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Use of hydrochemistry as a standalone and complementary groundwater age tracer

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SUMMARY

Groundwater age or residence time is the time water has resided in the subsurface since recharge. This can provide information on groundwater mixing and flow, and volumes of groundwater and recharge, etc. Groundwater age can be inferred from environmental tracers, such as SF_6 and tritium that have a known input to groundwater and/or undergo known alteration processes in groundwater. Multiple tracers are often applied complementarily in order to increase the robustness of age interpretations. To this end, it is desirable to develop cost-effective and easily applicable age tracers/techniques to supplement the existing ones.

A number of hydrochemical parameters are spatially and temporally widely available due to national and regional groundwater monitoring programmes. Their determination is cost-effective and relatively simple compared to existing age tracers. Hydrochemistry has been used as an age proxy but its use as an independent age tracer has only been demonstrated for water recharged weeks to months ago (relying on seasonal changes).

This study focuses on the Lower Hutt Groundwater Zone, New Zealand, and assesses whether hydrochemistry can be used as an independent indicator of groundwater age, or if not, whether hydrochemistry can be used to complement groundwater age measurements based on other tracers. This study also examines the use of hydrochemistry as an indicator for recharge sources and weathering processes. This study shows that, when used independently, hydrochemistry could only be used as an age proxy, but in combination with tritium measurements, hydrochemistry provided useful additional constraint on age of groundwater recharged days to ~100 years ago.

1. Introduction

Groundwater age helps characterize the complex and diverse recharge, mixing and flow processes of groundwater (Dillon, 2005; White and Rosen, 2001; Close et al., 2001). Groundwater age, which is defined more formally elsewhere (e.g. Kazemi et al. (2006), Clark and Fritz (1997)), is a measure of recharge year and hence residence time of a groundwater resource. Groundwater age information can aid assessment of not only recharge areas, flow paths and the amount of water that can be sustainably extracted, but also the lag-time and anticipated future loads of contaminants discharging from groundwater bodies.

Groundwater is usually sampled from a discharge point (e.g. springs or pumped wells) where groundwater from short and long flow paths in the aquifer mix. These samples therefore contain fractions of water of different ages rather than a single age (Małoszewski and Zuber, 1982). Recent studies have stressed the importance of inferring the age distribution rather than the mean age, because mean age is misleading in many contexts e.g. contaminant breakthrough can occur much earlier than at mean age
(e.g. McCallum et al., 2014; Suckow, 2014). Several approaches exist to estimate the groundwater's age distribution. The most widely applied technique makes use of natural or anthropogenic tracer substances with a known input to groundwater and/or known alteration processes in groundwater (e.g. radioactive decay), and a model that conceptualizes mixing of groundwater, also referred to as a mixing model. The simplest mixing models from which the age distribution is deduced are Lumped Parameter Models (LPMs). LPMs conceptualize groundwater mixing based on the aquifer geometry and allow for estimation of the groundwater's age distribution with little tracer data.

In general, LPMs are a function of mean residence time (MRT) and one or more mixing parameters. The most commonly applied

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LPMs are the Dispersion Model (DM), the Exponential Mixing Model (EMM), the Exponential Piston flow Model (EPM) and the Piston flow Model (PM). As an example, the EPM conceptualizing mixing of groundwater emerging from a partly unconfined aquifer is defined in Eq. (1). For a more detailed description of the most commonly used LPMs and discussion on the use of 'parametric' LPMs, their advantages and limitations, see Maloszewski and Zuber (1996), Zuber et al. (2001) and Jurgens et al. (2012).

$$\text{For } t' > MRT\left(1-\frac{1}{n}\right): \; f_{EPM} = \frac{n}{MRT} * \exp\left(-n * \frac{t'}{MRT} + n - 1\right); \quad \text{else}: \; f_{EPM} = 0, \tag{1}$$

with f_{EPM} as the age distribution according to the exponential piston flow model, MRT as the mean residence time; t' as transit time; t as observation time; n refers to the reciprocal of the ratio of exponential to total flow defined by Małoszewski and Zuber (1982); $1/n$ is in the following referred to as E/PM.

Inferring the age distribution from environmental tracers with the aid of these simplified LPMs relies on the relationship in Eq. (2), also referred to as convolution integral.

$$c_{obs}(t) = \int_0^\infty g(t') * c_{in}(t-t') * e^{-(\lambda t')} dt', \tag{2}$$

with $c_{obs}(t)$ as the observed tracer concentration in groundwater; $c_{in}(t'-t)$ is the tracer concentration in recharge as a function of time; t' = transit time, t = observation time, $e^{-(\lambda\tau)}$ refers to radioactive/biological decay of the tracer with decay rate λ; $g(t')$ is the mixing model or LPM from which the age distribution is deduced.

Age tracer measurements are only available for a limited number of groundwater sites, because their determination is relatively expensive and requires special lab equipment and expertise. In addition, the applicability and reliability of individual age tracers are limited to specific groundwater environments and each tracer's time/age application range is restricted.

This study is concerned with finding cost-effective, easily determinable tracers to increase the number of available robust groundwater age estimates. The use of commonly measured hydrochemistry[1] as a groundwater age tracer bears significant advantages to the use of established age tracers. Firstly, measurement is relatively cost-effective and simple. Secondly, it is routinely determined and data are spatially widely available over the past decades in line with major national and regional groundwater monitoring programs such as the National Groundwater Monitoring Program (NGMP) in New Zealand, or the National Ground Water Monitoring Network (NGWMN) in the USA. The potential of hydrochemistry for groundwater characterization has been discussed for decades (e.g. Freeze and Cherry, 1979; Drever, 1988; Langmuir, 1997; Robins, 1998). However, its use is challenging as groundwater chemistry can be influenced by many factors aside from residence time. Such factors include the abundance and type of minerals and microbes present and climatic conditions (Downes, 1985; Plummer et al., 1990; O'Brien et al., 1997; Kilchmann et al., 2004; Daughney and Reeves, 2005) and also anthropogenic factors such as land use and fertilizing practices (e.g. Morgenstern and Daughney, 2012; Böhlke, 2002a,b).

Time dependent processes/reactions that can result in hydrochemistry–RT relationships include mineral weathering, redox reactions, hydrolysis, precipitation, sorption, complexation and ion exchange reactions (e.g. Bethke, 2008). Of these reactions, mineral weathering is thought to be the most suitable for groundwater dating as occurs over a suitable timeframe. Ion exchange, hydrolysis, complexation, precipitation, dissolution and sorption are relatively rapid processes and therefore not expected to give hydrochemistry–RT relationships that can be used to date groundwater of MRT > months to years, although the confounding effect of these processes on the hydrochemistry–RT response does need to be considered. Hydrochemistry parameters have been successfully used to determine an age distribution for relatively young groundwaters with a mean age of the order of weeks to a few months. This method relied on significant seasonal variation of hydrochemistry in groundwater recharge (Anderson, 2005; Cox et al., 2007; Cirpka et al., 2007).[2] Over a wider age range, hydrochemistry has been used as an age proxy to distinguish older from younger groundwater and/or to support age information derived from environmental tracers with the aid of statistical tools or physical groundwater models (e.g. Allison and Hughes, 1978; Edmunds and Walton, 1980; Plummer and Sprinkle, 2001; Petrides et al., 2006; Lalbat et al., 2007; Daughney et al., 2010). Relationships between mean or apparent age inferred from environmental tracer data (e.g. Downes, 1985; Katz et al., 1995; Morgenstern et al., 2009, 2010, 2015; Rademacher et al., 2001, 2005; Peters et al., 2013), flow path or well depth (e.g. Taylor et al., 1992; Edmunds and Smedley, 2000; Edmunds et al., 2003; Hofmann et al., 2010) and flow path length and groundwater velocity (e.g. Kenoyer and Bowser, 1992; Pacheco and van der Weijden, 2012)), and hydrochemistry[3] have been established.

These relationships can be used to estimate mean/apparent age purely using hydrochemistry as illustrated in Fig. 1, but do not take account of groundwater mixing, nor can they be used to estimate the age distribution. These do not therefore (necessarily) represent processes/kinetics at piston (i.e. unmixed or homogenously mixed) flow.[4] Deviation of observed groundwater chemistry from piston flow relationships may contain information on groundwater mixing. Inferring such information may allow for the use of hydrochemistry as an age tracer to estimate the groundwater's age distribution over a wider age range than possible with the established technique that relies on seasonal variations. To the authors' knowledge this has never been assessed.

This study builds on the findings of the above mentioned studies and assesses the potential of hydrochemistry as an independent age proxy/tracer further. In particular, the potential use of commonly measured hydrochemistry parameters as complementary age tracers is assessed further. As such, this study presents a framework to identify hydrochemistry–time relationships and determine what age information (i.e. mean age and mixing model) these provide. Although the type(s) of reaction(s) that led to hydrochemistry–RT relationships are explored and weathering rates are

[1] In this study, the term 'commonly measured hydrochemistry' includes the concentration of major and trace ions, but does not include the concentrations of isotopic compounds, such as tritium and carbon, or other compounds, such as SF_6, that have been applied as groundwater age tracers through employment of their known input to groundwater and/or well-studied decay.

[2] The approach is similar to the use of stable isotope ratios for groundwater dating (e.g. McDonell et al., 1999; Rosen et al., 1999b; Stewart and Morgenstern, 2001). It relies on seasonal variation of hydrochemistry of recharge that is dampened over a period of months to a few years (depending on the groundwater environment and its signal dampening effect). The approach works well for inferring groundwater age distributions with a mean age of up to several months (e.g. has been used to characterize infiltration of river water into groundwater (Anderson, 2005; Cox et al., 2007; Cirpka et al., 2007)), but is of limited use for dating of water older than ~5 years. In addition, a large number (i.e. time series) data of hydrochemistry of recharge and hydrochemistry of groundwater are necessary for successful application of this approach.

[3] These relationships have been established for rock forming elements, such as Si, Na, Mg, and total dissolved solids (TDS) as well as constituents of microbial degradation, such as dissolved oxygen (DO) and pH.

[4] The rates inferred from these relationships are therefore not necessarily comparable to rates determined under piston flow in lab environments. Similarly, age estimated from these relationships does not necessarily represent mean or apparent water age (except for pure piston flow field environments) as the relationships are skewed depending on the degree of mixing.