Hydrol. Earth Syst. Sci. Discuss., 12, 1397–1436, 2015
www.hydrol-earth-syst-sci-discuss.net/12/1397/2015/
doi:10.5194/hessd-12-1397-2015

Hydrology and Earth System Sciences
Discussions
Open Access

Assessment of Halon-1301 as a groundwater age tracer

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Received: 21 November 2014 – Accepted: 19 January 2015 – Published: 30 January 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Groundwater dating is an important tool to assess groundwater resources in regards to their dynamics, i.e. direction and time scale of groundwater flow and recharge, to assess contamination risks and manage remediation. To infer groundwater age information, a combination of different environmental tracers, such as tritium and SF_6, are commonly used. However, ambiguous age interpretations are often faced, due to a limited set of available tracers and their individual restricted application ranges. For more robust groundwater dating multiple tracers need to be applied complementarily and it is vital that additional, groundwater age tracers are found to ensure robust groundwater dating in future.

We recently suggested that Halon-1301, a water soluble and entirely anthropogenic gaseous substance, may be a promising candidate, but its behaviour in water and suitability as a groundwater age tracer had not yet been assessed in detail. In this study, we determine Halon-1301 and infer age information in 17 New Zealand groundwaters and various modern (river) water samples. The samples are simultaneously analysed for Halon-1301 and SF_6, which allows identification of issues such as contamination of the water with modern air during sampling. Water at all analysed groundwater sites have also been previously dated with tritium, CFC-12, CFC-11 and SF_6, and exhibit mean residence times ranging from modern (close to 0 years) to over 100 years. The investigated groundwater ranged from oxic to highly anoxic, and some showed evidence of CFC contamination or degradation. This allowed us to make a first attempt of assessing the conservativeness of Halon-1301 in water, in terms of presence of local sources and its sensitivity towards degradation etc., which could affect the suitability of Halon-1301 as groundwater age tracer.

Overall we found Halon-1301 reliably inferred the mean residence time of groundwater recharged between 1980 and 2014. Where direct age comparison could be made 71 % of mean age estimates for the studied groundwater sites were in agreement with ages inferred from tritium and SF_6 (within ±2 years). The remaining (anoxic) sites

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showed reduced concentrations of Halon-1301 along with even further reduced concentrations of CFCs. The reason(s) for this need to be further assessed, but are likely to be caused by sorption or degradation of the compounds. Despite some groundwater samples showing evidence of contamination from industrial or agricultural sources via elevated CFC concentrations, no sample indicated significantly elevated concentration of Halon-1301, which may indicate a lack of local anthropogenic or geologic sources of Halon-1301 contamination.

1 Introduction

Groundwater dating is a widely applied technique to determine groundwater flow parameters, e.g. recharge source and rate, flow direction and rate, residence time and volume. Age in itself is also increasingly used as a stand-alone indication for quality and contamination risks. Tracers, such as tritium, SF_6 and various CFCs, are commonly used to infer groundwater age of relatively young groundwater (recharged < 100 years ago) by comparing their atmospheric history to their concentration found in groundwater. However, all tracers have a restricted application range and face individual limitations, which can lead to ambiguous age interpretations (e.g. Allison and Hughes, 1978; Edmunds and Walton, 1980; Visser, 2009; Beyer et al., 2015 and references therein). As examples of these limitations, SF_6 has natural sources (e.g. Bunsenberg and Plummer, 2000 and 2008; Stewart and Morgenstern, 2001; Koh et al., 2007), CFCs have a stagnant input function (Bullister, 2011), have anthropogenic point sources (e.g. in industrial and horticultural areas) (e.g. Oster et al., 1996; Stewart and Morgenstern, 2001; Bunsenberg and Plummer, 2008, 2010; Cook et al., 2006) and are known to be degradable in anaerobic environments (e.g. Lesage et al., 1990; Bullister and Lee, 1995; Oster et al., 1996; Shapiro et al., 1997). Ambiguous age interpretations with tritium can be faced due to similar rates of radioactive decay and decrease in atmospheric concentration, which leads to similar concentrations of tritium in groundwater recharged at different times. This is particularly relevant for the Northern Hemisphere, where con-

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centrations in young groundwater are still elevated due to H bomb testing in the 1970s (Morgenstern and Taylor, 2009; Morgenstern et al., 2010; Taylor et al., 1992). Additional interpretation issues follow from both the seasonal variability of groundwater recharge and tritium in rain. In these situations the tritium recharge is often estimated using recharge weighting techniques (Allison and Hughes, 1978; Stewart and Taylor, 1981; Engesgaard et al., 1996; Knott and Olipio, 2001; Morgenstern et al., 2010). These limitations with ambiguity and input uncertainty can be overcome by time series or multiple tracer observations. To ensure robust age interpretation of (relatively young) groundwater in future, there is a need for additional, complementary groundwater age tracers.

We previously and unexpectedly identified the presence of Halon-1301 ($CBrF_3$) within modern water samples. Our paper immediately following this discovery (Beyer et al., 2014) details this identification, discusses known Halon-1301 properties, and suggests this compound might have potential as a new, complementary groundwater age tracer (for water recharged < 100 years ago) to join the limited set of established compounds commonly used for this purpose. We did not infer ages from Halon-1301 concentrations in that paper. However we provided a first insight into its performance by approximating Halon-1301 ages derived from corrected CFC-13 data presented in Busenberg and Plummer (2008). In this work, we analyse Halon-1301 in a range of groundwater locations, infer Halon-1301 ages from its concentration, and compare these to groundwater ages previously inferred from other tracers. We additionally comment on (and analyse where possible) the various properties of Halon-1301 that have not previously been assessed in detail but may affect its wide-scale applicability as an age tracer.

As discussed in that earlier paper (Beyer et al., 2014), Halon-1301 appears to be a suitable groundwater age tracer, since it is soluble in water (saturation: $30\,mg\,L^{-1}$ at $20\,^{\circ}C$; in contact with modern air (3.2 pptv): $7.5\,fmol\,L^{-1}$ at $20\,^{\circ}C$, 10 m elevation) (Deeds, 2008) and its increasing atmospheric concentration has been determined in the atmosphere since the 1970s by NOAA (National Oceanic and Atmospheric Administration) and AGAGE (Advanced Global Atmospheric Experiment) and data from

1969 to 1977 are reconstructed by Butler et al. (1999) (Fig. 1). Open questions remain regarding its conservativeness and contamination potential in groundwater environments. These are:

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

To answer these questions, we analyse Halon-1301 in 17 New Zealand groundwater and various modern (river) water samples. The analysis allows for simultaneous determination of Halon-1301 and SF_6 (Beyer et al., 2014), which are both gaseous tracers with a similar behaviour in water. This allows us to identify issues, such as contamination, due to contact with air during sampling or local (anthropogenic) sources.

All groundwater samples have been previously dated with tritium, CFC-12, CFC-11 and SF_6. We determine piston and exponential piston flow ages for Halon-1301 and SF_6, as inferred by matching the historic input to the determined concentrations in the groundwater samples. Comparison of inferred Halon-1301 piston flow and exponential piston flow mean residence times (MRTs) to relatively robustly inferred tritium and SF_6

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MRTs enables for direct assessment of the performance of Halon-1301 as a groundwater age tracer. Because Halon-1301 and SF_6 are both gaseous tracers with a similar input function over several decades, they are expected to show similar transport and exchange process through the unsaturated zone. Gaseous tracers equilibrate with the atmosphere during transport through the unsaturated zone and therefore do not account for this unsaturated zone travel time. This contrasts with inferred tritium ages, which do account for travel time through the unsaturated zone. Comparison of age information inferred from tritium and 4 different gaseous tracers (SF_6, Halon-1301 and CFC-12 and CFC-11) allows for assessment of unsaturated zones processes of Halon-1301 or potential contamination/degradation. Since some of the anoxic samples clearly showed evidence of CFC degradation, comparison of Halon-1301 from these samples enables a first understanding of the potential for degradation of Halon-1301 in anoxic groundwater.

2 Methodology

2.1 Water samples

This study takes advantage of the relatively well defined age information of New Zealand groundwater inferred from time series tritium and SF_6 (and CFC) observations, particularly for confined aquifers (Morgenstern and Taylor, 2009; van der Raaij and Beyer, 2015). The inferred tritium ages are considered robust because of their well-defined input function (close proximity of our sampling sites to the high-resolution Kaitoke monitoring station) and because of long time series data in groundwater (Table 1). To enable a relatively comprehensive assessment of the potential of Halon-1301 as a groundwater age tracer, groundwater samples previously dated with tritium, SF_6 and CFCs covering a wide range of mean residence times and including anoxic and aerobic samples and samples with apparent contamination/degradation of CFCs are chosen. We analyse 35 groundwater samples from 17 different sites in the Wellington region from 3 different aquifer systems (Lower Hutt groundwater Zone, Wairarapa groundwater system and Wainuiomata aquifer) and 8 river and equilibrated tap water samples for Halon-1301 and SF_6, simultaneously. Groundwater samples in the Lower Hutt groundwater Zone (LHGWZ) and river water samples are collected as triplicates, of which 2 are analysed directly after sampling and 1 is analysed after 7 weeks storage at 14 °C. One river water sample is analysed after 1.23 years of storage at 14 °C. The location of the sampling sites and aquifer systems is illustrated in Fig. 2. The sampling sites, number of samples taken and corresponding aquifer systems are summarized in Table 1. Table 1 also includes the concentration of dissolved oxygen (DO), previously determined recharge temperature and amount of excess air (determined by Ar and N_2 analysis) (Jones and Gyopari, 2006; Stewart and Morgenstern, 2001; Tidswell et al., 2012) and the number of previously determined CFC (CFC-11 and CFC-12), SF_6 and tritium observations. The groundwater systems are briefly described in the following.

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

Generally the sampling procedure for determination of Halon-1301 is similar to the standard procedure for determination of water soluble gaseous tracers, such as SF_6 and CFCs. To ensure the sampling of fresh unexposed groundwater (i.e. not the water sitting in the dead volume of the well), the well is flushed until conductivity, pH and dissolved oxygen (DO) stabilizes. In the absence of measurement equipment the well is flushed at least 3 times of its volume (Daughney et al., 2006). To avoid alteration of Halon-1301 concentrations with UV light and contamination or adsorption of the gas

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tracers (Halon-1301 and SF_6) from/onto the sampling material, only brown borosilicate glass bottles and nylon tubing are used and the use of PTFE/Teflon or other fluorine baring plastics is avoided (Reynolds et al., 1990; van der Raaij and Beyer, 2015). To avoid contamination of the samples with modern air, sampling is carried out under rigorous exclusion of air by inserting a nylon tube to the bottom of the sampling bottle and filling it from the bottom. Then the volume of the bottle is let to overflow, so the water volume is replaced by several bottle volumes. The bottle is quickly capped and checked for presence of bubbles and if necessary the sampling process is repeated until no bubble is present.

River water and a variety of equilibrated (at close to constant temperature) tap water samples are taken as representative modern water sample and to verify solubility data. This method presupposes no contamination of SF_6 or Halon-1301 from air within our facilities, surrounding environment or river sampling locations, which seems reasonable, due to the lack of sources of these compounds in our close environment. Air samples are regularly analyzed to confirm the lack of elevated SF_6 and Halon-1301 concentrations in our facilities.

2.2 Analytical system

The water samples are purged with ultra-pure (analytical grade) nitrogen gas in a vacuum sparge chamber (Busenberg and Plummer, 2000). Purging with nitrogen at a flow rate of $70\,mL\,min^{-1}$ for 18 min is carried out to ensure complete degassing of the water sample in regards to removal of SF_6 and Halon-1301. The stripped gas then passes through a drying column (NaOH coated silica) to remove residual moisture and CO_2 to avoid interference in the detection system. To ensure consistent amounts of water sample are purged, the sparge chamber is filled until the filling mark (0.955 L) or the weight of the water sample is determined. If applicable, temperature and headspace volume are determined. Standard gas samples are pushed through a loop of known volume (9.97 ± 0.02 or 0.502 ± 0.001 mL) and the temperature and pressure are recorded to determine the amount of standard gas analyzed.

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The samples (standard gas and purged gas from water samples) are then simultaneously analyzed for Halon-1301 and SF_6 using a gas chromatograph with attached electron capture detector (GC/ECD) setup including 2 cryogenic traps for pre-concentration (Busenberg and Plummer, 2008; Beyer et al., 2014). The analytical setup also allows for simultaneous determination of CFC-12 (Busenberg and Plummer, 2008; Beyer et al., 2014). However an appropriately concentrated standard gas is needed to establish its calibration curve. CFC-12 concentrations and inferred CFC-12 ages are therefore not determined in the study.

In the following the determination of Halon-1301 and SF_6 concentrations in water samples and resulting recharge year are described, which involves the determination of a calibration curve, solubility and where required excess air and headspace correction.

2.3 Calibration

The amount of Halon-1301 and SF_6 in all groundwater samples is determined by establishing a calibration curve (least square fit, forced through 0/0) with approximately 10 mL (precisely 9.97 ± 0.02 mL) certified air standard at various pressures. The certified air standard contains 3.27 ± 1.55 ppt Halon-1301 and 7.53 ± 0.81 ppt SF_6 among other gases (supplied by the Scripps Institution of Oceanography in 2011). A calibration curve is established every day before measurement commences, since the performance of the GC/ECD can change from day to day, due to fluctuations in the environment (e.g. temperature) or aging of the material (e.g. column fill). Because Halon-1301 concentrations in 10 mL calibrated air standard do not sufficiently cover concentrations obtained in modern water samples, another standard gas containing 3.16 ± 0.3 ppb Halon-1301 and 1.02 ± 0.1 ppb SF_6 (prepared by New Zealand Industrial Gases (NZIG)) is used in a smaller standard loop of approximately 0.5 mL (precisely 0.502 ± 0.001 mL) at various pressures. Additionally tap water samples ranging from 1 to 15 L volume and 10 mL modern air samples at pressures from 1 to 3.5 bar are analyzed to assess the linearity of the ECD signal towards Halon-1301 concentrations in the concentration range obtained in old to modern 1 L water samples. If linearity is

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found, then previously determined calibration curves (using the calibrated air standard) are linearly up-scaled to estimate Halon-1301 concentrations in water. This is relevant for all groundwater samples for which calibration curves were established at the time of measurement with calibrated air only. We are aware that this introduces additional uncertainty which we take account of (see Sect. 3).

After determination of the molar amount of Halon-1301 (and SF_6) in a 1 L water sample purged in the vacuum sparge chamber, its equivalent atmospheric molar ratio at time of equilibrium (for groundwater samples at recharge) can be determined using the solubility relationship (Henrys law, described in Supplement S1). In contrast to the solubility of SF_6, which is well studied (Bullister, 2002; Wilhelm et al., 1977, Table 2), the solubility of Halon-1301 has only been reported in one study without provision of the measurement data ("grey" literature) (Deeds, 2008) and cannot be considered robust.

If applicable, the amount of Halon-1301 (and SF_6) in the water sample is corrected for headspace and/or excess air (previously determined by dissolved Ar and N_2 determination, Heaton and Vogel, 1981), also described in detail in Supplement S1.

2.4 Determination of recharge year

To infer the recharge year or residence time of the groundwater, the equivalent partial pressure of Halon-1301 and SF_6 in the atmosphere at time of recharge (determined as described above) is compared to their historic atmospheric records (illustrated in Fig. 1). Southern Hemisphere historic atmospheric Halon-1301 concentrations are summarized and smoothed by Newland et al. (2013). Data from 1969 to 1977 are reconstructed by Butler et al. (1999). Southern Hemisphere atmospheric SF_6 records (Cape Grim station) are available at the GMD/NOAA (http://www.esrl.noaa.gov/gmd/; Thompson et al., 2004) and CDIAC websites (Miller et al., 2008); data from 1973–1995 are reconstructed by Maiss and Brenninkmeijer (1998).

In simple terms the recharge year can be found when observed (equivalent) atmospheric concentrations match historic atmospheric concentrations. This can be done using a simple "lookup" table to infer the piston flow recharge year. However misleading age interpretations can be obtained when using piston flow assumptions, which do not take account of mixing processes of groundwater in the aquifer or during sampling (e.g. Eberts et al., 2012). Therefore lumped parameter modelling is often used to infer an age distribution and with it the mean residence time (MRT) of the groundwater samples from tracer observations (Maloszewski and Zuber, 1982; Juergens et al., 2012). In this study we use the commonly used exponential piston flow modelling (EPM), which has previously been found to best represent tritium (time series) and SF_6 observations in the studied groundwater. EP modelling is carried out using TracerLPM software (USGS) (Jurgens et al., 2012). For one point tracer observations, as obtained for Halon-1301 and SF_6 in this study, a range of EPMs with various exponential to total flow ratio (referred to as $1/n$; n has been defined as ratio of total to exponential flow by Maloszewski and Zuber, 1982) can be fit to the tracer observation. We constrain their $1/n$ ratio to the $1/n$ ratio previously inferred from tritium (time series) observations. We assume this approach is adequate under the assumption of steady state at each sampling location. MRTs (using EPM or PM) inferred from SF_6 and Halon-1301 concentrations are subsequently compared to previously determined MRTs inferred from tritium. We also comment on observed Halon-1301 concentrations in regards to previously observed degradation or contamination with CFCs (CFC-12 and CFC-11) in these wells.

2.5 Analytical uncertainty

Due to uncertainties related to the analytical procedure (calibration, analysis, etc.), the inferred recharge year and mean residence time (from Halon-1301 and SF_6 concentrations) can only be constrained to an age range. To determine the overall relative uncertainty, the EURACHEM/CITAC Guide CG4 (Ellison and Williams, 2012) is followed. This recommends the method described in Kragten (1994), which also implies a sensitivity analysis. The standard measurement error is determined as the total of

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the following (independent) uncertainties:

$$u_{\text{total}}(x) = \sqrt{u1^2 + u2^2 + u3^2 + u4^2 + u5^2 + u6^2 + u7^2}. \tag{1}$$

$u1$: Uncertainty from least square regression (calibration curve)
$u2$: Uncertainty in standard gas concentration
$u3$: Repeatability error from relative SD of replicates
$u4$: Uncertainty related to correction for headspace
$u5$: Uncertainty related to correction for excess air
$u6$: Uncertainty in recharge temperature
$u7$: Uncertainty in solubility

Replicate samples are analyzed to determine the repeatability of the analysis. The absolute SD is defined as:

$$\text{ASD}_i = \sqrt{\frac{\left(\sum\left[\left(a_i - \overline{x}_i\right)\right]^2\right)}{n-1}}. \tag{2}$$

where $a_i - \overline{x_i}$ is the difference between the concentrations obtained for one of the replicate samples a_i with overall mean value $\overline{x_i}$ for n samples and i number of replicates. The overall relative SD can then be determined as median of all replicate samples:

$$D_i = \sum\left(\frac{\text{ASD}_i}{\overline{x}_i}\right). \tag{3}$$

The limit of detection (LOD) is determined by taking into account the slope and SD of the calibration curve (Shrivastava and Gupta, 2011):

$$\text{LOD} = 3.3\frac{\text{SD}}{\text{slope}}. \tag{4}$$

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

3 Results and discussion

3.1 Calibration curve

Figure 3 illustrates the calibration curves of Halon-1301 obtained with the calibrated air standard (Scripps) and highly concentrated Halon-1301 standard (NZIG) with a nearly linear response of the ECD towards Halon-1301 concentration in the concentration range obtained for groundwater samples (signal up to 30 mV min^{-1} for modern water). Additional analysis of modern air at pressures ranging from 1 to 3.5 bar and analysis of water samples of 3 to 15 L (Fig. 4) confirm the nearly linear response of the ECD towards Halon-1301 concentrations in this concentration range. Only for very high amounts of Halon-1301 (signals of approximately one order of magnitude higher than obtained in modern water) does the quadratic regression fit slightly better than the linear regression. Given this evidence of a linear signal response up to concentrations obtained in modern water, we linearly up-scale the calibration curve of Halon-1301 obtained with the calibrated air standard to estimate concentrations of Halon-1301 in all groundwater samples. Using this approach we introduce additional uncertainty, which we take account of during discussion of the inferred MRTs (for further detail see Sect. 3.4: "Assessment of inferred Halon-1301 ages" and "Supplement S2 – Assessment of elevated Halon-1301 ages").

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3.2 Uncertainty

The analysis allows for an average repeatability of 3.6 % for Halon-1301 (2.8 % for SF_6) and 9.8 % (6.9 % for SF_6) average SD of the calibration curve. On average the overall analytical uncertainty in an average[1] New Zealand groundwater samples is 4.7 % for Halon-1301 (9.0 % for SF_6). This leads to a larger uncertainty in inferred piston flow age for waters recharged before 1975 and after about 2000 when using Halon-1301, due to its characteristic S-shaped input function (Fig. 5). The limit of detection (LOD) of the analytical setup is 0.32 $fmol\,L^{-1}$ for Halon-1301 (and 0.23 $fmol\,L^{-1}$ for SF_6), equivalent to a recharge year of 1975 for Halon-1301 (and 1979 for SF_6), at an average recharge temperature (12.1 °C), 10 m elevation and lack of excess air and headspace.

Sensitivity analysis shows that the most significant contributors to the overall uncertainty are uncertainties related to the calibration curve, repeatability, excess air and headspace correction for Halon-1301 and SF_6. Without considering headspace and excess air, the total uncertainty becomes only marginally smaller for Halon-1301 (4.4 % instead of 4.6 %), but significantly smaller for SF_6 (3.2 % instead of 9.0 %). The main uncertainty for the determination of Halon-1301 is related to the uncertainty of the calibration curve and repeatability. Detailed determined uncertainties for each groundwater sample are shown in Figs. 6 and 7 and Table 3.

We note if SF_6 alone is analysed using a different GC column it can be more accurately resolved with 4.5 % overall uncertainty (van der Raaij and Beyer, 2015). However our aim here is to simultaneously determine the two gaseous tracers SF_6 and Halon-1301 with a particular focus on resolving the Halon-1301 signal accurately. The higher uncertainty in SF_6 determination when using our approach may be resolved by adjustment of the column or ECD conditions or application of signal processing.

[1] A detailed study in New Zealand showed groundwater samples have on average a recharge temperature of 12.1 ± 1.8 °C; 2.9 ± 1 mL (STP) kg^{-1} excess air; a headspace volume of 0.5 ± 0.05 mL (van der Raaij and Beyer, 2015).

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Please note that the analytical setup also allows for simultaneous determination of CFC-12. This 3 way simultaneous determination of SF_6, Halon-1301, and CFC-12 allows for more robust groundwater dating, due to the ability to identify issues related to the limited application range of the individual tracers. These are contact with air during sampling (indicated by an increased concentration of all three gas tracers), degradation/contamination (indicated by a reduced/increased concentration of one or more of the gas tracers, respectively) or unsaturated zone processes, such as diffusion (lag-time)/retardation (indicated by a reduced concentration of all or one or more of the gas tracers, respectively, in comparison to tritium ages).

3.3 Solubility

To test the reported solubility of Halon-1301, we determine the Henry coefficient (Eq. S1 in Supplement) in equilibrated tap and river water samples and in relatively young groundwater (< 2 years MRT). These modern waters were collected for estimation of the solubility of Halon-1301. To estimate the robustness of the estimated Halon-1301 solubility, the solubility of SF_6 is also determined in these samples with the same method and compared to literature data.

Figure 6 shows the inferred solubility ($\ln K_H$) of SF_6 and Halon-1301 in modern groundwater and equilibrated tap and river water compared to solubilities reported by Deed (2008) and Bullister et al. (2002) for Halon-1301 and SF_6, respectively. Table 1 contains solubility parameters inferred from the found relationship in Fig. 6 along with previously reported solubility parameters. As can be seen, inferred solubility of SF_6 agrees well with its reported solubility, which indicates that our approach should give relatively robust Halon-1301 solubility estimates. Inferred solubility of Halon-1301 is significantly lower than given by Deed (2008). When using the Deed (2008) solubility parameters, Halon-1301 concentrations are obtained which result in significantly older inferred Halon-1301 ages compared to tritium and SF_6 ages with an average discrepancy of +12 years in equilibrated tap and river water. This offset is removed when using our estimated Halon-1301 solubility parameters.

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Due to absence of robust solubility data of Halon-1301, we use the solubility parameters estimated in this study (Table 3) to infer equivalent atmospheric Halon-1301 concentrations and with that infer Halon-1301 ages. Its estimated solubility has a relatively large uncertainty of 9.8 % (estimated for a regression analysis in Fig. 6). This uncertainty adds to the analytical uncertainty in equivalent atmospheric Halon-1301 concentration (estimated in the previous section), so that the overall uncertainty increases from 4.7 to 9.7 %. This increased uncertainty in turn affects the uncertainty in inferred Halon-1301 age as discussed in the following.

3.4 Assessment of inferred Halon-1301 ages

3.4.1 Overall

In the following we assess inferred Halon-1301 mean ages in comparison to inferred SF_6 and previously inferred tritium and CFC mean ages. We consider elevated concentrations of Halon-1301, SF_6 or CFCs (> 10 %) as "potentially contaminated" and highly elevated concentrations (> 25 %) as "highly contaminated". For signals at or below the limit of detection (LOD) only a lower limit of the mean age can be assigned (i.e. recharged before 1970). Details on individual piston and exponential piston flow model MRTs inferred from Halon-1301 and SF_6 (in this study) and tritium (from previous studies) are listed in Table 4, which are illustrated in Figs. 7 and 8.

Inferred piston flow (PM) SF_6 and Halon-1301 ages (Fig. 7) show that Halon-1301 ages are on average 5.4 years higher than inferred SF_6 ages (over the entire age range), caused by reduced concentrations of Halon-1301 compared to SF_6. However, piston flow ages are unrealistic, as they neglect mixing of water of different age in the subsurface or during sampling (e.g. Małoszewski and Zuber, 1982), also indicated by previously determined EPM ages inferred from tritium and SF_6 (e.g. Morgenstern and Taylor, 2009). In the following we apply an exponential piston flow model (EPM) and infer mean residence times (MRT) from Halon-1301 and SF_6 concentrations. The choice of lumped parameter model significantly affects the age interpretation with Halon-1301,

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due to its S-shaped input function, which is skewed due to mixing processes (depending on the lumped parameter model choice). This highlights the importance of considering mixing processes for inferring groundwater age from Halon-1301 observations. For SF_6, this is less of a problem, due to its nearly linear atmospheric input since the late 1980s. The sensitivity of Halon-1301 concentrations towards mixing of groundwater of different age also implies that groundwater dating with Halon-1301 may allow better constraining of the mixing parameters compared to SF_6.

3.4.2 Consistency of inferred Halon-1301 ages with inferred tritium and SF_6 ages using the EPM

When using the EPM, inferred Halon-1301 and SF_6 MRTs agree for the majority of sites (11 of 18). The remaining sites indicate higher MRTs inferred from Halon-1301 compared to SF_6. To assess whether these differences have been caused by processes affecting both gas tracers (such as lag-time in the unsaturated zone) or only Halon-1301 (such as potential degradation or sorption which does not occur for SF_6), inferred Halon-1301 and SF_6 MRTs are compared to previously inferred tritium MRTs in Fig. 8. Where present, samples exhibiting probable CFC degradation/contamination are highlighted.

At 1 of 18 sites both gases and tritium are close to the LOD, but evidence of slight contamination with modern air during sampling is found, indicated by elevated concentrations of both SF_6 and Halon-1301 which are incompatible with their low tritium concentrations. Evaluation of the performance of Halon-1301 as an age tracer in comparison to SF_6 and tritium is not possible for this sample, which was therefore excluded for the overall comparison. For the majority of the remaining 17 groundwater samples, inferred SF_6 ages agree well with previously determined tritium ages, which indicate that unsaturated zone processes are not significant in this study.

Inferred Halon-1301 MRTs of 12/17 sites are in agreement with inferred tritium and SF_6 MRTs (within ±2 years). This includes 4 older groundwater sites, which show concentrations at or close to LOD of tritium, and are also free of Halon-1301 (Fig. 9 and

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Table 4). For the remaining waters (all relatively old and anoxic), inferred Halon-1301 ages are higher compared to tritium/SF_6 ages. The reasons for this offset are discussed in the following subsection.

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

3.4.3 Conservativeness of Halon-1301

No unexplainable significantly elevated Halon-1301 concentrations are found, despite that the sites cover situations of land use and well construction that result in CFC contamination (Fig. 8 and Table 4). This indicates no issues related to contamination for Halon-1301 from local sources at the studied sites. This has to be evaluated further, e.g. in groundwater recharged close to airports, where Halon-1301 is still in use as a fire suppressant during fuelling of planes. The lack of elevated Halon-1301 concentrations may also indicates that interference of the Halon-1301 signal with CFC-13 or other co-eluting compounds (assessed in Beyer et al., 2014) is not an issue in the studied groundwater samples. However this needs to be assessed further in groundwater with elevated concentrations of CFC-13 or other potentially co-eluting compounds.

Significantly higher Halon-1301 MRTs to tritium and SF_6 MRTs (over an age range from 2.5 to 40 years MRT) are found in 5 of 17 groundwater samples, where direct age comparison could be made. There are several possibilities for higher inferred Halon-1301 groundwater ages as a result of reduced Halon-1301 concentrations, which we assess in detail in Supplement S2. A summary is presented in the following. Our assessment shows we can exclude degassing into headspace created by de-nitrification, production of methane or when groundwater is brought to the ground surface, since this would affect all determined gas tracers, to the highest extend the least water soluble SF_6, which we did not find in any of our samples. We can also exclude lag-time in the unsaturated zone, because this would also affect all gas tracers, dependent on their diffusion coefficient (Goody et al., 2006), which we did not find in any of our samples. Assuming that Halon-1301 behaves similarly to CFCs in regards to sorption to specific materials, we also consider the risk of sorption to well casing/sampling material to be minimal as we followed robust sampling procedure established for CFCs and SF_6 (using only borosilicate glass, stainless steel equipment and nylon tubing).

Potential degradation of Halon-1301 during storage is assessed by analysis of 6 groundwater samples from different sites (covering an age range from modern (< 1 year) to over 100 years MRT, and aerobic to anoxic waters) stored for 7 weeks. The simultaneous determination of SF_6 and Halon-1301 allows us to isolate Halon-1301 degradation, since SF_6 is not known to degrade in aerobic or anoxic environments. Hence an isolated reduced concentration in Halon-1301 would indicate Halon-1301 degradation, in contrast to a combined (Halon-1301 and SF_6) reduced concentration that would indicate e.g. escaping of gas into headspace. Figure 9 illustrates concentrations determined before and after storage are within statistical uncertainty, indicating that Halon-1301 is stable in aerobic and anoxic groundwater during storage for over 1 month at 14 °C. The concentration of Halon-1301 in 1 sample (river water) stored for over 1.2 years is also not significantly reduced compared to SF_6.

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

1. Increased inferred Halon-1301 ages in younger water samples with a MRT (tritium age) close to or below 15 years (applicable for 1 of 5 affected samples) are likely caused by uncertainties related to the recent levelling out atmospheric concentrations of Halon-1301 (AGAGE, 2014), which make it more difficult to constrain the age of younger waters.

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2. Increased inferred Halon-1301 ages in the remaining, particularly older samples with a MRT above 15 years are likely to be caused by (a) degradation, which is likely to occur under anaerobic/anoxic conditions (all affected samples are anoxic), (b) sorption to organic material in the aquifer (cannot be excluded for any of the sites).

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

4 Summary and conclusion

This paper provides an insight into the suitability of the gaseous, water soluble compound Halon-1301 as groundwater age tracer. We demonstrated the capability of the analytical setup for robust simultaneous determination of the gas tracers Halon-1301 and SF_6 (and CFC-12) on the same 1 L water sample, which provides an immense potential for more robust age interpretation of relatively young groundwater (recharged < 100 years). We estimated solubility, which is required to convert measured concentrations in water into atmospheric concentrations, from a range of equilibrated waters and relatively modern, aerobic groundwater. We found that the solubility of Halon-1301 found in this study did not match its reported solubility. Uncertainties arising from this estimation approach, led to higher uncertainty in inferred MRT up to

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16 years. More accurate determination of Halon-1301's solubility is required for better utilization of its potential as age tracer.

We used piston and exponential piston flow modelling (PM and EPM) to infer age from Halon-1301 (and SF_6) concentrations in groundwater. Significantly different age interpretations were found with both modelling approaches. Halon-1301 is particularly sensitive to the choice of LPM due to its S-shaped input function, which is considerably skewed during mixing processes in contrast to SF_6 with a nearly linear atmospheric record. This indicates that the determination of Halon-1301 may allow better constraint of the mixing model. Previously inferred CFC, SF_6 and tritium ages in the studied groundwater sites allowed us to compare the performance of Halon-1301 as an age tracer compared to other tracers.

Twelve of 17 groundwater samples where direct comparison of inferred ages could be made showed matching Halon-1301, SF_6 and/or tritium ages within ±2 years. We found no significantly increased Halon-1301 concentrations in any of the analysed groundwater samples which indicate no apparent sources of contamination of Halon-1301 in our study, despite that the sites included different land use environments and well construction that resulted in CFC contamination. This also indicates that interference with other co-eluting compounds is not an issue, since this would lead to increased concentrations of Halon-1301 determined in water.

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

Despite these not fully understood reduced concentrations, we showed that Halon-1301 has strong potential as a complementary groundwater age tracer. If used in combination with other established tracers, it is likely to aid in reducing the ambiguity in groundwater age interpretations obtained though tritium, SF_6 and fading out CFC concentrations, and improve constraining mixing models. Since Halon-1301 is a gaseous

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tracer, it has additional potential to be used to assess unsaturated as well as saturated zone processes, especially with respect to the simultaneous determination of CFC-12 and SF_6 on the proposed analytical setup. Due to its S-shaped, fading out atmospheric input and analytical detection limits, we suggest the appropriate application range for inference of groundwater age from Halon-1301 is for waters recharged between 1980 and 2005/08. Higher uncertainty will be present in age estimates for waters of earlier (from 1970s) or more modern recharge. The uncertainty in inferred Halon-1301 age can be reduced by more accurate determination of its solubility.

To confirm the absence of local sources, Halon-1301 needs to be assed further at sites with higher risk of local sources (e.g. close to airports). To assess whether reduced Halon-1301 concentrations in older anoxic waters are a result of degradation or sorption, Halon-131 needs to be assed in anoxic waters (preferably young – MRT < 5 years) that have been influenced by different compositions of bacteria and/or aquifer material, and/or in relatively old oxic sites (MRT > 5 years) with high organic content. Even if Halon-1301 is affected by degradation/sorption and/or contamination is occurring in specific areas, Halon-1301 is likely to be a more reliable groundwater age tracer than CFCs, which face issues regarding their reliably to infer groundwater age due to (anthropogenic) contamination, degradation (in anaerobic or anoxic waters) and fading out concentration in the atmosphere.

The Supplement related to this article is available online at doi:10.5194/hessd-12-1397-2015-supplement.

Acknowledgements. Greater Wellington Regional Council, especially Sheree Tidswell, is thanked for support and organisation of the sampling of the groundwater wells. Thanks to NIWA, especially Rowena Moss and Ross Martin, for provision of the NZIG Halon-1301, SF_6 standard gas mixture. This study is part of a PhD supported by GNS Science as part of the Smart Aquifer Characterization program funded by the New Zealand Ministry for Science and Innovation (http://www.smart-project.info/).

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Table 1. Summary of water samples analysed in this study: site name, amount of duplicates analysed, associated groundwater (GW) system, recharge temperature and excess air determined from noble gas analysis, dissolved oxygen (DO) and number of available CFC, tritium and SF_6 data.

Site name	# of samples	Groundwater system	recharge *T* [°C]	Excess air [ml (STP) L^{-1}]	DO [mg L^{-1}]	# SF_6 data	# CFC data	# tritium data
Wainuiomata	3	Wainuiomata	10.7 ± 1.8	0.6 ± 0.9	4.17	2	1	2
Avalon Studio	3	LHGWZ[c]	14.2 ± 1.9	−0.7 ± 0.9	4.82	1	2	4
IBM 2	3	LHGWZ[c]	12.3 ± 1.9	1.0 ± 0.8	0.31	4	3	9
Seaview Wools	3	LHGWZ[c]	15.8 ± 2.1	2.3 ± 0.9	0.22	2	1	3
River water (Hutt River)	4	LHGWZ[c]	15.4; 12.3	2.9 ± 1.8[a]	10.8	1	1	1
IBM 1	3	LHGWZ[c]	10.4 ± 1.5	0.8 ± 0.8	0.29	3	2	4
UWA3	3	LHGWZ[c]	12.1 ± 1.8[a]	2.9 ± 1.8[a]	4.19?	2	1	3
Shandon GC	3	LHGWZ[c]	9.7 ± 1.5	0.3 ± 0.8	0.11	3	2	1
Buick St	3	LHGWZ[c]	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[b]	2	1	1
CDC south	1	Wairarapa	10.7 ± 1.6	2.0 ± 0.8	1.16[b]	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

[a] if no data are available for this site, the average NZ recharge temperature of 12.1 ± 1.8 °C and average NZ excess air 2.9 ± 1 ml (STP) L^{-1} (van der Raaij and Beyer, 2014) are used;
[b] groundwater shows considerable amount of methane and is considered as anoxic, despite relatively high oxygen concentration;
[c] Lower Hutt Groundwater Zone.

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Table 2. Reported solubility parameters for Halon-1301 and SF_6 and *estimated solubility parameters for Halon-1301 with an uncertainty of 10 %.

		Parameters for Henry solubility coefficient [$mol\,L^{-1}\,atm^{-1}$]		
compound	Reference	A	B	C
Halon-1301	Deeds (2008)	−92.9683	140.1702	36.3776
SF_6	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_6 (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".

Site ID	Equivalent atmospheric concentration: Halon-1301 pptv	Halon-1301 ±[c] (incl. solub.)	Halon-1301 ±[c] (excl. solub.)	SF_6 pptv	SF_6 ±	Inferred MRT when using EPM: Halon-1301 MRT [years]	Halon-1301 +[c] (incl. solub.)	Halon-1301 −[c] (incl. solub.)	Halon-1301 +[c] (excl. solub.)	Halon-1301 −[c] (excl. solub.)	SF_6 MRT [years]	SF_6 +	SF_6 −	Previously det. age information: tritium n[d]	tritium MRT [years]	CFC-12/CFC-11 MRT [years]
Hutt River[a]	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[a]	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[b]	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[b]	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[a]	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[b]	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[a]	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[b]	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[a]	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[a]	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[a]	0.05	0.12	0.11	2.03	0.26	55	8	> 14	8	> 14	27	2	2	0.4	40	85
George[b]	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[b]	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[b]	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[a]	LOD	–	–	LOD	–	–	–	–	–	–	–	–	–	0.1	100	95
Warren[b]	0.05	0.01	0.00	0.12	0.01	234	6	6	6	6	215	10	5	0.9	140	n/a
UWA3[a]	LOD	–	–	LOD	–	–	–	–	–	–	–	–	–	var.	150	LOD/LOD
Finnlayson[b]	LOD	–	–	1.57	0.71	–	–	–	–	–	52	28	17	var.	LOD	LOD/LOD

[a] sampling date: 2 Dec 2013;
[b] sampling date: 10 Dec 2013;
[c] uncertainty (±1 SD) including/excluding uncertainty in solubility;
[d] n = mixing ratio (total to exponential flow), which has previously been inferred from tritium (time series) observations.

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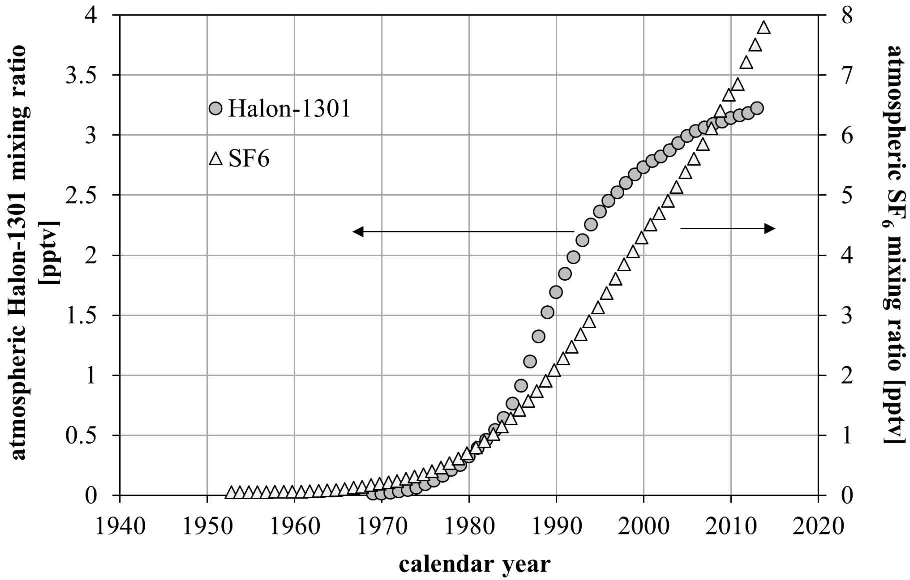

Figure 1. Historic records of Halon-1301 and SF_6 atmospheric mixing ratios [pptv] (Newland et al., 2013; Butler et al., 1999; Thompson et al., 2004; Miller et al., 2008; Maiss and Brenninkmeijer, 1998).

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Assessment of Halon-1301 as a groundwater age tracer

M. Beyer et al.

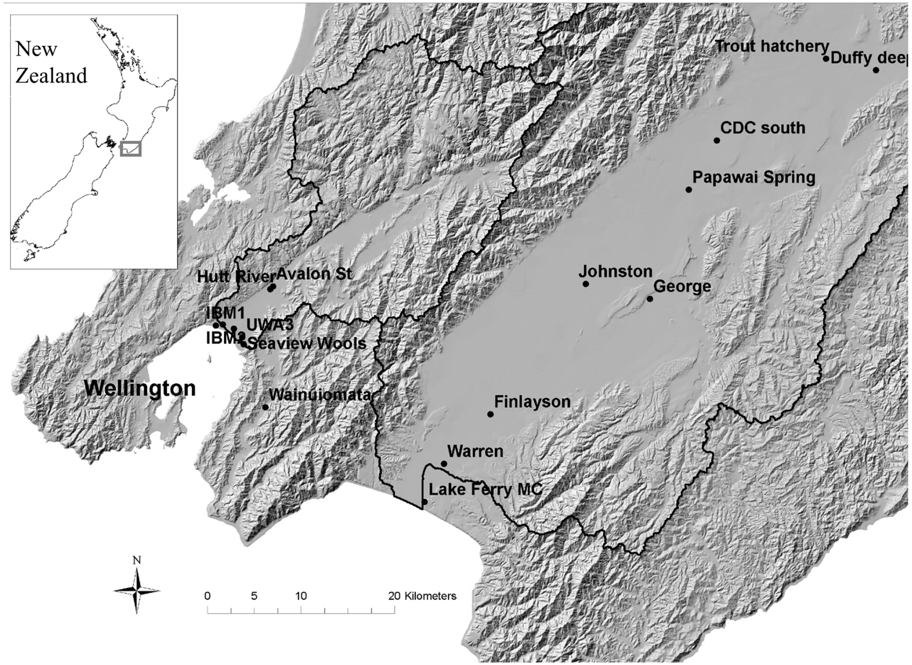

Figure 2. Groundwater wells and sampling locations in the Wellington Region New Zealand are displayed as points; the black outlines represent the 2 catchments Hutt Valley (left catchment) and Wairarapa (right catchment).

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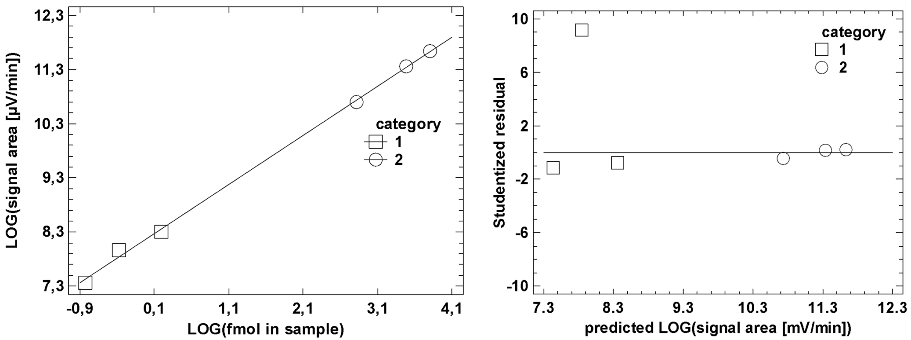

Figure 3. Calibration curve (left) and residual plot (right) for Halon-1301 using 10 mL calibrated air standard (category 1) and 0.5 mL highly concentrated Halon-1301 standard (NZIG) (category 2).

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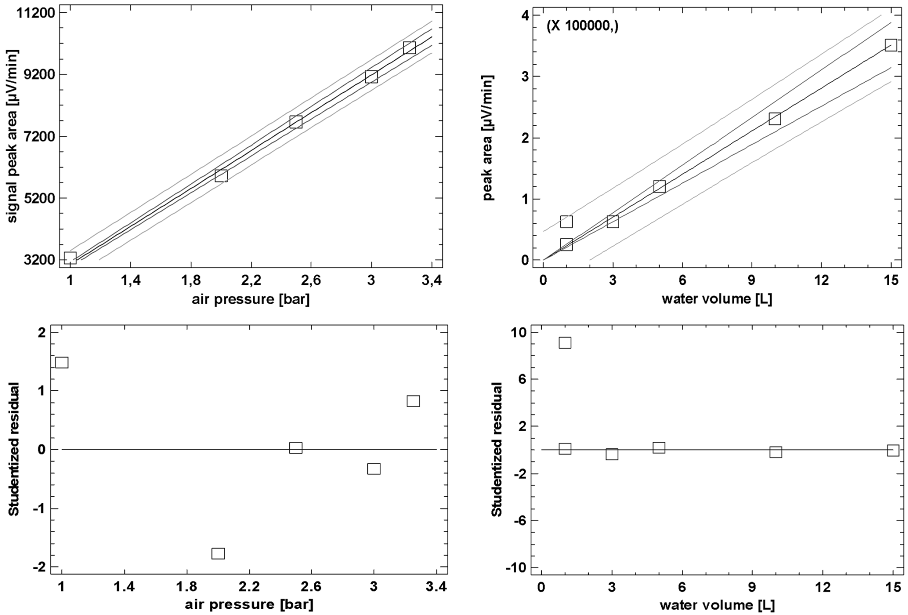

Figure 4. Assessment of linearity of the ECD signal towards Halon-1301 using 10 mL modern air at different pressures (left) and water at different volumes (right) showing an almost linear signal to pressure/volume (upper) and acceptable residuals (lower), lines in upper graphs represent the best least square fit, fit with SD of slope and 95 % confidence interval.

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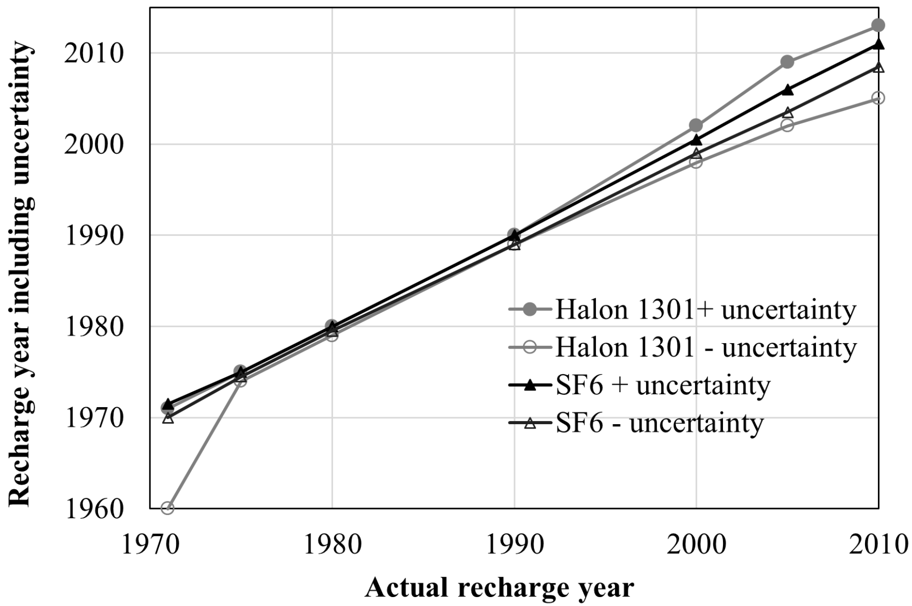

Figure 5. Effect of relative analytical uncertainty on inferred piston flow recharge year for SF_6 and Halon-1301.

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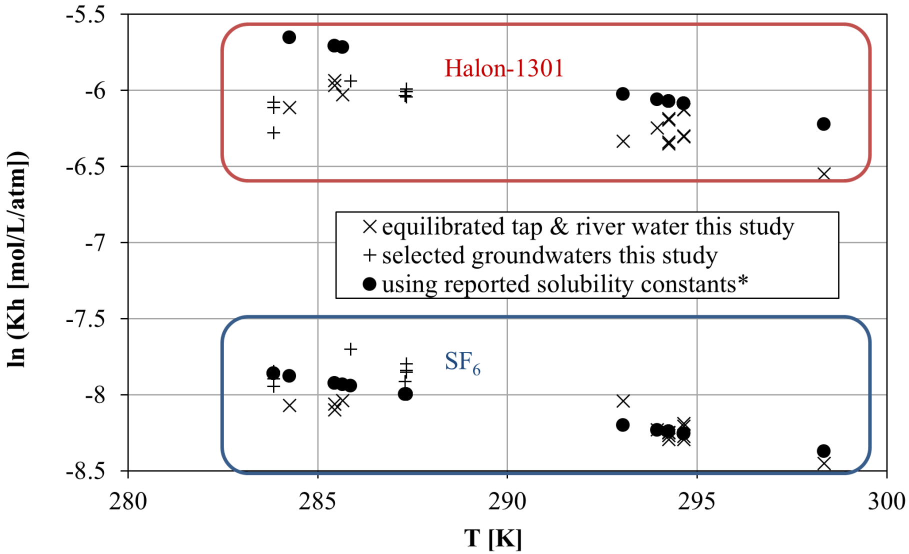

Figure 6. Estimated solubility of Halon-1301 and SF_6 in equilibrated tap water, river water, and aerobic young groundwater in comparison to reported solubility data. * Data from Deeds (2008) for Halon-1301 and Bullister et al. (2012) for SF_6.

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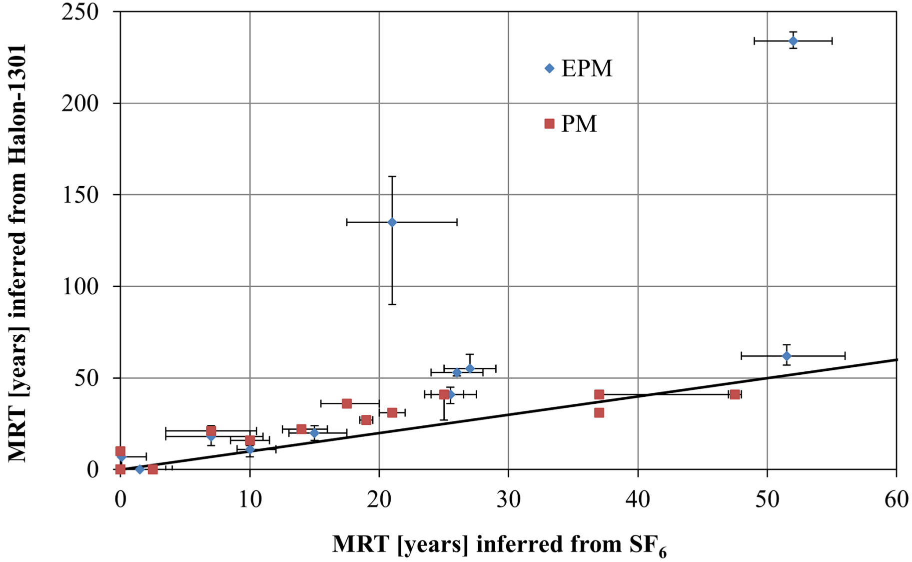

Figure 7. Piston flow and exponential piston flow ages (MRTs) inferred from Halon-1301 and SF_6 concentrations, including error bars (1 SD uncertainty as overall uncertainty including uncertainty in solubility).

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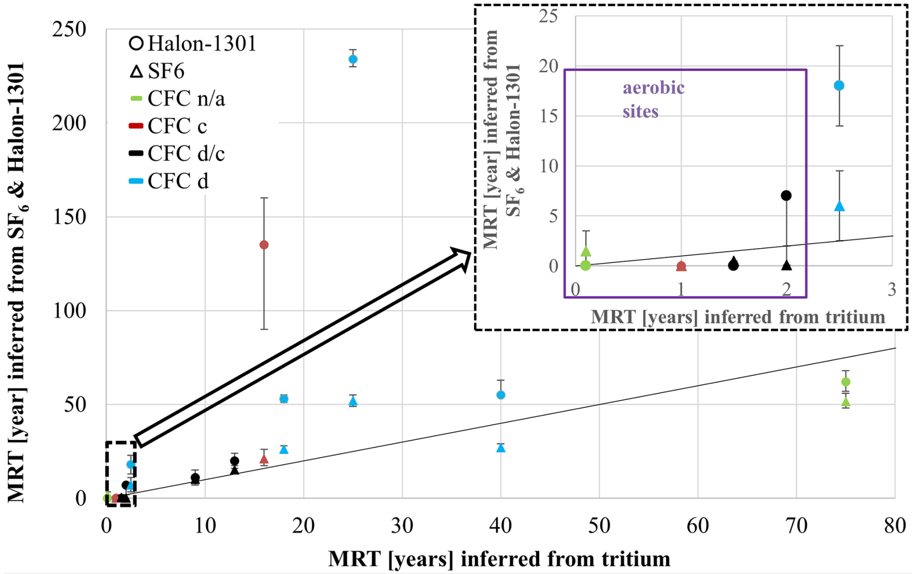

Figure 8. Summary of mean residence time including error bars (±1 SD uncertainty as overall uncertainty including uncertainty in solubility) inferred from Halon-1301, SF_6 and tritium observations using the exponential piston flow model, Halon-1301 and SF_6 were determined in this study, tritium was determined in previous study(s); data points are highlighted according to CFC-12/CFC-11 contamination/degradation (see legend); 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.

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Assessment of Halon-1301 as a groundwater age tracer

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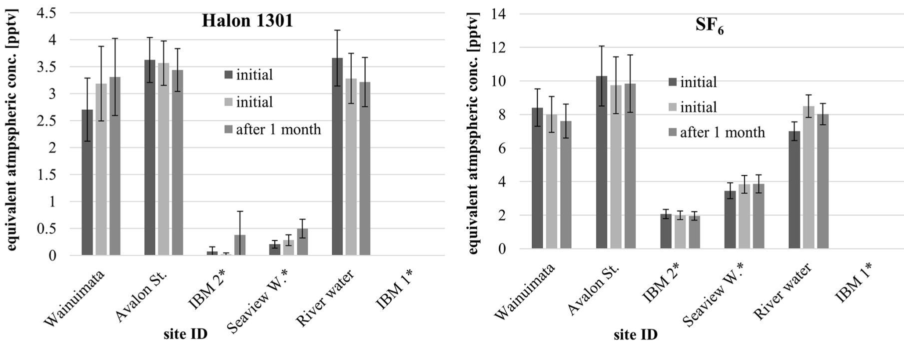

Figure 9. Comparison of Halon-1301 concentration in 1 L water samples analysed directly after sampling (2 of 3) and after 7 weeks storage (1.2 years for Hutt River water sample) at 14 °C (1 of 3). * Anoxic water samples.