



RESEARCH ARTICLE

# Estimation of Groundwater Residence Time Using Radiocarbon and Stable Isotope Ratio in Dissolved Inorganic Carbon and Soil CO<sub>2</sub>

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## Abstract

Estimation of residence time of groundwater, particularly in regions with inadequate surface waters are very important for formulating sustainable groundwater management policies. We developed a technique for extracting dissolved inorganic carbon (DIC) quantitatively from water for measuring its <sup>14</sup>C contents and presented the analytical details here. We also measured stable carbon isotope ratio ( $\delta^{13}\text{C}$ ) in soil CO<sub>2</sub> and groundwater DIC to correct the groundwater <sup>14</sup>C ages. In addition, <sup>14</sup>C in soil CO<sub>2</sub> were measured for making necessary correction in the initial activity of the recharging water. The corrected <sup>14</sup>C contents in the groundwater samples were used to estimate their residence times employing Lumped Parameter Models (LPM), a set of mathematical models to account for the processes that take place during transport from the recharge to the sampling spots. We present a case study focused on the calculation of radiocarbon ages and residence times for a groundwater sample collected from the campus of Physical Research Laboratory in Ahmedabad, Gujarat, India. The study also includes estimations of groundwater residence times using previously measured <sup>14</sup>C ages of groundwater samples from Gujarat, India. Various factors controlling the groundwater ages in the LPM and their applicability are discussed.

## 1. Introduction

Detailed knowledge of groundwater residence time is crucial for groundwater management, especially in regions with arid, semi-arid, and sub-humid climates where surface waters resources are inadequate to meet the day-to-day demand. In addition, contamination and risk assessment depend strongly on the residence time of groundwater. Groundwater residence time in an aquifer is the average time taken by a water molecule to travel from the recharge to the exit or monitoring site of the aquifer. Radiocarbon (<sup>14</sup>C) in dissolved inorganic carbon (DIC) is widely used to understand groundwater dynamics including estimation of its residence time, recharge and flow rates (Clark and Fritz 1997; Kalin 2000; Hamed et al. 2008; Iverach et al. 2017; Priestley et al. 2017; Herrera et al. 2021). With the development of accelerator mass spectrometry (AMS), precise determination of the ratios of <sup>14</sup>C/<sup>12</sup>C and <sup>14</sup>C/<sup>13</sup>C in sub milligram of carbon made it a popular technique for dating water samples. <sup>14</sup>CO<sub>2</sub> gets incorporated into groundwater through dissolution of CO<sub>2</sub> from the atmosphere and soil during recharge. Soil CO<sub>2</sub> mainly governs the DIC concentration of the recharging water while passing through the unsaturated zones as CO<sub>2</sub> concentration is very high in this zone due to root respiration and microbial decomposition of organic matter. Once water percolates down to the unsaturated zone, DIC becomes isolated from the modern <sup>14</sup>C and decays with time. Therefore, measurement of <sup>14</sup>C in groundwater can give an estimate of the age of the water. <sup>14</sup>C contents can be measured with a precision better than 1%.

Soil CO<sub>2</sub> is mainly controlled by decomposition of recent organic matter and root respiration and hence mostly modern in <sup>14</sup>C content although decomposition or oxidation of old organic matter may contribute significantly in some specific cases (Magnone et al. 2019). If a significant fraction of old carbon contributes to the DIC in recharge zone, the age of the groundwater will be overestimated. This needs to be ascertained and corrected wherever required. Contrarily, addition of post 1950 CE bomb carbon, released to the atmosphere due to nuclear weapon testing can lead to underestimation of the groundwater ages. Recent addition of carbon in groundwater DIC can be assessed measuring tritium in the same groundwater (Telloli et al. 2022). Potential <sup>14</sup>C contamination particularly, incorporation of atmospheric CO<sub>2</sub> in the aquifer and poor constraints on the sources of DIC in groundwater often leads to large uncertainty in <sup>14</sup>C content (Plummer and Glynn 2013; Han and Plummer 2016; Campeau et al. 2017) and lowering in the upper limit of the estimated radiocarbon ages of groundwater to less than 30 ka (Kalin 2000; Clark 2015), which is still good enough for most of the regional aquifers. Additionally, when aquitards store significant amount of water with different water transport rates and hence <sup>14</sup>C content, estimated groundwater ages may deviate significantly depending on the ratio of the fluid volume in aquitards to aquifers (Bethke and Johnson 2002). Therefore, precautions need to be taken to account the exchange with the aquitards while estimating age of groundwater.

The objectives of the present study are to develop a simple method for extracting CO<sub>2</sub> from groundwater DIC and measuring its <sup>14</sup>C contents and estimation of its residence time using various correction schemes and models. The correction schemes include estimating the contribution of DIC from carbonate rocks using δ<sup>13</sup>C in DIC and initial <sup>14</sup>C correction in the recharging water by measuring the <sup>14</sup>C in soil CO<sub>2</sub>, the main component of the groundwater DIC. Finally, the corrected <sup>14</sup>C ages of the DIC were used to estimate groundwater residence time using Lumped Parameter Models (LPM) that take care of the advection and dispersion during transit from the recharge to the monitoring site.

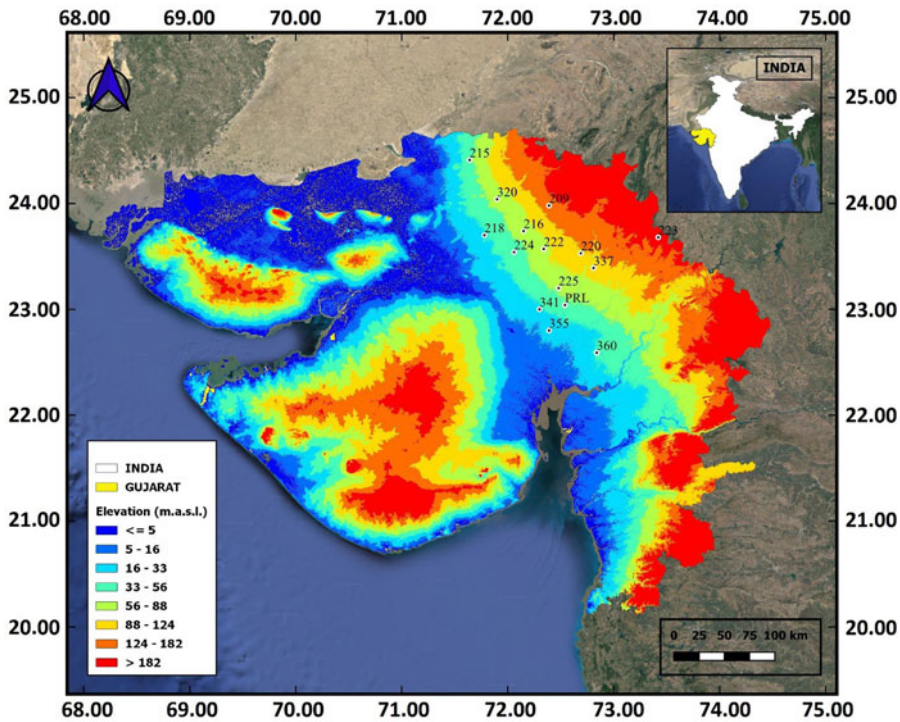
## 2. Materials and Methods

### 2.1. Groundwater and Soil CO<sub>2</sub> Sampling

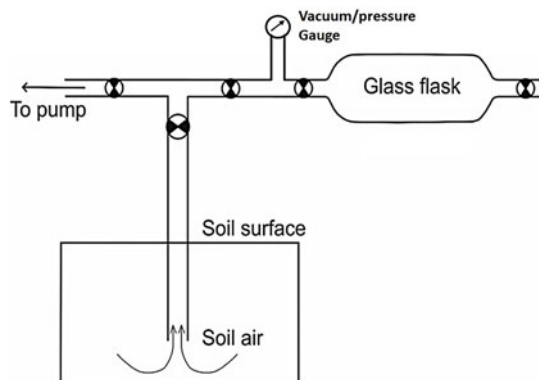
For demonstrating the performances of the developed techniques for <sup>14</sup>C and δ<sup>13</sup>C analysis in DIC and soil CO<sub>2</sub>, we carried out sampling and analysis of groundwater and soil CO<sub>2</sub> from the campus of Physical Research Laboratory (PRL) (Figure 1). Groundwater was collected from a borewell sucking water from a depth of ~90 m from the surface. Water samples were collected in 60 mL polypropylene narrow mouth bottles (Tarson, Kolkata, India) directly from a pipe sucking the groundwater before falling on the reservoir from which water is distributed. For soil CO<sub>2</sub> collection, a homemade customized vacuum system with pumping arrangement was utilized as shown in Figure 2. A stainless-steel pipe (~2 cm diameter) was introduced into the soil to the depth from which the soil air was to be collected. The soil material inside the pipe was removed and a new empty pipe was introduced into the hole. The empty spaces on the sides of the pipe were packed with soil materials to avoid contact with atmospheric air. The glass flask along with the pipeline was evacuated using a rotary vacuum pump. The flask was then filled to 1 atmosphere with the soil air from the desired depth, the pressure inside the flask was monitored using a pressure gauge. More details about the soil CO<sub>2</sub> extraction system are provided elsewhere (Mohanty et al. in preparation).

### 2.2. CO<sub>2</sub> Extraction from DIC of Groundwater

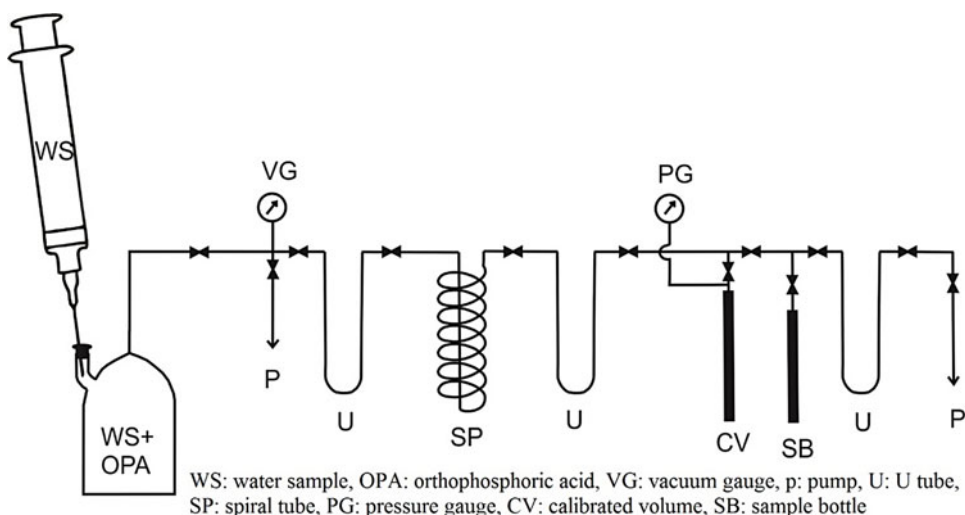
A schematic diagram for the extraction of DIC from water is shown in Figure 3. The extraction system was modified from some existing techniques (e.g., Carmi et al. 2007; Macchia et al. 2013; Ge et al. 2016; Takahashi et al. 2021). About 10 mL commercial orthophosphoric acid (85%) was taken in a flask of ~1 L capacity and was evacuated to ~1 × 10<sup>-2</sup> mbar. Using a syringe, 20–200 mL water was introduced into the flask. The amount of water for reaction depends on the concentration of DIC. The



**Figure 1.** Location for the groundwater sampling site, the campus of the Physical Research Laboratory (PRL). Locations of the sampling sites whose groundwater samples were dated previously by Agarwal et al. (2006) are also shown (the site number were taken from their published article). Samples with radiocarbon ages neither modern nor beyond radiocarbon dating limit are listed here.



**Figure 2.** Soil air sampling setup. The soil air samples are collected from a specific soil depth introducing the pipe to that depth and filling the pre-evacuated high vacuum glass flask.

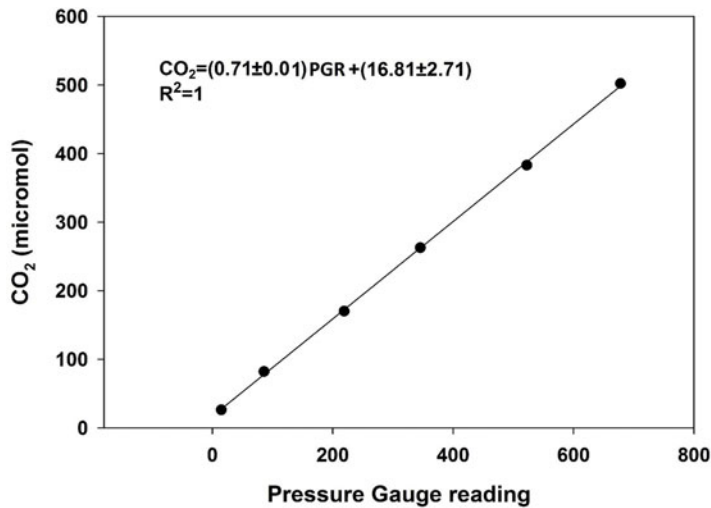


**Figure 3.** Glass vacuum line used for extraction of carbon dioxide from dissolved inorganic carbon and soil  $\text{CO}_2$ . Water samples are injected into the sample flask, reacted with orthophosphoric acid under vacuum, passed through tubes immersed in slush ( $-80^\circ\text{C}$ ) and liquid nitrogen ( $-196^\circ\text{C}$ ) and finally collected in the sample bottle.

flask was heated to  $\sim 60^\circ\text{C}$  using a hot plate and a magnetic stirrer was used for fast reaction and release of  $\text{CO}_2$ . The reaction was allowed to proceed for 15–20 minutes. The liberated  $\text{CO}_2$  was passed through a series of three U-tubes with first one immersed in alcohol-liquid nitrogen slush kept at  $-80^\circ\text{C}$  and the subsequent two in liquid nitrogen ( $\text{LN}_2$ ) at  $-196^\circ\text{C}$ . The U-tube immersed in the slush, trapped most of the moisture while  $\text{CO}_2$  passed through it and freezes in the two  $\text{LN}_2$  traps. One of the  $\text{LN}_2$  traps was a spiral tube to increase the  $\text{CO}_2$  freezing efficiency (Figure 3). The extracted  $\text{CO}_2$  was cleaned by freeze and thaw technique a few times while transferring from one trap to the other to remove remaining traces of water and other impurities. The amount of  $\text{CO}_2$  liberated was measured by expanding it in a calibrated volume connected to a pressure gauge. Finally, pure  $\text{CO}_2$  was collected in the pre-evacuated high vacuum glass ampule to load into the graphite preparation system. The complete extraction of  $\text{CO}_2$  from a water sample takes almost an hour. The vacuum system takes an additional half an hour for cleaning by pumping between two samples.

### 2.3. Estimation of $\text{CO}_2$ Yield from DIC

The liberated  $\text{CO}_2$  from the water samples was allowed to expand in a pre-calibrated volume attached to a pressure gauge (Setra DATUM 2000<sup>TM</sup>) to measure the  $\text{CO}_2$  content and hence DIC concentration in the sample. The gauge and attached volume were calibrated using pure  $\text{Na}_2\text{CO}_3$  powder. Precisely weighed  $\text{Na}_2\text{CO}_3$  was reacted with orthophosphoric acid in the flask at  $60^\circ\text{C}$  for half an hour and the liberated  $\text{CO}_2$  was extracted following the procedure discussed above. The amount of  $\text{Na}_2\text{CO}_3$  reacted varied from 2 to 53 mg. The liberated  $\text{CO}_2$  was expanded in the volume attached to the gauge and a calibration curve was prepared by plotting the amount of  $\text{CO}_2$  in micromole against the gauge reading (Figure 4). The amount of liberated  $\text{CO}_2$  in micromole was calculated from the actual weight of the  $\text{Na}_2\text{CO}_3$  powder used in the reaction. The amount of  $\text{CO}_2$  liberated from any sample with unknown concentration can be estimated directly from the gauge reading using the equation shown in Figure 4.



**Figure 4.** Calibration plot used for estimating the amount of CO<sub>2</sub> liberated from any sample.

#### 2.4. Extraction of CO<sub>2</sub> from Soil Air

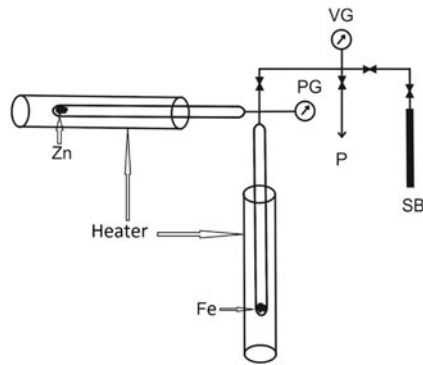
CO<sub>2</sub> from soil air for δ<sup>13</sup>C and <sup>14</sup>C measurements was extracted using the same glass vacuum line used for extracting DIC (Figure 3). Instead of using water flask, the glass flask containing soil air was connected and CO<sub>2</sub> was quantitatively extracted from the soil air using cryogenic technique. From the total amount of CO<sub>2</sub> and the volume of the flasks, the concentration of CO<sub>2</sub> was measured with a precision of ~1% (Mohanty et al. in preparation).

#### 2.5. Preparation of Standards

In absence of water standards for radiocarbon dating, we used carbonate standards for estimating the accuracy of the radiocarbon measurements for the present technique. The International Atomic Energy Agency's two carbonate standards viz. Carrara Marble (IAEA-C1) and Travertine (IAEA-C2) were used. The Carrara marble serves as background and Travertine has a radiocarbon content of  $41.14 \pm 0.03$  pMC (Rozanski 1991). The carbonate samples were finely powdered with agate-mortar and dried samples were loaded in the reaction flask followed by evacuation. About 20–30 mL of Milli Q water was introduced into the flask using a syringe through a rubber septum under vacuum condition. The carbonate powder was mixed with water to make the extraction procedure similar to that of water samples. About 5 mL orthophosphoric acid was then injected into the flask using a syringe. The CO<sub>2</sub> evolved was extracted following the same procedure as discussed for the water samples. This gives the estimate of the background and accuracy of the procedure followed for radiocarbon measurements in DIC samples.

#### 2.6. Graphite Preparation and <sup>14</sup>C Dating Using AMS

The purified CO<sub>2</sub> samples were converted into graphite using an in-house graphite preparation line (Figure 5). About 50 to 100 micromole CO<sub>2</sub> was transferred to a vacuum system in which pre-conditioned iron (~5 mg) and zinc (~25 mg) powders were loaded in the two arms of an L-shaped interconnected vacuum sealed quartz tubes (Jull et al. 1986). Iron and zinc powders were heated to appropriate temperatures for CO<sub>2</sub> reduction to elemental carbon (graphite) which deposit on the surface



**Figure 5.** Graphite preparation system. Fe: iron powder, Zn: zinc powder, PG: pressure gauge, VG: vacuum gauge, P: pump, SB: sample bottle to load CO<sub>2</sub> into the system.

of iron powder. Graphite precipitation using this technique takes 3 to 5 hours. The graphite-coated iron was then pressed into pellet and loaded into the source of the 1 MV accelerator mass spectrometer for <sup>14</sup>C measurements at Physical Research Laboratory (PRL) Ahmedabad, India (Bhushan et al. 2019). Using <sup>14</sup>C/<sup>12</sup>C or <sup>14</sup>C/<sup>13</sup>C for samples, ages were estimated (Donahue et al., 1990). Along with the samples, measurements of international standards such as Oxalic Acid I, Oxalic Acid II and background materials (anthracite) were made to estimate the background subtracted activity of samples and measure their radiocarbon ages. The ages were corrected for the isotopic fractionation during sample preparation and within the AMS (Donahue et al. 1990).

## 2.7. Radiocarbon Dating in Groundwater

Conventionally radiocarbon age (using Libby half-life of 5568 yr) of any sample is calculated using the basic decay equation given by

$$t = -\frac{5568}{\ln(2)} \ln\left(\frac{A}{A_0}\right) \quad (1)$$

Where A is the activity measured in a sample and A<sub>0</sub> is the initial activity. These activities are corrected for isotopic fractionation also called normalized activities (Stuiver and Polach 1977) “Closed system” is a basic requirement for radiocarbon age determination i.e., the system should remain closed to subsequent gains or losses of the carbon except through radioactive decay. However, most of the natural samples particularly subsurface water samples experience many physical and chemical processes and mixing with many different water channels during transport and within the aquifers altering the radiocarbon contents (Plummer and Glynn, 2013 and references therein). Decomposition of old organic matter or dissolution of carbonates may cause incorporation of DIC into groundwater in addition soil CO<sub>2</sub>. These two components might have different <sup>14</sup>C content compared to the original groundwater. In such cases actual <sup>14</sup>C content present in a groundwater sample can be different from that attained just by decay of the original <sup>14</sup>C content of the sample. Though, there is no standard way to correct for the incorporation of carbon from the surroundings, some schemes for radiocarbon age corrections in groundwater samples are discussed below.

If DIC in groundwater is solely derived from atmospheric CO<sub>2</sub> and/or the modern soil CO<sub>2</sub> and no mixing with other flow paths or incorporation of carbon from other sources take place, the determined



age will be close to its exact value. It is to be noted that the determined age should be corrected for age of the soil CO<sub>2</sub> particularly when the ages of CO<sub>2</sub> in the unsaturated zone are significantly old or if a significant fraction of carbon is originated from the post 1950 CE atmosphere (bomb carbon). For example, <sup>14</sup>C content of the soil CO<sub>2</sub> at Ti Tree (Australia) at a depth of 10 m is ~50 pMC though it is close to 100 pMC near the surface (Wood et al. 2015). Low <sup>14</sup>C contents in soil CO<sub>2</sub> in deeper soil layers were also observed at Saskatoon (Canada), North Dakota and Nevada (USA) (Bacon and Keller 1998; Thorstenson et al. 2016; Haas et al. 2016). On the other hand, presence of bomb carbon in unsaturated zone CO<sub>2</sub> or in organic matter (e.g., Blume et al. 2022; Laskar et al. 2012) may lead to underestimation of groundwater ages if not corrected. In most of the studies related to the groundwater dating, <sup>14</sup>C content in CO<sub>2</sub> in the unsaturated zone is assumed to be modern which may lead to significant discrepancies between the actual and measured ages. The <sup>14</sup>C contents are also expressed as percent modern carbon pMC = (A/A<sub>0</sub>)100% or in the form of delta notation such as D<sup>14</sup>C = (A/A<sub>0</sub>-1)1000‰ and or fraction modern F<sup>14</sup>C = A/A<sub>0</sub>. A sample with pMC greater than 100% or positive D<sup>14</sup>C or F<sup>14</sup>C greater than 1 indicate presence of bomb carbon.

Incorporation of carbon with different <sup>14</sup>C signature in groundwater DIC pool in some cases can be corrected using stable carbon isotope ratio (δ<sup>13</sup>C) in DIC as follows. Average δ<sup>13</sup>C values of C3 and C4 vegetation are ~ -27‰ and -13‰, respectively (Deines 1980; Khon 2010). The organic carbon present in soil under a particular vegetation type has similar or slightly enriched δ<sup>13</sup>C values (Laskar et al. 2010, 2013, 2016). The enrichment is due to incorporation of <sup>13</sup>C depleted CO<sub>2</sub> in the atmosphere during the industrial era (Suess Effect) (McCarroll and Loader 2004; Paul et al. 2020) and preferential removal of lighter carbon during decomposition by microbes (Laskar et al. 2016). Soil CO<sub>2</sub> has a δ<sup>13</sup>C value controlled by the decomposition of organic matter, root respiration and diffusive fractionation. As soil CO<sub>2</sub> mainly controls the DIC contents in the groundwater, its δ<sup>13</sup>C value can be used to estimate its fraction in DIC taking into account the appropriate fractionation factor (Szaran 1997). Therefore, by measuring δ<sup>13</sup>C values in soil CO<sub>2</sub> in recharge region and in DIC, contribution from other sources (bedrock) can be estimated and corrected for the <sup>14</sup>C activity in the sample. If <sup>14</sup>C dilution is caused by dissolution of carbonate of marine origin, the correction can be relatively easily made using δ<sup>13</sup>C values as these carbonates are free from <sup>14</sup>C and their δ<sup>13</sup>C values are 0 ± 2‰ (Ripperdan 2001) which is very different from soil CO<sub>2</sub> (~ -20‰). On the other hand, if dissolution takes place from soil carbonates formed by evaporation or lacustrine carbonates it may be difficult to estimate the contributions simply using δ<sup>13</sup>C of DIC due to weak constraints and possible overlapping in the range of their δ<sup>13</sup>C values with that dissolved from soil CO<sub>2</sub>. In addition, groundwater does not flow like the flow in a tube (piston flow), but encounter dispersion, advection and mixing making it a more complex system. Therefore, appropriate models are required to handle those mixing issues as discussed in Section 2.8.

A simple approach for correction of <sup>14</sup>C age in groundwater due to contamination from carbonate dissolution and decomposition of old organic matter is as follows. Suppose a groundwater sample is diluted due to incorporation of carbon from bedrocks and q is the dilution factor (see Equation 3 below), then the <sup>14</sup>C activity in the recharge area would be qA<sub>0</sub>, and the corresponding radiocarbon age of such a groundwater, as discussed elsewhere (e.g., Clark and Fritz 1997; Aggarwal et al. 2006; Cartwright 2020) would be

$$t = -\frac{5568}{\ln(2)} \ln\left(\frac{A}{qA_0}\right) \quad (2)$$

Unfortunately, determination of the dilution factor q is challenging in most of the cases. In case of dilution by marine carbonate under closed condition, the dilution factor q can be calculated using the following two-component isotopic mass balance equation:

$$\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{carb}} \times q + \delta^{13}\text{C}_{\text{recharge}} \times (1 - q) \quad (3)$$

where δ<sup>13</sup>C<sub>DIC</sub>, δ<sup>13</sup>C<sub>recharge</sub> and δ<sup>13</sup>C<sub>carb</sub> are the δ<sup>13</sup>C values observed in the DIC in the groundwater, DIC of recharging water and carbonate rocks in the aquifers, respectively. δ<sup>13</sup>C<sub>recharge</sub> can be obtained

from the  $\delta^{13}\text{C}$  value of soil  $\text{CO}_2$  as  $\delta^{13}\text{C}$  in bicarbonate (most of the DIC at neutral pH) is  $\sim 7.4\%$  higher than  $\delta^{13}\text{C}$  value of the soil  $\text{CO}_2$  at  $30^\circ\text{C}$  (Vogel et al. 1970; Mook et al. 1974; Deines et al. 1974; Szaran 1997). In the above isotopic mixing calculation (Equation 3), contribution from atmospheric  $\text{CO}_2$  is neglected because of the fact that most of the dissolution of  $\text{CO}_2$  in groundwater takes place in the unsaturated zone due to high concentration of  $\text{CO}_2$  in the latter. Soil  $\text{CO}_2$  from decomposition/oxidation of old organic matter if significant can be corrected using the  $^{14}\text{C}$  in soil  $\text{CO}_2$  in the recharge areas. The values of  $q$  can also be calculated from major ion geochemistry, graphical techniques and isotopic mass balance as discussed by many previous researchers (e.g., Vogel and Ehhlalt 1963; Vogel et al. 1970; Pearson and Hanshaw 1970; Mook 1972; Tamers 1975; Fontes and Garnier 1979; Clark and Fritz 1997; Geyh 2000; Agarwal et al. 2006; Coetsiers and Walraevens 2009; Blaser et al. 2010; Clark 2015; Han and Plummer 2016; Cartwright et al. 2020).

There can be more potential sources of DIC with different  $^{14}\text{C}$  content compared to the soil  $\text{CO}_2$  such as soil carbonate, carbonate nodules and addition of bomb carbon in groundwater which can alter the  $q$  value. Addition of such carbon in DIC would result in over or underestimation of groundwater residence time if not corrected. Estimation of the input of  $^{14}\text{C}$ -free DIC or any input into the DIC pool of an aquifer with different initial  $^{14}\text{C}$  content than the aquifer water is a major challenge in interpreting radiocarbon data in groundwater (Vogel and Ehhlalt 1963; Fontes 1992; Aravena et al. 1995; Kalin 2000; Coetsiers and Walraevens 2009; Han et al. 2012; Plummer and Glynn 2013; Han and Plummer 2016; Nydahl et al. 2020; Cartwright et al. 2020). As shown in Equation 3, for a two-component mixing, values of  $q$  may be calculated from the  $\delta^{13}\text{C}$  values of soil  $\text{CO}_2$ , DIC in groundwater and carbonate rocks (Pearson and Hanshaw 1970; Tamers 1975; Clark and Fritz 1997; Geyh 2000; Coetsiers and Walraevens 2009; Clark 2015; Han and Plummer 2016).

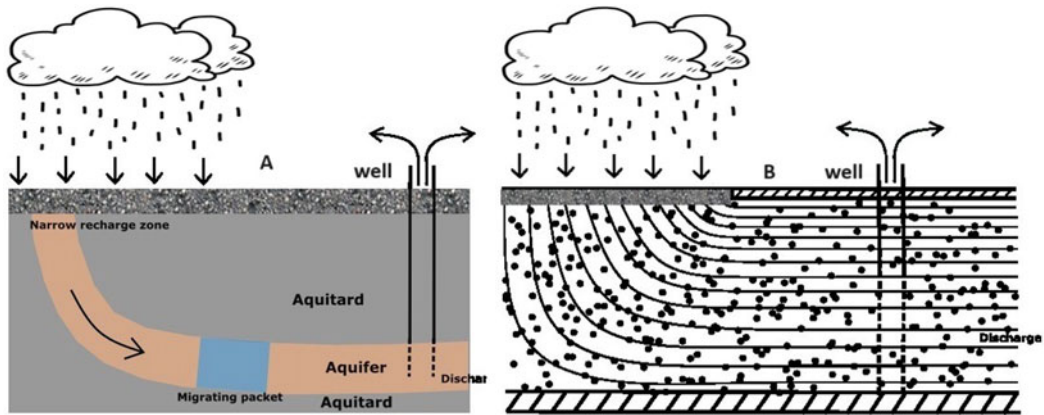
The ages estimated using decay equations (1 and 2) need to be converted into calendar ages using radiocarbon calibrations (e.g., Reimer et al. 2020; Hogg et al. 2020). Calibration is necessary to compare the obtained ages with other paleoclimate datasets. Other factors (e.g., hard-water effect) may cause erroneous estimation of radiocarbon ages and need to be carefully accounted before calibrations. The calibrated ages of groundwater can be considered as the residence times in some limited cases if all the water in an aquifer is recharged at the same time without much dispersion and advection during its transport. Hardly such simple systems exist as groundwater flows along paths of varying lengths and undergoes hydrodynamic dispersion and advection causing  $^{14}\text{C}$  content modification. In other words, a groundwater sample may contain many fractions of water from different origins and have a range of residence times rather than being of a single age (Maloszewski and Zuber 1982; Maloszewski 2000; Cox 2003; Suckow 2014).

## **2.8. Estimation of Residence Time of Groundwater Using Radiocarbon**

There is no standard way to account all the complexities discussed above. Researchers address these complexities using different models (Seltzer et al. 2021; Starn et al. 2021; Fareze et al. 2022). One approach is to use Lumped Parameter Models (LPM) (Maloszewski and Zuber 1982; Maloszewski and Zuber 1992; Maloszewski 2000; McGuire and McDonnell 2006; Jurgens et al. 2012; Cartwright et al. 2020) to estimate the groundwater residence times. LPM are mathematical models that deal with the transport of water from recharge zones to discharge regions based on aquifer geometry and flow configurations. The model's approach involves convolution of tracer input and decay functions with a weight factor and the obtained output is matched to a known time series (Maloszewski and Zuber 1982; Maloszewski et al. 2004). The models allow the variability of the  $^{14}\text{C}$  input, define a recharge zone, time taken by the water to penetrate the soil zone and the ratios of advection to dispersion. In other words, the model assumes more realistic and flexible flow path geometries, and the effects of dispersion may be taken into account to a large extent.

In the LPM, at steady state, the  $^{14}\text{C}$  content of groundwater  $^{14}\text{C}(t)$  at a time  $t$  in any outlet position in the aquifer can be calculated from the corrected  $^{14}\text{C}$  content of DIC in the recharging water ( $^{14}\text{C}_i$ ) using





**Figure 6.** Schematics of (A) piston flow model (after Bethke and Johnson, 2008) and (B) dispersion model (after Maloszewski and Zuber 1982).

exit age distribution function and the radioactive decay via the following convolution integral (Maloszewski and Zuber, 1982):

$${}^{14}C_t = \int_0^{\infty} C_i(t - \tau)g(\tau) \exp(-\lambda\tau)d\tau \quad (4)$$

Where  $\tau$  is the mean residence time,  $t - \tau$  is the time when the water recharged,  $\lambda$  is the decay constant and  $g(\tau)$  is the response function describing the distribution of flow paths and residence times in the aquifer. Depending on the aquifer geometries, different LPMs can be applied (e.g., Maloszewski and Zuber, 1982; Maloszewski and Zuber 1992; Amin and Campana, 1996; Cook and Bohlke 2000; Maloszewski 2000; Jurgens et al. 2012).

Here we used a tracer LPM program developed by Jurgens et al. (2012) to estimate the residence times of groundwater extracted from the PRL Campus. We also applied the LPM program on previously measured  ${}^{14}\text{C}$  ages in groundwater from different parts of Gujarat, Western India. We applied three different LPMs viz. piston flow model (PFM), dispersion model (DM) and binary mixing model (BMM) to show the variations in residence times under different dispersion and mixing parameters. Schematics of the PFM and DM are shown in Figure 6.

The PFM assumes that a tracer ( ${}^{14}\text{C}$ ) travels from the recharge area to the outlet position (e.g., a well) without mixing or hydrodynamic dispersion. For PFM, radiocarbon output for a constant input ( ${}^{14}\text{C}_i$ ), the solution of Equation (4) can be expressed as (Zuber and Maloszewski 2000):

$$C_{(t)} = C_i(t - \tau)\exp(-\lambda\tau) \quad (5)$$

The PFM is applicable to hydrogeologic settings with low dispersion, high linear velocity or short flow path from recharge to discharge region.  ${}^{14}\text{C}$  tracer can be assumed to follow piston-flow behaviour in shallow, short screened monitoring wells in unconfined aquifers or in confined aquifers with a relatively small recharge area.

The DM is based on a solution of a one dimensional advection dispersion equation for a semi-infinite medium with an instantaneous injection and detection of the tracer in the fluid flux. A solution for the Equation (4) for a constant input ( ${}^{14}\text{C}_i$ ) with advection and dispersion can be expressed as (Zuber and Maloszewski 2000):

**Table 1.** Yield of DIC extraction, measured using the present technique. Water samples with different DIC concentration are prepared by dissolving known amount of sodium carbonate. The solutions are then reacted with orthophosphoric acid and the amount of liberated CO<sub>2</sub> were measured. The measured amounts of CO<sub>2</sub> for different samples are compared to that actually present and the percentage yields are calculated

Sl no.	Weight in mg of Na <sub>2</sub> CO <sub>3</sub> dissolved	CO <sub>2</sub> expected in micromole	CO <sub>2</sub> obtained (micromole)	Yield (%)
1	23.45	221	224	101
2	28.42	268	241	90
3	36.24	342	331	97
4	23.95	226	200	89
5	27.8	262	265	101
6	30.96	292	270	93
7	25.34	239	242	101
8	27.47	259	261	101
9	28.57	270	274	102
10	17.97	170	171	101
11	15.0	142	143	101
Average yield ± 1σ				98 ± 5

$$^{14}\text{C}_t = ^{14}\text{C}_i \exp[(2P_D)^{-1} \times \{1 - (1 + 4\lambda P_D \tau)^{1/2}\}] \quad (6)$$

Where  $P_D$  is the dispersion parameter which is the reciprocal of Peclet number describing the relative importance of dispersion and advection. The Peclet number depends on the velocity of flow field and characteristics length of the system (Rapp 2017). The DM can give an approximate description of age distributions in samples from multiple aquifer configurations.

Binary mixing model (BMM) describes two-component mixtures in which each component can be obtained by a model. For example, a “BMM-PFM-DM” model describes a binary mixture in which one component of the mixture is modelled by using PFM ( $^{14}\text{C}_1$ ) and the other component by DM ( $^{14}\text{C}_2$ ) and the corresponding fractions are  $f_1$  and  $f_2(=1-f_1)$ . The output in a BMM is given by:

$$^{14}\text{C}_{\text{out}} = f_1 ^{14}\text{C}_1 + (1 - f_1) ^{14}\text{C}_2 \quad (7)$$

Binary mixing models can be appropriate for wells screened across multiple aquifer units and aquifers with short-circuit pathways that result in age mixtures of significantly different mean ages.

### 3. Results and Discussion

#### 3.1. Yield, Accuracy, and Reproducibility

The average yield of the DIC extraction of the present method is  $98 \pm 5\%$  (Table 1). The accuracy of measurements is estimated with IAEA standards Carrara Marble and Travertine (Table 2). Carrara marble is free of  $^{14}\text{C}$  and acts as a background while Travertine has a consensus radiocarbon content of  $41.14 \pm 0.03$  pMC. These carbonate standards are solid samples, but our actual samples are liquid. To make the processing of these solid standards identical with liquid samples, these samples were crushed and mixed with Milli Q water and then reacted with orthophosphoric acid. The measured  $^{14}\text{C}$  contents of Travertine is similar to the consensus value within the analytical uncertainty but it is slightly higher for the Carrara marble (background). The higher  $^{14}\text{C}$  content for the later is probably due to incorporation of air CO<sub>2</sub> into the MilliQ water, used with the carbonate powder for making the CO<sub>2</sub> extraction identical with the water samples. The effect of incorporation of air CO<sub>2</sub> significantly modified the  $^{14}\text{C}$  content of

**Table 2.** Radiocarbon dates of two international standards measured using the present technique (details of the standards are available in Rozanski et al. 1991)

Sample	Sample code	Measured $^{14}\text{C}$ activity (pMC)	Consensus $^{14}\text{C}$ activity (pMC)	
International Atomic Energy Agency (Vienna) standards				
IAEAC2	1	S31461/C2	$41.2 \pm 0.6$	$41.14 \pm 0.03$
Travertine	2		$41.8 \pm 0.6$	
	3		$41.6 \pm 0.6$	
	4		$40.7 \pm 0.6$	
IAEAC1	1	S51462/C1	$4.2 \pm 0.1$	$0.00 \pm 0.02$
Carrara Marble (background)	2		$2.3 \pm 0.8$	
	3		$2.9 \pm 0.2$	

the background sample (Carrara marble) but insignificant for relatively younger samples. The actual groundwater samples are expected to have less air  $\text{CO}_2$  contamination compared to these carbonate standards as they were carefully handled without exposing to the air.

The reproducibility of  $^{14}\text{C}$  measurements for the present technique has been estimated using multiple measurements of the groundwater samples collected from the PRL Campus. Radiocarbon age of this groundwater are presented in Table 3. The reproducibility of the radiocarbon age (standard deviation) for five PRL groundwater samples is  $\sim 160$  yr (Table 3).

### 3.2. Radiocarbon Age of PRL Groundwater

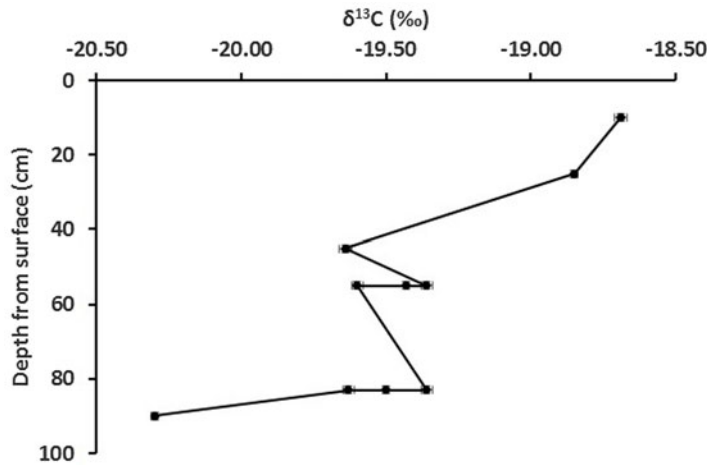
Groundwater samples collected from the PRL Campus were analyzed for  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  and are presented in Table 3. To constrain the contribution of soil  $\text{CO}_2$  in DIC, we measured the  $\delta^{13}\text{C}$  values in soil  $\text{CO}_2$  up to a depth of 90 cm inside the PRL campus.  $\delta^{13}\text{C}$  values and  $^{14}\text{C}$  ages of the soil  $\text{CO}_2$  are presented in Figure 7 and Table 4, respectively. Within the soil profile,  $\delta^{13}\text{C}$  varies between  $-18.7$  and  $-20.3\text{‰}$  with an average of  $-19.4 \pm 0.4\text{‰}$ . Considering the fractionation factor of  $7.4\text{‰}$  at  $30^\circ\text{C}$  (Szaran, 1997; Deines et al., 1974) between the  $\text{CO}_2$  and dissolved bicarbonate (dominant DIC species at a pH of  $\sim 7$ ),  $\delta^{13}\text{C}$  values in the latter is expected to be  $-12.1 \pm 0.4\text{‰}$ . However,  $\delta^{13}\text{C}$  values of the present groundwater varies between  $-8.8$  to  $-9.1\text{‰}$  indicating that the groundwater samples are significantly contaminated by carbon from other sources. We assume that the  $\delta^{13}\text{C}$  value in soil  $\text{CO}_2$  measured inside the PRL campus is the same as that in the recharge region as we do not see much spatial variation in the  $\delta^{13}\text{C}$  values of soil  $\text{CO}_2$  across Gujarat (Mohanty et al. in preparation). Assuming bedrock carbonates as the other contributor to the DIC (hard-water effect) with a  $\delta^{13}\text{C}$  value of  $\sim 0 \pm 2\text{‰}$  (Ripperdan 2001) and free from  $^{14}\text{C}$ , we correct its contribution to the radiocarbon ages calculating the factor  $q$  (Equation 3, Table 3). The factor  $q$  can also be affected by dissolution of soil carbonate from shallow zones with  $^{14}\text{C}$  content neither zero nor modern (e.g., Solder and Jurgens 2020) though the deep soil carbonates are mostly free from  $^{14}\text{C}$ . The contribution from soil carbonates and carbonate nodules are neglected in the present case as the contribution from dissolution of such carbonates in alluvial settings with relatively fast recharge is expected to be low. However, this needs to be tested measuring  $^{14}\text{C}$  content in soil DIC and soil carbonate. To validate the other assumption that the soil  $\text{CO}_2$  in the recharge zones that dissolves to from DIC, is modern, we measured the  $^{14}\text{C}$  content in soil  $\text{CO}_2$  at different depths inside PRL campus and found  $F^{14}\text{C}$  values in the range of 0.97 to 1 fraction modern or age from 0 to 210 BP with an average of 0.99 fraction modern or 90 BP in the top 90 cm of the soil profile (Table 4). Therefore, the  $^{14}\text{C}$  content of the soil  $\text{CO}_2$  in the recharge zone is mostly modern hence neglected in calculating the age of the groundwater.

**Table 3.** Radiocarbon ages of PRL groundwater samples (with Libby half-life). A  $\delta^{13}\text{C}$  value of soil  $\text{CO}_2$  of  $-19.4\text{‰}$  (average in the soil profile, see Table 4) is considered for the calculation. The median of the calibrated age is used for estimating mean residence time

Sample	$\delta^{13}\text{C}$ (VPDB)	Radiocarbon age (BP)	*Fraction of soil $\text{CO}_2$ contribution	†Corrected age (BP)
PRL-GW-S1	-9.1	5260 ± 40	0.75 ± 0.04	2880 ± 440
PRL-GW-S2	-8.9	5460 ± 50	0.74 ± 0.04	2970 ± 450
PRL-GW-S3	-8.9	5600 ± 40	0.74 ± 0.04	3110 ± 450
PRL-GW-S4	-8.8	5680 ± 70	0.73 ± 0.04	3080 ± 450
PRL-GW-S5	-8.9	5440 ± 120	0.73 ± 0.04	2840 ± 460
Average ± 1 $\sigma$	-8.9 ± 0.1	5490 ± 160	0.74 ± 0.08	2980 ± 110
Calibrated age range (calBP) (68.3%)			3340–3290 (8.3%)	
			3260–2990 (60.0%)	
			(Median: 3150)	
Mean residence time of PRL groundwater (in yr)				
Using piston flow model			Using dispersion model	
3240 (range: 3022–3432)			3360 (range: 3172–3547)	

\*Value of (1-q) in Equation (3).

†Correction is done using Equation (2).



**Figure 7.** Variation in  $\delta^{13}\text{C}$  in soil  $\text{CO}_2$  with depth in a soil profile inside the Campus of Physical Research Laboratory Ahmedabad.

The measured radiocarbon age of the PRL groundwater is  $5490 \pm 160$  BP (Table 3). This age is corrected using the measured  $\delta^{13}\text{C}$  value of the DIC and calculating the factor  $q$  (Equation 3 and Table 3). The corrected age is  $2980 \pm 110$  BP. This age is calibrated using OxCal version 4.4. The calibrated age of the PRL groundwater lies in the range of 2855 to 3442 cal BP with a median value of 3140 cal BP. The correction has been made using Equation (3). The mean residence times, calculated using the median of the calibrated age range are 3240 and 3360 yr, estimated by PFM and DM, respectively. For the DM, a dispersion parameter of 0.1 is assumed for the residence time calculation. This dispersion parameter corresponds to a Peclet number of  $\sim 10$  (see Section 3.3). A model estimated residence time is not a single value but a range with varying probability and the mean value is reported here.

### 3.3. Variation in Residence Times of Groundwater with Varying Radiocarbon Ages

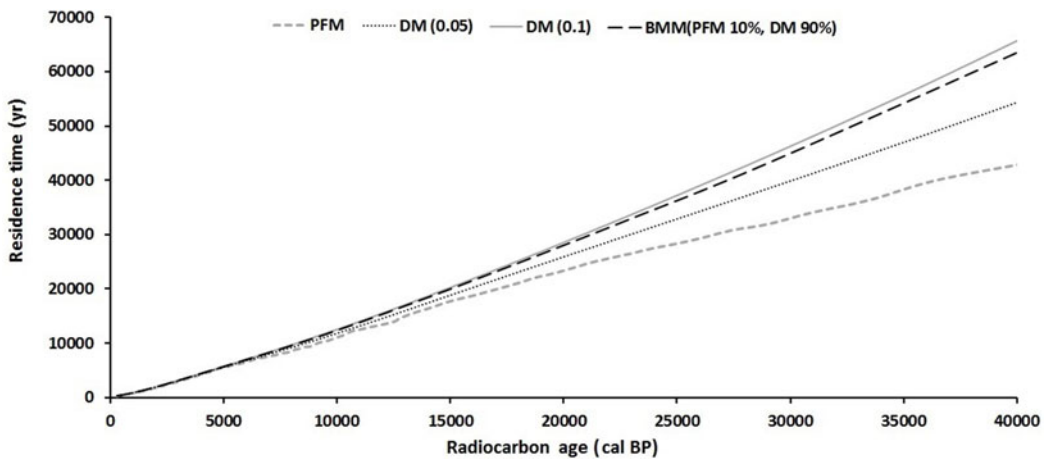
Variation in residence times of groundwater with variation in radiocarbon ages for PFM, DM and BMM are shown in Figure 8. The actual radiocarbon ages and the residence times obtained from PFM are not very different as in this model it is assumed that a water parcel once detached from the soil zone directly travels to the target site without significant advection and/or dispersion. However, water before reaching the target site of an aquifer, may encounter dispersion and advection causing significant change in its radiocarbon content which need to be taken into account before estimating its residence time. In the DM, these processes along the transport path and aquifer are taken into account by the dispersion parameter which is given by the inverse of Peclet number (Zuber and Maloszewski 2000). Peclet number for recharge patterns, topography and aquifer set up for the present case would vary in the range of 10–20 as discussed in Wilske et al. (2020) giving a dispersion parameter in the range of 0.05–0.1. For this range of dispersion parameters, the variation in the residence times of groundwater with radiocarbon ages are shown in Figure 8.

We also presented residence times estimated using a BMM with 10% contribution from PFM and 90% from DM with a dispersion parameter of 0.1. The BMM gives residence times intermediate of the PFM and DM (Figure 8). For radiocarbon ages of less than  $\sim 5000$  BP, the difference between the residences time estimated by various models is not significant and hence PFM or even the calibrated radiocarbon ages with proper corrections can represent the residence time. With increase in age, the deviation in the estimations of residence times increases compared to the radiocarbon ages or that

**Table 4.** Stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) and radiocarbon content ( $F^{14}\text{C}$ ) in soil  $\text{CO}_2$  at different depths in a soil profile from the Campus of Physical Research Laboratory. The reproducibility in  $\delta^{13}\text{C}$  measurement is  $\sim 0.1\%$ . 2 to 3 samples from the same depths (different samples) for some samples were collected, processed and analyzed for establishing the reproducibility of the method. Radiocarbon ages in BP are also presented

Depth (cm)	$\delta^{13}\text{C}$ (VPDB)	Radiocarbon content ( $F^{14}\text{C}$ )	Age in BP
10	-18.7	NM*	—
25	-18.8	$1.00 \pm 0.01$	$0 \pm 50$
45	-19.6	$0.99 \pm 0.01$	$60 \pm 60$
55(1)	-19.4	$0.99 \pm 0.01$	$90 \pm 40$
55(2)	-19.4	$0.99 \pm 0.01$	$80 \pm 50$
55(3)	-19.6	NM	—
83(1)	-19.4	$0.99 \pm 0.01$	$100 \pm 50$
83(2)	-19.6	NM	—
83(3)	-19.5	NM	—
90	-20.3	$0.97 \pm 0.01$	$210 \pm 50$

\*Not measured.



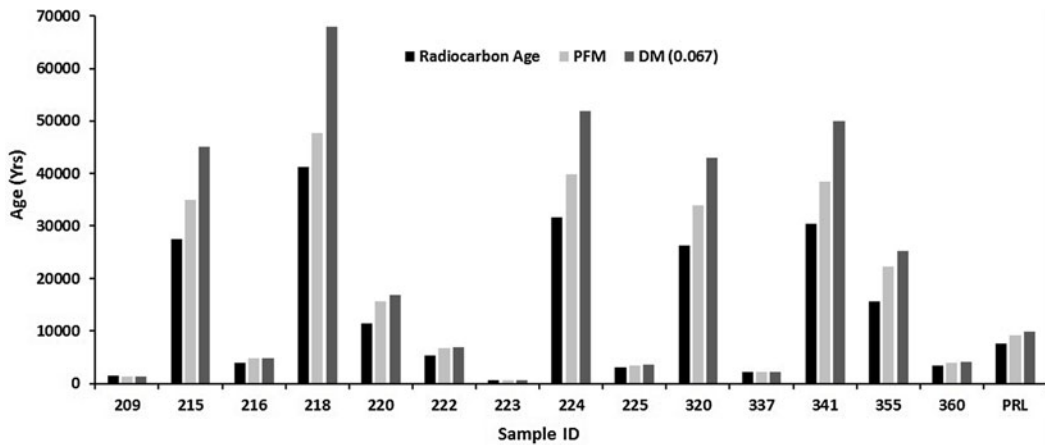
**Figure 8.** Estimated residence times with change in radiocarbon ages using piston flow model (PFM), dispersion model (DM) with a dispersion parameter of 0.1 and binary mixing model (BMM). Residence times corresponding to dispersion parameters of 0.05 and 0.1 for DM are shown. In the BMM, calculation is made with 10% contribution from PFM and 90% from DM.

estimated by PFM and hence it is better to use DM or other more appropriate models for older samples as recommended previously (e.g., Jurgens et al. 2012).

### 3.4. Residence Times of Groundwater with Available $^{14}\text{C}$ Dates from Gujarat, Western India

We also estimated the residence times of some groundwater samples from Gujarat which were dated previously using  $^{14}\text{C}$  technique (Agrawal et al. 2006). The locations of the sampling sites are given in Figure 1. The original radiocarbon ages and the residence times obtained using PFM and DM are presented in Figure 9. The PFM gives residence times close to that of the radiocarbon ages. However,





**Figure 9.** Residence times of the groundwater samples of Gujarat region using available radiocarbon dates from Agarwal et al (2006) (see Figure 1 for locations). Residence times estimated using piston flow model (PFM) and Dispersion Model (DM) with a dispersion parameter of 0.1 are shown along with the measured radiocarbon ages for different samples.

the residence times deviates significantly with the DM especially for older samples. The residence times for DM is estimated using a dispersion parameter of 0.1. The groundwater sample from PRL campus whose residence times is estimated here was also dated by Agarwal et al. (2006) and estimated a radiocarbon age of 7580 BP which is significantly higher than that measured in this study (Table 3). The difference is probably due to sampling from different aquifers or increased addition of modern waters due excessive extraction of groundwater during the last two decades.

The advantage of the present technique of CO<sub>2</sub> extraction from DIC is simple, quantitative and does not require carrier gas to extract the liberated CO<sub>2</sub>. The major limitations of estimating residence time using <sup>14</sup>C in DIC is the poor constraints of the sources of DIC and exchange of waters between aquifers and aquitards. Further investigations with measurements of more parameters particularly to better constrain the carbonate dissolution would help to estimate the <sup>14</sup>C contents of the groundwater DIC. Also, better mapping of the water contents in aquitards can better constrain the aquifer water age and hence groundwater residence time.

## Conclusions

We presented a simple CO<sub>2</sub> extraction system from DIC for radiocarbon dating of groundwater samples and estimated the <sup>14</sup>C ages of groundwater from the campus of Physical Research Laboratory Ahmedabad. δ<sup>13</sup>C values and <sup>14</sup>C ages of soil CO<sub>2</sub> up to a depth of 90 cm were measured to estimate the contribution of soil CO<sub>2</sub> in the DIC and age of the DIC in the recharge zone. δ<sup>13</sup>C values of the DIC were used to estimate the contribution of bedrock carbonates in groundwater and hence <sup>14</sup>C age correction. Soil CO<sub>2</sub> was found to be modern and hence the influence of age of it in the recharge zone in modulating the radiocarbon ages of groundwater was neglected. Residence times estimated using different LPM for a groundwater sample collected from the PRL Campus and some previously measured radiocarbon ages from Gujarat region were presented and discussed. Groundwater residence times can be estimated reasonably well using Piston Flow Model for young samples (<5000 yr) while for older samples, Dispersion Model or other more appropriate models should be used.

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