

## ***Interactive comment on “Using $^{14}\text{C}$ and $^3\text{H}$ to understand groundwater flow and recharge in an aquifer window” by A. P. Atkinson et al.***

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Dear authors, dear editors,

Please find my comments about the paper referred as HESS 11- 5953-2014 by Atkinson et al.

I hope these comments will be useful,

Best regards,

Guillaume Bertrand

General comments: In my opinion, this paper provides a good example of the appli-

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cation of natural tracers and especially the dating tracers to help the understanding of the groundwater flows. The text is well written, the pictures are clear. However, in some places, I have some comments (see details below), in particular about the use, or actually, the lack of use of  $^{18}\text{O}$ , that I would think interesting, knowing the apparent ages of water and considering the possible origin from the Barongarook High. Another important comment is about the reactivity of wells (with very old water) with the precipitation variability. In my opinion, it means that the system is somehow "double": There is a recharge from long groundwater flow systems (old waters) but also a recharge from potentially a vertical components. if the authors agree with that, I suggest to strengthen this aspect in the paper, that is not so much highlighted, including in the final conceptual scheme (see my suggestion). About the  $^{14}\text{C}$  and Cl relationships, this linear trend could be a bit more discussed, and in this perspective, I suggest to think about the role of evapotranspiration, not only in the quantity of recharge but also in the geochemical effect (chloride concentration) of evapotranspiration (see my comments below). Considering these observations, I suggest some minor revisions to improve and/or discuss these elements.

Specific remarks:

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

P5956 L 3" Understanding the capacity of rivers to recharge regional groundwater is important in understanding exchange within 5 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 bit useless. I suggest to remove.

P5956 L 16: " 1.1 Radiogenic tracers" This title is the only one in the introduction para-

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graph. Either an other paragraph is missing, either you need to remove this numbering and just include this paragraph in the introduction.

P5956 L 28: " Additionally, geogenic CO<sub>2</sub> and CO<sub>2</sub> generated by the breakdown of organic matter during methanogenesis may provide additional sources of 14C-free DIC" Yes but methanogenesis may be of 2 types

(1) CO<sub>2</sub> + 4 H<sub>2</sub> → CH<sub>4</sub> + 2H<sub>2</sub>O (2) CH<sub>3</sub>COOH → CH<sub>4</sub> + CO<sub>2</sub>

In the type (1) the 14C signature of methane is dependent on the initial signature of CO<sub>2</sub>, which can be rich in 14C (or not....if it is geogenic...). In addition I have a question about CH<sub>4</sub> which is gaseous. Is it integrated in the measurement of 14C in DIC? For example, Aravena and Wassenar (1995) distinguished clearly DIC DOC and CH<sub>4</sub>. Is there any fractionation of 14C of DIC (like for 13C) in case of methanogenesis? Similarly the type 2 leads to production CO<sub>2</sub> (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 "14C free 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 CO<sub>2</sub> previously affected by methanogenesis which lower 14C activities of DIC (e.g. Aravena et al., 1995)

Aravena , Wassenaar, Plummer. 1995. Estimating 14C Groundwater Ages in a Methanogenic Aquifer. *Water Resources Research*31(9): 2307–2317. Bertrand G., Celle-Jeanton H., Look S., Huneau F., Lavastre V. (2013). Contribution of δ<sup>13</sup>C<sub>DIC</sub> and PCO<sub>2</sub>eq measurements to the understanding of groundwater mineralization and carbon patterns in volcanic aquifers. Application to Argnat Basin (Massif Central). *Aquatic Geochemistry* 19(2): 147-171. DOI: 10.1007/s10498-012-9185-0 Federico C., Aiuppa A., Allard P., Bellomo S., Jean-Baptiste P., Parello F., Valenza M. (2002) : Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt

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Vesuvius, Italy. *Geochim. Cosmochim. Acta* 66 (6) : 963–981. 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 15 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 14C.

P 5962: "Ca and O<sub>4</sub> (Fig. 3d)". a S is missing for SO<sub>4</sub>

P 5964: " A handful of groundwater samples have a 1 : 1 Ca : SO<sub>4</sub> 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 precursor of about -23 permil what means that the speciation (which fractionate 13C (DIC), especially when carbonic acid becomes bicarbonates) is proportionally limited in comparison to CO<sub>2</sub> dissolution in the water.

P 5965: " Regardless, estimates using bore hydrographs indicate that significant groundwater recharge to the unconfined Eastern View aquifer in the valley occurs via 20 diffuse recharge." I can not understand the linkage with the recharge estimation you

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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.

P5968: " Additionally the activities of 3H in near-river bores are negligible, 5 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." 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 it is not the 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 ( p 5969), but how to explain the "young" 3H signature (equilibrium?, subsurface flow when it is raining?)

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." I agree that applying the Darcy law strengthen this hypothesis but 2 remarks 1) Up to now you did not proved it. 2) Related to this, 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 altitudinal 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.

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 relationship to river height (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

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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.

(See figure in the attached pdf)

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?

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 downstream area, where the evapo-transpiration is higher. You also mentionned 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.

(See figure in the attached pdf)

"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)

McEwan et al., 2006. Available via <http://www.clw.csiro.au/publications/science/2006/sr53-06.pdf>

What do you think?

Please also note the supplement to this comment:

<http://www.hydrol-earth-syst-sci-discuss.net/11/C2189/2014/hessd-11-C2189-2014-supplement.pdf>

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