



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



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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 ($^{14}\text{C}_0$) – 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 $\delta^{13}\text{C}$ 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 $^{14}\text{C}_0$ 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 $^{14}\text{C}_0$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $^{14}\text{C}_0$ 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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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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Contents

1. Introduction	120
2. Evolution of carbon isotopic composition in groundwater	121
2.1. Dissolution of soil gas CO_2 in water	123
2.2. Water–rock interaction (bicarbonate formation)	123
2.3. Water–soil gas interaction (carbon exchange under open-system conditions)	124
2.4. Water–rock interaction (carbon exchange under closed-system conditions)	124
3. Existing single-sample-based correction models	125
3.1. Empirical approach	125
3.2. Simple mixing models	125
3.2.1. Tamers' model	125
3.2.2. Pearson's model	126
3.3. Simple mixing accompanied by carbon exchange	127
3.3.1. Exchange with soil CO_2 (Mook's model)	127
3.3.2. Exchange with solid carbonate	128
3.3.3. Models considering either exchange with soil CO_2 or with solid carbonate	128
3.4. Mixed open- and closed-systems: the IAEA model	129
3.5. Other single-sample-based models	130
3.5.1. Oeschger's model	130
3.5.2. Cheng's model	130
4. Statistically-based models	130
4.1. Gonfiantini & Zuppi model	130
4.2. Extended Gonfiantini & Zuppi model	131
5. Geochemical mass-balance approach	132
6. Discussion of applications and limitation of radiocarbon dating models	133
7. Conclusions	137
Acknowledgments	138
Appendix A. The distribution of carbonate species as percentages of total dissolved inorganic carbon in water	138
Appendix B. De-normalization of ^{14}C data and use of radiocarbon calibration in hydrological investigations	138
Appendix C. Step by step guide to selecting appropriate model(s) for the groundwater system	138
References	138

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, $^{14}\text{C}_{\text{DIC}}$, 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), $^{14}\text{C}_0$:

$$t = -\frac{5730}{\ln 2} \ln \left(\frac{^{14}\text{C}_{\text{DIC}}}{^{14}\text{C}_0} \right) = -\frac{1}{\lambda_{14}} \ln \left(\frac{^{14}\text{C}_{\text{DIC}}}{^{14}\text{C}_0} \right). \quad (1)$$

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

The essential step in dating DIC is the estimation of $^{14}\text{C}_0$. Because DIC in groundwater is a mixture of carbon from different sources, estimation of $^{14}\text{C}_0$ 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 pedogenic 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 $^{14}\text{C}_0$. The single-sample-based models rely on mass balances of major

carbon species or carbon isotopes (^{14}C and ^{13}C) of DIC in water (Ingerson and Pearson, 1964; Tamers, 1967; Pearson and Hanshaw, 1970; Mook, 1972; Tamers, 1975; Wigley, 1976; Mook, 1976; Fontes and Garnier, 1979; Evans et al., 1978; Salem et al., 1980; Eichinger, 1983; Fontes, 1983; Geyh, 2000). However, there has been little guidance as to which of these models are best suited for application to prevailing hydrochemical conditions, if any. Indiscriminate application of these models to chemical and isotopic measurements in groundwater can result in large uncertainties in age estimates. Determination of the most appropriate model to use in a given system can be uncertain (Małoszewski and Zuber, 1991; Clark et al., 1997; Hinsby et al., 2002; Witczak et al., 2008; Aeschbach-Hertig et al., 2002). Małoszewski and Zuber (1991) pointed out that due to diffusion and exchange reaction in a dual-porosity fissured rock, the groundwater radiocarbon ages in carbonate formations are evidently too great and not explainable by models for the initial ^{14}C corrections. Aeschbach-Hertig et al. (2002) found that the correction models cannot explain the unexpectedly low ^{14}C values in some of the samples, where $\delta^{13}\text{C}$ and HCO_3^- values are approximately constant. Clark et al. (1997) found that it is difficult to isolate the radioactive decay signal, especially if the observed ^{14}C content is of the order of 1 pMC (percent of modern carbon), for waters that have undergone strong water–rock interaction.

In groundwater systems where a curved ^{14}C vs. $\delta^{13}\text{C}$ relationship exists, the Gonfiantini & Zuppi model (Gonfiantini and Zuppi, 2003; Han and Plummer, 2013) can be used to estimate groundwater radiocarbon ages and to describe the aquifer-specific value of λ_{13} , the apparent first-order rate constant for reactions occurring in the aquifer. The Gonfiantini & Zuppi model does not consider individual samples but instead obtains a statistical correlation between ^{14}C and ^{13}C data from the aquifer. Radiocarbon age is then estimated from the rate of change of $\delta^{13}\text{C}$. Where isotopic data for carbon sources are limited and/or reaction details are insufficient for construction of detailed adjustment models, the extended Gonfiantini & Zuppi model (Han and Plummer, 2013) can provide a useful approach to radiocarbon dating of DIC in aquifers. The main limitation of this model is that it cannot be used for ^{14}C age estimation if the ^{14}C and $\delta^{13}\text{C}$ data in the aquifer do not show a curved relationship.

In addition to the single-sample-based models and the statistical approach based on the observed (curved) relationship between ^{14}C and $\delta^{13}\text{C}$ data in the aquifer, other approaches, termed ‘extended geochemical mass balance approaches’, such as that implemented in NETPATH, have also been developed (Plummer, 1977; Wigley et al., 1978, 1979; Plummer et al., 1983, 1994; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; El-Kadi et al., 2011; Blaser et al., 2010). The ‘extended geochemical mass balance approaches’ typically apply single-sample-based models to the recharge zone or an initial point along a flow path to estimate the pre-nuclear-detonation ^{14}C content, and then apply geochemical modeling methods to evolve the ^{14}C geochemically (without decay) to a sample downgradient in the aquifer. These methods consider a large number of geochemical and isotopic processes/effects in aquifers that are not considered by the single-sample-based models, including an accounting for total dissolved carbon, TDC, (i.e., $\text{TDC} = \text{DIC} + \text{DOC} + \text{CH}_4$, where DOC is dissolved organic carbon and CH_4 is dissolved methane). Therefore, ‘extended geochemical mass balance approaches’ provide the most complete analysis of potential models and are capable of generating the most accurate estimates of $^{14}\text{C}_0$. Although the ‘extended geochemical mass-balance approach’ may provide a better understanding of the systems under investigation than that provided by the single-sample-based models, or the extended Gonfiantini & Zuppi model, some of the necessary chemical, mineralogical and isotopic data may not be available or can be uncertain.

Each model/approach is based on a set of assumptions regarding chemical reactions and isotopic fractionation that may occur during the evolution of the carbon isotopic composition of the DIC and affect the value of $^{14}\text{C}_0$ (Table 1).

The chemical and isotopic evolution of carbonate groundwater can be represented by varying extents of two limiting conditions: (1) chemical

and isotope exchange equilibrium between the soil gas CO_2 and the DIC in water, termed “open”, and (2) reaction of carbonate minerals (typically calcite and dolomite) with water that was initially in contact with a soil gas CO_2 reservoir, but which was isolated from the soil-gas CO_2 before carbonate dissolution, termed “closed”. Typically, the chemical and isotopic evolution of groundwater occurs between these two extreme cases, that is, an open system becomes closed to soil gas CO_2 before the DIC in water is fully equilibrated with the soil gas CO_2 and carbonate rock (Clark and Fritz, 1997; Gillon et al., 2009). These limiting and intermediate conditions have been considered in the development of the single-sample-based models.

The single-sample-based models have been discussed in detail in the literature (Fontes and Garnier, 1979; Fontes, 1983, 1992; Plummer et al., 1994; Kalin, 1999; Zhu and Murphy, 2000; Geyh, 2000, 2005; and Plummer and Glynn, 2013). In other studies, different models have been applied and compared by using data from specific groundwater systems (e.g. Fontes and Garnier, 1979; Eichinger, 1983; Hackley et al., 1992; Salle et al., 1996; Gallagher et al., 2000; Plummer and Sprinkle, 2001; Chen et al., 2003). In contrast to previous studies which focus mainly on (1) carbonate reactions, (2) estimation of $^{14}\text{C}_0$, and (3) estimation of groundwater ages using ^{14}C as a single indicator, recent studies (1) investigate other geochemical/physical processes to improve understanding of the processes occurring in the system and their effects on $^{14}\text{C}_0$ (e.g. Bishop et al., 1994; Clark et al., 1996; Boaretto et al., 2006; Coetsiers and Walraevens, 2009; Gillon et al., 2009; Blaser et al., 2010; Bates et al., 2011), (2) estimate the ^{14}C decrease rate affected by geochemical/physical processes and calculate groundwater age by using a statistical approach (Gonfiantini and Zuppi, 2003; Han et al., 2014), and (3) use combined chemical, isotope, and noble gas data to derive groundwater ages (e.g. Zuber et al., 2004; Carey et al., 2004; Edmunds et al., 2006; Kwicklis and Farnham, 2014). Recently, Han et al. (2012) suggested using a graphical method to recognize processes that may occur in groundwater systems that affect $^{14}\text{C}_0$ of DIC in the water sample. The use of graphs combined with measured values of ^{14}C , $\delta^{13}\text{C}$ and DIC in groundwater samples can aid in the evaluation of geochemical data. This evaluation leads to improved understanding of the processes occurring in the system and their effects on $^{14}\text{C}_0$. Ultimately, in conjunction with appropriate models, the graphical evaluation method can improve the estimation of radiocarbon age. When insufficient chemical and isotopic data limit successful application of the geochemical mass-balance method, the graphical method is used to review and analyze the single-sample-based models and the statistically-based approach of Gonfiantini and Zuppi (2003), to improve understanding of which models are most appropriate for the groundwater system.

2. Evolution of carbon isotopic composition in groundwater

In this section we discuss the geochemical processes that affect the carbon isotopic composition in groundwater, in the absence of ^{14}C decay. The parameters and notation used are described in Table 2.

‘Groundwater age’ refers to the number of years that have elapsed since the water sample was isolated from the atmosphere, i.e. time since recharge (IAEA, 2006). If the ^{14}C content of the DIC in the aquifer were only a function of radioactive decay, ^{14}C dating of DIC in groundwater would be a simple application of the ^{14}C decay equation. However, we encounter two main problems in ^{14}C dating of DIC in groundwater: (1) we have to know the amount of ^{14}C at the time of recharge (not to confuse with $^{14}\text{C}_0$ in Eq. (1)), and (2) we have to know the rate of ^{14}C decrease (not to confuse with ^{14}C decay constant λ_{14} in Eq. (1)). In other words, we have to (1) set the ^{14}C clock initially, and (2) make corrections to the ^{14}C clock speed. The ^{14}C content of DIC may change as a result of geochemical processes even without radioactive decay. These processes may occur before the start of the ^{14}C clock (i.e. under open-system conditions), which will change the ^{14}C content of DIC and will affect the initial clock setting. Geochemical processes

Table 1
Summary of radiocarbon adjustment models.

Single-sample-based models	Description
Vogel, Vogel and Ehhalt (Vogel, 1967, 1970; Vogel and Ehhalt, 1963; Geyh, 2000)	Empirical; based on assumptions. For process of carbon exchange between DIC and soil CO ₂ under specific geological settings. Under these settings the extent of exchange is assumed to be similar for all the waters.
Tamers (Tamers, 1967, 1975; Tamers and Scharpenseel, 1970)	Chemistry based; two-pool carbon atom mixing. For simple process of dissolution of carbonate by dissolved soil CO ₂ . The two mixing end members (with mixing ratio of 1:1) are (1) dissolved soil CO ₂ and (2) solid carbonate. This model assumes that 50% of the DIC is from solid carbonates and the other 50% is from soil CO ₂ .
Pearson (Ingerson and Pearson, 1964; Pearson and White, 1967; Pearson and Hanshaw, 1970; Pearson et al., 1972; Pearson and Swarzenki, 1974)	Isotope based; two-pool carbon isotope mixing. Similar to Tamers' model. The differences to Tamers' model are that (1) in this model two carbon-isotope sources, instead of two carbon-atom sources, are mixed, (2) this model can be used for carbon mixing in any ratio.
Mook (Mook, 1972, 1976, 1980)	Chemistry and isotope based; mixing and exchange. For the process of dissolution of carbonate by dissolved soil CO ₂ followed by carbon exchange between DIC and soil CO ₂ under open-system conditions. This is an extended model of Vogel that can be used for any extent of exchange.
Wigley (Wigley, 1976)	Isotope based; mixing; exchange. For carbon exchange between DIC and solid carbonate under closed-system conditions. Processes that affect the carbon isotopic composition of DIC before the system becomes closed to soil CO ₂ are not considered.
Evans (Evans et al., 1978)	
Eichinger (Eichinger, 1983)	
Fontes & Garnier (Fontes et al., 1978; Fontes and Garnier, 1979)	Chemistry and isotope based; mixing and exchange. For the process of dissolution of carbonate by dissolved soil CO ₂ followed by (1) carbon exchange between DIC and soil CO ₂ under open-system conditions or (2) carbon exchange between DIC and solid carbonate under closed-system conditions. Han & Plummer is a revised version of Fontes & Garnier that avoids underestimation of ¹⁴ C ₀ .
Han & Plummer (Han and Plummer, 2013)	
IAEA (Gonfiantini, 1972; Salem et al., 1980)	Isotope based; two-pool isotope mixing. Mixing end member A: DIC that was in equilibrium with soil CO ₂ before the system became closed to soil CO ₂ . Mixing end member B: DIC that was in equilibrium with solid carbonate.
Oeschger (Geyh, 2000)	Chemistry based; two-pool DIC mixing. For dilution of ¹⁴ C _{DIC} by additional ¹⁴ C-free DIC under closed-system conditions.
Cheng (Cheng, 1992)	Chemistry based; two-pool DIC mixing. For dilution of ¹⁴ C _{DIC} by additional ¹⁴ C-free DIC under closed-system conditions. This model assumes that the system had undergone carbon exchange with soil CO ₂ before being closed to soil CO ₂ .
Statistically-based models	Description
Gonfiantini & Zuppi (Gonfiantini and Zuppi, 2003)	Isotope based; exchange; exchange rate and statistics based. For carbon exchange between DIC and solid carbonate under closed-system conditions.
Extended G & Z (Han et al., 2014)	Isotope based; process rate and statistics based. For geochemical reactions that affect the carbon isotopic composition and can be represented by apparent first-order processes.
Geochemical mass-balance models	Description
Wigley et al., 1978, 1979; Plummer et al., 1983, 1990, 1994; Plummer and Sprinkle, 2001; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; Blaser et al., 2010; El-Kadi et al., 2011	Pairs of initial and final (evolved) water compositions are selected from the aquifer. A set of chemical, electron-transfer and isotope mass-balance equations is solved to calculate the amounts of minerals and gases that must dissolve or precipitate (de-gas) along the flow path to account for the observed chemical and isotopic composition at the end of the flow path. The ¹⁴ C content of DIC recharged to the aquifer is adjusted for geochemical reactions accounting for isotope dilution, isotope exchange, oxidation of DOC and isotope-fractionating processes, without radioactive decay. Reaction models (and modeled radiocarbon age) can be eliminated in cases in which the modeled $\delta^{13}\text{C}$ of DIC differs from the measured beyond the uncertainty of the data. For those models that cannot be eliminated, the adjusted radiocarbon age is calculated from the modeled ¹⁴ C ₀ using Eq. (1).

also can occur after the start of the ¹⁴C clock (i.e. under closed-system conditions), which will change the ¹⁴C content of DIC as ¹⁴C is decaying and will affect the apparent clock speed. Because it is usually difficult to estimate rate of change of ¹⁴C decrease due to geochemical processes, in Eq. (1) we assume that the decrease rate constant of ¹⁴C is λ_{14} (i.e. ¹⁴C decreases with a half-life of 5730 years in the groundwater system), and adjust all the geochemical effects on the initial ¹⁴C clock setting and ¹⁴C clock speed by using an adjusted 'initial' ¹⁴C value (¹⁴C₀).

Adjustment of the 'initial' ¹⁴C value is analogous to the problem of determination of elapsed time from an inaccurate clock. In the morning, we set the initial time correctly to eight o'clock when we start our working day (this is similar to 'estimation of the initial ¹⁴C content at the time of recharge'). At the end of our working day, our inaccurate clock reads seventeen o'clock. Then, knowing that our clock runs too fast (this is comparable to understanding the effect of dilution of ¹⁴C by dead carbon during the residence time that causes the ¹⁴C content to decrease faster than natural ¹⁴C decay), we determine, for example, by comparing our

clock with a correct one that our clock gains one hour in every eight hours (i.e. we have worked out an adjustment model for our clock, analogous to determination of an appropriate geochemical adjustment model in ¹⁴C dating). To estimate our actual working hours, we apply our adjustment model by calculating the elapsed time since nine o'clock instead of eight o'clock in the morning (i.e. we adjust the initial value by using our model so as to use the correct clock speed). So having adjusted the initial reading of our clock, we determine that the elapsed time since we began work that day is eight hours. Had we not corrected the initial clock reading, the uncorrected elapsed time (analogous to the uncorrected radiocarbon age) would be biased greater than the actual elapsed time, by one hour, in this example (analogous to the unadjusted radiocarbon age that typically is biased old).

The geochemical processes which affect the initial clock setting and the apparent clock speed may involve not only soil CO₂, but also CO₂ derived from fossil organic substances (Aravena et al., 1995; Hackley et al., 1992; Han et al., 2012; Pearson and Hanshaw, 1970; Plummer, 1977),

Table 2
Description of parameters and notation used.^a

Parameter	Description	Unit	Determination/calculation ^b
C_T	Total concentration of dissolved inorganic carbon ($C_a + C_b$) (see Appendix A)	mol/kg	C_T often is calculated in an aqueous speciation model by using the measured alkalinity and pH (e.g. Parkhurst and Appelo, 2013)
C_b	Concentration of HCO_3^-	mol/kg	C_b can be determined e.g. by acid titration
C_a	Concentration of $\text{CO}_{2(aq)}$	mol/kg	$C_a = C_T - C_b$
$^{14}\text{C}_{\text{DIC}}, \delta^{13}\text{C}_{\text{DIC}}$	Carbon isotopic composition determined from the sample	pMC, ‰	The values typically are measured.
$^{14}\text{C}_0, \delta^{13}\text{C}_0$	Initial carbon isotopic composition of DIC adjusted for geochemical reactions without decay.	pMC, ‰	$^{14}\text{C}_0$ and $\delta^{13}\text{C}_0$ are deduced from geochemical reactions by using different models. $^{14}\text{C}_0$ is calculated without considering ^{14}C decay.
$^{14}\text{C}_g, \delta^{13}\text{C}_g$	Carbon isotopic composition of soil gas CO_2 (Point A in Fig. 1)	pMC, ‰	In most cases $^{14}\text{C}_g$ can be assumed to be 100 pMC; $\delta^{13}\text{C}_g$ to be -26‰ (for C_3 plants) and -10 to -15‰ (for C_4 plants).
$^{14}\text{C}_{a1}, \delta^{13}\text{C}_{a1}$	Carbon isotopic composition of dissolved soil CO_2 in equilibrium with soil gas CO_2 (Point A1 in Fig. 1).	pMC, ‰	$^{14}\text{C}_{a1} = ^{14}\text{C}_g + 0.2\epsilon_{a/g} \approx 100$ pMC. $\delta^{13}\text{C}_{a1} = \delta^{13}\text{C}_g + \epsilon_{a/g}$
$^{14}\text{C}_s, \delta^{13}\text{C}_s$	Carbon isotopic composition of solid carbonate minerals. (Point M in Fig. 1).	pMC, ‰	For old marine carbonate, $^{14}\text{C}_s$ can be assumed to be 0 pMC; $\delta^{13}\text{C}_s$ to be 0.0 to $+2.5\text{‰}$.
$^{14}\text{C}_{a2}, \delta^{13}\text{C}_{a2}$	Carbon isotopic composition of HCO_3^- at Mook's point (Point A2 in Fig. 1).	pMC, ‰	$\delta^{13}\text{C}_{a2} = \delta^{13}\text{C}_g - \epsilon_{g/b}$ $^{14}\text{C}_{a2} = ^{14}\text{C}_g - 0.2\epsilon_{g/b} \approx ^{14}\text{C}_g$
$^{14}\text{C}_i, \delta^{13}\text{C}_i$	'Primary' carbon isotopic composition of DIC (usually at Tamers' point, Point O in Fig. 1).	pMC, ‰	$^{14}\text{C}_i \approx 0.5(^{14}\text{C}_{a1} + ^{14}\text{C}_s)$ $\delta^{13}\text{C}_i \approx 0.5(\delta^{13}\text{C}_{a1} + \delta^{13}\text{C}_s)$
$^{14}\text{C}_T, \delta^{13}\text{C}_T$	Carbon isotopic composition of DIC ($\text{CO}_{2(aq)}$ and HCO_3^-).	pMC, ‰	$^{14}\text{C}_T$ and $\delta^{13}\text{C}_T$ are deduced from geochemical reactions without considering ^{14}C decay.
$\delta^{13}\text{C}_E$	$\delta^{13}\text{C}$ value of DIC ($\text{CO}_{2(aq)}$ and HCO_3^-) in equilibrium with solid carbonate (Eichinger's Point, Point M" in Fig. 1).	‰	See Eqs. (36) and (37).
$\epsilon_{a/g}$	^{13}C fractionation factor of dissolved CO_2 with respect to gaseous CO_2 .	‰	$\epsilon_{a/g} = -373/T + 0.19$ ($\epsilon_{a/g} = -1.13\text{‰}$ at 10°C)
$\epsilon_{g/s}$	^{13}C fractionation factor of gaseous CO_2 with respect to solid carbonate mineral.	‰	$\epsilon_{g/s} = -5380/T + 9.15$ ($\epsilon_{g/s} = -9.85\text{‰}$ at 10°C)
$\epsilon_{g/b}$	^{13}C fractionation factor of gaseous CO_2 with respect to HCO_3^- .	‰	$\epsilon_{g/b} = -9483/T + 23.89$ ($\epsilon_{g/b} = -9.60\text{‰}$ at 10°C)
$\epsilon_{s/a}$	^{13}C fractionation factor of carbonate mineral with respect to dissolved CO_2 ($= \text{CO}_{2(aq)}$).	‰	$\epsilon_{s/a}$ is used only for derivation of Eq. (21)
$\epsilon_{s/b}$	^{13}C fractionation factor of carbonate mineral with respect to HCO_3^- .	‰	$\epsilon_{s/b} = -4232/T + 15.1$ ($\epsilon_{s/b} = +0.15\text{‰}$ at 10°C)

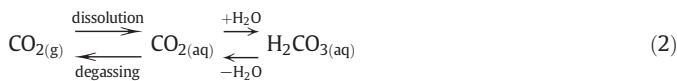
^a Units: mol/kg, moles per kilogram of water; pMC, percent of modern carbon; ‰, percent; ‰, per mil; T, temperature in degrees Kelvin; C, temperature in degrees Celsius. Isotopic values and the selected temperature are for example purposes. In application, the relationships should be constructed for conditions representative of the system under study. For discussion of unit pMC see Appendix B.

^b The equations for calculation of $\epsilon_{a/g}$, $\epsilon_{g/s}$, $\epsilon_{g/b}$, and $\epsilon_{s/b}$ are from Thode et al. (1965); Robinson and Clayton (1969); Emrich et al. (1970); Vogel et al. (1970); Mook et al. (1974); Mook (2000, 2006). $\epsilon_{i/j}$ ($=\delta_i - \delta_j$ at isotopic equilibrium) is the so-called "additive fractionation factor" commonly used in radiocarbon adjustment models. $\epsilon_{i/j}$ is related approximately to the equilibrium isotope fractionation factor, $\alpha_{i/j}$, by the relation $\epsilon_{i/j} \sim 10^3 \ln(\alpha_{i/j} - 1)$. $\epsilon_{i/j} = -\epsilon_{j/i}$ (e.g. $\epsilon_{g/s} = -\epsilon_{s/g}$). $\epsilon_{i/j}$ is approximately additive, for example, $\epsilon_{a/s} \sim \epsilon_{a/g} + \epsilon_{g/b} + \epsilon_{b/s}$. Thus, at 10°C , $\epsilon_{a/s} \sim -1.13 - 9.60 - 0.15 = -10.88\text{‰}$. Formally, $\alpha_{a/s} \equiv \alpha_{a/g}\alpha_{g/b}\alpha_{b/s}$.

and CO_2 of magmatic origin (Crossey et al., 2009; James et al., 1999; Lesniak, 1985; Yamada et al., 2010). In addition to CO_2 , the geochemical processes may involve carbonate from different sources. However, in most situations the evolution of carbon isotopic composition in ground-water involves four basic steps: (1) dissolution of soil gas CO_2 in water; (2) water–rock interaction (bicarbonate formation); (3) water–soil gas interaction (isotope exchange under open-system conditions); and (4) water–rock interaction (isotope exchange under closed-system conditions).

2.1. Dissolution of soil gas CO_2 in water

CO_2 is soluble in water:



where $\text{CO}_{2(g)}$ is the gaseous soil CO_2 and $\text{CO}_{2(aq)}$ is the dissolved CO_2 in water. The subscript g and aq represent gaseous, and dissolved states, respectively. (see Appendix A).

The carbon isotopic composition of $\text{CO}_{2(aq)}$ can be calculated as

$$\delta^{13}\text{C}_{a1} = \delta^{13}\text{C}_g + \epsilon_{a/g} \quad (3)$$

$$^{14}\text{C}_{a1} = ^{14}\text{C}_g + 0.2\epsilon_{a/g}. \quad (4)$$

Because $\epsilon_{a/g}$ represents the end (aqueous) state with respect to the initial (gaseous) state (Eq. (2)), the '+' sign is applied in Eqs. (3) and (4) before $\epsilon_{a/g}$. If the '−' sign is used, the value of $\epsilon_{g/a}$ has to be applied

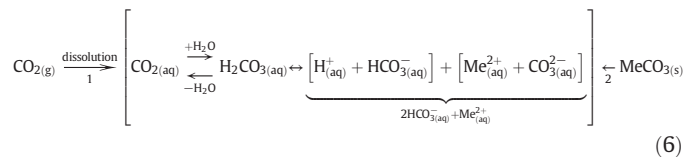
(the gaseous state with respect to the aqueous state, i.e., $\epsilon_{a/g} = -\epsilon_{g/a}$). In Eq. (4) the term $0.2\epsilon_{a/g}$ is used since isotope fractionation is approximately proportional to mass difference (Craig, 1954), i.e. the mass difference between ^{14}C and ^{12}C is about twice the mass difference between ^{13}C and ^{12}C . Because $0.2\epsilon_{a/g} < ^{14}\text{C}_g$,

$$^{14}\text{C}_{a1} \approx ^{14}\text{C}_g. \quad (5)$$

The carbon isotopic composition of $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$ are represented by points A and A1 (Eqs. (3) and (4)) in Fig. 1 (Han and Plummer plot), respectively. The reversible exchange of $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$ (Process (2)) is represented in Fig. 1 by the left–right arrow, A–A1.

2.2. Water–rock interaction (bicarbonate formation)

Because soils can contain carbonate minerals, the carbonic acid (H_2CO_3) produced in Reaction (2) can react with carbonate. During the reaction bicarbonate (HCO_3^-) is formed:



where Me is generally Ca or Mg. The subscript s represents solid state.

Assuming that sub-reactions 1 and 2 in Process (6) are irreversible (e.g. if the amount of $\text{CO}_{2(g)}$ taking part in the reactions is finite, and the dissolved carbonate does not re-precipitate), the reaction products

With increasing extent of reaction, increasing amounts of DIC ($\text{CO}_{2(\text{aq})} + \text{HCO}_3^-$) will exchange with solid carbonate. Consequently, the carbon isotopic composition of HCO_3^- changes from point O towards M' (arrow not drawn in Fig. 1). The carbon isotopic composition of the DIC changes along the direction indicated by arrow O–M". If the reaction extent is large, all the DIC will be in equilibrium with the solid carbonate. Similar to Eqs. (14) and (15), at equilibrium, the carbon isotopic composition of the DIC is (without ^{14}C decay)

$$\delta^{13}\text{C}_0 = \left(\frac{C_a}{C_T}\right)(\delta^{13}\text{C}_s - \varepsilon_{s/a}) + \left(\frac{C_b}{C_T}\right)(\delta^{13}\text{C}_s - \varepsilon_{s/b}) \quad (17)$$

$$^{14}\text{C}_0 = \left(\frac{C_a}{C_T}\right)(^{14}\text{C}_s - 0.2\varepsilon_{s/a}) + \left(\frac{C_b}{C_T}\right)(^{14}\text{C}_s - 0.2\varepsilon_{s/b}). \quad (18)$$

The values of Eqs. (17) and (18) are represented in Fig. 1 by point M".

In natural water systems, different combinations of the above evolutionary stages may occur to varying extents. Commonly, in soils containing solid carbonate, an infiltrating water reacts first with carbonate to form DIC ($\text{CO}_{2(\text{aq})}$ and HCO_3^-) (point O). During infiltration, the DIC in water exchanges carbon atoms with soil CO_2 (Process (11), arrow O–A3). If the DIC is equilibrated with soil CO_2 before the system becomes closed, further evolution will start from point A3 (For example the dashed line arrow A3–M" in Fig. 1 represents Process (16) that occurs in the aquifer after the system becomes closed to soil CO_2). On the other hand, if the DIC is not equilibrated with soil CO_2 before the system becomes closed, further evolution will start from a point on line O–A3 (e.g. Process (16), short-dashed-line arrow B–M"). A water system may evolve via only Process (2) (arrow A–A1 in Fig. 1), if no carbonate reacts (e.g. in silicate aquifers, or in cases where the water moves quickly into the groundwater system, also see Gillon et al., 2009). A water system may also evolve via Process (2) followed by Process (6) (arrow A–A1 and A1–O in Fig. 1) without Process (11), if the system becomes closed shortly after Process (6) (fast infiltration), and Process (16) may not occur under specific conditions (e.g. silicate aquifers). These combinations are discussed below as they relate to specific single-sample-based correction models.

3. Existing single-sample-based correction models

The models discussed in this section are presented using the symbols listed in Table 2. For simplicity and example purposes, the ^{14}C and $\delta^{13}\text{C}$ values of the soil CO_2 and carbonate mineral are assumed to be: $^{14}\text{C}_g = 100$ pMC and $\delta^{13}\text{C}_g = -26\text{‰}$ for $\text{CO}_{2(\text{g})}$; $^{14}\text{C}_s = 0$ pMC and $\delta^{13}\text{C}_s = 0\text{‰}$ for solid carbonate mineral. In reality, these values can change over time and space. The correctness of the ^{14}C age estimation thus not only depends on the correct use of the model but also depends on the estimated ^{14}C and $\delta^{13}\text{C}$ values of the soil CO_2 and carbonate mineral (see Appendix B; Wood et al., 2014).

3.1. Empirical approach

This approach, proposed by Vogel (Vogel, 1967, 1970; Vogel and Ehhlalt, 1963), uses an assumed value for $^{14}\text{C}_0$:

$$^{14}\text{C}_0 = B \quad (19)$$

where $B \approx 85$ pMC. The value of 85 pMC is typical for cases in which groundwater has evolved predominantly under open-system conditions.

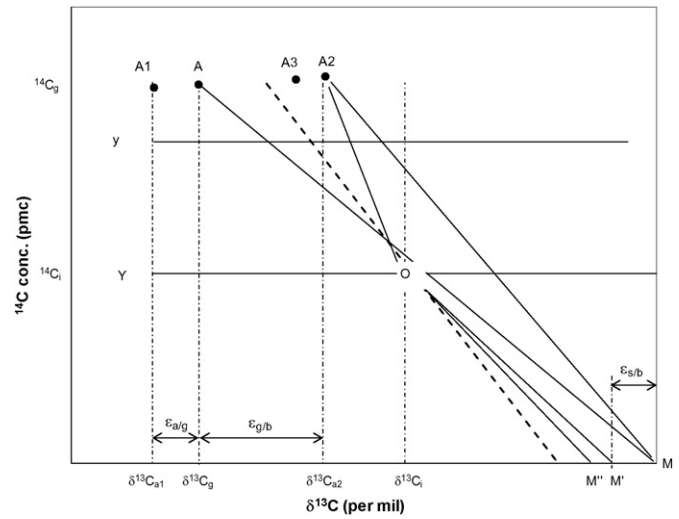


Fig. 2. The single-sample-based models for calculation of $^{14}\text{C}_0$ can be represented in the relationship of $^{14}\text{C}_{\text{DIC}}$ vs. $\delta^{13}\text{C}_{\text{DIC}}$ which can be described by a general linear equation (see Eq. (20)). The symbols are the same as in Fig. 1.

Vogel's model (assumption), Eq. (19), is represented on Fig. 2 by the line (line y) as

$$^{14}\text{C}_0 = A\delta^{13}\text{C}_{\text{DIC}} + B \quad (20)$$

where A and B are constants:

$$A = 0.$$

$$B = 85 \text{ (pMC)}.$$

In addition to $B = 85$ pMC, some alternative empirical values, more applicable to the $^{14}\text{C}_0$ values of DIC in spring water from specific geological settings, were calculated by Geyh (2000) (e.g. 55–65 pMC for uncovered karst; 90–100 pMC for crystalline rocks). It can be seen in Fig. 2 that Vogel's model is a specific case of other models because the 'Vogel's line', y, intercepts three other model lines in different ranges of $\delta^{13}\text{C}$ values.

This model is an empirical model (assumption) and has no underlying concept (Mook, 1976).

3.2. Simple mixing models

The simple mixing models consider $^{14}\text{C}_0$ to be a result of mixing of two carbon-bearing reservoirs. The two most commonly used simple mixing models are Tamers' and Pearson's models.

3.2.1. Tamers' model

Tamers' model (Tamers, 1967, 1975; Tamers and Scharpenseel, 1970) estimates $^{14}\text{C}_0$ based on a 'carbon chemical balance'. Tamers' model considers $^{14}\text{C}_0$ to be a result of Process (6). According to Tamers' model the DIC in water is a two-component mixture ($\text{CO}_{2(\text{aq})}$ and HCO_3^-), with one of the components, HCO_3^- , resulted from 1:1 mixing of two carbon-bearing reservoirs ($\text{CO}_{2(\text{g})}$ and $\text{MeCO}_3(\text{s})$). Thus, the ^{14}C value of the two component mixture can be expressed as (combining Eqs. (4) and (8), and neglecting $\varepsilon_{a/g}$):

$$^{14}\text{C}_0 = \frac{C_a}{C_T} ^{14}\text{C}_g + 0.5 \frac{C_b}{C_T} (^{14}\text{C}_g + ^{14}\text{C}_s) \quad (21)$$

Eq. (21) is an approximation of Eq. (8) and represents the mass balance of Process (6), neglecting the ^{14}C change caused by conversion of $\text{CO}_{2(\text{g})}$ to $\text{CO}_{2(\text{aq})}$ ($0.2\varepsilon_{a/g} \sim 0$, see Eq. (4)). More precisely, taking into account the contribution of dissolved CO_2 ($\text{CO}_{2(\text{aq})}$), Tamers' model can be

represented by

$$^{14}C_0 = ^{14}C_i = \left(\frac{C_a}{C_T}\right)^{14}C_{a1} + 0.5\left(\frac{C_b}{C_T}\right)^{14}C_{a1} + 0.5\left(\frac{C_b}{C_T}\right)^{14}C_s. \quad (22)$$

Similarly, the corresponding $\delta^{13}C$ value of the DIC is

$$\delta^{13}C_0 = \delta^{13}C_i = \left(\frac{C_a}{C_T}\right)\delta^{13}C_{a1} + 0.5\left(\frac{C_b}{C_T}\right)\delta^{13}C_{a1} + 0.5\left(\frac{C_b}{C_T}\right)\delta^{13}C_s, \quad (23)$$

where $^{14}C_i$ and $\delta^{13}C_i$ are identical to $^{14}C_0$ and $\delta^{13}C_0$ of the DIC in Tamers' model.

For a system containing only dissolved soil CO_2 , i.e. for a water system that has not contacted solid carbonate, $C_a \gg C_b$ and $C_T \approx C_a$, thus $^{14}C_i \approx ^{14}C_{a1} \approx ^{14}C_g$ (Eq. (4)). Because the dissolution of carbonate mineral (calcite in particular) is relatively rapid (see for example, Plummer et al., 1978; Dreybrodt and Scholz, 2011), soils containing even small amounts of calcite can lead to waters becoming significantly mineralized (Wigley, 1975). For most systems closed to soil CO_2 , the predominant dissolved carbon species is HCO_3^- , with $C_a \approx 0$, $C_b \approx C_T$ and $^{14}C_s = 0$ (Appendix A). Combining Eq. (4) and neglecting $^{14}C_s$, Eq. (21) can therefore be represented by

$$^{14}C_i \approx 0.5^{14}C_g \approx 0.5^{14}C_{a1}. \quad (24)$$

This model (Eq. (24)) represents a simple binary mixing of two end members, the dissolved CO_2 , and the carbonate mineral. It assumes that 50% of the DIC is from solid carbonates and the other 50% is from soil CO_2 .

Eq. (24) can be represented by Eq. (20), with

$$\begin{aligned} A &= 0. \\ B &= \frac{C_a}{C_T}^{14}C_{a1} + 0.5\frac{C_b}{C_T}(^{14}C_{a1} + ^{14}C_s) \approx 0.5\delta^{14}C_{a1}. \end{aligned}$$

Thus, Tamers' model can be represented in Fig. 2 by line Y.

From Eq. (9), assuming $\delta^{13}C_s \approx 0$, we obtain

$$\delta^{13}C_i = 0.5(\delta^{13}C_{a1} + \delta^{13}C_s) \approx 0.5\delta^{13}C_{a1}. \quad (25)$$

According to Tamers' model, samples with $^{14}C_{DIC}$ values of approximately $0.5^{14}C_{a1}$ have zero age, while samples with $^{14}C_{DIC}$ values less than $0.5^{14}C_{a1}$ have radiocarbon age. Samples with $^{14}C_{DIC}$ values higher than $0.5^{14}C_{a1}$ are considered to be 'contaminated'. In reality, however, many geochemical processes in addition to simple binary mixing (e.g. carbon exchange with solid carbonate or soil CO_2) may produce a sample with $^{14}C_{DIC}$ values either lower or higher than $0.5^{14}C_{a1}$. As a result, a sample with a $^{14}C_{DIC}$ value higher than $0.5^{14}C_{a1}$ may have a non-zero age and vice versa.

The point O in Fig. 2, represented by Eqs. (22) and (23), is referred to as 'Tamers' point'. Tamers' point is important because it represents the end point of Process (6) in carbon isotopic evolution of DIC, simple binary mixing of soil CO_2 and carbonate solid. Many models developed later make further corrections to Tamers' model (e.g. Oeschger, Wigley, Evans, Eichinger, Mook, Fontes & Garnier and Han & Plummer. See discussions below). For this reason, in Tamers' model (Eqs. (22) and (23)) we use $^{14}C_i$ and $\delta^{13}C_i$ instead of $^{14}C_0$ and $\delta^{13}C_0$. The values of $^{14}C_i$ and $\delta^{13}C_i$ in Eqs. (22) and (23) are referred to as the 'primary carbon isotopic composition of DIC' (see Table 2).

This model can only be used in cases where water that contains dissolved soil CO_2 reacts with carbonate under closed-system conditions to form HCO_3^- , and no further processes occur that can change ^{14}C content except for ^{14}C decay. In a natural groundwater system, however, such cases are rare.

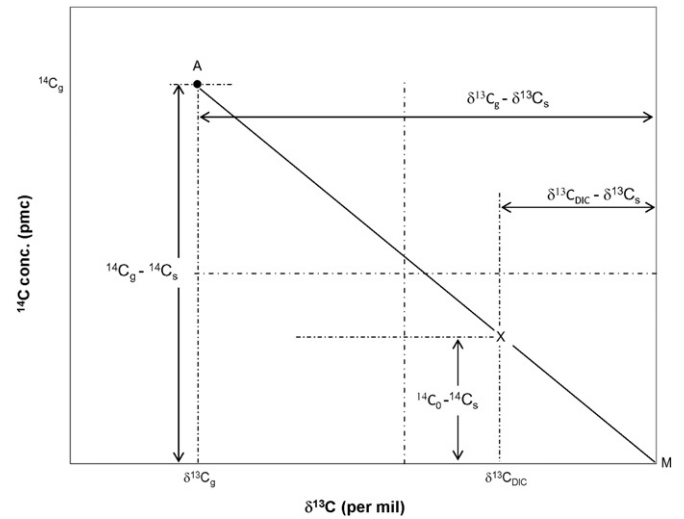


Fig. 3. Derivation of Pearson's model based on the $^{14}C_{DIC}$ vs. $\delta^{13}C_{DIC}$ relationship. Point x represents the isotopic composition of the sample.

3.2.2. Pearson's model

Pearson's model (Ingerson and Pearson, 1964; Pearson and White, 1967; Pearson and Hanshaw, 1970; Pearson et al., 1972; Pearson and Swarzenki, 1974) constructs an isotope mass balance to solve the simple mixing of soil $CO_{2(g)}$ and carbonate mineral. This model implies that the groundwater evolves chemically and isotopically by dissolution of carbonate mineral(s) under closed (to $CO_{2(g)}$ exchange) conditions while reacting with the dissolved CO_2 in the recharge water. Pearson's model neglects the dissolution of $CO_{2(g)}$ in water (namely, this model neglects the process represented by arrow A–A1 in Fig. 1). Pearson's model uses $^{14}C_g$ and $\delta^{13}C_g$ instead of $^{14}C_{a1}$ and $\delta^{13}C_{a1}$. Pearson's model can be derived by comparing the two triangles in Fig. 3: A–M– $\delta^{13}C_g$ and x–M– $\delta^{13}C_{DIC}$:

$$\frac{^{14}C_0 - ^{14}C_s}{\delta^{13}C_{DIC} - \delta^{13}C_s} = \frac{^{14}C_g - ^{14}C_s}{\delta^{13}C_g - \delta^{13}C_s}, \quad (26)$$

where $\delta^{13}C_{DIC}$ is the measured $\delta^{13}C$ value of the DIC. Eq. (26) can be rearranged to

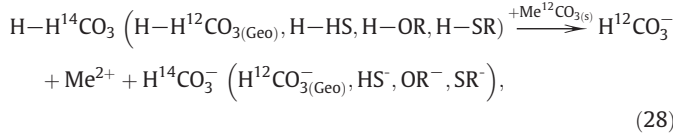
$$^{14}C_0 = \frac{^{14}C_g - ^{14}C_s}{\delta^{13}C_g - \delta^{13}C_s} (\delta^{13}C_{DIC} - \delta^{13}C_s), \quad (27)$$

Pearson's model (Eq. (27)) can be expressed in the form of Eq. (20), with

$$\begin{aligned} A &= \frac{^{14}C_g - ^{14}C_s}{\delta^{13}C_g - \delta^{13}C_s} \\ B &= -\frac{^{14}C_g - ^{14}C_s}{\delta^{13}C_g - \delta^{13}C_s} \delta^{13}C_s. \end{aligned}$$

Similar to Tamers' model, Pearson's model accounts for a simple binary mixing process under closed-system conditions. The difference between Pearson's model and Tamers' model is that Pearson's model uses two carbon-isotope sources instead of using two carbon-atom sources. While Tamers' model describes only mass balance of Process (6) and assumes that 50% of the DIC is from solid carbonates and the other 50% is from soil CO_2 , Pearson's model can be used for carbon mixing in any ratio. Of the two mixing end members, one is the initial ^{14}C -bearing soil CO_2 , (point A) and the other is the DIC produced by the dissolution of aquifer carbonates (point M).

Carbonate dissolution can be caused by cation exchange. In response to cation exchange more ^{14}C -free carbonate may dissolve (e.g. calcite dissolution accompanying Ca/Na exchange). In addition to cation exchange, the acids in water (inorganic acids e.g. $\text{CO}_{2(\text{aq})}$ from soil CO_2 , $\text{CO}_{2(\text{aq})}$ of geogenic origin, H_2S , or organic acids such as R-OH and R-SH) react with solid carbonates in the aquifer to produce HCO_3^- , e.g.



where $\text{H}_2^{12}\text{CO}_{3(\text{Geo})}$ denotes H_2CO_3 produced from geogenic CO_2 which does not contain ^{14}C . It is assumed that the solid carbonate does not contain ^{14}C (represented in the equation as $\text{Me}^{12}\text{CO}_{3(\text{s})}$).

Depending on the reactants, the reaction product, HCO_3^- , in Reaction (28) can have $^{14}\text{C}_0$ and $\delta^{13}\text{C}$ values (1) close to those of the solid carbonate (point M in Figs. 2 and 3), if the DIC is produced mainly from reactions between solid carbonates and acids that are not from soil CO_2 (i.e. without $\text{H}^{14}\text{CO}_3^-$ in Reaction (28)); (2) close to those of the soil CO_2 (point A), if solid carbonate is absent (e.g. silicate aquifer); or (3) plot at some intermediate value along Pearson's Line (line A–M, Figs. 2 and 3). In the situation where the $\text{CO}_{2(\text{aq})}$ originates only from dissolved soil CO_2 and is dominant over other acids, and solid carbonate is in excess, Pearson's model reduces to Tamers' model (i.e. ignoring the substances in the parentheses in Reaction (28)). Incongruent dissolution, leading to apparent isotope exchange between mineral and aqueous carbonate without concomitant changes in water chemistry is not included in Pearson's model. Because in Pearson's equation the carbon isotopic values of soil CO_2 are used, the straight line representing Pearson's model extrapolates to point A but not point A1 in Figs. 2 and 3.

Recharging water may contain more dissolved gas than can be explained by equilibrium solubility with the atmosphere as indicated by observations of dissolved gas concentrations in groundwater. This effect is called excess air (e.g. Herzberg and Mazor, 1979; Heaton and Vogel, 1981). The excess concentrations of various gases are often in accordance with air composition. Thus, in the absence of carbonate mineral(s) the isotopic composition of the DIC is at a point between point A and A1, i.e. the DIC is a mixture of gaseous and dissolved CO_2 (i.e. $\text{CO}_{2(\text{g})} + \text{CO}_{2(\text{aq})}$). For this reason, Pearson's model (Eq. (27)) can also be used by substituting $^{14}\text{C}_g$ and $\delta^{13}\text{C}_g$ with $^{14}\text{C}_{a1}$ and $\delta^{13}\text{C}_{a1}$. In this paper, we assume that there is no excess air in the system.

Compared to Tamers' model, the advantage of Pearson's model is that it takes into consideration the $\delta^{13}\text{C}$ data. Thus, ^{14}C dilution by additional dead carbon (e.g. carbon from fossil organic matter, magmatic CO_2 , cation exchange on clay minerals, etc.) can be recognized. The disadvantage of Pearson's model is that it considers only carbon mixing and it does not consider carbon exchange.

3.3. Simple mixing accompanied by carbon exchange

This approach assumes that the evolution of the carbon isotopic composition of the water consists of binary mixing (Processes (2) and (6)) accompanied by carbon exchange.

3.3.1. Exchange with soil CO_2 (Mook's model)

Mook (1972, 1976, 1980) proposed a model which accounts for not only carbonate dissolution caused by reaction with dissolved soil CO_2 (Process (6)), but also carbon exchange between DIC and gaseous CO_2 in the unsaturated zone (Process (11)). The equation for calculation of

the adjusted $^{14}\text{C}_0$ content is:

$$^{14}\text{C}_0 = \left[\frac{\text{C}_a}{\text{C}_T} ^{14}\text{C}_{a1} + 0.5 \frac{\text{C}_b}{\text{C}_T} (^{14}\text{C}_{a1} + ^{14}\text{C}_s) \right] + \left[^{14}\text{C}_g \left(1 - \frac{2\varepsilon_{g/b}}{1000} \right) - 0.5 (^{14}\text{C}_{a1} + ^{14}\text{C}_s) \right] \times \left\{ \frac{\delta^{13}\text{C}_{\text{DIC}} - \frac{\text{C}_a}{\text{C}_T} \delta^{13}\text{C}_{a1} - 0.5 \frac{\text{C}_b}{\text{C}_T} (\delta^{13}\text{C}_{a1} + \delta^{13}\text{C}_s)}{\delta^{13}\text{C}_g - \varepsilon_{g/b} \left(1 + \frac{\delta^{13}\text{C}_g}{1000} \right) - 0.5 (\delta^{13}\text{C}_{a1} + \delta^{13}\text{C}_s)} \right\}. \quad (29)$$

Assuming that $\text{C}_b/\text{C}_T = 1$ and $\text{C}_a/\text{C}_T = 0$, Eq. (29) can be simplified by combining Eqs. (22), (23) and the following equations

$$^{14}\text{C}_g \left(1 - \frac{2\varepsilon_{g/b}}{1000} \right) \approx ^{14}\text{C}_g - 0.2\varepsilon_{g/b} \quad (\text{assuming } ^{14}\text{C}_g = 100 \text{ pMC}) \quad (30)$$

$$\delta^{13}\text{C}_g/1000 \ll 1. \quad (31)$$

The combination gives

$$^{14}\text{C}_0 = ^{14}\text{C}_i + \left(^{14}\text{C}_g - 0.2\varepsilon_{g/b} - ^{14}\text{C}_i \right) \times \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_i}{\delta^{13}\text{C}_g - \varepsilon_{g/b} - \delta^{13}\text{C}_i} \quad (32)$$

where $^{14}\text{C}_i$ and $\delta^{13}\text{C}_i$ are the primary carbon isotopic composition of DIC (see Table 2).

Mook's model (Eq. (29)) consists of two parts. The first part is a pure closed-system model and accounts only for Process (6) under closed-system conditions (= Tamers' model, Eq. (22)). The second part of Mook's model (Eq. (29)) considers the process of carbon exchange between DIC and soil gas CO_2 in the unsaturated zone under open-system conditions. Influences of any processes after the system becomes closed are excluded. The second part of Mook's equation (Eq. (32)) is the additive correction term to Tamers' model accounting for exchange in an open system:

$$^{14}\text{C}_0 - ^{14}\text{C}_i = \left(^{14}\text{C}_g - 0.2\varepsilon_{g/b} - ^{14}\text{C}_i \right) \times \frac{\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_i}{\delta^{13}\text{C}_g - \varepsilon_{g/b} - \delta^{13}\text{C}_i}. \quad (33)$$

Assuming that carbon exchange between soil CO_2 and DIC in water does not change the chemical mass balance significantly, the

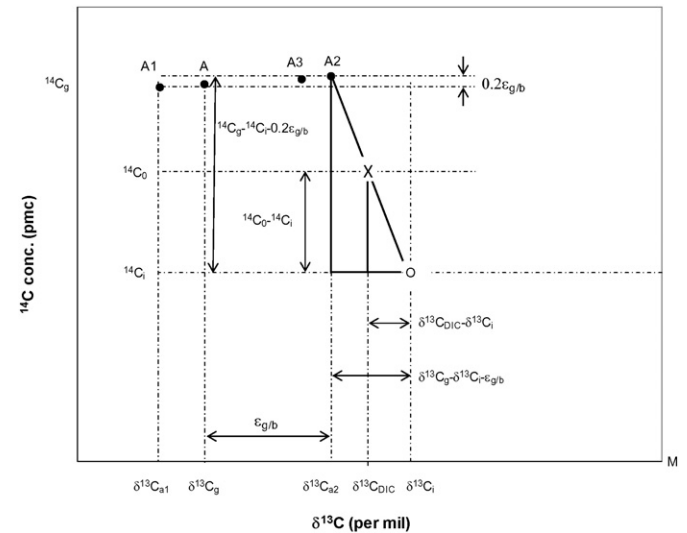


Fig. 4. Derivation of Mook's model based on a Han and Plummer plot. Mook's model makes an additive correction to Tamers' model. The additive term is $^{14}\text{C}_0 - ^{14}\text{C}_i$. Point A2 is referred to as 'Mook's point'. Point X represents the isotopic composition of the sample.

ratios C_a/C_T and C_b/C_T are determined by Process (6). Eq. (32) thus can be represented by a straight line $^{14}C_0 = A\delta^{13}C + B$ (Eq. (20)). Eq. (33) can also be derived from Fig. 4.

Thus, Eq. (32) can be represented in Fig. 2 by a straight line O–A2, referred to as “Mook’s line”, and Point A2 is referred to as “Mook’s point”.

As can be seen in Fig. 4, Mook’s model corrects $^{14}C_0$ starting from point O (Tamers’ point) towards point A2 ($\delta^{13}C_g - \epsilon_{g/b}$, $^{14}C_g - 0.2\epsilon_{g/b}$) instead of towards A3. The carbon isotopic composition of the DIC depends on the extent of the carbon exchange between DIC and CO_2 in the unsaturated zone. With increasing extent of the carbon exchange, the point representing the isotopic composition of the DIC will plot more closely to A2.

The advantage of Mook’s model is that it takes into consideration not only carbon mixing but also carbon exchange. The disadvantage of this model is that it does not account for carbon exchange that occurred in the saturated zone under closed-system conditions.

3.3.2. Exchange with solid carbonate

3.3.2.1. Wigley’s model

Wigley (1976) presented a model for correcting the effect of carbon exchange caused by closed-system incongruent dissolution (Process (16)):

$$^{14}C_0 = ^{14}C_i \times \left(\frac{\delta^{13}C_{DIC} + \epsilon_{s/b}}{\delta^{13}C_i + \epsilon_{s/b}} \right), \quad (34)$$

where $^{14}C_i$ and $\delta^{13}C_i$ are the carbon isotopic contents at the start of incongruent dissolution (i.e., at the start of closed-system conditions). The point represented by $^{14}C_i$ and $\delta^{13}C_i$ may or may not be at Tamers’ point. $\epsilon_{s/b}$ is the ^{13}C fractionation factor of carbonate mineral with respect to HCO_3^- . Wigley (1976) applied Eq. (34) to the groundwater system in the Chalk of the London Basin.

Eq. (34) can be represented by Eq. (20), with

$$A = \frac{^{14}C_i}{\delta^{13}C_i + \epsilon_{s/b}},$$

and

$$B = \frac{^{14}C_i \cdot \epsilon_{s/b}}{\delta^{13}C_i + \epsilon_{s/b}},$$

where $A < 0$ and $B < 0$. Assuming that the starting isotopic composition of the exchange process ($^{14}C_i$ and $\delta^{13}C_i$) is at point O (Tamers’ point), Eq. (34) can be represented by line O–M’ in Fig. 2.

Wigley’s model uses a multiplicative correction method, where $^{14}C_0$ is calculated by multiplying $^{14}C_i$ (the value before carbon exchange) with a correction factor obtained from $^{13}C_{DIC}$ values. Under closed-system conditions, a small amount of dissolved CO_2 contributes to DIC ($DIC \approx CO_{2(aq)} + HCO_3^-$). In Wigley’s model the contribution of $CO_{2(aq)}$ to the isotopic composition of the DIC is omitted. Hence, the value of M’ ($= \delta^{13}C_s - \epsilon_{s/b}$) in Fig. 2 differs from M’’ (Eq. (17)).

3.3.2.2. Evans’ model

Similar to Wigley’s model (Wigley, 1976), Evans et al. (1978) developed a model for correcting the effect of carbon exchange caused by incongruent dissolution:

$$^{14}C_0 = ^{14}C_i \times \left(\frac{\delta^{13}C_{DIC} + \epsilon_{s/b}}{\delta^{13}C_i + \epsilon_{s/b}} \right)^{\left(1 + \frac{\epsilon_{s/b}}{1000}\right)} \quad (35)$$

where $^{14}C_i$ and $\delta^{13}C_i$ are the carbon isotopic contents at the start of incongruent dissolution (i.e., at the start of closed-system conditions). Because the value $\epsilon_{s/b}/1000$ is very small ($\approx 10^{-4}$) at 10 °C $\epsilon_{s/b} \approx 0.15\%$

(Mook, 2000), Eq. (35) is practically identical with Eq. (34). As in Wigley’s model, the contribution of $CO_{2(aq)}$ to the isotopic composition of the DIC is omitted (Line O–M’ in Fig. 2).

3.3.2.3. Eichinger’s model

To correct for the effect of carbon exchange between the DIC and solid carbonate (Process (16)), Eichinger (1983) modified Tamers’ model by introducing a factor P to Tamers’ equation (Eq. (22), neglecting $^{14}C_s$):

$$^{14}C_0 = P \cdot \frac{(C_a + 0.5C_b)}{C_T} \cdot ^{14}C_g = P \cdot ^{14}C_i, \quad (36)$$

where

$$P = \frac{\delta^{13}C_{DIC} - \delta^{13}C_E}{\delta^{13}C_i - \delta^{13}C_E}. \quad (37)$$

$^{14}C_i$ and $\delta^{13}C_i$ are the carbon isotopic contents at the start of carbon exchange.

The term $\delta^{13}C_E$, denoted as Eichinger’s value, is the value of $\delta^{13}C$ of the DIC ($CO_{2(aq)}$ and HCO_3^-), calculated under the assumption that the groundwater is in isotopic equilibrium with the solid carbonate. The point M’’ in Figs. 1, 2, and 5 can be calculated from Eq. (17) and is denoted “Eichinger’s point”.

Eichinger’s model can be represented in Fig. 2 by line O–M’’. Fig. 5 shows the derivation of Eichinger’s model based on a Han and Plummer plot, where the model is represented by the thick straight line. Similar to Wigley’s model, Eichinger’s model corrects the initial value (often the initial value is at Tamers’ point) by multiplying by a factor. However, Eichinger’s model includes the contribution of $CO_{2(aq)}$ to the isotopic composition of the DIC.

The common advantage of the models of Wigley, Evans and Eichinger is that they consider not only carbon mixing but also carbon exchange. However, these models do not account for carbon exchange that occurred in the unsaturated zone under open-system conditions.

3.3.3. Models considering either exchange with soil CO_2 or with solid carbonate

3.3.3.1. Fontes and Garnier’s model (F & G’s model)

Fontes and Garnier (1979) proposed a model for correcting the ^{14}C for carbonate dissolution (Tamers’ model) and carbon

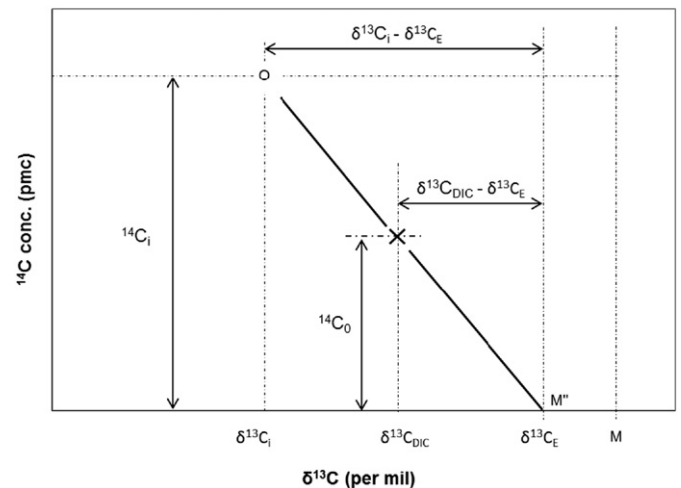


Fig. 5. Derivation of Eichinger’s model based on a Han and Plummer plot. The thick line represents the zero-age line according to Eichinger’s model. The symbol ‘X’ represents the sample from which the $^{14}C_0$ value is calculated. Point O, Tamers’ point, represents the initial carbon isotopic composition of the DIC before carbon exchange.

exchange:

$$^{14}C_0 = T + \left[\left(^{14}C_g - 0.2\epsilon_{g/s} - ^{14}C_s \right) \frac{\delta^{13}C_{DIC} - \frac{C_s}{C_T} \delta^{13}C_s - \left(1 - \frac{C_s}{C_T} \right) \delta^{13}C_g}{\delta^{13}C_g - \epsilon_{g/s} - \delta^{13}C_s} \right], \quad (38)$$

where the first part, T, is Tamers' model (Eq. (21)). C_s is the concentration of dissolved carbon coming from solid carbonate (see Reaction (2) in Process (6)). This single-enrichment factor model was initially proposed (Fontes et al., 1978; Fontes and Garnier, 1979) to account for not only carbon exchange between DIC and gaseous CO_2 under open-system conditions, but also the exchange between DIC and solid carbonate mineral under closed-system conditions.

Assuming $^{14}C_s = 0$, $\delta^{13}C_s = 0$, and $C_s/C_T = 0$, Eq. (38) can be represented by Eq. (20), with

$$A = \frac{^{14}C_g - 0.2\epsilon_{g/s}}{\delta^{13}C_g - \epsilon_{g/s}}$$

and

$$B = T - \left[\frac{0.5\delta^{13}C_g (^{14}C_g - 0.2\epsilon_{g/s})}{\delta^{13}C_g - \epsilon_{g/s}} \right].$$

Eq. (38) is represented by the dashed line in Fig. 2.

As pointed out by Han and Plummer (2013), the model of F & G has an inconsistency in conceptualization, resulting in underestimation of ^{14}C ages for groundwater systems that have undergone carbon exchange. The degree to which the ^{14}C age is underestimated increases with extent of carbon exchange. Examples show that in extreme cases, the error in calculated $^{14}C_0$ can be as high as 20 pMC.

3.3.3.2. Han & Plummer's model

Han and Plummer (2013) presented a model for correcting the ^{14}C for carbon exchange. The model has two forms, depending on whether the carbon exchange occurs predominantly in the unsaturated zone under open-system conditions, or in the saturated zone under closed-system conditions. Like Mook's model, this model consists of two parts. The first part, T, is Tamers' model (Eq. (21)). The second part is an additive correction term to Tamers' model:

$$^{14}C_0 = T + \left(^{14}C_x - ^{14}C_i - 0.2\epsilon_{x/b} \right) \times \frac{\delta^{13}C_{DIC} - \frac{C_a}{C_T} \delta^{13}C_{a1} - \frac{C_b}{C_T} \delta^{13}C_i}{\delta^{13}C_x - \delta^{13}C_i - \epsilon_{x/b}} \quad (39)$$

In situations where the carbon exchange occurs predominantly between soil CO_2 and HCO_3^- in the unsaturated zone under open-system conditions, the subscript x is replaced by g. In situations where the carbon exchange occurs predominantly between HCO_3^- and solid carbonate minerals in the saturated zone under closed-system conditions, the subscript x is replaced by s.

For situations where the exchange occurs predominantly between soil CO_2 and HCO_3^- , Eq. (39) is identical to Mook's model (Eq. (29)). Use of Eq. (39) results in two straight lines in Fig. 2: for $\delta^{13}C$ values more negative than $0.5\delta^{13}C_g$ (point O) the line is between points A2 and O (Mook's model); for $\delta^{13}C$ values less negative than $0.5\delta^{13}C_g$ the line is between points O and M' (similar to Eichinger's model).

Both of the models, Han & Plummer and Eichinger, generate the same correction for $\delta^{13}C_{DIC}$ values less negative than $0.5\delta^{13}C_g$, although, the models use different correction methods. Eichinger's model corrects $^{14}C_0$ by multiplying Tamers' value by a factor (Eq. (21), multiplicative correction). Han & Plummer's model corrects $^{14}C_0$ by subtracting a

value from Tamers' model (additive correction). Han & Plummer's model combines three models: Tamers', Mook's and Eichinger's. Therefore, Han & Plummer's model is more comprehensive than any other single-sample-based model, while correcting an error in the original model of Fontes and Garnier (1979).

The advantage of Han & Plummer's model is that it considers not only carbon mixing but also carbon exchange that occurred both in the saturated- and unsaturated zone. However, because this model does not consider changes in the concentration of DIC, it does not consider ^{14}C dilution caused by processes such as addition of dead carbon from oxidation of fossil organic matter, influx of magmatic CO_2 , or addition of DIC from dissolution of carbonate minerals accompanying Ca/Na cation exchange on clay minerals, etc.

3.4. Mixed open- and closed-systems: the IAEA model

Along the path from the recharge zone to the deeper aquifer, groundwater can experience both open- and closed-system conditions. Gonfiantini (1972) and Salem et al. (1980) presented a model, often referred to as the 'IAEA model', to account for both open- and closed-system evolution. The 'IAEA model' uses the following equation for estimating the initial ^{14}C contents:

$$^{14}C_0 = \frac{^{14}C_g \delta^{13}C_{DIC}}{\delta^{13}C_g + \epsilon_{b/g}} \times \left(1 + \frac{2\epsilon_{b/g}}{1000} \right) = \frac{100 - 0.2\epsilon_{g/b}}{\delta^{13}C_g - \epsilon_{g/b}} \delta^{13}C_{DIC}, \quad (40)$$

where $^{14}C_g$ is assumed to be 100 (pMC). $\epsilon_{b/g} = -\epsilon_{g/b}$ (Table 2).

A generalized equation of the IAEA model (Eq. (40)) can be obtained by dividing Eq. (15) by Eq. (14) (see Section 2) and ignoring the contribution of dissolved CO_2 ($CO_{2(a)}$):

$$^{14}C_0 = \frac{^{14}C_g - 0.2\epsilon_{g/b}}{\delta^{13}C_g - \epsilon_{g/b}} \delta^{13}C_{DIC}, \quad (41)$$

and represented by Eq. (20), with

$$A = \frac{^{14}C_g - 0.2\epsilon_{g/b}}{\delta^{13}C_g - \epsilon_{g/b}}$$

and

$$B = 0.$$

Thus, the generalized IAEA model (Eq. (41)) can be represented in Fig. 2 by line A2–M (compare Eqs. (12) and (13)).

Similar to Eichinger's model, the IAEA model corrects for the effect of carbon exchange between the DIC and solid carbonate. The main difference between Eichinger's model and the IAEA model is that Eichinger's model assumes groundwater evolves via Process (6) (point O, Fig. 2), followed by Process (16) under closed-system conditions. The IAEA model assumes groundwater evolves first via Process (6) (point O, Fig. 2), then via Process (11) until equilibrium is reached (point A2, an approximation of A3), followed by Process (16) under closed-system conditions (Fig. 2, line A2–M). While Eichinger's model considers the contribution of dissolved CO_2 to the DIC, the IAEA model considers only bicarbonate. Also, the IAEA model assumes that the solid carbonate has values of $^{14}C_s = 0$ and $\delta^{13}C_s = 0$ (point M in Fig. 2).

The IAEA model takes into consideration carbon exchange in the unsaturated zone. However, it is exclusively for cases where carbon exchange in the unsaturated zone has reached equilibrium under open-system conditions.

3.5. Other single-sample-based models

3.5.1. Oeschger's model

Another model was proposed in 1972 by Oeschger (Geyh, 2000) for correcting the ^{14}C affected by addition of dead carbon after the system becomes closed to soil CO_2 . For example, fossil organic matter contained in the aquifer system may be oxidized to produce CO_2 . Once formed, the CO_2 is likely to dissolve additional fossil carbonate producing ^{14}C -free HCO_3^- (see Processes (2) and (6)). The equation for estimation of $^{14}\text{C}_0$ is

$$^{14}\text{C}_0 = \frac{[\text{DIC}]_i}{[\text{DIC}]} \times ^{14}\text{C}_i, \quad (42)$$

where $[\text{DIC}]_i$ and $[\text{DIC}]$ are concentrations of the dissolved inorganic carbon before and after dilution by dead carbon, respectively. $^{14}\text{C}_i$ and $^{14}\text{C}_0$ are the ^{14}C content before and after dilution.

It can be seen that Oeschger's model corrects the dead carbon dilution effect by introducing a dilution factor of $[\text{DIC}]_i/[\text{DIC}]$ (<1). Oeschger's model only considers cases where the dilution of ^{14}C is caused by addition of dead carbon. It does not consider cases where ^{14}C dilution is caused by carbon exchange (i.e. no significant change in $[\text{DIC}]$ while ^{14}C is diluted).

Eq. (42) can be represented by Eq. (20), with

$$A = 0$$

$$B = \frac{[\text{DIC}]_i}{[\text{DIC}]} \times ^{14}\text{C}_i.$$

Oeschger's model can be represented in Fig. 2 by a horizontal line (not drawn in the figure). The value of B depends not only on the dilution factor $[\text{DIC}]_i/[\text{DIC}]$, but also on the value of $^{14}\text{C}_i$, which must be estimated. Clark and Fritz (1997) proposed a correction scheme for the factor $[\text{DIC}]_i/[\text{DIC}]$ based on the measured H_2S concentration; however, while the value of $^{14}\text{C}_i$ generally can be regarded as Tamers' value, the precise determination of $[\text{DIC}]_i/[\text{DIC}]$ is difficult in groundwater samples (Geyh, 2000). With the help of mass-transfer modeling it may be possible to estimate $[\text{DIC}]_i$ and $[\text{DIC}]$ (Plummer, 1977; Wigley et al., 1978, 1979; Plummer et al., 1983, 1994; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; El-Kadi et al., 2011; Blaser et al., 2010; Parkhurst and Appelo, 2013; Plummer and Glynn, 2013). The graphical method (Han et al., 2012) can also provide some information about changes in $[\text{DIC}]$ and carbon isotopic composition of DIC.

Oeschger's model can be used in cases where the concentration of DIC has increased in a groundwater system closed to soil CO_2 indicating that ^{14}C dilution is caused by processes such as addition of dead carbon from oxidation of fossil organic matter, influx of magmatic CO_2 , or addition of DIC from dissolution of carbonate minerals accompanying Ca/Na cation exchange on clay minerals, etc. It does not consider cases where ^{14}C dilution is caused by carbon exchange (i.e. no significant change in concentration of DIC while ^{14}C is diluted).

3.5.2. Cheng's model

Another model, proposed by Cheng (1992), accounts for the effects of both open- and closed-system dissolution of carbonate minerals. This model assumes that during infiltration the DIC in water exchanges carbon with soil CO_2 . After the system becomes isolated from the soil CO_2 reservoir the dissolved soil CO_2 reacts with limestone to produce additional HCO_3^- .

The equation of this model is

$$^{14}\text{C}_0 = Q ^{14}\text{C}_i, \quad (43)$$

where Q is a dilution factor accounting for dissolution of ^{14}C -free limestone after the system became closed. $^{14}\text{C}_i$ is the ^{14}C concentration of DIC at the point where the system became isolated from the soil CO_2 reservoir.

In simple carbonate aquifers where carbonate mineral dissolution occurs under closed-system conditions involving dissolved soil CO_2 , the change (increase) in DIC concentration between the initial water sample at the point where the system became isolated from the soil CO_2 reservoir and the final evolved closed-system water sample can be estimated by a DIC mass balance according to the reaction $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$. Therefore, approximately one-half of the increased DIC under closed-system conditions is derived from ^{14}C -free limestone and the dilution factor, Q, can be calculated based on chemical reaction stoichiometry.

Cheng's model is formally identical to Oeschger's model (see Eq. (42)). The only difference is that in Oeschger's model both of the reactants in the closed system, $\text{CO}_{2(\text{aq})}$ and carbonate, are ^{14}C -free. And in Cheng's model only the limestone is ^{14}C -free. Cheng's model is based on mass transfer and does not consider $\delta^{13}\text{C}$. Cheng's model can be represented in Fig. 2 by a horizontal line below point A3 (not drawn in the figure).

A problem of Cheng's model is apparent. Instead of using isotope species, Cheng's model uses the concentrations of the dissolved carbon species in water to account for the dilution of ^{14}C . In many cases, however, carbon exchange may occur without any changes in concentration of DIC, because the system is already at chemical equilibrium. Thus, the dilution of ^{14}C cannot be recognized without analyzing the ^{13}C data.

4. Statistically-based models

In most of the above discussed models (those that use $\delta^{13}\text{C}$ data for ^{14}C age calculations), $\delta^{13}\text{C}$ data are used to compute the 'extent' of carbon exchange between DIC and solid carbonate. Another approach to radiocarbon dating is to use $\delta^{13}\text{C}$ data calibrated to the 'rate' of the carbon exchange in the groundwater system.

In many groundwater systems the ^{14}C vs. $\delta^{13}\text{C}$ data of the DIC in water show a curved relationship (e.g. Deák, 1978; Deák et al., 1987; Dennis et al., 1997; Gonfiantini and Zuppi, 2003; Qin et al., 2005; Dulinski et al., 2013). For such systems the $\delta^{13}\text{C}$ data based on the rate of the carbon exchange can be used to estimate groundwater ages, as proposed by Gonfiantini and Zuppi (2003).

4.1. Gonfiantini & Zuppi model

Gonfiantini and Zuppi (2003) presented a model (G & Z's model) that can be used to estimate groundwater ages in cases where the ^{14}C vs. $\delta^{13}\text{C}$ data of the DIC in water show a curved relationship. Fig. 6

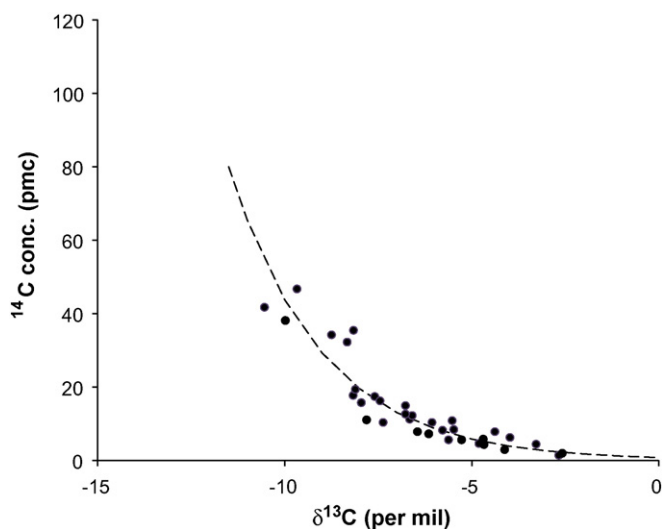


Fig. 6. The ^{14}C and $\delta^{13}\text{C}$ data show a curved relationship (dashed line). Data are from Gonfiantini and Zuppi (2003).

shows the curved ^{14}C vs. $\delta^{13}\text{C}$ relationship for DIC of the Libyan karst aquifers.

In their model Gonfiantini and Zuppi assume that the rate of carbon exchange between DIC and carbonate mineral is a first-order process and the rate constant of the process is constant with time. Because decay of ^{14}C also is a first-order process, the decrease in ^{14}C of the DIC can be represented by two simultaneous first-order processes (compare Eq. (1)):

$$t = -\frac{1}{\lambda_{14} + \lambda_{13}} \ln\left(\frac{^{14}\text{C}_{\text{DIC}}}{^{14}\text{C}_i}\right), \quad (44)$$

where λ_{13} is the carbon exchange rate constant (year^{-1}). $^{14}\text{C}_i$ is the ^{14}C value of the DIC at the start of the two processes (i.e. the ^{14}C value before decay and isotope exchange).

Under these assumptions Gonfiantini and Zuppi (2003) derived an equation from first principles which describes the curved relationship between the ^{14}C and $\delta^{13}\text{C}$ values. The equation is

$$\ln ^{14}\text{C}_{\text{DIC}} = \left(1 + \frac{\lambda_{14}}{\lambda_{13}}\right) \ln(-\delta^{13}\text{C}_{\text{DIC}} - \varepsilon_{\text{s/b}}) + \ln ^{14}\text{C}_i - \left(1 + \frac{\lambda_{14}}{\lambda_{13}}\right) \ln(-\delta^{13}\text{C}_i - \varepsilon_{\text{s/b}}), \quad (45)$$

where $^{14}\text{C}_i$ and $\delta^{13}\text{C}_i$ stand for the DIC isotopic composition at time $t = 0$, that is, when the groundwater enters the aquifer in the recharge area (the starting time of the exchange).

A plot of $\ln ^{14}\text{C}_{\text{DIC}}$ vs. $\ln(-\delta^{13}\text{C}_{\text{DIC}} - \varepsilon_{\text{s/b}})$ is a straight line (Fig. 7), and the slope of the correlation ($1 + \lambda_{14}/\lambda_{13}$) is used to compute the exchange rate constant λ_{13} . Thus, the overall rate constant for the first order ^{14}C decrease (decay + exchange) is $\lambda_{14} + \lambda_{13}$. The groundwater ages are then estimated by using Eq. (44) and the rate of carbon exchange.

By extrapolation to the ^{14}C content value of 100 pMC (^{14}C content of $\text{CO}_{2(\text{aq})}$), a $\delta^{13}\text{C}_i$ value of ca. -17.1‰ is obtained (point X in Fig. 7). In their calculations Gonfiantini and Zuppi used these values as the initial carbon isotopic composition.

4.2. Extended Gonfiantini & Zuppi model

Han et al. (2014) show that in addition to isotope exchange between DIC and solid carbonate, many other geochemical processes also may

cause a curved $^{14}\text{C}_{\text{DIC}}$ vs. $\delta^{13}\text{C}_{\text{DIC}}$ relationship if the kinetics of the reaction(s) can be treated as a single first-order or pseudo-first-order process. They show that a curved relationship of $^{14}\text{C}_{\text{DIC}}$ vs. $\delta^{13}\text{C}_{\text{DIC}}$ will be observed if (1) the change in $\delta^{13}\text{C}$ value in DIC is caused by a first-order or pseudo-first-order process, e.g. carbon exchange between DIC and solid carbonate, (2) the reaction/process progresses with the aging of the groundwater, i.e. with decay of ^{14}C in DIC, and (3) the magnitude of the rate of change in $\delta^{13}\text{C}$ value is comparable with that of ^{14}C decay.

Han et al. (2014) derived a model that can be used to estimate groundwater ages in cases where the ^{14}C vs. $\delta^{13}\text{C}$ data of the DIC in water show a curved relationship based on Fig. 8.

Assuming that the process that affects the ^{13}C composition of DIC is a first-order reaction (e.g. continuous addition of geogenic CO_2 to the system), from Fig. 8 (A) one obtains

$$(\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_{\text{DIC}}) = (\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_i) e^{-\lambda_{13}t} \quad (46)$$

where $\delta^{13}\text{C}_i$ and $\delta^{13}\text{C}_{\text{DIC}}$ are the ^{13}C content of the DIC at time zero and t , respectively. $\delta^{13}\text{C}_{\infty}$ is the ^{13}C content of the DIC as time $\rightarrow \infty$. λ_{13} is the apparent first-order rate constant of the reaction that affects the $\delta^{13}\text{C}$ value of the DIC. Eq. (46) is similar to the ^{14}C decay equation (Eq. (1)). There are two differences between Eq. (46) and Eq. (1): first, Eq. (46) describes a reaction, in that as time $\rightarrow \infty$, the $\delta^{13}\text{C}_{\text{DIC}}$ value approaches asymptotically a definite value, $\delta^{13}\text{C}_{\infty}$ (see Fig. 8); second, in Eq. (46) $\delta^{13}\text{C}_i$ is the initial value before the first-order process that affects the ^{14}C in addition to decay.

Taking the logarithm of both sides of Eq. (46) yields

$$\ln(\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_{\text{DIC}}) = \ln(\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_i) - \lambda_{13}t. \quad (47)$$

From the equation of ^{14}C decay + carbon exchange (Eq. (37)) one obtains

$$t = -\frac{1}{\lambda_{14} + \lambda_{13}} \ln ^{14}\text{C}_{\text{DIC}} + \frac{1}{\lambda_{14} + \lambda_{13}} \ln ^{14}\text{C}_i. \quad (48)$$

Combining Eqs. (47) and (48) yields Eq. (49)

$$\ln ^{14}\text{C}_{\text{DIC}} = \left(1 + \frac{\lambda_{14}}{\lambda_{13}}\right) \ln(\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_{\text{DIC}}) + \ln ^{14}\text{C}_i - \left(1 + \frac{\lambda_{14}}{\lambda_{13}}\right) \ln(\delta^{13}\text{C}_{\infty} - \delta^{13}\text{C}_i). \quad (49)$$

If the ^{14}C content of the reaction product (the newly formed DIC) is zero, the decrease in ^{14}C of the DIC will be caused by two parallel first-order processes following the relationship described by Eq. (44).

Eq. (49) is identical to Eq. (45) if we take $\delta^{13}\text{C}_{\infty} = \delta^{13}\text{C}_s - \varepsilon_{\text{s/b}}$ (i.e. the $\delta^{13}\text{C}_{\text{DIC}}$ value as the reaction time $\rightarrow \infty$, for isotope exchange between DIC and solid carbonate in carbonate aquifers).

The main difference between the statistically-based model and the single-sample-based models is that while the single-sample-based models assume that ^{14}C decreases with a constant half-life of 5730 years in the groundwater system and adjust the initial ^{14}C value taking the geochemical processes into account, the statistically-based model assumes a constant initial ^{14}C value and estimates ^{14}C decrease rate that is affected by geochemical processes.

In addition, the definition of the initial ^{14}C content, $^{14}\text{C}_i$ (Eq. (44)), is different than that used in the single-sample-based model (Eq. (1)). The initial $^{14}\text{C}_{\text{DIC}}$ value is representative for the entire system rather than for each individual sample. Therefore, the model avoids the effect of modern water components which might retain 'bomb' pulse signatures. In contrast to other single-sample-based models, this model uses a statistical method, and the λ_{13} value is estimated by correlation of isotopic data for water samples which may have a wide range of ages. Han et al. (2014) show that for waters with very low values of $^{14}\text{C}_0$ in

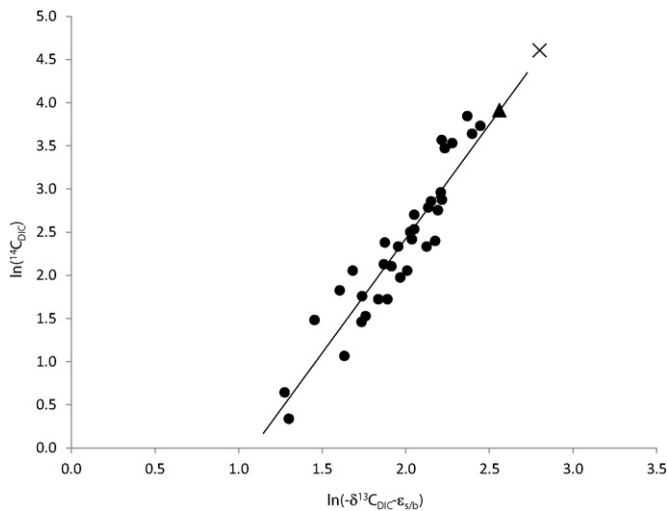


Fig. 7. $\ln(^{14}\text{C}_{\text{DIC}})$ vs. $\ln(-\delta^{13}\text{C}_{\text{DIC}} - \varepsilon_{\text{s/b}})$ for DIC of the Libyan karst aquifer. The straight line shows the regression of $\ln(^{14}\text{C}_{\text{DIC}})$ vs. $\ln(-\delta^{13}\text{C}_{\text{DIC}} - \varepsilon_{\text{s/b}})$. By extrapolation to the initial ^{14}C content value of 100 pMC ($^{14}\text{C}_i$), a $\delta^{13}\text{C}_i$ value of about -17.1‰ is obtained (point X). Point X is close to Mook's point. By extrapolation to the $^{14}\text{C}_i$ value of 50 pMC, a $\delta^{13}\text{C}_i$ value of about -12‰ is obtained (point \blacktriangle). Point \blacktriangle is close to Tamers' point.

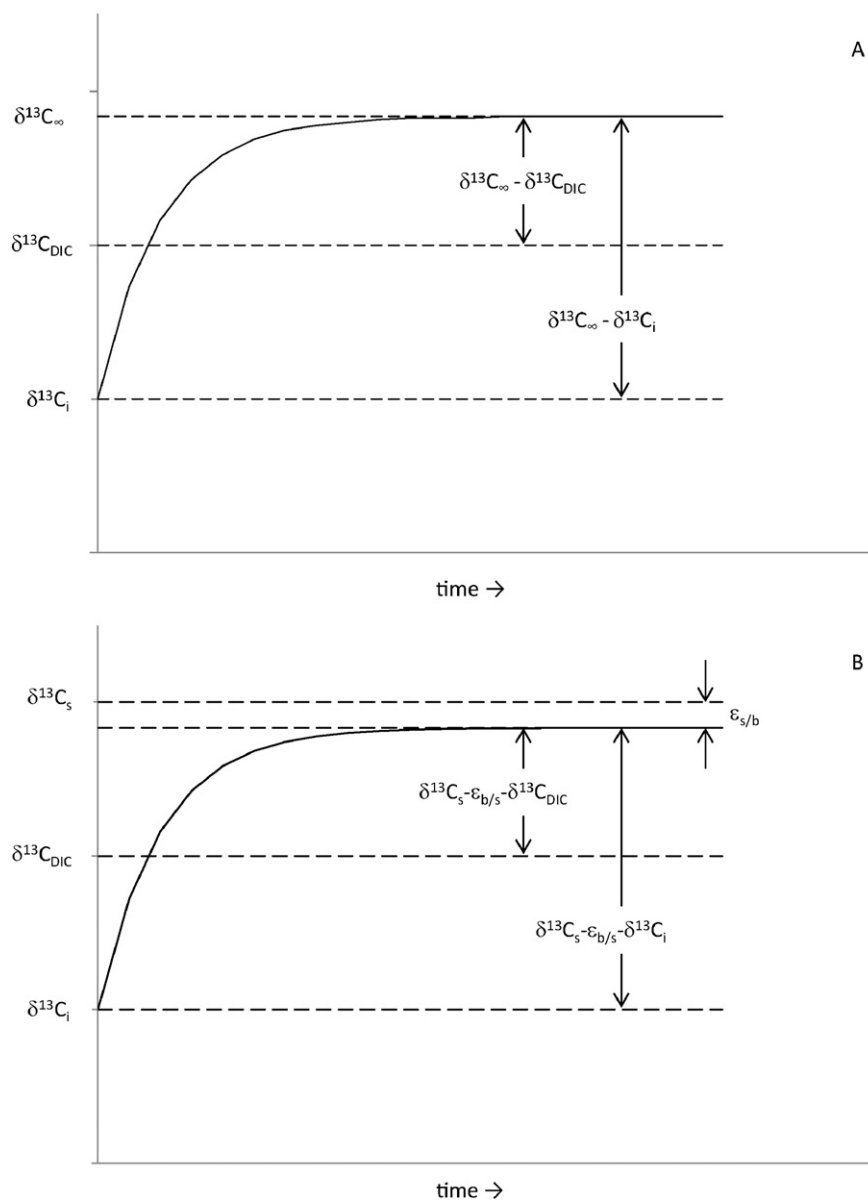


Fig. 8. Change (e.g. increase) in $\delta^{13}\text{C}_{\text{DIC}}$ in a first-order reaction. A: As time $\rightarrow \infty$, $\delta^{13}\text{C}_{\text{DIC}}$ approaches a definite value $\delta^{13}\text{C}_\infty$. At any given time the reaction rate is proportional to the substance concentration gradient ($\delta^{13}\text{C}_\infty - \delta^{13}\text{C}_{\text{DIC}}$). B: In carbon exchange between DIC and solid carbonate rock, as time $\rightarrow \infty$ the $\delta^{13}\text{C}$ value of DIC approaches a finite value $\delta^{13}\text{C}_s - \epsilon_{s/b}$.

Eq. (1), the model based on statistics may give more reliable age estimates than those obtained from single-sample-based models. In addition to groundwater age interpretation, the extended Gonfiantini & Zuppi model (Han et al., 2014) may also provide a useful tool for geochemical interpretations, e.g. estimating apparent rates of geochemical reactions and revealing the complexity of the geochemical environment.

The limitations of the extended Gonfiantini & Zuppi model (Han et al., 2014) are that (1) it does not consider concentrations of DIC. Thus, processes that dilute ^{14}C but cause no changes in $\delta^{13}\text{C}$ (e.g. addition of dead carbon from fossil organic matter that has similar $\delta^{13}\text{C}$ value to soil CO_2) cannot be recognized, and (2) it cannot be used if the ^{14}C and $\delta^{13}\text{C}$ data do not show a curved relationship.

5. Geochemical mass-balance approach

The geochemical mass-balance approach constructs balanced chemical reactions (models) that describe the chemical and isotopic evolution of an initial water composition (hypothetical or observed) to an observed final water composition in a groundwater system. The models

are constructed such that the calculated final water composition is identical to the observed. In so doing, the initial ^{14}C content of DIC (measured, or modeled using one or more of the above single-sample-based models) is adjusted for all the reactions, mass transfer, and isotope fractionation calculated to occur along the evolutionary path to the final water. The approach typically is non-unique given the potentially large number of phases that can react in groundwater systems. Each reaction model is a combination of masses of minerals and gases that must enter and/or leave (dissolve or precipitate) the initial water as it evolves chemically (and isotopically) to the final water. The range of valid reaction models, and possible adjusted radiocarbon ages, can be lowered by eliminating those models that are inconsistent with the observed $\delta^{13}\text{C}_{\text{DIC}}$, within uncertainty of the chemical and isotopic data. There is a large literature on the subject of geochemical modeling which is beyond the scope of this paper. See for example, Plummer, 1977; Plummer et al., 1983; Wigley et al., 1978, 1979; Plummer et al., 1994; Plummer and Sprinkle, 2001; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; El-Kadi et al., 2011; Blaser et al., 2010; and Plummer and Glynn, 2013, and references therein.

6. Discussion of applications and limitation of radiocarbon dating models

Of the possible processes that could have affected the ^{14}C data, how can one choose the best model? It should be pointed out that in choosing the model, 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 $^{14}\text{C}_0$ and limit the usefulness of radiocarbon as a dating tool for groundwater.

In quantitative analysis, internal standardization is an effective way to correct for changes in analyte concentration caused by sample manipulation steps prior to analysis. In a somewhat analogous way, the stable isotope, ^{13}C , can be used to correct for mixing and other carbon reactions occurring in groundwater systems, i.e., geochemical reactions/processes that affect the ^{14}C value.

DIC in groundwater is produced from and affected by different carbon-containing substances which may contain different amounts of ^{14}C and ^{13}C . The $^{14}\text{C}_0$ and $\delta^{13}\text{C}_{\text{DIC}}$ values of DIC are the results of different processes (e.g. mixing, fractionation, and exchange of isotopes). By knowing the processes, the ^{14}C and ^{13}C contents of DIC can be calculated under certain assumptions. In the case that ^{14}C has decayed, because ^{13}C is a stable isotope and participates in the same processes as ^{14}C , the $\delta^{13}\text{C}$ content of the DIC can be used to estimate the ^{14}C content in the absence of radioactive decay ($^{14}\text{C}_0$).

Tamers' model, although simple and does not consider ^{13}C , is important for understanding the evolution of carbon isotopic composition of the DIC in groundwater. The most important step of the evolution is the reaction between dissolved CO_2 and solid carbonate. After this step the carbon isotopic composition of the DIC will plot on the graph of ^{14}C vs. $\delta^{13}\text{C}$ relationship at point O (Tamers' point, Fig. 1). Further evolution will start from Tamers' point. This point (O) cannot be obtained by using Tamers' model because Tamers' model does not consider $\delta^{13}\text{C}$ values. However, Tamers point can be obtained by the material balance calculations (Eqs. (7) and (8)) involving both ^{14}C and ^{13}C or by geochemical modeling calculations as in PHREEQC (Parkhurst and Appelo, 2013; and references therein).

In contrast to Tamers' model, which includes carbon concentrations, Pearson's model is based entirely on isotopic data, with $\delta^{13}\text{C}$ data as a mixing indicator for two carbon sources. Although using isotopic data, like Tamers' model, Pearson's model is a mixing model.

The models of Mook, Wigley, Evans, Fontes & Garnier, Eichinger, and Han & Plummer consider, in addition to mixing process (Processes (2) and (6)), carbon exchange between different carbon species. Depending on the $\delta^{13}\text{C}$ value, Mook's model corrects the $^{14}\text{C}_0$ from Tamers' point towards point A2 (open-system evolution) (Fig. 1) by adding a correction term. Wigley's and Evans' models correct the $^{14}\text{C}_0$ from Tamers' point towards point M' (closed-system evolution) (Fig. 1). Eichinger's model corrects the $^{14}\text{C}_0$ from Tamers' point towards point M'' in a closed system (cf. Eqs. (17) and (18) and Fig. 1). The models of Wigley, Evans and Eichinger can give similar results. However, Eichinger's model is more accurate than those of Wigley and Evans, since it includes the contribution of $\text{CO}_{2(\text{aq})}$ in DIC (the model assumes that $\text{DIC} = \text{CO}_{2(\text{aq})} + \text{HCO}_3^-$). In contrast, the

models of Wigley and Evans omit the contribution of $\text{CO}_{2(\text{aq})}$ in DIC (the models assume that $\text{DIC} = \text{HCO}_3^-$). In all these models the carbon exchange starts from an initial state that can be described by Tamers' point. All the models can be represented by straight lines on Fig. 2.

As can be seen from Fig. 2, the straight line representing Fontes & Garnier's model has greater slope compared with the models of Wigley, Evans and Eichinger, and smaller slope compared with Mook's model. Assuming that the solid carbonate has an isotopic composition of $^{14}\text{C}_s = 0$ and $\delta^{13}\text{C}_s = 0$, the line representing Fontes & Garnier's model intersects at $\delta^{13}\text{C} \approx -5\text{‰}$ with the abscissa, a more negative value compared with that obtained by the models of Wigley, Evans and Eichinger. The reason is that Fontes and Garnier (1979) made an incorrect assumption in deriving their model (Han and Plummer, 2013).

In Fig. 1, groundwater data plotting along line A3–O represent different extents of “openness” of the system to soil gas CO_2 with points O and A3 represent the two extreme scenarios (Fig. 9): (1) DIC produced under conditions illustrated in the left side of Fig. 9 would plot near point O in Fig. 1. (2) DIC produced under conditions illustrated in the right side of Fig. 9 would plot near A3 (or approximately near A2). In most natural water systems, during infiltration, the DIC in water exchanges carbon atoms with soil CO_2 and the exchange often is not in equilibrium before the system becomes closed (DIC would plot on line A2–O, Mook's line). Two different models can be used to account for further carbon exchange between the DIC and solid carbonate under closed-system conditions: for the DIC produced in the first scenario Eichinger's model can be used (line O–M''); for the DIC produced in the second scenario the IAEA model can be used (line A2–M). Between the two extremes, further evolution occurs under closed-system conditions, as illustrated in Fig. 1 by line B–M'. However, while we use 100 pMC for $\text{CO}_{2(\text{g})}$ in soil air, there can be cases, such as infiltration through deep unsaturated zones, in which the soil air contain low $^{14}\text{CO}_2$ (perhaps through decay or more likely through water–rock reaction in the unsaturated zone (Wood et al., 2014)). At confinement this sample could appear old—even though it is modern. In other words, the points A2 and A3 in Fig. 1 plot lower than points A and A1.

In Fig. 10, the area enclosed by A3–O–M''–M–A2–A3 is referred to as ‘zero-age area’. The location of the zero-age area depends on values of ^{14}C and $\delta^{13}\text{C}$ data of soil $\text{CO}_{2(\text{g})}$ and solid carbonate. Samples plotting in the zero-age area have zero radiocarbon age, even though their ^{14}C content may be relatively low. Only groundwater samples plotting below this area may have radiocarbon ages of DIC greater than zero. Samples plotting above the zero-age area likely are mixtures containing a fraction of ^{14}C -bearing infiltration water.

Tamers' model cannot be applied to sample points that plot on the left side or the right side of Tamers' point (within the uncertainty of the data). This is because Tamers' model is a carbonate-dissolution-only (Processes (2) and (6)) model, and carbon exchange is not considered. For the samples represented by solid squares in Fig. 10, Tamers' model may be applied, i.e. the value of $^{14}\text{C}_0$ is the value of $^{14}\text{C}_{\text{DIC}}$ at Tamers' point (Even for these samples Tamers' model may give incorrect results if ^{14}C in these samples has been diluted by ^{14}C -free DIC

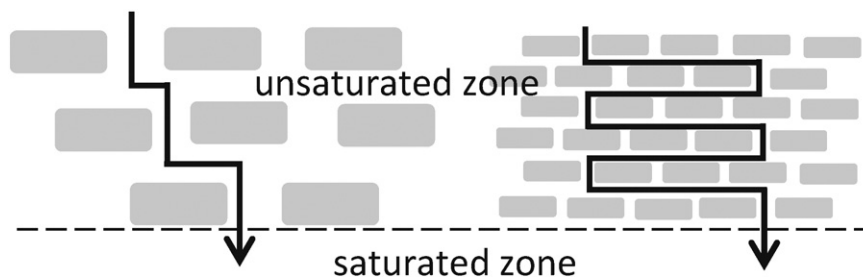


Fig. 9. Two extreme cases of water movement in a hypothetical karst system. Left: infiltration water saturated with soil CO_2 flows rapidly and the HCO_3^- is produced in the aquifer under closed-system conditions (Process (8)). Right: infiltration water saturated with soil CO_2 reacts with carbonate and moves slowly to allow carbon exchange between DIC and soil CO_2 until equilibrium (Process (11)).

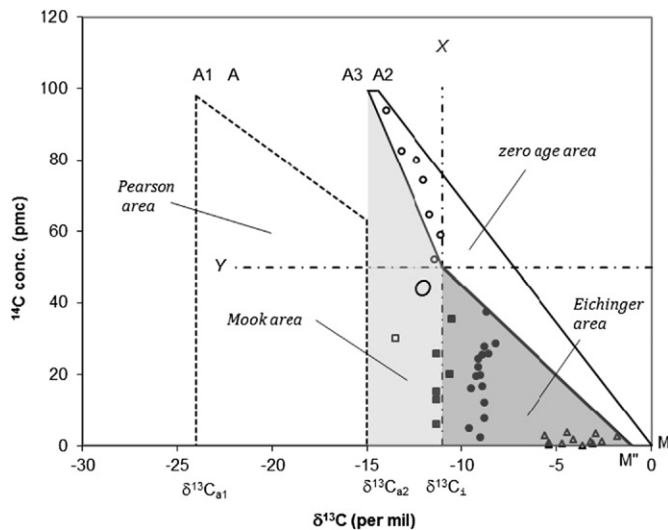


Fig. 10. Graphical presentation of data from Jirakova et al. (2009). Several groups of waters can be recognized by using the graphical method. ○: Samples with $\delta^{13}\text{C}_{\text{DIC}} < 0.5\delta^{13}\text{C}_g$; ■: Samples with $\delta^{13}\text{C}_{\text{DIC}} \approx 0.5\delta^{13}\text{C}_g$; ●: Samples with $\delta^{13}\text{C}_{\text{DIC}} > 0.5\delta^{13}\text{C}_g$; △: samples enriched in ^{13}C with $\delta^{13}\text{C}_{\text{DIC}}$ close to $\delta^{13}\text{C}_g$; □: A hypothetical sample not from Jirakova et al., 2009. See text for explanation of symbols and processes.

that was produced by decomposition of fossil organic matter. See discussion below).

In general the process of carbon exchange between DIC and soil CO_2 takes place in the unsaturated zone, before the water reaches the saturated zone. Typically, water infiltration is fast compared to ^{14}C decay. Therefore, in many cases the water samples can be found plotting on the Mook line, indicating young waters (see e.g. the empty circles in Fig. 10). The process of carbon exchange between DIC and solid carbonate takes place predominantly in the saturated zone, after the water has infiltrated below the water table and has become isolated from the soil-gas reservoir. The rate of this process is comparable to ^{14}C decay (Han et al., 2014). Therefore, water samples plot normally below the zero-age line, O–M'' (Eichinger) line (e.g. Fig. 10) and rarely on line O–M''.

Any $\delta^{13}\text{C}$ values that plot between $\delta^{13}\text{C}_{\text{a}2}$ and $0.5\delta^{13}\text{C}_g$ could be caused by carbon exchange between soil $\text{CO}_{2(\text{g})}$ and HCO_3^- in water (Process (11)). In general, Mook's model can be applied to sample points that plot within the light shaded shape in Fig. 10 (Mook area). For example, Mook's model can be applied to the waters represented by empty circles and the empty square; the age of the sample represented by an empty square in Fig. 10 may be estimated by using $^{14}\text{C}_0 = 80$ pMC.

$\delta^{13}\text{C}$ values, which are more negative than $\delta^{13}\text{C}_{\text{a}2}$, could be caused by evolution in the absence of carbonate. In such situations the DIC contains mainly dissolved CO_2 ($\text{CO}_{2(\text{a})}$). For samples that plot within the Pearson area (short dashed-line enclosed area in Fig. 10), Pearson's model can be applied.

The model of Han & Plummer is a combination of three models: Tamers', Mook's and Eichinger's models. If no carbon exchange occurs, the Han & Plummer model reduces to Tamers' model. If carbon exchange between the DIC and soil CO_2 occurs, but without exchange with solid carbonate, the model reduces to Mook's model. If carbon exchange between the DIC and solid carbonate occurs under closed-system conditions, but without exchange with soil CO_2 , the model reduces to Eichinger's model. Han & Plummer's model can be used for $\delta^{13}\text{C}$ values between $\delta^{13}\text{C}_{\text{a}2}$ and M'' (Fig. 2).

The IAEA model can be used for $\delta^{13}\text{C}$ values between $\delta^{13}\text{C}_{\text{a}2}$ and M (Fig. 2), similar to Han & Plummer's model. However, unlike Han & Plummer's model which assumes either open (Mook) or closed (Eichinger) systems, the IAEA model assumes mixed open and closed systems. The IAEA model assumes that the isotopic composition of the DIC evolved initially under completely open-system conditions, and

then evolved under closed-system conditions. While the results calculated from Han & Plummer's model can be biased to younger ages, the results calculated by the IAEA model may be biased to older ages. As shown in Fig. 10, a sample with zero-age may plot below the IAEA line (line A2–M) in the zero-age area, and interpreted as aged water by the IAEA model. On the other hand, an aged sample plotting below the zero-age area, but on the Han & Plummer line (line A3–O–M''), may be interpreted as zero-age water.

It can be seen in Fig. 2 that Vogel's empirical model is a specific case of other process based single-sample-based models (Pearson's, Mook's or the IAEA model). If the samples were analyzed for $\delta^{13}\text{C}$, the $\delta^{13}\text{C}_{\text{DIC}}$ values can be used to distinguish between specific cases of Pearson's, Mook's or the IAEA model, because the 'Vogel's line', y, intercepts with the three model lines in different ranges of $\delta^{13}\text{C}$ values.

Despite the problems, the single-sample-based models constitute the prevailing use of ^{14}C data in hydrogeology and hydrological studies in specific cases, particularly for geochemically simple groundwater systems. This is in part because (1) the single-sample-based models use simple algebraic equations with relatively few parameters, so that calculations can be easily performed, and (2) the models are applied to an individual water sample to estimate the ^{14}C age of DIC and are based on measured data that typically are available. In contrast, although the 'extended geochemical mass balance approaches' can be more accurate than the single-sample-based models, mineralogical, chemical and isotopic data needed for application of the 'extended geochemical mass balance approaches' may not be available or are uncertain. Thus, resort to appropriate single-sample-based models remains a viable approach to radiocarbon dating in groundwater systems. At least in application to many simple carbonate aquifers, they have been shown to provide realistic radiocarbon ages.

To avoid confusion, it is recommended to use four models, Pearson's model, Han & Plummer's model, the IAEA model, and Oeschger's model, instead of using the other single-sample-based models. These four models include all processes considered in single-sample-based models and incorporate useful parts of the single-sample-based models of Tamers, Mook, Fontes & Garnier, and Eichinger (Wigley's and Evans' model are similar to Eichinger's model). The $\delta^{13}\text{C}$ value of the DIC and concentration of DIC in the sample must be known to use the single-sample-based models correctly. For different ranges of $\delta^{13}\text{C}$ values, different models or parameters should be used (i.e. $\delta^{13}\text{C}_{\text{DIC}}$ data plotting right of Tamers' point, close to Tamers' point, between $\delta^{13}\text{C}_{\text{a}2}$ and $0.5\delta^{13}\text{C}_g$ or between $\delta^{13}\text{C}_{\text{a}1}$ and $\delta^{13}\text{C}_{\text{a}2}$). Incorrect use of the model or parameters can lead to completely different results. The graphical method (Han et al., 2012) can help in deciding which model should be applied (see Fig. 10).

Unlike the single-sample-based models, the model of Gonfiantini and Zuppi (2003) applies a statistical approach to a group of samples from the same aquifer to quantify the relationship between ^{14}C and $\delta^{13}\text{C}$ data. This relationship can be used to estimate groundwater ages, and to describe some characteristics of the aquifer (such as the average carbon exchange rate within the aquifer and the homogeneity of the aquifer geochemical environment). The model also can be used to recognize outliers from the relationship between ^{14}C and $\delta^{13}\text{C}$ data, and this information may be important for successful use of the single-sample-based models. The model of Gonfiantini and Zuppi (2003), which was proposed initially for special cases where the exponential curve of ^{14}C vs. $\delta^{13}\text{C}$ relationship is caused by carbon exchange, can be extended to more general cases (Han et al., 2014).

The application of single-sample-based and statistically-based models is summarized in Table 3.

Except for ^{14}C decay, any process that alters the ^{14}C content of the DIC typically (but not necessarily) will also alter the DIC concentration and the ^{13}C content of the DIC. For this reason, (1) models that do not use $\delta^{13}\text{C}$ data should not be used; and (2) not only $\delta^{13}\text{C}$, but also chemistry (at least $[\text{HCO}_3^-]$) data should be studied in order to use the models correctly.

Table 3

Application of single-sample-based and statistically-based radiocarbon adjustment models.

Model	Equation	Applicable range of $\delta^{13}\text{C}^a$	Possible bias	Applicable for hydrogeological environments
<i>Single-sample-based models</i>				
Vogel, Vogel and Ehrlert	19		Any	Slow infiltrating water (suggest using Mook's model because Mook's model considers $\delta^{13}\text{C}$ data)
Mook	29	$>\delta^{13}\text{C}_{a2}$ and $<\delta^{13}\text{C}_i$		
Tamers	22	$\delta^{13}\text{C}_i$	Any	Fast infiltrating water (e.g. groundwater recharge through sinkhole in karst areas); non-carbonate aquifer.
Pearson	27	Suggest use the model between $\delta^{13}\text{C}_{a1}$ and $\delta^{13}\text{C}_{a2}$	Older ^b	Fast infiltrating water (e.g. groundwater recharge through sinkhole in karst areas); non-carbonate aquifer. Addition of bicarbonate caused by cation exchange or reactions between acids and carbonate.
Wigley	34	$>\delta^{13}\text{C}_i$	Older ^b	Carbonate aquifer; addition of DIC that is in isotopic equilibrium with solid carbonate (e.g. DIC produced by geogenic CO_2)
Evans	35	$>\delta^{13}\text{C}_i$	Older ^b	
Eichinger	36, 37	$>\delta^{13}\text{C}_i$		
F & G	38	$>\delta^{13}\text{C}_{a2}$ ($<\delta^{13}\text{C}_i$ for open system)	Younger ^c	Non-carbonate or carbonate aquifer; addition of CO_2 ; addition of DIC that is in equilibrium with solid carbonate (e.g. DIC produced by geogenic CO_2)
H & P	39	$>\delta^{13}\text{C}_{a2}$ ($<\delta^{13}\text{C}_i$ for open system)	Younger	
IAEA	40, 41	$>\delta^{13}\text{C}_{a2}$ ($<\delta^{13}\text{C}_i$ for open system)	Older	Slow infiltrating water; affected by addition of DIC under closed-system conditions that is in equilibrium with solid carbonate
Oeschger	42			System affected by additional CO_2 under closed-system conditions (e.g. CO_2 produced by oxidation of organic matter, methanogenesis, geogenic CO_2)
Cheng	43			System affected by additional CO_2 under closed-system conditions (e.g. CO_2 produced by oxidation of organic matter, methanogenesis, geogenic CO_2)
<i>Statistically-based models</i>				
G & Z	44, 45	$>\delta^{13}\text{C}_{a2}$	Younger or older ^d	Carbonate aquifer
Extended G & Z	46, 49	$>\delta^{13}\text{C}_{a2}$	Younger or older ^d	Carbonate aquifer; system affected by additional CO_2 under closed-system conditions (e.g. CO_2 produced by oxidation of organic matter, methanogenesis, geogenic CO_2); groundwater mixing in a dual porous system

^a For $\delta^{13}\text{C}_i$ and $\delta^{13}\text{C}_{a2}$, see Table 2 and Fig. 1.^b The bias increases with extent of carbon exchange.^c The bias is caused by an inadequate conceptualization of the model.^d Depending on the selection of $\delta^{13}\text{C}_i$ and $^{14}\text{C}_i$.

While instructive and often quite useful, the models discussed in Sections 3 and 4 are based on simple chemical/physical concepts. Groundwater systems can be very complicated chemically and isotopically. For example, $^{14}\text{C}_0$ also may be modified by mixing of waters, cation exchange and/or proton exchange coupled with carbonate dissolution, methane production, oxidation of dissolved or particulate organic carbon, introduction of CO_2 from geogenic sources, and many other reactions/processes (see Han et al., 2012; Plummer and Glynn, 2013). Therefore, identification of all carbon sources and all reactions that affect carbon mass transfer is important in interpretation of ^{14}C data and can require application of geochemical modeling (Plummer, 1977; Wigley et al., 1978, 1979; Plummer et al., 1983, 1994; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; El-Kadi et al., 2011; Parkhurst and Appelo, 2013; Blaser et al., 2010; Plummer and Glynn, 2013). The graphical method (Han et al., 2012) can also provide some useful information about the complexity of the system.

Not all ^{14}C dilution by dead carbon is accompanied by a change in $\delta^{13}\text{C}_{\text{DIC}}$ value. One example is the case where $^{14}\text{C}_{\text{DIC}}$ is diluted by ^{14}C -free CO_2 that is produced by decomposition of fossil organic matter. Because fossil organic matter may have the same $\delta^{13}\text{C}$ value as that of the modern soil CO_2 , addition of ^{14}C -free DIC produced from fossil organic matter may not be recognized by a change in $\delta^{13}\text{C}_{\text{DIC}}$ value. Fig. 11 (data from Buckau et al., 2000) shows that addition of CO_2 produced by decomposition of fossil organic matter mainly dilutes ^{14}C of DIC and is accompanied by an increase in DIC concentration. A small change in $\delta^{13}\text{C}_{\text{DIC}}$ value is insignificant. The ^{14}C age of the samples would be biased to older values if Tamers' model is used (i.e. assuming that $^{14}\text{C}_0 = 50$ pMC). On the other hand, the ages would be correct if Oeschger's model is used (see Eq. (42)).

The application of the single-sample-based models implies conceptually that the water sample is unmixed or of a single age (e.g. from a confined and isolated aquifer or one subject to piston-type flow). However, most groundwater samples should be regarded as mixtures (see for example, Bethke and Johnson, 2008; Torgersen et al., 2013). In

some situations, mixing of waters causes continuous change of the ^{14}C value (with continuous change in $\delta^{13}\text{C}$ and/or DIC values), such as exponential mixing (e.g. mixing in a dual porous system; mixing due to dispersion). In such situations radiocarbon dating of the DIC (i.e. ^{14}C -bearing fraction of the water mixtures) can be treated by the extended G & Z model provided that the mixing rate is comparable to that of ^{14}C decay and can be regarded as a first-order reaction. For these types of mixtures the extended G & Z model can still give the correct ages of the ^{14}C -bearing water fraction by considering an additional rate of ^{14}C decrease (not to be confused with ^{14}C decay rate). In other situations where the mixtures consist of waters with distinctly different ages, such as binary mixtures, any resulting "age" is regarded as a "mixed age". This mixed age often has less meaning in groundwater dating, and a more physically based definition of groundwater age is needed. For example, a paleowater (with an age of millions of years) may appear to be less than 30 ka old with a mix of only 1% of water from the bomb era (post-1950s). This age gives no useful information about the system and may be misleading. For example, if this water has low noble gas temperature and apparently datable ^{14}C content, it may be erroneously interpreted as groundwater that was recharged during the last glacial maximum (LGM). It is thus important to recognize groundwater mixtures. It is not always possible to recognize the second type of mixtures. Obvious mixtures of the second type are samples with low $^{14}\text{C}_{\text{DIC}}$ but containing tritium or chlorofluorocarbons (IAEA, 2006; Plummer and Glynn, 2013; Mook, 2000; IAEA, 2013), or other tracers of anthropogenic origin.

Fig. 12 shows the evolution of the carbon isotopic composition of DIC in a karst system (unpublished data, Dajun Qin, Institute of Geology and Geophysics, Chinese Academy of Sciences, 2014) in which surface water mixes with old groundwater. Because none of the single-sample-based models consider mixing of waters, none of the single-sample-based models discussed in this paper can be applied to estimate the $^{14}\text{C}_0$ concentration. Still, the Han and Plummer plot (Fig. 12) is useful in tracing the evolutionary processes. An interpretation of the data in Fig. 12 is

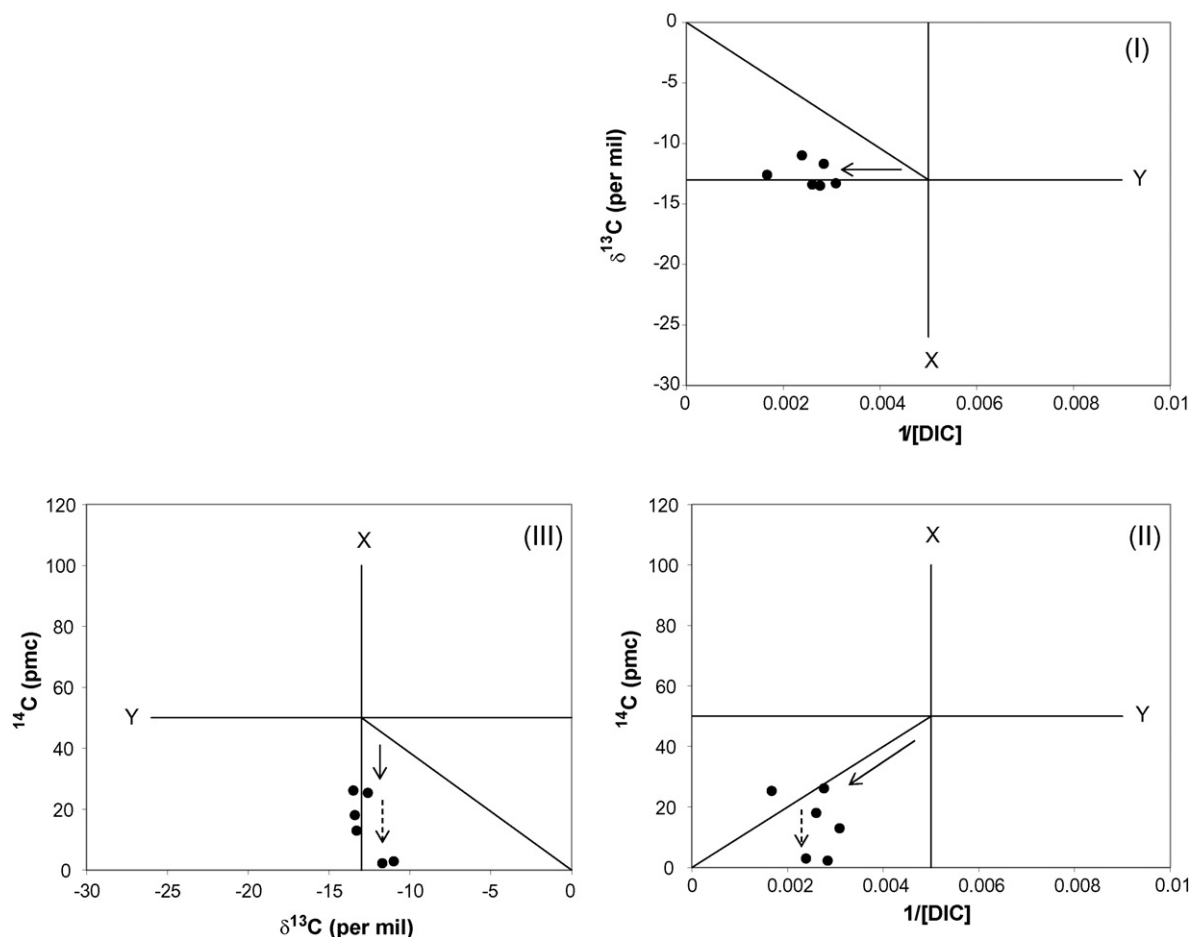


Fig. 11. Carbon isotopic and chemical data from Buckau et al. (2000). Full-line arrows: effect of addition of carbon produced by oxidation of organic matter. Dashed-line arrow: decay of ^{14}C . The initial DIC concentration before dilution can be determined from the crossing point of lines X and Y in sub-diagrams I and II (i.e. $\approx 1/0.005 = 200 \text{ mg/l}$).

that the DIC has equilibrated with soil CO_2 (see Fig. 9, right), causing the composition to move from point O along line A3–O to plot at A3. The DIC then exchanges carbon with aquifer carbonate under closed-system conditions, causing the carbon isotopic composition of DIC to move along line A3–M (similar to the IAEA model. Also see Fig. 2). The water then mixes with surface water, causing the carbon isotopic composition to shift up along the dashed line (mixing line). The surface (river) water has $^{14}\text{C}_{\text{DIC}} \approx 100 \text{ pMC}$ and $\delta^{13}\text{C}_{\text{DIC}}$ between points A3 and A6 (see Fig. 6), because this water has been affected not only by soil CO_2 but also atmospheric CO_2 .

In addition to mixing, evaporation of groundwater may also cause a sample point to plot above the zero-age area.

Even for unmixed samples and clearly physically defined ages, the dating results can still be uncertain. The uncertainty can be caused by uncertainties in assumed $\delta^{13}\text{C}_g$ and $^{14}\text{C}_g$ values. Because we are dating DIC in old samples, the soil CO_2 should be pre-bomb, which differs from modern recharge. While the plants may be predominantly C3 today, they may have been C4 in the past or mixtures of C3 and C4. Changes in solar flux, the Earth's geomagnetic field intensity, and the carbon cycle have impacted the ^{14}C content of the atmosphere in the past. Consequently, the ^{13}C and ^{14}C contents of soil gas CO_2 may have varied in the recharge zone with time (de Vries, 1958; Stuiver and Polach, 1977; Stuiver et al., 1986; Bard et al., 1990, 1993; Plummer and Sprinkle, 2001; Plummer and Glynn, 2013) (also see Appendix B).

Finally, because carbon and its isotopes often are involved in geochemical reactions that can affect interpretation of radiocarbon age in groundwater, it is best to include measurements of the concentrations of selected inert environmental tracers that can help, at least in part,

to corroborate interpreted radiocarbon ages or, alternatively, that can help recognize those radiocarbon ages that may require further interpretation (Kazemi et al., 2006). The presence of tritium, chlorofluorocarbons, and/or elevated $^{36}\text{Cl}/\text{Cl}$ ratios can indicate samples that are from the bomb era (post-1950s) or are mixed with post-bomb water, and thus may contain fractions of water with elevated ^{14}C from nuclear detonation (see for example Mook, 2000, 2006; Davis et al., 2003; Plummer and Glynn, 2013; Kwicklis and Farnham, 2014). If the radiocarbon age places the sample near the Last Glacial Maximum (LGM, 18 ka radiocarbon years), detection of shifts in stable isotope composition of groundwater and/or lowered dissolved gas- (N_2/Ar ; Heaton, 1981; Heaton et al., 1983; Heaton and Vogel, 1981), and noble-gas recharge temperatures (Herzberg and Mazor, 1979; Stute et al., 1995a, 1995b; Stute and Schlosser, 2000; Stute et al., 1992a) can help to corroborate the radiocarbon age. A depletion in stable isotope composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of groundwater in continental aquifers relative to that of modern water in the recharge zone can indicate water recharged during a past glacial period (Rozanski, 1985; Edmunds and Smedley, 2000; Stute and Deak, 1989; Stute and Schlosser, 1993; Plummer et al., 2012), but in some coastal aquifers, enrichment in stable isotope composition of groundwater has been noted at the LGM (Plummer, 1993; Stute and Talma, 1998), possibly indicating a change in moisture source and/or enrichment in ocean water isotopic composition (ice volume effect). Some success also is noted in corroboration of radiocarbon ages with ages based on in-situ accumulation of radiogenic ^4He (Andrews and Lee, 1979; Stute et al., 1992b; Aeschbach-Hertig et al., 2002; Carey et al., 2004; Plummer et al., 2012; Torgersen and Stute, 2013).

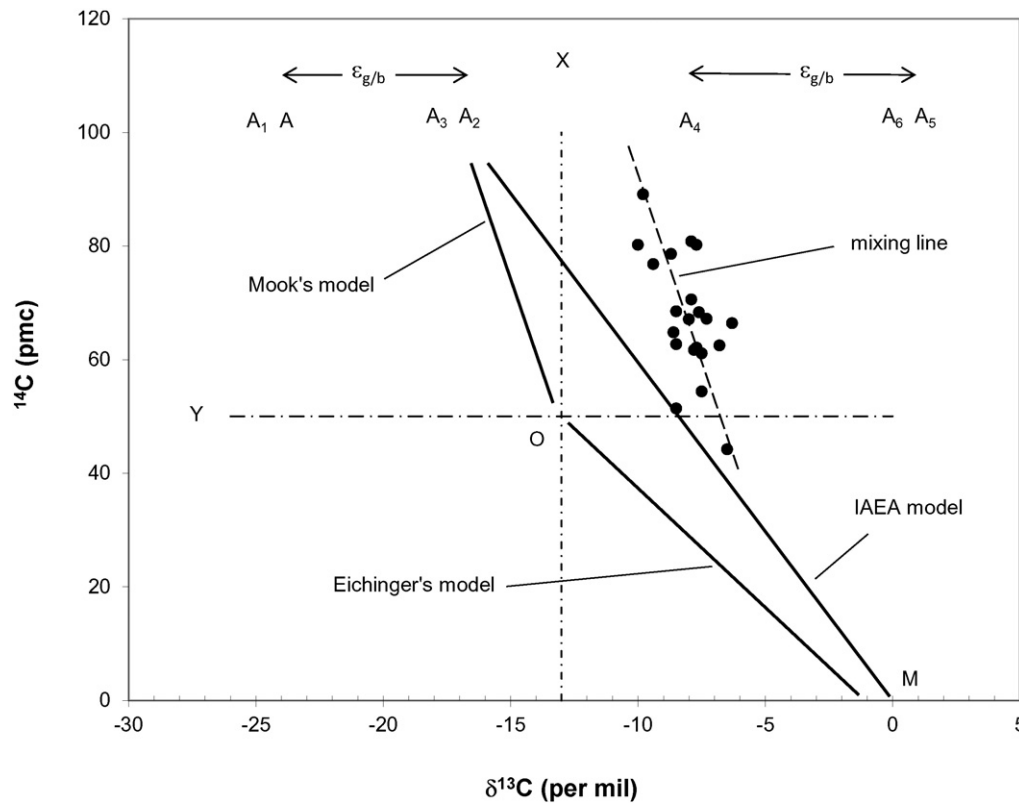


Fig. 12. Data from Qin et al. (unpublished data, Dajun Qin, Institute of Geology and Geophysics, Chinese Academy of Sciences, 2014) plotted in Han and Plummer plot. The waters are mixtures of karst groundwater (older end member) with river water (younger end member). A4: atmospheric CO_2 ($\delta^{13}\text{C} \approx -8\text{‰}$). A5: HCO_3^- in water equilibrated with atmospheric CO_2 . A6: DIC equilibrated with atmospheric CO_2 .

7. Conclusions

The evolution of carbon isotopic composition and concentration of DIC in groundwater typically involves four basic steps: (1) dissolution of soil gaseous CO_2 in water; (2) water–rock interaction (bicarbonate formation); (3) water–soil gas interaction (isotope exchange under open-system conditions); and (4) water–rock interaction (isotope exchange under closed-system conditions). Besides these four basic steps, the carbon isotopic composition and concentration of DIC can be affected by many other geochemical processes (Han et al., 2012; Plummer and Glynn, 2013).

Without accounting for decay of ^{14}C , the isotopic compositions of carbon-containing species (sources of DIC) and the reaction products, DIC, can be represented on a ^{14}C vs. $\delta^{13}\text{C}$ graph by using simple mass balance calculations. The calculated $^{14}\text{C}_0$ may differ depending on the applied models.

The single-sample-based models can be classified into four types: (1) empirical, (2) chemistry-based, (3) ^{13}C -based, and (4) a combination of chemistry and ^{13}C based. Most of the single-sample-based models can be represented by a linear relationship between ^{14}C and $\delta^{13}\text{C}$. Thus, with the help of the graphical method, comparison of age interpretation between different models is possible. The approach also allows ‘fitting’ of different models to the data and selection of models that best describe the observations.

The main advantage of the single-sample-based models is that they can be used for an individual water sample to estimate the ^{14}C age and are based on measured data that typically are available. The main disadvantage of these models is that selection of model may have significant effects on $^{14}\text{C}_0$ and can result in a wide range of estimates of ^{14}C ages.

In contrast to the single-sample-based models, the extended model of Gonfiantini & Zuppi is a statistical approach to estimate the relationship between ^{14}C and ^{13}C data. This relationship can be used to estimate groundwater ages and to describe the aquifer-specific value of λ_{13} , the

apparent first-order rate constant for reactions occurring in the aquifer. This model also can be applied to the ^{14}C and $\delta^{13}\text{C}$ data to identify outliers, that is, to identify samples that may have evolved under differing geochemical conditions. Another advantage of this model over the single-sample-based models is that selection of the model might be easier because observation of a curved relationship between ^{14}C and ^{13}C data may suggest use of this model. This model, although having many advantages over the single-sample-based models, cannot be used in cases where the ^{14}C and $\delta^{13}\text{C}$ data do not show a curved relationship.

The geochemical mass-balance approach may be used for more complicated cases including dissolved organic carbon (DOC) and methane (CH_4) (Plummer and Glynn, 2013). The main limitation of this approach is that sufficient chemical, mineralogical and isotopic data are not always available to yield accurate estimates of the adjusted radiocarbon age.

Practical guidelines to select appropriate model(s) for groundwater system are proposed: To avoid confusion, use of only four of the single-sample-based models (Pearson's model, Han & Plummer's model, the IAEA model, and Oeschger's model) is recommended. A revised version of the code NetpathXL implements the Han & Plummer model (Parkhurst and Charlton, 2008; U.S. Geological Survey, 2013). The IAEA model and Pearson's model can be applied using NETPATH and NetpathXL (Plummer and Glynn, 2013).

The $\delta^{13}\text{C}$ value of the DIC and the concentration of DIC in the sample must be known to use the single-sample-based models correctly, even for evolution of simple carbonate groundwater. For different ranges of $\delta^{13}\text{C}$ value (i.e. $\delta^{13}\text{C}_{\text{DIC}}$ data plotting right of Tamers' point, close to Tamers' point, between $0.5\delta^{13}\text{C}_g$ and $\delta^{13}\text{C}_{a2}$, or between $\delta^{13}\text{C}_{a1}$ and $\delta^{13}\text{C}_{a2}$) different models or parameters should be used. Incorrect use of the model or parameters can lead to completely different results.

In cases where a curved ^{14}C vs. $\delta^{13}\text{C}$ relationship exists, Gonfiantini & Zuppi's extended model can be used.

An initial scrutiny of the isotopic and chemical data is essential. The graphical method can help in deciding whether a model can be used or not, and which model should be applied for given isotopic and chemical data. In cases where the single-sample-based and statistically-based models cannot be used, more advanced dating models, e.g. use of geochemical modeling may provide a better understanding of the systems under investigation.

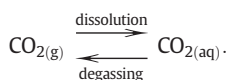
Steps in selecting appropriate model(s) for the groundwater system are summarized in [Appendix C](#).

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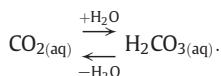
Appendix A. The distribution of carbonate species as percentages of total dissolved inorganic carbon in water

Gaseous CO_2 ($\text{CO}_{2(g)}$), can form in soils by plant-root respiration and microbial degradation of soil organic matter. During recharge, $\text{CO}_{2(g)}$ dissolves in infiltration water according to the reaction



The CO_2 acquires a shell of water molecules to become hydrated. In other words, it is caged by water molecules.

A small fraction of these hydrated carbon dioxide molecules react with the water to produce carbonic acid (molecular $\text{H}_2\text{CO}_{3(aq)}$ (see for example [Soli and Byrne, 2002](#))):



The equilibrium constant for this reaction is $10^{-2.93}$ at 25 °C ([Soli and Byrne, 2002](#)). The concentration of $\text{CO}_{2(aq)}$ in water therefore far exceeds that of $\text{H}_2\text{CO}_{3(aq)}$ (the concentration ratio $\text{CO}_{2(aq)}/\text{H}_2\text{CO}_{3(aq)}$ being on the order of 1000:1).

By convention, the dissociation of carbonic acid to form bicarbonate ion (HCO_3^-) is written as $[\text{CO}_{2(aq)} + \text{H}_2\text{O}] = \text{H}^+ + \text{HCO}_3^-$ ([Stumm and Morgan, 1996](#)), and dissociation of HCO_3^- to form CO_3^{2-} ion is written as $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$. The overall equilibria relations in the CO_2 – H_2O system are expressed:



where the first and second dissociation constants of carbonic acid dissociation are, at 25 °C and 1 atm pressure, $10^{-6.35}$ and $10^{-10.33}$, respectively ([Parkhurst and Appelo, 2013](#)).

At one atmosphere total pressure, the distribution of the carbonate species, $\text{CO}_{2(aq)}$ (neglecting $\text{H}_2\text{CO}_{3(aq)}$), HCO_3^- and CO_3^{2-} , in water depends on the solution pH value, water temperature and dissolved solute concentration. From the dissociation equilibria, the concentrations of $\text{CO}_{2(aq)}$ and HCO_3^- are equal at pH of 6.35 in dilute aqueous solutions at 25 °C. And the concentrations of HCO_3^- and CO_3^{2-} are equal at pH of 10.33. Aqueous models such as that of PHREEQC ([Parkhurst and Appelo, 2013](#)) can be used to calculate the distribution of carbonate species in aqueous solutions as a function of temperature, pressure and inorganic chemistry. [Fig. A.1](#) shows the distribution of the carbonate species as percentages of total dissolved

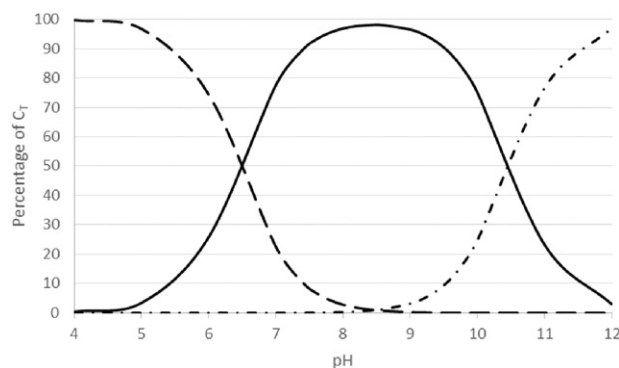


Fig. A.1. Distribution of carbonate species as percentages of total dissolved inorganic carbon in relation to solution pH. The values are calculated for fresh water (salinity = zero) and a temperature of 10 °C. Long-dashed line: $\text{CO}_{2(aq)}$; solid line: HCO_3^- ; dash-dot line: CO_3^{2-} .

inorganic carbon in relation to solution pH calculated at 10 °C and one atm. total pressure.

Depending on the type of soil and rock that has reacted with the groundwater, the pH value of groundwater typically ranges from about 6.0 to 8.5. As shown in the figure, for the pH range of 6.0 to 8.5, the contribution of CO_3^{2-} to the DIC is negligible. Therefore, in most situations encountered in the study of carbon isotopic composition of DIC in ground water, the predominant dissolved species in DIC are $\text{CO}_{2(aq)}$ and HCO_3^- , i.e. $\text{DIC} \approx \text{CO}_{2(aq)} + \text{HCO}_3^-$. For general discussions on the carbon isotopic composition of water we refer the reader to [Clark and Fritz, 1997](#); [Deines et al., 1974](#); [Wigley et al., 1978](#); [Mook \(2000\)](#), Vol. I, Chapter 9 “The chemistry of carbonic acid in water”; [Mook \(2006\)](#); [Plummer and Glynn \(2013\)](#), Chapter 4; [Wigley et al., 1978](#).

Appendix B. De-normalization of ^{14}C data and use of radiocarbon calibration in hydrological investigations

Radiocarbon dating of a carbonaceous sample can be done by measuring its ^{14}C content and comparing the result to the value of a ^{14}C standard of zero age using the equation:

$$t = -\frac{t_{1/2}}{\ln 2} \ln \left(\frac{^{14}\text{C}_{\text{sample}}}{^{14}\text{C}_{\text{std}}} \right) \quad (\text{B.1})$$

where t is the age of the sample; $t_{1/2}$ is the ^{14}C half-life; $^{14}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{std}}$ are the ^{14}C contents of the sample and standard, respectively.

The principle of radiocarbon dating, as represented by Eq. (B.1), is straightforward. However, before interpreting the age calculated by Eq. (B.1), several factors need to be taken into account to understand what the results actually mean.

Carbonaceous samples, such as samples of wood grown at the same time, assimilate the same atmospheric CO_2 , but can have apparently different ages because, due to isotopic fractionation, the measured ^{14}C contents can differ between samples. A typical example of isotopic fractionation is the apparent difference in ^{13}C contents in C3 and C4 plants, though each type of plant grew at the same time and assimilated the same atmospheric CO_2 . Thus, in order to be able to calculate the ^{14}C age of carbonaceous material based on the measured ^{14}C content, the following question has to be answered: How do I know that the difference in ^{14}C is purely due to decay? A normalization procedure is used to answer this question. The procedure uses the measured ^{13}C and ^{14}C data from the same sample and corrects the measured ^{14}C content to the same ^{13}C content, namely, $\delta^{13}\text{C} = -25\%$ with respect to VPDB (Vienna Pee Dee Belemnite, a Cretaceous belemnite from the Pee Dee formation in South Carolina, USA).

In radiocarbon dating of carbonaceous materials in geological and archeological studies, in order that the results can be comparable, the following equation is used to calculate the conventional ^{14}C age

$$t = -\frac{5568}{\ln 2} \ln \left(\frac{{}^{14}\text{C}_{\text{sample}}}{{}^{14}\text{C}_{\text{std}}} \right) \quad (\text{B.2})$$

where 5568 is the ^{14}C half-life determined by Libby (Stuiver and Polach, 1977). ${}^{14}\text{C}_{\text{sample}}$ and ${}^{14}\text{C}_{\text{std}}$ are the ^{14}C content of the sample and standard and both are normalized for deviations of the measured $\delta^{13}\text{C}$ from -25‰ . ${}^{14}\text{C}_{\text{sample}}$ and ${}^{14}\text{C}_{\text{std}}$ are represented in the same unit. By assigning the age of the standard in the year 1950 AD to be zero, and its ^{14}C content to be 100% at age of zero (100% of modern carbon), the ratio ${}^{14}\text{C}_{\text{sample}}/{}^{14}\text{C}_{\text{std}}$ in Eq. (B.2) is defined as ‘percent of modern carbon’ (pMC). Under the assumption that any sample with age of zero should have a ^{14}C content of 100%, pMC represents the proportion of ^{14}C content in the sample compared to its initial ^{14}C content (at age of zero in the year 1950 AD). Thus, with the unit pMC, the age of the sample calculated by using Eq. (B.2) is relative to 1950 AD, i.e. a sample from a tree that died in the year 1450 AD would have a ^{14}C age of 500 radiocarbon years (i.e. conventional radiocarbon age) BP (before present, i.e., years before 1950 AD).

To obtain calendar year ages, the conventional ^{14}C age calculated by using Eq. (B.2) is corrected and calibrated because: (1) Libby’s ^{14}C half-life has been revised to 5730 years (Godwin, 1962), and (2) the level of ^{14}C in the biosphere has not always been the same (i.e. ${}^{14}\text{C}_{\text{std}}$ in Eq. (B.2) has not always been 100 pMC) (de Vries, 1958; Stuiver et al., 1986; Bard et al., 1990, 1993).

Many calibration curves have been published using a variety of methods. Fig. B.1 is an example of a calibration curve. Because the calibration curves are obtained by first using the Libby half-life (Eq. (B.2)), using the Libby half-life has the advantage of maintaining consistency with the early papers, and also avoids the risk of a double correction for the Libby half-life value. Use of radiocarbon calibration corrects radiocarbon years to calendar years. In Fig. B.1, the point represents the ^{14}C age of the sample before (the conventional ^{14}C age) and after (the calendar age) correction. As can be seen in this

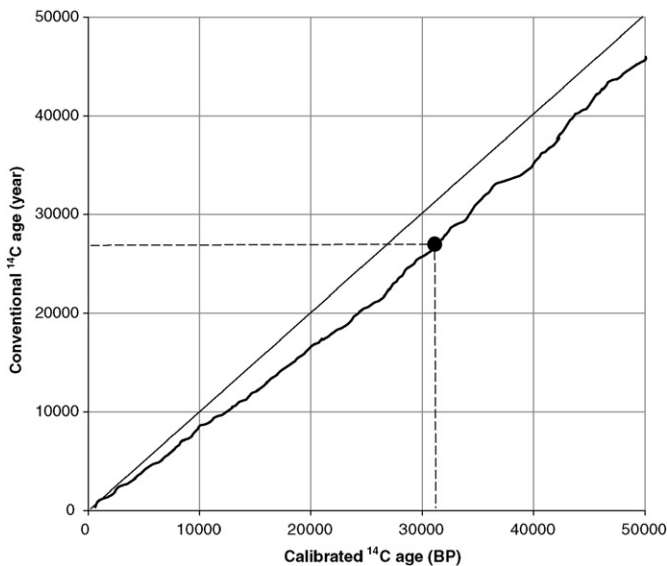


Fig. B.1. Curve for calibration of ^{14}C dates. This curve is for the northern hemisphere. (Reimer et al., 2013). The point “●” represents the ^{14}C ages of a sample before correction (i.e. conventional radiocarbon age, calculated by using Eq. (B.2) with the assumptions that the half-life of ^{14}C is 5568 years and the initial ^{14}C level is 100 pMC), and after correction (i.e. calendar age, based on other chronologies like tree ring, coral reef and lake varve records). The diagonal line shows where the curve would lie if the conventional ages and calendar ages were the same.

example, the age difference before and after correction is 31,200–26,900 = 4300 years. A common reference point is the last glacial maximum (LGM) which occurred at about 18,000 radiocarbon years BP, equivalent to about 22,000 calendar years BP (Fig. B.1).

In radiocarbon dating of carbonaceous material, it is standard practice to normalize ^{14}C measurements to a common $\delta^{13}\text{C}$ value of -25‰ , correcting for *in-vivo* fractionation processes that affect both ^{13}C and ^{14}C (Stuiver and Polach, 1977; Stuiver, 1980; Donahue et al., 1990; Mook and der Plicht, 1999). The conventional radiocarbon age does not account for reservoir effects (Stuiver, 1980). It assumes that all the samples obtain their carbon from the same carbon source (i.e. atmospheric CO_2). The conventional radiocarbon age applies best to dating of wood or other forms of carbonaceous material, or to dating of dissolved inorganic carbon (DIC) in some ground-water systems where the initial ^{14}C activity during recharge is near modern and geochemical reactions affecting DIC in the aquifer can be ignored, such as in some silicate aquifers. But more often, the conventional radiocarbon age is biased old in the dating of DIC in ground water due to geochemical reaction effects (reservoir effects). As can be seen in Fig. 1 (see the main paper), in most geochemical processes (as illustrated by the arrows), quite the contrary to *in-vivo* fractionation processes, $^{14}\text{C}_{\text{DIC}}$ decreases with increasing $\delta^{13}\text{C}_{\text{DIC}}$ (e.g., dissolution of carbonate rocks in ground-water, a non-fractionating process), and vice versa (e.g. carbon exchange between gaseous soil CO_2 and dissolved HCO_3^-).

In cases in which the $\delta^{13}\text{C}$ of DIC is significantly affected by water-rock reaction, it is recommended to “de-normalize” the commonly-reported normalized ^{14}C activity (Mook and der Plicht, 1999). For measurements based on the $^{14}\text{C}/^{12}\text{C}$ ratio, the normalized ^{14}C activities can be converted to non-normalized values in percent modern carbon (denoted here as “pmc”) by the equation (Mook and der Plicht, 1999),

$$\text{pmc} = \text{pMC} \left[\frac{\left(1 + \frac{\delta^{13}\text{C}_{\text{DIC}}}{1000} \right)}{0.975} \right]^2,$$

where pmc is the measured ratio ${}^{14}\text{C}_{\text{sample}}/{}^{14}\text{C}_{\text{std}}$ in Eq. (B.1) (in percent) before normalization, pMC is the commonly-reported normalized ^{14}C activity represented in percent of modern carbon, and $\delta^{13}\text{C}_{\text{DIC}}$ is the $\delta^{13}\text{C}$ of the DIC in per mil. For ^{14}C measurements based on the $^{14}\text{C}/^{13}\text{C}$ ratio,

$$\text{pmc} = \text{pMC} \left[\frac{\left(1 + \frac{\delta^{13}\text{C}_{\text{DIC}}}{1000} \right)}{0.975} \right].$$

In terms of pmc, Eq. (1) (see the main paper) becomes:

$$t = -\frac{5730}{\ln 2} \ln \left(\frac{{}^{14}\text{C}_{\text{DIC,pmc}}}{{}^{14}\text{C}_{0,\text{pmc}}} \right) \quad (\text{B.3})$$

where 5730 is the Cambridge half-life of ^{14}C (Godwin, 1962). ${}^{14}\text{C}_{\text{DIC,pmc}}$ is the ^{14}C content of the sample before normalization (or, de-normalized). ${}^{14}\text{C}_{0,\text{pmc}}$ is the initial ^{14}C content of the DIC (a carbon reservoir that is different to the atmospheric CO_2). In Eq. (B.3), ${}^{14}\text{C}_{0,\text{pmc}}$ is a function of many measured and assumed data/parameters, namely, ${}^{14}\text{C}_{0,\text{pmc}} = f({}^{14}\text{C}_g, \delta^{13}\text{C}_g, \delta^{13}\text{C}_{\text{DIC}}, \text{etc.})$. Usually, ${}^{14}\text{C}_{0,\text{pmc}}$ is determined by using an adjustment model applied to non-normalized values (e.g. ${}^{14}\text{C}_g, \delta^{13}\text{C}_g, \delta^{13}\text{C}_{\text{DIC}}$ are not normalized to $\delta^{13}\text{C} = -25\text{‰}$). The calculated age of the sample is relative to 1950 AD.

Although the correct half-life of 5730 years is used and corrections for the reservoir effect are accounted for in Eq. (B.3), depending on the water ages and goal of the research, there may be a need for ^{14}C age calibration, for the following reasons: (1) the older the waters are, the greater the uncertainty will be in the calculated ^{14}C ages from

Eq. (B.3); (2) groundwater flow models are more accurate if calibrated in calendar years rather than radiocarbon years; particularly for paleowaters (see Appendix A.3 in Chapter 4 of Plummer and Glynn, 2013); (3) two factors may affect age estimation uncertainty—(a) First, $^{14}\text{C}_0$ is calculated by using an adjustment model, in which the initial ^{14}C content is calculated using $\delta^{13}\text{C}_g$. Thus, the results may depend on the assumed $\delta^{13}\text{C}_g$. For example, $\delta^{13}\text{C}_g$ may change in response to climatic variations that cause changes in the relative proportions of plants utilizing the C3 and C4 photosynthetic pathways (Plummer and Sprinkle, 2001; Plummer and Glynn, 2013); (b) Second, although theoretically it is possible to assume a 'correct' $^{14}\text{C}_g$ value for the recharge area (a value that may be greater or smaller than 100 pmc for de-normalized values), however, in reality we do not know the (calibrated or calendar age) $^{14}\text{C}_g$ value in the past.

It is difficult to correct for the uncertainty caused by uncertainty in $\delta^{13}\text{C}_g$ assumption. However, as an approximation, we can avoid/correct for the uncertainty caused by assumption of $^{14}\text{C}_g$, by (1) assuming that $^{14}\text{C}_g$ is 100 pmc in the adjustment model, (2) using the Libby half-life value of 5568 years instead of 5730 years in Eq. (B.3), and (3) applying ^{14}C age calibration. Thus, by applying a radiocarbon calibration a calendar age relative to 1950 AD can be estimated (see for example Plummer and Glynn, 2013) which can be translated into a time period between point of recharge and sample location.

Appendix C. Step by step guide to selecting appropriate model(s) for the groundwater system

Step 1: Determine/assume the key ^{14}C and $\delta^{13}\text{C}$ values for the system. The key values include carbon isotopic compositions of the soil gas CO_2 , the carbonate rocks, temperature, pH, etc.

Step 2: Calculate values of ^{14}C and $\delta^{13}\text{C}$ for points A1 (using Eqs. (3) and (4)), A2 (using Eqs. (12) and (13)), O (using Eqs. (24) and (25)) and M' (using Eqs. (17) and (18)).

Step 3: Using the values calculated in Step 2 draw the Han & Plummer diagram specific to the system studied (Han et al., 2012, 2014; Han and Plummer, 2013).

Step 4: Plot the samples using determined values of ^{14}C , $\delta^{13}\text{C}$ and DIC (or HCO_3^-) concentration in the Han & Plummer diagram.

Step 5: Analyze the data ($^{14}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DIC}}$ and $\text{DIC}/\text{HCO}_3^-$) using the Han & Plummer diagram (see e.g. Figs. (10) and (11)). Refer to Table 3 to transform/convert the information (i.e. changes in $^{14}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DIC}}$ and $\text{DIC}/\text{HCO}_3^-$) into geochemical process(es) and hydrogeological environments.

Step 6: Referring to Fig. 10 decide which single-sample-based model best applies.

Step 7: If the ^{14}C and $\delta^{13}\text{C}$ data show a curved relationship, try the extended Gonfiantini & Zuppi's model and compare the results with those obtained from other single-sample-based model(s).

Step 8: If none of the single-sample-based models can be used and the extended Gonfiantini & Zuppi's model fails, consider (1) the water sample to be a mixture of waters that have distinctly different ages, or (2) the water has been affected by processes more complicated than listed in Table 3. Turn to geochemical modeling for detailed analysis. (See for example Plummer et al., 1983; Plummer et al., 1994; Parkhurst and Charlton, 2008; Coetsiers and Walraevens, 2009; El-Kadi et al., 2011; Parkhurst and Appelo, 2013; Blaser et al., 2010; Plummer and Glynn, 2013).

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