulate in solution as all groundwater samples are below saturation with respect to fluorite (Figure 3b). Concentrations of Cl^- in the alluvial groundwater range from 0.063 mmol/L to 26.73 mmol/L (average: 1.67 mmol/L). Unlike the other major ions, Cl^- concentrations through the vertical groundwater profile are relatively stable (Figure 3c). The relationship between Cl^- and the Cl/Br ratio shows that groundwater composition clusters from values below the seawater ratio to values close to seawater. The Cl/Br ratios are similar to ranges found in other alluvial groundwater systems but slightly lower than ratios observed in other GAB samples for Australian locations (Herczeg et al., 1991; Cendón et al., 2010; Cartwright et al., 2010). Additionally, t~~T~~he Cl/Br ratios in shallow samples connected to the river are consistent with expected ratios in rainfall (Short et al. 2017). The regional GAB samples (Radke et al. 2000) show a Cl/Br ratio more similar to seawater, with our samples from the LNA lying on a mixing trend between the two end-members (Figure 3c).

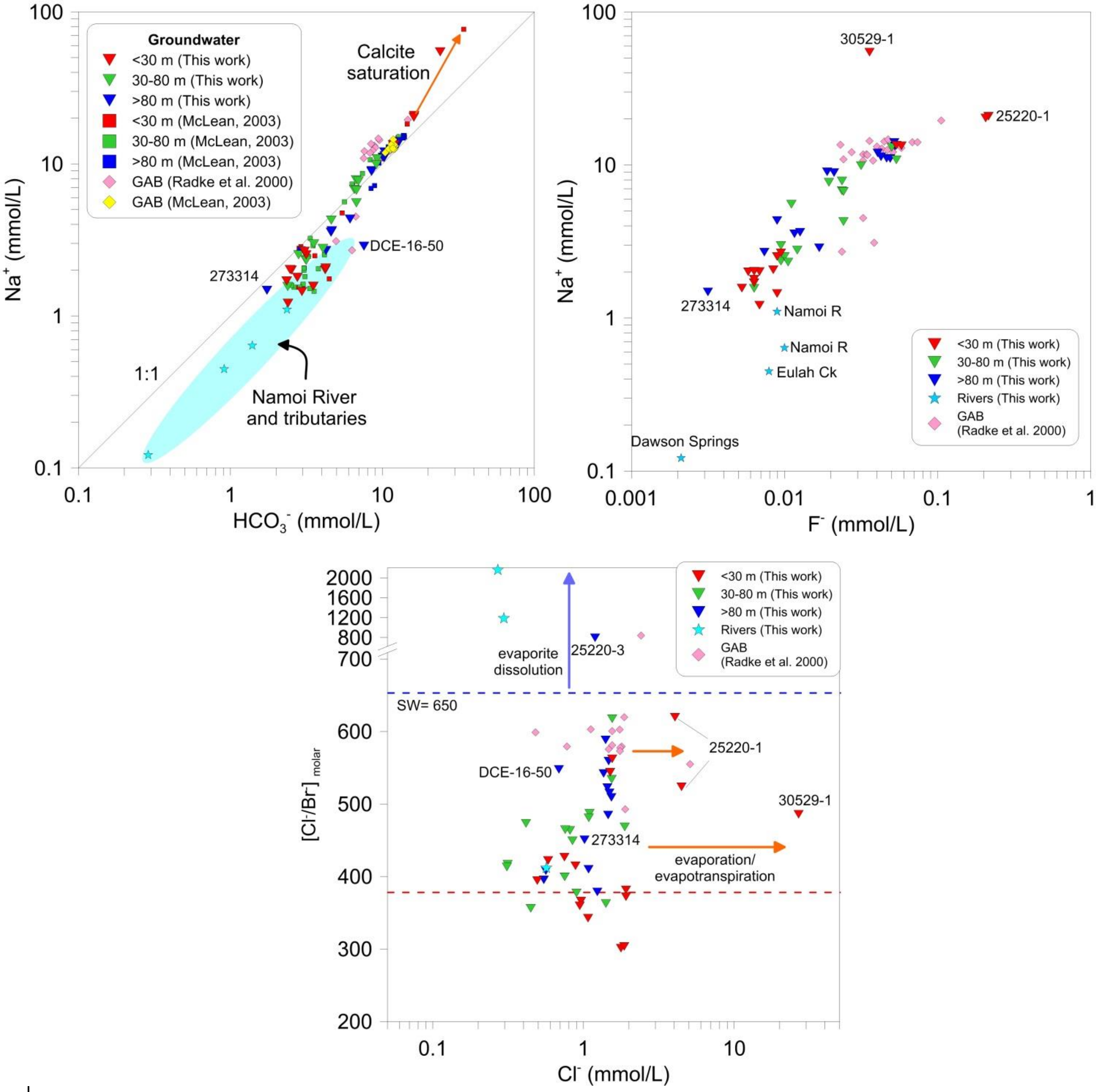


Figure 3. a) Na^+ vs HCO_3^- showing the mixing trend that the alluvial samples form between the Namoi River and samples from the GAB (Radke et al. 2000; McLean 2003). The shaded blue ellipse

represents all river chemistry data available for the Namoi River and tributaries (this work (n=4), McLean 2003 (n=4), Mawhinney 2011 (n=79)); b) Na^+ vs F^- and c) Cl^-/Br^- vs Cl^-, highlighting the mixing trend between the surface recharge and the GAB that we observe in other geochemical indicators. The red dotted line represents the Cl^-/Br^- ratio for rainfall and the blue dotted line is the seawater ratio. ~~b) Water stable isotopes in the LNA, showing the two separate mechanisms of recharge; surface water recharge plotting along an evaporation trend line and potential inflow from the GAB clustered with regional samples from the GAB (McLean 2003).~~

~~**Figure 4.** a) Na^+ vs F^- and b) Cl^-/Br^- vs Cl^-, highlighting the mixing trend between the surface recharge and the GAB that we observe in other geochemical indicators. The red dotted line represents the Cl^-/Br^- ratio for rainfall.~~

We identified one major outlier in the hydrochemical results, which was sample 273314. This sample is from 207 m bgs and the bore screen is classified as being in the GAB. However, the geochemical parameters for this deep GAB sample have a signature more similar to river water than what would be expected in the GAB 207 m bgs. The concentration of Na^+, HCO_3^-, Cl^-, F^- and the Cl/Br ratio in this sample plot closer to the river and shallow groundwater than the deeper groundwater system (Figure 3). Potential reasons for this are explored in detail below.

4.2 Water stable isotopes (δ^2H and $\delta^{18}O$)

~~The stable water isotope distribution in the LNA is shifted to the right of the nearest available local meteoric water lines (LMWL) (Macquarie Marshes and Gunnedah) (Figure 5; Supplementary Table 3).~~ The stable water isotopic values for this study range from -0.76‰ to 8.4‰ for $\delta^{18}O$ and -7.5‰ to -54.9‰ for δ^2H. Most groundwater samples cluster together at around -6‰ and -40‰ ($\delta^{18}O$ and δ^2H) and lie on the global meteoric water line (GMWL), to the right of the nearest available local meteoric water lines (LMWL) (Macquarie Marshes and Gunnedah) (Figure 4~~5~~; Supplementary Table 3). A group of mostly shallow samples collected from piezometers close to river channels follow an ~~groundwater~~ evaporation line. Our results are similar, including the shallow groundwater evaporative trend, to those recorded by McLean (2003). Water stable isotopic compositions for regional GAB samples range from -6.58‰ to -6.24‰ for $\delta^{18}O$ and -43.1‰ to -38.8‰ for $\delta^{2}H$ (McLean 2003) (Figure 4).

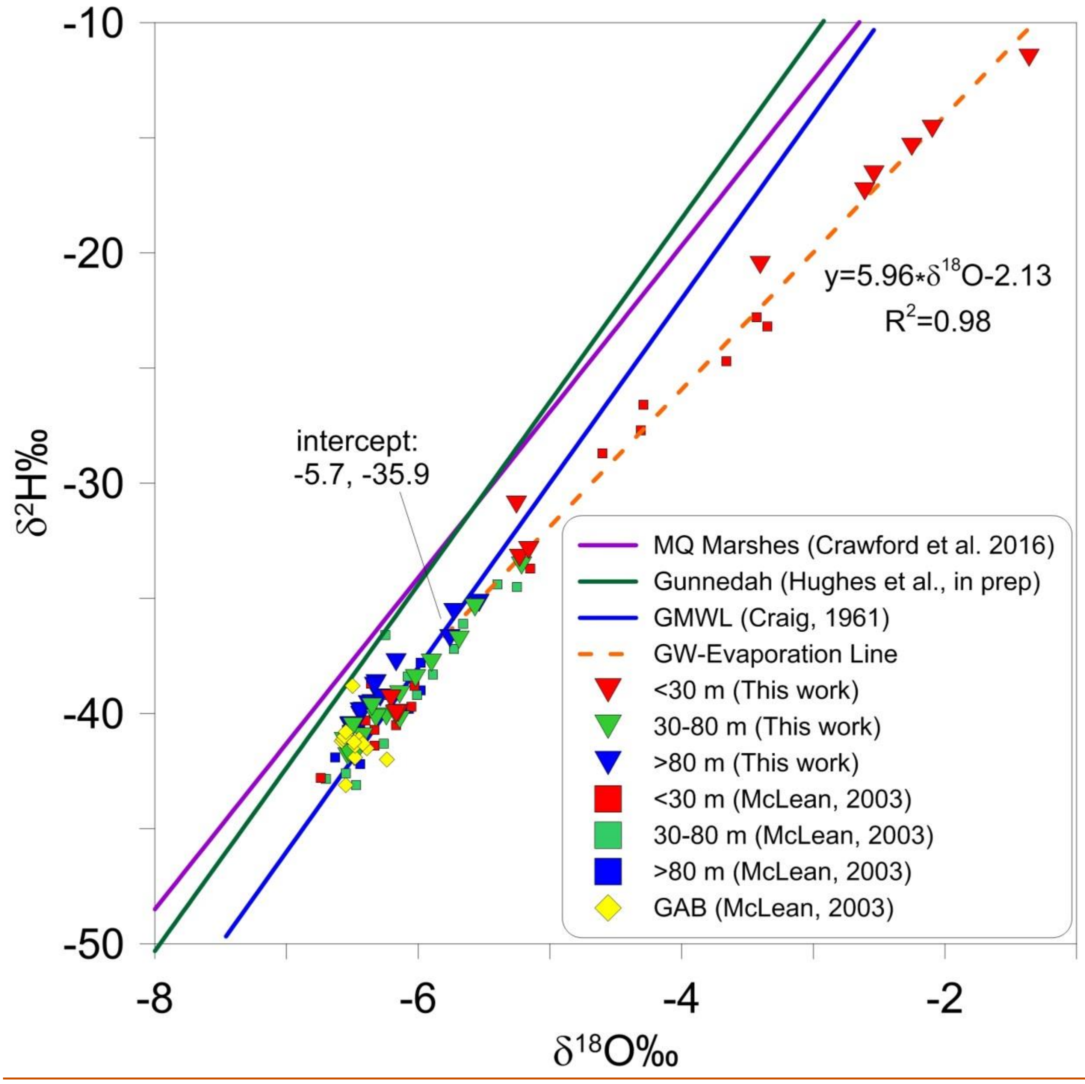
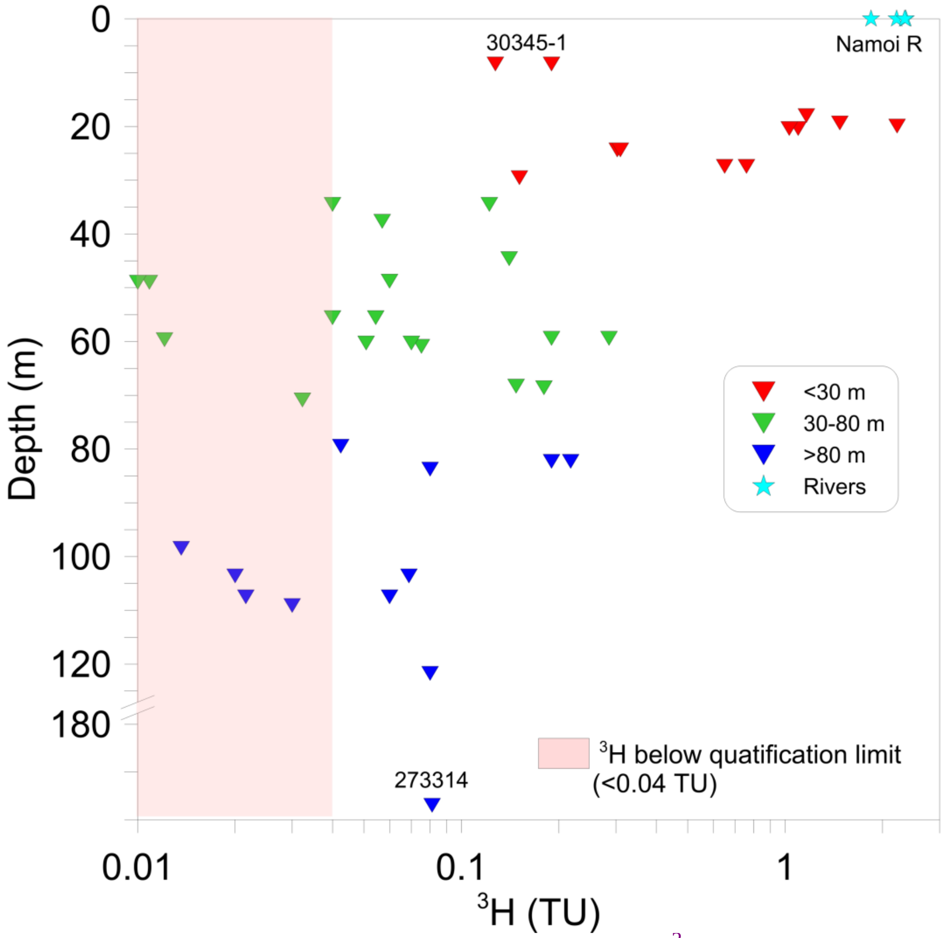


Figure 4. –Water stable isotopes in the LNA, showing the two separate mechanisms of recharge; surface water recharge plotting along an evaporation trend line and potential inflow from the GAB clustered with regional samples from the GAB (McLean 2003).~~a) Na^{+} vs F^{-} and b) Cl^{-}/Br^{-} vs Cl^{-}, highlighting the mixing trend between the surface recharge and the GAB that we observe in other geochemical indicators. The red dotted line represents the Cl^{-}/Br^{-} ratio for rainfall.~~

4.3~~4~~ Isotopic tracers (^{3}H, ^{14}~~^{3}~~C and ^{36}Cl)

Tritium activities vary throughout the study area, ranging from 0.01 TU to 2.36 TU (average: 0.42 TU). Tritium a~~with a~~ctivities generally decrease~~ing~~ with depth and distance from the river channel (Figure 5) (all data in Supplementary Table 3), with modern recharge evident in the high ^{3}H activities near the main river channels. However, ^{3}H above the detection limit



(0.04 TU) was measured at depth (down to 207 m bgs).~~,~~ The ^{3}~~-~~H activities we measured at depth are significant for Australian groundwater, as the peak of the bomb pulse in Australia was around 60 TU and ^{3}H in Australian rainfall as been at natural background concentrations for some time. ~~indicating that the extent of recharge from episodic flooding. Measuring 3H above the detection limit also shows that surface recharge reaches the deeper LNA relatively quickly (< 70 years).~~

Figure 5. Plot of depth vs ^{3}H, highlighting the ^{3}H activity throughout the vertical groundwater profile.

~~Past ^{3}H data from the region (Calf 1978) suggest that ^{3}H was already present in the deeper parts of the alluvial aquifer (> 70 m bgs) prior to a major flood in 1971, with activities ranging from 7.9 TU to 11.2 TU. This indicates good connectivity to the surface. Additionally, measurements of ^{3}H post flooding (16.6 to 20.7 TU) indicate that substantial recharge took place during this flood, highlighting the importance of surface water recharge to the LNA.~~

~~. The activities of ^{3}H in shallow groundwater samples near the main channels show areas with modern recharge. However, despite decreasing activities, ^{3}H remains relatively prevalent in the deeper part of the system. This indicates the extent of recharge from episodic flooding and shows that surface recharge reaches the deeper LNA (down to ~80 m bgs) relatively quickly (< 70 years). In February 1971, the region experienced the second largest flood on record. Pre-flood sampling of deep groundwater (> 70 m bgs) revealed ^{3}H activities ranging from 7.9 to 11.2 TU, in several bores located in the north of our study area (Calf 1978). The same monitoring bores in September 1971 and March 1972 ranged from 16.6 to 20.7 TU, with surface water in the Namoi River ranging from 16.9 to 22.3 TU (Calf 1978). Pre-flooding ^{3}H activities suggest that modern water was already present in deeper parts of the alluvial aquifer at this time, indicating good connectivity to the surface and that substantial recharge took place during this flood, highlighting the importance of surface water recharge to the LNA. It should be noted that the high ^{3}H values in the 1970s are a result of atmospheric nuclear bomb testing and can’t be compared with present day ^{3}H values.~~ The ^{14}C content in the groundwater ranged from 0.2 pmc to 107.6 pmc (average: 54.0 pmc). Generally, groundwater samples shallower than 30 m had a high ^{14}C content (> 90 pmc), which decreased with depth. There were 9 samples with a ^{14}C content below 1 pmc, indicating very old groundwater (> 30 ka), with total depths ranging from 35 m bgs to 207 m bgs.

~~It has been found that groundwater in the GAB recharge zone closest to the study area has a ^{36}Cl/Cl ratio up to ~ 200 (x10^{-15}) (Radke et al. 2000) with recharge values applied in calculations elsewhere in the GAB of 110 (x10^{-15}) (Moya et al. 2016). Water from the Namoi River has a ^{36}Cl/Cl ratio of ~ 420 (x10^{-15}), possibly affected by thermonuclear ^{36}Cl input from atmospheric bomb testing in the 1950s (Supplementary Table 4). We calculated ^{36}Cl agesresidence times from the equations of Bentley et al. (1986), assuming no other sources or sinks besides recharge and natural decay (eqn. 1):~~

~~$t = \frac{-1}{\gamma_{36}} \ln \frac{R-R_{se}}{R_0-R_{se}}$ (1)~~

~~where R = ^{36}Cl/Cl ratio measured in the sample, R_0 = the initial ^{36}Cl/Cl ratio (meteoric water), and R_{se} = the ^{36}Cl/Cl ratio under secular equilibrium (in this case the ^{36}Cl/Cl ratio from the Pilliga Sandstone). We used a R_0 value of 160 (x10^{-15}), which was an average of 10 samples compiled from studies in the Coonamble Embayment and reported in Radke et al. (2000). For R_{se} we used a value of 5.7 (x10^{-15}), which is appropriate for aquifers dominated by sandstone (this secular equilibrium value can vary according to the dominant lithology). This R_{se} value has been applied to ^{36}Cl/Cl calculations elsewhere in the GAB (Moya et al. 2016).~~

Our ^{36}Cl ~~calculations~~results ~~resulted in residence times~~ for the alluvial groundwater ranged~~ing~~ from 24.06 (x10^{-15}) to 455.35 (x10^{-15}) (average: 169.4 (x10^{-15}) (shown in the interpolation in Figure 2). It has been found that groundwater in the GAB recharge zone closest to the study area has a ^{36}Cl/Cl ratio up to ~ 200 (x10^{-15}) (Radke et al. 2000) with recharge values applied in calculations elsewhere in the GAB of 110 (x10^{-15}) (Moya et al. 2016). Water from the Namoi River has a ^{36}Cl/Cl ratio of ~ 420 (x10^{-15}), possibly affected by thermonuclear ^{36}Cl input from atmospheric bomb testing in the 1950s (Supplementary Table 4).

5 Discussion~~and Discussion~~

5.1 Identification of recharge and mixing between the GAB and the LNA

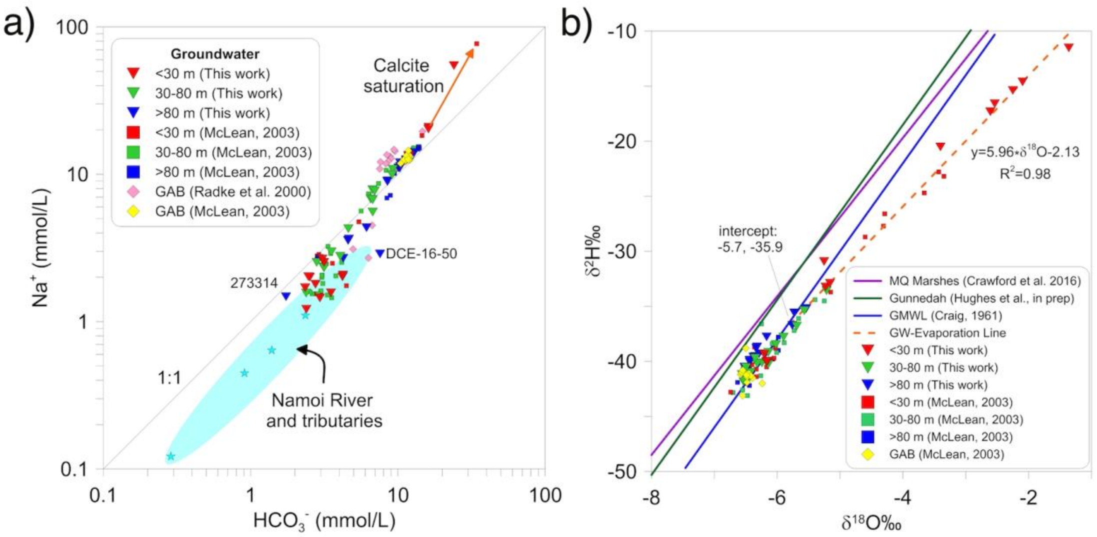
~~In the literature, mechanisms of recharge to the LNA are generally agreed upon, with a main surface water recharge component and a minor artesian component (Calf 1978; Merrick 2000; McLean 2003). We observe these two mechanisms in this study as well, however the relative contributions of these two components at any given time, and how this contribution changes over time, are difficult to constrain.~~ The δ^{18}O and δ^{2}H isotopic compositions suggest two mechanisms of recharge to the alluvium: artesian discharge and surface water infiltration. The regional GAB samples plot within the alluvial groundwater sample range, suggesting a GAB component in the alluvium. The ~~groundwater~~ evaporation line in Figure 4 indicates recharge to the alluvium via surface water infiltration. It also shows ~~and~~ a good connection between ~~modern~~ surface water that has undergone evaporation and shallow groundwater.

~~There is an excess of both Na$^+$ and HCO$_3^-$ in the groundwater of the LNA (Supplementary Table 2), compared to ion ratios expected from local rainfall sources and other shallow groundwater alluvial systems in eastern Australia (Martinez et al. 2017). Their abundance defines the ubiquitous presence of Na-HCO$_3$-type groundwater we observe throughout the study area.~~ Additional evidence for these two mechanisms of recharge is~~ly,~~ the composition of Na$^+$ and HCO$_3^-$ in the LNA.~~ suggests the 2 aforementioned mechanisms of recharge.~~ ~~The Na-HCO$_3$ ratio in GAB groundwater is generally 1:1 (ppm) (Radke et al. 2000; McLean 2003), which is reinforced by the position of the regional GAB samples in Figure 3a. The Namoi River and other regional streams have lower Na$^+$ and HCO$_3^-$ concentrations and a lower Na$^+$/HCO$_3^-$ ratio than both the historic GAB data and the deeper alluvial data collected in this study.~~ Figure 3a~~3a~~ shows a mixing line that the alluvial samples follow, plotting between the end-members of the GAB and the Namoi River, suggesting ~~.~~ ~~This suggests that there is~~ an increasing GAB contribution to the alluvial groundwater with depth. This also ~~suggests~~implies ~~and~~ that a continuum of mixing exists between the shallow and deep groundwater within the LNA. The shallow samples (25220-1 and 30259-1) that are more Na$^+$ enriched compared to samples from the GAB have undergone separate evapotranspiration processes and hence have a concurrent increase in Cl$^-$. Assuming that Cl$^-$ is behaving conservatively (Appelo & Postma 2005) we surmise that increases in dissolved major ion concentrations concomitant with increases in Cl$^-$ in the shallow groundwater are likely to be a result of evaporation.

Further hydrochemical evidence for these recharge mechanisms is the covariation of Na$^+$ and F$^-$, both interpreted as primarily derived from groundwater interaction with silicate minerals in this region (Airey et al. 1978; Herczeg et al. 1991; McLean 2003) (Figure 3b). Our alluvial samples fall on the mixing line between samples from the river and nearby tributaries and regional samples from the GAB (Radke et al. 2000), in a similar way to the Na-HCO$_3$ trend that we observe in Figure 3a. The Cl/Br ratios in the groundwater also support the mixing interpretation provided by the Na$^+$ and HCO$_3^-$ concentrations, contrary to the possibility of water rock interactions along the alluvium flowpath (Figure 3c). Furthermore, the relationship between ^{36}Cl and Na$^+$ provides additional evidence of mixing in the groundwater (Supplementary Figure 1).

Figure 3 also ~~show~~highlights the aforementioned deep outlying sample (273314), which was 207 m bgs in total depth, yet plots with the shallow alluvial and river samples. Figure 2 shows that this sample is situated just above the Napperby Formation. We hypothesise that this sample originated from surface recharge from the Namoi River (which is in contact with the underlying Digby Formation to the south of the study area), with negligible input from the more Na-HCO$_3$-rich groundwater in the Pilliga Sandstone, where the sample is ~~situated~~from. ~~We observe a similar geochemistry in ~~S~~s~~ample 30345-2 (Supplementary Tables 2 and 3), which is situated in the lower part of the LNA in proximity to the alluvial contact with the Napperby Formation (Figure 2) has a similar geochemistry. These results suggest the connection between deeper Triassic formations beneath the GAB and the Namoi River, which must be an important consideration in future water balance models of the catchment.

~~The evapotranspiration process is also shifting the groundwater composition towards calcite saturation. Both processes contribute to increasing the Na^+/HCO_3^- ratio. The evaporative enrichment is also evident in the concentration of F^-, Cl^- and the Cl^-/Br^- ratio (Figure 4). Evidence for the $CaCO_3$ precipitation is found in the calcrete material on the surface soils, which also occurs in other semi-arid environments due to this process (Meredith et al. 2016).~~

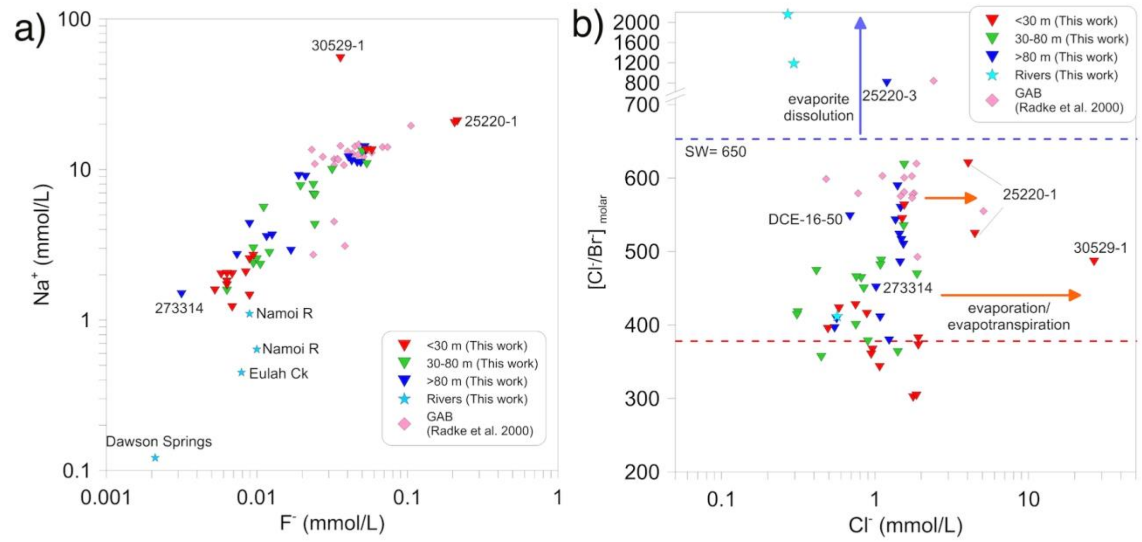


~~**Figure 3.** a) Na^+ vs HCO_3^- showing the mixing trend that the alluvial samples form between the Namoi River and samples from the GAB (Radke et al. 2000; McLean 2003). The shaded blue ellipse represents all river chemistry data available for the Namoi River and tributaries (this work (n=4), McLean 2003 (n=4), Mawhinney 2011 (n=79)); b) Water stable isotopes in the LNA, showing the two~~

~~separate mechanisms of recharge; surface water recharge plotting along an evaporation trend line and potential inflow from the GAB clustered with regional samples from the GAB (McLean 2003).~~

~~The δ^{18}O and δ^{2}H compositions suggest two mechanisms of recharge to the alluvium (Figure 3b; Supplementary Table 3): artesian discharge and surface water infiltration. The regional GAB samples (δ^{18}O and δ^{2}H: -6.58‰ to -6.24‰ and -43.1‰ to -38.8‰, respectively (McLean 2003)) plotted within the alluvial groundwater sample range (δ^{18}O and δ^{2}H: -7‰ to -6‰ and -44‰ to -37‰, respectively). This may suggests a GAB component in the alluvium. A second trend is observed with alluvial groundwater samples ranging from -3.4‰ to -1.4‰ for δ^{18}O and -20.5‰ to -11.5‰ for δ^{2}H plotting along an evaporation trend line that suggests good connection and mixing between modern surface water and shallow groundwater.~~

~~Further hydrochemical evidence for these recharge mechanisms come from assessing the covariation of Na^+ and F^-, both interpreted as primarily derived from groundwater interaction with silicate minerals in this region (Airey et al. 1978; Herczeg et al. 1991; McLean 2003) (Figure 4a). Our alluvial samples fall on the mixing line between samples from the river and nearby tributaries and regional samples from the GAB (Radke et al. 2000), in a similar way to the Na-HCO_3 trend that we observe in Figure 3a. The Cl^-/Br^- ratios in the groundwater also support the mixing interpretation provided by the Na^+ and HCO_3^- concentrations, contrary to the possibility of water rock interactions along the alluvium flowpath (Figure 4b).~~ ~~The Cl/Br ratios in shallow samples connected to the river are consistent with expected ratios in rainfall (Short et al. 2017).~~ ~~The regional GAB samples (Radke et al. 2000) show a Cl^-/Br^- ratio closer more similar to seawater, with our samples from the LNA lying on a mixing trend between the two end-members.~~



~~**Figure 4.** a) Na^+ vs F^- and b) Cl^-/Br^- vs Cl^-, highlighting the mixing trend between the surface recharge and the GAB that we observe in other geochemical indicators. The red dotted line represents the Cl^-/Br^- ratio for rainfall.~~

~~Figure 4a also reveals a deep outlying sample (273314), which was 207 m bgs in total depth (screened 182-195 m bgs), yet plots with the shallow alluvial and river samples. Additionally, many of the geochemical parameters (for example Na^+, F^-, HCO_3) in this sample have a signature more similar to river water rather than what would be expected in the GAB 207 m bgs (Supplementary Tables 2 and 3). Figure 2 shows that this sample is situated just above the Napperby Formation. This suggests that this sample originated from surface recharge from the Namoi River (which is in contact with the underlying Digby Formation to the south of the study area), with negligible input from the more Na-HCO_3-rich groundwater in the overlying Pilliga Sandstone. We observe a similar geochemistry in sample 30345-2 (Supplementary Tables 2 and 3), which is situated in the lower part of the LNA in proximity to the alluvial contact with the Napperby Formation (Figure 2). These results suggest the connection between deeper Triassic formations beneath the GAB and the Namoi River, which must be an important consideration in future water balance models of the catchment.~~

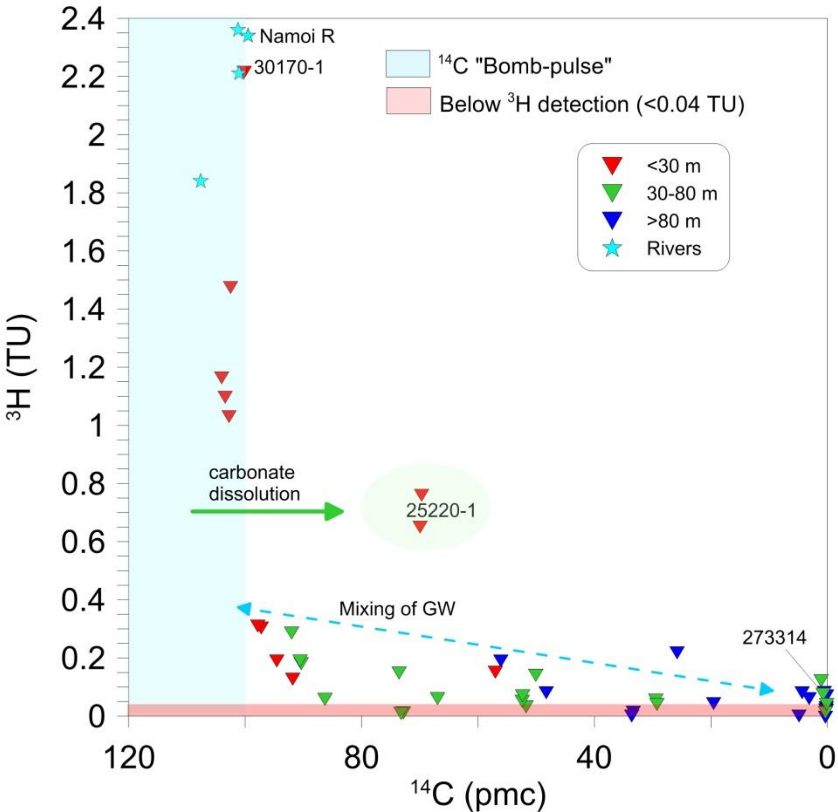
5.1.1~~2~~ *Mixing between groundwaters of varying residence times*

Major ion and water stable isotope data suggest two primary mechanisms of recharge to the LNA and show that mixing is occurring within the alluvium. ~~We use the that there is mixing of groundwater from the GAB and the LNA. We build upon this interpretation by evaluating the~~ ^{3}H activity and ^{14}C content~~s~~ in the alluvial groundwater to quantify the potential residence times of the groundwater sources that are mixing within the alluvium. Tritium activities above the detection limit at depth (down to 207 m bgs) indicates the extent of recharge from episodic flooding. Measuring ^{3}H above the detection limit at these depths also shows that surface recharge reaches the deeper LNA relatively quickly (< 70 years). Past ^{3}H data from the region (Calf 1978) suggest that ^{3}H was already present in the deeper parts of the alluvial aquifer (> 70 m bgs) prior to a major flood in 1971, with activities ranging from 7.9 TU to 11.2 TU. This indicates good connectivity to the surface. Additionally, measurements of ^{3}H post-flooding (16.6 to 20.7 TU) indicate that substantial recharge took place during this flood, highlighting the importance of surface water recharge to the LNA. ~~of the LNA and calculating residence times from ^{36}Cl, to quantify the extent of interaction between the two groundwater sources.~~

~~Tritium activities vary throughout the study area, with activities generally decreasing with depth and distance from the river channel (Supplementary Table 3). The activities of ^{3}H in shallow groundwater samples near the main channels show areas with modern recharge. However, despite decreasing activities, ^{3}H remains relatively prevalent in the deeper part of the system. This indicates the extent of recharge from episodic flooding and shows that surface recharge reaches the deeper LNA (down to ~80 m bgs) relatively quickly (< 70 years). In February 1971, the region experienced the second largest flood on record. Pre-flood sampling of deep groundwater (> 70 m bgs) revealed ^{3}H activities ranging from 7.9 to~~

~~11.2 TU, in several bores located in the north of our study area (Calf 1978). The same monitoring bores in September 1971 and March 1972 ranged from 16.6 to 20.7 TU, with surface water in the Namoi River ranging from 16.9 to 22.3 TU (Calf 1978). Pre-flooding ^{3}H activities suggest that modern water was already present in deeper parts of the alluvial aquifer at this time, indicating good connectivity to the surface and that substantial recharge took place during this flood, highlighting the importance of surface water recharge to the LNA. It should be noted that the high ^{3}H values in the 1970s are a result of atmospheric nuclear bomb testing and can't be compared with present day ^{3}H values.~~

The ~~prevalence~~ activities of ^{3}H above the detection limit throughout the vertical profile of the LNA~~system~~ (Figure 5~~indicating groundwater with a residence time of < 70 a~~) are ~~is not~~ inconsistent with the low ^{14}C contents in the groundwater. ~~(Supplementary Table 3).~~ The presence of measurable ^{3}H but negligible ^{14}C (close to 0 pmc) suggests that mixing is occurring between groundwater that is associated with modern recharge processes in the alluvium and groundwater that, as indicated by the ^{14}C content, is presumably much older. This older groundwater~~ as indicated by the ^{14}C content and~~ may be derived from artesian inflow. Figure 6~~5~~ shows ^{3}H activities above the detection limit in samples with ^{14}C content of



almost 0 pmc, suggesting that groundwater with a very low ^{14}C content is mixing with groundwater with a high ^{3}H activity. Even though ~~we see~~there is evidence of ^{14}C dilution in localised areas, we also observe mixing between groundwaters of widely different ^{14}C and ^{3}H values in the gradient of the samples in Figure 6~~5~~ (emphasised with a dotted blue line). This gradient would be steeper if there were mixing between groundwaters closer in residence times (Cartwright et al. 2013). ~~The outlying sample (25220-1) is interpreted to be undergoing carbonate dissolution as evidenced by calcrete material present in the surface soils.~~

Figure 6~~5~~. ^{3}H (TU) vs ^{14}C (pmc). This shows the mixing between groundwater with detectable ^{3}H activity (as indicated by the red band) and groundwater with very low ^{14}C content (as indicated by the dotted blue line).

5.2~~3~~ Extent of interaction between the GAB and the LNA

The ^{3}H and ^{14}C values show that there is mixing between groundwater of varying ~~values~~residence times, however they provide little constraint on the groundwaters with a ^{14}C content of close to 0 pmc (ie > 30 ka). This is where chlorine-36 dating can be a useful tracer because it can be used to identify the presence of groundwaters that are much older than the range provided by ^{14}C. ~~It has been found that groundwater in the GAB recharge zone closest to the study area has a ^{36}Cl/Cl ratio up to ~ 200 (x10^{-15}) (Radke et al. 2000) with recharge values applied in calculations elsewhere in the GAB of 110 (x10^{-15}) (Moya et al. 2016). Water from the Namoi River has a ^{36}Cl/Cl ratio of ~ 420 (x10^{-15}), possibly affected by thermonuclear ^{36}Cl input from atmospheric bomb testing in the 1950s (Supplementary Table 4). We calculated ^{36}Cl ages from the equations of Bentley et al. (1986), assuming no other sources or sinks besides recharge and natural decay (eqn. 1):~~

~~$t = \frac{-1}{\gamma_{36}} \ln \frac{R - R_{se}}{R_0 - R_{se}}$ (1)~~

~~where R = ^{36}Cl/Cl ratio measured in the sample, R_0 = the initial ^{36}Cl/Cl ratio (meteoric water), and R_{se} = the ^{36}Cl/Cl ratio under secular equilibrium (in this case the ^{36}Cl/Cl ratio from the Pilliga Sandstone). We used a R_0 value of 160 (x10^{-15}), which was an average of 10 samples compiled from studies in the Coonamble Embayment and reported in Radke et al. (2000). For R_{se} we used a value of 5.7 (x10^{-15}), which is appropriate for aquifers dominated by sandstone (this secular equilibrium value can vary according to the dominant lithology). This R_{se} value has been applied to ^{36}Cl/Cl calculations elsewhere in the GAB (Moya et al. 2016).~~

A plot of ^{36}Cl/Cl vs ^{14}C (pmc) (Figure 7~~6~~) shows a distinct mixing trend between groundwater with high and very low ^{14}C content. The 2 deep outlying samples (30345-2 and 273314; shaded yellow ellipse in Figure 7~~6~~) display different geochemical characteristics from the other samples, possibly because of their~~its~~ aforementioned proximity to the Napperby Formation (Figure 2). Figure 7~~6~~ shows the ^{36}Cl/Cl value range of GAB recharge, highlighting the alluvial samples with values lower than this GAB recharge value. This suggests that these alluvial groundwaters are influenced by artesian inflow of very old groundwater. This is evident in the natural neighbour interpolation in Figure 2.

The ~~In this case, the~~ longest residence time calculated from eqn. 1 for our study area is between 700 ka and ~900 ka. Using the two extremes of the ^{36}Cl/Cl range for GAB recharge (100 (x10^{15}) and 200 (x10^{15})) this calculated residence time would be slightly shorter or slightly longer, respectively.

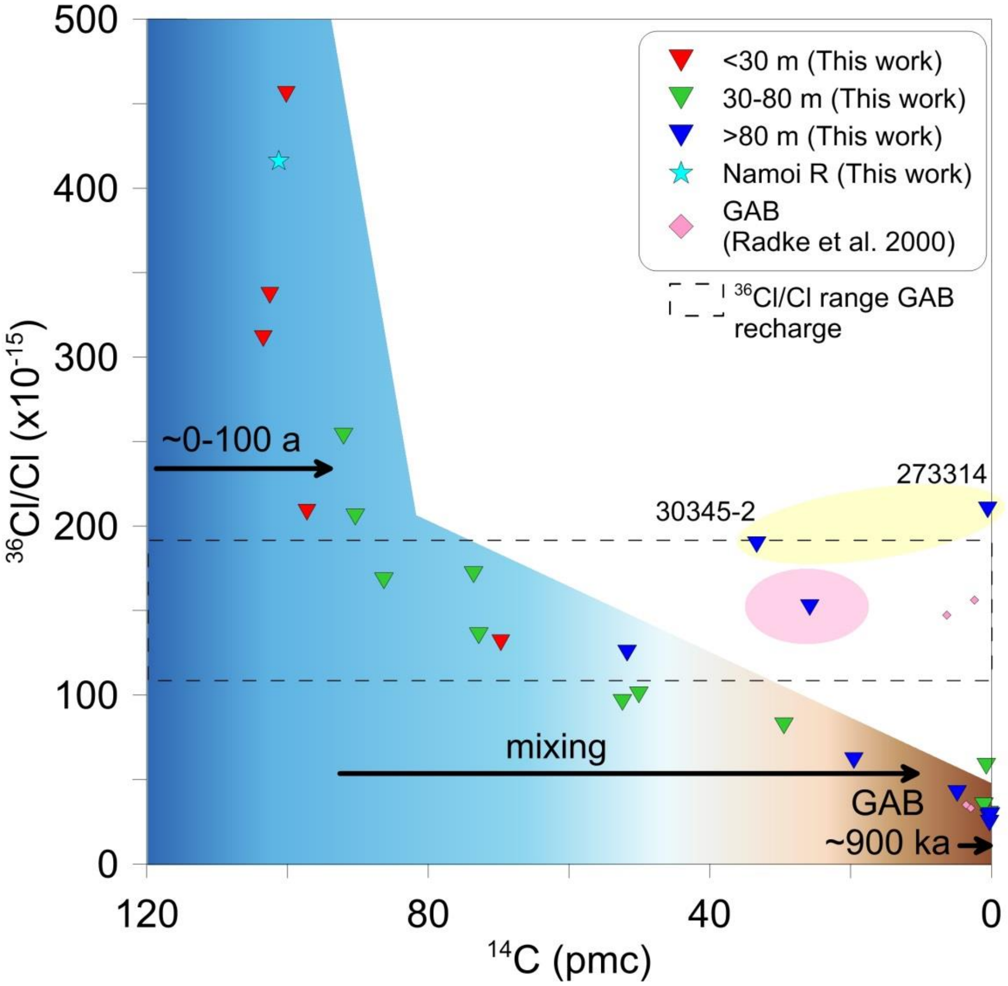


Figure 7~~6~~. ^{36}Cl/Cl (x10^{-15}) vs ^{14}C (pmc). The colour gradient represents the mixing between the two major sources: surface water recharge (blue = modern) and the GAB (brown = old). The shaded yellow ellipse encompasses the two outliers where the geochemistry is being influenced by proximity to the Napperby Formation. The shaded pink ellipse is sample 25327-3 located in the irrigation area.

The apparent degree of ^{36}Cl decay ~~we~~ observed in the alluvial groundwater samples is too large to be explained simply by radioactive decay as indicated by the measurable ^{14}C content in the same samples (Phillips 2000). This means that the time needed for the ^{36}Cl to decay as much as ~~we~~ observed would be well outside the range of ^{14}C dating (> 30 ka) and therefore ~~we would expect~~ all groundwater samples would be expected to have a ^{14}C content of 0 pmc, which is ~~we do~~ not observed. Furthermore, the decrease in ^{36}Cl is unlikely to result from dilution by ^{36}Cl-depleted sources such as evaporites, as the Cl$^-$ concentrations are similar in most samples (Figure 8~~7~~a and b). Therefore, mixing between groundwaters of different residence times is the most likely explanation for the observed ^{36}Cl signatures.

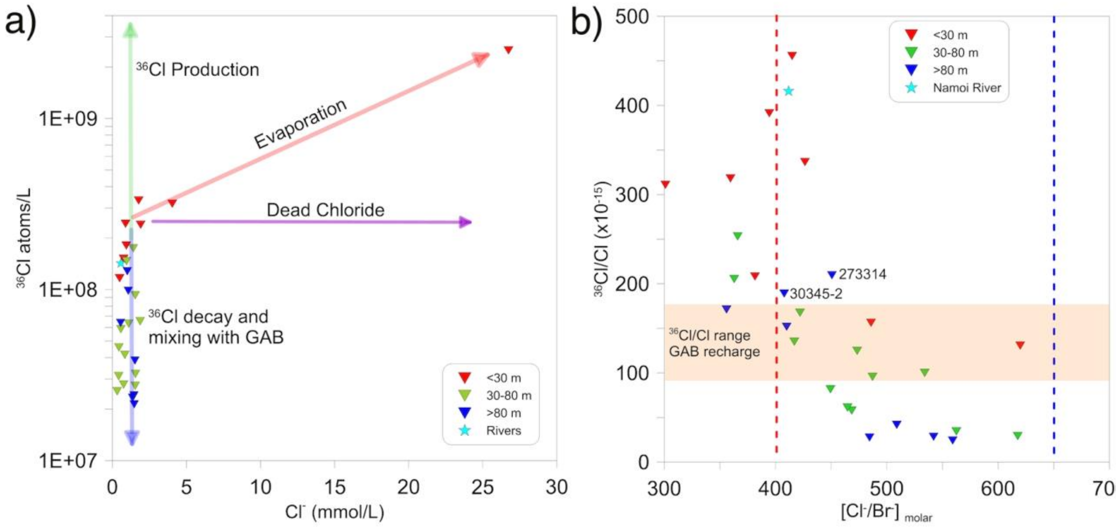


Figure 8~~7~~. a) ^{36}Cl vs Cl$^-$ concentration. The ^{36}Cl production arrow represents in situ ^{36}Cl production as a result of high U and Th in host rocks; b) ^{36}Cl/Cl ratio (x10^{-15}) vs Cl$^-$/Br$^-$. The dotted blue line represents the Cl$^-$/Br$^-$ ratio in seawater and the dotted red line represents the expected Cl$^-$/Br$^-$ ratio for rainfall at Narrabri based on distance from the coast (Short et al. 2017).

Our groundwater samples from the deep alluvium display lower ^{36}Cl/Cl ratios (down to 24 (x10^{-15})) than those measured in the GAB recharge zone. This indicates that there is very old groundwater in the deeper LNA (up to 900 ka), and that the mixing ~~that we~~ observed in our geochemical data could be taking place between groundwater with a residence time of less than 70 a (assumed using ^{3}H) and groundwater with a residence time of ~ 900 ka (calculated using ^{36}Cl; an approximation based on eqn. 1). In the study area, the only source of groundwater with a residence time of ~ 900 ka is the GAB.

To quantify the extent of interaction between the two groundwater sources, we use the concentration of the conservative chloride ion to determine an approximate percentage of GAB to alluvial groundwater at each sample location. To estimate the local surface infiltration end-member, ~~we used~~ a shallow groundwater sample with a high ^{3}H activity (sample 30170-1; 2.21 TU) was used. T~~We used t~~he average of all available GAB data was used for ~~as that of~~ GAB inputs. These end-members are mixed in varying proportions to obtain the Cl$^-$ concentration that we observe in all our groundwater samples. I~~n some instances, i~~f the Cl$^-$ concentration in the sample was lower than that in the representative local surface infiltration sample, a 100% LNA contribution is assumed. The representative sample used as the local surface infiltration end-member has been subject to some ~~is~~ evaporation~~ed~~ ~~(Figure 3b; Supplementary Table 2)~~ and therefore does not have the lowest Cl$^-$ concentration in the alluvium. If ~~we were to use~~ the sample with the lowest Cl$^-$ concentration was used as the surface water end-member, we would require a higher percentage of GAB contribution across the study area. Thus, the use of the evaporated sample as our end-member represents a conservative approach when considering the mixing components from both the LNA and the GAB. ~~to consider overall transport of Cl$^-$ from shallow groundwater.~~

The Cl mixing results provide an approximate mixing threshold with shallower samples generally containing a higher proportion of alluvial groundwater, which diminishes with depth. These mixing proportions show that some deeper samples in the LNA contain up to 70% GAB groundwater. Figure 9~~8~~ presents approximate contours for artesian discharge proportions into the LNA based on the Cl mixing approach. The dotted lines indicate areas where there is just one sample to inform the interpretation~~we have only one sample to inform interpretations~~, whereas the solid lines connect multiple samples that all displayed similar contributions fr~~r~~om the GAB.

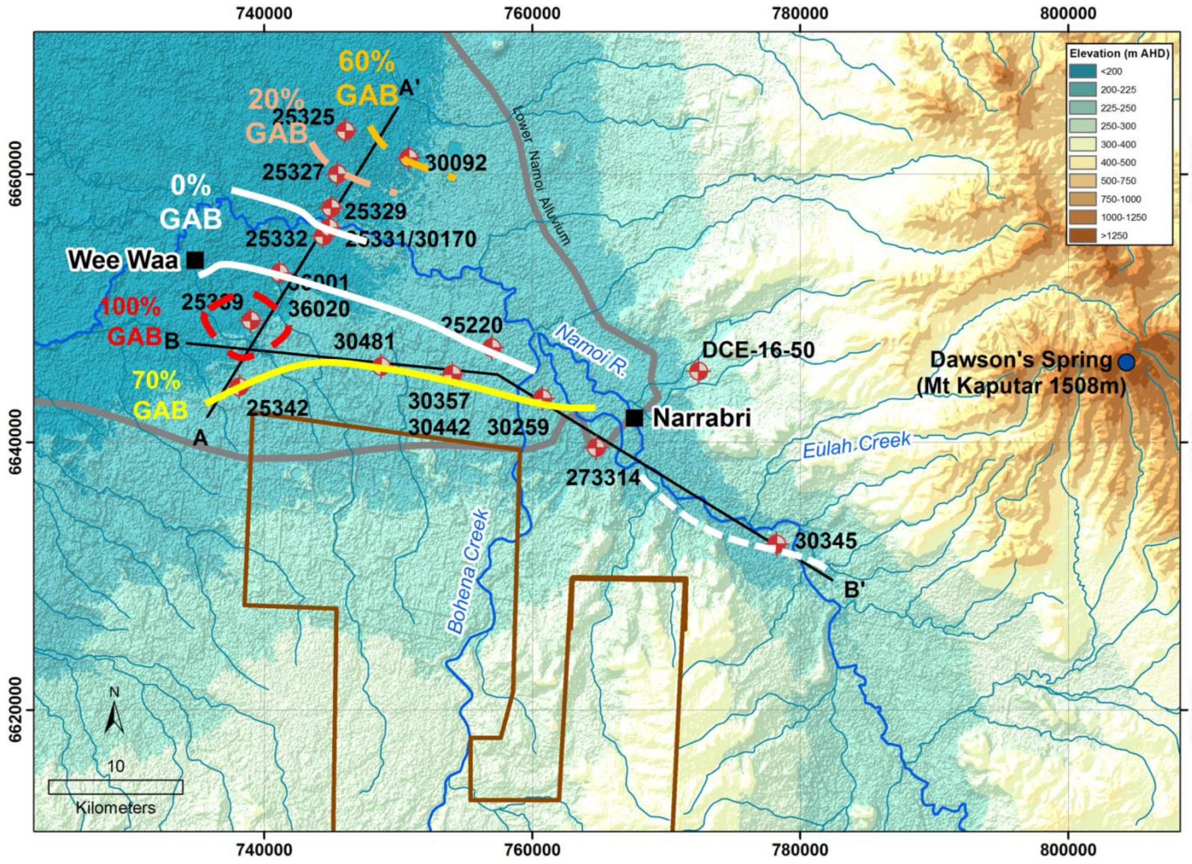


Figure 9~~8~~. Approximate percentages of GAB contribution to the LNA, calculated from multiple geochemical tracers and major ion data.

Artesian input can be inferred from nested piezometers at locations 30481 and 30259 (Figure 1). At these locations, the monitoring bore slotted in the lower portion of the LNA has a head higher than the monitoring bore slotted in the shallow portion of the LNA, indicative of upward flow. At all other locations artesian contributions cannot be discerned from head data. Comparing Figure 9~~8~~ to Figure 1 we show that groundwater geochemistry can provide a more accurate evaluation of GAB contribution to the LNA. Multiple geochemical tracers reveal that boreholes in the north and west of the study area may be experiencing much more GAB inflow than has been inferred in catchment water balance models (Merrick 2000~~1~~; Kelly et al. 2007; CSIRO 2007). This is most evident at sample 25342. It is not immediately apparent from the vertical heads in the hydrograph set at sample

25342 that there is any GAB inflow, yet based on the geochemical tracers this location is 100 % GAB groundwater. The water balance model ~~detailed~~described in Merrick (2000)~~Kelly et al. (2007)~~ ~~presented in Merrick (2001)~~ has GAB groundwater contributing 22% of all inflow into the LNA between Narrabri and Wee Waa (Figure 1). From the geochemistry alone it is not possible to make an estimate that can be directly compared to thate artesian discharge estimate.~~s presented in Merrick (2001).~~ However, it is apparent from the mixing results shown in Figure 9~~8~~ that a large portion of the study area has an ~~n~~ artesian input to the LNA that is likely to be greater than 22%. The above observations highlight why geochemical insights should ideally be used as one of the constraining data sets when doing water balance models in regions where there is both artesian discharge and surface water recharge to the alluvial aquifer. ~~Thuis indicates we show that it is necessary to consider the geochemistry of the groundwater in conjunction with water balance modelling to constrain estimates of artesian discharge to an alluvial aquifer.~~

5.3~~4~~ Temporal changes in the interaction between the LNA and the GAB

The multiple geochemical tracers we have used show substantial artesian discharge to the LNA, which is larger than that currently considered in groundwater models of the region (Merrick 2000~~1~~; Kelly et al. 2007; CSIRO 2007). Time series sampling can constrain~~s~~ how this GAB discharge ~~interaction between the GAB and the LNA~~ changes over time and is important for understanding future artesian contributions to the LNA. We use~~d~~ ^{14}C (pmc) data collected in 1978 (Calf), 2003 (McLean), 2010 (ANSTO data) and 2016 (this study) to observe how the ^{14}C content in the groundwater changes over that period~~ime~~. Even though dissolved inorganic carbon content and isotopic signature can be affected by processes involving both organic and inorganic carbon sources along its flow path, (which can alter the ^{14}C content) the application of ^{14}C data can still be useful as a tracer when investigating mixing and recharge processes (Meredith et al. 2016). This is especially the case if it is assumed that the processes that can potentially alter the ^{14}C signature do not change substantially over the period where different historical ^{14}C data are compared. Therefore, the historical ^{14}C data, coupled with data from this study could be used to estimate the changes in relative contributions of high ^{14}C contents from recent ~~groundwater~~ surface recharge ~~from the surface~~ (~ 100 pmc) versus low ^{14}C contents of the GAB ~~groundwater~~ discharge to the LNA. The dataset contains 14 bores from 5 nested sites and is the most comprehensive long-term time-series database for the study area, if not Australia, despite not being complete for all years.

Most of the samples displayed relatively consistent ^{14}C values across the years where data were available. However, we observed large changes in ^{14}C content in 5 monitoring bores; 4 showed an increase and 1 showed a decrease (bold text in Table 1). The borehole that displayed a decrease in ^{14}C (30092-2) between 2003 and 2016 suggests that there is an increasing GAB contribution over the time period at this site. Using the Cl^- concentration, this sample displayed 60% GAB contribution (Figure 9~~8~~), despite the vertical head gradients in the hydrograph showing no evidence of this (Figure 1). The remaining 4 monitoring bores, primarily located deeper in the LNA, have an increase in ^{14}C, suggesting a larger alluvial contribution at these locations over time. At monitoring bore 25332-4, ^{14}C increased between 1978 and 2010, then decreased between 2010 and 2016. These locations were in the northern part of the study area where there is extensive pumping for irrigation, suggesting that these changes in the ^{14}C contents are reflecting the extent of pumping occurring and associated surface water recharge with modern carbon versus artesian discharge. Therefore, measuring the ^{14}C in the groundwater at any future time and assessing how this has changed using past data is useful as a preliminary indicator for the current state of the system.

Table 1. Changes in ^{14}C content (pmc) in select boreholes in the study area between 1978-2016 (see Figures 1 and 8 for the locations of the bores). The 5 bores in bold text highlight where we observe changes in the ^{14}C content from 1978 to this study. Where available, the time of sampling is included.

Bore	Depth interval (mbgs)	Calf (1978)	McLean (2003)	ANSTO data (summer 2010)	This study (summer 2016)	This study (winter 2016)
25220/1	**24.4-30.5**	**28.15**	**ND**	**ND**	**69.66**	**69.94**
25220/3	97.5-109.7	0.99	ND	0.13	0.17	0.22
25325/2	36.9-38.4	83.63	ND	85.77	86.25	ND
25325/6	**67.1-70.1**	**65.31**	**ND**	**66.57**	**90.37**	**ND**
25332/1	17.7-21	103.61	ND	ND	102.48	ND
25332/2	38.1-41.1	99.19	ND	104.78	ND	ND
25332/3	50.9-55.5	94.70	ND	ND	ND	ND
25332/4	**66.8-69.8**	**49.33**	**ND**	**84.12**	**73.57**	**ND**
25327/1	18.9-21.9	123.36	101.3 (s)	ND	103.43	102.74
25327/2	57.9-60.9	84.16	93.78 (s)	ND	92.05	90.56
25327/3	**80.8-83.8**	**8.48**	**8.63 (s)**	**ND**	**25.79**	**56.08**
30092/1	17.7-20.7	ND	90.51 (w)	ND	ND	ND
30092/2	**48.2-49.4**	**ND**	**80.06 (w)**	**72.31**	**ND**	**66.92**
30092/4	108.2-110	ND	0.19 (w)	0.24	0.3	0.21

~~5.5 Implications for sustainable groundwater use~~

~~The continued sustainable access to groundwater is vital for irrigation, stock and domestic water supplies in the study area. Increased reliance by the irrigation industry on GAB groundwater with high Na^+ concentrations and very long residence times could have negative environmental impacts, such as producing sodic soils, as well as a significant economic impact. The difficulty in accurately constraining how the artesian contribution to the LNA will change over time means consistent monitoring of the groundwater is important for assessing changes to groundwater quality and quantity and the impact that this will have on the irrigation industry in the region. Additionally, the percentage extent of the interaction between the GAB and the LNA (Figure 8), and how this percentage changes over time depending on surface water recharge and increased groundwater extraction, has repercussions for the continued access and management of groundwater in the LNA. In regions where very old groundwater is used, assessments of sustainability must consider changing water quality (for example salinity and the sodium adsorption ratio (SAR)), as well as changes to~~

~~groundwater heads throughout the system, especially in recharge areas. Our results indicate that the head in the GAB needs to be carefully monitored and recharge areas in the alluvium and adjacent rock formations preserved.~~

6~~5~~ Conclusion

We have used multiple geochemical tracers to show that artesian discharge to a shallow alluvial aquifer is higher than previously derived from water balance models in the literature (Merrick 2000~~1~~; CSIRO 2007; Kelly et al. 2007). This finding is important when considering the sustainable use of connected alluvial and artesian systems. We have also provided a percentage estimate of GAB groundwater in each sample collected in the LNA using the concentration of Cl in the groundwater, showing that in some locations the ‘alluvial’ sample is comprised of up to 70% GAB groundwater. ~~Ongoing and increasing artesian inflow into the LNA will change the chemistry of the groundwater used for irrigation, which may have potential impacts on crop yield and soil health.~~

Isotopic tracers (^{3}H, ^{14}C, and ^{36}Cl) indicate that there is substantial mixing between two groundwater end-members~~s~~ of very different residence times (< 70 a and ~ 900 ka). This suggests interaction between modern surface recharge through the shallow LNA and variable artesian inflow at depth, dependent on where the sample is located in the system. Using~~We used~~ past ^{14}C data (1978, 2003, 2010), along with data from this study to show that there has been an increase in ^{14}C in the groundwater in some locations of the LNA in the last ~ 40 years. This suggests a greater contribution from modern river and flood recharge in locations proximal to the Namoi River since 1978, which could be induced by nearby groundwater abstraction for irrigation. In contrast, a sample farther from the river has displayed a steady decrease in ^{14}C content since 1978. How these trends change geographically throughout the system, and how they will behave in the future are difficult to constrain without continuous monitoring.

Recharge inputs to the LNA from the GAB were previously considered less than 22% (Merrick 2000~~1~~; CSIRO 2007; Kelly et al. 2007). However, the geochemical data reported above clearly indicate that ~~we have shown that~~ GAB discharge is occurring in locations where inflow is not apparent from the nested hydrograph data. This highlights the need to apply multiple groundwater investigation techniques (including flow modelling, hydrograph analysis, geophysics, and geochemistry) when inferring artesian discharge to an alluvial aquifer. This research has demonstrated ~~We have shown~~ that a multi-tracer geochemical approach is required to better determine artesian contributions to the alluvial aquifer and must be considered in constraining future models of the study system and elsewhere.

Acknowledgements

This research was funded by the Cotton Research and Development Corporation (CRDC). Charlotte Iverach was supported by scholarships from the Australian Government, ANSTO and CRDC. ANSTO support and analytical staff are thanked for their continuous efforts (Chris Dimovski, Henri Wong, Robert Chisari, Vladimir Levchenko, Krista Simon, Alan Williams, Simon Varley). The authors also thank Dr. Lisa Williams for editing and proofreading the manuscript. In addition, many thanks to the three reviewers, who provided constructive feedback and raised the overall quality of the paper.

Author contributions

Experimental conceptualisation and design was carried out by D.I.C & B.F.J.K. Fieldwork was conducted by C.P.I., D.I.C., S.I.H. & B.F.J.K. Additional data was contributed by

K.T.M. Geochemical analyses were conducted by C.P.I., D.I.C. & K.M.W. The manuscript was written by C.P.I with input from all authors.

Competing Interests

The authors declare that they have no conflict of interest.

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Figure 2. Two cross sections through the study area, showing the location and depth of the samples in the alluvium and their proximity to formations of the GAB. Contacts obtained from gas wells Nyora-1, Culgoora-1 and Turrawan-2, coinciding with our cross sections, are added. Their locations are displayed on the map. The chlorine-36 data interpolated using the 'natural neighbours' algorithm is shown in each cross section. ~~Chlorine-36 data interpolation is shown in each cross section using natural neighbour.~~

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