Author's response to reviewers

Response to referee #1 – G.Bertrand

First of all, we would like to thank Guillaume Bertrand for his positive and courteous comments. The suggestions made have been taken into consideration and we believe them to have significantly improved the paper. Comments have been addressed as outlined below (in red):

"It is important to document groundwater flow in such aquifer windows" I suggest to replace in by "from"

We will amend this as suggested (P5955).

P5956 L3" Understanding the capacity of rivers to recharge regional groundwater is important in understanding exchange within the hydrological cycle (Stichler et al., 1986; Chen and Chen, 2003). Furthermore, where surface-waters transport contaminants and have the potential to recharge the surrounding aquifer, this may lead to contamination and degradation of groundwater quality (Newsom and Wilson, 1988; Stuyfzand, 1989)" May be a bit repetitive with above and so a bituseless. I suggest to remove.

Response: This paragraph will be removed in the revised manuscript.

P5956 L 16: "1.1 Radiogenic tracers" This title is the only one in the introduction paragraph. Either another paragraph is missing, either you need to remove this numbering and just include this paragraph in the introduction.

Response: While there is probably not a problem with having a single sub-heading, we agree that this section does not need it and will remove it in the revised paper.

P5956 L 28: " Additionally, geogenic CO2 and CO2 generated by the breakdown of organic matter during methanogenesis may provide additional source s of 14C-free DIC". Yes but methanogenesis may be of 2 types

(1) $CO_2 + 4 H_2 \rightarrow CH_4 + 2H_2O$

(2) $CH_3COOH \rightarrow CH_4 + CO_2$

In the type (1) the 14C signature of methane is dependent on the initial signature of CO2, which can be rich in 14C (or not....if it is geogenic...). In addition I have a question about CH4 which is gaseous. Is it integrated in the measurement of 14C in DIC? For example, Aravena and Wassenar (1995) distinguished clearly DIC DOC and CH4. Is there any fractionation of 14C of DIC (like for 13C) in case of methanogenesis? Similarly the type 2 leads to production

CO2 (further transformed in methane)and methane....but are their signatures not similar to the initial organic matter (here acetic acid, but it is true for other molecules).

I suggest to eventually reword this part of paragraph to avoid any misunderstanding, sth like "14Cfree sources of DIC may occur within the aquifers. These sources may be "dead" geogenic carbon of degassing mantellic or sedimentary terrains (e.g. Bertrand et al., 2013; Federico et al.,....) or CO2 previsously affected by methanogenesis which lower 14C activities of DIC (e.g. Aravena et al., 1995).

Response: Methane was not integrated into the DIC measurement (DIC was transformed into CO_2 by acidification with phosphoric acid and then reduced to a graphite target). The reviewer commented on the possible fractionation of ^{14}C during methanogenesis. Briefly, there are two main mechanisms of methane generation (as noted by the reviewer). Firstly, breakdown of long chain organic molecules leads eventually to acetate fermentation that has a net reaction of the form: $2CH_2O \rightarrow CO_2 + CH_4$ and secondly the direct reduction of DIC in the groundwater via: $CO_2 + 4H^+ \rightarrow CH_4 + 2H_2O$ (Clark and Fritz, 1997; Valentine et al., 2004; Leybourne et al., 2006). ^{13}C fractionations between CO_2 and CH_4 are 60-80‰ for CO_2 reduction and 20-50‰ for acetate fermentation. Thus, both processes can produce DIC that is enriched in ^{13}C. If acetate fermentation occurs, the enrichment is due to the subsequent dissolution of ^{13}C-enriched CO_2 into the groundwater, while if direct reduction of DIC occurs the enrichment is due to the removal of low $\delta^{13}C$ CH_4. The impact on ^{14}C activities differs markedly between the two processes. In the case of acetate fermentation, ^{14}C-free CO_2 is generated from old organic matter that subsequently lowers the $a^{14}C$ of the DIC. In the case of DIC reduction the $^{14}C/^{12}C$ fractionation is approximately twice the $^{13}C/^{12}C$ fractionation (Clarke and Fritz, 1997), so if methanogenesis raises $\delta^{13}C$ values by 10‰ (1%), there will be a ~2% increase in $a^{14}C$.

While recognising that methanogenesis can potentially have an impact on ^{14}C ages in some groundwater systems, for the following reasons we consider that it is unlikely to be a significant process in the Gellibrand Valley:

1. The groundwater in this region contains dissolved oxygen and there are no reported occurrences of methane in the groundwater from the Gellibrand Valley
2. There are no extensive occurrences of organic carbon such as coal layers or organic-rich shales, which limits the capacity for acetate fermentation.
3. There is no groundwater with anomalously high $\delta^{13}C$ values (which should be result from both methanogenesis pathways).
4. In regions where DIC reduction has occurred, the groundwater generally has low to negligible SO_4 and NO_3 concentrations as bacterial sulphate reduction and denitrification occur prior to DIC reduction (Coetsiers and Walraevens, 2009); however this is not the case in the Gellibrand Valley.

While there is unlikely to be methanogenesis in this region, we have reworded the material as suggested and will add the above arguments to section 5.3 (P5966) to clarify that we did consider this possibilty.

P 5959: "Radioactive tracers 14C and 3H are used to determine residence times and define groundwater flow paths whilst major ion chemistry is employed to determine dominant geochemical processes. Water table fluctuations and groundwater electrical conductivities are also continuously monitored. These easily measurable, robust parameters can be used to observe changes in storage and infer sources of aquifer recharge (Vogt et al., 2010) and allow for comparison with radioisotopes in understanding the dynamics of groundwater systems."Eventually comment: Actually the EC and water level analyses as used by Vogt et al. is rather to analyse the transit time between a source already known (a loosing channel) and an area of the adjacent aquifer. The difference between the two kinds of approach- isotopic and physico-chemical- is rather in the targeted time-scales: short for EC, water-level (and also temperature, to be complete), longer for 3Hand 14C.

Response: The different time-scales that the various isotopic and physico-chemical approaches target is an important point, this will be added to the revised manuscript (P 5959).

P 5962: "Ca and O4 (Fig. 3d)". a S is missing for SO4

Response: This is correct and will be amended in the revised manuscript.

P 5964: " A handful of groundwater samples have a 1: 1 Ca : SO4 ratio indicating some minor gypsum dissolution may take place. Together, the major ion geochemistry suggests that water-rock interaction is limited with minimal silicate weathering, negligible dissolution of halite and carbonate minerals and some minor 5 dissolution of gypsum." I agree, and I suggest also to mention the low pH observed in your data (between 4.8 and 6), suggesting a pretty limited speciation DIC through weathering processes. (NB: This can also be viewed through 13C signature of DIC close to biogenic precusor of about -23 per mil what means that the speciation (which fractionate 13C (DIC), especially when carbonic acid becomes bicarbonates) is proportionnaly limited in comparison to CO2 dissolution in the water.

Response: We will add a sentence concerning the pH of groundwater samples and the limitation this has on DIC speciation to the revised manuscript (p5964). It is important to make this point as the low δ^{13}C values also limit the possibility of methanogenesis.

P 5965: "Regardless, estimates using bore hydrographs indicate that significant groundwater recharge to the unconfined Eastern View aquifer in the valley occurs via diffuse recharge" I can not understand the linkage with the recharge estimation you did in the paragraph. From an estimation at the annual scale, how can you conclude the recharge is diffuse (or on the contrary punctual?). Please clarify.

Response: We were using diffuse here in the context of spatially widespread rather than localised recharge from features such as rivers, lakes etc. This is a term that appears in many papers and textbooks. However, there seems some confusion with temporally continuous vs. punctuated recharge, which we agree that out data does not constrain. To make it clearer, this sentence will be reworded to 'recharge to the unconfined Eastern View aquifer in the valley occurs via direct infiltration of precipitation'

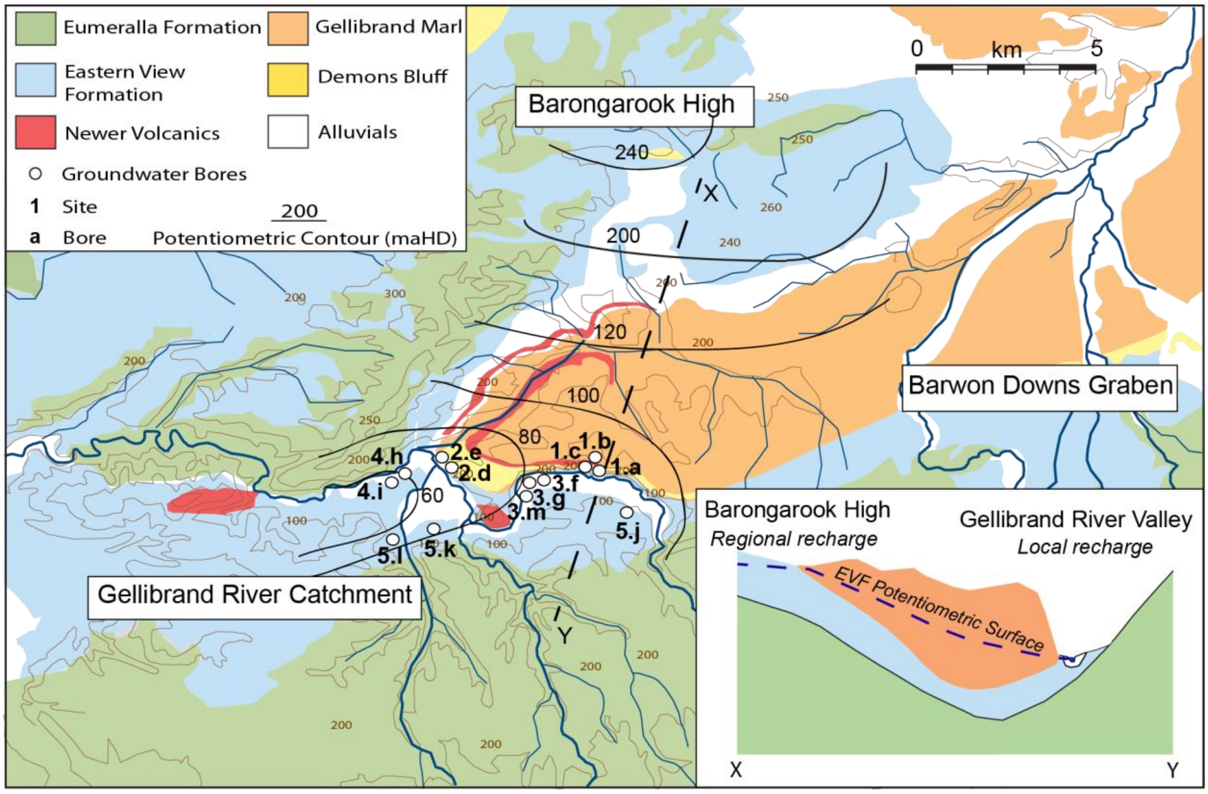
P5968:" Additionally the activities of ^{3}H in near recharge from the river does not penetrate more than a few metres into the adjacent aquifer. Thus, flow through the river bank or river flooding does not recharge in the Gellibrand Valley." Does it mean that it is rather the aquifer which discharge in the river? Or that the aquifer and the river are hydraulically disconnected? I know that this is not the hot topic of your paper, but I think the reader would be interested (well, I am...) by a rapid concrete conclusion concerning the river. I see that you mention that the river might be recharged by this regional gw flow (p5969), but how to explain the "young" 3H signature (equilibrium?, subsurface flow then it is raining?)

Response: From previous work, we know that groundwater discharges into the river under all but the highest flows, and this was the subject of a separate paper (Atkinson et al., 2013). During low to moderate flows, ^{3}H activities decline downstream in the Gellibrand River, suggesting an input of old water (most probably regional groundwater) into the river (Atkinson et al., 2013). The "young" ^{3}H signature during rainfall is explained by water derived from the upper catchment. The upper catchment of the Gellibrand River drains basement rocks and contributes up to 50% of river discharge during high flow events. Water in the upper catchment has relatively short (a few years) residence times and ^{3}H activities between 2 to 2.2TU.

We will emphasise this point in the updated manuscript to make the hydrological context more complete.

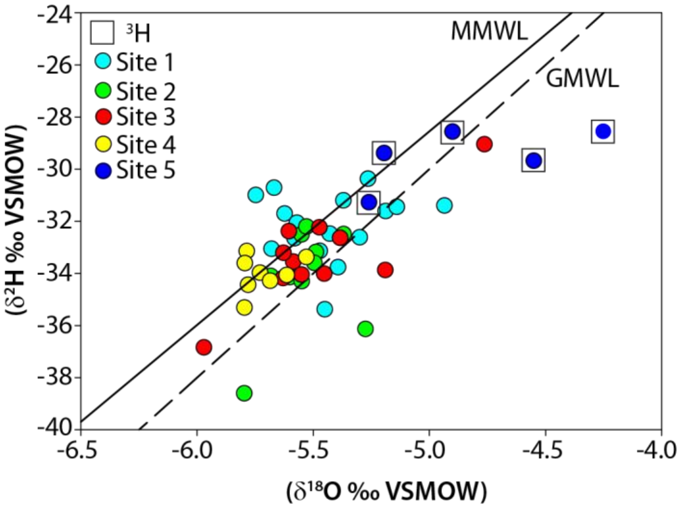
P 5968: "Most of the groundwater originates on the Barongarook High, and this region potentially provides a substantial proportion of baseflow to the Gellibrand River. "Darcy law strengthen this hypothesis but 2 remarks 1) up to now you did not include the 18O and 2H in your discussion. I suggest you to use, if possible, the 18O data coupled with a regional altitude gradient of 18O in precipitation (you showed that gw originates from rainwater and that the evaporation does not affect significantly the isotopic signatures), to calculate a recharge altitude. Hopefully this recharge altitude will correspond to the altitude of Barongarook High. If not, you have to discuss the possible paleoclimatic effect.

Response: This was a good suggestion that made us examine our data more completely. To investigate this we have regrouped groundwater bores into sites based on location within the valley. This separates bores that are situated in the near river environment (Sites 1-4) from those situated further back on the floodplain (Site 5).



The replotted δ^2H and δ ^{18}O data are shown below. The difference in height between the Barongarook High and the Gellibrand Valley is ~150m, which assuming typical fractionation gradients of -0.15‰ to -0.5‰ per 100 m for δ^{18}O (Clark & Fritz, 1997) should result in δ^{18}O values being -0.25‰ to -0.75‰ lower in waters derived from the Barongarook High vs. those that are locally recharged in the valley. Revisiting the stable isotope data, groundwater in the regional system (Sites 1 to 4) does have lower δ^{18}O values than the groundwater recharged in the aquifer window (Site 5). The trend of the waters away from the Meteoric Water Line to higher δ^{18}O values most likely represents evaporation that is commonly recorded in stable isotope signatures in SE Australian groundwater; however, the observation that all the waters from the aquifer window have higher δ^{18}O values most likely reflects the altitude effect. Further to this, combining stable isotope data with ^{3}H data further shows the separation between ‘young’ water recharged within the valley (site 5) and ‘old’ regional groundwater recharged on the Barongarook High. There is one sample from site 3 that appears not to fit this pattern (high δ^{18}O, ^{3}H-free and a ^{14}C age of 980 years). This sample may be more evaporated than the other regional groundwater samples; however overall these data are consistent and help in the interpretation of the flow system.

We will incorporate this material in the revised manuscript



There are some contradictory clues that you need to solve (or that you need to discuss). If I summarize, you show that groundwater levels is sensitive to rainfall rate, including the water level in the regional groundwater flow system. When looking at the EC, you said that " groundwater EC was constant throughout the study period and there is no inverse relation (Fig 6). I am not totally agree as if you increase the scale, you can see that EC is moving especially at the end of your campaign. River height can be seen as a proxy of the rain rate and also of the groundwater rate, as you show in figure 2 that the gw depth are changing especially when rain rate increase.

Response: There does appear to be some dilution of EC later in the later part of the record during high flow (June-July 2013). During high flow events there may be some minor infiltration of river water into the aquifer, we have noted this in the revised manuscript. However, it remains that the river is not a dominant source of recharge to the aquifer.

So my question is as following: How can one explain that gw presenting old recharge apparent age implying long transit time, can be so reactive to rain rate change?

Response: The response of water table and deeper aquifers to rainfall is well understood. Briefly, recharge following a rain event raises the level of the water table and can change hydraulic gradients which results in phenomena such as discharge areas temporally becoming recharge areas (e.g. Cartwright et al., 2007), enhanced baseflow to rivers (e.g. Brodie et al., 2008) and increased discharge of artesian groundwater (Unland et al., 2014). This process may be termed hydraulic loading or floodplain loading. In a system such as the Gellibrand, there is recharge through the floodplain which produces a fluctuation of the water table. The pressure pulse created by this is transmitted to the deeper aquifers, even though physical mixing of water between the deeper and very shallow system is limited. The boundary between the deeper and shallower groundwater may be hydrodynamic (i.e. maintained by the upward head gradients in the deeper water) or there may be some separation due to clay layers in the alluvial sediments which would produce a semi-confined aquifer system.

We will expand on our explanation in section 5.2 (p 5964) of the revised paper and have also modified Fig. 8 (shown below) to show this more clearly.

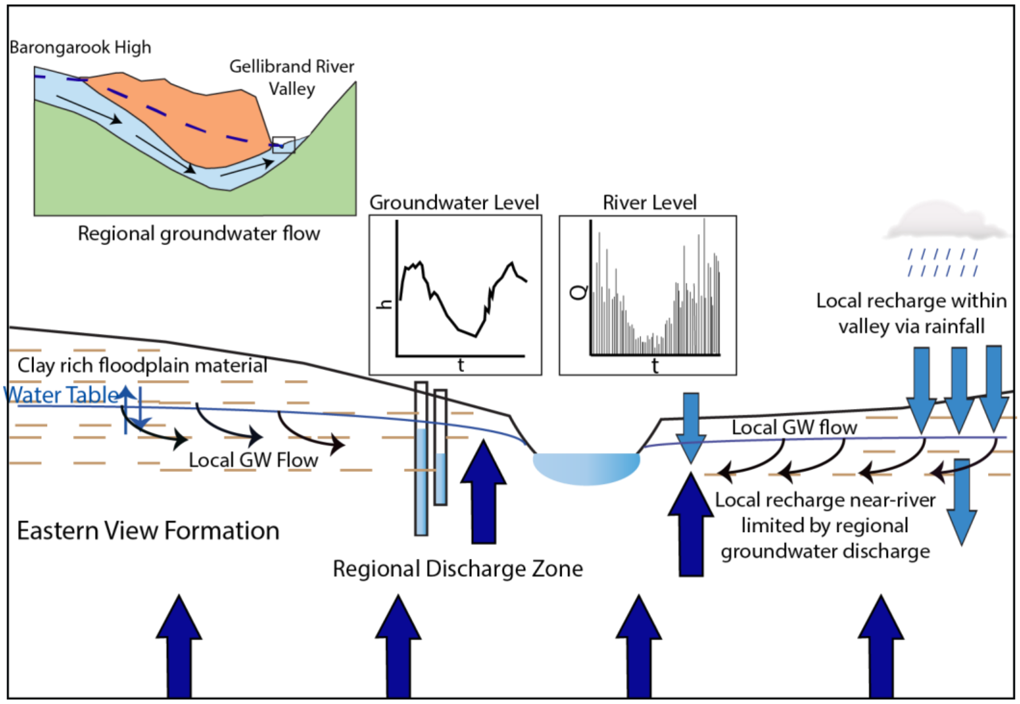
In my opinion, a possible way to explain that, and to try to explain the good correlation between 14C and Cl, is to take into account that a part of the recharge is local, even in a so-called discharge area. The term discharge area is true from a point of view of the regional gw system, but it can not exclude the influence of a vertical component of the recharge from the surface, affecting the chloride content, especially in dowstream area where the evapo-transpiration is higher. You also mentionned that the older water are genrally found close to the river, i.e from an hydrogeological point of view, where the gw is the most shallow, and where, may be, the gwater might be significantly caught by trees, thought that the gw is in the root zone,what could affect the Cl content.

"In many arid/semi-arid areas there are naturally high concentrations of salts stored in soil and groundwater systems due to factors such as low relief, little or no surface drainage, and high rates of evapotranspiration (Herczeg et al., 2001)." (From McEwan et al., 2006.) What do you think?

Local recharge certainly plays a role to the valley margins, however in the near-river environment it appears unlikely to be important at the depths that we have sampled. This is supported by several lines of evidence. Firstly upwards head gradients imply a regional discharge zone which is maintained annually – this would limit the downward movement of local recharge. Secondly, where locally recharged groundwater is present at the edge of the floodplain (Sites 5j, k and l) ^{3}H activities are between 1.02 to 1.47 TU at depths of 21-42m. If local recharge is important in the near-river environment we would expect to see high ^{3}H activities in the groundwater bores which are screened at much shallower depths (generally between 11.2 and 17 m). As none of the bores in the near-river environment have ^{3}H activities above detection levels, it is unlikely that local recharge infiltrates to the depth in the aquifer that we have sampled.

We agree that evapotranspiration is the likely driver of the ^{14}C v Cl trend for the reasons that the reviewer stated; however, we consider that this takes place in the regional recharge area, rather than within the valley. The interpretation that evapotranspiration during recharge is the dominant process in determining the salinity of groundwater in a common one for SE Australia (including the study of Herczeg et al., 2001) and generally there is an inverse correlation between recharge rate and salinity (water from zones of low recharge has undergone higher degrees of evaporation and has higher Cl concentrations). The variation in recharge rates also produces a well-documented correlation between Cl concentrations and ^{14}C ages (Leaney et al., 2003; Cartwright et al., 2006). By contrast if evapotranspiration occurred in the near-river environment it would likely increase Cl concentrations but will have no effect on the ^{14}C of groundwater and is therefore unlikely to produce the observed Cl v ^{14}C trend.

We will expand on the discussion of these processes in the manuscript in order to make clear that we believe it is the regional groundwater that drives the observed trends, and clarify the processes which govern local groundwater flow. We also believe that the updated groundwater flow conceptual model makes these processes more apparent to the reader.



References

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Hofmann, H., Unland, N.P., Cendón, D.I., and Chisari, R.: 2013. A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry. Hydrol Process. Available Online. DOI: 10.1002/hyp.10122)

Brodie, R,S., Hostetler, S., Slatter, E, 2008. Comparison of daily percentiles of streamflow and rainfall to investigate stream-aquifer connectivity. Journal of Hydrology, 328, 56-67.

Cartwright, I., Weaver, T.R., Fifield, L.K., 2006. Cl/Br ratios and environmental isotopes as indicators of recharge variability and groundwater flow: An example from the southeast Murray Basin, Australia. Chemical Geology 231, 38-56

Cartwright, I., Weaver T.R., Stone, D., Reid, M., 2007. Constraining modern and historical recharge from bore hydrographs, ^{3}H, ^{14}C and chloride concentrations: Applications to dual-porosity aquifers in dryland salinity areas, Murray Basin, Australia. Journal of Hydrology, 332, 69-92.

Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis, New York, 328p.

Coetsiers, M., Walraevens, K., 2009. A new correction model for ^{14}C ages in aquifers with complex geochemistry - Application to the Neogene Aquifer, Belgium. Applied Geochemistry 24, 768-776.

Herczeg, A.L., Dogramaci, S.S., Leaney, F.W., 2001. Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. Marine and Freshwater Resources 52, 41-52

Leaney, F.W., Herczeg, A.L.,Walker, G.R., 2003. Salinization of a fresh palaeo-ground water resource by enhanced recharge. Ground Water, 41. 84-92

Leybourne, M.I., Clark, I.D., Goodfellow, W.D., 2006. Stable isotope geochemistry of ground and surface waters associated with undisturbed massive sulfide deposits; constraints on origin of waters and water-rock reactions. Chemical Geology 231, 300-325.

Unland, N.P., Cartwright, I., Cendón, D.I., Chisari, R., 2014. Residence times and mixing of water in river banks: implications for recharge and groundwater – surface water exchange. Hydrology and Earth System Sciences Discussions 11, 1651-1691.

Valentine, D.L., Chidthaisong, A., Rice, A., Reeburgh, W.S., Tyler, S.C., 2004. Carbon and hydrogen isotope fractionation by moderately thermophilic methanogens. Geochimica et Cosmochimica Acta 68, 1571-1590

<u>Response to Referee # 2</u>

We would like to thank the reviewer for their comments. The suggestions made have substantially improved the quality of the manuscript and they have been addressed as outlined below (in red).

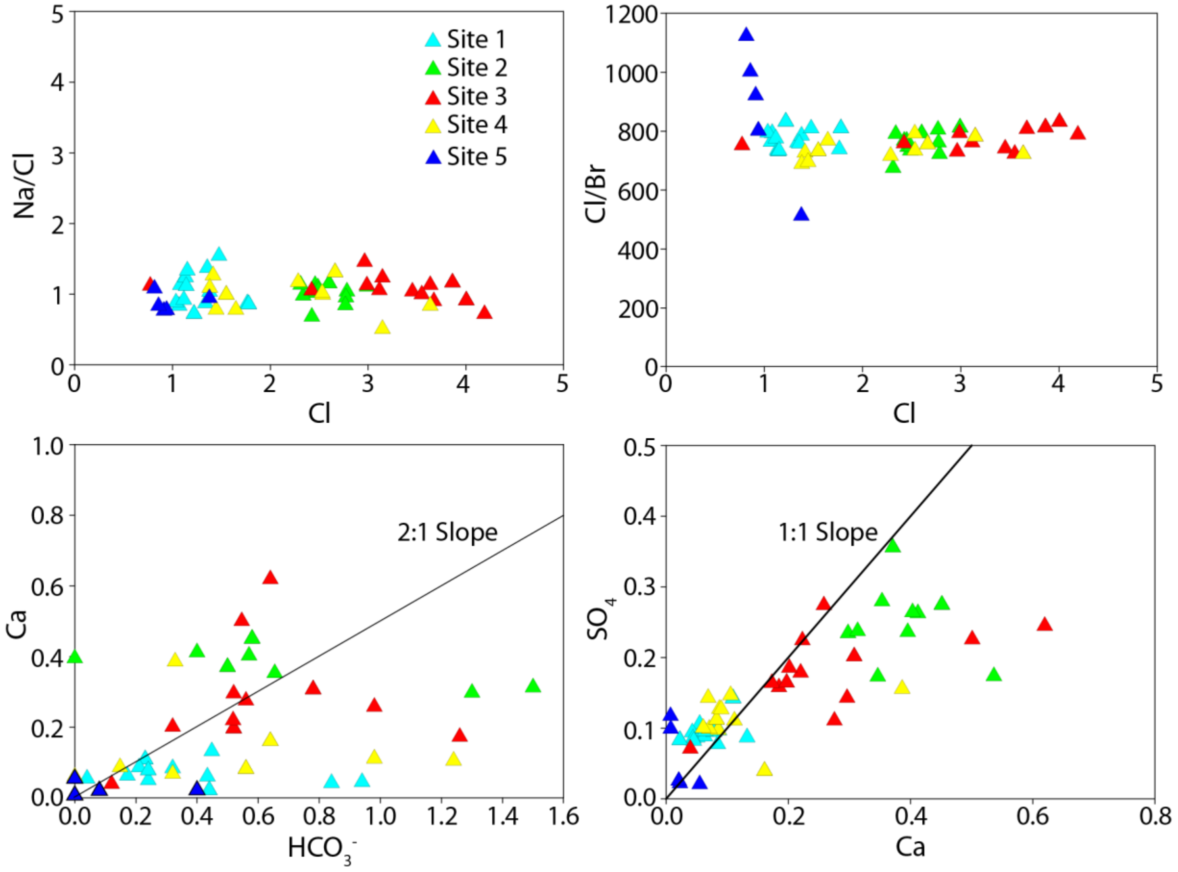
General comments:

This paper describes the hydrogeological study of the “aquifer window” (indeed, the discharge zone) of the Eastern View formation, a confined aquifer located in southeast Australia, with a major focus on groundwater/surface water interactions. The tools used are long-term river water levels and water table levels, major ion geochemistry, stable isotopes of water and carbon, and radiogenic 14C and 3H.

The paper is well written and the figures are clear, despite some modifications pro-posed thereafter. Still, in my opinion, the discussion could be notably enhanced, as the potential of the geochemical tools is not really exploited. Indeed, most considerations on the hydrogeological flow pattern that compose the conclusion could have been attained mainly based on the available water level data, i.e. without requiring costly 3H and 14C analysis. Nonetheless, I believe there is a very interesting potential for reaching an upper level of knowledge of the hydrogeological context by optimizing the available material. Therefore, if the paper pretends using environmental tracers to understand groundwater flow and recharge in the study area, the manuscript should go deeper into geochemical and isotopic interpretation and try to provide quantitative results on the water balance in the valley. I therefore recommend “major” revisions.

According to the authors, “major ion chemistry of groundwater is similar across the catchment, and the groundwater is Na-Cl type”. Then, a written description of the proportion of several species is provided as well as some indicators (Figure 3). Nonetheless, the contribution of these considerations, conducted at a general scale, is not clear regarding the aim of the paper. Why are all dots graphically undifferentiated? Is there really no geochemical distribution of water types, no different mineralization processes? I believe improved graphical representations of geochemistry could help the authors to go deeper into the interpretation, and provide more efficient and convincing elements to the reader. Rather than simply describing mineralization processes, the interest of such approach would be to define specific geochemical features of groups of samples and to attend to identify and quantify mixing processes between water masses.

Response: To take this into account we have grouped groundwater bores across the catchment into different sites based on location. The bores have been separated into 5 different sites, four of which are groundwater bores located < 15 m of the river and 1 site composed of bores located further back on the valley floodplain. By doing this it is easier to assess whether there is a difference in chemistry between those bores which sample regional groundwater (Sites 1-4 – old ^{14}C ages and tritium free) and those which sample local groundwater which has been recharged within the valley (Site 5 –groundwater with high ^{3}H and ^{14}C activities).



The only real difference between the geochemistry of the local and regional groundwater is that the Site 5 samples from the edge of the valley have lower salinity than those from the other sites. Since evapotranspiration is the major process in determining the salinity of the groundwater, it implies that the samples recharged at the edge of the valley have undergone less evapotranspiration than samples derived from the regional recharge area on the Barongarook High. This is not unexpected as the regional groundwater was recharged prior to land-clearing (~200 years ago) when the landscape was dominated by eucalypt forest with high transpiration rates while current recharge through the Gellibrand valley is through cleared grasslands that have lower transpiration rates. However, on the ion vs. ion plots there is little distinction between the various waters; hence the major ion ratios are not a good discriminator of the water origins.

We will introduce the differentiation between different sites in the revised manuscript and note that the major ions do not discriminate between the groundwater from the various regions.

Similarly, stable isotopes of water might provide additional information. But, why was such scale chosen in Fig. 4? What is it supposed to show? To my mind, it impeaches visualizing any process that could take place, any potential differentiation between groups of samples based on fractionation processes. Ideally, a dual "Barongarook High" and "Gellibrand River Valley" signature might be found inside the Eastern View formation, with the corresponding altitudinal gradient of precipitation. As well, a slight differentiation might be found between groundwater recharged from infiltration of Gellibrand river and from local precipitation in the valley, as boreholes k and l, located where the Eastern View formation outcrops in the valley, do feature evaporated signature (when plotted on a more representative scale).

Response: The replotted δ^2H and δ ^{18}O data are shown below (using the distinction between the sites discussed above). The difference in height between the Barongarook High and the Gellibrand Valley is ~150m, which assuming typical fractionation gradients of -0.15‰ to -0.5‰ per 100 m for δ^{18}O (Clark & Fritz, 1997) should result in δ^{18}O values being -0.25‰ to -0.75‰ lower in waters derived from the Barongarook High vs. those that are locally recharged in the valley. Revisiting the stable isotope data, groundwater in the regional system (Sites 1 to 4) does have lower δ^{18}O values than the groundwater recharged in the aquifer window (Site 5). The trend of the waters away from the Meteoric Water Line to higher δ^{18}O values most likely represents evaporation that is commonly recorded in stable isotope signatures in SE Australian groundwater; however, the observation that all the waters from the aquifer window have higher δ^{18}O values most likely reflects the altitude effect. Further to this, combining stable isotope data with ^{3}H data further shows the separation between 'young' water recharged within the valley (site 5) and 'old' regional groundwater recharged on the Barongarook High. There is one sample from site 3 that appears not to fit this pattern (high δ^{18}O, ^{3}H-free and a ^{14}C age of 980 years). This sample may be more evaporated than the other regional groundwater samples; however overall these data are consistent and help in the interpretation of the flow system. We will incorporate this material in the revised manuscript

The interpretation of geochemistry seems to consider that the river is the only possible source of recharge to the aquifer in the valley. What about groundwater recharged from rainfall infiltration on the unconfined surface of the Eastern View formation inside the valley? Its role is cited when describing potentiometric data, but seems to have been forgotten for geochemical interpretation. Indeed, potentiometric data does indicate that such recharge happens at important levels, as shown in Fig. 2 for piezometer "j", located in the Southern part of the valley. By the way, why isn't water table data for piezometers k and l, also located southwards, displayed here? If available, it could provide a confirmation of such process.

Response: The aim of the paper was to look at the impact of recharge from within the valley from rainfall, recharge within the valley from the river and regional recharge on the Barongarook High on the groundwater within the Gellibrand Valley. As suggested we have split the bores into different sites and this clarifies that there is recharge at the southern edge of the valley via rainfall (site 5). Recharge from local rainfall is evident mainly from ^{3}H activities (groundwater from bores at the southern edge of the valley all contain substantial ^{3}H) and also from the stable isotope signatures.

The water table data for other piezometers is taken from data loggers that were installed at the beginning of the study whereas piezometers K and l were not part of the initial investigation. We have added the water level data that is available at the Victorian Water Resources Data Warehouse for bores k and l, which show yearly recharge cycles and provide confirmation of recharge via rainfall in the valley.

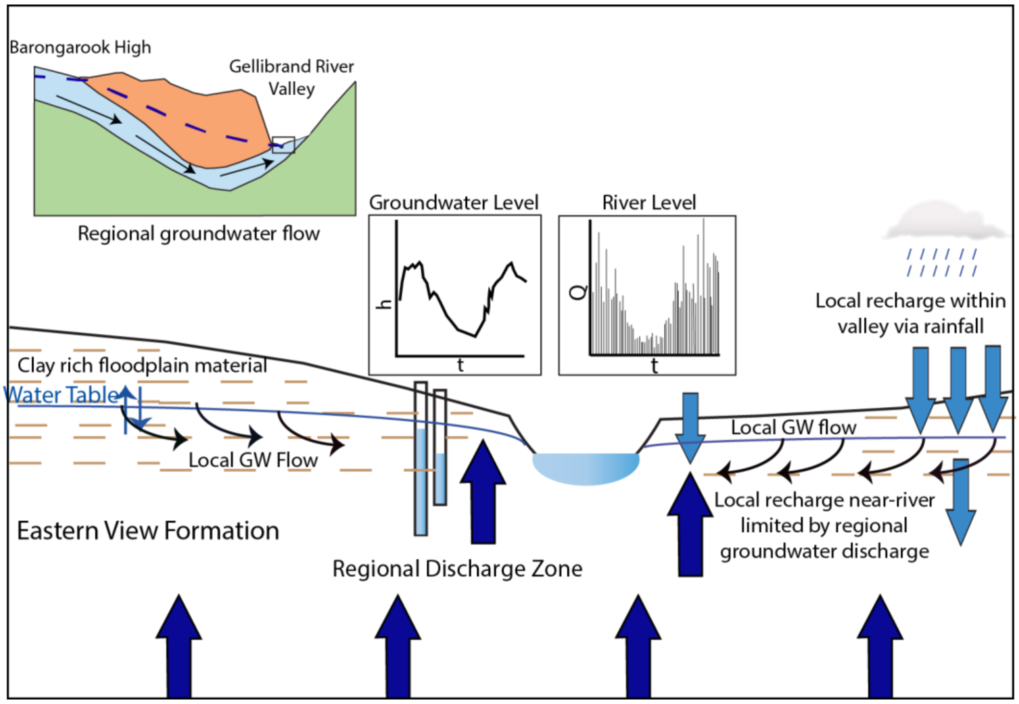
Overall while there is recharge in the valley as evidenced by the fluctuating groundwater heads, there remains a separation between the deeper and shallow groundwater. Notably, side from the southern edge of the valley, groundwater from only a few metres below the water table has relatively old ^{14}C ages, is ^{3}H free, and has stable isotope values consistent with it being derived from the Barongarook High. Similarly recharge from the river does not penetrate more than a few metres into the aquifers. This leads to the conceptualisation of the flow system shown on Fig. 8 whereby we have a very local and a regional groundwater system interacting in the valley.

We will discuss the role of local recharge in the geochemical interpretation, and make clear throughout the paper that local groundwater flow processes and recharge within the valley are being considered. The role of the local GW component is also more clear in the revised conceptual model (Fig. 8).

The role of recharge from rainfall infiltration on the unconfined surface of the Eastern View formation inside the valley is also absent of the conceptual flow model from the Gellibrand River Valley (Fig. 8), although its impact on groundwater recharge is probably the main driver of water table variations measured in the aquifer, later transmitted to the river by groundwater discharge as supposed by the regional configuration of the aquifer and confirmed by the upward vertical head gradient in the valley (Fig. 2a). The contribution of infiltrated river water to the recharge of the Eastern View formation, if it exists, will be limited to periods where the upward vertical gradient is downward. As aforementioned, these conceptual considerations do not necessarily require geochemical or isotopic analysis of groundwater.

Response: We have improved the conceptual model to make clear the distinction between the regional and local systems which exist in the valley and how local recharge is impeded in the near-river zone. Although conceptually this may be deduced from water level data alone, in reality there are not sufficient bores (nor monitoring data from the existing bores) to do this. Additionally, the hydrometric data does not help understand the timescales of groundwater flow nor the residence times of groundwater, which are important for the understanding and management of this groundwater system.

This is an important point that we will incorporate into the Discussion section of the revised manuscript.



Regarding the interpretation of 14C and 3H, I would propose some clues to reach a more integrated interpretation. As described in several textbooks (e.g. Cook and Böhlke, 2000), the spatial distribution of groundwater ages differs according to the aquifer geometry and to the flow configuration. In addition, depending on the length of the screen inside the aquifer, groundwater pumped from a well or tubewell might result from a distribution of ages, as it is representative of several flow lines. To take into account these features in the interpretation of the tracers, some tools exist, like the physical modeling of groundwater flow or Lumped Parameter Models (LPM, e.g. Zuber and Maloszewski 2001; Jurgens et al. 2012; Suckow 2012). I would suggest trying to reproduce the conceptual model of groundwater flow pattern through one of those tools in order to deduce the respective contribution of groundwater recharged inside the valley and originated from the

Barongarook High. To my understanding, this would be one of the most interesting way to fit to the title of the paper by “using 14C and 3H to understand groundwater flow and recharge in an aquifer window”.

Response: Using LPM’s to interpret ^{14}C and ^{3}H was considered. The most common LPMs that are considered are the exponential-piston flow model (EPF) and the dispersion model (DM). The EPF accounts for groundwater flow paths of different length within the aquifer with an exponential distribution. In this study the Eastern View aquifer is confined along most of its length so that flow closely approximates piston flow. Additionally in this study the bores have screens of 1-2 m. Such screen lengths are many times smaller than the thickness of the Eastern View Formation and likely integrate a small range of flow paths, again approximating piston flow. The DM models dispersion within a single flow path and the key parameter is essentially the Peclet number (v.x)/D (where D is the dispersivity, v is velocity, and x is distance). The dispersivity is given by a.v where a is the dispersion coefficient. For a groundwater system with typical hydraulic gradients of 10^{-4} to 10^{-3} and hydraulic conductivities appropriate for sands of 10^{-8} to 10^{-6} m/s, the Darcy flux is 10^{-12} to 10^{-9} m^{3}/m^{2}/sec. Assuming a porosity of 0.3, yields velocities of $3.3\text{x}10^{-12}$ to $3.3\text{x}10^{-9}$ m/s. Dispersion coefficients for regional systems are likely ~100 m (Domenico and Schwartz, 1997: Physical Hyrdogeology, Wiley), implying D = $3\text{x}10^{-10}$ to $3\text{x}10^{-7}$ m^{2}/day. For a flowpath that is 10,000 m long all Peclet numbers calculated using the above values are >1 implying (as is commonly the case for regional flow systems) advection dominates dispersion and under such circumstances the DM approximates a piston flow model. The above discussion implies that the flow system approximates piston flow and although it was not explained in those terms, the way that the calculations were done for the regional groundwater was by assuming a piston flow model.

We will make more comments as to the choice of flow model in the revised manuscript.

For the bores at the southern margins of the valley that are recharged locally we will determine ages from the ^{3}H data using lumped parameter modelling and incorporate ages into the revised manuscript. In this cases (short flow path and an unconfined aquifer) an EPF model would be appropriate.

Some specific observations

- Figure 8 indicates groundwater levels lower than river levels, i.e. supposing losing conditions. Are water levels in this figure really to scale? - Regional potentiometric data: it would be interesting to know where were measured the potentiometric heads used for this map. - Number/name of the groundwater bores: why not use the same names everywhere? I would recommend generalizing the use of letters a, b, c as Table 1 provides the “official” name.

Response: This has been amended to indicate gaining conditions. Water levels in this figure are not to scale, and are used to emphasise upward head-gradients in the near-river environment. The potentiometric data used are from nested piezometers, with the data available at the Victorian Water Resources Data Warehouse. We have used the generalized letters throughout the manuscript (with the official names listed in Table 1). We have redrawn Fig. 8 to try and make water levels more representative.

Author's Response to Main Editor

Comment from editor are in black, comments from authors are in red:

Dear Authors,

Your work is a good demonstration of how the isotopic, hydrochemical and hydrological data should be combined to gain insights into the structure and dynamics of groundwater flow, especially that the manuscript addresses also a hot topic in groundwater resources management which are groundwater-surface water interactions. However some aspects of the manuscript require reworking.
Reviewers' objections to the manuscript, with which I generally agree, run along two lines:

- underutilization of the isotopic and geochemical methods which are used here, except the 14C dating, mostly in a qualitative manner

- the presented picture of the interactions between the deep, shallow groundwater and surface water is not fully convincing.

Please make sure that your responses to reviewers' comments are integrated into the revised version of the manuscript.

Response: Firstly thank you for your positive comments.

We have integrated all reviewer comments and focused on addressing the two major comments in the revised manuscript. This has been achieved through better utilization and more thorough assessment of the geochemical and isotopic data, and a clearer discussion of the groundwater dynamics which operate within the Gellibrand Valley throughout the manuscript. These changes have significantly improved the quality of the paper.

Specific changes:

(1) Groundwater samples are now grouped into 5 different sampling sites (4 near-river, 1 floodplain) to emphasise the distinction between the regional and local groundwater (Section 4.2 – Groundwater Geochemistry).

(2) We have been able to separate regionally recharged and locally recharged groundwater through the improved use of the stable isotope data. We have incorporated the proposed altitudinal effect on regionally recharged groundwater (Section 5.1, lines 1061-1078), and added a more complete discussion on the possible causes of stable isotope variations (Section 5.1, lines 1061 – 1078).

(3) We have improved the use of ^{3}H data through the implementation of lumped parameter modelling. This is used to constrain the ages of groundwater locally recharged within the valley (Section 5.4: 1190-1210).

Combined, the improved use of the geochemical and isotopic data leads to a much clearer picture of the groundwater dynamics operating within the Gellibrand Valley. This culminates in the groundwater conceptual model, which we have modified in accordance with the reviewers comments and it now better visually represents the processes operating within the valley (Figure 8) as well as being supplemented by a clearer discussion of these processes (Section 5.5: 1236-1259).

Please see below for revised manuscript.

Additionally, I would like to raise the following questions.

1. If the river is gaining than its hydrology and chemical and isotopic signatures should be influenced by the discharging groundwater. Refer to the results presented in the companion paper (Atkinson et al., 2013) which might confirm such influence. Furthermore, can a water budget be set for some river reaches showing fluxes of water coming from deep groundwater, floodplain infiltration, headwaters, etc.? Stable isotopes of water could be helpful here.

Although the river chemistry is certainly influenced by discharging groundwater (Atkinson et al., 2013), it is difficult to ascertain whether it is deep regional or local groundwater which discharges into the river as the only difference between these end these members is a small difference in the overall abundance of major ions (i.e. there are no clear geochemical indicators of deep vs. shallow groundwater). There is also little fluctuation in stable isotopes downstream (Atkinson et al., 2013) and while there are some differences in the stable isotope ratios of local and deeper groundwater (as discussed in this paper), they are too subtle to be used to separate groundwater components in the river. The decrease in ^{3}H downstream indicates a large proportion of discharging groundwater must be old (and most likely of regional origin) and this is discussed in the companion paper. Although separating the chemical signatures of these different end members would provide an interesting addition to the manuscript, it is also not within the scope of this study which focuses on the groundwater itself.

2. Grouping the groundwater samples on plots was a good idea. What if the stable isotopic compositions of groundwater averaged for each site were plotted against the MWLs and river water and precipitation signals? In the corrected version of Fig. 4 one can see a trend between sites 1 to 4 towards the more negative values. Is it really there and can this reflect recharge in different climatic conditions? Discuss stable isotopes versus 14C age of groundwater. Finally, the question of the evaporative enrichment is not thoroughly discussed. Could it be hidden in the scatter of data?

Plotting averages for each site results in the same trend as the corrected version of Fig.4. We considered the altitudinal effect based on the reviewers comments, however we have included in our discussion the possibility that this effect may be climatic in lines 363-368. We have also incorporated stable isotope v ^{14}C values of groundwater in Figure 4 (b). There is little displacement of groundwater from the meteoric water line implying that changes in the stable isotope values due to evaporation are minor. Groundwater elsewhere in southeast Australia show displacements of up to several per mil (e.g. Herczeg et al., 2001). We examined the stable isotope data again with the separation between sites but there are no distinct or statistically justifiable trends. This is probably to be expected as the Otway region is higher rainfall and lower temperature than many other regions (such as the Murray Basin where evaporation trends are common; hence, evaporation will be lower but transpiration relatively high due to the dense eucalyptus vegetation (lines 1044-1047 & lines 1055-1059).

Several minor corrections needed:

- change scaling of the vertical axes in figures 3a and 3b to make them correspond to the range of data

The original scale was chosen in order to easily identify geochemical processes (large variations, particularly in Cl/Br ratios can occur). The scale chosen is therefore appropriate in demonstrating that halite dissolution and rock weathering play little role in altering groundwater chemistry. This makes the figures more easily comparable to those from other papers addressing the geochemistry of groundwater in southeast Australia.

- add information on water sample volumes and handling of samples before analyses

We have added information on water sample volumes and handling in the methods section (Lines 868-870).

- add “DIC” subscripts to del13C in Table 1 or explain in the Methods section that carbon isotopic composition is measured for DIC

This has been amended.

- chapter 4.5 should refer to Fig. 5 instead of Fig.

This has been amended.

Using ^{14}C and ^{3}H to understand groundwater flow and recharge in an aquifer window

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Abstract

Knowledge of groundwater residence times and recharge locations are vital to the sustainable management of groundwater resources. Here we investigate groundwater residence times and patterns of recharge in the Gellibrand Valley, southeast Australia, where outcropping aquifer sediments of the Eastern View Formation form an ‘aquifer window’ that may receive diffuse recharge from rainfall and recharge from the Gellibrand River. To determine recharge patterns and groundwater flowpaths, environmental isotopes (^{3}H, ^{14}C, δ^{13}C, δ^{18}O, δ^{2}H) are used in conjunction with groundwater geochemistry and continuous monitoring of groundwater elevation and electrical conductivity. The water table fluctuates by 0.9 to 3.7 m annually, implying recharge rates of 90 and 372 mm yr^{-1}. However, residence times of shallow (11 to 29 m) groundwater determined by ^{14}C are between 100 and 10,000 years, ^{3}H activities are negligible in most of the groundwater, and groundwater electrical conductivity remains constant over the period of study. Deeper groundwater with older ^{14}C ages has lower δ^{18}O values than younger shallower groundwater, which is consistent with it being derived from greater altitudes. The combined geochemistry data indicate that local recharge from precipitation within the valley occurs through the aquifer window, however much of the groundwater in the Gellibrand Valley predominantly originates from the regional recharge zone, the Barongarook High. The Gellibrand Valley is a regional discharge zone with upward head gradients that limits local recharge to the upper 10 m of the aquifer. Additionally, the groundwater head gradients adjacent to the Gellibrand River are generally upwards, implying that it does not recharge the surrounding groundwater and has limited bank storage. ^{14}C ages and Cl concentrations are well correlated and Cl concentrations may be used to provide a first-order estimate of groundwater residence times. Progressively lower chloride concentrations from 10,000 years BP to the present day are interpreted to indicate an increase in recharge rates on the Barongarook High.

1. Introduction

Groundwater residence time can be defined as the period of time elapsed since the infiltration of a given volume of water (Campana & Simpson, 1984), or perhaps more accurately, the mean time that a mixture of waters of different ages have resided in an aquifer (Bethke & Johnson, 2008). The residence time of water within an aquifer is a key parameter in describing catchment storage and may be used to estimate historical recharge rates (Le Gal La Salle et al., 2001; Cook et al., 2002; Cartwright & Morgenstern, 2012; Zhai et al., 2013), elucidate groundwater flowpaths (Gardner et al., 2011; Smerdon et al., 2012), calibrate hydraulic models (Mazor & Nativ, 1992; Reilly et al., 1994; Post et al., 2013) and characterize the rate of contaminant spreading (Böhlke and Denver 1995; Tesoriero et al.,2005). From a water resource perspective, information on groundwater residence times is required for sustainable aquifer management by identifying the risk posed to groundwater reserves against over-exploitation (Foster & Chilton, 2003), climate change (Manning et al., 2012) and contamination (Böhlke, 2002).

Unconfined aquifers may be recharged over broad regions leading to young groundwater at shallow depths over broad areas (Cendón et al., 2014). On the other hand, the residence time of groundwater in confined aquifers generally increases away from discrete recharge areas. The geology of catchments is often complex and heterogeneous and outcrops of aquifers in more than one location may provide ‘windows’ for groundwater recharge (Meredith et al., 2012). It is important to document groundwater flow from such aquifer windows. If they act as recharge areas, changes in land-use such as agricultural development may introduce contaminants to the deeper regional groundwater systems. By contrast, if they are local discharge areas, use of regional groundwater from these areas may impact rivers, lake or wetlands that are receiving groundwater.

Rivers may also recharge shallow groundwater if the hydraulic gradient between the river and the groundwater is reversed during high flows (Doble et al., 2012). Episodic recharge of aquifers by large over-bank floods is also locally important (Moench & Barlow, 2000; Cendón et al., 2010; Doble et al., 2012), particularly in arid areas (Shentsis & Rosenthal, 2003); however, the potential for over-bank events to recharge aquifers in temperate areas is still poorly understood. Additionally, during high flow, water from rivers is likely stored temporarily in the banks (McCallum et al., 2010, Unland et al., 2014); however, the depth and lateral extent to which bank exchange water infiltrates the aquifer is not well documented. Lastly, knowledge of residences times of groundwater in close proximity to the river can provide important information on groundwater-river interactions (Gardner et al., 2011). Local groundwater flowpaths in connection with rivers are often underlain by deeper regional flowpaths (Tóth, 1963) however the role these flowpaths play in contributing to river baseflow remains unclear (Sklash & Farvolden, 1979; McDonnell, 2010; Frisbee & Wilson, 2013; Goderniaux et al., 2013). This may be elucidated from understanding residence times of near-river groundwater (Smerdon et al., 2012).

Radioactive environmental isotopes, in particular ^{14}C and ^{3}H have proven useful tools for determining groundwater residence times (Vogel, 1974; Wigley, 1975). Produced in the atmosphere via the interaction of N_2 with cosmic rays, ^{14}C has a half life of 5730 years and can be used to trace groundwater with residence times up to 30 ka. The use of ^{14}C in dating groundwater was first discussed by Muennich (1957), and has subsequently been widely used due to the ubiquitous presence of dissolved inorganic carbon (DIC) in groundwater (Cartwright et al., 2012; Samborska et al., 2012; Stewart, 2012). The calculation of ^{14}C ages may be complicated if groundwater DIC is derived from a mixture of sources (Clark and Fritz, 1997). Where a large proportion of DIC is derived from the dissolution of ^{14}C-free carbonate minerals in the aquifer matrix, the ^{14}C originating from the atmosphere or soil zone will be significantly diluted. Additional sources of ^{14}C free DIC include old geogenic carbon from igneous degassing (Bertrand et al., 2013; Frederico et al., 2002) or CO_2 produced together with methane from old organic carbon in the aquifer matrix (Aravena et al., 1995). Groundwaters recharged post 1950 may have anomalously high ^{14}C activities (a^{14}C) due to the ^{14}C produced during atmospheric nuclear tests. Objective ^{14}C dating requires recognition and quantification of these processes. A number of models based on both major ion and stable C isotope geochemistry have been proposed to correct apparent ^{14}C ages (Han & Plummer, 2013)

With a significantly shorter half-life (12.33 years), ^{3}H can be used to date groundwater with residence times of up to 100 years (Vogel et al., 1974).With the decay of the 1960s ^{3}H bomb-pulse peak in the southern hemisphere to near background levels unique ages may now be determined from single ^{3}H measurements (Morgenstern et al., 2010). As ^{3}H is part of the water molecule, there is negligible change to ^{3}H activities other than decay, and ^{3}H is an excellent tracer for the movement of water through hydrological systems (Michel, 2004). Used in conjunction with ^{14}C data, ^{3}H may also be used to study mixing in shallow aquifers (Le Gal La Salle 2001; Cartwright & Morgenstern, 2012).

2. Study Site

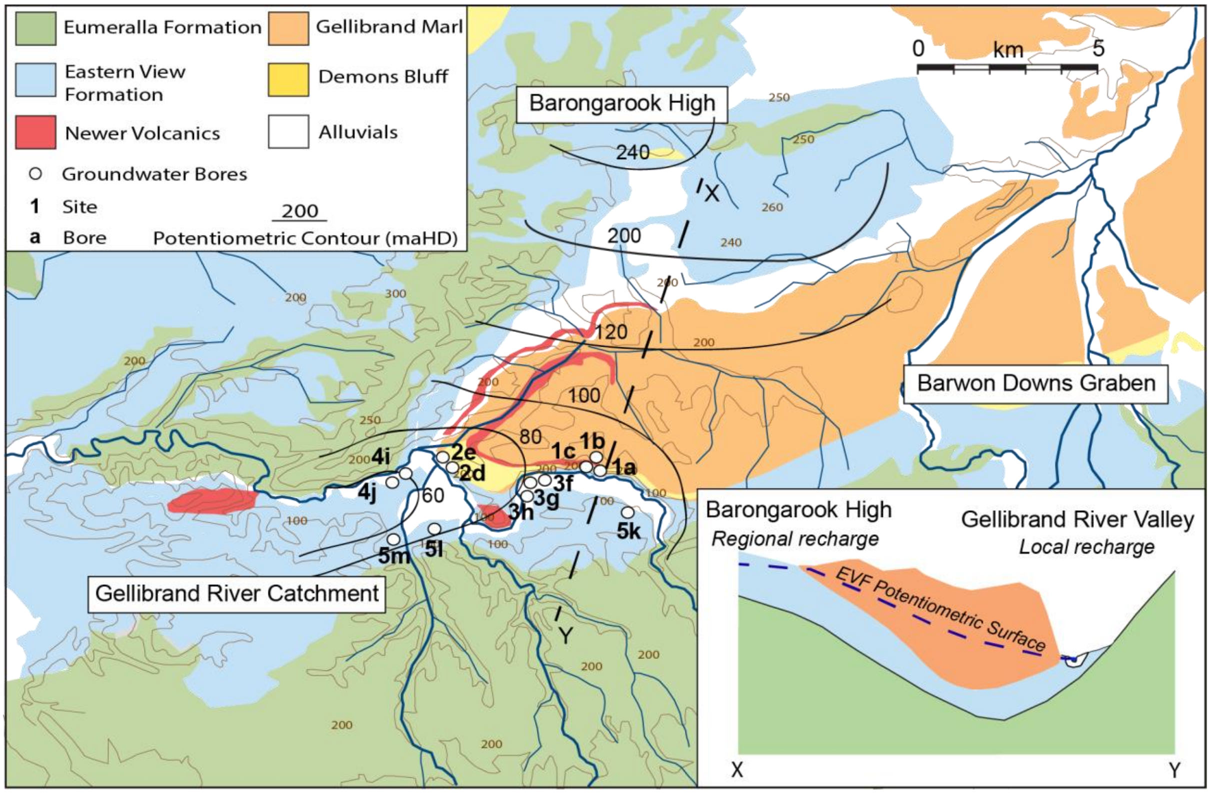

Figure 1 – Geology, groundwater flow, and cross sectional view of the upper part of the Gellibrand River Catchment (the Gellibrand Valley). Potentiometric contours for the Eastern View Formation are created from groundwater data (Water Resources Data Warehouse, 2013) and are expressed in metres above Australian Height Datum (mAHD). Sampled groundwater bores are also shown. Letters refer to bores in Table 1.

The Otway Basin is located in southwest Victoria, covering an area of 150,000 km^2. The basin was formed during the Cretaceous rifting of Australia and Antarctica (Briguglio et al., 2013) and is infilled with Upper Cretaceous and Cenozoic siliciclastic and calcareous sediments that form several aquifers and aquitards. The basin is divided into a number of sub-basins with regional groundwater flow paths originating at topographic highs. The Gellibrand River Catchment is one of these sub-basins. This study focuses on a 250 km^2 upland area of the Gellibrand River Catchment (known as the Gellibrand Valley), which lies at the foothills of the Otway Ranges, directly south of the Barongarook High (Fig.1).

Cretaceous Otway Group sediments of the Eumeralla Formation form the basement of the catchment and crop out in areas of higher relief. The Eumeralla Formation consists of thickly bedded siltstone, mudstone and volcanolithic sandstone. It has a low primary porosity and hydraulic conductivity and acts as a poor aquifer (Lakey & Leonard, 1982). Cenozoic sediments of the Wangerrip group overlie the bedrock and form major aquifers in the region to which flow is constrained (Van den Berg, 2009). The primary aquifer in the study area is the Eastern View Formation or the equivalent Dilwyn Formation (Van den Berg 2009; Petrides & Cartwright 2006; Atkinson et al., 2013) that is composed of gravel, fine to coarse grained sand, and major clay layers. The Eastern View Formation comprises predominantly quartz, feldspars and carbonates (< 2 %) and has hydraulic conductivities of 10^{-2} to 10^{2} m d^{-1} (Hortle et al., 2011). The Eastern View Formation is underlain by another productive aquifer, the Pebble Point Formation, however this is much thinner and is separated from the above layers by the Pember Mudstone. To the north, the Eastern View Formation is confined by the Gellibrand Marl, which is a regional aquitard that comprises 100 to 200 m of clay, and the Demons Bluff formation, which comprises fine-grained silts. Basaltic intrusions of the Quaternary Newer Volcanics are also present. The floodplain is covered with recent alluvial deposits of sand and clay. Regional groundwater recharge occurs on the Barongarook High where the Eastern View Formation crops out. Groundwater flows southwest along the Gellibrand River Catchment from the Barongarook High as well as eastward into the Barwon Downs Graben. However there is also potential for localised recharge within the Gellibrand Valley, where outcropping sediments of the Eastern View Formation, potentially act as an aquifer window (Fig. 1).

The Gellibrand Valley contains a mixture of cool temperate rainforest on the valley sides and cleared agricultural pasture through which the Gellibrand River flows. Rainfall across the catchment averages ~1000 mm yr^{-1}, with the majority of rainfall falling in the Australian winter between June and September (Bureau of Meteorology, 2013). The Gellibrand River is gaining and groundwater contributes between 10 and 50% to total river flow dependent on flow conditions (Atkinson et al., 2013). River flows are between 5 x 10^{4} m^{3} day^{-1} and 2 x 10^{6} m^{3} day^{-1} (Fig. 2c), with low flows during summer months (December to March) and high flows and flooding during winter (June to August) (Victorian Water Resources Data Warehouse, 2013). During flooding there is the potential for aquifer recharge from overbank flow.

Although groundwater residence times in the Otway Basin have been explored in the Gambier Embayment (Love et al., 1994) and nearby Barwon River Graben (Petrides & Cartwright, 2006), little is known of the residence times of groundwater in the Gellibrand River Catchment. This is despite the groundwater in Eastern View Formation being a potential valuable water resource (Petrides & Cartwright, 2006). Here we evaluate groundwater residence times in the Gellibrand Valley where the Eastern View Formation is exposed, forming an aquifer window, and regular episodic river floods occur, to understand the origins of groundwater within the valley and to identify whether groundwater recharge via rainfall and/or the river occurs in this part of the groundwater system. This is important in understanding the potential impacts of landuse change and pollution in the catchment as well as understanding the dynamics of recharge in catchments where aquifer material is exposed in more than one location. It is also important to fully understand groundwater systems such as this that have the potential to be developed as significant water resources. Radioactive tracers ^{14}C and ^{3}H are used to determine residence times and define groundwater flow paths whilst major ion chemistry is employed to determine dominant geochemical processes. Water table fluctuations and groundwater electrical conductivities are also continuously monitored. These easily measurable, robust parameters can be used to observe changes in storage and infer sources of aquifer recharge (Vogt et al., 2010) and allow for comparison with radioisotopes in understanding the dynamics of groundwater systems. Together, isotopic and physico-chemical approches provide insight on both short-term recharge processes (electrical conductivity, water levels) and long-term recharge processes (^{3}H and ^{14}C).

3. Methods

A number of groundwater monitoring bores that form part of the Victorian State Observation Bore network are present in the Gellibrand Valley (Victorian Water Resources Data Warehouse, 2013). These are screened in the Eastern View Formation, with depths of between 0 and 42 m. Bores located within 25 m from the Gellibrand River generally have screen depths between 11 and 15 m, whilst bores located on the flood plain have depths between 21 and 42 m. Groundwater from the Eastern View Formation was sampled from 13 bores. 10 of these are located within 25 m from the river in a 14 km^2 area of the catchment (Sites 1 to 4 in Fig. 1), with 3 further samples taken from bores situated further back on the flood plain between 1 and 2 km from the river (Site 5 in Fig. 1). Groundwater was sampled using an impeller pump set in the screen, with 2 to 3 bore volumes purged before sampling. In the field, samples for anion analysis were filtered through 0.45µm cellulose nitrate filters, whilst samples for cation analysis were filtered and acidified with high purity 16 N HNO_3 to pH < 2. Additionally, electrical conductivity (EC) and pH of groundwater were measured in the field using a calibrated TPS WP-81 conductivity/pH meter and probes. To assess transient changes in groundwater levels and EC, Aqua Troll 200 (In-Situ) data loggers were deployed in June 2011. A significant drop in EC in near-river groundwater is shown in some bores following flooding in June 2012 when bores were overtopped. However immediately upon pumping in October 2012 (bores 3g, 4i) and April 2013 (bore 1b), the EC of the groundwater returned to pre-flood EC values. We interpret this as floodwater that infiltrated down the bore which was not displaced by groundwater prior to pumping, and these data have been omitted. Rainfall samples were also collected in the catchment throughout the study period for chemical analysis.

Cations were analysed on filtered, acidified samples using a Thermo Finnigan X Series II Quadrupole ICP-MS. Anions were measured on filtered unacidified samples using a Metrohm ion chromatograph. The precision of major ion concentrations based on replicate analyses is ±2 %. Charge balances are within ±5 %. Stable isotope ratios were measured using Finnigan MAT 252 and ThermoFinnigan DeltaPlus Advantage mass spectrometers. $\delta^{18}O$ values were measured via equilibration with He-CO_2 at 32°C for 24 to 48hr in a Finnigan MAT Gas Bench whilst $\delta^{2}H$ values were measured by the reaction of water samples with Cr at 850°C using a Finnigan MAT H/Device. Both $\delta^{18}O$ and $\delta^{2}H$ were measured against an internal standard that has been calibrated using the IAEA, SMOW, GISP and SLAP standards. Data was normalised following methods outlined by Coplen (1988) and are expressed relative to V-SMOW where $\delta^{18}O$ and $\delta^{2}H$ values of SLAP are -55.5‰ and -428‰ respectively. Precision is ±1‰ for $\delta^{2}H$ and ±0.2‰ for $\delta^{18}O$.

^{14}C and ^{3}H samples of groundwater were measured at the Australian Nuclear Science and Technology Organisation (ANSTO) and the Tritium and Water Dating Laboratory, Institute of Geological and Nuclear Sciences (GNS), (New Zealand). For ^{14}C analysis performed at

ANSTO, CO_2 was extracted from water samples in a vacuum line using orthophosphoric acid and converted to graphite through reduction with excess H_2 gas in the presence of an iron catalyst at 600°C. ^{14}C concentrations were measured using a 10kV tandem accelerator mass spectrometer. $\delta^{13}C$ values for these samples are derived from the graphite fraction used for radiocarbon via EA-IRMS.

For ^{14}C samples measured at GNS, CO_2 was extracted from groundwater samples through addition of orthophosphoric acid. CO_2 was made into a graphite target and analysed by AMS. An aliquot of the extracted CO_2 was used for $\delta^{13}C$ analysis. ^{14}C activities are expressed as pMC (percent modern carbon) where pMC = 100% corresponds to 95% of the ^{14}C concentration of NBS oxalic acid standard (Stuiver and Polach, 1977), with a precision of $^{14}C/^{12}C$ ratios of ±0.5 (Fink et al 2004). At both ANSTO and GNS, samples for ^3H were distilled and electrolytically enriched prior to being analysed by liquid scintillation counting as described by Neklapilova et al. (2008a,b) and Morgenstern and Taylor (2009). ^3H activities are expressed in Tritium Units (TU) with a relative uncertainty of ± 5 % and a quantification limit of 0.13 to 0.14 TU at ANSTO and 0.02 TU and a relative uncertainty of 2 % at GNS.

(4) Results

(4.1) Groundwater elevations

Groundwater elevations decrease from 230 m relative to the Australian Height Datum (AHD) on the Barongarook High to <60 mAHD within the Gellibrand Valley (Fig.1), with groundwater flowing from the Barongarook High towards the Gellibrand Valley and then westward. Groundwater elevations from all depths and positions within the Gellibrand Valley are in phase and fluctuate between 1 and 3 m annually (Fig. 2a). The water table rises between June and August following winter rainfall (Fig. 2c) and head gradients at nested sites are upwards (Fig. 2b). The Gellibrand River has high water levels that result in flooding during winter months (June to August) and low flows in summer (December to March) (Fig. 2c).

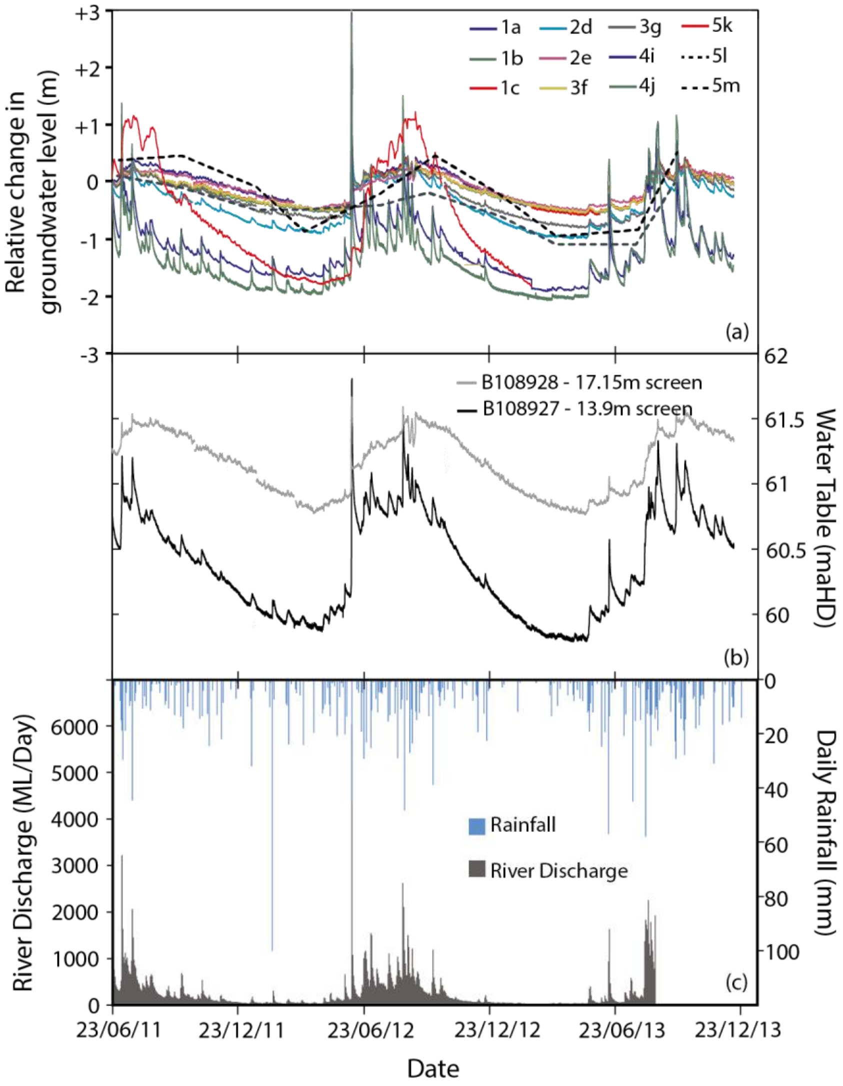

Figure 2 - (a) Groundwater elevations in bores display clear annual cycles (b) Groundwater head-gradients in the Gellibrand Valley are upwards implying a discharge zone (Victorian Water Resources Data Warehouse, 2013) (c) Flow in the Gellibrand River. Baseflow conditions during summer months transition into high flows in winter following winter rainfall. (Bureau of Meterology, 2013)

(4.2) Groundwater Geochemistry

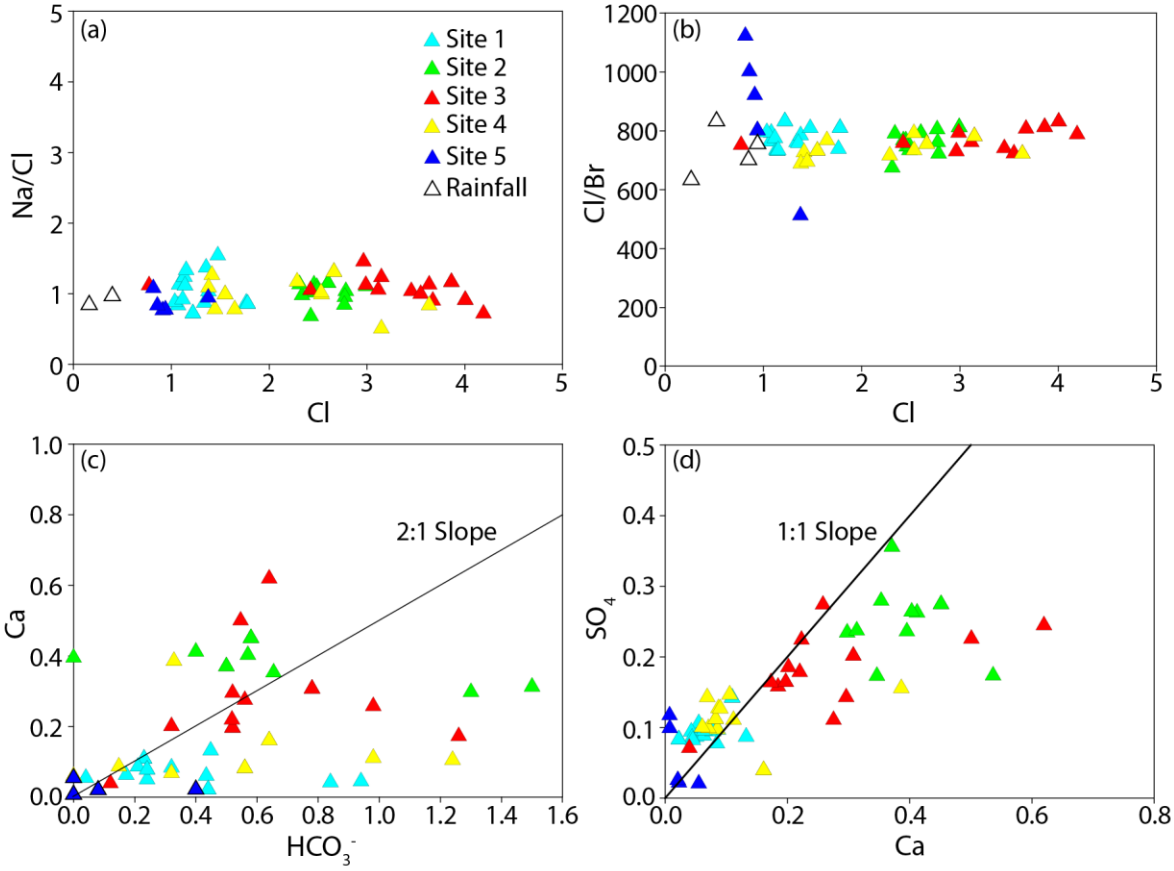

Figure 3 – Geochemical characteristics of groundwater in the Eastern View Formation; (a) mCl/Br v mCl (b) mNa/Cl v mCl (c) mCa v mHCO$_3$ (d) mSO$_4$ v mCa. Rainfall samples are also plotted where measured. Data is from Table 1 with repeat measurements over the sampling period included.

The chemistry of groundwater in the Gellibrand Valley is summarised in Table 1. Groundwater is oxic, with electrical conductivities between 140 and 600 µS cm^{-1} and pH values ranging from 4.8 to 6.0. Groundwater from close proximity to the river (Sites 1 to 4) generally has higher EC values (144 to 545 µS cm^{-1}) than groundwater further back on the floodplain at site 5 (149 to 220 µS cm^{-1}). Despite the range of salinity, the relative proportions of the major ions in groundwater are similar across the catchment. The groundwater is Na-Cl type. Cl constitutes between 68 and 92% of total anions on a molar basis, with HCO_3 accounting for 0 to 25%. Increases in Cl concentrations are associated with a decrease in HCO_3. Na comprises between 60 and 85% of total cations with Ca constituting 1 to 10%, Mg constituting 0 to 10% and K constituting 0 to 10%. Increased Na concentrations are associated with decreases in both Ca and Mg concentrations. Molar Cl/Br ratios are between 400 and 600 and do not increase with increasing Cl (Fig. 3b), molar Na/Cl ratios are 0.7 to 1.3 and also remain stable with increasing Cl concentrations (Fig. 3a). Na/Cl ratios of groundwater samples are similar to those measured in rainfall in southeast Australia (Blackburn and Mcleod, 1983) and the Cl/Br ratios are also similar to those expected for local rainfall (Cartwright et al., 2006). There is a weak correlation between Ca and HCO_3 (Fig. 3c) and between Ca and SO_4 (Fig. 3d).

(4.3) ^{13}C, $a^{14}C$ and ^{3}H concentrations

The $a^{14}C$ of groundwater ranges from 29 to 101.5 pMC. ^{3}H activities are below detection for the majority of groundwater samples (Table 1), with the exception of bores 5k, 5l and 5m which have activities of 1.02, 1.47 and 1.24 TU, respectively. Groundwater from these bores has $a^{14}C$ >90 pMC. The distribution of $a^{14}C$ and ^{3}H values across the catchment is heterogeneous with no relationship to depth or along lateral groundwater flowpaths. A strong inverse correlation (R^2 = 0.87) is observed between $a^{14}C$ and Cl concentrations (Table 1). A similar correlation is also observed for Na (R^2 = 0.855), K (R^2 = 0.82), Ca (R^2 = 0.6) and Mg (R^2 = 0.54).

(4.4) Stable Isotopes (δ^{2}H, δ^{18}O, δ^{13}C)

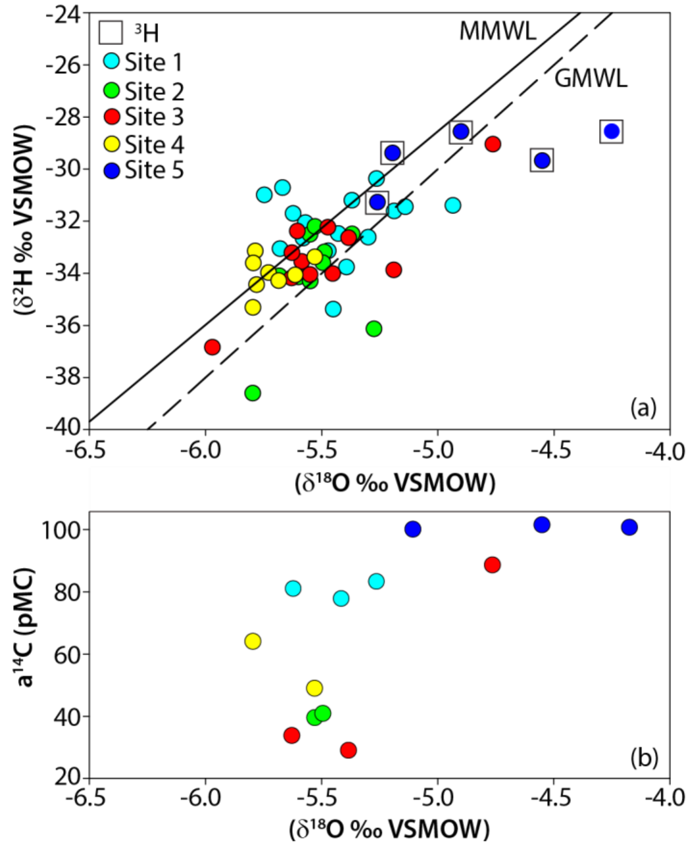

Figure 4 – *(a)* ^{2}H vs ^{18}O values of the Gellibrand River and surrounding groundwater sampled over March 2011 – August 2013 and the weighted average for rainfall from Adelaide and Melbourne. MMWL = Melbourne Meteoric Water Line (Hughes and Crawford, 2012). GMWL = Global Meteoric Water Line (Clarke and Fritz, 1997). Groundwaters with ^{3}H activities > 1 TU are also highlighted. Data is from Table 1 with repeat measurements over the sampling period included. (b) a^{14}C vs ^{18}O of groundwater samples.

δ^{18}O and δ^{2}H values of groundwater define a narrow field (δ^{18}O = -4 to -6 ‰ and δ^{2}H = -28 to -40 ‰) that is close to both the global and local meteoric water lines (Fig. 4a). The Gellibrand Valley is located between Melbourne and Adelaide, with groundwater generally plotting between the average isotopic compositions of meteoric waters located in those areas. Groundwater samples from site 5 are enriched in both δ^{18}O (+ 0.7 ‰) and δ ^{2}H (+ 3.5 ‰) relative to groundwater from sites 1 to 4 and have ^{3}H activities >1 TU (Fig. 4a). Additionally samples that are enriched in $\delta^{18}O$ have $a^{14}C$ >100 pMC (Fig. 4b). $\delta^{13}C$ values of DIC from groundwater range from -19.8 to -25 ‰, with an average of 21.7‰ (Table 1)

(4.5) Continuous Electrical Conductivity

Continuous groundwater EC records for a number of near-river bores and 5k, which is situated on the flood-plain, are shown in conjunction with changes in river height for the study period (Fig. 5). Groundwater EC in all bores for the majority of the dataset show little or no response to changes in river height, although minor dilution of groundwater EC occurs during high flow events in August and September 2013. Minor changes in EC correlate to sampling events in which groundwater bores were pumped

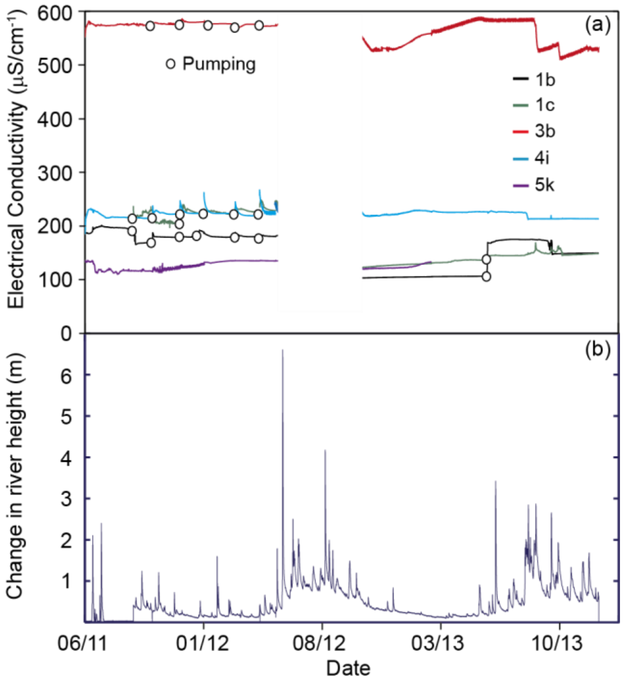

Figure 5 – (a) Continuous electrical conductivity monitoring of near-river groundwater. (b). Changes in river height over the study period. Groundwater EC and river level data from deployed Aqua troll 200 (In-Situ) Data Loggers.

(5) Discussion

(5.1) Groundwater Chemistry

Understanding geochemical processes in groundwater is required for correction of ^{14}C ages and in documenting groundwater flow and recharge. Processes which govern the evolution of groundwater geochemistry and sources of solutes in the Eastern View Formation can be determined from the major ion geochemistry. The observation that Cl/Br ratios are between 500 and 1000, which is similar to those expected in rainfall, and do not increase with increased TDS implies that evapotranspiration rather than halite dissolution is the major process controlling groundwater salinity (Herczeg et al., 2001; Cartwright et al., 2006). This conclusion is also consistent with an absence of halite in the aquifer lithologies. The δ^{18}O and δ^{2}H values of groundwater generally lie close to the meteoric water line and do not define evaporation trends, implying that transpiration in the soil zone or upper parts of the aquifer is likely to be more dominant over evaporation. Na/Cl ratios in groundwater are also similar to those in local rainfall (~1) implying that silicate weathering is limited (e.g., Edmunds et al., 2002), whilst the increase in Na concentrations at the expense of Ca may indicate ion exchange reactions on the surface of clay minerals (e.g., Herczeg et al., 2001). That Ca and $mHCO_3$ are poorly correlated suggests that negligible dissolution of calcite has occurred. A handful of groundwater samples have a 1:1 $Ca:SO_4$ ratio indicating some minor gypsum dissolution may take place. Together, the major ion geochemistry suggests that water-rock interaction is limited with minimal silicate weathering, negligible dissolution of halite and carbonate minerals and some minor dissolution of gypsum. As is the case elsewhere in southeast Australia, including within the Otway basin, the primary geochemical process is evapotranspiration promoted by the moderate rainfall and water-efficient native vegetation, and the groundwater salinity is largely controlled by the degree of evapotranspiration during recharge (Herczeg et al., 2001; Bennetts et al., 2006; Petrides & Cartwright, 2006).

Groundwater from the near-river sites 1 to 4 has lower $\delta^{18}O$ and $\delta^{2}H$ values relative to that from the floodplain away from the river at site 5. In a catchment of < 250 km^2 with a^{14}C varying between 29.1 to 101.5 pMC, climatic influences and the altitude effect are the most likely drivers in variability between groundwater samples (e.g., Dansgaard, 1964). As there is potential for groundwater recharge on the elevated Barongarook High and within the Gellibrand Valley; the depleted stable isotope signature of groundwater at sites 1 to 4 relative to groundwater samples from site 5 may reflect altitudinal differences of groundwater recharged at these locations. Assuming typical altitudinal gradients in rainfall of -0.15‰ to -0.5‰ per 100 m for $\delta^{18}O$ (Clark & Fritz, 1997) and an elevation difference of ~150m between the Gellibrand Valley and the Barongarook High, groundwater recharged on the Barongarook High is expected to be depleted in ^{18}O by -0.25‰ to -0.75‰ relative to that which is locally recharged in the valley. $\delta^{18}O$ values of groundwater from sites 1 to 4 are ~ -0.7‰ lower than groundwater from site 5. Thus, the stable isotopes indicate that water in the near-river environment may have been recharged from the Barongarook High, whilst water from the floodplain is recharged locally within the valley. This is supported by the negligible ^{3}H activities at sites 1 to 4, which indicate old water, and elevated activities at site 5 indicating recently recharged water. It is possible that the differences in stable isotopes between the sites are driven by climatic factors rather than altitude.

It is also possible that the variations in $\delta^{18}O$ values represent variation in the climate during recharge. While this has been proposed elsewhere in the Otway Basin (Love et al., 1994), in this part of the Otway Basin climatic variation has not been recorded in groundwater δ^{18}O values (Petrides and Cartwright, 2006). The lack of a systematic variation in δ^{18}O values with a^{14}C in groundwater from sites 1 to 4 also indicates that a climatic influence on δ^{18}O values is unlikely.

(5.2) Water Table Fluctuations

Annual cycles of groundwater elevations are present in all groundwater bores, which are screened 11 to 40 m below the ground surface. The fluctuations in groundwater levels across the Gellibrand Valley are likely a pressure response to recharge on the flood plain following rainfall events via hydraulic loading (Cartwright et al., 2007; Brodie et al., 2008; Unland et al., 2014). The magnitude of annual water table fluctuations recorded in data loggers is similar to those over the previous 30 years (Fig.6).

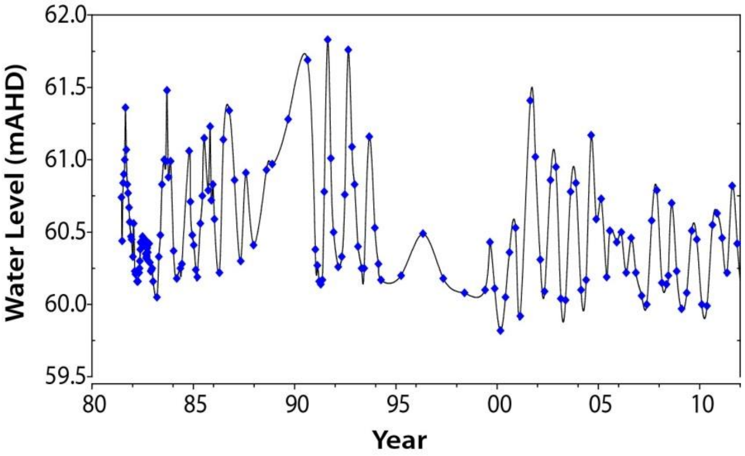

Figure 6 – Historical water table fluctuations 1988-2011 for bore 108927 (Victorian Water Resources Data Warehouse, 2013). The magnitude of annual recharge cycles are coherent with those recorded in data loggers over the study period (2011 to 2013)

Recharge was estimated for years 2012 and 2013 using the water-table fluctuation method Eq.(1):

$$R = S_y * \Delta h / \Delta t \tag{1}$$

(Scanlon et al., 2002), where S_y is specific yield, Δh is the change in water table height between the hydrograph recession and hydrograph peak and Δt is time. The water table rise is estimated as the difference between peak groundwater levels and the extrapolated antecedent recession. The estimate of recharge from this method is sensitive to the estimate of the specific yield. S_y is assumed to be 0.1 which is close to the measured effective porosity of the Eastern View Formation (Love et al., 1993), and takes into account the presence of finer sized sediments such as silt and clay in the aquifer. Annual water table fluctuations are between 0.9 and 3.7 m across all bores, which for S_y values of 0.1, imply that R = 130 to 372 mm yr^{-1} in 2012 (mean of 200 mm yr^{-1}) and 90 to 300 mm yr^{-1} in 2013 (mean of 164 mm yr^{-1}). This equates to between 11 and 32 % of rainfall in 2012 and 12 and 28 % of rainfall in 2013. The bores are screened 11.2 to 42 m below the ground surface and thus these recharge estimates will be minima due to the attenuation of pressure variations with depth (Scanlon et al., 2002). Recharge estimates are also susceptible to the value of specific yield, particularly where the aquifer is composed of finer sized sediments such as silt and clay. Regardless, estimates using bore hydrographs indicate that significant groundwater recharge to the unconfined Eastern View aquifer in the valley occurs via direct infiltration of precipitation.

(5.3) *^{14}C ages*

As groundwater in the Eastern View Formation contains dissolved oxygen and nitrate (Victorian Water Resources Data Warehouse, 2013), δ^{13}C values are low, and there are no reported occurrences of methane or coal seams within the Gellibrand River Catchment, methanogenesis is unlikely to be a source of DIC. Likewise there are no obvious sources of geogenic CO_2 in this area. Based on the major ion geochemistry, only minor calcite dissolution occurs in the Eastern View Formation, which is to be expected as the Cenozoic aquifers are siliceous and contain only minor carbonate minerals. While only minor carbonate dissolution is likely, determination of groundwater residence times requires this to be taken into account. If it is assumed that closed system dissolution of calcite in the aquifers is the major process, the fraction of C derived from the soil zone (*q*) may be derived from the $\delta^{13}C$ values of DIC ($\delta^{13}C_{DIC}$), carbonate ($\delta^{13}C_{cc}$) and recharging water ($\delta^{13}C_r$) via Eq.(2):

$$q = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{cc}}{\delta^{13}C_r - \delta^{13}C_{cc}} \qquad (2)$$

(Clark & Fritz 1997). The calcite is assumed to have a $\delta^{13}C$ of ~0‰ (Love et al., 1994; Petrides and Cartwright, 2006) as is appropriate for marine sediments. $\delta^{13}C_r$ is calculated from the $\delta^{13}C$ of the soil carbon in the recharge zone. Pre-land clearing vegetation in southeast Australia was dominated by eucalypts that have $\delta^{13}C$ values of -30 to -27 ‰ (Quade et al., 1995). Assuming a ~4 ‰ ^{13}C fractionation during outgassing (Cerling et al., 1991), $\delta^{13}C$ values of soil CO_2 would be -26 to -23 ‰ (average of -24.5 ‰). At 20 °C and pH 6.5, $\delta^{13}C_r$ calculated from the fractionation data of Vogel et al. (1970) and Mook et al. (1974) is ~ -20 ‰. Although the calculated $\delta^{13}C_r$ values require the pH and temperature of recharge and the $\delta^{13}C$ of the soil zone CO_2 to be estimated, they are similar to those from other studies in southeast Australia and consistent with the predicted $\delta^{13}C$ values of DIC in equilibrium with calcite in the regolith (Quade et al., 1995; Cartwright, 2010). Calculated q values are between 0.85 and 0.97 (Table 2), implying that only 10% to 15% of DIC in groundwater from the Eastern View formation is derived from calcite in the aquifer, this is similar to the expected contribution of calcite dissolution in siliceous aquifers (Vogel et al., 1970) and similar to other estimates from the Otway Basin (Love et al., 1994; Petrides and Cartwright, 2006).

Using the q values from Table 2, ^{14}C ages (t) corrected for closed-system calcite dissolution are calculated from Eq. (3); where a^{14}C is the activity of ^{14}C in groundwater DIC, and $a_o{}^{14}$C is the activity during recharge (assumed to be 100 pMC).

$$t = -8376 \ln\left(\frac{a^{14}C}{q.a_o{}^{14}C}\right) \qquad (3)$$

Radiocarbon ages for groundwater in the Eastern View Formation range from 380 to 9260 years (Table 2) with the exception of bores 5k, 5l and 5m which have a^{14}C >100 pMC and represent groundwater that has a component of water recharged during or after the atmospheric nuclear tests in the 1950s to 1960s. The majority of ^{14}C ages however, suggest that groundwater in the valley, especially in the near-river environment has long residence times (Fig. 7).

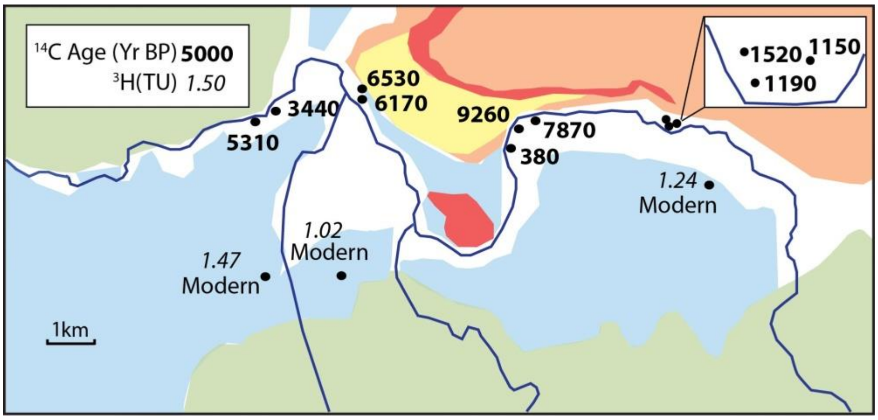

Figure 7 – Groundwater residences times within the Gellibrand Valley. Residence times up to 9260 years are found in close proximity to the river. Modern local groundwaters with a^{14}C > 100 pMC are situated back on the floodplain. Data from Tables 1 and 2.

(5.4) ^{3}H Activities and Recharge Rates

With a shorter half-life, ^{3}H activities can infer the presence of modern groundwater. The water table fluctuations imply that the Gellibrand Valley receives considerable recharge year (90 to 370 mm yr^{-1}), and although head gradients at nested sites are upwards implying that the valley is a groundwater discharge zone (Fig. 2b), these may be reversed during periods of high rainfall. If local recharge is significant in recharging the groundwater system across the valley, it would be expected that the groundwater would have relatively high ^{3}H activities. Recently-recharged groundwater in other Victorian catchments has ^{3}H activities up to 3.6 TU (Cartwright & Morgenstern, 2012).

^{3}H activities across most of the groundwater from the Gellibrand Valley are negligible, and with ^{14}C ages of 380 to 9260 years, much of the groundwater is regional, originating from the Barongarook High. The exception to this is groundwater from the southern edge of the valley (Site 5) where the Eastern View Formation overlies the basement rock (Eumeralla Formation) and ^{3}H activities and ^{14}C activities are substantially higher than groundwater from sites 1 to 4. The mean residence times of water samples from the southern margin of the valley (Site 5) were evaluated from ^{3}H activities using the TracerLPM Excel workbook (Jurgens et al., 2012). As the aquifer is unconfined throughout the valley, and bore screens sample only part of the aquifer, the partial exponential model (PEM) is applied, with the PEM ratio calculated for bores 5k, 5l and 5k as the ratio of the unsampled thickness of the aquifer to the sampled thickness (Jurgens et al., 2012). A value of 2.7 TU was used to represent modern and pre-bomb pulse rainfall based on the ^{3}H activity of rainfall measured at Monash University and expected ^{3}H values in Southern Victoria (Tadros et al., 2014). For intervening years, the mean weighted average of ^{3}H activities in precipitation in Melbourne was extracted from the

International Atomic Energy Agency Melbourne record (International Atomic Energy Association, 2014). Calculated groundwater ages of 65 years (5k) 73 years (5l) and 59 years (5m) indicate that groundwater away from the river is modern and likely recharged from direct infiltration of precipitation. This supports $\delta^{18}O$ and $\delta^{2}H$ data which suggests that sites 1 to 4 sample old, regional groundwater recharged on the Barongarook High, whilst site 5 samples locally recharged groundwater within the valley. Although groundwater levels across sites 1 to 5 demonstrate annual recharge cycles, in the near-river environment (sites 1 to 4) much of the regional groundwater is from within 5 to 10 m of the water table, suggesting that any local recharge penetrates only to a limited depth, and does not mix with the bulk of the water in the Eastern View Formation. Conversely the high ^{3}H activities and ^{14}C activities at site 5, which occur in groundwater from depths of 21 – 42 m, imply that recharge to the deeper parts of the aquifer locally occurs at the southern edge of the floodplain.

The Gellibrand River has the potential to recharge regional groundwater during high river stages and episodic floods. Aquifer recharge from surface water can be assessed by combining data from groundwater EC values and ^{3}H activities. The EC of river water varies between 120 and 200 µS cm^{-1} and is lower than that of groundwater in the catchment throughout the year. ^{3}H activities of river water are between 1.24 and 2.0 TU during baseflow conditions (Atkinson et al., 2013), and may be higher during high flow events as local modern rainfall (with ^{3}H activities of 2.4 to 3.2 TU: Tadros et al., 2014) and relatively 'young' water draining the upper catchment likely comprise a significant component of river flow at those times. Significant amounts of aquifer recharge through overbank events or bank exchange should result in groundwater with low EC values, and high ^{3}H activities near the river. Except for in June 2012 when the bores were overtopped and a limited to response to high river flow events (June to July 2013), groundwater EC remains relatively constant throughout the study period and there is only a minor inverse relationship with river height (Fig. 6). This indicates there is little exchange of river water to the depth of the aquifer sampled by the bores. Additionally the activities of ^{3}H in near-river bores are negligible, again suggesting that recharge from the river does not penetrate more than a few metres into the adjacent aquifer. Thus, flow through the river bank or river flooding does not appear to be a significant mechanism of recharge in the Gellibrand Valley. Instead, with upward head gradients and evidence for limited recharge in the near-river environment, the river likely acts as a groundwater discharge zone for the majority of the year, supplied by a combination of regional groundwater from the Barongarook High and local groundwater recharged within the valley.

(5.5) Groundwater Flowpaths and Conceptual Model

Radiocarbon ages are up to 10 ka implying that the groundwater in the Gellibrand Valley has a long residence time; in turn this implies that the area is a regional discharge zone. Most of the groundwater originates on the Barongarook High, and this region potentially provides a substantial proportion of baseflow to the Gellibrand River. The large range of ^{14}C ages in the Gellibrand Valley is a likely result of heterogeneous geology, where the presence of low hydraulic conductivity sediments such as silt and clays in the Eastern View Formation lead to variable velocities along groundwater flowpaths. Groundwater travel times may also be determined using the present day hydraulic gradients. From Darcy's law and assuming a porosity of 0.1 (Love et al., 1994) and a hydraulic conductivity of 0.2 to 2 m day^{-1} (Love et al., 1993) calculated travel times are between 1000 and 10 000 years, which are similar to those implied by the ^{14}C ages. This and the depleted stable isotope signature of groundwater samples form sites 1 to 4 supports the idea that groundwater in the valley is predominantly regional groundwater derived by recharge on the Barongarook High. The high ^{3}H activities in groundwater bores from site 5 situated away from the river imply local recharge via precipitation recharges the aquifer to depths of 21 to 42 m at the southern edge of the floodplain. However for the most-part, shallow groundwater in the Gellibrand Valley, including in the near-river environment is predominantly regional groundwater. Though groundwater elevations display clear annual cycles and winter months are punctuated by high river flow, localised recharge from both of these processes combined is stored in the upper 10 m of the aquifer. The infiltration of precipitation within the Gellibrand Valley is likely limited by the presence of silts and clays on the floodplain and riverbanks. This is coupled with strong upwards hydraulic gradients in the Eastern View Formation, driven by regional groundwater flow from the Barongarook High, which ensure that recharge in the near-river environment does not penetrate deep within the aquifer (Fig. 8).

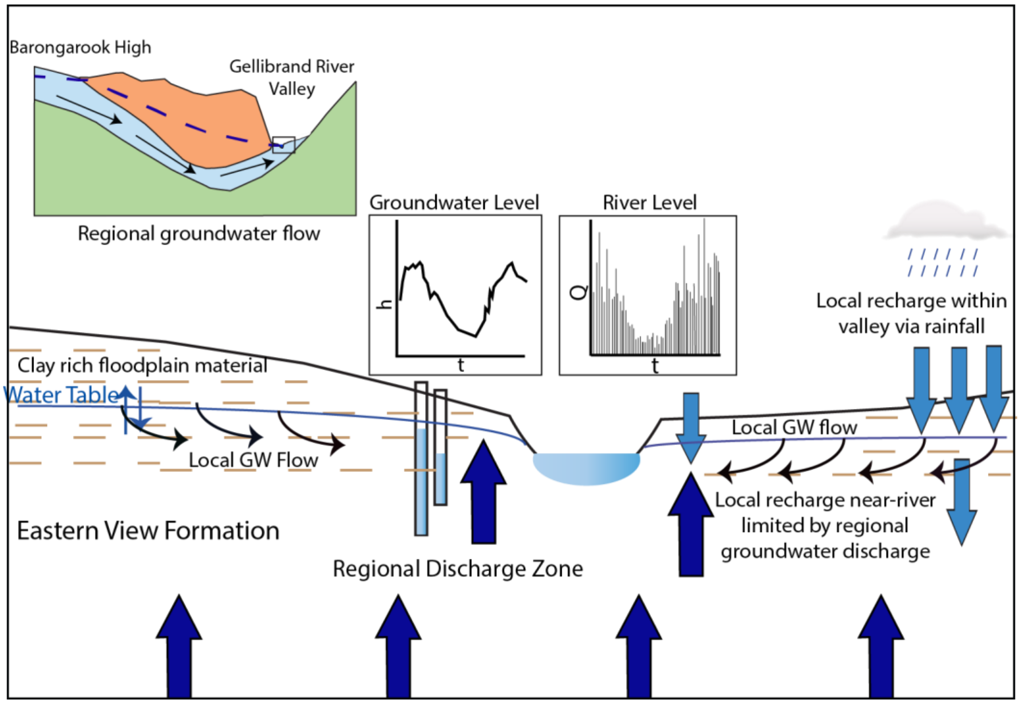

Figure 8 – Groundwater flow conceptualisation in the Gellibrand Valley. Though appreciable amounts of recharge are estimated from bore hydrographs and high river flows, the depth to which recharging waters infiltrate into the Eastern View Formation (downward leakage) is limited by strong upward head gradients, and a floodplain which consists of appreciable amounts of silt and clay.

(5.6) ^{14}C ages & Cl

The good correlation of a^{14}C with chloride implies that chloride concentrations correspond to groundwater age (Fig. 9). Correlations between ^{14}C and Cl have also been documented in groundwater from the Eastern View Formation in other regions of the Otway Basin (Love et al., 1994). In assessing this relationship, chloride sources must be considered. That the Cl/Br ratios in the groundwater are similar to those of rainfall preclude significant halite dissolution by the groundwater from the Eastern View Formation, and there are no extensive occurrences of halite in the aquifer matrix.

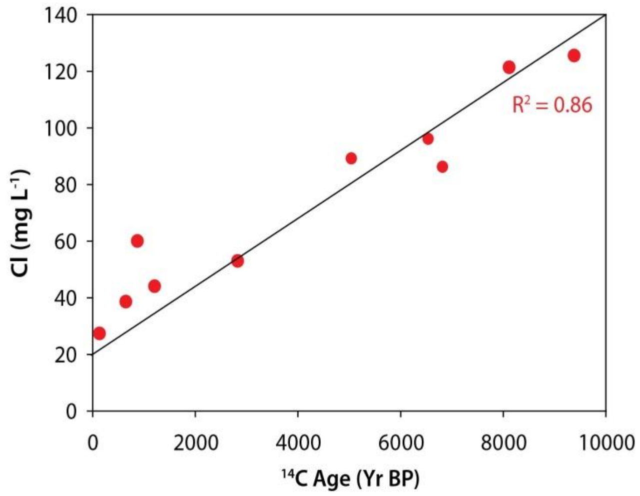

Figure 9 – ^{14}C age v Cl. ^{14}C ages are taken from the calcite corrected ages in *Table 1*

We propose three possible explanations of this trend. Firstly, the relationship between a^{14}C and Cl may be explained by mixing of low salinity groundwater that is locally recharged within the valley (Site 5) and high salinity regional groundwater from the Barongarook High (Sites 1 to 4). However, groundwater samples from site 5 which have high a^{14}C and low Cl also have high ^{3}H activities (0.99 to 1.47 TU) suggesting if mixing has occurred it must do so at a very slow rate otherwise the resultant groundwater (Sites 1 to 4) would be expected to contain measurable ^{3}H. This implies that mixing between the shallow groundwater system and the deeper groundwater is limited.

It is possible that the Cl concentrations in groundwater preserve a record of climate variability. In the Otway Basin Love et al. (1994) report a decrease in Cl concentrations in groundwater recharged between 18 and 10 ka, followed by an increase in Cl concentrations in groundwater recharged from 10 ka to the present day, which they attribute to increased evapotranspiration rates during a warming Holocene climate. However, in this study decreasing Cl concentrations with increasing a^{14}C would imply that recharge rates on the Barongarook high increased from 10,000 years BP to the present, which is not likely given the warming trend over that period.

It is more likely that the correlation between a^{14}C and Cl concentrations reflects spatially variable recharge on the Barongarook High due to the heterogeneous sediments within the Eastern View Formation. Evapotranspiration during recharge is commonly the dominant process in determining the salinity of groundwater in SE Australia (Herczeg et al., 2001). Low recharge rates result in higher degrees of evapotranspiration and higher salinity groundwater, and the resultant correlation between Cl concentrations and ^{14}C ages has been noted in other catchments (Leaney et al., 2003; Cartwright et al., 2006). Variable recharge rates could result in a wide range of recharge ages in the Gellibrand Valley, with the high Cl low a^{14}C groundwater being derived from regions with locally low recharge rates. Regardless of which model is correct, the chloride measurements provide a useful first order estimate of groundwater residence times.

(6) Conclusion

Though widely available water-table measurements offer an insight into recharge, the dynamics of groundwater flow systems and recharge patterns can only be fully understood when combined with geochemical data, in particular radiogenic tracers such as ^{3}H and ^{14}C. These can be used to assess the importance of recharge and discharge in aquifer windows, which in turn defines groundwater pathways and allows the potential fate of pollutants to be assessed. Here shallow (11 to 42 m) groundwater bores indicate a significant amount of recharge occurs in the Gellibrand River Valley (90 to 370 mm yr^{-1}). However, the groundwater at 5 to 10 m below the water table has ^{14}C ages between 350 and 10,000 years, and below detection ^{3}H activities. Furthermore, there is no indication of water from the river penetrating more than ~10 m following flood events. In the Gellibrand River Valley, outcropping aquifer sediments act as a regional discharge zone. Upwards head gradients are maintained for long periods of time and aided by the presence of silts and clays on the floodplain, this limits the depth to which diffuse and localised recharge (via over-bank events and bank exchange) penetrate the aquifer.

There is most likely a shallow local flow system within the Gellibrand River Valley that has limited connectivity with the deeper groundwater, particularly in the near-river environment. This potentially limits the spread of pollutants such as nitrate and pesticides that may derive from the agricultural activities into the regional groundwater. Future land-use, climate change or groundwater exploitation that occurs on the Barongarook High or in the Gellibrand River Catchment is likely to affect both the chemistry of groundwater and groundwater fluxes to the Gellibrand River, highlighting the importance of protecting regional recharge zones.

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References

Alley, W.M., Healy, R.W., LaBaugh J.W., and Reilly, T.E.: Flow and storage in groundwater systems. (Review: hydrology). Science, 296: 1985-1990 DOI:10.1126/science.106712, 2002.

Aravena, R., Leonard, I., Wassenaar, L., and Plummer, N.: Estimating ^{14}C Groundwater Ages in a Methanogenic Aquifer. Water Resour Res, 9: 2307-2317. DOI: 10.1029/95WR01271, 1995.

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Hofmann, H., Unland, N.P., Cendón, D.I., and Chisari, R.: A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry. Hydrol Process. Available Online. DOI: 10.1002/hyp.10122, 2013.

Bennetts, D.A., Webb, J.A., Stone, D.J.M., and Hill, D.M.: Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. J Hydrol, 323: 178-192. DOI: http://dx.doi.org/10.1016/j.jhydrol.2005.08.023, 2006.

Bertrand, G., Celle-Jeanton, H., Loock, S., Huneau, F., Lavastre, V.: Contribution of δ^{13}CCITD and PCO2 eq measurements to the understanding of groundwater mineralization and carbon patterns in volcanic aquifers. Application to Argnat Basin (Massif Central). Aq. Geochem. 19 (2): 147-171. DOI: 10.1007/s10498-012-9185-0, 2013.

Bethke, C.M. and Johnson, T.M.: Groundwater Age and Groundwater Age Dating. Annual Review of Earth Planet Sc lett, 36: 121-152. DOI: 0.1146/annurev.earth.36.031207.124210, 2008.

Blackburn, G. and Mcleod, S.: Salinity of atmospheric precipitation in the Murray-Darling drainage division, Australia. Soil Research, 21: 411-434. DOI: http://dx.doi.org/10.1071/SR9830411, 1983.

Böhlke, J.K. and Denver, J.M.: Combined Use of Groundwater Dating, Chemical, and Isotopic Analyses to Resolve the History and Fate of Nitrate Contamination in Two Agricultural Watersheds, Atlantic Coastal Plain, Maryland. Water Resour Res, 31: 2319-2339. DOI: 10.1029/95wr01584, 1995.

Böhlke, J.K.: Groundwater recharge and agricultural contamination. Hydrogeol J, 10: 153-179. DOI: 10.1007/s10040-001-0183-3, 2002.

Briguglio, D., Kowalczyk, J., Stilwell, J.D., Hall, M., and Coffa, A.: Detailed paleogeographic evolution of the Bass Basin: Late Cretaceous to present. Aust Journal Earth Sci, 60: 719-734. DOI: 10.1080/08120099.2013.826282, 2013.

Bureau of Meteorology, 2013. Commonwealth of Australia Bureau of Meteorology. http://www.bom.gov.au, last access: 14 January 2014.

Campana, M.E. and Simpson, E.S.: Groundwater residence times and recharge rates using a discrete-state compartment model and ^{14}C data. J Hydrol, 72: 171-185. DOI: http://dx.doi.org/10.1016/0022-1694(84)90190-2, 1984.

Cardenas, M.B.: Potential contribution of topography-driven regional groundwater flow to fractal stream chemistry: Residence time distribution analysis of Tóth flow. Geophys Res Lett, 34: L05403. DOI: 10.1029/2006gl029126, 2007.

Cartwright, I., Weaver, T.R., and Fifield, L.K.: Cl/Br ratios and environmental isotopes as indicators of recharge variability and groundwater flow: An example from the southeast Murray Basin, Australia. Chem. Geol, 231: 38-56. DOI: http://dx.doi.org/10.1016/j.chemgeo.2005.12.009, 2006.

Cartwright, I. and Morgenstern, U.: Constraining groundwater recharge and the rate of geochemical processes using tritium and major ion geochemistry: Ovens catchment, southeast Australia. J Hydrol, 475: 137-149. DOI: http://dx.doi.org/10.1016/j.jhydrol.2012.09.037, 2012.

Cartwright, I., Weaver, T.R., Cendón, D.I., Fifield, L.K., Tweed, S.O., Petrides, B., and Swane I.: Constraining groundwater flow, residence times, inter-aquifer mixing, and aquifer properties using environmental isotopes in the southeast Murray Basin, Australia. Appl Geochem, 27: 1698-1709. DOI: http://dx.doi.org/10.1016/j.apgeochem.2012.02.006, 2012.

Cartwright, I., Fifield, L.K., and Morgenstern, U.: Using ^{3}H and ^{14}C to constrain the degree of closed-system dissolution of calcite in groundwater. App Geochem, 32: 118-128. DOI: http://dx.doi.org/10.1016/j.apgeochem.2012.10.023, 2013.

Cendón, D.I., Larsen, J.R., Jones, B.G., Nanson, G.C., Rickleman, D., Hankin, S.I., Pueyo, J.J., and Maroulis, J.: Freshwater recharge into a shallow saline groundwater system, Cooper Creek floodplain, Queensland, Australia. J Hydrol, 392: 150-163. DOI: http://dx.doi.org/10.1016/j.jhydrol.2010.08.003, 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., and Chisari, R.: Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura-Mangrove Mountain aquifer, NSW, Australia. Aust J of Earth Sci, 1-25 http://dx.doi.org/10.1080/0812099.2014.894628, 2014.

Cerling, T.E., Solomon, D.K., Quade, J., and Bowman, J.R.: On the isotopic composition of carbon in soil carbon dioxide. Geochim Cosmochim Ac, 55: 3403-3405. DOI: http://dx.doi.org/10.1016/0016-7037(91)90498-T, 1991.

Chen, X. and Chen, X.: Stream water infiltration, bank storage, and storage zone changes due to stream-stage fluctuations. J Hydrol, 280: 246-264. DOI: http://dx.doi.org/10.1016/S0022-1694(03)00232-4, 2003.

Clark, I.D. and Fritz, P.: Environmental Isotopes in Hydrogeology. Lewis, New York, USA, 1997.

Cook, P., Herczeg, A., and Kalin, R.: Radiocarbon Dating of Groundwater Systems. In: Environmental Tracers in Subsurface Hydrology, Springer US, pp: 111-144, 2000.

Cook, P.G. and Robinson, N.I.: Estimating groundwater recharge in fractured rock from environmental ^{3}H and ^{36}Cl, Clare Valley, South Australia. Water Res Res, 38: 11-11-11-13. DOI: 10.1029/2001wr000772, 2002.

Coplen, T.B.: Normalization of oxygen and hydrogen isotope data. Chem. Geol., 72: 293-297. DOI: 10.1016/0168-9622(88)90042-5, 1988.

Dansgaard, W.: Stable isotopes in precipitation. Tellus., 16 (4): 436-468. DOI:10.1111/j.2153-3490.1964.tb00181.x, 1964.

Doble, R.B.P., McCallum, J., and Cook, P.: An analysis of river bank slope and unsaturated flow effect on bank storage. Groundwater, 50: 77-86. DOI: 0.1111/j.1745-6584.2011.00821.x, 2012.

Edmunds, W.M., Carrillo-Rivera, J.J., and Cardona, A.: Geochemical evolution of groundwater beneath Mexico City. J Hydrol, 258: 1-24. DOI: http://dx.doi.org/10.1016/S0022-1694(01)00461-9, 2002.

Fink, D., Hotchkis, M., Hua, Q., Jacobsen, G., Smith, A.M., Zoppi, U., Child, D., Mifsud, C., van der Gaast, H., Williams, A., and Williams, M.: The ANTARES AMS facility at ANSTO. Nuclear Instruments and Methods in Physics Research B 223-224, 109-115, 2004.

Foster, S.S.D., and Chilton, P.J.: Groundwater: the processes and global significance of aquifer degradation. Philosophical Transactions of the Royal Society of London Series B-Biological Sciences, 358: 1957-1972. DOI: 10.1098/rstb.2003.1380, 2003.

Frederico, C., Aiuppa, A., Allad, P., Bellomo, S., Jean-Baptiste, P., Parello, F., Valenza, M.: Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt Vesuvius, Italy. Geochim. Cosmochim. Acta, 66(6): 963-981, 2002.

Frisbee, M.D., Wilson, J.L., Gomez-Velez, J.D., Phillips, F.M., and Campbell, A.R.: Are we missing the tail (and the tale) of residence time distributions in watersheds? Geophys Res Lett, 40: 4633-4637. DOI: 10.1002/grl.50895, 2013.

Gardner, W.P., Harrington, G.A., Solomon, D.K., and Cook, P.G.: Using terrigenic ^{4}He to identify and quantify regional groundwater discharge to streams. Water Resour Res, 47: W06523. DOI: 10.1029/2010wr010276, 2011.

Goderniaux, P., Davy, P., Bresciani, E., de Dreuzy, J.R., and Le Borgne, T.: Partitioning a regional groundwater flow system into shallow local and deep regional flow compartments. Water Resour Res, 49: 2274-2286. DOI: 10.1002/wrcr.20186, 2013.

Han, L.F. and Plummer, L.N.: Revision of Fontes & amp; Garnier's model for the initial ^{14}C content of dissolved inorganic carbon used in groundwater dating. Chem. Geol., 351: 105-114. DOI: http://dx.doi.org/10.1016/j.chemgeo.2013.05.011, 2013.

Herczeg, A.L., Dogramaci, S.S., and Leaney, F.W.J.: Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. Mar. Freshw. Res., 52: 41-52. DOI: http://dx.doi.org/10.1071/MF00040, 2001.

Hilscherova, K., Dusek, L., Kubik, V., Cupr, P., Hofman, J., Klanova, J., and Holoubek, I.: Redistribution of organic pollutants in river sediments and alluvial soils related to major floods. Journal of Soils and Sediments, 7: 167-177. DOI: 10.1065/jss2007.04.222, 2007.

Hortle, A., de Caritat, P., Stalvies, C., and Jenkins, C.: Groundwater monitoring at the Otway project site, Australia. Energy Procedia, 4: 5495-5503. DOI: http://dx.doi.org/10.1016/j.egypro.2011.02.535, 2011.

Hughes, C.E. and Crawford, J.: A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. J Hydrol, 464: 344-351. DOI: http://dx.doi.org/10.1016/j.jhydrol.2012.07.029, 2012.

Jurgens B.C., Böhlke J.K., Eberts S.M.: TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data: U.S. Geological Survey Techniques and Methods Report 4- F3, 60p, 2012.

Krüger, F., Meissner, R., Gröngröft, A., and Grunewald, K.: Flood Induced Heavy Metal and Arsenic Contamination of Elbe River Floodplain Soils. Acta hydroch hydrob, 33: 455-465. DOI: 10.1002/aheh.200400591, 2005.

Leaney, F.W., Herczeg, A.K., Walker, G.R.: Stable isotope geochemistry of ground and surface waters associated with undisturbed massive sulphide deposits; constraints on origin of waters and water-rock reactions. Chemical Geology, 2006.

Leonard, J., Lakey, R., and Cumming, S.: Gellibrand groundwater investigation interim report. Geologic Survey of Victoria. Department of Minerals and Energy. Unpublished Report, 1981

Le Gal La Salle, C., Marlin, C., Leduc, C., Taupin, J.D., Massault, M., and Favreau, G.: Renewal rate estimation of groundwater based on radioactive tracers (3H, 14C) in an unconfined aquifer in a semi-arid area, Iullemeden Basin, Niger. J Hydrol, 254: 145-156. DOI: http://dx.doi.org/10.1016/S0022-1694(01)00491-7, 2001.

Love, A.J., Herczeg. A.L., Armstrong, D., Stadter, F., and Mazor, E.: Groundwater flow regime within the Gambier Embayment of the Otway Basin, Australia: evidence from hydraulics and hydrochemistry. J Hydrol, 143: 297-338. DOI: http://dx.doi.org/10.1016/0022-1694(93)90197-H, 1993.

Love, A.J., Herczeg, A.L., Leaney, F.W., Stadter, M.F., Dighton, J.C., and Armstrong, D.: Groundwater residence time and palaeohydrology in the Otway Basin, South Australia: ^{2}H, ^{18}O and ^{14}C data. J Hydrol, 153: 157-187. DOI: http://dx.doi.org/10.1016/0022-1694(94)90190-2, 1994.

Manning, A.H., Clark, J.F., Diaz, S.H., Rademacher, L.K., Earman, S., and Plummer, N.L.: Evolution of groundwater age in a mountain watershed over a period of thirteen years. J Hydrol, 460: 13-28. DOI: http://dx.doi.org/10.1016/j.jhydrol.2012.06.030, 2012.

Mazor, E., and Nativ, R.: Hydraulic calculation of groundwater flow velocity and age: examination of the basic premises. J Hydrol, 138: 211-222. DOI: http://dx.doi.org/10.1016/0022-1694(92)90165-R, 1992.

McCallum, J.L., Cook, P.G., Brunner, P., and Berhane, D.: Solute dynamics during bank storage flows and implications for chemical base flow separation. Water Resour. Res., 46: W07541. DOI: 10.1029/2009wr008539, 2010.

McDonnell, J.J., McGuire, K., Aggarwal, P., Beven, K.J., Biondi, D., Destouni, G., Dunn, S., Kirchner, J.A., Kraft, P., Lyon, S., Maloszewski, P., Newman, B., Pfister, L., Rinaldo, A., Rodhe, A., Sayama, T., Seibert, J., Solomon, K., Soulsby, C., Stewart, M., Tetzlaff, D., Tobin, C., Troch, P., Weiler, M., Western, A., Wörman, A., and Wrede, S.: How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. Hydrol Process, 24: 1745-1754. DOI: 10.1002/hyp.7796, 2010.

Meredith, K.T., Cendón, D.I., Pigois, J-P., Hollins, S.E., and Jacobsen, G.: Using ^{14}C and 3H to delineate a recharge 'window' into the Perth Basin aquifers, North Gnangara groundwater system, Western Australia. Sci Total Environ, 414, 456-469, 2012.

Michel, R.L.:Tritium hydrology of the Mississippi River basin. Hydrol Process, 18: 1255-1269. DOI: 10.1002/hyp.1403, 2004.

Moench, A.F. and Barlow, P.M.: Aquifer response to stream-stage and recharge variations. I. Analytical step-response functions. J Hydrol, 230: 192-210. DOI: http://dx.doi.org/10.1016/S0022-1694(00)00175-X, 2000.

Mook, W.G., Bommerson, J.C., and Staverman, W.H.: Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet Sc Lett, 22: 169-176. DOI: http://dx.doi.org/10.1016/0012-821X(74)90078-8, 1974.

Morgenstern, U. and Taylor, C.B.: Ultra low-level tritium measurement using electrolytic enrichment and LSC. Isot environ and healt s, 45(2) 96-117, 2009.

Morgenstern, U. Stewart, M.K., and Stenger, R.: Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. Hydrol. Earth Syst. Sci., 14: 2289-2301. DOI: 10.5194/hess-14-2289-2010.

Muennich, K.O.: Messung des ^{14}C-Gehaltes von hartem Grundwasser. Naturwissenschaften 34, 32-33, 1957.

Neklapilova, B.: Conductivity measurements and large volumes distillation of samples for Tritium analysis. ANSTO internal guideline. Technical Report ENV-I-070-002, ANSTO – Institute for Environmental Research, Australia, 2008a.

Neklapilova, B.: Electrolysis and small volume distillation of samples for tritium activity analysis, ANSTO internal guideline. Technical Report ENV-I-070-003, ANSTO – Institute for Environmental Research, Australia, 2008b.

Newsom, J.M. and Wilson, J.L.: Flow of Ground Water to a Well Near a Stream – Effect of Ambient Ground-Water Flow Direction. Ground Water, 26: 703-711. DOI: 10.1111/j.1745-6584.1988.tb00420.x, 1988.

Payton Gardner, W., Susong, D.D., Kip Solomon, D., and Heasler, H.: Snowmelt hydrograph interpretation: Revealing watershed scale hydrologic characteristics of the Yellowstone volcanic plateau. J Hydrol, 383: 209-222. DOI: http://dx.doi.org/10.1016/j.jhydrol.2009.12.037, 2010.

Petrides, B. and Cartwright, I.: The hydrogeology and hydrogeochemistry of the Barwon Downs Graben aquifer, southwestern Victoria, Australia. Hydrogeol J, 14: 809-826. DOI: 10.1007/s10040-005-0018-8, 2006.

Post, V.E.A., Vandenbohede, A., Werner, A.D., Maimun, S., and Teubner, M.D.: Groundwater ages in coastal aquifers. Adv in Water Resour, 57: 1-11. DOI: http://dx.doi.org/10.1016/j.advwatres.2013.03.011, 2013.

Quade, J., Chivas, A.R., and McCulloch, M.T.: Strontium and carbon isotope tracers and the origins of soil carbonate in South Australia and Victoria. Palaeogeogr Palaeocl, 113: 103-117. DOI: http://dx.doi.org/10.1016/0031-0182(95)00065-T, 1995.

Reilly, T.E., Plummer, L.N., Phillips, P.J., and Busenberg, E.: The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer. Water Resour Res, 30: 421-433. DOI: 10.1029/93wr02655, 1994.

Samborska, K., Różkowski, A., and Małoszewski, P.: Estimation of groundwater residence time using environmental radioisotopes (14C,T) in carbonate aquifers, southern Poland. Isot Environ Healt St, 49: 73-97. DOI: 10.1080/10256016.2012.677041, 2012.

Scanlon, B., Healy, R., and Cook, P.: Choosing appropriate techniques for quantifying groundwater recharge. Hydrogeol J, 10: 18-39. DOI: 10.1007/s10040-001-0176-2, 2002.

Shentsis, I. and Rosenthal, E.: Recharge of aquifers by flood events in an arid region. Hydrol Process17: 695-712. DOI: 10.1002/hyp.1160, 2003.

Sklash. M.G. and Farvolden, R.N.: The role of groundwater in storm runoff. J Hydrol, 43: 45-65. DOI: http://dx.doi.org/10.1016/0022-1694(79)90164-1, 1979.

Smerdon, B.D., Payton Gardner, W., Harrington, G.A., and Tickell, S.J.: Identifying the contribution of regional groundwater to the baseflow of a tropical river (Daly River, Australia). J Hydrol, 464â€“465: 107-115. DOI: http://dx.doi.org/10.1016/j.jhydrol.2012.06.058, 2012.

Stewart, M.K.: A 40-year record of carbon-14 and tritium in the Christchurch groundwater system, New Zealand: Dating of young samples with carbon-14. J Hydrol, 430: 50-68. DOI: http://dx.doi.org/10.1016/j.jhydrol.2012.01.046, 2012.

Stichler, W., Maeszewski, P., and Moser, H.: Modelling of river water infiltration using oxygen-18 data. J Hydrol, 83: 355-365. DOI: http://dx.doi.org/10.1016/0022-1694(86)90161-7, 1986.

Stuvier, M. And Polach, H.A.: Reporting of ^{14}C data. Radiocarbon, 19: 355-363, 1977.

Stuyfzand, P.J.: Hydrology and water quality aspects of rhine bank groundwater in The Netherlands. J Hydrol, 106: 341-363. DOI: http://dx.doi.org/10.1016/0022-1694(89)90079-6, 1989.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E., and Chisari, R.: Tritium in Australian Precipitation: a 50 Year Record. J Hydrol. DOI: http://dx.doi.org/10.1016/j.jhydrol.2014.03.031, 2014.

Tesoriero, A.J., Spruill, T.B., Mew, H.E., Farrell, K.M., and Harden, S.L.: Nitrogen transport and transformations in a coastal plain watershed: Influence of geomorphology on flow paths and residence times. Water Resour Res, 41: W02008. DOI: 10.1029/2003wr002953, 2005.

Tóth, J.: A theoretical analysis of groundwater flow in small drainage basins. J Geophys Res, 68: 4795-4812. DOI: 10.1029/JZ068i016p04795, 1963.

Unland, N.P., Cartwright, I., Cendón, D.I., and Chisari, R.: Residence times and mixing of water in river banks: implications for recharge and groundwater – surface water exchange. Hydrol. Earth Syst. Sci. Discuss., 11: 1651-1691. DOI: 10.5194/hessd-11-1651-2014, 2014.

Van den Berg, A.H.M., Rock unit names in western Victoria, Seamless Geology Project. Geological Survey of Victoria Report 130. GeoScience Victoria, State of Victoria, Department of Primary Industries, 2009.

Victorian Water Resources Data Warehouse: Victorian Department of Sustainability and Environment Water Resources Data Warehouse, available at http://www.vicwaterdata.net, last access: January 2014.

Vogel, J.C., Grootes, P.M., and Mook, W.G.: Isotopic fractionation between gaseous and dissolved carbon dioxide. Z. Physik, 230: 225-238. DOI: 10.1007/bf01394688, 1970.

Vogel, J.C., Thilo, L., and Van Dijken, M.: Determination of groundwater recharge with tritium. J Hydrol, 23: 131-140. DOI: http://dx.doi.org/10.1016/0022-1694(74)90027-4, 1974.

Vogt, T., Hoehn, E., Schneider, P., Freund, A., Schirmer, M., and Cirpka, O.A.: Fluctuations of electrical conductivity as a natural tracer for bank filtration in a losing stream. Adv

Water Resour, 33: 1296-1308. DOI: http://dx.doi.org/10.1016/j.advwatres.2010.02.007, 2010.

Wigley, T.M.L.: Carbon 14 dating of groundwater from closed and open systems. Water Resour Res, 11: 324-328. DOI: 10.1029/WR011i002p00324, 1975.

Zhai, Y., Wang, J., Teng, Y., and Zuo, R.: Hydrogeochemical and isotopic evidence of groundwater evolution and recharge in aquifers in Beijing Plain, China. Environmental Earth Sciences, 69: 2167-2177. DOI: 10.1007/s12665-012-2045-9, 2013.

Table 1 – Screen depth, Cl, ^{18}O, ^{2}H, ^{13}C, a^{14}C and ^{3}H activities of groundwater samples. [a]Refers to bore name on the Victorian Water Resources Data Warehouse. [b] Measured as depth to the middle of the well screen. [c]^{3}H activities that are below detection.

Sample No.	**Screen Depth (m)**	**EC (μS cm^{-1})**	**Cl**	**Br**	**Na**	**Ca**	**Mg**	**K**	**HCO_3^-**	**SO_4^{2-}**	**δ^{18}O**	**δ^{2}H**	**$\delta^{13}C_{DIC}$ (‰PDB)**	**a^{14}C**		**^{3}H**	
						(mg/L)					**(‰VSMOW)**			**pMC**	**1σ**	**TU**	**1σ**
1a (108899)[a]	29[b]	282	60	0.18	35.1	4.8	2.9	2.2	0.23	0.14	-5.6	-32.7	-21.4	81	0.34	*bd*[c]	-
1b (108916)	14.5	197	38.6	0.12	29.3	3.4	4.1	1/9	0.24	0.09	-5.3	-30.4	-22.1	83.3	0.28	*bd*	-
1c (108917)	14.5	238	44	0.08	20.3	1.0	2.6	0.7	0.44	0.08	-5.3	-31.1	-21.5	77.8	0.29	*bd*	-
2d (108927)	14	430	86	0.07	69.1	16.3	9.9	7.4	0.5	0.36	-5.6	-32	-20	39.5	0.2	*bd*	-
2e (108928)	17	446	96	0.08	76.3	19.9	11	8.6	0.58	0.27	-5.5	-33.6	-19.8	40.9	0.21	*bd*	-
3f (108933)	11.2	491	121	0.1	84	8.6	5.3	9.1	0.52	0.16	-5.6	-34.1	-20.1	33.8	0.20	*bd*	-
3g (108934)	11.5	545	125	0.06	103.8	13.5	8.5	10.5	0.78	0.2	-5.8	-32.4	-20.4	29	0.16	*bd*	-
3h (108935)	11.5	144	27	0.04	19.9	1.7	2.7	0.7	0.12	0.07	-4.8	-31.2	-21.3	88.6	0.17	*bd*	-
4i (108940)	11.5	243	53	9.02	35.4	3.6	3.21	2.2	0.56	0.11	-5.8	-34	-22.3	64	0.24	*bd*	-
4j (108941)	11.5	414	89	0.03	80.3	7.1	3.9	11.5	0.64	0.03	-5.7	-34.3	-21.5	49	0.21	*bd*	-
5k (110737)	42	149	31	0.02	16.9	0.9	2.3	0.7	0.08	0.03	-5.1	-29.4	-22.4	100	0.3	1.24	0.06
5l (80732)	21	200	48	0.1	30	0.33	4.2	0.5	0	0.1	-4.5	-29.7	-24.2	101.5	0.17	1.02	0.03
5m (80735)	21	217	30	0.03	16.5	0.32	10.5	3.6	0	0.11	-4.2	-29.1	-25.3	100.7	0.17	1.47	0.04

Table 2 – Radiocarbon ages of groundwater in the Gellibrand Catchment corrected for calcite dissolution. Uncertainties are calculated varying q by ± 0.1 plus the analytical uncertainty of a^{14}C from *Table 1*

Sample	q	Radiocarbon Age (years)	Uncertainty
1a	0.93	1150	+ 630 / - 980
1b	0.96	1190	+ 360 / - 940
1c	0.93	1520	+ 590 / - 970
2d	0.86	6530	+ 940 / - 1050
2e	0.86	6170	+ 950 / - 1060
3f	0.87	7870	+ 950 / - 1050
3g	0.89	9260	+ 930 / - 1040
3h	0.93	380	+ 630 / - 380
4i	0.97	3440	+ 290 / - 930
4j	0.93	5310	+ 630 / - 980

Figure Captions

Figure 1 – Geology, groundwater flow, and cross sectional view of the upper part of the Gellibrand River Catchment (the Gellibrand Valley). Potentiometric contours for the Eastern View Formation are created from groundwater data (Water Resources Data Warehouse, 2013) and are expressed in metres above Australian Height Datum (mAHD). Sampled groundwater bores are also shown. Letters refer to bores in Table 1.

Figure 2 - (a) Groundwater elevations in bores display clear annual cycles (b) Groundwater head-gradients in the Gellibrand Valley are upwards implying a discharge zone (Victorian Water Resources Data Warehouse, 2013) (c) Flow in the Gellibrand River. Baseflow conditions during summer months transition into high flows in winter following winter rainfall. (Bureau of Meterology, 2013)

Figure 3 – Geochemical characteristics of groundwater in the Eastern View Formation; (a) mCl/Br v mCl (b) mNa/Cl v mCl (c) mCa v $mHCO_3$ (d) mSO_4 v mCa. Rainfall samples are also plotted where measured. Data is from Table 1 with repeat measurements over the sampling period included.

Figure 4 – (a) ^{2}H vs ^{18}O values of the Gellibrand River and surrounding groundwater sampled over March 2011 – August 2013 and the weighted average for rainfall from Adelaide and Melbourne. MMWL = Melbourne Meteoric Water Line (Hughes and Crawford, 2012). GMWL = Global Meteoric Water Line (Clarke and Fritz, 1997). Groundwater with ^{3}H activities > 1 TU are also highlighted. Data is from Table 1 with repeat measurements over the sampling period included. (b) a^{14}C vs ^{18}O of groundwater samples.

Figure 5 - (a) Continuous electrical conductivity monitoring of near-river groundwater. **5** (b). Changes in river height over the study period. Groundwater EC and river level data from deployed Aqua troll 200 (In-Situ) Data Loggers.

Figure 6 – Historical water table fluctuations 1988-2011 for bore 108927 (Victorian Water Resources Data Warehouse, 2013). The magnitude of annual recharge cycles are coherent with those recorded in data loggers over the study period (2011 to 2013)

Figure 7 – Groundwater residences times within the Gellibrand Valley. Residence times up to 9260 years are found in close proximity to the river. Modern local groundwaters with a^{14}C > 100 pMC are situated back on the floodplain. Data from Tables 1 and 2.

Figure 8 – Groundwater flow conceptualisation in the Gellibrand Valley. Though appreciable amounts of recharge are estimated from bore hydrographs and high river flows, the depth to which recharging waters infiltrate into the Eastern View Formation (downward leakage) is limited by strong upward head gradients, and a floodplain which consists of appreciable amounts of silt and clay.

Figure 9 – ^{14}C age v Cl. ^{14}C ages are taken from the calcite corrected ages in *Table 1*