Earth-Science Reviews 152 (2016) 119–142

Contents lists available at ScienceDirect

Earth-Science Reviews

journal homepage: www.elsevier.com/locate/earscirev

A review of single-sample-based models and other approaches for radiocarbon dating of dissolved inorganic carbon in groundwater

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ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form 22 October 2015
Accepted 5 November 2015
Available online 10 November 2015

Keywords:
Radiocarbon
Dating
Groundwater
Models
Graphical
Review

ABSTRACT

Numerous methods have been proposed to estimate the pre-nuclear-detonation ^{14}C content of dissolved inorganic carbon (DIC) recharged to groundwater that has been corrected/adjusted for geochemical processes in the absence of radioactive decay ($^{14}C_0$) — a quantity that is essential for estimation of radiocarbon age of DIC in groundwater. The models/approaches most commonly used are grouped as follows: (1) single-sample-based models, (2) a statistical approach based on the observed (curved) relationship between ^{14}C and $\delta^{13}C$ data for the aquifer, and (3) the geochemical mass-balance approach that constructs adjustment models accounting for all the geochemical reactions known to occur along a groundwater flow path. This review discusses first the geochemical processes behind each of the single-sample-based models, followed by discussions of the statistical approach and the geochemical mass-balance approach. Finally, the applications, advantages and limitations of the three groups of models/approaches are discussed.

The single-sample-based models constitute the prevailing use of ^{14}C data in hydrogeology and hydrological studies. This is in part because the models are applied to an individual water sample to estimate the ^{14}C age, therefore the measurement data are easily available. These models have been shown to provide realistic radiocarbon ages in many studies. However, they usually are limited to simple carbonate aquifers and selection of model may have significant effects on $^{14}C_0$ often resulting in a wide range of estimates of ^{14}C ages.

Of the single-sample-based models, four are recommended for the estimation of $^{14}C_0$ of DIC in groundwater: Pearson's model, (Ingerson and Pearson, 1964; Pearson and White, 1967), Han & Plummer's model (Han and Plummer, 2013), the IAEA model (Gonfiantini, 1972; Salem et al., 1980), and Oeschger's model (Geyh, 2000). These four models include all processes considered in single-sample-based models, and can be used in different ranges of ^{13}C values.

In contrast to the single-sample-based models, the extended Gonfiantini & Zuppi model (Gonfiantini and Zuppi, 2003; Han et al., 2014) is a statistical approach. This approach can be used to estimate ^{14}C ages when a curved relationship between the ^{14}C and ^{13}C values of the DIC data is observed. In addition to estimation of groundwater ages, the relationship between ^{14}C and $\delta^{13}C$ data can be used to interpret hydrogeological characteristics of the aquifer, e.g. estimating apparent rates of geochemical reactions and revealing the complexity of the geochemical environment, and identify samples that are not affected by the same set of reactions/processes as the rest of the dataset. The investigated water samples may have a wide range of ages, and for waters with very low values of ^{14}C, the model based on statistics may give more reliable age estimates than those obtained from single-sample-based models. In the extended Gonfiantini & Zuppi model, a representative system-wide value of the initial ^{14}C content is derived from the ^{14}C and $\delta^{13}C$ data of DIC and can differ from that used in single-sample-based models. Therefore, the extended Gonfiantini & Zuppi model usually avoids the effect of modern water components which might retain 'bomb' pulse signatures.

The geochemical mass-balance approach constructs an adjustment model that accounts for all the geochemical reactions known to occur along an aquifer flow path (Plummer et al., 1983; Wigley et al., 1978; Plummer et al., 1994; Plummer and Glynn, 2013), and includes, in addition to DIC, dissolved organic carbon (DOC) and methane (CH_4). If sufficient chemical, mineralogical and isotopic data are available, the geochemical mass-balance method can yield the most accurate estimates of the adjusted radiocarbon age. The main limitation of this approach is that complete information is necessary on chemical, mineralogical and isotopic data and these data are often limited. Failure to recognize the limitations and underlying assumptions on which the various models and approaches are based can result in a wide range of estimates of $^{14}C_0$ and limit the usefulness of radiocarbon as a dating tool for groundwater. In each of the three generalized approaches (single-sample-based models, statistical approach,

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http://dx.doi.org/10.1016/j.earscirev.2015.11.004

and geochemical mass-balance approach), successful application depends on scrutiny of the isotopic (^{14}C and ^{13}C) and chemical data to conceptualize the reactions and processes that affect the ^{14}C content of DIC in aquifers. The recently developed graphical analysis method is shown to aid in determining which approach is most appropriate for the isotopic and chemical data from a groundwater system.

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1. Introduction

The possibility of using cosmogenic ^{14}C (half-life of 5730 ± 40 years (Godwin, 1962)) for estimating chronologies in regional groundwater systems on the ten thousand year timescale (today, using modern analytical methods, the approximately 0–45,000 year timescale) has been recognized since the pioneering work of K.O. Münnich (1957); Münnich and Vogel, 1962; Münnich et al., 1967). Numerous studies have applied radiocarbon dating to estimate radiocarbon age of dissolved inorganic carbon (DIC) in groundwater, estimate modern and paleorecharge rates to aquifers, recognize non-renewable paleowaters, extract paleoclimate information from the groundwater archive, calibrate groundwater flow models, and investigate the availability and sustainability of groundwater resources in regions of rapid population growth (see for example, summaries by Fontes and Garnier, 1979; Fontes, 1992; Kalin, 1999; Geyh, 2005; Plummer and Glynn, 2013). Despite widespread use of ^{14}C, interpretation of radiocarbon age of dissolved inorganic carbon (DIC) in groundwater still is limited by many uncertainties in determining the pre-nuclear-detonation ^{14}C content of DIC in recharge areas to aquifers and in accounting for the important chemical and physical processes that alter the ^{14}C content along groundwater flow paths. Therefore, with the measured amount of ^{14}C in the DIC, $^{14}C_{DIC}$, the basic equation for groundwater dating using ^{14}C, Eq. (1), depends on knowing the amount of the ^{14}C after adjustment for the geochemical and physical processes in the aquifer (without radioactive decay), $^{14}C_0$:

$$t = -\frac{5730}{\ln 2}\ln\left(\frac{^{14}C_{DIC}}{^{14}C_0}\right) = -\frac{1}{\lambda_{14}}\ln\left(\frac{^{14}C_{DIC}}{^{14}C_0}\right). \quad (1)$$

In Eq. (1), t is the groundwater age, λ_{14} is the ^{14}C decay constant, and $^{14}C_{DIC}$ is the measured ^{14}C value of the DIC.

The essential step in dating DIC is the estimation of $^{14}C_0$. Because DIC in groundwater is a mixture of carbon from different sources, estimation of $^{14}C_0$ requires an understanding of the carbon-bearing reactants and the reactions affecting their concentration in groundwater. The reactants include different sources of CO_2 (e.g. soil gas CO_2, CO_2 from oxidation of fossil organic matter, CO_2 from methane oxidation, and CO_2 of geogenic origin) and different sources of carbon from carbonate rocks (mainly limestone and dolostone). Further, the ^{14}C and ^{13}C content of additional sources of carbon to the groundwater DIC, such as carbon from pedigenic calcite in arid and semi-arid regions (Wallick, 1976; Marshall et al., 1993), or calcite cement in sandstones or calcite in fracture coatings, can differ isotopically from the predominant limestone and/or dolostone lithology of the carbonate aquifer.

Numerous models and approaches have been proposed to estimate $^{14}C_0$. The single-sample-based models rely on mass balances of major