Research Paper

Use and application of CFC-11, CFC-12, CFC-113 and SF_6 as environmental tracers of groundwater residence time: A review

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ABSTRACT

Groundwater residence time is a fundamental property of groundwater to understand important hydrogeological issues, such as deriving sustainable abstraction volumes, or, the evolution of groundwater quality. The anthropogenic trace gases chlorofluorocarbons (CFC-11, CFC-12 and CFC-113) and sulphur hexafluoride (SF_6) are ideal in this regard because they have been released globally at known rates and become dissolved in groundwater following Henry's Law, integrating over large spatial (global) and temporal (decades) scales. The CFCs and SF_6 are able to date groundwater up to ~ 100 years old with the caveat of certain simplifying assumptions. However, the inversion of environmental tracer concentrations (CFCs and SF_6) to derive groundwater age rests on the accurate determination of groundwater recharge parameters, namely temperature, elevation, salinity and excess air, in addition to resolving the potential for contamination, degradation and unsaturated zone effects. This review explores the fundamentals of CFC-11, CFC-12, CFC-113 and SF_6 as environmental tracers of groundwater age and recommends complementary techniques throughout. Once this relatively simple and inexpensive technique has been used to determine initial concentrations at the recharge zone, setting the groundwater dating 'clock' to zero, this review then explores the meaning of groundwater 'age' in relation to measured environmental tracer concentrations. It is shown that the CFCs and SF_6 may be applied to a wide-range of hydrogeological problems and suggests that environmental tracers are particularly powerful tools when integrated with numerical flow and transport models.

1. Introduction

Water, unlike other commodities, has no substitute, is essential to virtually every aspect of the human endeavour and is recognised as a universal basic human right (United Nations Committee on Economic, Social and Cultural Rights, 2003). Groundwater, vastly exceeds all other freshwater resources on the planet (Shilomanov and Rodda, 2003), supplying billions of people with their primary source of drinking water (Morris et al., 2003) and potentially over half of the world's irrigation water (Siebert et al., 2010). In times of drought, this 'invisible asset' forms a strategic reserve in rural, semi-arid and arid regions where groundwater is often the only source of freshwater (Famiglietti, 2014). The availability of 'good quality' groundwater, both directly and indirectly, ensures global energy, water and food security (Dalin et al., 2017), in addition to the health of many ecosystems (Alley et al., 2002).

Recent hydrological modelling (Wada et al., 2014) and satellite-based estimates (Rodell et al., 2009; Famiglietti, 2014) have revealed alarming rates of groundwater depletion worldwide. Increasing groundwater pumping rates for irrigation is causing water tables to fall dramatically across large areas of northern China, India, Pakistan, Iran, the Middle East, Mexico and the western United States (Rodell et al., 2009; Wada et al., 2014), primarily due to increasing global population and embedded food consumption (Dalin et al., 2017). As much as 11 percent of the world's food is now produced by pumping non-renewable groundwater, meeting today's food needs with tomorrow's water (Postel, 2010). Groundwater pumping in excess of the natural recharge rate raises serious questions about the long-term sustainability of global food production (Wada et al., 2012), whilst

leading to environmental issues such as land subsidence and seawater intrusion. Indeed, human-induced aquifer depletion and contamination is now widespread in both the developing and developed world (Konikow and Kendy, 2005; Rodell et al., 2009; Famiglietti, 2014; Wada et al., 2014).

The sustainable supply of 'good quality' groundwater is a crucial socioeconomic challenge of our time, particularly as global population, industrialisation and agricultural intensification are projected to increase (Gleeson et al., 2012). Yet, the sustainable supply of groundwater is difficult to quantify due to the wide range of mean groundwater ages (residence times), which for an individual aquifer may range from <10 years to > 1,000,000 years (McMahon et al., 2011; Holland et al., 2013). Groundwater age, which we define more formally in section 3, is a measure of the 'recharge year' or recharge rate of a groundwater resource (Cook and Solomon, 1997). This property of groundwater may be used to assess the volume of water that can be sustainably abstracted, to constrain timescales of water-rock interaction processes, or, to assess the vulnerability and response of a groundwater resource to contaminant release or climate change.

There is clearly the need for a straightforward and simple to use technique which can quantify timescales of groundwater recharge, flow and transport processes. In doing so, it will also be possible to better manage (use, value and protect) this vital resource and understand the processes controlling the distribution of contaminants in space and time. This paper reviews the use and value of specific environmental tracers for obtaining such measures of groundwater residence time.

1.1. Why environmental tracers?

Hydrogeological investigations typically proceed from a hydraulic perspective. In hydraulic-based numerical models of non-fractured systems, hydraulic conductivities and hydraulic gradients are generally combined with Darcy's Law to estimate advective flow velocities and transport rates. Because the hydraulic conductivity of the subsurface is highly variable (Schwartz and Zhang, 2003) and the recharge rate is often estimated as a fitting parameter to hydraulic-based models (Cook and Solomon, 1997), model predictions (flow velocities and transport rates) may be subject to a high-degree of uncertainty (Zuber et al., 2011). A far more direct approach is the observation of mass transport through measuring tracers (Cook and Solomon, 1997).

A *tracer* in hydrogeology is any substance in groundwater, or, property of the water molecule that can be measured and used to infer environmental processes (Cook and Herczeg, 2012). The atmospheric trace gases CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113) and SF_6 (sulphur hexafluoride) are ideal in this regard because they are widespread across the surface of the earth, have been released at known rates over many decades, become dissolved in groundwater according to Henry's Law and typically behave conservatively. Hence, they provide information on processes that occur over large spatial and temporal scales (on the order of decades). The CFCs and SF_6 have been applied as tracers of groundwater age (Cook and Solomon, 1997; Darling et al., 2012), to trace water or contaminant sources (Darling et al., 2010), to trace chemical reactions such as sulphate reduction or denitrification (Visser et al., 2009), to develop conceptual models of groundwater flow and resolve mixing processes (Gooddy et al., 2006), and to calibrate numerical flow and transport models (Reilly et al., 1994; Szabo et al., 1996; Portniaguine and Solomon, 1998; Zuber et al., 2005; Ginn et al., 2009; Leray et al., 2012; Massoudieh et al., 2014). The efficacy and wide range of applications of the CFCs and SF_6 as environmental tracers is indisputable.

1.2. Review outline

This review focuses on the tracing and age dating of 'modern' groundwater (<100 years old) components using CFC-11, CFC-12, CFC-113 and SF_6. Such techniques are vital because modern groundwater is the most abundant and easily-accessible part of the active hydrologic cycle, being approximately three times larger than fresh surface water (Gleeson et al., 2016). Yet, modern groundwater is the most vulnerable to industrial/agricultural contamination, land-use changes (Alley et al., 2002) and the adverse effect of climate change (Taylor et al., 2013).

In section 2, we discuss the sampling method and the various factors for consideration to determine atmospheric equilibrium concentrations of the CFCs and SF_6. This is to set the groundwater dating 'clock' at the recharge zone to determine age. In section 3, we define groundwater age and discuss the underlying assumptions and limitations of groundwater age dating based on the CFCs and SF_6 tracer techniques. In section 4, we discuss the combination of independent hydraulic and tracer based techniques in numerical modelling studies to improve the quantification of flow and transport systems. In section 5, we discuss the potential for linking groundwater age to hydrochemistry. Finally, in section 6, the authors own conclusions are discussed with regards to the CFCs and SF_6 as tracers of groundwater age. Recommendations for complementary techniques are made throughout.

2. Theory

The production of CFC-12 and CFC-113 began in the early 1940s and was quickly followed by CFC-11 in the 1950s and SF_6 in the 1950s. CFC-11 and CFC-12 were mainly used for refrigeration and air-conditioning, whereas CFC-113 was mainly used by the electronics industry in the manufacture of semiconductor chips (Jackson et al., 1992) and SF_6 was mainly used for its electrical and thermal insulation properties. Inevitably, these gases leaked into the wider environment and became well-mixed in the atmosphere (Plummer et al., 2006). The concentrations of the CFCs rose until the 1990s when restrictions were imposed on the CFCs to protect the ozone layer as a result of the Montreal Protocol. The concentration of SF_6 (a potent greenhouse gas) has risen monotonically since the early 1960s and is still rising (Fig. 1).
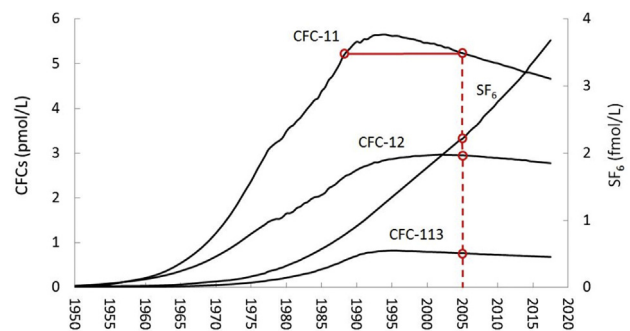
Figure 1. The variation in concentrations of the CFCs and SF_6 over time in groundwater at equilibrium with the Northern Hemispheric atmosphere assuming a temperature of 10 °C (typical of the UK). Note the difference in axial scale between the CFCs (pmol/L) and SF_6 (fmol/L). Based on data from the U.S. Geological Survey (http://water.usgs.gov/lab/software/air_curve/). The solid red line indicates a non-unique groundwater age obtained from a single measurement of CFC-11. This issue may be overcome by measuring several tracers simultaneously (illustrated by the dashed red line for an example recharge year of 2005).

2.1. Sampling and analysis

An advantage of the CFCs and SF$_6$ tracer techniques is the speed, relatively low cost and ease of sampling and analysis, especially when compared to radio-isotope techniques, such as ^{3}H/^{3}He which requires weeks to months for counting or ingrowth (Clarke et al., 1976). The sample collection is done by the USGS single bottle method (Plummer et al., 2006). The sampling requires no specialist equipment or expertise where a 'diffusion barrier' is created during sampling to avoid re-equilibration with the atmosphere (Plummer et al., 2006; Darling et al., 2012). The equipment should also be checked to avoid contamination from pumps and tubing (Dunkle et al., 1993; Cook and Solomon, 1995). This is best done by obtaining an 'old' (>100 years old) groundwater sample in which the anthropogenic trace gases are below detection limit (Darling et al., 2012). The CFCs and SF$_6$ are measured by gas chromatography with an electron-capture-detector (GC-ECD) following 'purge and trap' cryogenic pre-concentration (Warner and Weiss, 1985; Busenberg and Plummer, 2000). The detection limit for CFCs in water is 0.01 pmol/L and for SF$_6$ is 0.1 fmol/L (Gooddy et al., 2006). The CFCs and SF$_6$ are calibrated to bulk air standards collected from an atmospheric monitoring station, preferably from the AGAGE network (http://agage.mit.edu/).

2.2. Setting the 'clock'

The input function for the CFCs and SF$_6$ is determined by their atmospheric concentration as a function of time. The atmospheric trace gases CFC-11, CFC-12, CFC-113 and SF$_6$ are well-mixed and become dissolved in groundwater following their Henry's Law solubilities (Warner and Weiss, 1985; Bu and Warner, 1995; Busenberg and Plummer, 2000). The concentrations of CFC-11, CFC-12, CFC-113 and SF$_6$ in groundwater at equilibrium with the Northern Hemispheric atmosphere are shown in Fig. 1, assuming a temperature of 10 °C and one atmosphere (sea level). It should also be noted that there is a slight time lag in Southern Hemispheric concentrations relative to the Northern Hemisphere by 1−2 years (Plummer et al., 2006).

In theory, it is possible to simply match the measured concentrations of the CFCs and SF$_6$ in a sample to a particular recharge year in Fig. 1 to determine groundwater age. This assumes no mixing and equilibrium with the atmosphere. Hence, groundwater age simply refers to the time elapsed since last contact with the atmosphere, or since rainfall. However, a groundwater sample is rarely a single recharge year due to in-aquifer mixing (diffusion and dispersion), large well-screen length leading to the sampling of different flow paths (Weissmann et al., 2002), and mixing within the well-bore during sampling. The issue of mixing for environmental tracer and groundwater 'age' interpretation is discussed in Section 3.

2.3. Additional considerations for setting the 'clock'

2.3.1. The unsaturated zone

The unsaturated zone may present certain issues for the interpretation of dissolved CFCs and SF$_6$ because dissolved gases may be transported by both the aqueous and gaseous phases. If recharge occurs from surface waters, or, the unsaturated zone is relatively thin, the composition of the unsaturated zone atmosphere maps back to the atmosphere (Cook and Solomon, 1995). However, issues may arise due to diffusive transport of the CFCs and SF$_6$ through thick unsaturated zones. This 'time lag' will be a function of the individual tracer diffusion coefficient and solubility in water, in addition to the moisture content of the unsaturated zone (Weeks et al., 1982; Cook and Solomon, 1995). However, diffusion coefficients in the gaseous phase are typically several orders of magnitude higher than the aqueous phase (Cook and Solomon, 1995). Therefore, in most practical situations, the effect of the unsaturated zone on equilibrium concentrations is negligible (Plummer et al., 2006).

2.3.2. Recharge temperature

The solubilities of gases are a function of temperature, pressure and salinity (Henry's Law). As temperature increases the solubility decreases, leading to lower concentrations, or vice versa. Typically, pressure and salinity are well constrained (Kipfer et al., 2002) and recharge temperature must be accurately resolved (Fig. 2). In some instances the recharge temperature may simply be estimated from the shallow groundwater temperature (Plummer et al., 2006). However, the recharge temperature is most precisely determined from measurements of other dissolved gases, such as nitrogen and argon (Heaton and Vogel, 1981), or the noble gases (Mazor, 1972; Andrews and Lee, 1979; Aeschbach-Hertig et al., 2000; Peeters et al., 2003). The accurate reconstruction of the recharge temperature is extremely important for palaeo-climate studies (Stute et al., 1995; Aeschbach-Hertig et al., 2000) and there are least-squares fitting computer routines which facilitate the automated calculation of this parameter (Peeters et al., 2003). However, in modern (<55 years) groundwater dating studies, the determination of the recharge temperature is usually a trivial issue. An uncertainty in the recharge temperature of ±2 °C typically leads to a an age
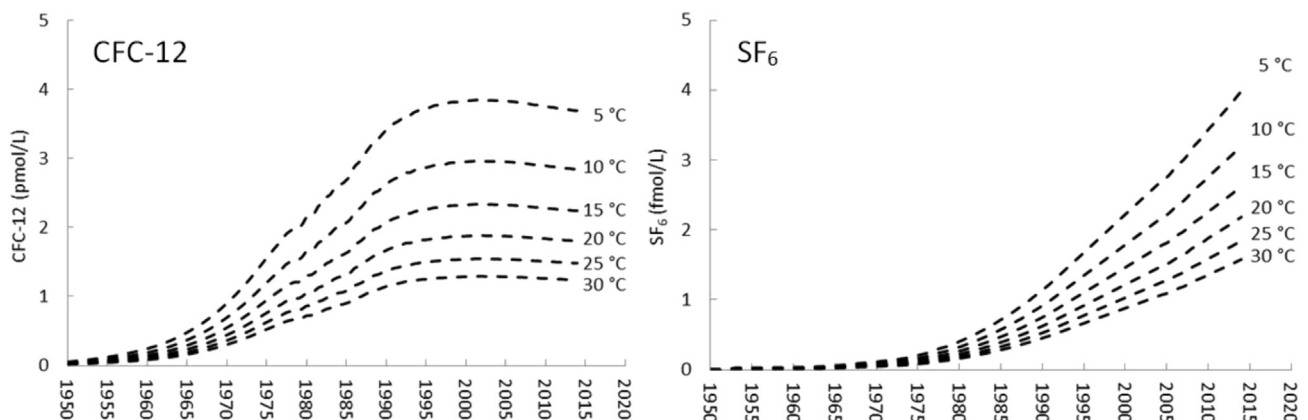
Figure 2. The concentration of CFC-12 and SF$_6$ in equilibrium with Northern Hemispheric atmosphere at sea level as a function of temperature. Note difference in axial scales for CFC-12 and SF$_6$.

uncertainty of <3 years for groundwater samples obtained prior to 1990 (Plummer et al., 2006). Non-unique groundwater ages may arise in post-1990 groundwater dating studies. This is due to the post-1990 reduction in atmospheric CFC concentrations as a result of the Montreal Protocol. This problem may be overcome by measuring several tracers simultaneously (e.g., CFC-11, CFC-12 and SF_6) to obtain a unique age (a simple case is illustrated in Fig. 1). This of course assumes no groundwater mixing occurs (see section 3).

2.3.3. Excess air and degassing

The forced dissolution of microscopic air bubbles during recharge results in a temperature-independent excess of dissolved gases. The formation of 'excess air' (Heaton and Vogel, 1981) remains incompletely understood (Aeschbach-Hertig and Solomon, 2013), but is mainly due to seasonal water table fluctuations (Ingram et al., 2007; Aeschbach-Hertig et al., 2008), in addition to the nature of matrix porosity and fracturing (Darling et al., 2012). There is typically a few cm^3/L of excess air in groundwater sampled from sedimentary aquifers (Beyerle et al., 1999; Gooddy et al., 2006). However, excess air may vary considerably and must be carefully considered, particularly for the sparingly soluble gases used in groundwater dating (e.g., SF_6 or ^{3}He). The excess air parameter is best estimated from the measurements other dissolved gases (e.g., the noble gases) as discussed above. The correction factors for CFC-12 and SF_6 are shown in Fig. 3. The relative insolubility of SF_6 compared to the CFCs means that excess air must be accurately resolved to establish equilibrium concentrations.

However, concentrations of gases below that predicted by the solubility equilibrium relationship (Henry's Law) are becoming increasingly common (Brennwald et al., 2005; Fortuin and Willemsen, 2005; Jones et al., 2014), particularly in groundwater

dating studies (Klump et al., 2006; Visser et al., 2007; Van Geen et al., 2013). This is primarily due to organic matter metabolism resulting in subsurface biogenic gas production post-recharge, e.g. the formation of CH_4 in anoxic groundwater (Fortuin and Willemsen, 2005), or the denitrification of N_2 gas beneath agricultural areas (Visser et al., 2007, 2009). This 'degassing' produces a gas phase below the groundwater table which causes dissolved gases to repartition between a mobile aqueous phase and a gas phase (Fry et al., 1995; Visser et al., 2007). This is particularly problematic for the sparingly soluble anthropogenic gases (i.e., SF_6) which may be completely stripped from solution (below detection) following recharge. Again, complementary techniques are required, because the degassing phenomenon is easily resolvable when measurements of the noble gases are available (Kipfer et al., 2002; Visser et al., 2007).

2.3.4. Atmospheric pressure and salinity

Atmospheric pressure decreases exponentially with increasing altitude, decreasing the partial pressures of atmospheric gases, reducing equilibrium concentrations in water (including the CFCs and SF_6). In most practical situations some knowledge of the recharge elevation is known. Conversely, temperature typically decreases with increasing altitude with an average 'lapse rate' of 6.5 °C (ICAO, 1964), increasing the solubility of atmospheric gases in water (although local factors must be taken into consideration). Therefore, the altitude and temperature corrections tend to cancel out, rather than reinforce one another (see Darling et al., 2012).

A high electrical conductivity of 1000 µS/cm may be expected in arid/semi-arid regions, or, in chemically evolved groundwater. This equates to a salinity value of <1 parts per thousand by weight, ‰ (Wüest et al., 1996), which results in a correction of <1% for
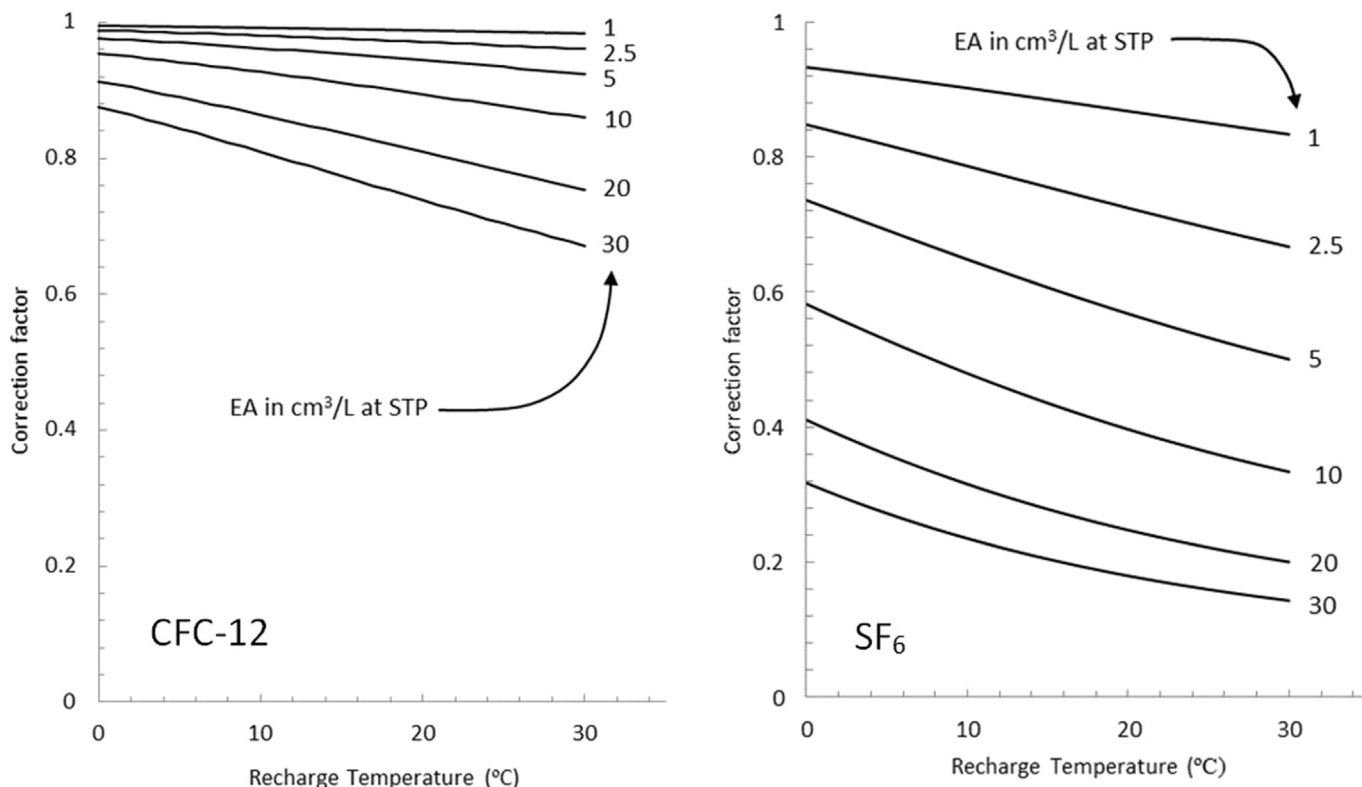

Figure 3. Graph showing correction factors for Excess Air (EA) as a function recharge temperature.

dissolved CFCs and SF_6 concentrations (Warner and Weiss, 1985; Busenberg and Plummer, 2000). Crucially, of interest is the salinity at the time of infiltration, which is typically close to zero. Hence, corrections for salinity are not typically required in groundwater dating studies (Kipfer et al., 2002; Plummer et al., 2006).

2.3.5. Additional contamination from anthropogenic and terrigenic sources

The CFCs are susceptible to contamination in urban/peri-urban environments, particularly in aquifers where rapid flow may occur through fractured horizons (Morris et al., 2006a, b). The CFCs may reach concentrations in excess of atmospheric equilibrium concentrations due to inputs from industrial activities and leaking landfills (Darling et al., 2012). Contamination may arise from atmospheric (Oster et al., 1996), or from subsurface (Darling et al., 2010) sources. Because atmospheric equilibrium concentrations of the CFCs are so low (pmol/L), only minor contamination is required to render the CFCs somewhat meaningless in terms of tracers of groundwater age. Taking a simple case, one-tenth of the CFC-12 present in a refrigerator of older design could theoretically contaminate a moderately sized aquifer to more than 10 times current atmospheric equilibrium concentrations (Morris et al., 2006a). At a simplistic level, such contamination may be used as a tracer of modern groundwater inputs.

Sulphur hexafluoride is far less susceptible to contamination, although concentrations in excess of atmospheric equilibrium have been found in areas of high-voltage electricity supply equipment, Mg and Al smelting and landfills (Fulda and Kinzelbach, 2000; Santella et al., 2008). However, anomalously high concentrations due to terrigenic production are a far greater concern for SF_6. Elevated concentrations have been found in sedimentary aquifers (von Rohden et al., 2010) and in aquifers containing fluorite or metallic sulphide mineralisation (Harnisch and Eisenhauer, 1998; Koh et al., 2007).

2.3.6. Microbial breakdown

The CFCs may be subject to microbial degradation under anoxic conditions where CFC-11 is typically degraded more rapidly than CFC-12, as has been reported in a number of studies (Khalil and Rasmussen, 1989; Oster et al., 1996; Hinsby et al., 2007; Horneman et al., 2008). Reduction effects may be revealed by measuring the field parameters dissolved oxygen (DO) and oxidation/reduction potential (ORP) during sampling, or, by differences in tracer ages established from concentrations of CFC-11, CFC-12, CFC-113 and SF_6 (section 3). Under highly reducing conditions the CFCs may be degraded to concentrations that are below detection. Therefore, it is extremely important to be aware of redox conditions during sampling for the CFCs. However, a detectable concentration of dissolved oxygen during sampling does not preclude reduction effects. This is because of the potential for changes in redox conditions along the groundwater flow path, or, the mixing of different flow paths containing different dissolved O_2 concentrations during sampling.

2.3.7. Other factors for consideration

The potential for sorption of the CFCs is minimal and generally only tends to affect aquifers with a matrix that is high in organic carbon content (Plummer et al., 2006). Sorption tends to effect CFC-12 to CFC-11 to CFC-113 in increasing order of magnitude when sorption does occur (Ciccioli et al., 1980). There is also limited evidence for thermal effects where CFC-12 has been preferentially removed from solution. This limited evidence was established from groundwater issuing from two small springs in Belgium and the UK (Darling et al., 2012).

2.4. Theory summary

The CFCs and SF_6, like all hydrological tracers, have advantages and disadvantages. Sampling and analysis, in addition to the corrections for temperature, pressure and salinity are relatively simple and straightforward. These corrections are made to determine atmospheric equilibrium concentrations at the time of groundwater recharge to set the dating 'clock' to zero. There are several non-correctable factors which require careful consideration, such as contamination of the CFCs (typically anthropogenic in origin) and SF_6 (typically terrigenic in origin), in addition to the degradation of the CFCs under reducing conditions (typically revealed by field parameters DO and ORP). However, contamination may be useful for 'fingerprinting' water sources. Ultimately, the quality of the atmospheric equilibrium 'signal' for the purpose of groundwater age dating will depend on the accuracy of the above corrections and the extent to which contamination, degradation, thermal and sorption effects change concentrations during transport. In the authors experience, it is possible to quantify the above parameters with a high degree of certainty. In doing so, it is possible to determine the efficacy and application of the CFCs and SF_6 as tracers of groundwater age.

3. Groundwater age

The definition of groundwater age is complicated and covered by many authors (Małoszewski and Zuber, 1982; Clark and Fritz, 1997; Kazemi et al., 2006; Bethke and Johnson, 2008; Suckow, 2014). There are many terms in the literature which in some way attempt to describe groundwater 'age' and this review does not attempt a complete review of all the definitions, and the sometimes minor differences in the meaning of age. Instead, a disambiguation of the terms is presented by discussing three basic concepts of groundwater age as follows (Suckow, 2014): (i) a simple definition that assumes no mixing, (ii) a more complicated definition that treats groundwater as a population of individual ages and assumes knowledge of aquifer geometry and mixing of different ages, and (iii) a definition with unit time that assumes no knowledge of the geometry or mixing of different ages.

3.1. Definitions

3.1.1. Tracer age

Groundwater age cannot be measured directly and is inferred from environmental tracers, or, from simulations in hydrogeological models (Suckow, 2014; Turnadge and Smerdon, 2014). In this instance groundwater age is estimated from measured concentrations of anthropogenic trace gases. Hence, the measured groundwater age is actually a *tracer age* and only if the tracer exactly follows the process in question (e.g., advective transport, mixing or a chemical reaction) can the tracer considered an *ideal tracer* (Suckow, 2014). The CFCs and SF_6 could be described as ideal tracers of mass transport if they behave exactly as the water molecule. However, the applied tracers may be transported slightly differently to the water molecule (e.g., due to concentration gradients or diffusion), or subject to degradation. Therefore, it is important to explicitly state here that groundwater ages determined from tracer concentrations are in fact *tracer ages*.

3.1.2. Idealised age (assume no mixing)

Here we define: "the (highly) *idealised groundwater age* is the time difference that a water parcel needs to travel from the groundwater surface to the position where the sample is taken" (Torgersen et al., 2013). This definition is advantageous for groundwater dating methods based on dissolved gases (e.g.,

[3]H/[3]He, CFCs and SF_6) because this is a measure of time since water was last in contact with the atmosphere. Hence, the groundwater dating 'clock' starts when groundwater is no longer in contact with the atmosphere. The age (residence time) of groundwater is then determined by simply matching a particular recharge year in Fig. 1 to the measured concentration in a sample. This assumes an infinitesimal small particle (or parcel) of groundwater and flow as if along a tubular flow line, with no mixing between the moment of recharge and the moment of sampling. This is also known as the 'piston flow' model of groundwater flow (Małoszewski and Zuber, 1982).

3.1.3. Groundwater age distributions

Groundwater mixing occurs in-aquifer (diffusion and dispersion), due to large well-screens sampling different flow lines, and within the well-bore during sampling. In most practical situations a sample is obtained from a discharge point where flow lines converge (e.g., springs or pumped wells). Therefore, the idealised definition of groundwater age (section 3.1.2) exposes a simple problem, because it is now generally accepted that a sample equivalent to a point in space in a flow field will comprise a population of individual ages (Suckow, 2014; Turnadge and Smerdon, 2014), even if samples are obtained from discrete sampling depths, < 1 m (Weissmann et al., 2002).
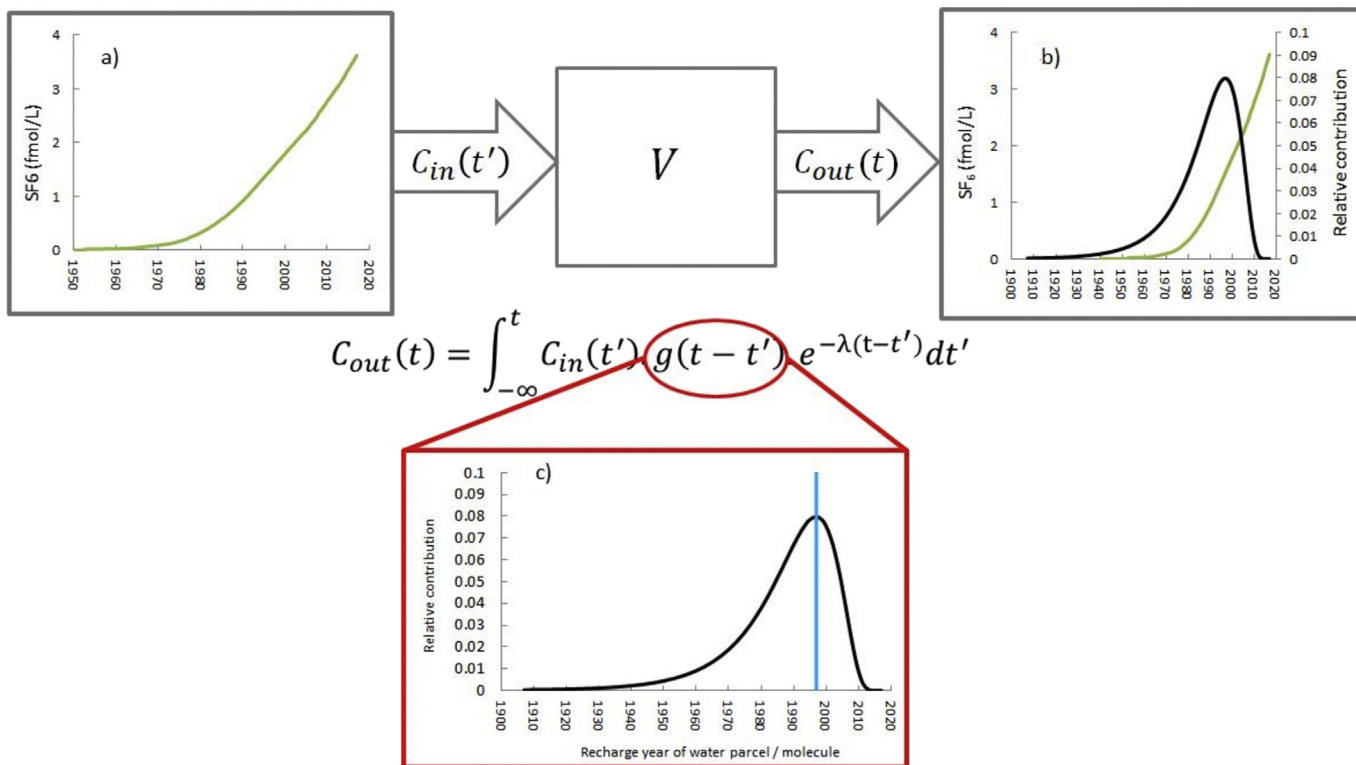
3.1.4. Lumped parameter models

In the early years of isotope hydrology techniques were developed to bridge the gap between age as a scalar value (infinitesimal small particle) and the concept of real-world samples as a mixture of different ages. These simple lumped parameter models (LPMs) treat the aquifer as a 'black box' and do not require any physical knowledge of the system prior to interpretation (Małoszewski and Zuber, 1982). These models combine the concept of residence time as a distribution with a measurable tracer concentration according to a convolution integral (Fig. 4). The measured concentration as a function of time, $C_{out}(t)$ is given as:

$$C_{out}(t) = \int_{-\infty}^{t} C_{in}(t') \cdot g(t - t') \cdot e^{-\lambda(t-t')} dt' \quad \text{(pmol/L or fmol/L)}$$

(1)

where, $C_{in}(t')$ is the input concentration of the applied tracer as function of time and $(t - t')$ is the time difference between the input time t' and the time of sampling t'. As shown in Fig. 4, the convolution integral attributes a weight function $g(t - t')$ describing what percentage each individual age contributes to the whole mean. Hence, age is incorporated using convolution, summing up all concentrations as a function of time in an aquifer volume (Fig. 4). The $e^{-\lambda(t-t')}$ term accounts for radioactive decay if required (Małoszewski and Zuber, 1982). The above mathematical formalism is equivalent to the concept of idealised age defined above, but instead assumes a population of idealised ages. This approach attempts to describe all the properties of the system using only a few parameters, hence the term 'lumped parameter models'. The LPMs may be adapted to measured concentrations by varying the weighting function to minimise the difference between model output and measured tracer concentrations (e.g., least squares fitting).

This modelling approach is dominated by the specification of the weight function $g(t - t')$ as shown in Fig. 4, defining the relative contribution for each age in the convolution integral. There are

Figure 4. The application of lumped parameter models to link the concept of groundwater age as a distribution (blue line is the *mean residence time*) to a measured concentration. Fig. 4a shows the variation in concentration of SF_6 over time in groundwater at equilibrium with the Northern Hemispheric atmosphere (as shown in Fig. 1). Fig. 4b shows the relative contribution of each groundwater age (as shown in Fig. 4c) as function of the SF_6 concentration over time. The lumped parameter models assume that the age distribution is described by a weighting function $g(t - t')$, which is in effect an age distribution. All the input concentrations of the applied tracer are summed up as a function of time according to the convolution integral. Adapted from Suckow (2014).

various LPMs with different weighting functions. For example, the piston flow model uses a Dirac delta distribution whereas the exponential model uses an exponential distribution (Małoszewski and Zuber, 1982). The LPM approach highlights the importance of the shape of the age distribution. A simple case is considered in Fig. 4, illustrating a groundwater sample obtained in 2017 with a SF_6 concentration of 0.93 fmol/L (Fig. 4b). This fictitious sample has a log-normal distribution with a mean residence time and piston flow age of 20 years (recharge year 1990). If constant nitrate input entered a watershed during the last 15 years and behaved conservatively, the outflow of the piston flow model will not contain any nitrate. Whereas the outflow of the log-normal distribution will contain >30% of groundwater that is < 15 years old (Fig. 4b). Therefore, it is also important to state the assumptions of the applied dating method, since it is the shape of the age distribution that will determine the 'breakthrough' of a contaminant (Fogg et al., 1999; Weissmann et al., 2002; Suckow, 2014; Turnadge and Smerdon, 2014).

The CFCs and SF_6 have significantly different input functions as function of time (Fig. 1). Therefore, a basic way of resolving mixing processes is to plot CFC-12 versus SF_6 (Fig. 5). The piston flow model of age results in a 'bow shape' plot owing to the different input functions for the tracers. The other extreme of groundwater flow is the binary mixing models which assumes the mixing of old (>100 years) tracer free groundwater with modern groundwater recharged in 2017 (Fig. 5). The binary mixing model may be adapted to any particular recharge year. The exponential mixing and exponential piston flow models proposed by Małoszewski and Zuber (1982) assume an exponential distribution for the weighting function as discussed above. Hence, due to the exponential nature of groundwater mixing it may be possible to date groundwater up to 100 years old using CFC-12 and SF_6, provided certain simplifying assumptions are fulfilled (e.g., steady state conditions and simple aquifer geometry). Therefore, through measuring two tracers simultaneously it may be possible to reveal distributions of groundwater age and resolve mixing processes without any prior knowledge of the physical properties of the aquifer system (Gooddy et al., 2006). An exponential distribution of age and a mean residence time of 20 years is shown in Fig. 5 (red markers, sampled in

Figure 5. Example plot of CFC-12 versus SF_6 showing the piston flow model, the exponential piston flow model and the exponential mixing model with ages shown. The binary mixing model shows the mixing of tracer free water with recharge in 2017 expressed as a percentage. Plotted using USGS Tracer Model (https://water.usgs.gov/lab/software/tracer_model/).

2017). However, these LPMs assume steady-state conditions and relatively simple aquifer geometry (Małoszewski and Zuber, 1982; Cook and Herczeg, 2012).

3.1.5. Apparent age

Although not the focus of this review, the $^3H/^3He$ and ^{14}C groundwater dating techniques require a mathematical formula. Age in this instance is referred to as the '$^3H/^3He$ apparent age' or the 'conventional radiocarbon age' respectively (Suckow, 2014). As discussed, in practical situations samples are obtained from a pumped well (large well-screen) or a spring where flow lines converge. The mixing of groundwater ages contributes to the calculated $^3H/^3He$ and ^{14}C age in an unknown way and mean residence time is meaningless because the age distribution is *a priori* unknown. Therefore, a new term is required and *apparent tracer age* is the most useful description found in the literature (Suckow, 2014). The term 'apparent' is applied because the age represents an unknown average of idealised ages (infinitesimal small particles).

The $^3H/^3He$ and ^{14}C have different formulas. The $^3H/^3He$ age involves radioactive decay and simultaneous measurement of the parent (^3H) and daughter (^3He) isotopes:

$$\tau = \frac{1}{\lambda} \cdot \ln\left(1 + \frac{^3He_{trit}}{^3H}\right) \ \text{(years)} \tag{2}$$
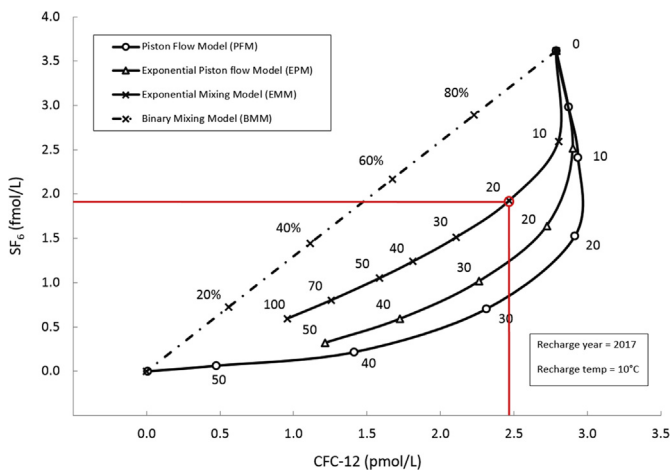
whereas, the ^{14}C age involves an initial concentration (C_0) and radioactive decay:

$$\tau = \frac{1}{\lambda} \ln\left(\frac{C_0}{C(t)}\right) \ \text{(years)} \tag{3}$$

The decay constant (λ) is 12.32 years for ^3H (Lucas and Unterweger, 2000) and 5730 years for ^{14}C (Kalin, 2000). Hence, these techniques integrate over vastly different age ranges and may lead to different apparent ages, even when applied on the same sample (Bethke and Johnson, 2008; McCallum et al., 2014, 2015). This is due to the nature of hydraulic conductivity variance (heterogeneity) which may lead to wide distributions of groundwater age and conflicting age estimates (McCallum et al., 2015). Again, the shape of the age distribution requires careful consideration when interpreting tracer data.

3.1.6. Groundwater age summary

As has been demonstrated, the inversion of tracer concentrations to derive groundwater 'age' or mean residence time has to be transformed to 'apparent age' or 'modelled age' due to the fact that 'age' is always linked to a mathematical model. The highly idealised age assumes no mixing and an infinitesimal small particle, which does not exist. Thus, simple lumped parameter models were developed to present a more accurate description of reality, treating groundwater as a population of idealised ages, comprising various distributions of age (e.g., Dirac delta and exponential distributions). However, the LPM approach is unsuitable in transient flow fields (e.g., large scale anthropogenic stresses) and in practical situations the age distribution is *a priori* unknown. Further, the inversion of tracer concentrations to derive age distributions is a non-unique process, even when several tracers are measured simultaneously (McCallum et al., 2014, 2015). Yet, it is this parameter that is of most value when guiding water resource management (Fogg et al., 1999; Weissmann et al., 2002; Turnadge and Smerdon, 2014). A potential complementary technique is the use of hydrological models to simulate age distributions and tracer concentrations directly.

4. Hydrological models

Hydrological models are traditionally developed based on lithology and hydrologic data (e.g., water levels, recharge area and precipitation rates) to estimate groundwater recharge, flow, contaminant transport, and more recently, groundwater age. In practice, the recharge rate is often estimated from meteorological data and knowledge of the geology is incomplete. Accordingly, assumptions must be made about the subsurface, such as relative homogeneity. Model properties such as hydraulic heads, hydraulic conductivities, storage and porosity are measured, or, estimated from literature values. Groundwater models, of non-fractured aquifers, then typically solve Darcy's Law in three-dimensions to simulate flow velocities. The advection-dispersion equation is generally combined with simulated flow velocities to estimate solute transport rates, and more recently, statistical descriptions of groundwater age (Turnadge and Smerdon, 2014). However, the hydraulic conductivity of earth materials is highly variable, therefore model predictions (flow velocities and transport rates) may be subject to a high-degree of uncertainty (Zuber et al., 2011).

Age information, such as tracers of age (e.g., CFCs and SF_6), provide one means by which hydrological modellers can reduce uncertainty and refine understanding of subsurface flow systems. Hydraulic heads traditionally form the primary calibration targets in hydrological models. The inclusion of tracer concentrations as secondary calibration targets then facilitates the exploration of alternative calibration methods, towards more refined and realistic models with reduced uncertainty (Reilly et al., 1994; Szabo et al., 1996; Portniaguine and Solomon, 1998; Castro and Goblet, 2005; Zuber et al., 2005; Ginn et al., 2009; Leray et al., 2012; Massoudieh et al., 2014). The combination of hydraulic and tracer methods in the calibration process creates a linkage between independent measurements, providing a feedback that improves quantification of the flow and transport system. A numerical approach also circumvents the need for groundwater 'age' altogether through focussing on measured concentrations as calibration targets directly, rather than age (Suckow, 2014; Turnadge and Smerdon, 2014). Numerical approaches can also evaluate scenarios of changing hydraulic stresses (transient flow conditions).

5. Hydrochemistry

The hydrochemistry of groundwater is influenced by climate, the source of recharge, lithology, aquifer confinement, and the residence time of groundwater in the subsurface (Freeze and Cherry, 1979; Hiscock, 2009). As residence time increases the dissolution of the aquifer matrix occurs, leading to an increase of certain compounds (depending on lithology), particularly the six major ions (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^{2-}). In addition, biological oxidation occurs, leading to an increase in oxygen-rich compounds such as nitrate and iron oxide (Hiscock, 2009). With a combination of appropriate age tracers, it may be possible to constrain reaction times in the subsurface and obtain hydrochemical information (Böhlke and Denver, 1995).

However, in the literature to date, no definitive relationship between groundwater age and hydrochemistry has been established. Indeed, the use of age tracer data to infer hydrochemical processes remains highly controversial in certain research areas, such as the release of arsenic to porewater (Charlet and Polya, 2006). This is because in reality natural processes are highly complex, for example due to the mixing flow lines and transient kinetics induced by heterogeneity or seasonal climate (e.g., monsoon cycle). Further, the relationship between groundwater age/mean residence time and hydrochemistry may not be related to a single process, such as dry/wet deposition, biogeochemical cycling and

cation exchange (Plummer et al., 1990), and may vary from system to system due to individual aquifer idiosyncrasies. The age-hydrochemistry relationship may also be influenced by human activities, such as land-use changes, fertilisation and increased groundwater pumping rates for irrigation (Harvey et al., 2006; Klump et al., 2006; McArthur et al., 2010). Despite these complications, groundwater age clearly plays an essential role in determining contamination risk from the surface and age tracer techniques can help delineate wellhead protection areas (Molson and Frind, 2012). At a fundamental level, the development of a robust conceptual model is needed prior to investigation before age tracer data can be reliably used to make estimates of hydrochemical reactions and contamination risk.

The application of tracers under all hydrochemical conditions remains challenging due to the requirement for tracer specific expertise (Cook and Herczeg, 2012). When we consider the very low solubility tracers (e.g., ^{3}He and SF_6) and the correction methods required to obtain age information (e.g., noble gases), it becomes clear that a high level of expertise is required for each tracer. The tracers themselves may also be subject to chemical reactions (e.g., microbial degradation) and may not be able to provide quantitative information on groundwater age. In addition, the applied tracers can only typically provide information on part of the potential age distribution, for example the CFCs and SF_6 cover the age range <100 years, whereas the age range from 50 to 1000 years remains challenging to date (Cook and Herczeg, 2012). Consequently, constraining reaction times and contamination risk on timescales of 50 to 1000 years also remains challenging.

As a side note, age tracer data may be used to assess steady-state flow conditions, which can indirectly aid in the interpretation of hydrochemical data. For example, if groundwater age changes as a function of time at an observation location due to changing flow conditions, then clearly the hydrochemistry will also be in transient-state. Further, decreasing groundwater age could be an indicator of land-use intensification, for example increased groundwater pumping rates leading to a decrease in groundwater age at depth (Klump et al., 2006; Stute et al., 2007; McArthur et al., 2010).

6. Conclusion

This review has explored the application of the CFCs and SF_6 as quantitative tracers of groundwater 'age'. Due to differing input functions, applicability and limitations related to current 'modern' groundwater dating techniques (<55 years), a combination of dating tools is recommended for more robust age interpretation. In this regard, the highly complementary CFCs and SF_6 dating techniques are recommended. In principle, resolving recharge temperature, pressure, salinity, excess air and degassing is relatively simple and straightforward, particularly when using the highly complementary noble gases. In doing so, the groundwater dating 'clock' is set to zero at the recharge zone. The simultaneous measurement of CFC-11, CFC-12 and SF_6 can also identify the various non-correctable factors (e.g., degradation, contamination and sorption) to determine the efficacy of the CFCs and SF_6 as tracers of groundwater age.

The term 'age' in relation to groundwater is complicated, therefore three basic concepts of groundwater age were defined; (i) idealised age, (ii) age as a distribution and (iii) apparent age (Suckow, 2014). Simple 'lumped parameter models' (LPMs) incorporate the concept of idealised age (infinitesimal small particle) and age as a distribution (mean residence time). The LPM approach is extremely useful in data poor environments because the environmental tracers (CFCs and SF_6) integrate over large temporal (decades) and spatial (global) scales. As a simple first-pass analysis,

LPMs can resolve mixing processes whilst encouraging the investigator to interpret groundwater 'age' not as a scalar value, but rather as a distribution of ages. This is extremely important for water resource management and understanding the spatial and temporal trends of contaminants (Weissmann et al., 2002). Accordingly, it is also encouraged that the underlying assumptions of age calculations are explicitly stated when discussing groundwater age. These concepts are of particular value when communicating and collaborating with adjacent sciences.

The rapid advancement of numerical modelling techniques over recent decades now means that flow models can be calibrated to independent hydraulic and tracer measurements. This is typically achieved by simulating theoretical distributions of groundwater age (solution of the advection-dispersion equation). This parameter is *a priori* unknown in hydrogeological investigations, yet of most value from a resource management perspective. It is also possible to investigate the potential biases of fluid dating techniques through simulating age distributions, such as those discussed in this review. Hence, simulating distributions of age can offer significant improvement in conceptual understanding, particularly when communicating to a non-technical audience (Turnadge and Smerdon, 2014). It is suggested that this approach should be adopted where possible. However, such an approach is typically prohibitively expensive and limited to a few real-world cases due to the complexities of linking simulated age distributions to measured tracer concentrations.

A key scientific challenge faced by hydrogeologists is the quantification of recharge rates, flow rates and velocities like distance velocity or Darcy velocity, in addition to dispersivity and storativity in complex three-dimensional geologic and potentially transient conditions. This is in order to manage groundwater resources at the scale of interest (Larocque et al., 2009). The direct observation of mass transport through measuring the tracers discussed in this review can directly contribute quantification of these parameters and is the topic of a future publication.

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