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Discussions

Interactive comment on "Assessment of Halon-1301 as a groundwater age tracer" *by* M. Beyer et al.

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Response to Anonymous Referee #2

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 12, 1397, 2015.

Dear reviewer,

Many thanks for your constructive and helpful feedback on our manuscript. In the following we comment on each of your remarks and state which changes have been made according to your feedback.

Kind regards

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Interactive Discussion
Discussion Paper

Monique Beyer

I agree with the comments and remarks of reviewer 1, and concur with his opinion on the potential usefulness of this manuscript for groundwater dating. The methodology presented by the authors seems sound, and is presented in a very clear and systematic manner. I also find the response of the authors to the comments of reviewer 1 convincing and satisfactory (with the exception of the MRT comparison, which I come back to further below). Thus, I will simply add additional suggestions along the same lines as reviewer 1. But for minor modifications, the manuscript seems to me ready for publication specific comments:

P1398:

L1-3: “assess” twice in the first sentence.

L8: there are other ways to complement tracer information. Discharge recession analysis or groundwater level fluctuations, for instance.

⇒ We agree and changed these as suggested.

L9: “vital” may be a bit strong. How about “useful”?

⇒ Thanks for this comments. We changed ‘vital’ to ‘important’ and added: . . .need to be applied complementarily ‘(or other characterization methods need to be used to complement tracer information)’

L20: “investigated aquifer” may be more correct than “investigated groundwater”.

⇒ Thanks for pointing this out. We changed ‘investigated groundwater’ to ‘investigated groundwater samples’.

P1399: L4: “revealed by elevated CFC concentrations” rather than “via elevated...” L5: “no sample showed” rather than “no sample revealed” L6: “the absence” and not “the lack”

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⇒ We agree and changed these as suggested.

L 11: “standalone indication for quality”. References?

⇒ Thanks for pointing this out. We added relevant references (the New Zealand drinking water standard and the European Water Framework Directive). We removed ‘standalone’ to avoid confusion, since groundwater age data are used in combination with hydrochemistry data to assess the quality and contamination risks of groundwater (according to these 2 references).

L25: “can be calculated from tritium measurements” rather than “with tritium can be faced” L27: “this is particularly true” rather than “this is particularly relevant” P1400: L2: Is there a reason for not citing the papers in chronological order (either from younger to older or the other way around)?

⇒ We agree and changed these accordingly.

L5: An important reference is missing: Grabczak, J., P Maloszewski, et aL (1984). "Estimation of the tritium input function with the aid of stabile isotopes." Catena 11(2/3): 105-114. In my opinion the soundest way to weight the tritium input function.

⇒ Thanks for pointing this out. We added this reference to our paper.

L8: Your statement is too performative. If the limitations you mention can be overcome, why would we need “complementary groundwater age tracers” ? I do not disagree with you, but I think such a statement needs qualification. As it is, it reads more like an activist appeal to politicians than an scientific utterance.

⇒ We agree and changed ‘ensure’ to ‘allow for’ making the sentence less perfomative.

L11: “in” instead of “within” P1401: L4: “like THE structurally similar CFCs” L 9: “Does its use as a fire suppressing agent” rather than “Does its use for fire suppression” L 12: “note” is unnecessary L 17: Would not “aquifer” be more appropriate than “groundwater L 20: How about “In this way, problems such as contamination due to contact with air

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during sampling or local (anthropogenic) sources can be identified"? "Issues" is not a good synonym for "problems" in this context

⇒ We agree and changed these accordingly

P1402: L4: Are the diffusion rates in air (and water) similar? Differences between deuterium and oxygen-18 for instance are quite significant, if I remember well

⇒ We agree and changed this to: 'Because Halon-1301 and SF6 are both gaseous tracers, they are expected to show similar transport and exchange processes through behaviour in the unsaturated zone.'

L17: Is the groundwater in New Zealand so homogeneous that you can refer to it as just that, "groundwater"? P1403: L7: "is shown" rather than "is illustrated" L12: One does not determine observations. How about "the number of CFC (...), SF6 and tritium observations available for these sites" ? L16: "and is recharged both by rain and river infiltration" rather than "both rain and river recharged" L25: "not the water stagnating" rather than "not the water sitting"

⇒ We agree and changed these following your suggestions.

L27: This is not clear. Did you always measure pH, conductivity and DO, or only sometimes? Which sites were sampled how?

→ Thanks for pointing this out. In fact for all wells DO, Cond. and pH were measured. We changed this to: 'wells were flushed at least 3 times of their volume until DO, Cond. and pH were stabilized.'

P1404: L6: "Then the bottle is left to overflow," L12: "no contamination by SF6 or Halon-1301 from the air" L14: "in the surrounding areas" and not "in our close environment"

⇒ We agree and changed these accordingly.

P1405: L14: Is there a good reason to drop the intercept term? Helsel and Hirsch, in their excellent book entitled "Statistical methods in water resources", USGS, book 4,

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chapter 3 (chapter 9, P238-239), warn against it.

⇒ Thanks for this comment. We added the following as a foot note to the paper. 'We analysed blank samples (only containing N2) which indicated 0 signal for SF6 and Halon-1301. Additionally the statistical difference between the intercept of the calibration curves for SF6 and Halon-1301 (when not forced through 0/0) were not significant (at 99% confidence). The intercept of the calibration curve was therefore considered insignificantly different from 0, hence the calibration curve was forced through 0/0 to simplify the calibration procedure and to ensure 0 signal is interpreted as a concentration of 0 (fmol/L, e.g.). This procedure is following the suggestions of Helsel and Hirsch (2002) and Caulcutt and Boddy (1983).'

P1406: L5: "which we took into account", not "which we took into account of" P1407: L6: "we use the commonly used" is a bit ponderous. How about "we adopt the commonly used" ? L25: "This guide recommends" instead of "This recommends" P1408: L3: This is where dropping the intercept term of the regression becomes problematic, because it can influence the uncertainty estimate of the whole regression. The same applies to the SD introduced L18. P1411, L8: There is one "(" too many.

⇒ We agree and made changes as suggested.

P1412, L19-25: Maybe you could drop this paragraph altogether? After all, you argue that so-called "apparent" piston-flow ages are "unrealistic" (and I agree). They are also useless in practice (unless the geometry of the groundwater system and sampling design lead to the sampling of parallel streamlines, of course) and tend to confuse people. I should think that in the present study, only EPM ages are relevant at all. I would also for the same reason, and because it clutters the plot, drop the PF points on figure 7.

⇒ Thanks for this comment. We decided to keep this paragraph (and Fig. 7) as it shows that for Halon-1301 the (right) choice of mixing model is particularly important for the determination of groundwater age from Halon-1301 concentrations. We ar-

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gue that due to this one may be able to better constrain the mixing model with aid of (time-series) Halon-1301 data than when using SF6 (due to their characteristic input functions - Halon-1301 with a S-shaped atmospheric trend and SF6 with a nearly linear atmospheric trend).

P1413: L10: The relationship between Halon-1301 and SF6 looks indeed rather linear, but what was exactly your criterion for "agreement"? You use further below the word agreement again, so I think you should explain what "disagreement" would look like. Line 27 for instance, you mention an interval of +/-2 years. It is only in your conclusion that you seem to explicitly recognise the interval of +/-2 years as your criterion for "agreement". Would not a relative measure be more adequate, since the MRTs span an order or magnitude?

⇒ We agree and changed the requirement for agreement/disagreement from 'within +/-2 years' to 'within uncertainty bounds of 1 SD (except for 1 site (Johnston) where we considered 1.1 SD as acceptable)' Using a relative difference as criterion for agreement is in principle better, but would not reflect the uncertainty in inferred age. In addition a relative difference would be slightly difficult to determine (and potentially misleading) when looking at modern water samples (close to 0 years old) – we cannot precisely determine if the water is 1 or 5 days old and this was not the purpose of this study. The purpose was to show that inferred Halon-1301 ages agree with SF6 and/or tritium within an acceptable range (we chose within 1 (or 1.1 for the Johnston well) sigma uncertainty bounds, as commonly used within the science community to differentiate significant from insignificant.

L18: "At one of the eighteen sites" instead of "At 1 of 18 sites" L16: "of twelve out of seventeen" instead of "of 12/17" P1414, L13: This sentence is awkward. P1415, L5: You do not find "lag-time" in a sample as you would measure concentration, you can only calculate it from the data P1416, L11: "is only likely to occur" instead of "is likely only occurring" L26: cross out the "," P1417, L16: "despite of the fact that" instead of "despite that". Further below (L25), "Despite of these" instead of "Despite these".

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Check how to use “despite” properly P1418, L9: “of local contamination sources”

⇒ Thanks for these comments. We agree and changed these following your suggestions.

Table 1: The units are missing for SF6, CFC and tritium

⇒ Thanks for pointing this out. This column shows the number of available SF6, tritium and CFC measurements, so no unit. We changed the column header from ‘# SF6 data’ to ‘# of SF6 data’ for more clarity.

Figure 1: I would plot both y-axis labels turned counter clockwise. As it is, one need to twist the head first in one direction, then in the other

⇒ We agree and changed this accordingly.

Figure 7: As I wrote above, I think you should use the EPM ages only

⇒ Thanks for this comment. We decided to keep the Figure please see comment above (for P1412, L19-25) for detail on the reasoning behind this decision.

Figure 8 and Table 3: Apparently, this figure shows the 12 sites for which the estimated ages were presented in the text to lie within two years between tritium and Halon-1301 (P1417, L12). The discrepancy between MRTs obtained from tritium and those calculated from Halon-1301 or SF6 seem much higher than that on the figure, and so is the difference between the MRTs given in column 9 and 16 of table 3. Reviewer 1 also pointed to this, and I do not think the authors clarified that point in their answer.

⇒ Thanks for pointing this out. We hope this is less confusion now that we changed the criterion for agreement/disagreement to +/- 1 SD (with an exception of 1 site where we considered 1.1 SD as acceptable) and added more info for clarification to the paper (please see comment on P1413: L10 for details). With this criterion inferred Halon-1301 MRTs do agree with inferred SF6 and/or tritium MRTs.

Figure 9: Bar plots do not allow to grasp synoptic differences, and this one is no excep-

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tion. If you want to show the differences, or the absence of differences at two points in time, not on a station to station basis, but for the entire dataset, a scatter plot of initial versus final equivalent atmospheric concentrations might be much clearer, as it would show a possible general trend at first sight. I am also not quite sure of the meaning of the sentence “analysed directly after sampling (2 of 3)” in the caption. Does that mean that the two first bars for each site labeled “initial” were replicates?

⇒ Thanks for these comments. We would like to comment on your last comment (reg. replicate samples) first: Yes, the first two bars were replicate water samples (in fact all 3 were replicate samples from which two of them were analysed shortly after sampling and the third one was analysed after storage) to illustrate the variation from water sample to water sample (the analytical uncertainty is illustrated as error bars). ⇒ To your fist comment (reg. change this plot to a scatter plot): We agree in principle with your comment. We think in our case, however, significant differences are relatively easy to spot as the uncertainty in Halon-1301 concentrations is relatively large (a significant difference would need to lie outside the range of analytical uncertainty). In addition we think a scatter plot would be confusing as there are two initial samples and each well would plot rather randomly across the figure.

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