

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

M. Beyer et al.

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My apologies, I have previously accidentally uploaded the penultimate version of the response to reviewer 1. Please disregard our previous post and find the ultimate version of the response to reviewer 1 below.

Kind regards

Monique Beyer

Dear reviewer,

C593

Many thanks for your feedback on our manuscript which will greatly enrich our paper. In the following we comment on each of your remarks and state which changes will be made according to your feedback once we have also received comments from the 2nd reviewer.

Kind regards

Monique Beyer

Anonymous Referee #1; Received and published: 1 March 2015: Water age dating is of fundamental importance in hydrology and hydrogeology since it provides quantitative information on the time scales of water movement through catchments. This has implications for both water resources, fluxes and processing times of biogeochemically relevant ions and molecules. Despite the importance of water age dating, there are very few tools that can be used in a quantitative manner to measure water residence times. The paper presented by Beyer et al further investigates the use of Halon-1301 as a new tracer for dating of young water in groundwater systems. Thus the paper makes a potentially important contribution to the available methods for dating groundwater. Technically the paper is sound and in my opinion needs only minor revisions. My main concern is that this new tracer actually gives us no new information to the methods already available. SF6 for example is actually more sensitive as atmospheric concentrations are rapidly increasing, making it a more suitable gaseous tracer. Moreover, tritium is considered the most robust tracer, especially in the southern hemisphere. So I would ask the authors what Halon-1301 provides that tritium and SF6 don't. This may lie in finding a unique solution to model parameters, but if so this needs to be further explored in the paper.

→ We suggest that the mixing model and mixing parameter may be better constrained with Halon-1301, due to its S-shaped input function (compared to SF6 with a nearly linear input function). However, we do not have time series data to support this supposition. This needs to be evaluated further. More generally, the simultaneous deter-

C594

mination of Halon-1301 and SF6 (2 gaseous tracers) has the advantage over single SF6 analysis that causes for differences in gas (e.g. SF6) and tritium ages can be identified, such as unsaturated zone travel time or contact with air during sampling, as we showed in our study. Halon-1301 can also aid to better constrain the unsaturated zone travel time (if applicable). In addition, each tracer, including SF6 and tritium, can be subject to contamination or uncertainties like contamination. A third tracer can help identify such problems and improve the robustness of the dating. We will try to bring out the above mentioned points more in our paper.

Minor points: The paper is rather difficult to read, and I found myself often being caught up in the grammar than concentrating on the ideas presented in the paper. This is mostly because the paper is written in present tense, which is quite strange, especially when referring to samples taken and measured in the past. I would highly recommend that the authors change the text to past tense, as this will help with many of the disconcerting sentences and allow the reader to better concentrate on the ideas and methods rather than constantly having the feeling that something is wrong with the grammar.

→Thanks for this comment. We have tried this and agree that the past tense improves the readability of the paper. We will change the tense to past tense.

P1405 Line 15: the authors give first an approximate measured volume (10ml) and then the exact volume ($9.97 \pm 0.02\text{ml}$). This is redundancy, just give one or the other, I suggest that the exact volume is given, although this has also been discussed in the methods section.

→We agree and will change this to ' $9.97 \pm 0.02\text{ml}$ (in the following referred to as 10ml).

P1406 Line10-15: The authors state that the data from Deeds 2008 cannot be considered robust because they come from a PhD thesis. In my experience some very good data is contained in PhD work that unfortunately never gets published. Thus while the authors may be correct as suggested later in the paper, the fact that the data come

C595

from a PhD thesis is in my opinion no grounds for the data to be considered in error.

→ We will state more clearly in our paper that the solubility estimation for Halon-1301 in Deeds (2008) have been constructed using the solubility estimation methods of Meylan and Howard (1991) and Meylan et al. (1996). Actual measurements of the solubility of Halon-1301 are not available in literature (according to our searches and further backed up by personal communication with Daniel Deeds, 06/03/2015).

P1406 Lines 20-25: How sure can the authors be that Halon-1301 is well mixed across the atmosphere of the southern hemisphere?

→ We will add the following to the paper: The differences in Halon-1301 concentrations between the southern and northern hemisphere are very low (see Montzka et al., 2003 and Butler et al., 1998). Although a comprehensive analysis of potential local sources has not yet been carried out, studies such as that by Barletta (2011) in Los Angeles, US, have not found local enhancement of Halon-1301 in city environments. Butler et al. state that the sources of Halon-1301 in the southern hemisphere have only a minor contribution to the overall concentration of Halon-1301 in the atmosphere. In addition, the Wellington area is dominated by maritime air masses. Local sources (if present) are expected to have an insignificant effect on the atmospheric concentration of Halon-1301 (as we confirmed with regular measurements of local air). These findings support our assumption that concentrations of Halon-1301 in our study area are fairly well mixed and that southern hemisphere atmospheric concentrations can be used to estimate concentrations of Halon-1301 in recharge. There is only 1 study we are aware of, that showed unusual fluctuations of Halon-1301 in the atmosphere in Krakow and at Kasprowy Wierch station in Poland. The group is still investigating reasons, but speculate it may be attributed to local sources from close-by city/industry environments [Bartyzel, 2015].

P1410 section 3.2: There is a fundamental difference between quantification limit and detection limit. Thus the authors cannot calculate a water age at the detection limit

C596

(since this statistic only determines if the gas can be detected or not), but need instead to do this at the limit of quantification. Other than this, the authors have provided a very robust estimation on error and error propagation.

→ We agree and now state the minimum determinable recharge year at the LOQ.

P1401: Solubility: there is a lot of noise in the data generated by the authors, much more than in Deeds 2008. Why is this and why didn't the authors do the solubility experiments in the classical way of exposing a known volume of water to a known concentration of Halon-1301? The noise in the data can also be seen in SF6.

→ Measurement of the solubility of Halon-1301 is beyond the scope of this study. Due to the extremely low solubility of Halon-1301, specialised equipment is required. We make an estimate that is sufficient to demonstrate that Halon-1301 has potential as age tracer, and make the case that accurate solubility is required to encourage research groups specialised in this to measure the solubility. The solubility reported by Deeds (2008) has been estimated using structural estimation methods, therefore the solubility data plotted in Deeds (2008) appear to be smooth. We estimated the solubility using modern groundwater and river water. The scatter in the data can be explained by unaccounted heterogeneity, unaccounted mixing of water and uncertainty in recharge temperature, etc. We will add these points to our paper.

General: Halon-1301 vs other tracers: the authors state that the data agree very well with a few exceptions. Firstly, there is no Halon-1301 or SF6 plotted in Figure 8 where ages are compared between 3H and CFCs. This makes it difficult for me as the reviewer to evaluate how well the ages agree. When looking at table 3 I found it hard to identify which MRTs correlated with which tracer. But if I understood the table properly, there are many dates that are quite different e.g. Lake Ferry MC, Seaview Wools, IBM2. If I am mistaken I would ask the authors to make the table clearer.

→ Thanks for this comment and sorry about the confusion. Fig. 8 plots Halon-1301 and SF6 ages vs. tritium ages with a colour code highlighting if CFC contamination

C597

or degradation had been observed. We will change the legend and description of the figure to make this clearer.

General: There are also MRTs listed that are below the quantification limit of the tracers. → The inferred MRT is dependent on the mixing model and mixing parameter, so it may be possible that MRTs stated in Table 3 are below the piston flow MRT equivalent to the LOD of Halon-1301.

General: One of the assumptions in the models used to quantify the MRT is that the MRT and the distribution of residence times around the mean is stationary. Is this a reasonable assumption at the sites studied here? This may have implications for comparing data measured in the paper with previous measurements of 3H.

→ Since we only determine 1 Halon-1301 measurement at each site, it is not possible to constrain both the mixing parameter and the MRT. We therefore use the mixing parameter inferred with tritium and SF6 time series data to infer MRTs from Halon-1301 concentrations. For that we assume steady state flow conditions in each well from the time of the first tritium and SF6 measurement until the time of the Halon-1301 measurement. Assessment of historical hydrochemistry data (using trend and seasonality analysis) suggests this is a reasonable assumption. - We will add the latter point to our paper.

Plots: please indicate if the lines are 1:1 lines, which would be good, or simply lines of best fit. 'ff' is given in italics in all words.

→ We agree with this and will add a 1:1 line to each figure (where appropriate).

References: Meylan, W. M., Howard, P. H. and Boethling, R. S. (1996), Improved method for estimating water solubility from octanol/water partition coefficient. *Environmental Toxicology and Chemistry*, 15: 100–106. doi: 10.1002/etc.5620150205.

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C598

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Bartyzel, J. (2015). Wykorzystanie środowiskowych znaczników gazowych (SF₆, SF₅CF₃, CCl₂F₂, CBrF₃) do datowania wód podziemnych – zagadnienia metodyczne i zastosowania. PhD thesis at the University of AGH University of Science and Technology in Kraków, Poland.

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