

**Dear Markus Hrachowitz,**

**Many thanks for your and the two reviewers helpful feedback on our manuscript.**

**We agree with your comment regarding the clarification of the use of Halon-1301 as a complementary age tracer (as opposed to using it as a stand-alone tracer). Following your feedback, we have added a paragraph in the summary and conclusion to highlight this.**

**We agree with both reviewers' comments and have made changes accordingly. Please find below the detailed comments on both reviewers' feedback and the changes we have made to the manuscript following their suggestions.**

**Please also find below the changed manuscript with highlighted changes as uploaded. All authors have sighted and are happy with this version of the document.**

**Kind regards**

**Monique Beyer**

## Response to Anonymous Referee #1

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

Dear reviewer,

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 2<sup>nd</sup> 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. SF<sub>6</sub> 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 SF<sub>6</sub> 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 SF<sub>6</sub> 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 determination of Halon-1301 and SF<sub>6</sub> (2 gaseous tracers) has the advantage over single SF<sub>6</sub> analysis that causes for differences in gas (e.g. SF<sub>6</sub>) 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 SF<sub>6</sub> 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 be-

cause 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 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 (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 Figure8 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 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 SF<sub>6</sub> 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 SF<sub>6</sub> 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.

Meylan, W. M. and Howard, P. H. (1991), Bond contribution method for estimating henry's law constants. *Environmental Toxicology and Chemistry*, 10: 1283–1293. doi: 10.1002/etc.5620101007.

Montzka, S. A. and P. J. Fraser (2003), Controlled substances and other gases, in *scientific Assessment of Ozone Depletion: 2002*, pp. 1 – 87, World Meteorol. Org., Geneva.

Butler, J. H., S. A. Montzka, A. D. Clarke, J. M. Lobert, and J. W. Elkins (1998), Growth and distribution of halons in the atmosphere, *J. Geophys. Res.*, 103(D1), 1503–1511, doi:10.1029/97JD02853.

Barletta, B., P. Nissenson, S. Meinardi, D. Dabdub, F. Sherwood Rowland, R. A. VanCuren, J. Pederson, G. S. Diskin, and D. R. Blake (2011) HFC-152a and HFC-134a emission estimates and characterization of CFCs, CFC replacements, and other halogenated solvents measured during the 2008 ARCTAS campaign (CARB phase) over the South Coast Air Basin of California, *Atmos. Chem. Phys.*, 11(6), 2655-2669.

Bartyzel, J. (2015). Wykorzystanie środowiskowych znaczników gazowych (SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub>, CCl<sub>2</sub>F<sub>2</sub>, CBrF<sub>3</sub>) do datowania wód podziemnych – zagadnienia metodyczne i zastosowania. PhD thesis at the University of AGH University of Science and Technology in Kraków, Poland.

## 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 (highlighted in bold) we comment on each of your remarks and state which changes have been made according to your feedback.

Kind regards

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”

→ **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 ‘stand-alone’ 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 stable 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 a scientific utterance.

→ **We agree and changed 'ensure' to 'allow for' making the sentence less performative.**

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

→ **Thanks for these comments. We agree and changed this accordingly.**

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 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 SF<sub>6</sub> 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"

→ **Thanks for these comments. We agree and changed these accordingly.**

L12: One does not determine observations. How about "the number of CFC (...), SF<sub>6</sub> and tritium observations available for these sites" ?

→ **We agree and changed this to: previously taken CFC, SF<sub>6</sub> and tritium measurements.**

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

→ **Thanks for pointing this out. We added the following as a foot note to the paper. ‘We analysed blank samples (only containing N<sub>2</sub>) 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 argue 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?

→ **Thanks for this comment. 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.

→ **Thanks for these comments. We agree and changed these as suggested.**

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”. 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 exception. 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 first 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.**

## 1 Changed manuscript with highlighted changes:

### 3 Assessment of Halon-1301 as a groundwater age tracer

5 Monique Beyer<sup>1,2</sup>, Rob van der Raaij<sup>2</sup>, Uwe Morgenstern<sup>2</sup>, Bethanna Jackson<sup>1</sup>

6 [1] {School of Geography, Environment and Earth Sciences, Victoria University of Wellington,  
7 Wellington, New Zealand}

8 [2] {Department of Hydrogeology, GNS Science, Avalon, New Zealand}

9 Correspondence to: M. Beyer (Monique.beyer@vuw.ac.nz)

#### 11 Abstract

12 Groundwater dating is an important tool to assess groundwater resources in regards to their  
13 dynamics, i.e. direction and time scale of groundwater flow and recharge, contamination risks and  
14 manage remediation. To infer groundwater age information, a combination of different  
15 environmental tracers, such as tritium and SF<sub>6</sub>, are commonly used. However, ambiguous age  
16 interpretations are often faced, due to a limited set of available tracers and their individual  
17 restricted application ranges. For more robust groundwater dating multiple tracers need to be  
18 applied complementarily (or other characterization methods need to be used to complement tracer  
19 information). It is important that additional, groundwater age tracers are found to ensure robust  
20 groundwater dating in future.

21 We have recently suggested that Halon-1301, a water soluble and entirely anthropogenic gaseous  
22 substance, may be a promising candidate, but its behaviour in water and suitability as a groundwater  
23 age tracer had not yet been assessed in detail. In this study, we determined Halon-1301 and inferred  
24 age information in 17 New Zealand groundwater samples and various modern (river) water samples.  
25 The samples were simultaneously analysed for Halon-1301 and SF<sub>6</sub>, which allowed for identification  
26 of issues such as contamination of the water with modern air during sampling. All analysed  
27 groundwater sites had also been previously dated with tritium, CFC-12, CFC-11 and SF<sub>6</sub>, and  
28 exhibited mean residence times ranging from modern (close to 0 years) to over 100 years. The  
29 investigated groundwater samples ranged from oxic to highly anoxic. All samples with available CFC  
30 data were either degraded and/or contaminated in one or both CFC-11 and CFC-12. This allowed us  
31 to make a first attempt of assessing the conservativeness of Halon-1301 in water, in terms of  
32 presence of local sources and its sensitivity towards degradation etc., which could affect the  
33 suitability of Halon-1301 as groundwater age tracer.

34 Overall we found Halon-1301 reliably inferred the mean residence time of groundwater recharged  
35 between 1980 and 2014. Where direct age comparison could be made 71% of mean age estimates  
36 for the studied groundwater sites were in agreement with ages inferred from tritium and SF<sub>6</sub> (within  
37 an uncertainty of 1 standard deviation). The remaining (anoxic) sites showed reduced concentrations  
38 of Halon-1301 along with even further reduced concentrations of CFCs. The reason(s) for this need  
39 to be further assessed, but are likely to be caused by sorption or degradation of the compounds.  
40 Despite some groundwater samples showing evidence of contamination from industrial or

41 agricultural sources (inferred by elevated CFC concentrations), no sample showed significantly  
42 elevated concentration of Halon-1301, which suggests no local anthropogenic or geologic sources of  
43 Halon-1301 contamination.

## 44 1 Introduction

45 Groundwater dating is a widely applied technique to determine groundwater flow parameters, e.g.  
46 recharge source and rate, flow direction and rate, residence time and volume. Age in itself is also  
47 increasingly used as a indication for quality and contamination risks (e.g. the New Zealand drinking  
48 water standard [Ministry of Health, 2008] and the European Water Framework Directive [EU  
49 Legislature, 2000]).

50 Tracers, such as tritium, SF<sub>6</sub> and various CFCs, are commonly used to infer groundwater age of  
51 relatively young groundwater (recharged <100 years ago) by comparing their atmospheric history to  
52 their concentration found in groundwater. However, all tracers have a restricted application range  
53 and face individual limitations, which can lead to ambiguous age interpretations [e.g. Allison and  
54 Hughes, 1978; Edmunds and Walton, 1980; Visser, 2009; Beyer et al., 2014a and references therein].  
55 As examples of these limitations, SF<sub>6</sub> has natural sources [e.g. Bunsenberg and Plummer 2000 and  
56 2008; Stewart and Morgenstern, 2001; Koh et al. 2007], CFCs have a stagnant input function  
57 [Bullister, 2011], have anthropogenic point sources (e.g. in industrial and horticultural areas) [e.g.  
58 Oster et al. 1996; Stewart and Morgenstern, 2001; Bunsenberg and Plummer, 2008 & 2010; Cook et  
59 al., 2006] and are known to be degradable in anoxic environments [e.g. Lesage et al., 1990; Bullister  
60 and Lee, 1995; Oster et al., 1996; Shapiro et al., 1997]. Ambiguous age interpretations can be  
61 inferred from tritium measurements due to similar rates of radioactive decay and decrease in  
62 atmospheric concentration, which leads to similar concentrations of tritium in groundwater  
63 recharged at different times. This is particularly true for the northern hemisphere, where  
64 concentrations in young groundwater are still elevated due to H bomb testing in the 1970s [Taylor et  
65 al., 1992; Morgenstern and Taylor, 2009; Morgenstern et al. 2010]. Additional interpretation issues  
66 follow from both the seasonal variability of groundwater recharge and tritium in rain. In these  
67 situations the tritium recharge is often estimated using recharge weighting techniques [Allison and  
68 Hughes, 1978; Stewart and Taylor, 1981; Grabczak et al., 1984; Engesgaard et al., 1996; Knott and  
69 Olipio, 2001, Morgenstern et al., 2010]. These limitations with ambiguity and input uncertainty can  
70 be overcome by time series or multiple tracer observations. To allow for more robust age  
71 interpretation of (relatively young) groundwater in future, there is a need for additional,  
72 complementary groundwater age tracers.

73 We have previously and unexpectedly identified the presence of Halon-1301 (CBrF<sub>3</sub>) in modern  
74 water samples. Our paper immediately following this discovery [Beyer et al, 2014b] has detailed this  
75 identification, has discussed known Halon-1301 properties, and has suggested this compound might  
76 have potential as a new, complementary groundwater age tracer (for water recharged <100 years  
77 ago) to join the limited set of established compounds commonly used for this purpose. We have not  
78 inferred ages from Halon-1301 concentrations in that paper. However we have provided a first  
79 insight into its performance by approximating Halon-1301 ages derived from corrected CFC-13 data  
80 presented in Busenberg and Plummer, [2008]. In this work, we analysed Halon-1301 in a range of  
81 groundwater locations, inferred Halon-1301 ages from its concentration, and compared these to  
82 groundwater ages previously inferred from other tracers. We additionally commented on (and  
83 analysed where possible) the various properties of Halon-1301 that had not previously been  
84 assessed in detail but may affect its wide-scale applicability as an age tracer.

85 As discussed in that earlier paper [Beyer et al., 2014b], Halon-1301 appears to be a suitable  
86 groundwater age tracer, since it is soluble in water (saturation: 30 mg/L at 20°C; in contact with  
87 modern air (3.2 pptv): 7.5 fmol/L at 20°C, 10 m elevation) [Deeds, 2008] and its increasing  
88 atmospheric concentration has been determined in the atmosphere since the 1970s by NOAA  
89 (National Oceanic and Atmospheric Administration) and AGAGE (Advanced Global Atmospheric  
90 Experiment) and data from 1969 to 1977 were reconstructed by Butler et al. (1999) (Fig. 1). Open  
91 questions remained regarding its conservativeness and contamination potential in groundwater  
92 environments. These are:

- 93 • Is Halon-1301 degrading like the structurally similar CFCs in anoxic groundwater [e.g. Plummer  
94 and Busenberg 1999] or due to hydrolysis [e.g. Butler et al., 1991; Sturges et al., 1991; Kanta Rao  
95 et al., 2003]?
- 96 • Does Halon-1301 sorb to organic material in soil or elute from sampling material as suggested for  
97 CFCs [Reynolds et al., 1990; Cook and Solomon, 1995]?
- 98 • Does its use as a fire suppression agent and occurrence as a by-product during pesticide (Fipronil)  
99 production lead to 'local' contamination of groundwater?
- 100 • Can the interference of CFC-13 or other co-eluting compounds and Halon-1301 signals lead to  
101 overestimated Halon-1301 concentrations in water (potential co-eluting candidates are listed in  
102 Beyer et al., [2014b])?
- 103 • Most importantly, do the overall answers to these questions mean Halon-1301 can be used to  
104 reliably infer groundwater age in a wide variety of environments, and if so under what specific  
105 conditions, over what age ranges, etc.?

106 To answer these questions, we analysed Halon-1301 in 17 New Zealand groundwater samples and  
107 various modern (river) water samples. The analysis allowed for simultaneous determination of  
108 Halon-1301 and SF<sub>6</sub> [Beyer et al., 2014b], which are both gaseous tracers with a similar behaviour in  
109 water. In this way, problems such as contamination due to contact with air during sampling or local  
110 (anthropogenic) sources could be identified.

111 All groundwater samples have been previously dated with tritium, CFC-12, CFC-11 and SF<sub>6</sub>. We  
112 determined piston and exponential piston flow ages for Halon-1301 and SF<sub>6</sub>, as inferred by matching  
113 the historic input to the determined concentrations in the groundwater samples. Comparison of  
114 inferred Halon-1301 piston flow and exponential piston flow mean residence times (MRTs) to  
115 relatively robustly inferred tritium and SF<sub>6</sub> MRTs enabled for direct assessment of the performance  
116 of Halon-1301 as a groundwater age tracer. Because Halon-1301 and SF<sub>6</sub> are both gaseous tracers,  
117 they are expected to show similar behaviour in the unsaturated zone. Gaseous tracers equilibrate  
118 with the atmosphere during transport through the unsaturated zone and therefore do not account  
119 for this unsaturated zone travel time. This contrasts with inferred tritium ages, which do account for  
120 travel time through the unsaturated zone. Comparison of age information inferred from tritium and  
121 4 different gaseous tracers (SF<sub>6</sub>, Halon-1301 and CFC-12 and CFC-11) allowed for assessment of  
122 unsaturated zones processes or potential contamination/degradation of Halon-1301. Since some of  
123 the anoxic samples clearly have shown evidence of CFC degradation, comparison of Halon-1301  
124 from these samples enabled a first understanding of the potential for degradation of Halon-1301 in  
125 anoxic groundwater systems.

126 Figure 1 here.....

## 127 2 Methodology

### 128 2.1 Water samples

129 This study took advantage of the relatively well defined age information of New Zealand  
130 groundwater inferred from time series tritium and SF<sub>6</sub> (and CFC) observations, particularly for  
131 confined aquifers [Morgenstern and Taylor, 2009, van der Raaij and Beyer, 2014]. The inferred  
132 tritium ages were considered robust because of their well-defined input function (close proximity of  
133 our sampling sites to the high-resolution Kaitoke monitoring station) and because of long time series  
134 data in groundwater (Tab. 1). To enable a relatively comprehensive assessment of the potential of  
135 Halon-1301 as a groundwater age tracer, groundwater samples previously dated with tritium, SF<sub>6</sub>  
136 and CFCs covering a wide range of mean residence times and including anoxic and oxic samples and  
137 samples with apparent contamination/degradation of CFCs were chosen. We analysed 35  
138 groundwater samples from 17 different sites in the Wellington region from 3 different aquifer  
139 systems (Lower Hutt groundwater Zone, Wairarapa groundwater system and Wainuiomata aquifer)  
140 and 8 river and equilibrated tap water samples for Halon-1301 and SF<sub>6</sub>, simultaneously.  
141 Groundwater samples in the Lower Hutt groundwater Zone (LHGWZ) and river water samples were  
142 collected as triplicates, of which 2 were analysed directly after sampling and 1 was analysed after 7  
143 weeks storage at 14°C. One river water sample was analysed after 1.23 years of storage at 14°C. The  
144 location of the sampling sites and aquifer systems is shown in Fig. 2. The sampling sites, number of  
145 samples taken and corresponding aquifer systems are summarized in Tab. 1. Table 1 also includes  
146 the concentration of dissolved oxygen (DO), previously determined recharge temperature and  
147 amount of excess air (determined by Ar and N<sub>2</sub> analysis) [Jones and Gyopari, 2006; Stewart and  
148 Morgenstern, 2001; Tidswell et al., 2012] and the number of previously taken CFC (CFC-11 and CFC-  
149 12), SF<sub>6</sub> and tritium measurements. The groundwater systems are briefly described in the following.

150 Both the Wairarapa and the Lower Hutt Groundwater Zone (LHGWZ) have formed in alluvial basins  
151 filled with greywacke gravel and marine deposits during glacial and interglacial periods. The  
152 Wairarapa is unconfined and is recharged both by rain and river infiltration while the LHGWZ is  
153 mostly confined and mainly river recharged. More detailed descriptions of the Lower Hutt  
154 Groundwater System can be found in [Grant-Taylor, 1967; Reynolds, 1993; Gyopari, 2013] and of the  
155 Wairarapa groundwater system in [Begg et al., 2005 and Jones and Gyopari, 2006] The Wainuiomata  
156 aquifer is a shallow, unconfined aquifer, which has formed in an alluvial valley filled with alluvial  
157 gravel and sand [Jones and Barker, 2005; WRC, 1993].

158 Figure 2 here.....

159 Table 1 here....

160 For determination of Halon-1301, a sampling procedure similar to the standard procedure for  
161 determination of water soluble gaseous tracers, such as SF<sub>6</sub> and CFCs was followed. To ensure the  
162 sampling of fresh unexposed groundwater (i.e. not the water stagnating in the dead volume of the  
163 well), the well was flushed at least 3 times of its volume and until conductivity, pH and dissolved  
164 oxygen (DO) stabilized [Daughney et al., 2006]. To avoid alteration of Halon-1301 concentrations  
165 with UV light and contamination or adsorption of the gas tracers (Halon-1301 and SF<sub>6</sub>) from/onto  
166 the sampling material, only brown borosilicate glass bottles and nylon tubing were used and the use  
167 of PTFE/Teflon or other fluorine bearing plastics was avoided [Reynolds et al., 1990; van der Raaij and  
168 Beyer, 2014]. To avoid contamination of the samples with modern air, sampling was carried out  
169 under rigorous exclusion of air by inserting a nylon tube to the bottom of the sampling bottle and

170 filling it from the bottom. Then the bottle was let to overflow, so that the water volume was  
171 replaced by several bottle volumes. The bottle was quickly capped and checked for presence of  
172 bubbles and if necessary the sampling process was repeated until no bubble is present.

173 River water and a variety of equilibrated (at close to constant temperature) tap water samples were  
174 taken as representative modern water sample and to verify solubility data. This method  
175 presupposed no contamination by SF<sub>6</sub> or Halon-1301 from the air within our facilities, surrounding  
176 environment or river sampling locations, which seemed reasonable, due to the lack of sources of  
177 these compounds in the surrounding areas. Air samples were regularly analyzed to confirm the lack  
178 of elevated SF<sub>6</sub> and Halon-1301 concentrations in our facilities.

## 179 2.2 Analytical system

180 The water samples were purged with ultra-pure (analytical grade) nitrogen gas in a vacuum sparge  
181 chamber [Busenberg and Plummer, 2000]. Purging with nitrogen at a flow rate of 70 mL/min for 18  
182 min was carried out to ensure complete degassing of the water sample in regards to removal of SF<sub>6</sub>  
183 and Halon-1301. The stripped gas then passed through a drying column (NaOH coated silica) to  
184 remove residual moisture and CO<sub>2</sub> to avoid interference in the detection system. To ensure  
185 consistent amounts of water sample were purged, the sparge chamber was filled until the filling  
186 mark (0.955 L) or the weight of the water sample was determined. If applicable, temperature and  
187 headspace volume were determined. Standard gas samples were pushed through a loop of known  
188 volume (9.97+/-0.02 ml or 0.502 +/- 0.001 ml, in the following referred to as 10 ml and 0.5 ml,  
189 respectively) and the temperature and pressure were recorded to determine the amount of  
190 standard gas analyzed.

191 The samples (standard gas and purged gas from water samples) were then simultaneously analyzed  
192 for Halon-1301 and SF<sub>6</sub> using a gas chromatograph with attached electron capture detector  
193 (GC/ECD) setup including 2 cryogenic traps for pre-concentration [Busenberg and Plummer, 2008  
194 and Beyer et al., 2014b]. The analytical setup also allowed for simultaneous determination of CFC-12  
195 [Busenberg and Plummer, 2008; Beyer et al, 2014b]. However an appropriately concentrated  
196 standard gas is needed to establish its calibration curve. CFC-12 concentrations and inferred CFC-12  
197 ages were therefore not determined in the study.

198 In the following the determination of Halon-1301 and SF<sub>6</sub> concentrations in water samples and  
199 resulting recharge year are described, which involves the determination of a calibration curve,  
200 solubility and where required excess air and headspace correction.

## 201 2.3 Calibration

202 The amount of Halon-1301 and SF<sub>6</sub> in all groundwater samples were determined by establishing a  
203 calibration curve (least square fit, forced through 0/0<sup>1</sup>) with approximately 10 ml certified air  
204 standard at various pressures. The certified air standard contained 3.27 +/- 1.55 ppt Halon-1301 and  
205 7.53 +/- 0.81 ppt SF<sub>6</sub> among other gases (supplied by the Scripps Institution of Oceanography in  
206 2011). A calibration curve was established every day before measurement commenced, since the  
207 performance of the GC/ECD can change from day to day, due to fluctuations in the environment (e.g.

<sup>1</sup> We analysed blank samples (only containing N<sub>2</sub>) which indicated 0 signal for SF<sub>6</sub> and Halon-1301. Additionally the statistical difference between the intercept of the calibration curves for SF<sub>6</sub> 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 suggestion of Helsel and Hirsch (2002) and Caulcutt and Boddy (1983).

208 temperature) or aging of the material (e.g. column fill). Because Halon-1301 concentrations in 10 ml  
209 calibrated air standard did not sufficiently cover concentrations obtained in modern water samples,  
210 another standard gas containing  $3.16 \pm 0.3$  ppb Halon-1301 and  $1.02 \pm 0.1$  ppb SF<sub>6</sub> (prepared by New  
211 Zealand Industrial Gases (NZIG)) was used in a smaller standard loop of approximately 0.5 ml at  
212 various pressures. Additionally tap water samples ranging from 1 to 15 L volume and 10 ml modern  
213 air samples at pressures from 1 to 3.5 bar were analyzed to assess the linearity of the ECD signal  
214 towards Halon-1301 concentrations in the concentration range obtained in old to modern 1 L water  
215 samples. If linearity was found, then previously determined calibration curves (using the calibrated  
216 air standard) were linearly up-scaled to estimate Halon-1301 concentrations in water. This was  
217 relevant for all groundwater samples for which calibration curves have been established at the time  
218 of measurement with calibrated air only. We were aware that this introduced additional uncertainty  
219 which we took into account (see Results section).

220 After determination of the molar amount of Halon-1301 (and SF<sub>6</sub>) in a 1 L water sample purged in  
221 the vacuum sparge chamber, its equivalent atmospheric molar ratio at time of equilibrium (for  
222 groundwater samples at recharge) was determined using the solubility relationship (Henry's law,  
223 described in Supplementary Material S1). In contrast to the solubility of SF<sub>6</sub>, which has been well  
224 studied and directly measured [Bullister, 2002; Wilhelm et al 1977, Tab. 2], the solubility parameters  
225 of Halon-1301 have only been estimated by Deeds (2008) using the solubility estimation methods of  
226 Meylan and Howard (1991) and Meylan et al. (1996). Actual solubility measurements of Halon-1301  
227 are not available in literature (according to our searches and further backed up by personal  
228 communication with Daniel Deeds, 06/03/2015). We used modern (equilibrated tap and river)  
229 water to estimate solubility to validate the solubility estimates. If applicable, the amount of Halon-  
230 1301 (and SF<sub>6</sub>) in the water sample was corrected for headspace and/or excess air (previously  
231 determined by dissolved Ar and N<sub>2</sub> determination [Heaton and Vogel, 1981]), also described in detail  
232 in Supplementary Material S1.

233 Table 2 here....

#### 234 **2.4 Determination of recharge year**

235 To infer the recharge year or residence time of the groundwater, the equivalent partial pressure of  
236 Halon-1301 and SF<sub>6</sub> in the atmosphere at time of recharge (determined as described above) was  
237 compared to their historic atmospheric records (illustrated in Fig. 1). Southern hemisphere  
238 atmospheric SF<sub>6</sub> records (Cape Grim station) are available at the GMD/NOAA  
239 [<http://www.esrl.noaa.gov/gmd/>; Thompson et al., 2004] and CDIAC websites [Miller et al., 2008];  
240 data from 1973-1995 have been reconstructed by Maiss and Brenninkmeijer (1998). Southern  
241 hemisphere (Cape Grim) atmospheric Halon-1301 concentrations have been summarized and  
242 smoothed by Newland et al. (2013). Data from 1969 to 1977 have been reconstructed by Butler et al.  
243 (1999). We assumed that Halon-1301 concentrations are well mixed across the atmosphere of the  
244 southern hemisphere as suggested by Montzka et al. (2003) and Butler et al. (1998) and local  
245 sources of Halon-1301 are lacking as indicated by regular analysis of local air in this study, so that  
246 southern hemisphere atmospheric concentrations could be used to estimate concentrations of  
247 Halon-1301 in recharge.

248 Although a comprehensive analysis of potential local sources has not yet been carried out, studies  
249 such as that by Barletta (2011) in Los Angeles, US, have not found local enhancement of Halon-1301  
250 in city environments. We are aware of only one study that has found unusual fluctuations of Halon-  
251 1301 in the atmosphere: in two stations in Poland, at Krakow and Kasprowy Wierch stations. The



252 research group is still investigating reasons, but speculate it may be attributed to local sources from  
253 close-by city/industry environments [Bartyzel, 2015]

254 In simple terms the recharge year can be found when observed (equivalent) atmospheric  
255 concentrations match historic atmospheric concentrations. This can be done using a simple 'lookup'  
256 table to infer the piston flow recharge year. However misleading age interpretations can be obtained  
257 when using piston flow assumptions, which do not take account of mixing processes of groundwater  
258 in the aquifer or during sampling [e.g. Eberts et al., 2012]. Therefore lumped parameter modelling is  
259 often used to infer an age distribution and with it the mean residence time (MRT) of the  
260 groundwater samples from tracer observations [Maloszewski and Zuber, 1982; Juergens et al.,  
261 2012]. In this study we adopt the commonly used exponential piston flow modelling (EPM), which  
262 had previously been found to best represent tritium (time series) and SF<sub>6</sub> observations in the studied  
263 groundwater. EP modelling was carried out using TracerLPM software (USGS) [Jurgens et al, 2012].  
264 For one point tracer observations, as obtained for Halon-1301 and SF<sub>6</sub> in this study, a range of EPMs  
265 with various exponential to total flow ratio (referred to as 1/n; n has been defined as ratio of total to  
266 exponential flow by Maloszewski and Zuber, (1982)) could be fit to the tracer observation. Since the  
267 mixing parameter could not be adequately constrained with a 1 point measurement of Halon-1301  
268 and SF<sub>6</sub>, we constrained their 1/n ratio to the 1/n ratio previously inferred from tritium (time series)  
269 observations. We assumed this approach was adequate under the assumption of steady state at  
270 each sampling location, which has been indicated by assessment of time series hydrochemistry data  
271 (using trend and seasonality analysis). MRTs (using EPM or PM) inferred from SF<sub>6</sub> and Halon-1301  
272 concentrations were subsequently compared to previously determined MRTs inferred from tritium.  
273 We also commented on observed Halon-1301 concentrations in regards to previously observed  
274 degradation or contamination with CFCs (CFC-12 and CFC-11) in these wells.

## 275 2.5 Analytical uncertainty

276 Due to uncertainties related to the analytical procedure (calibration, analysis, etc.), the inferred  
277 recharge year and mean residence time (from Halon-1301 and SF<sub>6</sub> concentrations) can only be  
278 constrained to an age range. To determine the overall relative uncertainty, the EURACHEM/CITAC  
279 Guide CG4 [Ellison and Williams, 2012] was followed. This guide recommends the method described  
280 in Kragten (1994), which also implies a sensitivity analysis. The standard measurement error was  
281 determined as the total of the following (independent) uncertainties:

$$282 \quad u_{total}(x) = \sqrt{u1^2 + u2^2 + u3^2 + u4^2 + u5^2 + u6^2 + u7^2} \quad (6)$$

283 u1: Uncertainty from least square regression (calibration curve)

284 u2: Uncertainty in standard gas concentration

285 u3: Repeatability error from relative standard deviation of replicates

286 u4: Uncertainty related to correction for headspace

287 u5: Uncertainty related to correction for excess air

288 u6: Uncertainty in recharge temperature

289 u7: Uncertainty in solubility

290 Replicate samples were analyzed to determine the repeatability of the analysis. The absolute

$$291 \quad \text{standard deviation is defined as: } ASD_i = \sqrt{\frac{\sum[(a_i - \bar{x}_i)]^2}{n-1}} \quad (7)$$

292 where  $a_i - \bar{x}_i$  is the difference between the concentrations obtained for one of the replicate  
293 samples  $a_i$  with overall mean value  $\bar{x}_i$  for  $n$  samples and  $i$  number of replicates. The overall relative

294 standard deviation can then be determined as median of all replicate samples:  $D_i = \Sigma \left( \frac{ASD_i}{\bar{x}_i} \right)$ .  
295 (8)

296 The limit of detection (LOD) and limit of quantification (LOQ) were determined by taking into  
297 account the slope and standard deviation (SD) of the calibration curve [Shrivastava and Gupta,  
298 2011]:  $LOD = 3.3 \frac{SD}{slope}$  and  $LOQ = 10 \frac{SD}{slope}$  (9)

299  
300 Nomenclature: In the following the various forms of modern water (river and equilibrated tap water)  
301 are summarized and referred to as 1 sample type, namely modern water. Hence all comparisons are  
302 made in relation to a total of 18 (17 groundwater + 1 modern water) samples. The term age or  
303 recharge year refers to an age or recharge year distribution, which is a function of mean residence  
304 time (MRT) and mixing parameter (e.g. ratio of exponential to total flow for the EPM).

305

### 306 **3 Results and Discussion**

#### 307 **3.1 Calibration curve**

308 Figure 3 illustrates the calibration curves of Halon-1301 obtained with the calibrated air standard  
309 (Scripps) and highly concentrated Halon-1301 standard (NZIG) with a nearly linear response of the  
310 ECD towards Halon-1301 concentration in the concentration range obtained for groundwater  
311 samples (signal up to 30 mV/min for modern water). Additional analysis of modern air at pressures  
312 ranging from 1 to 3.5 bar and analysis of water samples of 3 to 15 L (Fig. 4) confirmed the nearly  
313 linear response of the ECD towards Halon-1301 concentrations in this concentration range. Only for  
314 very high amounts of Halon-1301 (signals of approximately one order of magnitude higher than  
315 obtained in modern water) did the quadratic regression fit slightly better than the linear regression.  
316 Given this evidence of a linear signal response up to concentrations obtained in modern water, we  
317 linearly up-scaled the calibration curve of Halon-1301 obtained with the calibrated air standard to  
318 estimate concentrations of Halon-1301 in all groundwater samples. Using this approach we  
319 introduced additional uncertainty, which we took account of during discussion of the inferred MRTs  
320 (for further detail see Section 3.4: 'Assessment of inferred Halon-1301 ages' and 'Supplementary  
321 Material S2-Assessment of elevated Halon-1301 ages').

322 Figure 3 and 4 here.....

#### 323 **3.2 Uncertainty**

324 The analysis allowed for an average repeatability of 3.6 % for Halon-1301 (2.8 % for SF<sub>6</sub>) and 9.8 %  
325 (6.9 % for SF<sub>6</sub>) average standard deviation of the calibration curve. On average the overall analytical  
326 uncertainty in an average\* New Zealand groundwater samples was 4.7 % for Halon-1301 (9.0 % for  
327 SF<sub>6</sub>). This led to a larger uncertainty in inferred piston flow age for waters recharged before 1975  
328 and after about 2000 when using Halon-1301, due to its characteristic S-shaped input function (Fig.  
329 5). The limit of detection (LOD) and limit of quantification (LOQ) of the analytical setup was 0.32  
330 fmol/L and 0.98 fmol/L for Halon-1301, respectively (and 0.23 fmol/L and 0.69 fmol/L for SF<sub>6</sub>,  
331 respectively). The LOQ was equivalent to a recharge year of 1975 for Halon-1301, at average  
332 recharge temperature (12.1°C), 10 m elevation and lack of excess air and headspace. \* A detailed

333 study in New Zealand has shown groundwater samples have on average a recharge temperature of  
334 12.1 +/-1.8°C; 2.9 +/- 1 ml (STP)/kg excess air; a headspace volume of 0.5 +/-0.05 ml. [van der Raaij  
335 and Beyer, 2014]

336 Figure 5 here.....

337 Sensitivity analysis showed that the most significant contributors to the overall uncertainty were  
338 uncertainties related to the calibration curve, repeatability, excess air and headspace correction for  
339 Halon-1301 and SF<sub>6</sub>. Without considering headspace and excess air, the total uncertainty became  
340 only marginally smaller for Halon-1301 (4.4 % instead of 4.6 %), but significantly smaller for SF<sub>6</sub> (3.2  
341 % instead of 9.0 %). Detailed determined uncertainties for each groundwater sample are shown in  
342 Figs. 6 and 7 and Table 3.

343 We note if SF<sub>6</sub> alone was analysed using a different GC column it could be more accurately resolved  
344 with 4.5 % overall uncertainty [van der Raaij and Beyer, 2014]. However our aim here was to  
345 simultaneously determine the two gaseous tracers SF<sub>6</sub> and Halon-1301 with a particular focus on  
346 resolving the Halon-1301 signal accurately. The higher uncertainty in SF<sub>6</sub> determination when using  
347 our approach may be resolved by adjustment of the column or ECD conditions or application of  
348 signal processing.

349 Please note that the analytical setup also allows for simultaneous determination of CFC-12. This 3  
350 way simultaneous determination of SF<sub>6</sub>, Halon-1301, and CFC-12 may allow for more robust  
351 groundwater dating, due to the ability to identify issues related to the limited application range of  
352 the individual tracers. These are contact with air during sampling (indicated by an increased  
353 concentration of all three gas tracers), degradation/ contamination (indicated by a  
354 reduced/increased concentration of one or more of the gas tracers, respectively) or unsaturated  
355 zone processes, such as diffusion (lag-time) or retardation (indicated by a reduced concentration of  
356 all or one or more of the gas tracers, respectively, in comparison to tritium ages).

### 357 3.3 Solubility

358 To test the reported solubility of Halon-1301, we determined the Henry coefficient (Eqn. S1 in  
359 Supplementary Material) in equilibrated tap and river water samples and in relatively young  
360 groundwater (<2 years MRT). These modern waters were collected for estimation of the solubility of  
361 Halon-1301. To estimate the robustness of the estimated Halon-1301 solubility, the solubility of SF<sub>6</sub>  
362 was also determined in these samples with the same method and compared to literature data.

363 Figure 6 shows the inferred solubility (ln K<sub>H</sub>) of SF<sub>6</sub> and Halon-1301 in modern groundwater and  
364 equilibrated tap and river water compared to solubilities estimated by Deeds [2008] and Bullister et  
365 al. [2002] for Halon-1301 and SF<sub>6</sub>, respectively. Table 1 contains solubility parameters inferred from  
366 the found relationship in Fig. 6 along with previously reported solubility parameters. As can be seen,  
367 inferred solubility of SF<sub>6</sub> agreed well with its reported solubility, which indicated that our approach  
368 should give relatively robust Halon-1301 solubility estimates. Inferred solubility of Halon-1301 was  
369 significantly lower than estimated by Deeds [2008]. When using the Deeds [2008] estimated  
370 solubility parameters, Halon-1301 concentrations were obtained which resulted in significantly older  
371 inferred Halon-1301 ages compared to tritium and SF<sub>6</sub> ages with an average discrepancy of +12 years  
372 in equilibrated tap and river water. This offset was removed when using our estimated Halon-1301  
373 solubility parameters.

374 Due to absence of robust solubility data of Halon-1301, we used the solubility parameters estimated  
375 in this study (Tab. 3) to infer equivalent atmospheric Halon-1301 concentrations and with that infer  
376 Halon-1301 ages. Accurate measurement of the solubility of Halon-1301 is beyond the scope of this  
377 study. Due to the extremely low solubility of Halon-1301, specialised equipment is required. The  
378 estimated solubility had a relatively large uncertainty of 9.8% (estimated for a regression analysis in  
379 Fig. 6), due to scatter in the data which may have been caused by uncertainty in recharge  
380 temperature, unaccounted heterogeneity or mixing of water, etc. The uncertainty in solubility added  
381 to the analytical uncertainty in equivalent atmospheric Halon-1301 concentration (estimated in the  
382 previous section), so that the overall uncertainty increased from 4.7 to 9.7%. This increased  
383 uncertainty in turn affected the uncertainty in inferred Halon-1301 age as discussed in the following.

384 Tab. 3 here...

385 Fig. 6 here...

### 386 3.4 Assessment of inferred Halon-1301 ages

#### 387 3.4.1 Overall

388 In the following we assessed inferred Halon-1301 mean ages in comparison to inferred SF<sub>6</sub> and  
389 previously inferred tritium and CFC mean ages. We considered elevated concentrations of Halon-  
390 1301, SF<sub>6</sub> or CFCs (>10%) as 'potentially contaminated' and highly elevated concentrations (>25%) as  
391 'highly contaminated'. Details on individual piston and exponential piston flow model MRTs inferred  
392 from Halon-1301 and SF<sub>6</sub> (in this study) and tritium (from previous studies) are listed in Tab. 3.

393 Inferred piston flow (PM) SF<sub>6</sub> and Halon-1301 ages (illustrated in Fig. 7) showed that Halon-1301  
394 ages were on average 5.4 years higher than inferred SF<sub>6</sub> ages (over the entire age range), caused by  
395 reduced concentrations of Halon-1301 compared to SF<sub>6</sub>. However, piston flow ages are unrealistic,  
396 as they neglect mixing of water of different age in the subsurface or during sampling [e.g.  
397 Małozzewski and Zuber, 1982], also indicated by previously determined EPM ages inferred from  
398 tritium and SF<sub>6</sub> [e.g. Morgenstern and Taylor, 2009]. In the following we applied an exponential  
399 piston flow model (EPM) and inferred mean residence times (MRT) from Halon-1301 and SF<sub>6</sub>  
400 concentrations. The choice of lumped parameter model significantly affected the age interpretation  
401 with Halon-1301, due to its S-shaped input function, which is skewed due to mixing processes  
402 (depending on the lumped parameter model choice). This highlighted the importance of considering  
403 mixing processes for inferring groundwater age from Halon-1301 observations. For SF<sub>6</sub>, this was less  
404 of a problem, due to its nearly linear atmospheric input since the late 1980s. The sensitivity of Halon-  
405 1301 concentrations towards mixing of groundwater of different age also implied that groundwater  
406 dating with Halon-1301 may allow better constraining of the mixing parameters compared to SF<sub>6</sub>.  
407 However, time series Halon-1301 data are necessary to confirm this supposition.

408 Fig. 7 here...

#### 409 3.4.2 Consistency of inferred Halon-1301 ages with inferred tritium and 410 SF<sub>6</sub> ages using the EPM

411 When using the EPM, inferred Halon-1301 and SF<sub>6</sub> MRTs agreed for the majority of sites (for 12 out  
412 of 18 sites) as summarized in Tab. 3. Inferred MRTs were considered as agreeing (i.e. insignificantly  
413 different) when their uncertainty bounds of 1 SD (except for 1 site where we accepted 1.1 SD)

414 overlapped. The remaining sites indicated higher MRTs inferred from Halon-1301 compared to SF<sub>6</sub>.  
415 To assess whether these differences had been caused by processes affecting both gas tracers (such  
416 as lag-time in the unsaturated zone) or only Halon-1301 (such as potential degradation or sorption  
417 which does not occur for SF<sub>6</sub>), inferred Halon-1301 and SF<sub>6</sub> MRTs were compared to previously  
418 inferred tritium MRTs in Fig. 8. Where present, samples exhibiting probable CFC  
419 degradation/contamination are highlighted in Fig. 8. Comparison to inferred CFC ages could not be  
420 made, because all samples (with available CFC data) were either degraded and/or contaminated in  
421 one or both of CFC-11 and CFC-12.

422 At one of the 18 sites both gases and tritium were close to the LOD, but evidence of slight  
423 contamination with modern air during sampling was found, indicated by elevated concentrations of  
424 both SF<sub>6</sub> and Halon-1301 which were incompatible with their low tritium concentrations. Evaluation  
425 of the performance of Halon-1301 as an age tracer in comparison to SF<sub>6</sub> and tritium was not possible  
426 for this sample, which was therefore excluded for the overall comparison. For the majority of the  
427 remaining 17 groundwater samples, inferred SF<sub>6</sub> ages agreed well with previously determined  
428 tritium ages, which indicated that unsaturated zone processes were not significant in this study.

429 Inferred Halon-1301 MRTs of 12 out of 17 sites were in agreement with inferred tritium and/or SF<sub>6</sub>  
430 MRTs (within an uncertainty of ~1 SD). This included 4 older groundwater sites, which showed  
431 concentrations at or close to LOD of tritium and SF<sub>6</sub>, and were also free of Halon-1301 (Fig. 9 and  
432 Tab. 3). For the remaining waters (all relatively old and anoxic), inferred Halon-1301 ages were  
433 higher compared to tritium/SF<sub>6</sub> ages. The reasons for this offset are discussed in the following  
434 subsection.

435 As can be seen in Tab. 3, the relatively large uncertainty in estimated solubility led to additional  
436 uncertainty in inferred Halon-1301 ages (compared to estimates assuming only a 1% uncertainty in  
437 solubility, for demonstration purposes). We found up to 16 years higher uncertainty in inferred  
438 Halon-1301 MRTs when accounting for the current uncertainty in solubility. Inferred Halon-1301  
439 ages can potentially be better constrained with a more accurate solubility estimate. This also means  
440 the full potential of Halon-1301 as an age tracer cannot yet be realised due to absence of accurate  
441 /robust solubility data.

442 Figure 8 and Table 3 here.....

### 443 3.4.3 Conservativeness of Halon-1301

444 No significantly elevated Halon-1301 concentrations were found, despite that the sites cover  
445 situations of land use and well construction that result in CFC contamination. A significantly elevated  
446 Halon-1301 concentration was only found for one site in concert with an elevated SF<sub>6</sub> concentration,  
447 suggesting that the sample was contaminated with air during sampling (Fig. 8 and Tab. 3). This  
448 indicated no issues related to contamination for Halon-1301 from local sources at the studied sites.  
449 This has to be evaluated further, e.g. in groundwater recharged close to airports, where Halon-1301  
450 is still in use as a fire suppressant during fuelling of planes. The lack of elevated Halon-1301  
451 concentrations may also indicate that interference of the Halon-1301 signal with CFC-13 or other co-  
452 eluting compounds (as has been assessed in Beyer et al., 2014b) was not an issue in the studied  
453 groundwater samples. However, this needs to be assessed further in groundwater with elevated  
454 concentrations of CFC-13 or other potentially co-eluting compounds.

455 Significantly higher Halon-1301 MRTs to tritium and SF<sub>6</sub> MRTs (over an age range from 2.5 to 40  
456 years MRT) were found in 5 of 17 groundwater samples, where direct age comparison could be

457 made. These samples also showed evidence of significant (even higher) degradation and/or  
458 contamination of one or both CFC-11 and CFC-12. There are several possibilities for higher inferred  
459 Halon-1301 groundwater ages as a result of reduced Halon-1301 concentrations, which we assessed  
460 in detail in Supplementary Material S2. A summary is presented in the following. Our assessment  
461 showed we could exclude degassing into headspace created by de-nitrification, production of  
462 methane or when groundwater is brought to the ground surface, since this would have affected all  
463 determined gas tracers, to the highest extent the least water soluble SF<sub>6</sub>, which we did not find in  
464 any of our samples. We could also exclude lag-time in the unsaturated zone, because this would  
465 have also affected all gas tracers, dependent on their diffusion coefficient [Goody et al., 2006] and  
466 we did not find decreased concentrations of both Halon-1301 and SF<sub>6</sub> in any of our samples.  
467 Assuming that Halon-1301 behaved similarly to CFCs in regards to sorption to specific materials, we  
468 also considered the risk of sorption to well casing/sampling material was minimal as we followed  
469 robust sampling procedure established for CFCs and SF<sub>6</sub> (using only borosilicate glass, stainless steel  
470 equipment and nylon tubing).

471 Potential degradation of Halon-1301 during storage was assessed by analysis of 6 groundwater  
472 samples from different sites (covering an age range from modern (< 1 year) to over 100 years MRT,  
473 and oxic to anoxic waters) stored for 7 weeks. The simultaneous determination of SF<sub>6</sub> and Halon-  
474 1301 allowed us to isolate Halon-1301 degradation, since SF<sub>6</sub> is not known to degrade in oxic or  
475 anoxic environments. Hence an isolated reduced concentration in Halon-1301 would indicate Halon-  
476 1301 degradation, in contrast to a combined (Halon-1301 and SF<sub>6</sub>) reduced concentration that would  
477 indicate e.g. escaping of gas into headspace. Figures 9 illustrates concentrations determined before  
478 and after storage were within statistical uncertainty, indicating that Halon-1301 was stable in oxic  
479 and anoxic groundwater during storage for over 1 month at 14°C. The concentration of Halon-1301  
480 in 1 sample (river water) stored for over 1.2 years was also not significantly reduced compared to  
481 SF<sub>6</sub>.

482 The remaining possibilities for reduced Halon-1301 concentrations (i.e. increased inferred ages)  
483 were:

- 484 I) Increased inferred Halon-1301 ages in younger water samples with a MRT (tritium age) close  
485 to or below 15 years (applicable for 1 of 5 affected samples) were likely caused by  
486 uncertainties related to the recent levelling out atmospheric concentrations of Halon-1301  
487 [AGAGE, 2014], which made it more difficult to constrain the age of younger waters.
- 488 II) Increased inferred Halon-1301 ages in the remaining, particularly older samples with a MRT  
489 above 15 years were likely caused by a) degradation, which is only likely to occur under  
490 anoxic/anoxic conditions (all affected samples are anoxic); b) sorption to organic material in  
491 the aquifer (could not be excluded for any of the sites).

492 Further studies are needed to confirm whether Halon-1301 is degradable or reduced concentrations  
493 are a result of sorption/retardation in the aquifer. This can be studied by determination of Halon-  
494 1301 in relatively old (MRT of > 5 years) oxic groundwater and/ or relatively young (MRT < 5 years)  
495 anoxic groundwater. Reduced concentrations of Halon-1301 in relatively old oxic water could  
496 confirm sorption/retardation, since degradation is likely only occurring in anoxic water. Similarly  
497 analysis of relatively young anoxic/ anoxic groundwater, where sorption/degradation has not likely  
498 affected the concentration of Halon-1301 (due to a relatively short travel time in the aquifer and the

509 currently levelling out atmospheric trend), and reduced concentrations could confirm degradation of  
500 Halon-1301.

501 Figure 9 here....

#### 502 **4 Summary and Conclusion**

503 This paper provided an insight into the suitability of the gaseous, water soluble compound Halon-  
504 1301 as groundwater age tracer. We demonstrated the capability of the analytical setup for robust  
505 simultaneous determination of the gas tracers Halon-1301 and SF<sub>6</sub> (and CFC-12) on the same 1 L  
506 water sample, which provided an immense potential for more robust age interpretation of relatively  
507 young groundwater (recharged <100 years). We estimated solubility, which is required to convert  
508 measured concentrations in water into atmospheric concentrations, from a range of equilibrated  
509 waters and relatively modern, oxic groundwater. We found that the solubility of Halon-1301 found  
510 in this study did not match its reported solubility. Uncertainties arising from this estimation  
511 approach, led to higher uncertainty in inferred MRT up to 16 years. More accurate determination of  
512 Halon-1301's solubility is required for better utilization of its potential as age tracer.

513 We used piston and exponential piston flow modelling (PM and EPM) to infer age from Halon-1301  
514 (and SF<sub>6</sub>) concentrations in groundwater. Significantly different age interpretations were found with  
515 both modelling approaches. Halon-1301 was particularly sensitive to the choice of LPM due to its S-  
516 shaped input function, which is considerably skewed during mixing processes in contrast to SF<sub>6</sub> with  
517 a nearly linear atmospheric record. This indicated that the determination of Halon-1301 may allow  
518 better constraint of the mixing model. However, further study is needed to support this supposition  
519 with time series Halon-1301 data. Previously inferred CFC, SF<sub>6</sub> and tritium ages in the studied  
520 groundwater sites allowed us to compare the performance of Halon-1301 as an age tracer compared  
521 to other tracers.

522 Twelve of 17 groundwater samples where direct comparison of inferred ages could be made,  
523 showed matching Halon-1301, SF<sub>6</sub> and/or tritium ages within an uncertainty of ~1 SD. We found no  
524 significantly increased Halon-1301 concentrations in any of the analysed groundwater samples  
525 which indicated no apparent sources of contamination of Halon-1301 in our study, despite the fact  
526 that the sites included different land use environments and well construction that resulted in CFC  
527 contamination. This also indicated that interference with other co-eluting compounds was not an  
528 issue, since this would have led to increased concentrations of Halon-1301 determined in water.

529 Analysis of stored groundwater samples indicated that Halon-1301 was stable in oxic to anoxic water  
530 stored up to 7 weeks at 14°C. Reduced concentration of Halon-1301 (along with significantly even  
531 further reduced concentration of CFC-12 and -11) at 5 of 17 sites needs to be assessed further. It is  
532 unclear if reduced concentrations were caused by degradation or retardation of Halon-1301 in the  
533 aquifer.

534 Despite these not fully understood reduced concentrations, we showed that Halon-1301 has strong  
535 potential as a complementary groundwater age tracer. If used in combination with other established  
536 tracers, it is likely to aid in reducing the ambiguity in groundwater age interpretations obtained  
537 though tritium, SF<sub>6</sub> and fading out CFC concentrations, and improve constraining mixing models.  
538 Since Halon-1301 is a gaseous tracer, it has additional potential to be used to assess unsaturated as  
539 well as saturated zone processes, especially with respect to the simultaneous determination of CFC-  
540 12 and SF<sub>6</sub> on the proposed analytical setup. Due to its S-shaped, fading out atmospheric input and  
541 analytical detection limits, we suggest the appropriate application range for inference of  
542 groundwater age from Halon-1301 is for waters recharged between 1980 and 2005/2008. Higher

543 uncertainty will be present in age estimates for waters of earlier (from 1970s) or more modern  
544 recharge. The uncertainty in inferred Halon-1301 age can be reduced by more accurate  
545 determination of its solubility.

546 To confirm the absence of local **contamination** sources, Halon-1301 needs to be assed further at  
547 sites with higher risk of local sources (e.g. close to airports). To assess whether reduced Halon-1301  
548 concentrations in older anoxic waters are a result of degradation or sorption, Halon-131 needs to be  
549 assed in anoxic waters (preferably young - MRT < 5 years) that have been influenced by different  
550 compositions of bacteria and/or aquifer material, and/or in relatively old oxic sites (MRT > 5 years)  
551 with high organic content. Even if Halon-1301 is affected by degradation/sorption and/or  
552 contamination is occurring in specific areas, Halon-1301 is likely to be a more reliable groundwater  
553 age tracer than CFCs, which face issues regarding their reliability to infer groundwater age due to  
554 (anthropogenic) contamination and degradation in anoxic waters, **as we observed in this study.**  
555 **Concentrations in the atmosphere are also fading out, which will make CFCs even less reliable in the**  
556 **future.**

557 **We suggest that Halon-1301 (or any other tracer) is used complementarily together with other**  
558 **tracers, to compensate for individual tracer limitations. We do not suggest that Halon-1301 is used**  
559 **as a stand-alone tracer (although in our study area it was significantly more reliable than CFCs, which**  
560 **are commonly used alone in the literature). Specifically, we recommend the simultaneous**  
561 **determination of Halon-1301 with SF<sub>6</sub> and CFC-12, using the cost-effective method presented in this**  
562 **study. This allows for the determination of 3 complementary age tracers in the same water sample,**  
563 **which may enable more precise determination of groundwater age (and mixing), assessment of**  
564 **unsaturated zone processes, and increase robustness as the three tracers together allow**  
565 **identification and exclusion of problem samples; e.g. where contact with air has occurred during**  
566 **sampling, or where degradation of one or more of the age tracers has occurred.**

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747 **Tables and Figures**

748 **Table 1: summary of water samples analysed in this study: site name, amount of duplicates**  
 749 **analysed, associated groundwater (GW) system, recharge temperature and excess air determined**  
 750 **from noble gas analysis, dissolved oxygen (DO) and number of available CFC, tritium and SF<sub>6</sub> data;**  
 751 **<sup>a</sup> if no data are available for this site, the average NZ recharge temperature of 12.1 +/- 1.8 C and/or**  
 752 **average NZ excess air 2.9 +/- 1 ml (STP) L-1 [van der Raaij and Beyer, 2015] are used; LHGWZ<sup>+</sup>**  
 753 **Lower Hutt Groundwater Zone; <sup>b</sup> groundwater shows considerable amount of methane and is**  
 754 **considered as anoxic, despite relatively high oxygen concentration**

Site name	# of water samples	Groundwater system	recharge T [°C]	Excess air [ml(STP)/L]	DO [mg/L]	# of SF <sub>6</sub> data	# of CFC data	# of tritium data
Wainuiomata	3	Wainuiomata	10.7 ± 1.8	0.6 ± 0.9	4.17	2	1	2
Avalon Studio	3	LHGWZ <sup>+</sup>	14.2 ± 1.9	-0.7 ± 0.9	4.82	1	2	4
IBM 2	3	LHGWZ <sup>+</sup>	12.3 ± 1.9	1.0 ± 0.8	0.31	4	3	9
Seaview Wools	3	LHGWZ <sup>+</sup>	15.8 ± 2.1	2.3 ± 0.9	0.22	2	1	3
River water (Hutt River)	4	LHGWZ <sup>+</sup>	15.4; 12.3	2.9+/-1.8 <sup>a</sup>	10.8	1	1	1
IBM 1	3	LHGWZ <sup>+</sup>	10.4 ± 1.5	0.8 ± 0.8	0.29	3	2	4
UWA3	3	LHGWZ <sup>+</sup>	12.1 ± 1.8 <sup>a</sup>	2.9 ± 1.8 <sup>a</sup>	4.19?	2	1	3
Shandon GC	3	LHGWZ <sup>+</sup>	9.7 ± 1.5	0.3 ± 0.8	0.11	3	2	1
Buick St	3	LHGWZ <sup>+</sup>	10.8 ± 1.2	0.6 ± 0.6	0.26	1	2	2
Duffy deep	1	Wairarapa	14.0 ± 0.1	2.1 ± 0.2	2.28 <sup>b</sup>	2	1	1
CDC south	1	Wairarapa	10.7 ± 1.6	2.0 ± 0.8	1.16 <sup>b</sup>	3	2	3
George	1	Wairarapa	20.0 ± 2.4	5.5 ± 0.9	0.02	2	1	2
Finlayson	1	Wairarapa	20.7 ± 1.5	-3.4 ± 0.8	0.02	2	1	1
Warren	1	Wairarapa	9.4 ± 1.8	3.0 ± 1.0	0.22	1	0	1
Johnston	1	Wairarapa	10.3 ± 1.8	0.1 ± 1.0	0.26	2	1	3
Trout hatchery	1	Wairarapa	14.2 ± 1.5	-0.3 ± 0.8	6.12	2	1	0
Papawai Spring	1	Wairarapa	12.7 ± 1.5	-0.4 ± 0.8	5.52	2	1	1
Lake Ferry MC	1	Wairarapa	11.4 ± 1.7	2.4 ± 0.8	2.84	1	0	2
equilibr. water	4	-	14.4; 19.8	n/a	-	1	1	n/a

755

756 **Table 2: Reported solubility parameters for Halon-1301 and SF<sub>6</sub> and \*estimated solubility**  
 757 **parameters for Halon-1301 with an uncertainty of 10%**

compound	Reference	parameters for Henry solubility coefficient [mol/L/atm]
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		A	B	C
Halon-1301	Deeds, 2008	-92.9683	140.1702	36.3776
SF <sub>6</sub>	Bullister, 2002	-96.5975	139.883	37.8193
Halon-1301	Our study*	1176.87	-1649.55	-576.81

**Table 3: summary of exponential piston flow ages (MRT) inferred from Halon-1301 and SF<sub>6</sub> (determined in this study), tritium, CFC-12/ CFC-11 (determined in previous studies); contaminated samples (>10%) are displayed 'C', highly contaminated samples (>25%) are displayed as 'HC'; 'D' refers to potentially degraded; signals below or at LOD are illustrated 'LOD'**

<sup>a</sup> sampling date: 02/12/2013; <sup>b</sup> sampling date: 10/12/2013; <sup>c</sup> uncertainty (+/- 1 SD) including/excluding uncertainty in solubility, <sup>d</sup> n = mixing ratio (total to exponential flow), which has previously been inferred from tritium (time series) observations

Site ID	equivalent atmospheric concentration					inferred MRT when using the EPM								previously det. age information		
	Halon-1301			SF <sub>6</sub>		Halon-1301					SF <sub>6</sub>			tritium		CFC-12/ CFC-11
	pptv	+/- <sup>c</sup> (incl. solub.)	+/- <sup>c</sup> (excl. solub.)	pptv	+/-	MRT [years]	+ <sup>c</sup> (incl. solub.)	- <sup>c</sup> (incl. solub.)	+ <sup>c</sup> (excl. solub.)	- <sup>c</sup> (excl. solub.)	MRT [years]	+	-	n <sup>d</sup>	MRT [years]	MRT [years]
Hutt River <sup>a</sup>	3.72	0.65	0.56	7.14	0.56	0	HC	4	C	2	1.5	2	1.4	var.	0	n/a
Avalon Studio <sup>a</sup>	3.60	0.46	0.19	10.02	1.74	0	C	2	C	0	HC	HC	0.1	var.	1.0	C/n/a
Pawai Springs <sup>b</sup>	3.77	0.59	0.28	10.63	1.34	C	HC	0	C	0	HC	HC	0.1	var.	1.0	C/HC
Trout Hatchery <sup>b</sup>	3.47	0.52	0.18	9.14	1.14	0	C	7	0	0	C	C	0.5	var.	1.5	C/12
Wainuiomata <sup>a</sup>	2.95	0.78	0.67	8.21	1.09	7	C	11	7	9	0.1	1.9	C	var.	2.0	HC/24
Johnston <sup>b</sup>	2.22	0.35	0.16	6.04	0.85	18	5	5	2.5	2	7	4	3.5	0.8	2.5	19/D
Shandon GC <sup>a</sup>	2.66	0.26	0.11	5.23	0.34	11	4	4	1	2	10	2	1	var.	9.0	27/C
CDC south <sup>b</sup>	2.06	0.22	0.09	4.43	0.34	20	4	4	1.5	2	15	2.5	2	0.9	13	C/D
Seaview Wools <sup>a</sup>	0.25	0.12	0.11	3.65	0.50	135	25	45	23	38	21	5	3.5	0.8	16	C/C
Buick <sup>a</sup>	0.57	0.05	0.02	2.77	0.23	53	2	2	1	1	26	2	2	0.7	18	21/D
IBM 2 <sup>a</sup>	0.05	0.12	0.11	2.03	0.26	55	8	>14	8	>14	27	2	2	0.4	40	85
George <sup>b</sup>	0.05	0.00	0.00	1.65	0.10	234	5	4	2	4	52	3	3	0.9	25	D/D



Duffy deep <sup>b</sup>	1.22	0.13	0.05	3.19	0.12	41	4	5	2	2	25.5	2	1.5	0.9	>21	39/D
Lake Ferry MC <sup>b</sup>	0.62	0.09	0.04	1.30	0.12	62	6	5	3	2	51.5	4.5	3.5	0.8	75	-
IBM 1 <sup>a</sup>	LOD	-	-	LOD	-	-	-	-	-	-	-	-	-	0.1	100	95
Warren <sup>b</sup>	0.05	0.01	0.00	0.12	0.01	234	6	6	6	6	215	10	5	0.9	140	n/a
UWA3 <sup>a</sup>	LOD	-	-	LOD	-	-	-	-	-	-	-	-	-	var.	150	LOD/ LOD
Finnlayson <sup>b</sup>	LOD	-	-	1.57	0.71	-	-	-	-	-	52	28	17	var.	LOD	LOD/ LOD

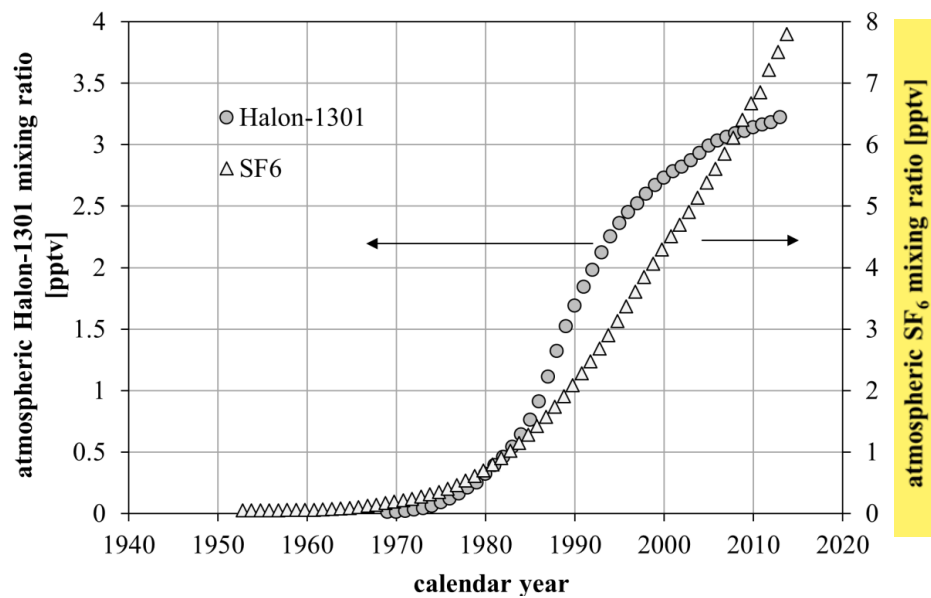


Figure 1: historic records of Halon-1301 and SF<sub>6</sub> atmospheric mixing ratios [pptv] [Newland et al., 2013; Butler et al., 1999; Thompson et al., 2004; Miller et al. 2008; Maiss and Brenninkmeijer, 1998]

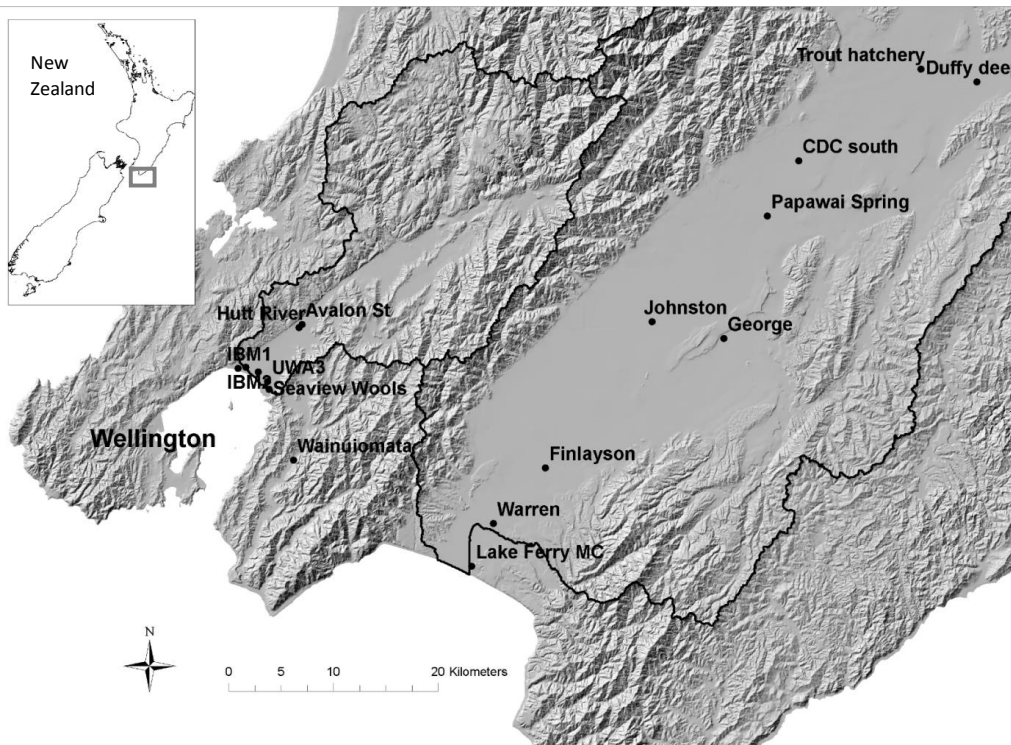


Figure 2: groundwater wells and sampling locations in the Wellington Region New Zealand are displayed as points; the black outlines represent the 2 catchments Hutt Valley (left catchment) and Wairarapa (right catchment)

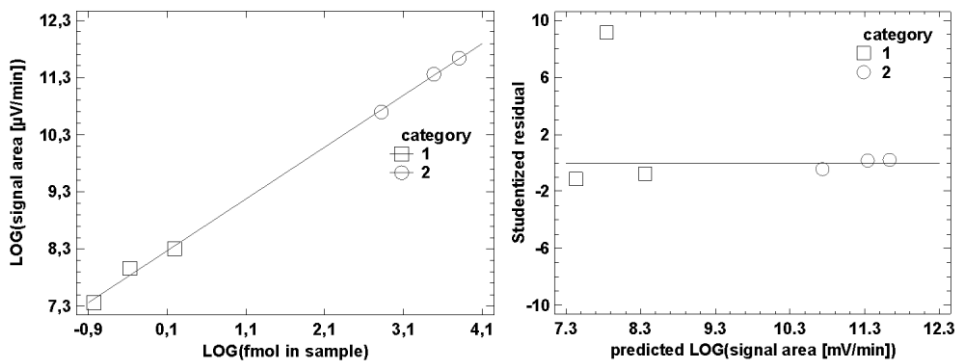


Figure 3: calibration curve (LEFT) and residual plot (RIGHT) for Halon-1301 using 10ml calibrated air standard (category 1) and 0.5ml highly concentrated Halon-1301 standard (NZIG) (category 2)

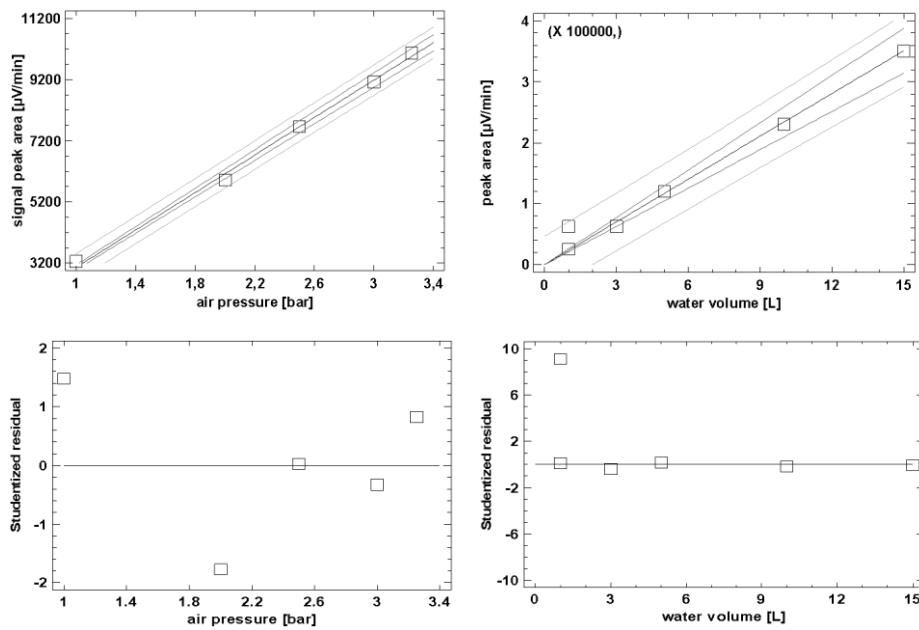


Figure 4: assessment of linearity of the ECD signal towards Halon-1301 using 10ml modern air at different pressures (LEFT) and water at different volumes (RIGHT) showing an almost linear signal to pressure/volume (UPPER) and acceptable residuals (LOWER), lines in upper graphs represent the best least square fit, fit with standard deviation of slope and 95% confidence interval

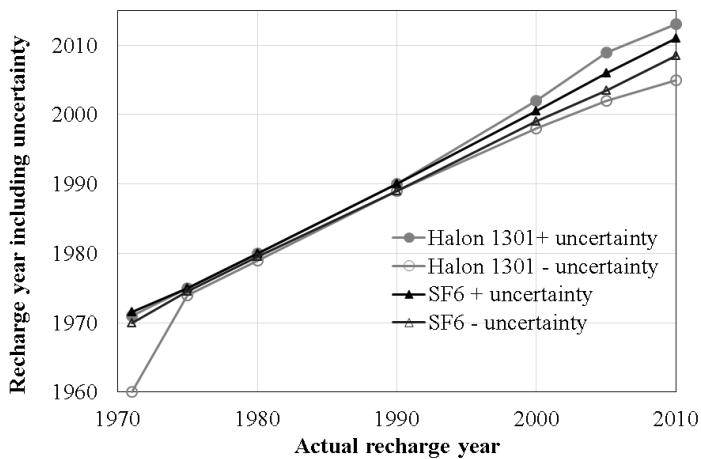
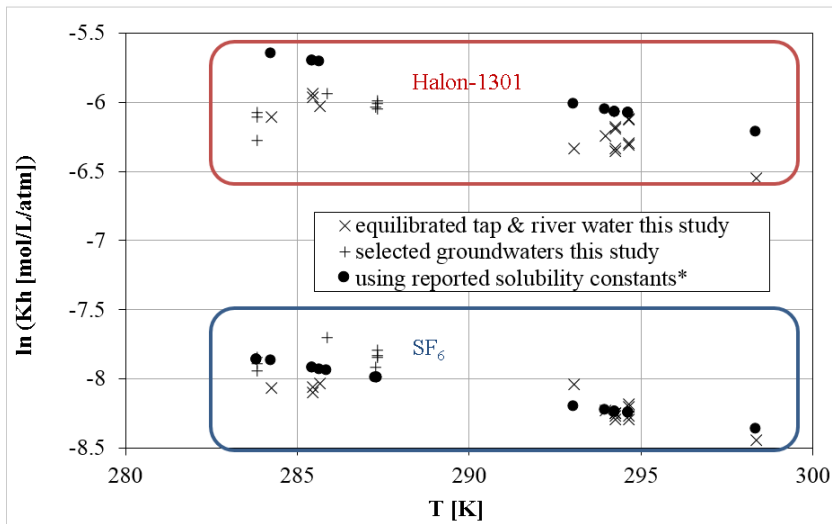
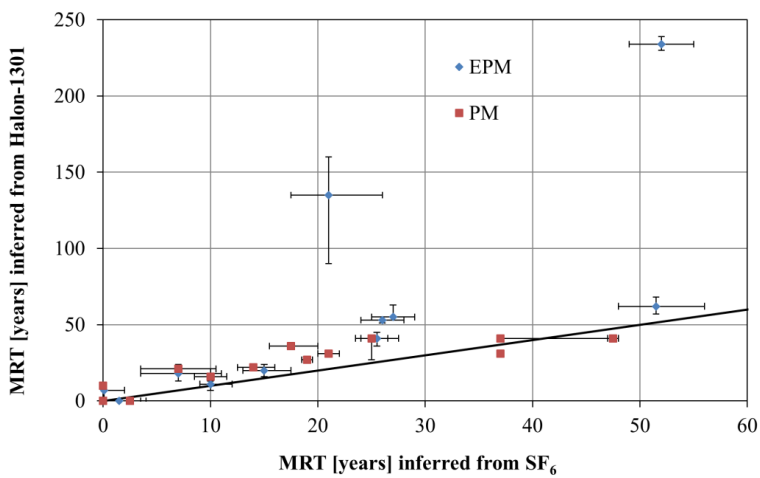


Figure 5: effect of relative analytical uncertainty on inferred piston flow recharge year for SF<sub>6</sub> and Halon-1301



**Figure 6: estimated solubility of Halon-1301 and SF<sub>6</sub> in equilibrated tap water, river water, and oxic young groundwater in comparison to reported solubility data, \* data from Deeds, (2008) for Halon-1301 and Bullister et al., 2012 for SF<sub>6</sub>**



**Figure 7: piston flow and exponential piston flow ages (MRTs) inferred from Halon-1301 and SF<sub>6</sub> concentrations, including error bars (+/- 1 SD analytical uncertainty including uncertainty in solubility)**

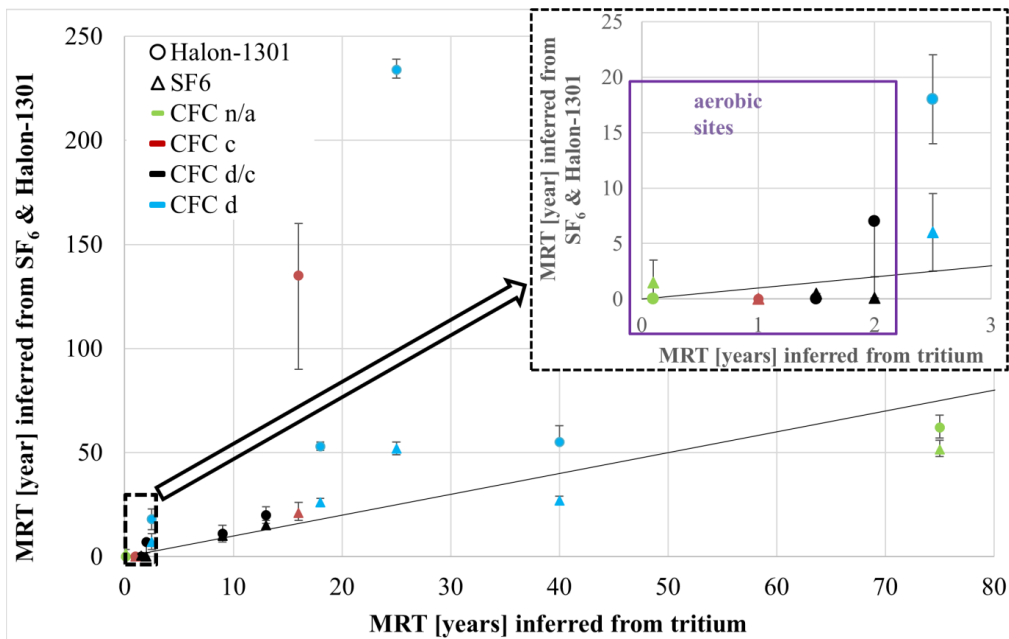


Figure 8: summary of mean residence time including error bars (+/- 1 SD analytical uncertainty including uncertainty in solubility) inferred from Halon-1301, SF<sub>6</sub> vs mean residence times inferred from tritium using the exponential piston flow model, data points are highlighted according to CFC-12/CFC-11 contamination/degradation (see legend); Halon-1301 and SF<sub>6</sub> were determined in this study, tritium and the CFCs were determined in previous study(s); the abbreviations 'c' and 'd' in the legend refer to: contaminated and degraded in one or both CFCs, respectively; c/d refer to contamination and degradation was observed for either CFC-12 or CFC-11; 'n/a' refers to no available CFC data.

**Comment [MB1]:** We swapped information around to make it easier to understand that Halon and SF<sub>6</sub> inferred ages are plotted vs tritium

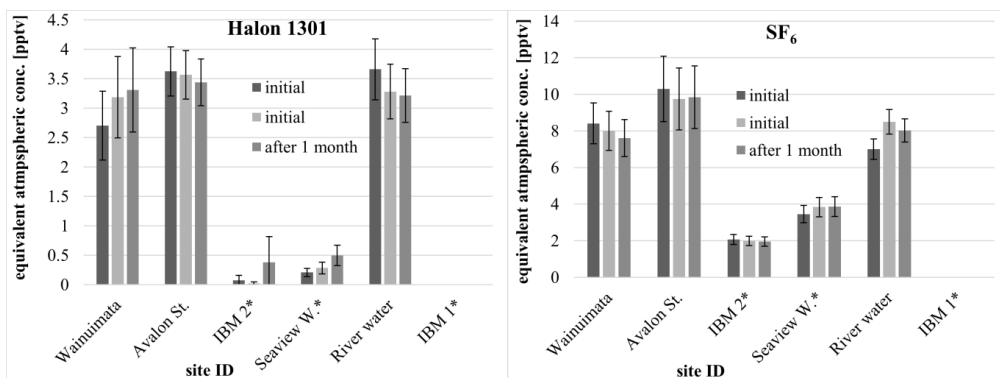


Figure 9: comparison of Halon-1301 concentration in 1 L water samples analysed directly after sampling (2 of 3) and after 7 weeks (1.2 years for Hutt River water sample) storage at 14°C (1 of 3), \* anoxic water samples