

# Review of techniques for dating young groundwater (<100 years) in New Zealand

Monique Beyer,<sup>1,2,\*</sup> Uwe Morgenstern<sup>2</sup> and Bethanna Jackson<sup>1</sup>

<sup>1</sup> School of Geography, Environment and Earth Sciences, Victoria University of Wellington, New Zealand. Corresponding author: Monique.Beyer@vuw.ac.nz

<sup>2</sup> Department of Hydrogeology, Institute of Geological and Nuclear Science, New Zealand.

## Abstract

This literature review summarizes existing methods for dating groundwater and their limitations, with a particular focus on dating techniques for young groundwater (<100 years) in New Zealand. After pointing out the importance and purpose of groundwater dating, we present the definition and accompanying assumptions of inferred groundwater age, which highlight the complexity of groundwater age interpretation. A selection of the most commonly used dating techniques for young groundwater in the New Zealand context is presented. Due to their limited application ranges and the often ambiguous age interpretations inferred using just a single technique, it is apparent that there is a need to develop further complementary dating techniques for more robust groundwater dating. Potential new groundwater dating tools are proposed and their limitations discussed, namely using atmospheric tracers SF<sub>5</sub>CF<sub>3</sub> and Halon-1301, and techniques for inferring age from hydrochemistry. These approaches seem promising, as the two tracers complement those currently in use, and hydrochemistry data is widely available.

## Keywords

groundwater, groundwater dating, hydrochemistry, SF<sub>5</sub>CF<sub>3</sub>, Halon-1301

## Introduction

There is an increasing demand for adequate quantities of 'good quality' groundwater, with increasing population, industrialization, agricultural intensification and climate change (Gleeson *et al.*, 2012), along with increasing recognition of the importance of groundwater quality in maintaining ecological functions (for freshwater and other ecological niches). However, groundwater has become subject to major human-induced contamination (Sampat, 2000). Groundwater recharge areas are increasingly affected by factors such as land use, water supply and sewage system infrastructure. There are also natural sources of groundwater pollution such as heavy metals, derived for example from geothermal processes or volcanic rock, or increased salinity levels due to saltwater intrusion.

The complex and diverse recharge, mixing and flow processes need to be better understood in order to manage and protect groundwater resources (White and Rosen, 2001; Dillon *et al.*, 1989; Close *et al.*, 2001). There are currently two main approaches to characterize groundwater systems and their residence times, flows, recharge source, and aquifer volumes. In the first, hydrogeological models are developed, based on lithology and hydrological data (e.g., water level, recharge area and porosity) to investigate groundwater flow, recharge and more recently to estimate

groundwater age (e.g., Cornaton, 2012). In the second, tracer substances, such as stable- and radio-isotopes and hydrochemical tracers, are studied to infer groundwater age, i.e., time of recharge or residence time and/or recharge source (e.g., Małozzewski and Zuber, 1982; Nir, 1986).

Groundwater age, which we define more formally in the next section, is a measure of ‘recharge year’ and turnover (or residence) time of a groundwater resource. It can be used to help assess not only the amount of water that can be sustainably extracted, but also the lag time and future load of contaminants discharging from groundwater bodies. For example, younger waters are generally more likely to be contaminated with man-made substances, due to recent leaching of pollutants (e.g., nitrate) into the groundwater. In contrast, a longer residence time of the water in the subsurface is likely to be associated with a lower risk of anthropogenic contamination, due to recharge at times with lower or no anthropogenic pollution, along with a higher potential of microbial (or other) degradation of pollutants with time. Groundwater dating also enables us to assess recharge areas, flow paths and mixing processes.

We first present the definition of groundwater age, its determination and assumptions for groundwater dating. Currently used groundwater dating techniques are then reviewed, with a focus on methods which cover the age range (in order of decades) of relatively young groundwater (<100 years). The limitations of these currently available groundwater dating tools are discussed and opportunities for new complementary techniques and their limitations presented.

We focus on dating young groundwater, since groundwater for drinking and irrigation in New Zealand (and many other places around the world), is abstracted primarily from shallow aquifers, due to their easier accessibility. These shallow aquifers contain

mainly younger groundwater, are highly prone to anthropogenic contamination and seasonal depletion and need to be studied for their protection and sustainable management.

## Groundwater age

### Definition

The definition of groundwater age is quite complicated, as described in, e.g., Mazor (1996), Clark and Fritz (1997), Kendall and McDonnell (1998), Phillips and Castro (2003) and Kazemi *et al.* (2006). Groundwater age cannot be measured directly but is inferred from simulations in hydrological models or from the concentration of age tracers by comparison of their measured input (recharge) and output concentrations. Groundwater age indicates the time since the water was recharged by infiltrating precipitation or surface water. However this time estimate can vary with the tracer and method used. For example groundwater ages inferred from non-gaseous tracers include transport through the unsaturated zone and transport on the surface (e.g., in streams). In contrast gaseous tracers do usually not include this time.

Groundwater is usually sampled from a discharge point with converging flow lines (springs, pumped wells), which leads to mixing of groundwater from short and long flow paths in the aquifer. These samples therefore contain a distribution of ages rather than a single age (Małozzewski and Zuber, 1982). The age distribution is complex to represent. Commonly the mean residence time is used for illustration, comparison and further modelling. However, it is important to keep in mind the age distribution, as contamination can occur much earlier than at the mean residence time. To overcome this problem, a distributional threshold can be used, e.g., as reflected by the New Zealand Ministry of Health (2008) drinking water standard, which requires that less than 0.005% of the water be less than one year old.

### Age determination and associated assumptions

The most commonly applied techniques to infer groundwater age use environmental tracers, such as the man-made gaseous compounds chlorofluorocarbons (CFCs) and sulfur-hexafluoride (SF<sub>6</sub>), or tritium and carbon 14. These tracers can be used to infer groundwater age due to their time-dependent input to the groundwater system via recharge and/or due to their time-dependent alteration by processes such as radioactive decay. In addition, some groundwater dating techniques can be applied only locally, such as assessing the extent of damping of seasonally changing hydrochemistry (Stichler and Moser, 1979), tracking of an induced tracer, e.g., dye or chloride (Flury and Wai, 2003; Moore, 2005), or groundwater dating approaches still being developed, such as inference of groundwater age from hydrochemistry (kinetics) (e.g., Daughney *et al.*, 2010) or hydrological models (e.g., Cornaton, 2012).

Generally, the age distribution is inferred by matching measured tracer concentrations to simulated concentrations using simplified 'lumped parameter' models. These account for groundwater mixing processes based on simplified aquifer geometries (e.g., a partly confined/unconfined aquifer) and assumptions regarding the conservativeness and retardation properties of the tracer in question. Despite their simplicity, they have been shown to explain observed tracer concentrations in many applications (e.g. Małoszewski and Zuber, 1982; Cook and Böhlke, 2000). However, with insufficient tracer data, often more than one model can fit observed data, leading to multiple possible (ambiguous) age interpretations. This is a particular problem for complex groundwater systems such as dual porosity aquifers, where a fraction of groundwater may be effectively stagnant and contain significantly older water

(and corresponding tracer signature) than that within the remainder of the system. The extent and time frame of exchange of an age tracer from stagnant to flowing groundwater depends on the nature of the tracer and its diffusion coefficients (a function of the rock type as well as the specific tracer). Age interpretation of this mixed fraction can sometimes be used to study such mixing processes, but a sufficiently large set of tracer data is necessary (e.g., Worthington, 2007; Stewart and Thomas, 2008).

There is also a Bayesian approach, from which the age distribution can be determined from a large set of observed tracer concentrations without assumptions of the shape of the lumped parameter model. However a sufficiently rich dataset is seldom available to use this approach (Fienen *et al.*, 2006; Cirpka *et al.*, 2007).

More recently, more complex hydrological models have been used to assess the age distribution at discharge points, e.g., by using particle tracking techniques or direct age simulation (e.g., Goode, 1996; Cornaton, 2012). These models are proving very valuable as hypothesis testing tools, but are very 'data hungry', as well as being time consuming to set up and parameterise.

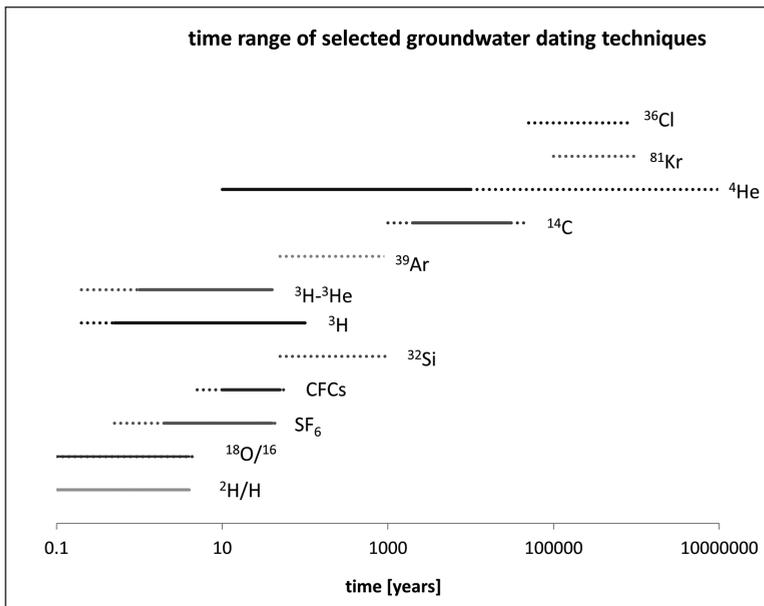
Steady-state conditions are often assumed in both the simple and more complex modelling approaches. However, inferred groundwater age (distribution) at an observation site may change over time, e.g., seasonally, due to a change in recharge or increased abstraction. If sufficient tracer data are available, age tracers can be used to verify steady-state or non-steady state conditions (Morgenstern *et al.*, 2010). Non-steady state (transient) parametric approaches may be used to infer groundwater age, but require confinement (magnitude and direction) of the unsteady changes (Ozyurt and Bayari, 2005).

## Comparison of current groundwater dating techniques

### General

Comprehensive summaries and comparison of available groundwater dating techniques (widely applied and still in development) have been published in recent decades, such as Mazor (1996), Clark and Fritz (1997), Kendall and McDonnell (1998), Cook and Herczeg (2000), Phillips and Castro (2003), Kazemi *et al.* (2006) and IAEA (2013). Further publications cover more limited selections of groundwater dating techniques and age tracer substances in detail. Ekwurzel *et al.* (1994) and Cook and Solomon (1997) compare CFC, krypton-85 ( $^{85}\text{Kr}$ ) and tritium/helium ( $^3\text{H}/^3\text{He}$ ) dating. Stewart and Morgenstern (2001) review groundwater age tracers used in New Zealand, including the stable isotope ratios  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/\text{H}$ , the radio-isotopes tritium (tritium/helium) and

carbon-14, and gas tracers CFCs and  $\text{SF}_6$ . Bethke and Johnson (2008) evaluate the role of hydrological models, carbon-14 ( $^{14}\text{C}$ ), tritium ( $^3\text{H}$ ), helium-4 ( $^4\text{He}$ ), argon-40 ( $^{40}\text{Ar}$ ) and anthropogenic compounds (chloride-36 ( $^{36}\text{Cl}$ ),  $^3\text{H}$ ,  $^{85}\text{Kr}$ , CFCs,  $\text{SF}_6$ ) in groundwater dating. The work of Visser (2009) summarizes  $^3\text{H}/^3\text{He}$ , pollutant concentrations (e.g., nitrate), CFCs,  $\text{SF}_6$  and particle tracking methods for groundwater dating. USGS (1999) summarize the use and limitations of CFC and  $\text{SF}_6$  as groundwater age tracers for dating young groundwater. Edmunds (2009) gives a very comprehensive review of the development of groundwater characterization tools from past till the present. Zuber *et al.* (2011) provides a critical review of the limitations of currently available groundwater dating techniques, with a focus on how these affect the robust calibration of flow and transport models.



**Figure 1** – Time ranges of selected groundwater dating techniques. Dotted lines indicate ranges where age interpretations are not robust due to problems with detection limits or transport behaviour in groundwater, or because their application has not been widely assessed (after Glynn and Plummer, 2005; Cook and Salomon, 1997; Cook and Herczeg, 2000).

The above-mentioned literature can be consulted for further detail. In summary, each dating method has specific limitations, and covers specific time spans which influence their applicability. The time spans of selected 'state-of-the-art' techniques are summarised in Figure 1 (opposite); it shows that no technique is applicable over the entire age range.

In the following, detailed limitations for selected techniques for young (<100 years) groundwater dating used in New Zealand are discussed, including the use of tracers ( $\text{SF}_6$ , CFCs and tritium) for groundwater dating and hydrological models.

### Age tracers for young groundwater

The most widely applied age tracers for dating groundwater recharged since the 1950s are tritium (tritium/ $^3\text{He}$  in northern hemisphere), sulfur hexafluoride ( $\text{SF}_6$ ) and chlorofluorocarbons (CFCs: CFC-12, CFC-11, and CFC-113) (e.g., Busenberg and Plummer, 2000, 2008; Taylor *et al.*, 2001; Stewart and Morgenstern, 2001; van der Raaij, 2003; Morgenstern and Daughney, 2012; van der Raaij and Beyer, under review). Groundwater dating with these tracers utilizes their known input function in meteoric water, illustrated in Figure 2, and known radioactive decay (for tritium).

Please note that stable isotopes (ratios) of hydrogen and oxygen are also widely applied, but are mainly used to characterize the recharge source of the groundwater and only robustly cover a small age range from months to years (relying on seasonal changes) (Stewart and Morgenstern, 2001; McDonnell *et al.*, 1999; Rosen *et al.*, 1999). They are therefore not further assessed in this study. Tracer tests involving application of dye and other artificial locally applied tracers are also not covered here.

*Tritium* ( $^3\text{H}$ ) is the heaviest hydrogen isotope and occurs naturally, produced by spallation reactions in the atmosphere due

to cosmic ray interaction with atmospheric gases. Atmospheric thermonuclear bomb tests (mainly between 1954 and 1963) have led to global spike(s) in atmospheric tritium concentration, with magnitude and characteristics differing between the northern and southern hemisphere (Fig. 2). The estimation of tritium recharge to the groundwater system is complicated, since it is dependent on the amount and timing of recharge. The seasonally varying tritium signal in the atmosphere can in some cases be amplified or dampened by seasonally varying recharge (Stewart and Taylor, 1981). Tritium recharge can be estimated by weighting its atmospheric concentration according to recharge estimates (Allison and Hughes, 1978; Stewart and Taylor, 1981; Engesgaard *et al.*, 1996; Knott and Olipio, 2001; Morgenstern *et al.*, 2010).

Tritium, as a radio-isotope, decays with a half-life of 12.32 years and the remaining traces of tritium from the bomb test spike(s) in groundwater infiltrated around 55 years ago. Tritium therefore allows the dating of waters with mean residence times varying from 250 years to 0.2-0.5 years, dependent on detection limits, sampling frequency and applied lumped parameter model. However the rate of radioactive decay and decrease in the atmosphere have led to similar concentrations in groundwater recharged after the nuclear bomb tests. Problems of ambiguity are faced, especially in the northern hemisphere (Morgenstern and Taylor, 2009; Morgenstern *et al.* 2010; Taylor *et al.*, 1992). To overcome this issue, tritium time series or the combination of a single tritium measurement with a complementary age tracer, e.g., tritium's daughter product  $^3\text{He}$ , CFCs, or  $\text{SF}_6$  are necessary (Tolstikhin and Kamenski, 1969; Schlosser *et al.*, 1988). In areas where tritium is being emitted, e.g., nuclear waste disposal sites, landfills or close to nuclear power plants, the atmospheric

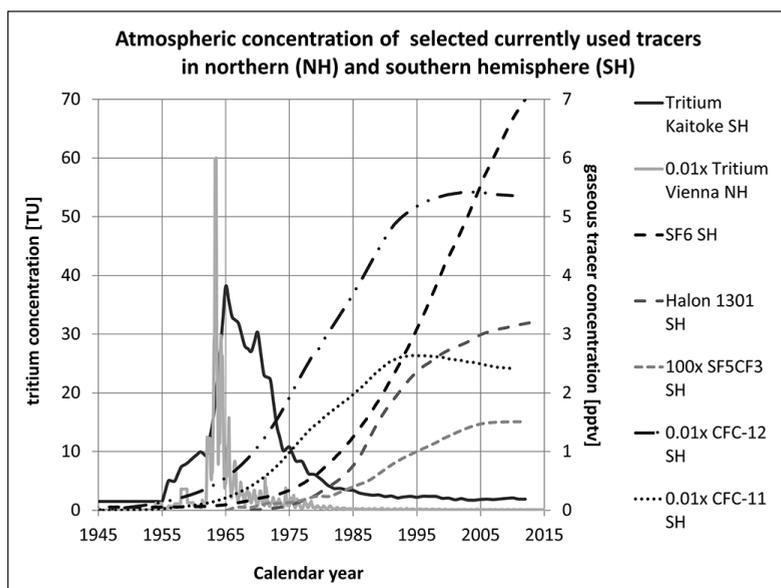
tritium signal can be significantly disturbed, which may prevent the use of tritium for age interpretation in these areas (e.g., Hughes *et al.*, 2010, Mutch and Mahony, 2008; Galeriu *et al.*, 2005).

*Chlorofluorocarbons (CFCs)* (CFC-11, CFC-12 and CFC-113) have gradually increased in the atmosphere since the 1930s due to their use as repellent and refrigerant gas (Fig. 2). CFCs can therefore be used to date groundwater recharged after the late 1940s/1950s, depending on the limit of detection of the analysis. CFCs are still being released from industrial waste, e.g., old refrigerants and air-conditioning units. However the restriction of CFC emissions since the late 1980s, due to their ozone depleting effect (Montreal Protocol), led to a leveling out and subsequent decrease in atmospheric concentrations (Fig. 2). This will compromise the use of CFC techniques in the future, leading to ambiguous age interpretations (Bullister, 2011). Further complications with the use of CFCs as groundwater age tracers are that they are biodegradable in anaerobic groundwater environments and tend to sorb to organic matter in soils (Lesage *et al.*, 1990; Bullister and Lee, 1995; Shapiro *et al.*, 1997; Happell *et al.*, 2003; Hinsby *et al.*, 2007; Horneman *et al.*, 2008). In addition, past and present release of local anthropogenic CFCs from sources in urban and industrial areas (e.g., Szabo *et al.*, 1996) can lead to contamination of groundwater and the inability to infer groundwater age from CFC concentrations. Such cases are known as 'excess' CFCs (e.g., Oster *et al.*, 1996; Stewart and Morgenstern, 2001; Bunsenberg and Plummer, 2008, 2010; Cook *et al.*, 2006). However, with improving knowledge of CFC contamination sources it may be possible to use excess CFCs as indicators for recharge sources (van der Raaij and Beyer, under review). In some cases, excess CFCs may also be used to estimate the extent and source of contamination

plumes (e.g., Thompson and Hayes, 1979; Busenberg *et al.*, 1993).

SF<sub>6</sub> is widely used for electrical insulation, which has led to a continuous increasing atmospheric concentration since the 1970s (Fig. 2). Therefore SF<sub>6</sub> can be used to date groundwater recharged since the 1970s, dependent on the limit of detection of the analysis. Although SF<sub>6</sub> is a greenhouse gas, it is unlikely that its production and release will be limited soon because its atmospheric concentration is still relatively low compared to other greenhouse gases. The steadily increasing input is expected to allow increasingly accurate dating of water younger than 40 years. SF<sub>6</sub> is not biodegradable and is stable in groundwater, even in anoxic environments. Point sources or enrichment in urban air can lead to higher concentrations or excess SF<sub>6</sub> in some areas and the inability to use SF<sub>6</sub> for groundwater dating. This is generally not a problem in New Zealand (Santella *et al.*, 2003, 2008; van der Raaij and Beyer, under review). SF<sub>6</sub> also has natural sources such as hot springs, volcanic areas, carbonate aquifers and silicigenous rock, which may affect groundwater interpretation with SF<sub>6</sub> (e.g., Bunsenberg and Plummer 2000, 2008; Stewart and Morgenstern, 2001; Koh *et al.*, 2007; van der Raaij, 2003).

Elevated gas tracer concentrations of SF<sub>6</sub> and CFCs (and <sup>3</sup>He for use of tritium in northern hemisphere) may occur due to excess air (air bubbles entrapped during recharge). This can be significant, in particular for less soluble gases such as SF<sub>6</sub> (and <sup>3</sup>He). On the other hand, due to their volatile character, gas tracer loss can occur due to degassing with gas produced from biological processes (such as methane or nitrogen). Both excess air and degassing can lead to nonconforming, ambiguous age interpretations using SF<sub>6</sub> and CFCs (and tritium/<sup>3</sup>He in northern hemisphere) (e.g., Visser *et al.*, 2008; Visser, 2009; Van Breukelen *et al.*, 2003; Morgenstern *et al.*, 2004).



**Figure 2** – Southern hemisphere (SH) atmospheric concentration of CFC-12, CFC-11, SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub> and Halon-1301 from the 1940s till date, according to data from Sturges *et al.* (2000, 2012), Busenberg and Plummer (2008), Bullister (2011), Newland *et al.* (2013) and Fraser *et al.* (1999); tritium input in SH from GNS Science (Morgenstern and Taylor, 2009) and in the northern hemisphere (NH) from IAEA GNIP (Jurgens *et al.*, 2012).

The use of different age tracers can result in different age interpretations, depending on whether the age estimate includes or excludes travel time within the unsaturated zone, or re-setting the ‘age clock’ through re-equilibration with atmospheric air.

For tritium, a non-gaseous tracer, the ‘clock’ starts counting as soon as the rain recharge infiltrates into the soil. Age estimates inferred from tritium concentrations therefore include the passage of the water through the unsaturated zone. In addition, if water enters the aquifer, then re-emerges to the surface, and again enters the aquifer after a short time, the ‘clock’ is not altered significantly during this surface contact, assuming additional recharge containing modern tritium is negligible. This is because the tritium signal is not affected significantly during contact with air. Tritium can therefore also be used as an age tracer for surface waters such as streams and rivers.

On the other hand, the gas tracers SF<sub>6</sub> and CFCs dissolved in recharging water are in equilibrium with the atmosphere in the unsaturated zone, hence the gas tracer ‘clock’ does not start counting until the recharge has entered the saturated zone (the water table). In addition, dissolved gas tracers re-equilibrate with the atmospheric air; hence their ‘clock’ is reset to zero when groundwater reappears at the surface.

In moist unsaturated zones a lag time needs to be taken into account, due to slower diffusive transport (Cook and Salomon, 1997), for both gaseous age tracers and tritium.

### Hydrological models

Hydrological models are widely applied in New Zealand and elsewhere to estimate groundwater flow, recharge, discharge, chemical transport and, more recently, simulation of groundwater age. Groundwater

models usually utilise Darcy's law to simulate flow and transport of groundwater in an aquifer. The hydraulic head gradient and porosity of a given aquifer are determined from observation bores to estimate its hydraulic conductivity and flow velocities. Chemical transport and, more recently, direct age simulation models generally combine the water flow equations with the advection-dispersion equation. It is extremely difficult to adequately characterise the properties of a groundwater system, due to the heterogeneity of the subsurface and the cost of observation bore surveys (Zuber *et al.*, 2011; Castro and Goblet, 2005). Therefore simplified assumptions of relatively homogeneous subsurface properties are often made. Steady-state conditions are also often assumed, due to the high computational cost of characterising a transient groundwater system, particularly under conditions with limited measurements where large numbers of simulations are required to estimate hydraulic parameters (hydraulic conductivity, porosity, etc.). The characterisation and resulting model estimations are hence subject to significant uncertainty.

Age tracers are one means by which groundwater modellers can reduce this uncertainty and refine their understanding of the subsurface flow systems. Calibration of hydrological models with age tracer data can lead to refined, more realistic hydrological models with reduced uncertainty (Castro *et al.*, 1998; Castro and Goblet, 2005; Stute and Schlosser, 2000; Konikow *et al.*, 2008; Cornaton, 2012).

### **Complementary groundwater dating tools**

Due to the complexity of groundwater flow, and the ambiguities and limited application range of given single methods, many studies have stressed the importance of using multiple methods to infer groundwater age more robustly (e.g., Scanlon *et al.*, 2002, USGS, 1999, Zuber *et al.*, 2011). This has been a theme in the literature since the

early studies of Allison and Hughes (1978) and Edmunds and Walton (1980), which showed a combination of hydrochemistry and isotopes are important to adequately characterise groundwater recharge and groundwater flow.

With a range of dating techniques, including isotopes, hydrochemistry, gas tracers, and implementation of hydrological models, it is possible to identify multidimensional and complex aquifer geometry (e.g., Taylor *et al.*, 2001; Glynn and Plummer, 2005), non-steady state conditions through discrepancies in inferred groundwater ages determined by different methods (e.g., Mazor and Nativ, 1992; Ayotte *et al.*, 2011), changes in inferred groundwater age due to irrigation with older groundwater (Close *et al.*, 2011; Hofmann *et al.*, 2010), temporal changes with climate (river or rain recharge), Gueller *et al.*, 2002; Reilly *et al.* 1994; McMahon *et al.*, 2011), issues of gas tracers with contamination, and/or travel time of recharging water through the unsaturated zone (Morgenstern and Daughney, 2012; Hölting *et al.*, 1995).

Multiple dating tools are essential for robust groundwater dating to overcome the ambiguities generally encountered when using a single method. However, as all techniques have limitations, dating cannot always be robust, even when using a combination of different dating techniques. In addition, some dating techniques, such as the use of CFCs, are becoming less useful as their atmospheric concentrations diminish. The development of further methods is imperative to extend the application range of groundwater dating methods, to replace those that will become less applicable, and to further reduce ambiguities in age interpretation. A combination of tracers with different input functions or transport parameters is recommended to allow for the study of more complex groundwater processes such as double porosity transport. In the following, two additional gaseous tracers and the use of

hydrochemistry as a groundwater age proxy are assessed as potential complementary groundwater dating tools.

## Potential complementary groundwater dating tools

### Gas tracers: SF<sub>5</sub>CF<sub>3</sub> and Halon-1301

For a compound to be of wide-spread applicability as a groundwater tracer, it is important that

- a) the tracer has a resolved atmospheric input,
- b) it is sufficiently soluble and easily detectable in water,
- c) it is stable in the atmosphere and generally conservative in groundwater, and
- d) it lacks significant local anthropogenic or natural contamination sources that would interfere with the groundwater age interpretation.

Based on these criteria, we suggest that both Trifluoromethyl-sulfurpentafluoride (SF<sub>5</sub>CF<sub>3</sub>) and Bromotrifluoromethane (Halon-1301, CF<sub>3</sub>Br) have potential as new age tracers, as they have long lifetimes, monitored concentrations in the atmosphere, and potentially conservative behavior in groundwater (Busenberg and Plummer, 2008, 2010; Sturges *et al.*, 2000; Takahashi *et al.*, 2002; IPCC, 2001; Beyer *et al.*, 2014).

SF<sub>5</sub>CF<sub>3</sub> is known to have a synthetic non-point source, most probably related to the production of certain fluorochemicals (Santoro, 2000; Sturges *et al.*, 2012). Its concentration in the atmosphere has been increasing since the 1960s, mimicking the historic pattern of SF<sub>6</sub> concentrations (Fig. 2) (Sturges *et al.*, 2000). After reaching a concentration of 0.15 pptv in the southern hemisphere, an abrupt levelling out of atmospheric SF<sub>5</sub>CF<sub>3</sub> has been observed since 2002/2003 (Sturges *et al.*, 2012).

Halon-1301 was used as a refrigerant gas and as an effective fire suppression agent prior to being banned from general use in the

mid-90s (Montreal Protocol) due to its ozone depleting effect (Montzka *et al.*, 2011). Now it is still used in rare cases for fire suppression at high-value facilities (such as airports). The atmospheric concentration of Halon-1301 started increasing from 1970, and since about 2000 has been slowly levelling out (Fig. 2) (Butler *et al.*, 1999; Newland *et al.*, 2013). Its atmospheric concentration has been predicted, using a modelling approach, to start declining between 2020 and 2030, with uncertainty depending on the model parameters used, such as atmospheric lifetime (e.g., Newland *et al.*, 2013).

Busenberg and Plummer (2008) developed a sampling and analysis technique for SF<sub>5</sub>CF<sub>3</sub> and were the first to demonstrate the application of SF<sub>5</sub>CF<sub>3</sub> for groundwater dating (Busenberg and Plummer, 2010). However, SF<sub>5</sub>CF<sub>3</sub> has an extremely low aqueous concentration, which complicates its determination. The analysis technique developed by Busenberg and Plummer (2008, 2010) is time-consuming and requires several hundred litres of water. Refinement of the sampling and analysis technique to a more user-friendly technique with improved quantification and smaller sample size may significantly enhance its use as a groundwater age tracer.

Halon-1301 is also present in recent and modern groundwater, although this has been recognized only recently, as it had previously been misidentified as CFC-13. Beyer *et al.* (2014) correct this misidentification, and show that the setup developed by Busenberg and Plummer (2008) can also be used to determine Halon-1301 in groundwater samples. Halon-1301 generally has a similar signal intensity to SF<sub>6</sub>, which may indicate a similar application range in terms of recharge year. However, the behavior of Halon-1301 in water and its feasibility as a groundwater age tracer has not been assessed in detail. Further work is needed to evaluate its conservativeness, such as degradability

and contamination potential from local (anthropogenic) sources, which may affect the interpretation of age from its concentration.

Due to their levelling out or already decreasing atmospheric concentration both tracers have only a limited application time until they have fully faded out in the atmosphere and in groundwater (similar to CFCs). However, for a few decades they have potential to significantly reduce the ambiguity in age interpretation related to limitations of other dating techniques, such as degradability and sources of excess SF<sub>6</sub> and CFCs, and they can replace rapidly fading out CFCs.

### Hydrochemistry

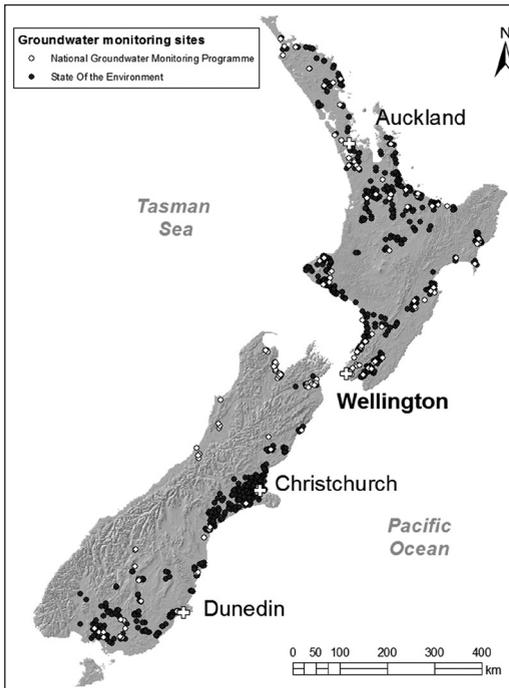
The hydrochemistry of groundwater is known to be mainly influenced by reaction times of the groundwater in the subsurface and by lithology, but also by confinement, geographic area/climate and recharge source (Freeze and Cherry, 1979; Chebotarev, 1955; Rosen, 2001; Daughney and Reeves, 2006). As groundwater resides in the subsurface, dissolution of aquifer material and biological oxidation processes take place, leading to an increase in certain compounds (such as the major ions Si, Na, and K) and a decrease in oxygen and subsequently oxygen-rich compounds (such as nitrate and iron oxide) (Freeze and Cherry, 1979; Chebotarev, 1955). With a combination of appropriate hydrochemistry parameters, it may be possible to obtain groundwater age information (Daughney *et al.*, 2007, 2010).

The potential of hydrochemistry for groundwater dating has been known for decades, since early studies by Chebotarev (1955), Krauskopf (1956) and Garrels and Christ (1964), who assessed the kinetics of processes that determine the hydrochemical composition. If reliable correlations can be established between hydrochemistry parameters and groundwater age, the use of hydrochemistry data as a proxy for

groundwater age would offer significant improvements because of their relatively simple, routine determination and their generally wide availability over the past decades in line with major national and regional groundwater monitoring programs (such as the State of the Environment (SoE) Monitoring network of the Regional Councils and the National Groundwater Monitoring Program (NGMP) in New Zealand, or National Ground Water Monitoring Network (NGWMN) in the USA). Daughney *et al.* (2007) states there are 17 parameters from over 100 NGMP sites and additionally around 1000 State of the Environment (SoE) groundwater monitoring sites available across New Zealand, illustrated in Figure 3. In contrast, age tracer data are available for only a small fraction of monitoring sites (estimated 20%).

Promising correlations have been established between one or more hydrochemistry parameters (especially increasing concentration of rock-forming elements, such as Si, Na, Mg; total dissolved solids and pH, and decreasing concentrations of constituents of microbial degradation, e.g., dissolved oxygen) and age information gained from tracer data (e.g., Downes, 1985; Morgenstern *et al.*, 2009, 2010, Rademacher *et al.*, 2001, 2005) or correlation of hydrochemistry with flow path or well depth (e.g., Taylor *et al.*, 1992; Hofmann *et al.*, 2010; Edmunds *et al.*, 2003). An example of an established hydrochemistry mean residence time relationship under piston flow can be found in Figure 4 (data from Morgenstern *et al.*, 2010). This correlation can potentially be used to estimate the groundwater's mean residence time for locations in the same aquifer with an unknown mean residence time, but known hydrochemistry.

However in the literature to date, no one has been able to establish a distinct relation between groundwater age and hydrochemistry. This is because natural processes are more

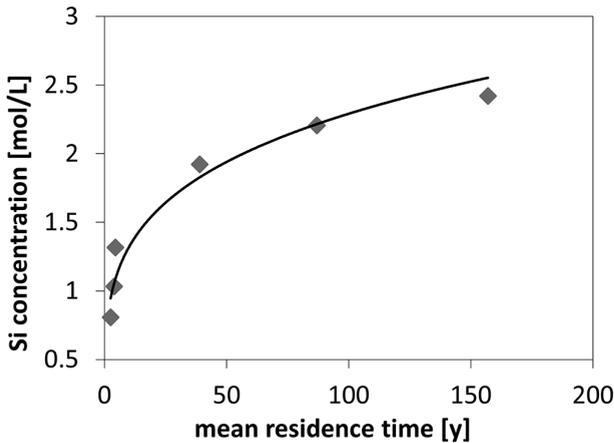


**Figure 3** – Groundwater monitoring sites across New Zealand with available hydrochemistry data.

complicated, for example the mixing of water from different flow lines and the varying kinetics induced by inhomogeneous aquifer material or seasonal climate. In addition, its universal application under all environmental and geological conditions is complicated. The relationships found between hydrochemistry and groundwater age/mean residence time often can not be related to single processes and seem to vary from aquifer to aquifer, due to a complex combination of processes such as dry deposition, cation exchange, vegetative cycling and enhanced weathering kinetics due to biological degradation (O'Brien *et al.*, 1997; Furman *et al.*, 1998; Downes, 1985; Daughney and Reeves, 2005; Plummer *et al.*, 1990; Kilchmann *et al.*, 2004). The hydrochemistry – age relationship also can be influenced by human activities, such as land use and fertilizing, affecting hydrochemistry (e.g., Morgenstern and Daughney, 2012).

A better understanding of individual aquifer idiosyncrasies and how these affect relationships between hydrochemistry and age are needed before hydrochemical monitoring datasets can be reliably used to make age estimates.

Overall, few studies have attempted to directly link groundwater age (mean residence time) and hydrochemistry. One exception is the study by Daughney *et al.* (2010), using discriminant analysis and hydrochemistry observations to assign an age range to groundwater samples from all over New Zealand. This illustrates that statistical approaches may be suitable data reduction tools and could be used to untangle the complexity of aquifer processes that influence hydrochemistry (Dalton and Upchurch, 1978; Lawrence and Upchurch, 1982; Meng and Maynard, 2001; Adams *et al.*, 2001; Locsey and Cox, 2003; Daughney *et al.*, 2007). Inverse modeling may then be used to identify underlying reactions (Parkhurst and Appelo, 1999; Plummer and Back, 1980; Plummer *et al.*, 1991), and have been applied by Busby *et al.* (1991); Rowe and Brantley (1993); Furman *et al.* (1998); Hidalgo *et al.* (2001); Thyne *et al.* (2004); Lecomte (2005); Zhenxue *et al.* (2006) and others. Once the underlying processes/reactions are untangled, hydrochemical modelling may be used to investigate reaction kinetics, which may then be used to infer groundwater age. The assessment of aquifer (material) or geology-dependent kinetics appear to be necessary, since field or naturally occurring mineral weathering kinetics are often different (by several orders of magnitude!) from laboratory results (e.g., White and Brantley, 2003). There is a need to establish a 'database', including inferred reaction kinetics of lab and field kinetics in different hydrological and geological settings, to find adequate estimates for specific reaction kinetics for field environments that can in future potentially be used to directly infer groundwater age



**Figure 4** – Example for potential groundwater dating with hydrochemistry using the established relationship between silica concentration and groundwater mean residence time (piston flow) following a power law function (data from Morgenstern *et al.* (2010)).

(distribution) from a set of hydrochemistry data in any given aquifer.

As a side note, hydrochemistry is also useful to determine if groundwater observations indicate steady state, which can indirectly aid age interpretation. If groundwater age has changed over time at a given observation bore due to changing flow conditions, the hydrochemistry will have changed as well (e.g., Mendizabal *et al.*, 2012; Daughney and Reeves, 200). A change in hydrochemistry can also indicate land-use intensification, but is not necessarily an indicator of a change in groundwater age (Morgenstern and Daughney, 2012; Daughney and Reeves, 2006). Additionally hydrochemistry data contain information about the aquifer material and (microbial) processes in the aquifer, which may be important for assessing contamination risk. It is therefore important to look further into the topic of using hydrochemistry for groundwater characterization, as also pointed out by Glynn and Plummer (2005).

## Conclusion

Due to differing applicability, limitations and ambiguities related to current state-of-the-art groundwater dating techniques (for dating young groundwater with <100 years mean residence time), a combination of dating tools is recommended for more robust groundwater age interpretation. New dating techniques are needed to complement existing ones. Two promising new gas tracers, SF<sub>5</sub>CF<sub>3</sub> and Halon-1301, have been described. They have suitable tracer properties, but have not yet been widely applied, partly due to technical challenges in measuring their very low concentrations in groundwater (for SF<sub>5</sub>CF<sub>3</sub>) or only recent discovery and insufficient assessment (Halon-1301). Improvements in detection limits and sampling procedure (reducing sample volume, time and cost) for SF<sub>5</sub>CF<sub>3</sub> and assessment of relevant properties of Halon-1301 as an age tracer, such as conservativeness in water, are the subject of further studies being carried out by the authors.

Hydrochemistry data has the potential to be better used to assist with groundwater age determination. Hydrochemistry data, which are widely available and routinely determined, can contain age information. In combination with the development of appropriate methods (statistical, process modeling, diagnostic or otherwise), hydrochemistry data may be capable of providing a complementary groundwater dating technique. This would require establishing distinct relationships between hydrochemical signatures and groundwater ages for a variety of geological, climatic and flow/mixing regimes. In our future studies, we plan to investigate the complex relationships between hydrochemistry and inferred ground-

water age (distribution), and examine the kinetics in the field environment using statistical data reduction techniques and inverse modeling to untangle the underlying processes and enable subsequent kinetic modeling as part of the New Zealand government-funded 'Smart Aquifer Characterization' Project.

## References

- Adams, S.; Titus, R.; Pietersen, K.; Tredoux, G.; Harris, C. 2001: Hydrochemical characteristics of aquifers near Sutherland in the western Karoo, South Africa. *Journal of Hydrology* 241(1): 91-103.
- Allison, G.B.; Hughes, M.W. 1978: The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer, *Australian Journal of Soil Research* 16: 181-195.
- Ayotte J.D.; Szabo, Z.; Focazio M.J.; Eberts, S.M. 2011: Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water supply wells. *Applied Geochemistry* 26: 747-762.
- Bethke, C.M.; Johnson, T.M. 2008: Groundwater age and groundwater age dating. *Annual Review of Earth and Planetary Sciences* 36: 121-152.
- Beyer, M.; van der Raaij, R.; Morgenstern, U.; Jackson, B. (2014) Potential groundwater age tracer found: Halon 1301 (CF<sub>3</sub>Br), as previously identified as CFC-13 (CF<sub>3</sub>Cl), *Water Resources Research* 50, doi:HYPERLINK "<http://dx.doi.org/10.1002/2014WR015818>" \o "Link to external resource: 10.1002/2014WR015818" 10.1002/2014WR015818.
- Bullister, J. 2011: Atmospheric CFC-11, CFC-12, CFC-113, CCl<sub>4</sub> and SF<sub>6</sub> Histories (1910-2011). Ocean CO<sub>2</sub>, carbon dioxide information analysis centre, online resource [http://cdiac.ornl.gov/oceans/new\\_atmCFC.html](http://cdiac.ornl.gov/oceans/new_atmCFC.html), accessed 1/10/2012.
- Bullister, J.L.; Lee, B.S. 1995: Chlorofluorocarbon-11 removal in anoxic marine waters. *Geophysical Research Letters* 22: 1893-1896.
- Busby, J.F.; Plummer, L.N.; Lee, R.W.; Hanshaw, B.B. 1991: Geochemical evolution of water in the Madison Aquifer in parts of Montana, South Dakota, and Wyoming. *U.S. Geological Survey Open File Report: F1-F89*.
- Busenberg, E.; Weeks, E.P.; Plummer, L.N.; Bartholomay R.C. 1993: Age dating ground water by use of chlorofluorocarbons (CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>), and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho. U.S. Geological Survey Water-Resources Investigations 93-4054, 47.
- Busenberg, E.; Plummer, L.N. 2000: Dating young groundwater with sulphur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. *Water Resources Research* 36: 3011-3030.
- Busenberg, E.; Plummer, L.N. 2008: Dating groundwater with trifluoromethyl sulfur-pentafluoride (SF<sub>5</sub>CF<sub>3</sub>), sulfurhexafluoride (SF<sub>6</sub>), CF<sub>3</sub>Cl (CFC-13) & CF<sub>2</sub>Cl<sub>2</sub> (CFC-12). *Water Resources Research* 44: 2431-2449.
- Busenberg, E.; Plummer, L.N. 2010: A rapid method for the measurement of sulfur hexafluoride (SF<sub>6</sub>), trifluoromethyl sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>), and Halon 1211 (CF<sub>2</sub>ClBr) in hydrologic tracer studies. *Geochemistry Geophysics Geosystems* 11: 10.
- Butler, J.H.; Battle, M.; Bender, M.L.; Montzka, S.A.; Clarke, A.D.; Saltzman, E.S.; Sucher, C.M.; Severinghaus, J.P.; Elkins, J.W. 1999: A record of atmospheric halocarbons during the twentieth century from polar firn air. *Nature* 399, (6738): 749-755.
- Castro, M.C.; Goblet, P. 2005: Calculation of ground water ages – A comparative analysis. *Ground Water* 43(3): 368-380.
- Castro, M.C.; Goblet, P.; Ledoux, E.; Violette, S.; De Marsily, G. 1998: Noble gases as natural tracers of water circulation in the Paris Basin: 2. Calibration of a groundwater flow model using noble gas isotope data. *Water Resources Research* 34(10): 2467-2483.
- Chebotaev, I.I. 1955: Metamorphism of natural waters in the crust of weathering. *Geochimica et Cosmochimica Acta* 8, 22-48, 137-170, 198-212.

- Cirpka, O.A.; Fienen, M.N.; Hofer, M.; Hoehn, E.; Tessarini, A.; Kipfer, R.; Kitanidis, P.K. 2007: Analyzing bank filtration by deconvoluting time series of electric conductivity. *Ground Water* 45: 318-328, doi:10.1111/j.1745-6584.2006.00293.x
- Clark, I.D.; Fritz, P. 1997: *Environmental isotopes in hydrogeology*. New York, Lewis Publishers, 328 p.
- Close, M.; Morgenstern, U.; van der Raaij, R. 2011: A Review on the Impact of Irrigation on Age Dating and Geochemistry of Shallow Groundwater – implications for the Wairau Plains. Report prepared for Marlborough District Council, ESR report number: CSC 11005.
- Close, M.E.; Rosen, M.R.; Smith, V.R. 2001: Fate and transport of nitrates and pesticides in New Zealand's aquifers. In: *Groundwaters of New Zealand*. Rosen, M.R. and White P.A. (eds): 185-220.
- Cook, P.G.; Herczeg, A.L. 2000: *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Publishers, Boston.
- Cook, P.G.; Böhlke, J.K. 2000: Determining timescales for ground-water flow and solute transport. In: *Environmental tracers in subsurface hydrology*. Cook, P.G. and Herczeg, A.L. (eds.) Kluwer, Boston, 1-3.
- Cook, P.G.; Solomon, D.K. 1997: Recent advances in dating young groundwater: Chlorofluorocarbons,  $^3\text{H}/^3\text{He}$  and  $^{85}\text{Kr}$ . *Journal of Hydrology* 191(1-4): 245-265.
- Cook, P.G.; Plummer, N.L.; Solomon, D.K.; Busenberg, E.; Han, L.F. 2006: Effects and processes that can modify apparent CFC age. In: *Use of chlorofluorocarbons in hydrology*. IAEA, Vienna, 31-58.
- Cornaton, F.J. 2012: Transient water age distributions in environmental flow systems: The time-marching Laplace transform solution technique. *Water Resource Research* 48.
- Dalton, M.G.; Upchurch, S.B. 1978: Interpretation of hydrochemical facies by factor analysis. *Ground Water* 16(4): 228-233.
- Daughney C.J.; Baker, T.; Jones, A.; Hanson, C.; Davidson, P.; Thompson, M.; Reeves, R.R.; Zemansky, G.M. 2007: Comparison of sampling methods for state of the environment monitoring in New Zealand. *Journal of Hydrology (New Zealand)* 46: 19-31
- Daughney, C.J.; Reeves, R.R. 2005: Definition of hydrochemical facies in the New Zealand, National Groundwater Monitoring Programme. *Journal of Hydrology (New Zealand)* 44: 105-130.
- Daughney, C.J.; Reeves, R.R. 2006: Analysis of temporal trends in New Zealand's groundwater quality based on data from the National Groundwater Monitoring Programme. *Journal of Hydrology (NZ)* 45(1): 41-62.
- Daughney, C.J.; Morgenstern, U.; van der Raaij, R.; Reeves, R.R. 2010: Discriminant analysis for estimation of groundwater age from hydrochemistry and well construction: application to New Zealand aquifers. *Hydrogeology Journal* 18(2): 417-428.
- Dillon, P.J.; Close, M.E.; Scott, R.I. 1989: Diffuse Source Nitrate Contamination of Groundwater in New Zealand and Australia. Hydrology and Water Resources Symposium, Christchurch, New Zealand, 351-355.
- Downes, C.J. 1985: Redox reactions, mineral equilibria, and ground water quality in New Zealand aquifers. In: *Ground Water Quality*. Ward, C.H.; Giger, W.; McCarty, P.L. (eds.). Wiley & Sons, NY.
- Edmunds, W.M. 2009: Geochemistry's vital contribution to solving water resource problems. *Applied Geochemistry* 24: 1058-1073.
- Edmunds, W.M.; Shand, P.; Hart, P.; Ward, R.S. 2003: The natural (baseline) quality of groundwater: a UK pilot study. *Science of The Total Environment* 310(1-3): 25-35.
- Edmunds, W.M.; Walton, N.R.G. 1980: A geochemical and isotopic approach to recharge evaluation in semi-arid zones, past and present. *Arid Zone Hydrology. Investigations with Isotope Techniques*, IAEA, Vienna, 47-68.
- Ekwurzel, B.; Schlosser, P.; Smethie Jr., W.M.; Plummer, L.N.; Busenberg, E.; Michel, R.L.; Weppernig, R.; Stute, M. 1994: Dating of Shallow Groundwater: Comparison of the Transient Tracers  $^3\text{H}/^3\text{He}$ , Chlorofluorocarbons, and  $^{85}\text{Kr}$ . *Water Resources Research* 30(6): 1693-1708.
- Engesgaard, P.; Jensen, K.H.; Molson, J.; Frind, E.O.; Olsen, H. 1996: Large-Scale Dispersion in a Sandy Aquifer: Simulation of Subsurface Transport of Environmental Tritium. *Water Resources Research* 32(11): 3253-3266, doi:10.1029/96WR02398.

- Fienen, M.N.; Luo, J.; Kitanidis, P.K. 2006: A Bayesian geostatistical transfer function approach to tracer test analysis. *Water Resources Research* 42: doi:10.1029/2005 WR004576.
- Flury, M.; Wai, N.N. 2003: Dyes as tracers for vadose zone hydrology. *Reviews of Geophysics* 41(1): 2-1-2-37.
- Fraser, P. J.; Oram, D. E.; Reeves, C. E.; Penkett, S. A.; McCulloch, A. 1999: Southern hemisphere halon trends (1978-1998) and global halon emissions. *Journal of Geophysical Research* 104: 15,985-15,999.
- Freeze, R.A.; Cherry, J.A. 1979: *Groundwater*. Prentice-Hall, Englewood Cliffs, New Jersey.
- Furman, T.; Thompson, P.; Hatchl, B. 1998: Primary mineral weathering in the central Appalachians: a mass balance approach - An example from the basal Chilhowee group (uppermost Proterozoic to lower Cambrian) of the southcentral Appalachians. *Geochimica et Cosmochimica Acta* 62(16): 2889-2904.
- Galeriu, D.; Heling, R.; Melintescu, A. 2005. The dynamics of tritium-including OBT-in the aquatic food chain. *Fusion Science and Technology*, 48(1): 779-782.
- Garrels, R.M.; Christ, C.L. 1964: *Solutions Minerals and Equilibria*. Harper and Row, New York.
- Gleeson, T.; Wada, Y.; Bierkens, M.F.P.; van Beek, L.P.H. 2012: Towards Sustainable Groundwater Use: Setting Long-Term Goals, Backcasting, and Managing Adaptively. *Ground Water* 50(1): 19-26.
- Glynn, P.D.; Plummer, L.N. 2005: Geochemistry and the understanding of ground-water systems. *Hydrogeology Journal* 13: 263-287.
- Goode, DJ. 1996: Direct simulation of ground-water age. *Water Resources Research* 32: 289-296.
- Gueler, C.; Thyne, G.D.; McCray, J.E.; Turner, A.K. 2002: Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeology Journal* 10(4): 455-474.
- Happell, J.D.; Price, R.M.; Top, Z.; Swart, P.K. 2003: Evidence for the removal of CFC-11, CFC-12, and CFC-113 at the groundwater-surface water interface in the Everglades. *Journal of Hydrology* 279 (1-4): 94-105.
- Hinsby, K.; Højberg, A.L.; Engesgaard, P.; Jensen, K.H.; Larsen, F., Busenberg, E.; Plummer, L.N. 2007: Transport and degradation of chlorofluorocarbons (CFCs) in the pyritic Rabis Creek aquifer, Denmark. *Water Resources Research* 43(10).
- Hidalgo, M.C.; Cruz-Sanjulian, J. 2001: Ground water composition, hydrochemical evolution and mass transfer in a regional detrital aquifer (Baza Basin, southern Spain). *Applied Geochemistry* 16: 745-758.
- Hofmann, T.; Darsow, A.; Gröning, M.; Aggarwal, P.; Suckow, A. 2010: Direct-push profiling of isotopic and hydrochemical vertical gradients. *Journal of Hydrology* 385 (1-4): 84-94.
- Höltling, B.; Härtlé, T.; Hohberger, K.-H.; Nachtigall, K.H.; Villinger, E.; Weinzierl, W.; Wrobel, J.-P. 1995: Konzept zur Ermittlung der Schutzfunktion der Grundwasserüberdeckung. *Geologie Jahrbuch. C* 63: 5-24.
- Horneman, A.; Stute, M.; Schlosser, P.; Smethie Jr., W.; Santella, N.; Ho, D.T.; Mailloux, B.; Gorman, E.; Zheng, Y.; van Geen, A. 2008: Degradation rates of CFC-11, CFC-12 and CFC-113 in anoxic shallow aquifers of Arahazar, Bangladesh. *Journal of Contaminant Hydrology* 97: 27-41.
- Hughes, C.E.; Cendon, D.I.; Harrison, J.J.; Hankin, S.; Johansen, M.P.; Payne T.E. 2010: Movement of a tritium plume in shallow groundwater at a legacy low-level radioactive waste disposal site in eastern Australia. *Journal of Environmental Radioactivity* 102: 943-952.
- IAEA 2013: *Isotope Methods for Dating Old Groundwater*. International Atomic Energy Agency, Vienna, April, 2013. STI/PUB/1587, 357 p., available online: <http://www-pub.iaea.org/books/IAEABooks/8880/Isotope-Methods-for-Dating-Old-Groundwater>.
- IPCC (Intergovernmental Panel on Climate Change) 2001: *Climate Change 2001: The Scientific Basis*. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, J.T. Houghton et al. (eds.), Cambridge Univ. Press, New York, 881 p.
- Jurgens, B.C.; Böhlke, J.K.; Eberts, S.M. 2012: TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data. U.S. Geological Survey Techniques and Methods Report 4-F3.

- Kazemi, G.A.; Lehr, J.H.; Perrochet, P. 2006: *Groundwater Age*: John Wiley & Sons, Hoboken, NJ, 325 p.
- Kendall, C.; McDonnell, J.J. 1998: *Isotope tracers in catchment hydrology*. Elsevier.
- Kilchmann, S.; Waber, H.N.; Parriaux, A.; Bensimon, M. 2004: Natural tracers in recent groundwaters from different Alpine aquifers. *Hydrogeology Journal* 12(6): 643-661.
- Knott, J.F.; Olimpio, J.C. 2001: Estimation of Recharge Rates to the Sand and Gravel Aquifer Using Environmental Tritium, Nantucket Island, Massachusetts. U.S. Geological Survey Water-Supply Paper 2297.
- Koh, D.C.; Plummer, L.N.; Busenberg, E.; Kim, Y. 2007: Evidence for terrigenous SF<sub>6</sub> in groundwater from basaltic aquifers, Jeju Island, Korea: Implications for groundwater dating. *Journal of Hydrology* 339(1-2): 93-104.
- Konikow, L.F.; Hornberger, G.Z.; Putnam, L.D.; Shapiro, A.M.; Zinn, B.A. 2008: The use of groundwater age as calibration target. *IAHS-AISH Publications* 320, 250-256.
- Krauskopf, K.B. 1956: Dissolution and precipitation of silica at low temperatures. *Geochimica et Cosmochimica Acta* 10: 1-26.
- Lawrence, F.W.; Upchurch, S.B. 1982: Identification of recharge areas using geochemical factor analysis. *Ground Water* 20(6): 680-687.
- Lecomte, K.L.; Pasquini, A.I.; Depetris, P.J. 2005: Mineral Weathering in a Semiarid Mountain River: Its assessment through PHREEQC inverse modelling. *Aquatic Geochemistry* 11(2): 173-194.
- Lesage, S.; Jackson, R.E.; Priddle, M.W.; Riemann, P.G. 1990: Occurrence and fate of organic solvent residues in anoxic groundwater at the Gloucester landfill, Canada. *Environmental Science and Technology* 24: 559-566.
- Locsey, K.L.; Cox, M.E. 2003: Statistical and hydrochemical methods to compare basalt- and basement rock-hosted ground waters: Atherton Tablelands, north-eastern Australia. *Environmental Geology* 43(6): 698-713.
- Małoszewski, P.; Zuber, A. 1982: Determining the turnover time of groundwater systems with the aid of environmental tracers. *Journal of Hydrology* 5: 207-231.
- Mazor, E. 1996: Chemical and Isotopic Groundwater Hydrology: The Applied Approach. Marcel Dekker Inc.
- Mazor, E.; Nativ, R. 1992: Hydraulic calculation of groundwater flow velocity and age: examination of the basic premises. *Journal of Hydrology* 138: 211-222.
- McDonell, J.J.; Rowe, L.K.; Stewart, M.K. 1999: A combined tracer-hydrometric approach to assess the effect of catchment scale on water flow path, source, and age. Integrated methods in Catchment Hydrology – Tracer, Remote Sensing and New Hydrometric Techniques. Proceedings of IUGG 99 Symposium HS4, Birmingham, July. IAHS Publication No. 258.
- McMahon, P.B.; Plummer, L.N.; Bohlke, J.K.; Shapiro, S.D.; and Hinkle, S.R. 2011: A comparison of recharge rates in aquifers of the United States based on groundwater-age data. *Hydrogeology Journal* 19(4): 779-800.
- Mendizabal, I.; Baggelaar, P.K.; Stuyfzand, P.J. 2012: Hydrochemical trends for public supply well fields in The Netherlands (1898-2008), natural backgrounds and upscaling to groundwater bodies. *Journal of Hydrology* 450-451: 279-292.
- Meng, S.X.; Maynard, J.B. 2001: Use of statistical analysis to formulate conceptual models of geochemical behavior: Water chemical data from the Botucata Aquifer in Sao Paulo state, Brazil. *Journal of Hydrology* 250(1): 78-97.
- Montzka, S. A.; Reimann, S.; Engel, A.; Krüger, K.; O'Doherty, S.; Sturges, W.; Blake, D.; Dorf, M.; Fraser, P.; Froidevaux, L.; Jucks, K.; Kreher, K.; Kurylo, M.; Mellouki, A.; Miller, J.; Nielsen, O.-J.; Orkin, V.; Prinn, R.; Rhew, R.; Santee, M.; Stohl, A.; Verdonik, D. 2011: Ozone-Depleting Substances (ODSs) and Related Chemicals. Chapter 1 in Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project Report No. 52, World Meteorological Organization, Geneva, Switzerland, 516 p.
- Moore, R.D. 2005: Introduction to Salt Dilution Gauging for Streamflow Measurement Part III: Slug Injection Using Salt in Solution. *Watershed Management Bulletin* 8(2): 1-28.
- Morgenstern, U.; Daughney, C.J. 2012: Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification: The National Groundwater Monitoring Programme of New Zealand. *Journal of Hydrology*, 456/457: 79-93.

- Morgenstern, U.; Brown, L.J.; Begg, J.; Daughney, C.; Davidson, P. 2009: Linkwater catchment ground-water residence time, flow pattern, and hydrochemistry trends. *Institute of Geological and Nuclear Sciences science report 2009/08*: 47.
- Morgenstern, U.; Reeves, R.; Daughney, C.; Cameron, S.; Gordon, D. 2004: Groundwater Age and Chemistry, and Future Nutrient Load for Selected Rotorua Lakes Catchments. *Institute of Geological and Nuclear Sciences science report 2004/31*: 74.
- Morgenstern, U.; Stewart, M.K.; Stenger, R. 2010: Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. *Hydrology and Earth System Sciences 14*: 2289-2301.
- Morgenstern, U.; Taylor, C.B. 2009: Ultra low-level tritium measurement using electrolytic enrichment and LSC. *Isotopes in environmental and health studies 45(2)*: 96-117.
- Mutch, R.D.; Mahony, J. D. 2008: A study of tritium in municipal solid waste leachate and gas. *Fusion Science and Technology 54*: 305-310.
- New Zealand Ministry of Health 2008: Drinking-water Standards for New Zealand 2005 (Revised 2008), Wellington: Ministry of Health; <http://www.health.govt.nz/publication/drinking-water-standards-new-zealand-2005-revised-2008-0>.
- Newland, M.J.; Reeves, C.E.; Oram, D.E.; Laube, J.C.; Sturges, W.T.; Hogan, C.; Begley, P.; Fraser, P.J. 2013: Southern hemispheric halon trends and global halon emissions, 1978–2011. *Atmospheric Chemistry and Physics 13*: 5551-5565, doi:10.5194/acp-13-5551-2013.
- Nir, A. 1986: Role of tracer methods in hydrology as a source of physical information: basic concepts and definitions—time relationship in dynamic systems. In: *Mathematical models for interpretation of tracer data in groundwater hydrology*, IAEA, TECDOC-381. IAEA, Vienna, Austria, 7-44.
- O'Brien, A.K.; Rice, K.C.; Bricker, O.P.; Kennedy, M.M.; Anderson, R.T. 1997: Use of geochemical mass balance modelling to evaluate the role of weathering in determining stream chemistry in five mid-Atlantic watersheds on different lithologies. *Hydrological Processes 11*: 719-744.
- Oster, H.; Sonntag, C.; Munnich, K.O. 1996: Groundwater age dating with chloro-fluorocarbons. *Water Resources Research 32(10)*: 2989-3001.
- Ozyurt, N.N.: Bayari, C.S. 2005: Unsteady state lumped parameter modeling of  $^3\text{H}$  and CFCs transport: analyses of mean residence time in a mountainous karstic aquifer. *Hydrologic Processes 19(17)*: 3269-3284.
- Parkhurst, D.L.; Appelo, C.A.J. 1999: User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report 99-4259*: 312 p.
- Phillips, F.M.; Castro, M.C. 2003: Groundwater dating and residence-time measurements. In *Treatise on Geochemistry, Vol. 5: Surface and Ground Water, Weathering, and Soils*, J.I. Drever (ed.), Oxford: Elsevier: 451-97.
- Plummer, L.N.; Back, W.W. 1980: The mass balance approach – Application to interpreting the chemical evolution of hydrological systems. *American Journal of Science 280*: 130-142.
- Plummer, L.N.; Prestemon, E.C.; Parkhurst, D.L. 1991: An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH. *U.S. Geological Survey of Water Resources Investigations Report 91-4078*, Reston, Virginia.
- Plummer, L.N.; Busby, J.F.; Lee, R.W.; Hanshaw, B.B. 1990: Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. *Water Resources Research 26*: 1981-2014.
- Rademacher, L.K.; Clark, J.F.; Clow, D.W.; Hudson, G.B. 2005: Old groundwater influence on stream hydrochemistry and catchment response times in a small Sierra Nevada catchment: Sagehen Creek, California, *Water Resource Research 41*, W02004.
- Rademacher, L.K.; Clark, J.K.; Hudson, G.B.; Erman, D.C.; Erman, N.A. 2001: Chemical evolution of shallow groundwater as recorded by springs, Sagehen Basin, Nevada County, California, *Chemical Geology 179*: 37-51.
- Reilly, T.E.; Plummer, L.N.; Phillips, P.J.; Busenberg, E. 1994: The use of simulation and multiple environmental tracers to quantify flow in a shallow aquifer, *Water Resources Research 30(2)*: 421-433.

- Rosen, M.R.; Bright, J.; Carran, P.; Stewart M.K.; Reeves, R. 1999: Estimating rainfall recharge and soil water residence time in Pukekohe, New Zealand, by combining geophysical, chemical and isotopic methods. *Groundwater* 37(6): 836-844.
- Rosen, M.R. 2001: Hydrochemistry of New Zealand's Aquifers. In: *Groundwaters of New Zealand*. Rosen, M.R. and White, P.A. (eds.): 77-110.
- Rowe, Jr. G.L.; Brantley, S.L. 1993: Estimation of the dissolution rates of andesitic glass, plagioclase and pyroxene in a flank aquifer of Poás Volcano, Costa Rica. *Chemical Geology* 105: 71-87.
- Sampat, P. 2000: Groundwater Shock the Polluting of the World's Major Freshwater Stores. *World Watch* 13(1).
- Santella, N.; Ho, D.T.; Schlosser, P.; Stute, M. 2003: Distribution of atmospheric SF<sub>6</sub> near a large urban area as recorded in the vadose zone. *Environmental Science and Technology* 37(6): 1069-1074.
- Santella, N.; Ho, D.T.; Schlosser, P.; Stute, M. 2008: Widespread elevated atmospheric SF<sub>6</sub> mixing ratios in the Northeastern United States: Implications for groundwater dating. *Journal of Hydrology* 349(1-2): 139-14.
- Santoro, M.A. 2000: Clarifying the SF<sub>5</sub>CF<sub>3</sub> record. *Science* 290: 935.
- Scanlon, B.R.; Healy, R.W.; Cook P.G. 2002: Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeology Journal* 10: 18-39.
- Schlosser, P.; Stute, M.; Dorr, H.; Sonntag, C.; Munnich, K.O. 1988: Tritium/<sup>3</sup>He dating of shallow groundwater. *Earth and Planetary Science Letters* 89(3-4): 353-362.
- Shapiro, S.D.; Schlosser, P.; Smethie, W.M.; Stute, M. 1997: The use of H-3 and tritogenic He-3 to determine CFC degradation and vertical mixing rates in Framvaren Fjord, Norway. *Marine Chemistry* 59 (1-2): 141-157.
- Stewart, M.; Morgenstern, U. 2001: Age and Source of Groundwaters from Isotopic Tracers. In: *Groundwaters of New Zealand*. Rosen, M.R. and White P.A. (eds.), 161-183.
- Stewart, M.K.; Thomas, J.T. 2008: A conceptual model of flow to the Waikoropupu Springs, NW Nelson, New Zealand, based on hydrometric and tracer (<sup>18</sup>O, Cl, <sup>3</sup>H, and CFC) evidence. *Hydrology and Earth System Sciences* 12: 1-19.
- Stewart, M.K., Taylor, C.B. 1981: Environmental isotopes in New Zealand hydrology: 1. Introduction. The role of oxygen-18, deuterium, and tritium in hydrology. *New Zealand Journal of Science* 24(3/4): 295-311.
- Stichler, W.; Moser, H. 1979: An example of exchange between lake and groundwater. In: C. Mortimer (ed.), *Application of nuclear techniques to the study of lake dynamics. Isotope Hydrology*, IAEA, Vienna, 115-119.
- Sturges, W.T.; Oram, D.E.; Laube, J.C.; Reeves, C.E.; Newland, M.J.; Hogan, C.; Martinerie, P.; Witrant, E.; Brenninkmeijer, C.A.M.; Schuck, T.J.; Fraser, P.J. 2012: Emissions halted of the potent greenhouse gas SF<sub>5</sub>CF<sub>3</sub>. *Atmospheric Chemistry and Physics* 12.
- Sturges, W.T.; Wallington, T.J.; Hurley, M.D.; Shine, K.P.; Sihra, K.; Engel, A.; Oram, D.E.; Penkett, S.A.; Mulvaney, R.; Brenninkmeijer, C.A.M. 2000: A potent greenhouse gas identified in the atmosphere: SF<sub>5</sub>CF<sub>3</sub>. *Science* 289: 611-613.
- Stute, M.; Schlosser, P. 2000: Tritium/<sup>3</sup>He measurements as calibration tools in groundwater transport modelling. *IAHS-AISH Publications* 262: 33-38.
- Szabo Z.; Rice D.E.; Plummer L.N.; Busenberg E.; Drenkard S.; Schlosser, P. 1996: Age-dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain. *Water Resources Research* 32(4): 1023-1038.
- Takahashi, K.; Nakayama, T.; Matsumi, Y.; Solomon, S.; Gejo, T.; Shigemasa, E.; Wallington T.J. 2002: Atmospheric lifetime of SF<sub>5</sub>CF<sub>3</sub>. *Geophysical Research Letters* 29 (15): 7/1-17/4
- Taylor, C.B.; Trompeter, V.J.; Brown, L.J. 2001: The Manawatu Aquifers, North Island, New Zealand: Clarification of Hydrogeology Using a Multidisciplinary Environmental Tracer Approach. *Hydrological Processes* 15: 3269.
- Taylor, C.B.; Brown, L.J.; Cunliffe, J.J.; Davidson, P.W. 1992: Environmental tritium and <sup>18</sup>O applied in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand. *Journal of Hydrology* 138: 269-319.

- Thompson, G.M.; Hayes, J.M. 1979: Trichlorofluoromethane in groundwater: A possible tracer and indicator of groundwater age. *Water Resources Research* 15(3): 546-554.
- Thyne, G.; Güler, C.; Poeter, E. 2004: Sequential Analysis of Hydrochemical Data for Watershed Characterization. *Ground Water* 42: 711-723.
- Tolstikhin, I.N.; Kamenski, I.L. 1969: Determination of groundwater age by the T-3 He method. *Geochemistry International* 6: 810-811.
- US Geological Survey 1999: Tracing and Dating Young Ground Water, US Department of the Interior, Fact Sheet-134-99, available online: <http://pubs.usgs.gov/fs/FS-134-99/pdf/fs-134-99.pdf>.
- Van Breukelen, B.M.; Röling, W.F.M.; Groen, J.; Griffioen, J.; Van Verseveld, H.W. 2003: Biogeochemistry and isotope geochemistry of a landfill leachate plume. *Journal of Contaminant Hydrology* 65(3-4): 245-268.
- Van der Raaij, R. W. 2003: Age-dating of New Zealand groundwaters using sulphur hexafluoride. Unpublished MSc thesis, Victoria University, Wellington.
- Van der Raaij, R.; Beyer, M. (under review) Use of CFCs and SF<sub>6</sub> as groundwater age tracers in New Zealand, submitted to *Journal of Hydrology New Zealand*, 2013.
- Visser, A. 2009: Trends in groundwater quality in relation to groundwater age. PhD thesis, Netherlands Geographical Studies 384, Faculty of Geosciences, Utrecht University, Netherlands.
- Visser, A.; Schaap, J.D.; Broers, H.P.; Bierkens, M.F.P. 2008: Degassing of <sup>3</sup>H/<sup>3</sup>He, CFCs and SF<sub>6</sub> by denitrification: Measurements and two-phase transport simulations. *Journal of Contaminant Hydrology* 103(3-4): 206-218.
- White, A.F.; Brantley, S.L. 2003: The effect of time on the weathering of silicate minerals: Why do weathering rates differ in the laboratory and field? *Chemical Geology* 202: 479-506.
- White, P.A.; Rosen, M.R. 2001: Introduction. In: *Groundwaters of New Zealand*. Rosen, M.R. and White P.A. (eds.), 1-3.
- Worthington, S.R.H. 2007: Ground-water residence times in unconfined carbonate aquifers. *Journal of Cave and Karst Studies* 69(1): 94-102.
- Zhenxue, D.; Samper, J.; Ritzi, R. Jr. 2006: Identifying geochemical processes by inverse modeling of multicomponent reactive transport in the Aquia aquifer. *Geosphere* 2(4): 210-219.
- Zuber, A.; Róžański, K.; Kania, J.; Purtschert, R. 2011: On some methodological problems in the use of environmental tracers to estimate hydrogeologic parameters and to calibrate flow and transport models. *Hydrogeology Journal* 19(1): 53-69.

