This is a much better paper than the original version and I consider that it is suitable for publication in HESS following moderate revisions. I have made several specific comments below that are mainly concerned with the details of the paper. The overall methodology and conclusions are sound and the aims and objectives are generally clear.

We thank the reviewer for taking the time to go through our manuscript again. We have addressed all specific comments below. All line numbers below refer to the track changed document.

The one major concern that I have is with the calculation of 36Cl residence times. The interpretation of 36Cl is difficult in the best of circumstances due to problems with defining the 36Cl input function over time (given that the rainfall patterns, distance from the coast, input of dust etc is likely very different several hundred thousand years ago to today). Additionally, in many studies (including this one), the in situ production rate of 36Cl is assumed rather than measured and the definition of residence times via Eq. (1) implicitly assumes piston flow which is also unlikely. In groundwater such as that discussed in this study, there is also the problem of mixing which means than the calculations can only be carried out in waters that can be guaranteed to be the pre-mixing endmembers (which given the extent of mixing may be difficult). The fact that the GAB groundwater has long (several 100 ka) residence times is well established in previous studies and this paper does not add to that understanding. It would be sufficient to note that the low 36Cl activities are consistent with the old GAB groundwater and focus on the mixing.

We agree about the shortcomings of 36Cl/Cl to calculate meaningful groundwater residence times and we do make these shortcomings clear in the introduction (lines 95-102). Previous literature in the GAB (Bentley et al. 1986; Radke et al. 2000; Love et al. 2000; Moya et al. 2016) and the Coonamble Embayment (Radke et al. 2000; Mahara et al. 2007) have constrained GAB groundwater residence times using similar or the same methods (this is outlined at lines 408-413 in the revised manuscript). Therefore, the ‘old’ nature of GAB groundwater has been established in most cases with the same methods and uncertainties. However, we have followed the reviewer’s advice above and removed all references to residence times associated with 36Cl from the discussion.

All references to 36Cl in the results section are purely the 36Cl results from our samples so that section remains (lines 535-540).

The initial discussion regarding 36Cl (636-645) just discusses Figure 7 and the distinct mixing trend between the samples so that remains.

At line 648 is where we first mention residence time calculations using 36Cl. These lines have been deleted.

Lines 654-667 remain because they are just discussing the 36Cl values in relation to the 14C values that we obtained for our samples.

Lines 674-680 remove all trace of residence time estimation. At line 676 “up to 900 ka” has been removed and replaced with “conceivably older than that of the GAB recharge zone”.

“…groundwater with a residence time of 900 ka (calculated using eqn 1.)” has been changed to “…groundwater with low 36Cl activities, consistent with old GAB groundwater” (lines 679-680). The final sentence (line 680) regarding how the “only source of groundwater with a residence time of 900 ka in the study area is the GAB” has been deleted, as this is now evident in the previous sentence.

Lines 817-818: mention of residence time has been removed and 900 ka has been replaced with “old groundwater consistent with the GAB”.

Lines 39-40 in the abstract have removed reference to 900 ka and instead mention groundwater that is potentially hundreds of thousands of years old, which is consistent with that of the GAB.

The residence times have also been removed from Figure 7 and replaced with ‘alluvial’ and ‘GAB’.

These are all the instances where we refer to residence times calculated from 36Cl. They have all been removed and instead the low 36Cl data from the LNA has been used to compare with the GAB.

Specific Comments

Lines 50-55. Strictly recharge is infiltration of rainfall, what you are discussing here is mixing between recently recharged waters and older upward flowing groundwater. Since your main story is mixing and the water balance then I would frame the first sentences around that topic.

The first sentence of the introduction has been changed to focus on mixing rather than recharge. It has been changed to “Groundwater type mixing in an alluvial aquifer can occur between recently recharged groundwater (via infiltration from the land surface) and groundwater discharging into the alluvium from surrounding geological…” (lines 53-55 in the revised manuscript). Additionally, lines 58-59 have been modified to reflect mixing rather than recharge. “Additional uncertainties when allocating recharge to each source include…” has been changed to “Additional uncertainties confounding source attribution include…” (lines 60-61).

Lines 62-75. Similar comments apply. The Scanlon study is specific to recharge but some of the others deal with mixing in aquifers.

At line 68 we have included “…discharge from…” when mentioning artesian sources, to make the distinction between recharge and discharge. At line 74 we have changed “..can improve our understanding of recharge processes…” to “…can improve our understanding of groundwater mixing processes…”. At lines 84-85 we have changed “…proportioning sources of recharge to groundwater resources" to "…proportioning input sources for groundwater that has mixed origins".

Lines 79-83. Not very clearly expressed. It would be good to reference Jascheko (2016, Chemical Geology, 427, 35-42) who deals with this in some detail.

This has been better expressed at lines 90-93 in the revised manuscript. We have deleted the sentence regarding different tracers for a given window of time and included a sentence on the hindrance that calculation assumptions can have on interpretations. (line 90-91). We have cited the above reference at this location. We now mention that "multiple tracers are **useful for covering** the relevant time scales **and uncertainties associated with** the large range of groundwater residence times" (lines 92-93) (new text in bold).

Lines 89-93. The interpretation of 36Cl is also hampered by uncertainties in the input function. Because rainfall R36Cl values vary temporally due to climate variations the input function at any time in the past may not be the same as it is today (e.g., Phillips et al., 2000. In: Cook & Herczeg, Environmental Tracers in Subsurface Hydrology. pp. 299-348).

This additional difficulty in the interpretation of 36Cl (regarding the input function and changing rainfall) and reference has been added at lines 101-104. However, this is the case for all pre-existing 36Cl/Cl work in the GAB. Whether climatic variations are more important than groundwater flow assumptions, neotectonic movements or even point source contributions from high U/Th concentration rocks, is a matter of conjecture. We provide a dataset and interpretations that can be compared to other work in the area.

The introduction could be clearer and framed more specifically around understanding mixing between groundwater from different sources in aquifers. As it is you use recharge and discharge alternately to describe the input of the deeper waters in the alluvials. Also it would be good to note that geochemistry allows us to understand long-term patterns of mixing and groundwater flow whereas using hydraulic heads (especially in systems perturbed by land clearing or water abstraction) only informs present day groundwater flow.

We have changed the introduction to better reflect a focus on mixing rather than recharge (as per the first two comments above). We have carefully gone through the introduction and changed any mention of input of artesian water to 'discharge' rather than recharge, so that there is consistency (this includes at lines 68, 73, and 87).

Lines 126-139 (in the revised manuscript) have been changed to reflect the final sentence in the review comment. Line 130 is now a new paragraph (forming the concluding paragraph of the introduction). Lines 126-129 have been added, as per the reviewer's suggestion, to note that geochemical data can give us insights into long term patterns and trends, whereas hydrologic data (such as hydraulic heads) can give us insights on seasonal pumping impacts, and current local and catchment-scale groundwater flow paths.

While the choice of references is always personal, there has been more done in this field than is apparent from the introduction. For example, the numerous references by Edmunds (especially the review in Applied Geochemistry, 24, 1058-1073). These are also several Australian examples of the use of major ions, stable isotopes, and radioactive isotopes by CSIRO (Herczeg and co-workers) and the Monash (Cartwright and co-workers) groups.

We have included Edmunds (2009) in the references in the introduction, when highlighting the importance of geochemistry for other groundwater processes (line 76 in the revised manuscript). References from Herczeg et al. 1991 and Cartwright et al. 2010, 2013 are also included throughout the manuscript (lines 466, 567, 622, 97).

Lines 109-115. This is a rather convoluted way to say that you use the radioisotopes to determine mixing between waters with long and short residence times. It is obvious that determining residence times in mixed waters is nigh on impossible and I don't think that you need this as your explanation above is clear.

We have removed lines 109-113. We have left the last sentence to illustrate the global relevance of our study (lines 137-139 in the revised manuscript).

Line 134 (and elsewhere) ML is a commonly used unit in Australia but less so elsewhere. Suggest using m3 (which is the conventional SI unit).

We have changed all ML to m3. (lines 169 and 174 and 249-253).

Section 2 is much more relevant and informative than in the previous version of the paper. Adding the groundwater flow directions to one of the maps and the cross-sections would be good.

The major direction of groundwater flow actually follows the B-B' cross section line in Figure 2. In the interest of not making the maps too busy, we have mentioned in the caption that the major flow direction is from the SE to the NW following the B-B' line.

Lines 245-246. Can you give typical screen intervals (it is important as interpretation of geochemistry from short-screened wells is much easier than from those with long screens)?

We have provided the average length of the screened interval across all samples (average length of 5.6 m) at line 295-296. The specific depth of the start and end of all screen intervals are detailed in the tables in the supplementary.

Lines 268-275. A bit of a longwinded way of saying that you used existing data to characterise the GAB groundwater.

We have removed the lines stating our intentions during the sampling campaign (at line 319 in revised manuscript) to shorten this paragraph. We now simply state that we couldn't access any GAB bores so we used past data. We have also cut some words at lines 320 and 336 to condense this section.

Lines 278-283. This point about the aquifer structure was made earlier. While it might be of local interest, I am not sure that it is worth repeating through the paper (and in many ways it is misplaced as you are stating a conclusion in the methods section). It is a common observation globally that geological formations (which might be determined on ages) do not always form separate aquifers. Your explanation on lines 178-183 explains it well enough.

We have removed this section (removed at line 340 in revised manuscript) as we have already stated it previously and is misplaced in the methods.

Lines 290-291. That is precision not accuracy.

We have changed 'results are accurate to' to 'results have a precision of' at lines 347-348 in the revised manuscript.

Lines 335-339. You seem to be describing the procedure for getting the CBE correct. If you determined NH4 and the subsequent CBE was OK, then just make sure that the NH4 concentrations are in the table and report your final CBEs.

We thank the reviewer for noting this detail that we have overlooked many times, and we apologise for not finding it and remedying it earlier. We did a qualitative field analysis, which suggested the presence of NH4, however we were unable to properly measure it along with the other ions. Therefore, to avoid confusion, we have eliminated its mention and instead reported the outlying charge balances (-7.8 % for sample 25327-1 and -5.8 % for sample 36001-1). This is at line 404 in the revised manuscript.

Lines 342-348. These details are getting beyond strict methodology and it would be better to discuss the exact compositions of the endmembers when you present the results of the calculations.

We have deleted these lines at 408 in the new manuscript from the methods. The lines detailing the general Cl concentration of surface water and GAB groundwater have been moved down to lines 689-691 in the new manuscript (in the discussion section). This then flows onto the discussion regarding the Cl mixing in our study.

Lines 349-359. This section is fine. However, as noted elsewhere these calculations do not add much to the paper and are highly speculative given that mixing has occurred.

We have modified this section to state that we calculate residence time estimations from 36Cl to allow a direct comparison, under similar assumptions, with other estimates obtained from

GAB groundwater elsewhere. Even though we don’t explicitly put a residence time on the groundwater using the 36Cl anymore, we still think it is important to show that some of our alluvial samples were in the same calculation range as other GAB groundwater and that the methods we used are the same for residence times calculations for GAB groundwater in the literature (lines 409-441 in the revised manuscript).

Lines 363-403. This section describing the geochemistry is far better than in the first version of the paper. The only thing that I would suggest adding is the standard deviation to the average concentrations.

We have included standard deviations to all average concentrations in this section (lines 446-461 in new manuscript).

Fig. 3a. It is not clear what the calcite saturation line is (explain in caption or text).

We have added to the caption for Figure 3a: “The orange calcite saturation line indicates samples that are more enriched due to separate evapotranspiration and calcite precipitation”.

Lines 406-414 (and elsewhere). Given the quoted precision your δ2H values should not have decimal places and δ18O values should only have 1 decimal place.

Any future use of this research would be compromised by an artificially introduced rounding error. For example, rounding up δ2H from -10.4 to -10 and δ18O from -3.86 to -3.9 would change a d-excess calculation by approximately 1‰. It is common practice to report one decimal figure for δ2H and two decimal figures for δ18O for the precisions reported. Furthermore, in some instances stable isotope runs have even better precision on individual runs than reported but a general long term precision is reported.

Lines 410-412. Add a reference for the evaporation trend and perhaps rephrase it as “define a trend to the right of the meteoric water line with a slope of XX that is consistent with evaporation (REF)”.

We have deleted “follow an evaporation line” and replaced it with the reviewer’s suggestion (lines 495-496 in the revised manuscript). We have included a reference to show that this is consistent with evaporation (Cendón et al. 2014). This reference shows a water stable isotope plot with a groundwater evaporation line trending to the right of the meteoric water line.

Cendón, D.I. et al. Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura-Mangrove Mountain aquifer, NSW, Australia. *Aus. J. Earth Sci.* **61(3)**, 475-499, 2014.

Lines 409-410. Are the local sites close? Given that your samples seem to lie on the GMWL, I’m not sure whether the LMWLs are relevant (?)

Gunnedah is 86 km away from the study site and the Macquarie Marshes are 210 km away. Whilst they are not extremely close, considering the low relief orography in Australia, they are relevant. They are the closest LMWL's for this study site and so we believe they are important to put our data into regional context. Therefore, we have left the mention to them in text (line 493 in revised manuscript).

Lines 422-433. Here and elsewhere I would specify "<0.04 TU" rather than "detection limit" in the text as it is more specific.

We have changed "above the det limit" or "below the det limit" to > 0.04 TU and < 0.04 TU at all locations where it was mentioned (including lines 516, 593-594, 602, 608 in the revised manuscript).

However, we were imprecise with our words when we referred to the 0.04 TU threshold as a 'detection limit'. It is actually a quantification limit, meaning that we can still detect values below 0.04 TU, however there is too much uncertainty to use them confidently. We set the limit at 50 % uncertainty and so if the analysis uncertainty is 50% or higher, then we say it is below the quantification limit. Keeping the values that were below the quantification limit allows us to plot our data against other isotopes like 14C.

Any mention of 'detection' has been changed in text as per reviewer's suggestion above, or has been changed to 'quantification' (in Figures 5 and 6).

Lines 423-425. The statement that you have modern recharge is an interpretation. Try to rephrase it so you explain to the reader why you said this (eg "The highest 3H activities of XX are near the river… these are similar to those of modern rainfall(?)… this implies…"). On that point I presume that you can infer a modern rainfall 3H activity from the Tadros (2014) compilation and that would be worth doing.

We have deleted this sentence as it was and changed it to: "The highest ^{3}H activities of 2.31 TU and 2.36 TU are from a sample 40 m from the river and from the Namoi River itself, respectively. These are very similar to modern rainfall in Australia (2-3 TU (Tadros et al. 2014)), which suggests modern recharge near the river channels" (lines 511-515). Tadros et al. 2014 has been added to the reference list as well.

Lines 426-429. This is true but the explanation is a little brief for anyone not familiar with southern hemisphere 3H. A couple more sentences would be helpful.

We have added a qualifier saying "…the peak of the bomb pulse in Australia was only 60 TU**, compared to locations in the northern hemisphere. This is primarily because most thermonuclear testing was undertaken in the northern hemisphere far from Australia and mixing is limited between the atmospheric convection cells in the northern and southern hemispheres.** Therefore, 3H in Australian rainfall has been at background…." (new text in bold; lines 517-521 in revised manuscript). This places the 3H Australian concentrations into context for international readers.

Fig. 5. Suggest plotting the samples that are below detection on the left hand axis as the 3H values have no actual meaning. The same is true in your tables (ie designate these as "<0.04" or "bd" rather than quoting actual values).

Please see our response above regarding quantification limits. The legend in figures 5 and 6 has been changed to state 'quantification limit' rather than 'detection'.

Lines 492 to 497. This section is not very clearly expressed. You could add a few more details (eg where in the region these observations come from and whether the data are from the same wells). Also you should stress that both observations (the high initial 3H and the subsequent increase in 3H) imply recharge from the surface.

This has been rewritten to better express what we are trying to say (lines 596-602 in the revised manuscript). We have changed the beginning to "Tritium data from the 1970's collected from bores that were included in our sampling campaign (25329 and 25332) (Calf 1978) suggest…" We have also emphasised that both observations imply recharge from the surface and noted this at lines 600-602.

Line 492. Where does the estimate of <70 years come from?

This estimate at lines 595-596 comes from the half-life of 3H. We are saying that if we can measure 3H > 0.04 TU at depth (207 m bgs), then 3H has not undergone decay longer than 70 years at this stage. Hence, if we can detect 3H at depth it must have been recharged in a timeframe of < 70 years.

Lines 503 to 505. Does this interpretation agree with the major ion geochemistry? For example if your deeper water is 14C-free and the surface water has a 14C activity close to 100 pMC, then given the relative HCO3 concentrations how much old water do you need to add to reduce the 14C down to the observed values? What then would the predicted 3H activities of the mixed water be? The interpretation is plausible but it would be good to see it confirmed.

We thank the reviewer for these comments and ideas. This suggestion is looking for complementary mixing indicators, which would reinforce the concept already illustrated by the Cl mixing calculations and with the 36Cl vs 14C plot, and even the 36Cl/Cl vs Na plot that is included in the supplementary. We feel that the requested additional calculations are beyond the scope of the manuscript and do not provide critical insights. The reviewer's suggestions could form the basis of material for a new paper.

Fig. 6. I found the reversed axis for 14C confusing (is there any reason why 0 is not at the left especially since 3H is plotted conventionally). Also due to the waters containing different DIC concentrations, mixing lines are curved (if you know the relative DIC

concentrations, you should be able to predict whether the curvature is concave or convex).

Yes, we reversed the 14C axis to intuitively place samples with proximity to surface on the top left-hand corner. However, it was easy enough to reverse and we have done so to facilitate interpretation. The new Figure 6 contains the reversed 14C axis following reviewer advice. The blue dotted mixing line in Figure 6 was not a calculated mixing line, but rather simply a visual aid for readers, to highlight that there is this mixing between groundwaters. This is why the line isn't curved.

Lines 531-562. As outlined above, I think that estimating residence times using 36Cl in waters that have undergone mixing is not very convincing. It is clear from the available literature that the GAB waters have residence times of several hundred thousand years and this study does not add to that understanding. I strongly suggest that this section is reframed to discuss the mixing with a statement referenced to previous works that the low 36Cl in GAB groundwater is a consequence of the (already established) long residence times.

As detailed above, all mention of residence times calculated directly from our 36Cl values have been removed. Instead we now frame the discussion as mixing between very young groundwater and groundwater that is potentially hundreds of thousands of years old, which has 36Cl values consistent with those from the GAB (Bentley et al. 1986; Radke et al. 2000; Love et al. 2000; Mahara et al. 2009; Moya et al. 2016).

Lines 546-547. The Cl/Br ratios are a better indication of the lack of halite dissolution than the Cl concentrations.

Yes, we agree and this can be readily observed in Figure 3c, which also indicates expected Cl/Br ratios trends following dissolution of evaporites.

Lines 593-597. As in the introduction, it is worth stressing here that the geochemistry provides an indication of the long-term groundwater flow and mixing whereas hydraulics in perturbed systems show how the system is currently functioning.

Reference to the long-term insights from the geochemical data, contrasted to the current system functioning using hydraulic heads has been mentioned again at lines 727-729.

Section 5.3. This section appears almost as an afterthought (it has its own introduction, data description, and interpretations) and is speculative. While the data is interesting they are not that well integrated with the main part of the paper. I suggest shortening the material and noting that the 14C contents in some of the groundwater has changed over time implying a dynamic system without trying to over interpret it. As it is, the data seems to have been collected without a specific hypothesis in mind (eg collecting

from an area before and after groundwater extraction was established) and so are not that easy to interpret with any confidence.

We have shortened this section, including removing the detailed speculation of why each bore that had a different 14C activity may be experiencing different rates of GAB inflow. We have changed this section now to better reflect that it is important that temporal changes in the extent of groundwater mixing are considered to make judgements about how the system may change into the future or with increased groundwater abstraction. We maintain that the 14C data from our study and the past data may offer some preliminary insights into how the extent of mixing has changed, with a higher pmc now reflecting increased modern infiltration. However, the over interpretation in this section has been removed, as per the reviewer's suggestion. All specific changes between lines 746 and 784 are shown in the track changed document.

Conclusions. These are a summary of the paper. Given HESS is an international journal, it would be good to emphasise what is of broader interest. Some of that material (changes over time, general utility of tracers) appears in Section 5 but probably would be better here to round off the study.

We have removed a portion of the conclusion that was focused on the detailed findings of section 5.3 (and very site specific oriented as well), as the weight put on that section has now been greatly reduced. At lines 813-815 we include why out findings are important globally and lines 844-847 already has a concluding sentence that presents our findings with a broader interest. Since one of the major findings of this manuscript was the difference between water balance modelling estimates of GAB contribution and our findings using geochemistry, it is necessary to reference local sites in the conclusion. However, we have attempted to convey through the conclusion and the final paragraphs of the introduction too that water balance models, globally, must consider geochemistry because of the discrepancies that we find in our study and the ramifications for the sustainable use of groundwater.

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 and groundwater that is potentially hundreds of thousands of years old, which is consistent with that of the GAB. 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 regional scale water balance modelling estimates that attributed 22% of all inflow for the corresponding zone within the LNA to GAB discharge. 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.

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1 Introduction

Groundwater type mixing in an alluvial aquifer can occur between recently recharged groundwater (via infiltration from the land surface) and groundwater discharging 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 spatial and temporal data resolution, as well as heterogeneity in hydrogeological properties can result in considerable uncertainty when proportioning contributions from various sources in groundwater with mixed origins (Anderson & Woessner 1992; Beven 2009; Gardner et al. 2012). Additional uncertainties confounding source attribution include change in the magnitude of groundwater gradients and directions over time due to ongoing groundwater abstraction (for irrigation, stock and domestic water supplies), and the impact that this and flood frequency may have on the extent of artesian discharge and groundwater mixing. These complexities make it challenging to accurately proportion contributions from various sources to an alluvial aquifer and to guide water allocations.

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Water balance modelling of alluvial aquifers is commonly used to quantify and proportion recharge inputs from river leakage, floodwaters, areal (diffuse recharge) and discharge from 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 the need to use multiple techniques (including hydrochemical insights) to increase the reliability of recharge and discharge estimates. Geochemical data can improve our understanding of groundwater mixing 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 (Edmunds 2009; Martinez et al.

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2017). Therefore, the integration of geochemical evidence to constrain aquifer water balance models provides a more rigorous approach for proportioning input sources for groundwater that has mixed origins (Raiber et al. 2015; Currell et al. 2017).

Radioactive isotopic tracers that provide insights into groundwater residence times can constrain mechanisms of recharge and discharge, 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 both physical and chemical processes and calculation assumptions can affect the interpretation of groundwater residence times (Jasechko 2016). Therefore, multiple tracers are useful for covering the relevant time scales and uncertainties associated with the large range of groundwater residence times. 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 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. Additionally, the interpretation of ^{36}Cl can be affected by the input function, as ^{36}Cl values from rainfall vary temporally. This means that the input function for rainfall from any time in the past may be different from current conditions (Phillips 2000). However, 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).

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These isotopes can also be used for tracer mixing 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), and proportioning their relative contributions in a groundwater sample 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). This is because groundwater geochemical data give insights into long-term patterns of mixing and groundwater flow, whereas other hydrologic data (such as hydraulic head differences) provide insights on seasonal pumping impacts, and current local and catchment-scale groundwater flow paths.

Here, we 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 and discharge pathways and occurrences of groundwater mixing in the LNA. 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). 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.

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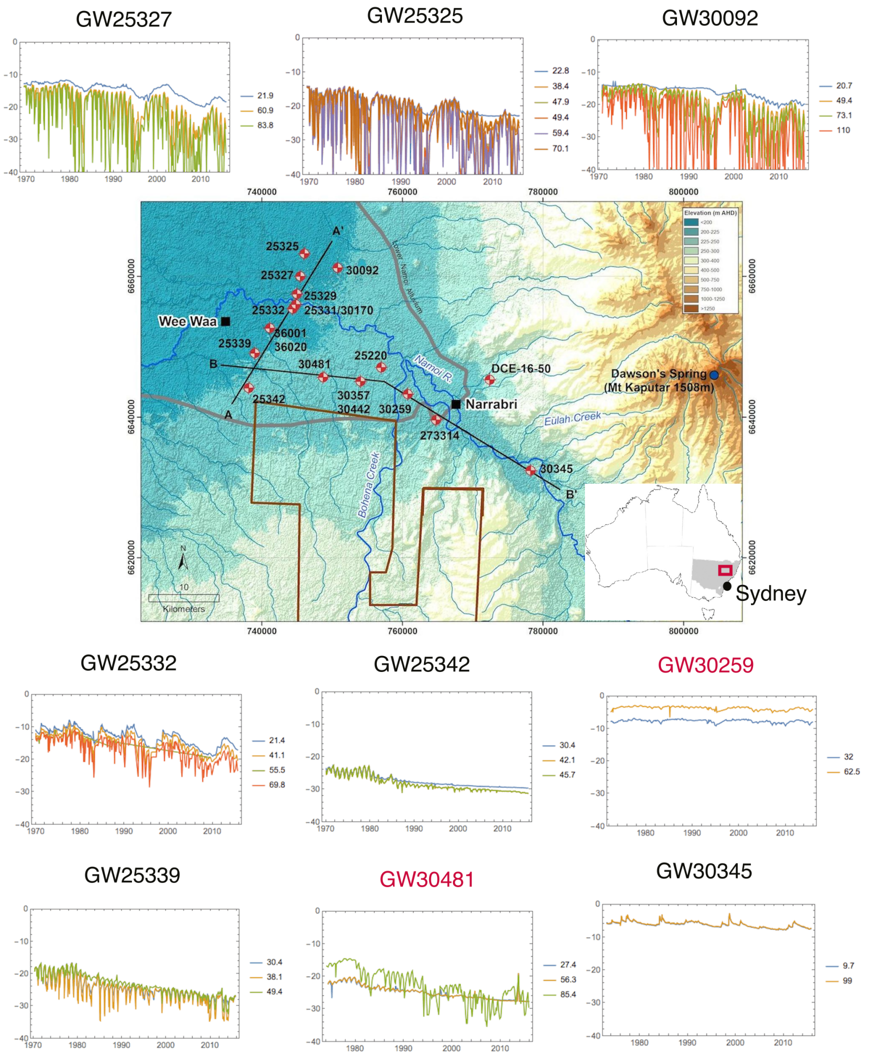

Figure 1. Map of the study area and sample locations, along with the location of the study area in Australia. Accompanying hydrographs show the groundwater level response in different piezometers throughout the study area (groundwater level data sourced from BOM 2017). The different colours in the hydrographs 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). Peak extraction of approximately 170 x 10^6 m^3 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 x 10^6 m^3/year (Lower Namoi Groundwater 2008).

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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 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).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). The boundary between the Triassic and Jurassic lies west of monitoring bore 30345. The Jurassic formations important to this study are the Purlawaugh Formation (carbonaceous claystone, siltstone, sandstone and subordinate coal), Pilliga Sandstone (medium to coarse quartzose sandstone) and the 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.

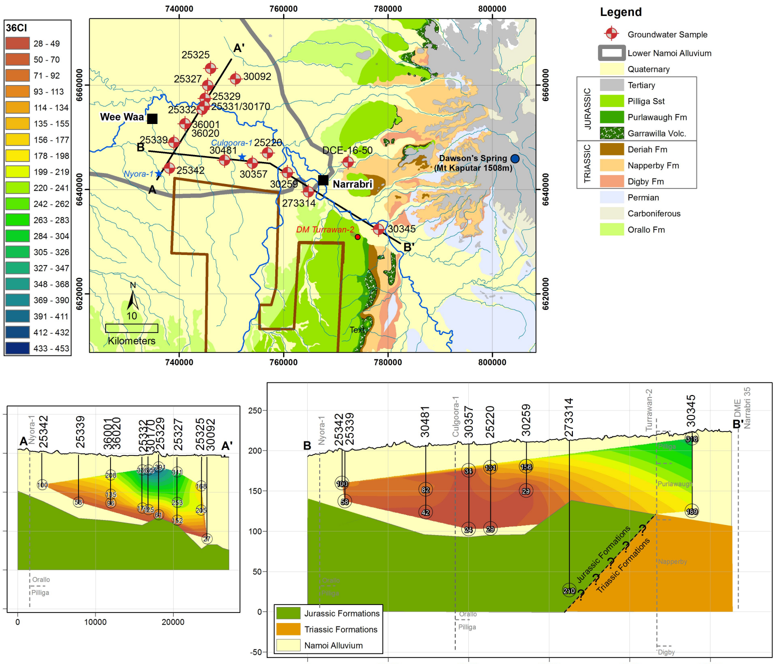

Figure 2. A geological map of the study area and two cross sections through the study area, showing the location and depth of the samples in the alluvium and their proximity to formations of the GAB. Contacts obtained from gas wells Nyora-1, Culgoora-1 and Turrawan-2, coinciding with our cross sections,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

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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, recent studies in the Namoi Catchment suggest that the rigid subdivision in to the Narrabri, Gunnedah, and Cubbaroo formations 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 (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, hydraulic conductivity generally increases with depth.

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 in the study area because of the local and national economic importance of the LNA. However, the hydrochemistry of the groundwater in the region has not been used in conjunction with water balance modelling prior to this study (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 2000; summarised 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 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; CSIRO 2007) or as a complex evapotranspiration function (Giambastiani et al. 2012)); verification measures and pragmatic goals. One MODFLOW derived water balance model proportioned the recharge for the water budget period 1980-1994 as following: flood and diffuse rain recharge 24.1 x 10^5 m^3/year, stream recharge 33.7 x 10^5 m^3/year, up gradient alluvial inflow 3.06 x 10^5 m^3/year, and artesian (GAB) recharge 9.5 x 10^5 m^3/year. In that model, artesian recharge was inferred to 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 42.7 x 10^5 m^3/year of the total recharge to the LNA. Thus, according to the model, GAB 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;CSIRO 2007; Kelly et al. 2007).

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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 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, 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 from 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 (average length of screened interval: 5.6 m (see Supplementary Table 2 for individual bores)), 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. Drop-tube extensions were used with the Bennett pump to place the pump intake just above the screen. 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.

We were not able to access any previously sampled GAB bores within the study area. Thus, better constrain GAB groundwater characteristics, we 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

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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.

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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. Samples for δ^2H and δ^{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 have a precision of ± 1‰ for δ^2H and ± 0.15‰ for δ^{18}O.

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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.

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 (-7.8 %) and 36001-1 (-5.8 %). 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 selected to provide conservative approximations.

Despite limitations, ^{36}Cl residence times for selected low ^{36}Cl/Cl samples were calculated from the equations of Bentley et al. (1986). This allows a direct comparison, under similar assumptions, with other estimates obtained from GAB groundwater elsewhere (Bentley et al. 1986; Radke et al. 2000; Love et al. 2000; Moya et al. 2016) and within the Coonamble Embayment (Radke et al. 2000; Mahara et al. 2007). These calculations assume a piston flow setting with no other sources or sinks besides recharge and natural decay (eqn. 1):

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

where R = ^{36}Cl/Cl ratio measured in the sample, R_0 = the initial ^{36}Cl/Cl ratio (meteoric water), 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

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Moved down [1]: 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.

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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) and is similar to that calculated from drill-core samples recovered in the GAB by Mahara et al. (2009).

4 Results

4.1 Major ion chemistry

The groundwater of the alluvial aquifer is predominantly Na-HCO_3-type water, with concentrations ranging from 0.12 mmol/L to 54.6 mmol/L (average: 6.85 mmol/L; std dev: 8.7 mmol/L) for Na^+ and 0.29 mmol/L to 24.0 mmol/L (average: 6.43 mmol/L; std dev: 4.8 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 concentrations 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.

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; std dev: 0.04 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; std dev: 3.7 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, 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 more similar to seawater, with our samples from the LNA lying on a mixing trend between the two end-members (Figure 3c).

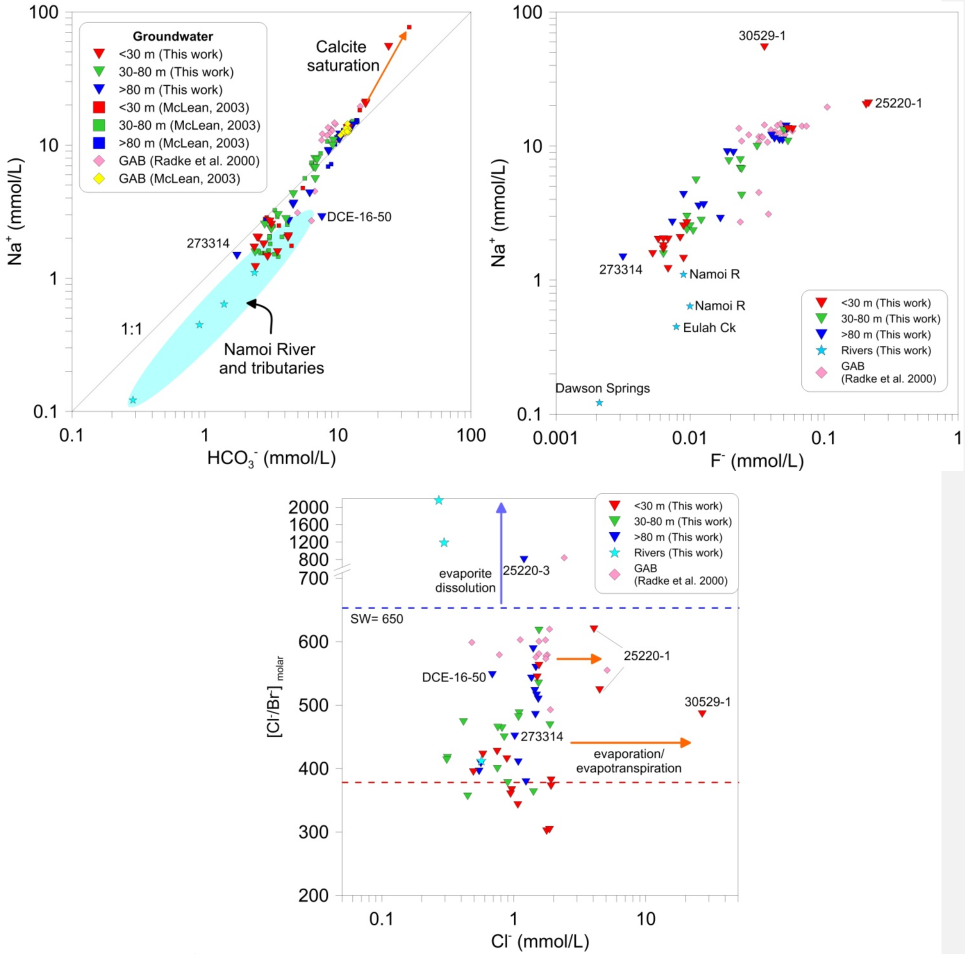

Figure 3. a) Na^+ vs HCO_3^- showing the mixing trend that the alluvial samples form between the Namoi River and samples from the GAB (Radke et al. 2000; McLean 2003). The orange calcite saturation line indicates samples that are more enriched due to separate evapotranspiration and calcite precipitation. 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.

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 Stable water isotopes (δ^2H and $\delta^{18}O$)

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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; Supplementary Table 3). A group of mostly shallow samples collected from piezometers close to river channels define a trend to the right of the GMWL with a slope of 5.96, which is consistent with evaporation (Cendón et al. 2014). 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 δ^2H (McLean 2003) (Figure 4).

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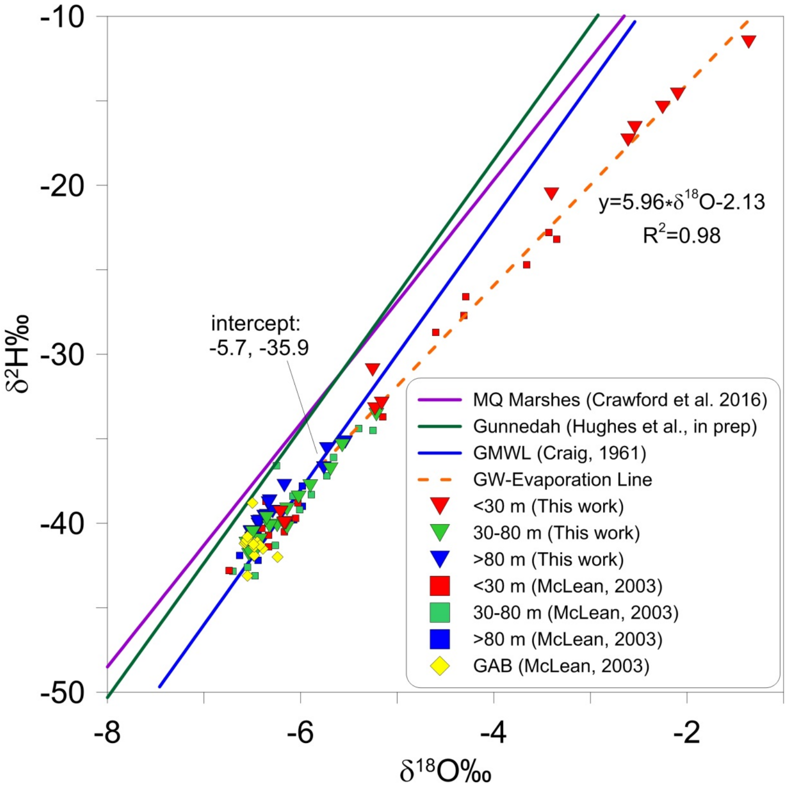

Figure 4. Water stable isotopes in the LNA, showing the two separate mechanisms of recharge; surface water recharge plotting along an evaporation trend line and potential inflow from the GAB clustered with regional samples from the GAB (McLean 2003).

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

Tritium activities vary throughout the study area, ranging from below the quantification limit (< 0.04 TU) to 2.36 TU (average: 0.42 TU). Tritium activities generally decrease with depth and distance from the river channel (Figure 5) (all data in Supplementary Table 3). The highest ^{3}H activities of 2.31 TU and 2.36 TU are from a sample 40 m from the river and the

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Namoi River itself, respectively. These are very similar to modern rainfall in Australia (~ 2-3 TU (Tadros et al. 2014)), which suggests modern recharge near the river channels However, ^{3}H > 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 only around 60 TU compared to locations in the northern hemisphere. This is primarily because most thermonuclear testing was undertaken in the northern hemisphere far from Australia and mixing is limited between the atmospheric convection cells in the northern and southern hemispheres. Therefore, ^{3}H in Australian rainfall has been at natural background concentrations for some time (Tadros et al. 2014).

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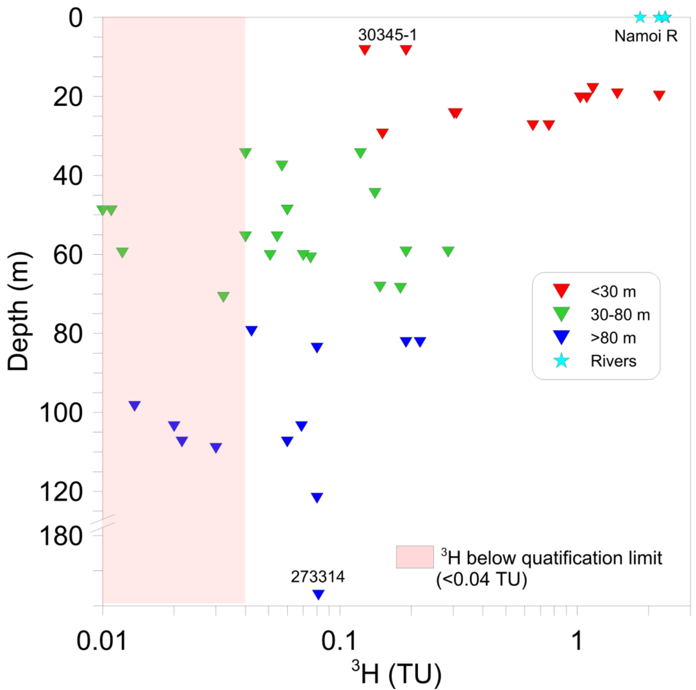

Figure 5. Plot of depth vs ^{3}H, highlighting the ^{3}H activity throughout the vertical groundwater profile. Samples that fall within the pink zone on the left are below the quantification limit (< 0.04 TU). These

data are not included in our interpretation of how ^{3}H changes with depth. They are presented to convey the relative proportions of interpretable versus non-interpretable data.

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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 old groundwater (> 30 ka), with total depths ranging from 35 m bgs to 207 m bgs.

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Our ^{36}Cl results for the alluvial groundwater ranged 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}) (Supplementary Table 4).

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5 Discussion

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

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 evaporation line in Figure 4 indicates recharge to the alluvium via surface water infiltration. It also shows a good connection between surface water that has undergone evaporation prior to recharge.

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Additional evidence for these two mechanisms of recharge is the composition of Na^{+} and HCO$_3^{-}$ in the LNA. Figure 3a shows a mixing line that the alluvial samples follow, plotting between the end-members of the GAB and the Namoi River, suggesting an increasing GAB contribution to the alluvial groundwater with depth. This also implies 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 evapoconcentration.

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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 highlights the 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 from. 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) has a similar geochemistry. These results suggest the connection between deeper Triassic formations

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beneath the GAB and the Namoi River, which must be an important consideration in future water balance models of the catchment.

5.1.1 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. ^{3}H activity and ^{14}C content in the alluvial groundwater to quantify the potential residence times of the groundwater sources that are mixing within the alluvium. Tritium activities > 0.04 TU at depth (down to 207 m bgs) indicates the extent of recharge from episodic flooding. Measuring ^{3}H > 0.04 TU at these depths also shows that surface recharge reaches the deeper LNA relatively quickly ($<$ 70 years). Tritium data from the 1970's collected from bores that were included in our sampling campaign (25329 and 25332) (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 and recharge from the surface. Additionally, measurements of ^{3}H in these bores post-flooding (16.6 to 20.7 TU) indicate that substantial recharge from the surface took place during this flood. This highlights the importance of surface water recharge to the LNA. The activities of ^{3}H > 0.04 TU throughout the vertical profile of the LNA (Figure 5) are inconsistent with the low ^{14}C contents in the groundwater. 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 may be derived from artesian inflow. Figure 6 shows ^{3}H activities > 0.04 TU 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 there is evidence of ^{14}C dilution in localised areas, we also observe mixing

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between groundwaters of widely different ^{14}C and ^{3}H values in the gradient of the samples in Figure 6 (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).

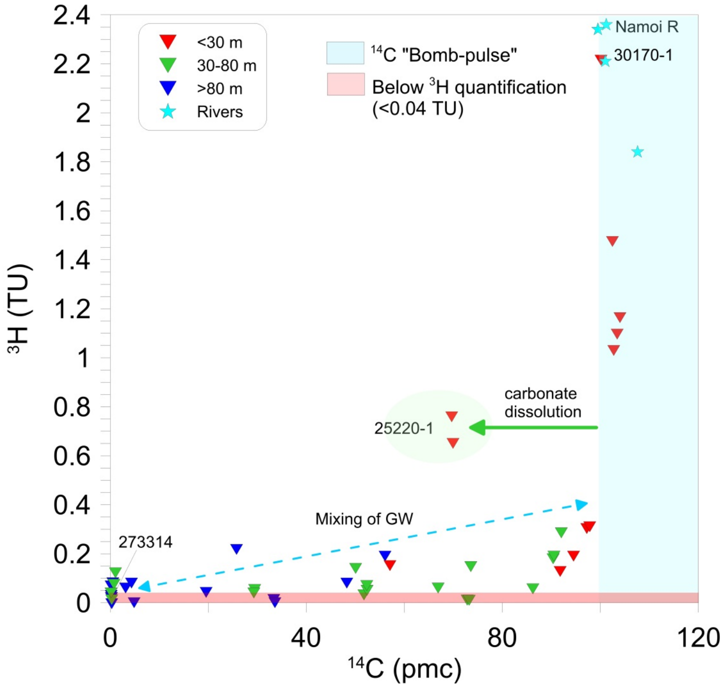

Figure 6. ^{3}H (TU) vs ^{14}C (pmc). This shows the mixing between groundwater with quantifiable ^{3}H activity (as indicated by the red band) and groundwater with very low ^{14}C content (as indicated by the dotted blue line).

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5.2 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 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.

A plot of ^{36}Cl/Cl vs ^{14}C (pmc) (Figure 7) 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) display different geochemical characteristics from the other samples, possibly because of their proximity to the Napperby Formation (Figure 2). Figure 7 shows the ^{36}Cl/Cl value range of GAB recharge, highlighting the alluvial samples with values lower than this GAB recharge value. Calculations suggest that these particular groundwater samples are potentially hundreds of thousands of years old, which is consistent with groundwater from the GAB. This implies that these alluvial groundwaters are influenced by artesian inflow of very old groundwater. This is evident in the natural neighbour interpolation in Figure 2.

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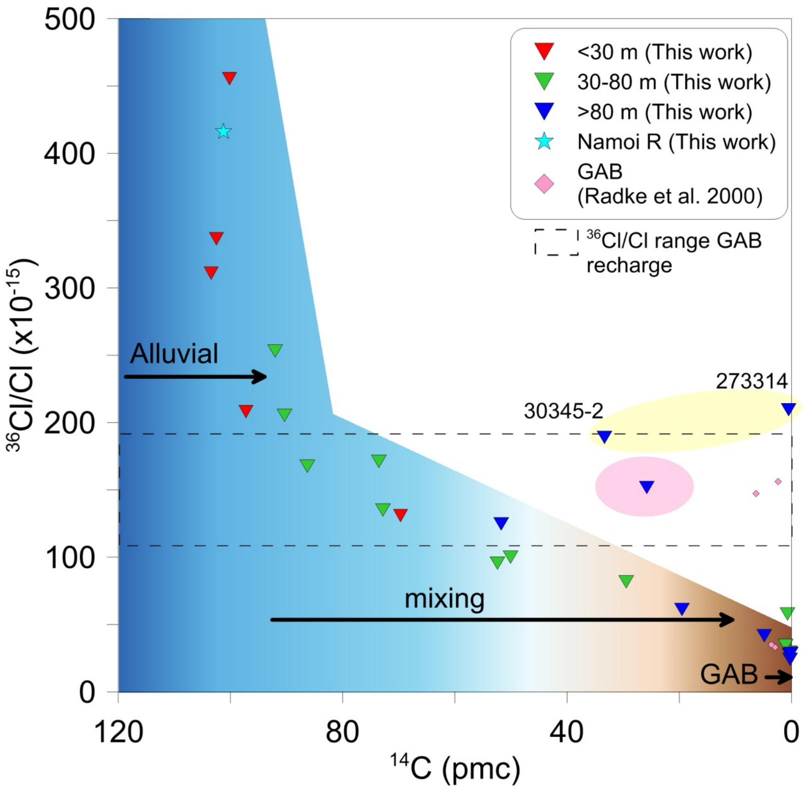

Figure 7. ^{36}Cl/Cl (x10^{-15}) vs ^{14}C (pmc). The colour gradient represents the mixing between the two major sources: surface water recharge (blue = modern) and the GAB (brown = old). The shaded yellow ellipse encompasses the two outliers where the geochemistry is being influenced by proximity to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

The apparent degree of ^{36}Cl decay 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 observed would be well outside the range of ^{14}C dating (> 30 ka) and therefore all groundwater samples would be expected to have a ^{14}C content of 0 pmc, which is not

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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 8a and b). Therefore, mixing between groundwaters of different residence times is the most likely explanation for the observed ^{36}Cl signatures.

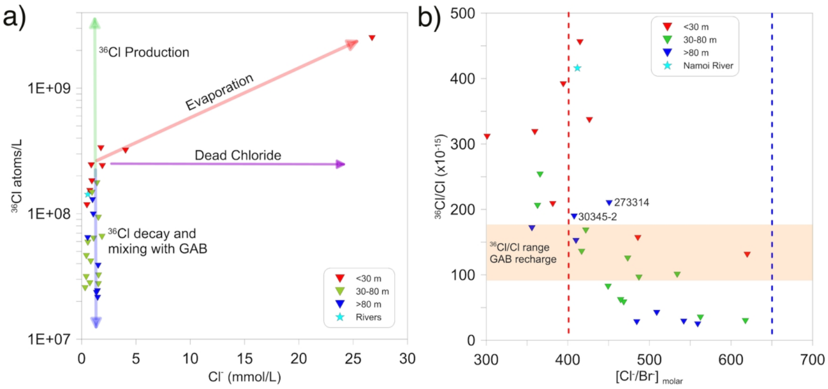

Figure 8. a) ^{36}Cl vs Cl$^-$ concentration. The ^{36}Cl production arrow represents potential in situ ^{36}Cl production from the high U and Th content in the host rocks; b) ^{36}Cl/Cl ratio (x10^{-15}) vs Cl$^-$/Br$^-$. The dotted blue line represents the Cl$^-$/Br$^-$ ratio in seawater and the dotted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

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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 (conceivably older than that of the GAB recharge zone) and that the mixing observed in our geochemical data could be taking place between groundwater with a residence time of less than 70 years (assumed using ^{3}H) and groundwater with low ^{36}Cl activities, consistent with GAB groundwater that is potentially hundreds of thousands of years old (Radke et al. 2000).

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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. 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). To estimate the local surface infiltration end-member, a shallow groundwater sample with a high ^{3}H activity (sample 30170-1; 2.21 TU) was used. The average of all available GAB data was used for GAB inputs. These end-members are mixed in varying proportions to obtain the Cl^- concentration that we observe in all our groundwater samples (via inverse modelling calculations). If 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 evaporation and therefore does not have the lowest Cl^- concentration in the alluvium. If 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.

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 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, whereas the solid lines connect multiple samples that all displayed similar contributions from the GAB.

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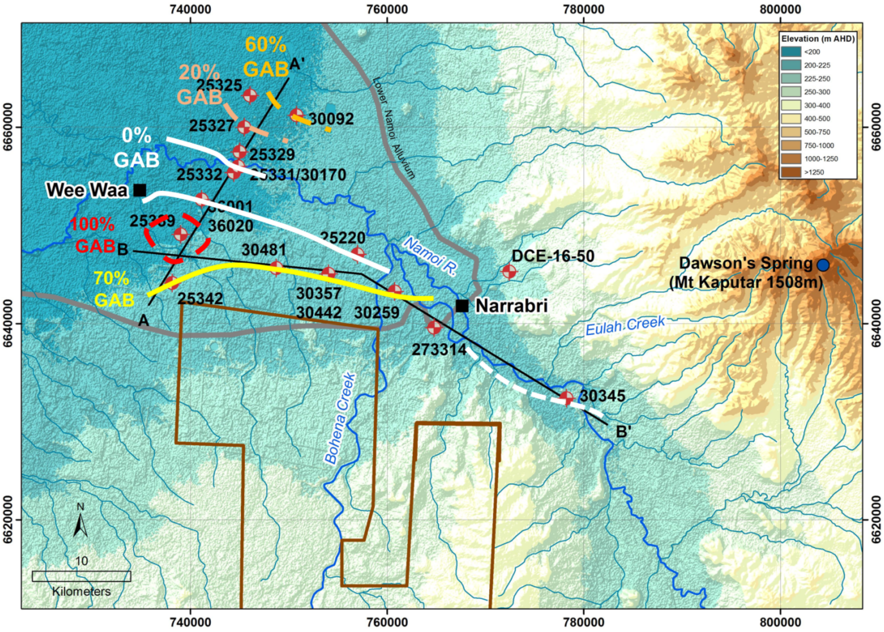

Figure 9. Approximate percentages of GAB contribution to the LNA, calculated from multiple geochemical tracers and major ion data.

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 to Figure 1 we show that groundwater geochemistry can provide a more accurate evaluation of GAB contribution to the LNA. This is because the geochemical data can elucidate groundwater mixing processes and provide longer term insights compared to the hydraulic head data. 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; Kelly et al.

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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 described in Merrick (2000) 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 that artesian discharge estimate. However, it is apparent from the mixing results shown in Figure 9 that a large portion of the study area has an 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.

5.3 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; Kelly et al. 2007; CSIRO 2007). However, it is difficult to constrain how the extent of artesian discharge has changed over time and how it may continue to change. Time series sampling can constrain how this GAB discharge will change and is important for understanding future artesian contributions to the LNA. Past ^{14}C (pmc) data collected from the same bores in 1978 (Calf), 2003 (McLean), 2010 (ANSTO data) and 2016 (this study) enable us to observe how the ^{14}C content in the groundwater has changed over time. The historical ^{14}C data, coupled with data from this study, has the potential to be used as a preliminary indicator of changes in the relative contributions of high ^{14}C contents from recent surface recharge (~ 100 pmc) versus low ^{14}C contents of the GAB discharge to the LNA. The

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Deleted: 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,

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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). This suggests that the varying contributions of older and younger groundwater has changed over time, which could be a preliminary indicator of increased surface recharge to various sites, or increased artesian discharge to others. 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. However, consistent data collection and incorporation of other factors that may affect groundwater mixing (such as rate of groundwater extraction and amount of surface infiltration) are necessary to make inferences about temporal changes in the interaction between the LNA and the GAB.

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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. ND = no data.

Bore	Depth interval (m bgs)	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

6 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; CSIRO 2007; Kelly et al. 2007). 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. Our findings are important when considering the global importance of groundwater and the sustainable use of connected alluvial and artesian systems, globally.

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Isotopic tracers (^{3}H, ^{14}C, and ^{36}Cl) indicate that there is substantial mixing between two groundwater end-members of very different residence times (< 70 years and very old groundwater consistent with the GAB). 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. We have also used past ^{14}C data (1978, 2003, 2010), along with data from this study to show that these data can be used as a preliminary indicator of how the extent of interaction between the GAB and the LNA has changed over time. Yet,

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how these trends change geographically throughout the system, and how they will behave in the future are difficult to constrain without continuous monitoring.

In the interval of the Lower Namoi studied discharge from the GAB into the LNA was previously considered to contribute approximately less than 22% of the input water to the LNA (Merrick 2000; CSIRO 2007; Kelly et al. 2007). However, the geochemical data reported above clearly indicate 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 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.

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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.

6 References

Abid, K., Dulinski, M., Ammar, F.H., Rozanski, K. & Zouari, K. Deciphering interaction of regional aquifers in Southern Tunisia using hydrochemistry and isotopic tools. *Appl. Geochem.* **27**, 44-55, 2012.

Acworth, R.I., Timms, W.A., Kelly, B.F.J., McGeeney, D.E., Ralph, T.J., Larkin, Z.T. & Rau, G.C. Late Cenozoic paleovalley fill sequence from the Southern Liverpool Plains, New South Wales – implications for groundwater resource evaluation. *Aus. J. Earth. Sci.* **62(6)**, 657-680, (2015).

Airey, P.L., Calf, G.E., Campbell, B.L., Habermehl, M.A., Hartley, P.E., & Roman, D., 1979. Aspects of the isotope hydrology of the Great Artesian Basin, Australia. In: Isotope Hydrology 1978, 1, P. 205–219. Proceedings International Symposium on Isotope Hydrology - International Atomic Energy Agency and United Nations Educational, Scientific and Cultural Organisation, Neuherberg, Fed. Rep. Germany, 19–23 June 1978. International Atomic Energy Agency, Vienna, 1979.

Amiri, V., Nakhaei, M., Lak, R. & Kholghi, M. Geophysical, isotopic, and hydrogeochemical tools to identify potential impacts on coastal groundwater resources from Urmia hypersaline Lake, NW Iran. *Environ. Sci. Poll. Res.* **23(16)**, 16738-16760, 2016.

Anderson, M.P. & Woessner, W.W. Applied Groundwater Modelling: Simulation of Flow and Advective Transport. Academic Press. ISBN: 0-12-059485-4, 1992.

Andrews, J. N. & J.-C. Fontes, Comment on chlorine 36 dating of very old groundwater, 3, Further results on the Great Artesian Basin, Australia by T. Torgersen et al., *Water Resour. Res*., **296**, 1871–1874, 1993.

Barnett B, Townley LR, Post V, Evans RE, Hunt RJ, Peeters L, Richardson S, Werner AD, Knapton A and Boronkay A. Australian groundwater modelling guidelines, Waterlines report, National Water Commission, Canberra, 2012.

Barrett, C. Upper Namoi groundwater source – status report 2011. NSW Department of Primary Industries, Office of Water, Sydney, 2012.

Bentley, H.W., Phillips, F.M., Davis, S.N., Habermehl, M.A., Airey, P.L., Calf, G.E., Elmore, D., Gove, H.E. Torgersen, T. Chlorine 36 dating of very old groundwater. 1. The Great Artesian Basin, Australia. *Water Resour. Res.* **22(13)**, 1986.

Beven, K. Environmental Modelling: An Uncertain Future? Routledge, ISBN-13: 978-0415457590
ISBN-10: 0415457599, 2009.

Calf, G.E. An investigation of recharge to the Namoi Valley aquifers using environmental isotopes. *Aust. J. Soil Res.* **16**, 197-207, 1978.

Cartwright, I., Weaver, T., Cendón, D.I. & Swane, I. Environmental isotopes as indicators of inter-aquifer mixing, Wimmera region, Murray Basin, Southeast Australia. *Chem. Geol.* **277**, 214-226, 2010.

Cartwright, I., Fifield, L.K. & Morgenstern, U. Using ^{3}H and ^{14}C to constrain the degree of closed-system dissolution of calcite in groundwater. *Appl. Geochem.* **32**, 118-128, 2013.

Cendón, D.I., Larsen, J.R., Jones, B.G., Nanson, G.C., Rickleman, D., Hankin, S.I., Pyeyo, J.J. & Maroulis, J. Freshwater recharge into a shallow saline groundwater system, Cooper Creek floodplain, Queensland, Australia. *J. Hydrol.* **392 (3-4)**, 150-163, 2010.

Cendón, D.I., Hankin, S.I., Williams, J.P., Van der ley, M., Peterson, M., Hughes, C.E., Meredith, K., Graham, I.T., Hollins, S.E., Levchenko, V. & Chisan, R. Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura-Mangrove Mountain aquifer, NSW, Australia. *Aus. J. Earth Sci.* **61(3)**, 475-499, 2014.

Chen, Z., Nie, Z., Zhang, G., Wan, L. & Shen, J. Environmental isotopic study on the recharge and residence time of groundwater in the Heihe River Basin, northwestern China. *Hydrogeol. J.* **14(8)**, 1635-1651, 2006.

Clark, I.D. & Fritz, P. Age Dating Old Groundwater *in* Environmental Isotopes in Hydrogeology. CRC Press, USA, 1997.

Costelloe, J.F., Irvine, E.C., Weestern, A.W. & Tyler, M. Identifying fluvial recharge and artesian upwards leakage contributions to arid zone shallow, unconfined groundwater. *Chem. Geol.* **326-327**, 189-200, 2012.

CSIRO. Water availability in the Namoi. A report to the Australian Government from the CSIRO Murray-Darling Basin Sustainable Yields Project. CSIRO, Australia. 154pp., 2007.

Currell, M.J., Werner, A.D., McGrath, C., Webb, J.A. & Berkman, M. Problems with the application of hydrogeological science to regulation of Australian mining projects: Carmichael Mine and Doongmabulla Springs. *J. Hydrol.* **548**, 674-682, 2017.

Dawes, W.R., Gilfedder, M., Walker, G.R. & Evans, W.R. Biophysical modelling of catchment-scale surface water and groundwater response to land-use change. *Math. Comp. Sim.* **64 (1)**, 3-12, 2004.

Department of Primary Industries (DPI) Water. NSW Government. *Namoi Alluvium Water Resource Plan (GW14), Status and Issues Paper*, available at: http://www.water.nsw.gov.au/__data/assets/pdf_file/0020/701732/Status-and-Issues-Paper-Namoi-GW-WRP.pdf, 2017.

Duvert, C., Stewart, M.K., Cendón, D.I. and Raiber, M. Time series of tritium, stable isotopes and chloride reveal short-term variations in groundwater contribution to a stream. *Hydrol. Earth Syst. Sci*. **20**, 257-277, 2016.

Edmunds, W.M. Geochemistry's vital contribution to solving water resource problems. *Appl. Geochem.* **24**, 1058-1073, 2009.

Fink, D., Hotchkis, M., Hua, Q., Jacobsen, G., Smith, A.M., Zoppi, U., Child, D., Mifsud, C., van der Gaast, H., Williams, A. & Williams, M. The ANTARES AMS facility at ANSTO. *Nuc. Instr. Meth. Phys. Res. Sect. B: Beam Interac. Mat. Atoms* **223-224**, 109-115, 2004.

Gardner, W.P., Harrington, G.A. & Smerdon, B.D. Using excess ^{4}He to quantify variability in aquitard leakage. *J. Hydrol.* **468-469**, 63-75, 2012.

Giambastiani, B.M.S., McCallum, A.M., Andersen, M.S., Kelly, B.F.J. & Acworth, R.I. Understanding groundwater processes by representing aquifer heterogeneity in the Maules Creek Catchment, Namoi Valley (New South Wales, Australia), *Hydrogeol. J.* **20(6)**, 1027-1044, 2012.

Golder Associates Santos Gunnedah Basin CSG Project. Groundwater impact study – Kahlua pilot test. Report No. 107626100-005-Rev1. Golder Associates, Australia. 2010.

Herczeg, A.L., Torgersen, T., Chivas, A.R. & Havermehl, M.A. Geochemistry of ground waters from the Great Artesian Basin, Australia. *J. Hydrol.* **126**, 225-245, 1991.

Hocking, M. & Kelly, B.F.J. Groundwater recharge and time lag measurement through Vertosols using impulse response functions. *J. Hydrol.* **535**, 22-35, 2016.

Iverach, C.P., Cendón, D.I., Hankin, S.I., Lowry, D., Fisher, R.E., France, J.L., Baker, A. & Kelly, B.F.J. Assessing connectivity between an overlying aquifer and a coals seam gas resource using methane isotopes, dissolved organic carbon and tritium. *Sci. Rep*. **5**, 1-11, 2015.

Jasechko, S. Partitioning young and old groundwater with geochemical tracers. *Chem. Geol.* **427**, 35-42, 2016.

Kalaitzis, P. & Jamieson, M. Draft Status Report for the Alluvial Groundwater Resources of the Lower Namoi Valley NSW. Land and Water Conservation Groundwater Unit Barwon Region, 121pp., 2000.

Kelly, B.F.J., Merrick, N., Dent, B., Milne-Home, W. & Yates, D. Groundwater Knowledge and Gaps in the Namoi Catchment Management Area. Cotton Catchment Communities CRC, University of Technology, Sydney – National Centre for Groundwater Management Report, NCGM 2007/1, 70pp., 2007.

Kelly, B.F.J., Timms, W.A., Andersen, M.S., McCallum, A.M., Blakers, R.S., Smith, R., Rau, G.C., Badenhop, A., Ludowici, K. & Acworth, R.I. Aquifer heterogeneity and response time: the challenge for groundwater management. *Crop & Past. Sci.* **64**, 1141-1154, 2013.

Kelly, B.F.J., Timms, W., Ralph, T.J., Giambastiani, B.M.S., Communian, A., McCallum, A.M., Andersen, M.S., Blakers, R.S., Acworth, R.I. & Baker, A. A reassessment of the Lower Namoi Catchment aquifer architecture and hydraulic connectivity with reference to climate drivers. *Aus. J. Earth Sci.* **61**, 501-511, 2014.

Lower Namoi Groundwater, NSW Government Department of Water and Energy, DWE_08_011, 2008, http://www.water.nsw.gov.au/__data/assets/pdf_file/0005/548699/wsp_namoi_gw_info_sheet.pdf

Love, A.J., Herczeg, A.L., Sampson, L., Cresswell, R.G., & Fifield, L.K. Sources of chloride and implications for 36Cl dating of old groundwater, southwestern Great Artesian Basin, Australia, *Water Resour. Res.* **36**, 1561-1574, 2000.

Mahara, Y., Habermehl, M.A., Miyakawa, K., Shimada, J. and Mizuochi, Y. Can the 4He clock be calibrated by 36Cl for groundwater dating? Nucl. Instr. Meth. in Phys. Res. Sect. B: Beam Interactions with Materials and Atoms **259**, 536-546, 2007.

Mahara, Y., Habermahl, M.A., Hasegawa, T., Nakata, K., Ransley, T.R., Hatano, T., Mizuochi, Y., Kobayashi, H., Nimomiya, A., Senior, B.R., Yasuda, H. & Obta, T. Groundwater dating by estimation of groundwater flow velocity and dissolved 4He accumulation rate calibrated by 36Cl in the Great Artesian Basin, Australia. *Earth Planet. Sci. Lett.* **287**, 43-56, 2009.

Martin, H.A. Cenozoic climatic change and the development of the arid vegetation in Australia. *J. Arid Environ.* **66(3)**, 533-563, 2006.

Martinez, J.L., Raiber, M. & Cendón, D.I. Using 3D geological modelling and geochemical mixing models to characterise alluvial aquifer recharge sources in the upper Condamine River catchment, Queensland, Australia. *Sci. Tot. Environ.* **574**, 1-18, 2017.

Mawhinney, W. *Namoi Water Quality Project 2002-2007 – Final report*, NSW Office of Water, Sydney, 39 pp, 2011. Available at: http://pandora.nla.gov.au/pan/126486/20110413-1101/namoiwater.pdf

McLean, W.A. *Hydrogeochemical evolution and variability in a stressed alluvial aquifer system: Lower Namoi River catchment, NSW.* PhD thesis, University of New South Wales, Sydney (unpublished), 2003.

Meredith, K.T., Han, L.F., Hollins, S.E. Cendón, D.I., Jacobsen, G.E. & Baker, A. Evolution of chemical and isotopic composition of inorganic carbon in a complex semi-arid zone environment Consequences for groundwater dating using radiocarbon. *Geochim. et Cosmochim. Acta* **188**, 352-367, 2016.

Merrick, N.P. *Optimisation Techniques for Groundwater Management*. PhD Thesis, University of Technology, Sydney (unpublished), 551p.

Deleted:

Mook & van der Plicht. Reporting 14C activities and concentrations. *Radiocarbon* **41**, 227-239, 1999.

Moya, C.E., Raiber, M., Taulis, M. and Cox, M.E. Using environmental isotopes and dissolved methane concentrations to constrain hydrochemical processes and inter-aquifer mixing in the Galilee and Eromanga Basins, Great Artesian Basin, Australia. *J. Hydrol.* **539**, 304-318, 2016.

Nishiizumi, K. 10Be,26Al,36Cl, and 41Ca AMS standards: Abstract O16-1. In 9th Conference on Accelerator Mass Spectrometry, page 130, 2002.

NSW Pinneena Groundwater Database, NSW Government DPI Water, available at: http://allwaterdata.water.nsw.gov.au/water.stm, (last access: 19 May 2017), 2017.

Phillips, F.M. Chlorine-36, *in* Environmental Tracers in Subsurface Hydrology. Pp 299-348, 2000

Plummer & Glynn. Radiocarbon dating in groundwater systems. In: Isotope methods for dating old groundwater: — Vienna : International Atomic Energy Agency, 2013. Pp. 33-89, STI/PUB/1587, 2013.

Powell, J. & Scott, F. A representative irrigation farming system in the Lower Namoi Valley of NSW: an economic analysis. Economic Research Report No. 46, Industry and Investment NSW, 63pp., 2011.

Price, G. & Bellis, L. Namoi Catchment Water Study Independent Report Final Study Report. Schlumberger Water Services (Australia) Pty Ltd, 50371/P4-R2 FINAL, 129pp., 2012.

Puls, R.W. & Barcelona, M.J. Low-flow (minimal drawdown) groundwater sampling procedures. EPA/540/S-95/504, 10pp., 1996.

Radke, B.M., Ferguson, J., Cresswell, R.G., Ransley, T.R. & Habermehl, M.A. Hydrochemistry ad implied hydrodynamics of the Cadna-owie-Hooray Aquifer Great Artesian Basin. *Bureau of Rural Sciences, Canberra,* 2000.

Raiber, M., Webb, J.A., Cendón, D.I., White, P.A. & Jacobsen, G.E. Environmental isotopes meet 3D geological modelling: Conceptualising recharge and structurally-controlled aquifer connectivity in the basalt plains of south-western Victoria, Australia. *J. Hydrol.* **527**, 262-280, 2015.

Rawling, G.C. & Newton, B.T. Quantity and location of groundwater recharge in the Sacramento Mountains, south-central New Mexico (USA), and their relation to the adjacent Roswell Artesian Basin. *Hydrogeol. J.* **24(4)**, 757-786, 2016.

Reilly T.E. and Harbaugh A.W. Guidelines for Evaluating Ground-Water Flow Models, USGS Scientific Investigations Report 2004-5038, available at: https://pubs.usgs.gov/sir/2004/5038/PDF.htm, 2004.

Robertson, W.D. & Cherry, J.A. Tritium as an indicator of recharge and dispersion in a groundwater system in Central Ontario. *Water Resour. Res.* **25(6)**, 1097-1109, 1989.

"Drilling Methods Bring Spectacular Yield Increases." Rural Forum for Applied Research *in* North Western Courier [Narrabri] 11 Dec. 1967: 2. Print.

Salameh, E. & Tarawneh, A. Assessing the imapcts of uncontrolled artesian flows on the management of groundwater resources in the Jordan Valley. *Environ. Earth Sci.* **76**, 2017.

Scanlon, B.R., Healy, R.W. & Cook, P.G. Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeol. J.* **10 (1)**, 18-39, 2002.

Schilling, K.E., Jacobsen, P.J., Libra, R.D., Gannon, J.M., Langel, R.J. & Peate, D.W. Estimating groundwater age in the Cambrian-Ordovician aquifer in Iowa: implications for biofuel production and other water uses. *Environ. Earth Sci.* **76(2)**, 2016.

Sharma, P., Kuhik, P.W., Fehn, U., Gove, H.E., Nishiizumi, K. & Elmore, D. *Nucl. Instr. Meth. B***.** **52**, 410-415, 1990.

Short, M.A., de Caritat, P. & McPhail, D.C. Continental-scale variation in chloride/bromide ratios of wet deposition. *Sci. Tot. Environ.* 574, 1533-1543, 2017.

Stone, J.O., Allan, G.L., Fifield, L.K., et al. Cosmogenic chlorine-36 from calcium spallation. *Geochim. et Cosmochim. Acta* **60**:679–692, 1996.

Smithson, A.*Lower Namoi Groundwater Source: Groundwater Management Area 001 Groundwater Status Report 2008*, NSW Department of Water and Energy, Sydney, 2009.

Tadros, N.Z. The Gunnedah Basin, New South Wales. Vol. 12. *Department of Mineral Resources, Coal and Petroleum Geology Branch*, 1993.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E. & Chisari, R. Tritium in Australian precipitation: A 50 year record. *J. of Hydrol.* **513**, 262-273, 2014.

Torgersen, T., Habermehl, M.A., Phillips, F.M., Elmore, D., Kubik, P., Jones, G.B., Hemmick, T. & Gove, H.E. Chlorine 36 Dating of Very Old Groundwater: 3. Further studies in the Great Artesian Basin, Australia. *Water Resour. Res.* **27(12)**, 3201-3213, 1991.

Tosaki, Y., Tase, N., Massmann, G., Nagashima, Y., eki, R., Takahashi, T., Sasa, K., Sueki, K., Matsuhiro, T., Miura, T. & Bessho, K. Application of ^{36}Cl as a dating tool for modern groundwater. *Nuc. Instr. Methods in Phys. Res. Sect. B: Beam Interact. with Mat. and Atoms.* **259(1)**, 479-485, 2007.

Wilcken, K.M., Fink, D., Hotchkis, M.A.C., Garton, D., Button, D., Mann, M., Kitchen, R., Hauser, T. & O'Connor, A. Accelerator Mass Spectrometry on SIRIUS: New 6 MV spectrometer at ANSTO, *Nucl. Inst. & Meth. in Phys. Res. B* xxx, xxx-xxx http://dx.doi.org/10.1016/j.nimb.2017.01.003, 2017.

Williams, R.M., Merrick, N.P. & Ross, J.B. Natural and induced recharge in the Lower Namoi Valley, New South Wales *in* Sharma, M.L. (ed.) *Groundwater Recharge,* Proceedings of the Symposium on Groundwater Recharge, 239-253, 1989.

Zhang, L., Walker, G.R. & Dawes, W.R. Water balance modelling: concepts and applications. In. *Regional Water and Soil Assessment for Managing Sustainable Agriculture in China and Australia.* ACIAR Monograph No. 84, 31-47, 2002.

List of Figures

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.

Figure 2. A geological map of the study area and 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 general direction of groundwater flow is from SE-NW, aligning with the B-B' line on the map. The chlorine-36 data interpolated using the 'natural neighbours' algorithm is shown in each cross section.

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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 orange calcite saturation line indicates samples that are more enriched due to separate evapotranspiration and calcite precipitation. 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.

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).

Figure 5. Plot of depth vs ^{3}H, highlighting the ^{3}H activity throughout the vertical groundwater profile. Samples that fall within the pink zone on the left are below the quantification limit (< 0.04 TU). These data are not included in our interpretation of how ^{3}H changes with depth. They are presented to convey the relative proportions of interpretable versus non-interpretable data.

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

Figure 7. ^{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.

Figure 8. a) ^{36}Cl vs Cl$^-$ concentration. The ^{36}Cl production arrow represents potential in situ ^{36}Cl production from the high U and Th content in the 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).

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

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Deleted: 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).