

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).

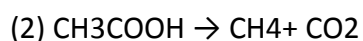
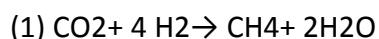
P5956 L3 " Understanding the capacity of rivers to recharge regional groundwater is important in understanding exchange within the hydrological cycle (Stichler et al., 1986; Chen and Chen, 2003). Furthermore, where surface-waters transport contaminants and have the potential to recharge the surrounding 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



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 previously 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 CO₂ by acidification with phosphoric acid and then reduced to a graphite target). The reviewer commented on the possible fractionation of ¹⁴C 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: 2CH₂O -> CO₂ + CH₄ and secondly the direct reduction of DIC in the groundwater via: CO₂ + 4H⁺ -> CH₄ + 2H₂O (Clark and Fritz, 1997; Valentine et al., 2004; Leybourne et al., 2006). ¹³C fractionations between CO₂ and CH₄ are 60-80‰ for CO₂ reduction and 20-50‰ for acetate fermentation. Thus, both processes can produce DIC that is enriched in ¹³C. If acetate fermentation occurs, the enrichment is due to the subsequent dissolution of ¹³C-enriched CO₂ into the groundwater, while if direct reduction of DIC occurs the enrichment is due to the removal of low δ¹³C CH₄. The impact on ¹⁴C activities differs markedly between the two processes. In the case of acetate fermentation, ¹⁴C-free CO₂ is generated from old organic matter that subsequently lowers the a¹⁴C of the DIC. In the case of DIC reduction the ¹⁴C/¹²C fractionation is approximately twice the ¹³C/¹²C fractionation (Clarke and Fritz, 1997), so if methanogenesis raises δ¹³C values by 10‰ (1%), there will be a ~2% increase in a¹⁴C.

While recognising that methanogenesis can potentially have an impact on ¹⁴C 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 δ¹³C values (which should be result from both methanogenesis pathways).
4. In regions where DIC reduction has occurred, the groundwater generally has low to negligible SO₄ and NO₃ 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 possibility.

P 5959: "Radioactive tracers ^{14}C 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 losing 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 ^3H and ^{14}C .

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 SO_4

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

P 5964: " 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 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 ^{13}C signature of DIC close to biogenic precursor of about -23 per mil what means that the speciation (which fractionate ^{13}C (DIC), especially when carbonic acid becomes bicarbonates) is proportionally limited in comparison to CO_2 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 $\delta^{13}\text{C}$ 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 our 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 ^3H 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?)

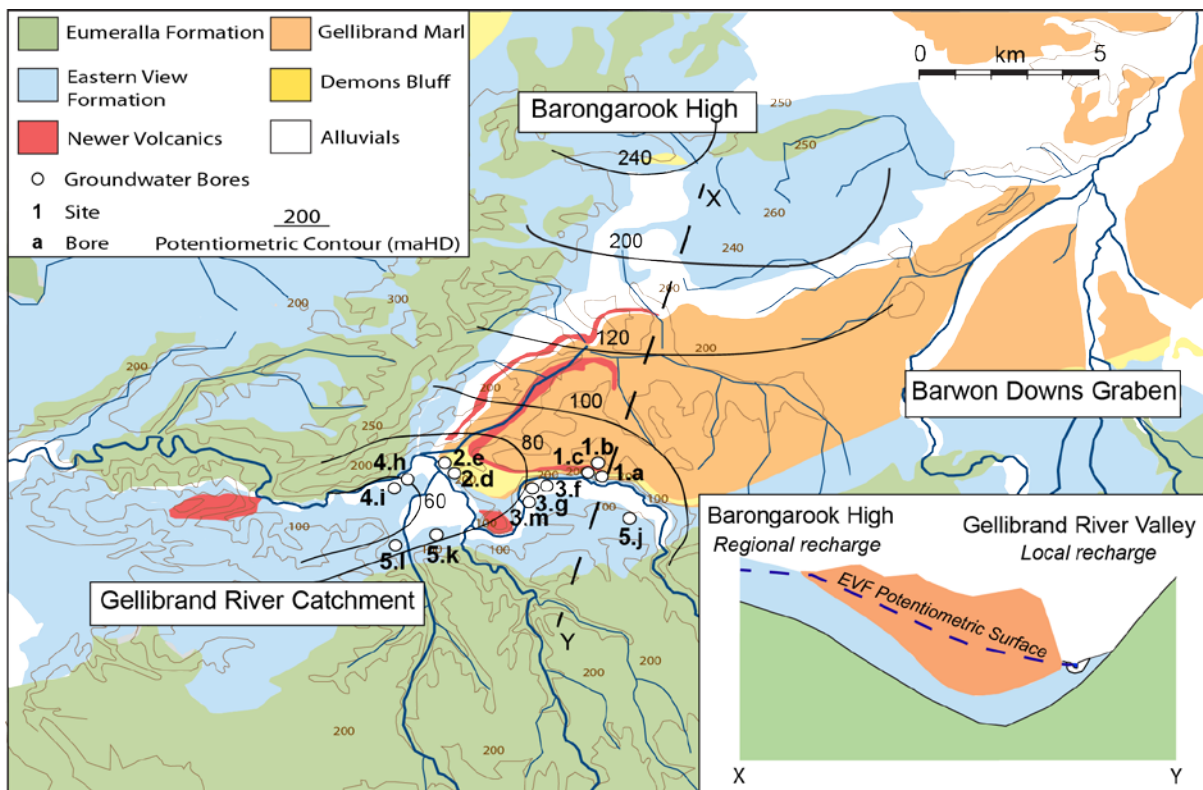
Response: From previous work, we know that groundwater discharges into the river under all but the highest flows, and this was the subject of a separate paper (Atkinson et al., 2013). During low to moderate flows, ^3H activities decline downstream in the Gellibrand River, suggesting an input of old water (most probably regional groundwater) into the river (Atkinson et al., 2013). The "young" ^3H 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 ^3H 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 ^{18}O and ^2H in your discussion. I suggest you to use, if possible, the ^{18}O data coupled with a regional altitude gradient of ^{18}O 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.

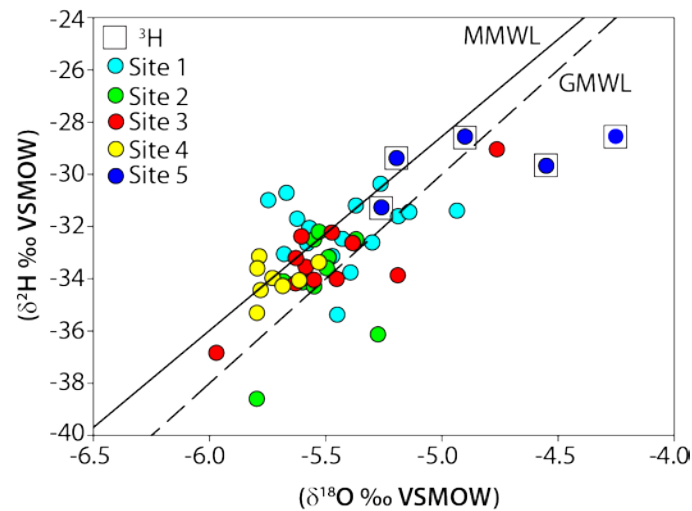
Response: This was a good suggestion that made us examine our data more completely. To investigate this we have regrouped groundwater bores into sites based on location within

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 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data are shown below. The difference in height between the Barongarook High and the Gellibrand Valley is $\sim 150\text{m}$, which assuming typical fractionation gradients of -0.15‰ to -0.5‰ per 100 m for $\delta^{18}\text{O}$ (Clark & Fritz, 1997) should result in $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values than the groundwater recharged in the aquifer window (Site 5). The trend of the waters away from the Meteoric Water Line to higher $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values most likely reflects the altitude effect. Further to this, combining stable isotope data with ^3H 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 $\delta^{18}\text{O}$, ^3H -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 ^{14}C 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 downstream area where the evapo-transpiration is higher. You also mentioned that the older water are generally 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.

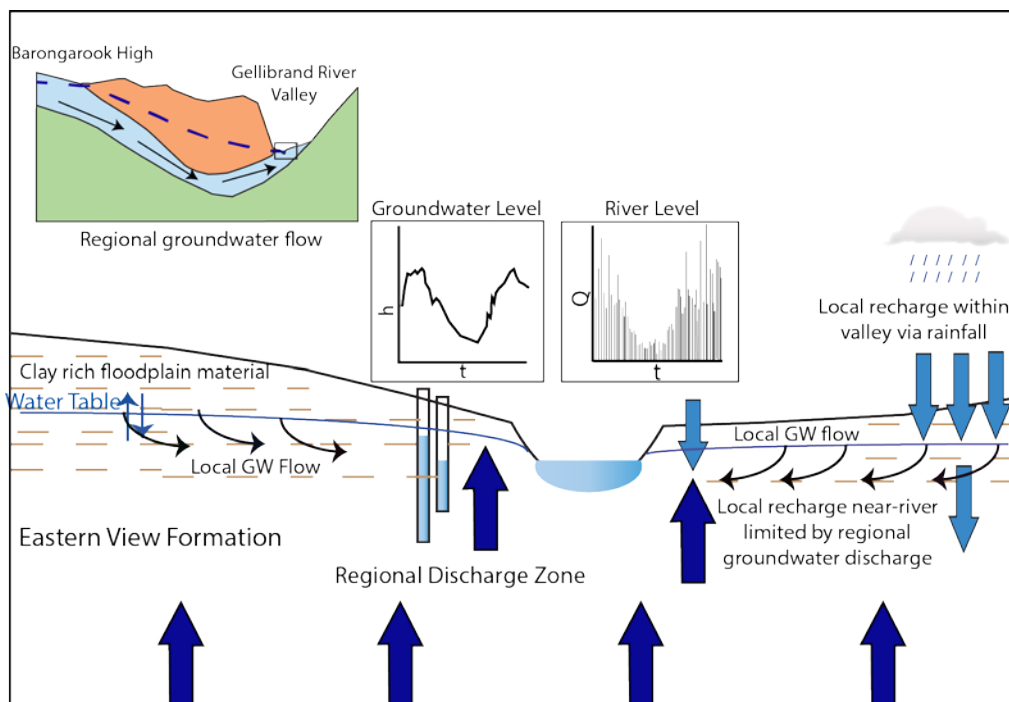
"In many arid/semi-arid areas there are naturally high concentrations of salts stored in soil and groundwater systems due to factors such as low relief, little or no surface drainage, and high rates of evapotranspiration (Herczeg et al., 2001)." (From McEwan et al., 2006.) What do you think?

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) ^3H 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 ^3H 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 ^3H 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.



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