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Partitioning young and old groundwater with geochemical tracers

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ABSTRACT

Groundwater age—defined as the time elapsed since the groundwater entered the subsurface—is a helpful indicator of groundwater quality and renewal. Some tracer-based groundwater age calculations require assumptions about the distribution of ages in the groundwater sample that, unfortunately, cannot be validated. Here, straightforward mixing models are developed that do not require a priori knowledge of age distributions and are able to quantify the fraction of a groundwater sample that recharged more recently than calendar year 1953 (using tritium) or within the past ~12 thousand years (using carbon-14). Calculations of young and old groundwater can be used to map groundwater velocities in flow systems driven by diverse climate conditions, groundwater extraction rates, rock types, topographic gradients and plant populations.

1. Introduction

Ages of groundwater in the natural environment have long been examined using radiochemical and technogenic gas contents of groundwater samples (e.g., von Buttlar and Wendt, 1958; Thatcher et al., 1961; see Bethke and Johnson, 2008). Quantifying groundwater age can help to estimate groundwater renewal fluxes (Le Gal La Salle et al., 2001; Chen et al., 2005; McMahon et al., 2011; Hagedorn, 2015), assess groundwater pollution vulnerabilities (Aggarwal et al., 2000; Cartwright and Weaver, 2005; Manning et al., 2005; Klump et al., 2006; Gurdak and Qi, 2006; Stute et al., 2007; Hoque and Burgess, 2012; Molson and Frind, 2012), determine continental weathering rates (Maher, 2010; 2011; Frisbee et al., 2013a, b; Maher and Chamberlain, 2014), and test hydrologic models (Kirchner, 2006; Vaché and McDonnell, 2006). Unfortunately, reported mean groundwater ages often vary widely when determined with different geochemical tracers (e.g., Corcho Alvarado et al., 2007; Kulongoski et al., 2008; Jiráková et al., 2010; Frisbee et al., 2013a, b; Mažeika et al., 2013).

Calculated water ages vary widely when determined using different tracers because each individual tracer is only useful for examining portions of potential age distributions (Waugh et al., 2003). Current groundwater age calculations rarely consider the potential for irregular, multimodal age distributions. This is problematic because spasmodic groundwater age distributions are expectedly widespread, because groundwater samples are often pumped from wells with long screens that draw shallow and deep storage unevenly, and because these same wells often have imperfect seals that permit rapid downward flows through gravel packs or well annuluses (Edmunds et al., 1984; Varni and Carrera, 1998; Plummer et al., 2000; Bethke and Johnson, 2002; Weissmann et al., 2002; Castro and Goblet, 2005; Chen et al., 2003; 2005; Bethke and Johnson, 2008; Jurgens et al., 2014). Mixtures of recent recharge and much older groundwater are evident in samples collected from many globally-distributed and diverse aquifer systems (e.g., Sonnenthal and Bodvarsson, 1999; Le Gal La Salle et al., 2001; Dogramaci and Herczeg, 2002; Harvey et al., 2006; Cartwright et al., 2007; Ma et al., 2008; Currell et al., 2010; Hamed et al., 2011; Varsányi et al., 2011; McMahon et al., 2013; Stadler et al., 2012; Samborska et al., 2013; Unland et al., 2014). Further, mixtures of recent and much older waters occur naturally without pumping-induced mixing, as evidenced by natural springs that discharge groundwaters bearing low radiocarbon concentrations but also measureable tritium (e.g., Thomas et al., 2003).

These widespread groundwaters with age distributions that span orders of magnitude are unlikely to be represented by smooth, unimodal distributions. Lumped parameter models are widely applied to calculate groundwater ages, but require users to assume constant flow and ascribe a known age distribution (Suckow, 2014; Lamontagne et al., 2015); unfortunately, true groundwater age distributions are "difficult (to impossible) to determine" (Torgersen et al., 2013). Because of their reliance on ascribing age distributions, current calculated groundwater ages may differ from true ages by substantial margins due to their vulnerability to the aggregation errors brought about by groundwater mixing and the nonlinear relationship between tracer concentration and water age (see Bethke and Johnson, 2008; Cornaton et al., 2011; Frisbee et al., 2013a, b; Torgersen et al., 2013; McCallum et al., 2015; Kirchner, 2016a; 2016b). While some studies have skillfully considered and quantified mixtures of young and old groundwater by combining

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lumped parameter and mixing models (e.g., Stanton et al., 2007; Solomon et al., 2010; Samborska et al., 2013), even the age distributions applied to fractions of samples may be impossible to validate (Torgersen et al., 2013). A broadly-applicable framework that is free from aggregation error and uses multiple groundwater tracers to quantify depth-distributions of young and old groundwater and their associated uncertainties remains unavailable.

The objective of this study is to apply measured groundwater tracer activities to quantify the fraction of a sample that recharged (i) more recently than the year 1953 (post-1953 groundwater: $F_{post\text{-}1953}$), or (ii) more recently than the Holocene–Pleistocene transition (11,700 years ago; Holocene groundwater: $F_{Holocene}$). This work builds from calculations presented in numerous other works (e.g., Goode, 1996; Dassi et al., 2005; Stanton et al., 2007; Stute et al., 2007; Solomon et al., 2010; Massoudieh et al., 2012; Samborska et al., 2013; Visser et al., 2013; Jurgens et al., 2014; Massoudieh et al., 2014; McCallum et al., 2014; Gleeson et al., 2016; Kirchner, 2016a; 2016b; Jasechko et al., 2016). For example, Goode (1996) showed that the product of groundwater age and its mass (i.e., the "age mass") is conserved during transport, and highlighted the importance of groundwater mixing on groundwater age estimates (see also Bethke and Johnson, 2002). Solomon et al. (2010) and Stanton et al. (2007) partition fractions of decades-old water in the sample, combining exponential and binary mixing models to estimate the age of a partitioned fraction of the water sample. Massoudieh et al. (2014) estimated discretized age distributions of groundwater samples using multiple geochemical tracers, focusing on the distribution of a sample that recharged more recently than the year 1950. Several studies have applied mixing models based on stable oxygen, hydrogen and radiocarbon isotope contents to estimate fractions of Pleistocene groundwater in samples (e.g., Dassi et al., 2005; Samborska et al., 2013; Jurgens et al., 2014); other studies have applied mixing models based on ^{3}H or ^{3}H–^{3}He to estimate fractions of decades-old groundwater in a sample (e.g., Stute et al., 2007).

The approach presented here differs from previously described approaches in one or more of the following ways. The ^{3}H-based equations presented here (Section 2.1) use time series of precipitation ^{3}H sourced from recently-developed global interpolations of precipitation ^{3}H (Jasechko and Taylor, 2015); account for radioactive decay prior to sampling and chemical analysis; and consider that the groundwater sample could be a mixture of groundwaters characterized by an irregular, multimodal age distribution. The ^{14}C-based equations presented here (Section 2.2) account for $^{14}C_{CO_2}$ variations throughout the Quaternary, upgradient carbonate mineral dissolution, past radiocarbon decay, and groundwater mixing that leads to an unspecified distribution of ages in the groundwater sample that could be smooth or irregular, unimodal or multimodal.

2. Partitioning young and old groundwater

This section describes an approach for calculating fractions of groundwater samples comprised of post-1953 groundwater (Section 2.1) and Holocene groundwater (Section 2.2). The Supplementary Information presents example calculations of each parameter and tabulates lists of calculation assumptions (Tables S1–S4).

2.1. Partitioning post-1953 groundwater fractions

Tritium in groundwater can be used to calculate the fraction of a water sample that recharged more recently than the year 1953. The year 1953 is selected as a threshold age because widespread nuclear weapons testing in the atmosphere between 1953 and 1963 artificially increased precipitation tritium to ~5 to ~500 times that of natural pre-bomb levels (Figs. 1 and 2). The mass fraction of a water sample that recharged more recently than the year 1953 ($F_{post\text{-}1953}$ = [mass of post-1953 groundwater in the sample] / [mass of the sample]) is described by (e.g., Jasechko et al., 2014):

$$F_{post\text{-}1953} = \frac{{}^{3}H_{sample} - {}^{3}H_{pre\text{-}1953}}{{}^{3}H_{post\text{-}1953} - {}^{3}H_{pre\text{-}1953}} \quad (1)$$

where $^{3}H_{sample}$ represents the tritium activity measured in a water sample, and $^{3}H_{pre\text{-}1953}$ and $^{3}H_{post\text{-}1953}$ represent decay-corrected tritium activities of groundwater that recharged during or prior to 1953 ($^{3}H_{pre\text{-}1953}$) and after 1953 ($^{3}H_{post\text{-}1953}$).

While $^{3}H_{sample}$ can be measured, $^{3}H_{pre\text{-}1953}$ and $^{3}H_{post\text{-}1953}$ must be estimated by reconstructing precipitation tritium time series and decay correcting these time series to the date that the groundwater sample was analyzed ($^{3}H_{decay\ corrected}$)

$${}^{3}H_{decay\ corrected} = \left({}^{3}H_{precip(t)}\, e^{-0.693\left(t_{sample}-t\right)/(12.3\ years)}\right)_{t} \quad (2)$$

where ${}^{3}H_{precip(t)}$ is the precipitation tritium content at time t, and t_{sample} is the date that the groundwater sample was analyzed for its tritium content. Annual precipitation ^{3}H values were input into Eq. (2); the annual precipitation ^{3}H values were calculated by precipitation-amount-weighting monthly precipitation ^{3}H interpolations using long term monthly average precipitation rates (New et al., 2002; see Table S1).

Spatiotemporal distributions of ${}^{3}H_{precip(t)}$ have been estimated using global historical precipitation ^{3}H records (Fig. 2; global interpolations shown in Supplementary Information of Jasechko and Taylor, 2015); defining a local precipitation ^{3}H input curve is crucial given the substantial differences in tritium time series around the globe (Stewart et al., 2012; Fig. 2). $^{3}H_{pre\text{-}1953}$ is defined as $^{3}H_{decay\ corrected}$ evaluated for dates prior to calendar year 1953, and $^{3}H_{post\text{-}1953}$ is defined as $^{3}H_{decay\ corrected}$ evaluated from calendar year 1953 to the date the sample was analyzed (t_{sample}). Evaluating $^{3}H_{pre\text{-}1953}$ and $^{3}H_{post\text{-}1953}$ over each time interval yields a range of possible groundwater tritium values that can be entered into Eq. (1) to calculate $F_{post\text{-}1953}$ (example shown in Table S3). By calculating fractions of young water, the proposed approach avoids aggregations errors otherwise introduced by the combination of groundwater mixing and the nonlinear relationship of tracer content and average groundwater age (Weissmann et al., 2002; Newman et al., 2010; Torgersen et al., 2013; McCallum et al., 2015).

2.2. Partitioning Holocene groundwater fractions

This section derives a ^{14}C-based approach to calculate the fraction of a groundwater sample that recharged within the past 11,700 years (i.e., the Pleistocene–Holocene transition). 11,700 years ago is proposed as a ^{14}C-based young water fraction threshold to enable $^{18}O/^{16}O$ and $^{2}H/^{1}H$ data to be used as a potential, secondary age tracer, because Pleistocene precipitation $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios differed from Holocene ratios in many regions (Rozanski, 1985; Clark et al., 1998; Edmunds and Milne, 2001; Aeschbach-Hertig et al., 2002; Beyerle et al., 2003; Edmunds, 2009; Corcho Alvarado et al., 2011; Jiráková et al., 2011; McIntosh et al., 2012; Samborska et al., 2013; Ferguson and Jasechko, 2015; Jasechko et al., 2015):

Unlike ^{3}H, which is part of the water molecule, ^{14}C-based mixing models must also consider potential dissolved inorganic carbon (DIC) concentration differences between Holocene groundwater and pre-Holocene paleowater (Maloszewski and Zuber, 1982). The ^{14}C-based mass fraction of a water sample younger than 11,700 years in its age ($F_{Holocene}$ = [mass of Holocene groundwater in sample] / [mass of the sample]) can be calculated as following:

$$F_{Holocene} = \frac{[DIC]_{sample}\,{}^{14}C_{sample} - [DIC]_{paleo}\,{}^{14}C_{paleo}}{[DIC]_{Holocene}\,{}^{14}C_{Holocene} - [DIC]_{paleo}\,{}^{14}C_{paleo}} \quad (3)$$

where [DIC] represents the dissolved inorganic carbon concentration and ^{14}C represents radiocarbon activity. Subscripts refer to three