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FIELD DEGASSING AS A NEW SAMPLING METHOD FOR ^{14}C ANALYSES IN OLD GROUNDWATER

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ABSTRACT. Radiocarbon (^{14}C) activity in groundwater can be used to determine subsurface residence time up to ~40 kyr, providing crucial information on dynamic properties of groundwater and on paleoclimate. However, commonly applied sampling methods for dissolved inorganic carbon (DIC- ^{14}C) are prone to low level of modern atmospheric contamination, resulting in underestimation of groundwater ages that cluster around 30–40 kyr. We extract CO_2 gas from groundwater using a device originally developed for studies of noble gas radionuclides. Carbon is collected in the gas phase, eliminating the possibility of fostering microbial activities and aqueous chemical reactions during sample storage. This method collects CO_2 - ^{14}C and radiokrypton (^{81}Kr and ^{85}Kr) samples simultaneously. The presence of any shorter-lived ^{85}Kr is used to evaluate the degree of atmospheric contamination during sampling or mixing of young groundwater. Most groundwater samples showed lower CO_2 - ^{14}C activities than those of DIC- ^{14}C , presumably due to the absence of atmospheric contamination. Samples with ^{81}Kr age exceeding 150 kyr have no detectable CO_2 - ^{14}C except where mixing sources of young groundwater is suspected. These field data serve as confirmations for the reliability of the newly presented sample collection and CO_2 - ^{14}C method, and for the outstanding roles of radiokrypton isotopes in characterizing old groundwater.

KEYWORDS: dissolved $^{14}\text{CO}_2$, field degassing, groundwater residence time.

INTRODUCTION

Cosmogenic radiocarbon (^{14}C) is produced by the nuclear reaction $^{14}\text{N}(\text{n,p})^{14}\text{C}$ in the upper atmosphere and has a generally accepted half-life of 5730 yr. The cosmogenic isotope is incorporated into the geochemical carbon cycle, penetrates into the subsurface, and interacts with the biosphere in the soil where partial pressure of CO_2 often becomes elevated (Brook et al. 1983). Dissolved CO_2 in water dissociates and forms bicarbonate and carbonate ions, which are together considered as dissolved inorganic carbon (DIC). In an ideal case, the ^{14}C activity of DIC in phreatic zone of groundwater is close to that of atmospheric air, and with the isolation of water mass from the atmosphere the radioactive decay dating clock starts. Decades of ^{14}C dating application on DIC in groundwater revealed that ^{14}C activities can be modified by numerous geochemical processes both in phreatic and confined conditions, in most cases admixture of ^{14}C -free carbon resulting in age overestimations. Nevertheless, sophisticated correction methods for such effects continue to develop (e.g. Plummer and Sprinkle 2001; Han and Plummer 2016), and ^{14}C has been extensively used for the determination of groundwater residence time in order to constrain the recharge rate, flow dynamics, and paleoclimates [Plummer and Glynn (2013) and references therein].

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Table 1 List of ^{14}C sampling methods. The \times symbols indicate “problematic” or “disadvantageous,” whereas the \circ symbols indicate “advantageous” or “not a concern.” “Inhibitors” and “filters” are countermeasures commonly taken against the potential problems.

Method	DIC analyzed	Reduced H_2O to transport	Time	Biological activity	Carbonate mixing	Scalability	pH limitation	Risk of air intake	Storage
Direct deposition ^a	Total	\circ	\times	\circ	\times	\circ	\circ	\times	NaOH in glass bottle
Gas evolution ^b	Total	\circ	\times	\circ	\times	\circ	\circ	\circ	NH_4OH in glass bottle
Bulk ^c	Total	\times	\circ	Inhibitors	Filter	\times	\circ	\times	Bulk water in glass bottle
Super head space ^d	CO_2	\circ	\circ	\circ	\circ	\times	$<7^f$	\circ	Molecular sieve cartridge
Field degassing ^e	CO_2	\circ	\circ	\circ	\circ	\circ	$<8.2^g$	\circ	Metal gas container

^aGleason et al. (1969); Plummer and Sprinkle (2001).

^bFeltz and Hanshaw (1963); Hanshaw et al. (1965).

^cMcNichol (1994).

^dGarnett et al. (2016).

^eThis work.

^fThe authors state as conservative limit.

^gHighest pH actually measured.

Sample collection methods for ¹⁴C analyses are listed in Table 1. Because large quantities of carbon (3 g) were required for ¹⁴C analyses by decay counting, DIC in groundwater has traditionally been acquired by separating DIC from a large volume of groundwater (≥50 L) via chemical treatments: the gas evolution method acidifies the sample using H₂SO₄ to liberate CO₂, which is then absorbed by hyperalkaline solution (NaOH or NH₄OH) and precipitated as SrCO₃ or BaCO₃ (Feltz and Hanshaw 1963; Hanshaw et al. 1965). The method had not been commonly applied in the field due probably to the relatively complex operation, but it has been refined and widely used in laboratories for efficiently extracting DIC from environmental water samples (e.g. Gao et al. 2014; Gospodinova et al. 2016). A simpler and widely used method (direct deposition) is to precipitate DIC in the form of carbonate (SrCO₃ or BaCO₃) by adding hyperalkaline solution and an appropriate salt (e.g. SrCl₂; Gleason et al. 1969; Plummer and Sprinkle 2001). As recently demonstrated (Aggarwal et al. 2014), the hyperalkaline solution exposed to the modern atmosphere is prone to rapid uptake of atmospheric CO₂.

Accelerator mass spectrometry (AMS) dramatically decreased the required sample size for the ¹⁴C analyses to 0.05–1 L and enabled transport of bulk water sample (bulk method). Naturally occurring bulk water, if stored untreated, risks occurrence of biological and chemical processes that modify ¹⁴C activity of DIC. As countermeasures, inhibitors of microbial activity are often added in the field, and water samples are occasionally filtered, during which exposure of the small-size samples to modern atmosphere or CO₂ loss by decompression is possible. Furthermore, ¹⁴C contamination may occur during sample storage (Takahashi et al. 2016). Aggarwal et al. (2014) also suspect that some AMS analyses may have been prone to such contamination based on the data from literatures where ¹⁴C measurements level out around a few % modern carbon (pMC) over hundreds of kilometers. As a consequence of modern atmospheric contamination, the ¹⁴C age of old groundwater would be substantially underestimated, and the hydrological system of the region would be severely misinterpreted. The degree of modern atmospheric contamination during sampling and sample processing depends primarily on the details of the operations performed, introducing unsystematic biases that cannot be interpreted in a generalized way. Aggarwal et al. (2014) suggested to collect (and seal) old groundwater samples in plastic containers submerged in an overflowing container. This will minimize the atmospheric contamination, but makes the procedure of adding chemicals more complex. Sample collection methods and sample storage containers for DIC-¹⁴C have recently been going through a phase of re-evaluation (e.g. Nakata et al. 2016; Takahashi et al. 2016).

The advent of atom trap trace analyses (ATTA) at Argonne National Laboratory enabled the analyses of radiokrypton isotopes that are ideal tracers of groundwater age (Chen et al. 1999; Du et al. 2003; Sturchio et al. 2004). ATTA is currently the only method capable of determining the isotopic abundance of the long-lived isotope ⁸¹Kr ($t_{1/2} = 229,000$ yr). Krypton-81 is an excellent tracer of old groundwater age and therefore provides the means of evaluating the hydrological significance of ¹⁴C leveling off as mentioned above (i.e. technical problem versus homogeneous reservoir). A detectable ⁸⁵Kr ($t_{1/2} = 10.8$ yr) activity concentration in deep wells clearly indicates young water mixing or atmospheric contamination during sampling. It is therefore ideal to use these three isotope tracers together to assess the age structure of low-¹⁴C groundwater.

At present, the quantity of Kr used for each analysis is about 10 μL-STP (Jiang et al. 2012; Lu et al. 2014), which can be extracted from 100–200 L of groundwater. Because of the relatively large sample size, krypton and other bulk gases dissolved in groundwater are extracted in the field and stored in compressed gas cylinders (e.g. Purtschert et al. 2013; Yokochi 2016). During this process, proven to be robust against modern atmospheric contamination, dissolved CO₂ is also extracted. In favorable cases, a significant fraction of DIC resides as dissolved CO₂ in

groundwater. Because the DIC chemical and isotope equilibrium occurs with an e-folding time scale of 10–25 s (Zeebe and Wolf-Gladrow 2001), ^{14}C isotopic abundance of CO_2 extracted by field degassing is likely to represent DIC of the groundwater, with minor isotopic fractionations that can be corrected for. Water-rock interaction and subsurface geochemical processes prior to sampling still require geochemical correction scheme (Plummer and Glynn 2013). This method collects ^{14}C and radiokrypton samples simultaneously, which is ideal for evaluating the degree of atmospheric contamination during sampling. Moreover, carbon is collected in the gas phase, eliminating the possibility of fostering microbial activities and aqueous chemical reactions. Recently, Garnett et al. (2016) presented a field CO_2 extraction method using headspace (super headspace method) for ^{14}C analyses, similarly highlighting the sample preservation capability.

We herein present case studies where groundwater ages of ^{81}Kr , ^{85}Kr , and ^{14}C of CO_2 from bulk gas samples are compared with those of DIC- ^{14}C . The samples for ^{14}C in gaseous CO_2 and radiokrypton isotope analyses were simultaneously collected via field degassing. Our goal is to demonstrate the feasibility and advantages of analyzing ^{14}C in CO_2 as well as of using it together with noble gas radionuclides from the same bulk gas extracted in the field.

HYDROGEOLOGICAL BACKGROUND

The first set of samples was collected from the Judea Group carbonate aquifer and the underlying Kurnub Group sandstone aquifer in the Negev desert, Israel, in May 2014. These aquifers are precious sources of fresh and brackish water, and have been studied extensively (e.g. Issar et al. 1972; Adar et al. 1992; Yechieli et al. 1992; Rosenthal et al. 2007). The Upper Cretaceous Judea Group carbonate aquifer in the studied region was probably replenished in the southern flanks of the Judea mountains, central to northeastern Sinai, and over the Negev Highlands. The Lower Cretaceous to Jurassic Kurnub (Nubian) sandstone aquifer extends beneath the Arabian Peninsula and the Sahara with two major clear hydrological discontinuities along the Gulf of Suez and the Jordan-Arava Rift Valley. The main recharge of Sinai-Negev Kurnub aquifer occurs in central Sinai where there are large exposures of Nubian sandstone. Additional small recharge zones are located in the erosion cirques of the northern Negev and Sinai deserts. ^{14}C data in the literature indicate the “fossil” nature of water in both the Judea and Kurnub aquifers (Issar et al. 1972; Kronfeld et al. 1993; Vengosh et al. 2007; Burg et al. 2013). In most cases, those ^{14}C analyses were conducted using the conventional method where BaCl_2 solution was added to the samples in the field, together with NaOH , to precipitate the carbonates as BaCO_3 . The arid climate causes multiple difficulties in applying ^{14}C dating of groundwater using DIC; the faint biological activities result in low P_{CO_2} of the soil and hence relatively low DIC concentration in groundwater, which makes samples sensitive to mixing, both via modern atmospheric air contamination during sampling, and via chemical reactions with minerals in the subsurface. After applying corrections for the effect of chemical exchanges between groundwater and minerals in both phreatic and confined aquifers, the authors concluded that the groundwater from deep aquifers of the region was predominantly recharged during the last glacial period, around 25 kyr (Issar et al. 1972; Gat and Issar 1974; Vengosh et al. 2007). The current sampling campaign was primarily aimed for ^{81}Kr dating, and water samples for ^{14}C analyses in DIC were not collected during this campaign. Therefore, the ^{14}C isotopic abundances of CO_2 in these samples are compared with published DIC- ^{14}C values in the literature (Carmi 1987; Kronfeld et al. 1993; Vengosh et al. 2007; Burg et al. 2013).

The second sampling campaign took place in June 2015 in southern Florida. The Floridan aquifer system is one of the most productive aquifers on Earth. It underlays the entire state of Florida and

beyond, consisting of a sequence of hydraulically connected carbonate rocks with minor amounts of evaporites of Paleocene to Miocene age (Bush and Johnson 1988). The recharge occurs near the potentiometric mound at Polk City, and the flow is south and outward (east and west) from the ridge of the peninsula. Low ¹⁴C activities of DIC were reported even at locations close to the recharge zone, partly due to the geochemical reactions that dilute the original ¹⁴C signal. Plummer and Sprinkle (2001) applied thorough correction of possible effects and concluded that most wells have adjusted ¹⁴C ages of 20–30 kyr and thus recharged during the last glacial period. A cavernous zone, known as the Boulder Zone, occurs in the southern Florida at depth where the chemical composition of the water is comparable with seawater and relatively high but not modern ¹⁴C activity was reported (Meyer 1989; Morrissey et al. 2010). In Florida, two samples near the recharge zone and two high-salinity samples from the Boulder Zone were collected.

METHODS

The field degassing device (Yokochi 2016) is equipped with a commercial membrane contactor, Liqui-Cel Extra-Flow. These membrane contactors permeate gas and serve as physical barriers to separate liquid water from the gas phase (Probst et al. 2006; Purtschert et al. 2013). A conceptual diagram of the devices is shown in Figure 1, with a projected configuration for radiocarbon sampling (i.e. small sample size) using a two-valve sample container. As filtered water runs through the shell-side of the contactor (MC), dissolved gas is pumped out from the lumen-side and compressed into a sample container. The operation is relatively simple: After connecting the water inlet, outlet, and sample container, the operator activates the pump and extracted gas comes out from the pump outlet. In both campaigns, carbon dioxide and krypton were collected together with other bulk gases (5–10 LSTP) from groundwater using the field degassing device (see for detail Yokochi 2016). Sample gas cylinders were shipped to the University of Chicago or University of Bern for Kr separation (Yokochi et al. 2008; Purtschert et al. 2013; Yokochi 2016), and gas splits of ~50 mL STP were set aside for the separation of CO₂. The abundances of radiokrypton isotopes were measured by ATTA at Argonne National Laboratory (Jiang et al. 2012).

In the field, temperature, pH, and conductivities were measured. In Florida, DIC-¹⁴C sample bottles were placed and overflowed for several minutes inside a bucket filled with water from the sampled well, then capped underwater without adding the inhibitor of biological activity, following the recommendation by Aggarwal et al. (2014). The samples were kept in a refrigerator except during transport, shipped directly from the field site to the AMS facility at the University of Georgia, and were analyzed within 3 weeks. The gas split container was connected to a vacuum line, and CO₂ gas samples were sealed in 6-mm Pyrex tubes after cryogenic separation. The analyses of ¹⁴C were performed at the University of Georgia AMS facility. There, H₂S and H₂O were removed catalytically and cryogenically, and CO₂ was graphitized with Fe catalyst (Vogel et al. 1984).

RESULTS AND DISCUSSIONS

Carbon-14, Krypton-81 and -85 abundances of gas samples collected via field gas extraction are listed in Table 2, together with ¹⁴C data of CO₂, DIC from the literature for Israeli samples and for four DIC samples from Florida. Table 3 includes δ¹³C of DIC and CO₂ gas, as well as input and output parameters of correction for isotope fractionations. Krypton-81 abundance ranged between 0.49 ± 0.04 and 1.05 ± 0.05 relative to the modern atmospheric concentration. Krypton-85 activities were below 1% of modern atmosphere except for two samples. It suggests that the contamination by modern atmospheric air is insignificant in most CO₂ gas samples. The ¹⁴C abundances of CO₂ gas of all but two samples were comparable or lower than that of DIC (Figure 2).

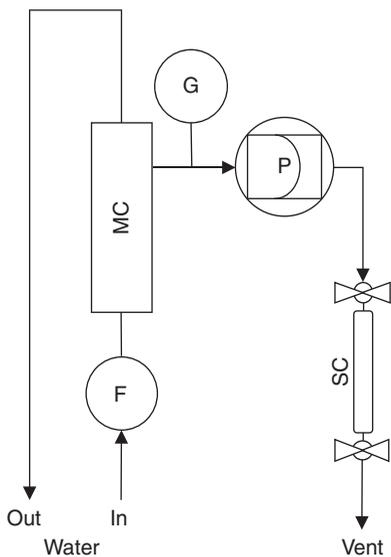


Figure 1 Conceptual diagram of a field gas extraction apparatus using a Liqui-Cel membrane contactor (MC), with a projected configuration for ^{14}C sampling using a double ended sample container (SC). The letters F, G, and P denote “filter,” “pressure gauge,” and “pump.” Arrows show water and gas flow directions. For portability, a 12 VDC battery-operated vacuum pump may be implemented as Device A in Yokochi (2016).

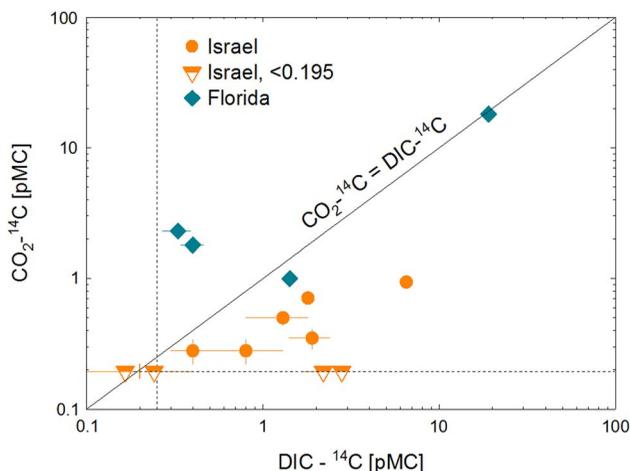


Figure 2 ^{14}C isotopic abundance [pMC] of dissolved inorganic carbon (DIC) is plotted against that of CO_2 gas extracted in the field. DIC data of Israeli samples are from the literature. The dotted lines are the detection limit of ^{14}C , and half-filled symbols represent data below detection limits. The solid line represents equal activity between DIC and CO_2 . All but two gaseous CO_2 samples had lower ^{14}C activity than DIC samples from the same well.

The field degassing method requires a sufficient amount of gaseous CO_2 dissolved in the groundwater samples. Furthermore, the observed $\delta^{13}\text{C}$ and ^{14}C abundances need to be corrected for isotopic fractionation and mixing prior to geochemical interpretation. Therefore, general aspects of DIC chemical speciation and dissolved gas chemistry are first addressed in order to assess the accuracy and applicability of the method. Comparisons of different tracer ages and their implications follow.

DIC Speciation, Dissolved Gas Chemistry, and Atmospheric Contamination

Carbon dioxide in soil gas dissolves in water, $[\text{CO}_{2,aq}]$, at the unsaturated zone to reach solubility equilibrium following Henry's law. The partial pressure of CO_2 in soil gas can be significantly higher by >100 fold than that in the atmosphere due to subsurface biological activities (Brook et al. 1983). A fraction of $[\text{CO}_{2,aq}]$ forms carbonic acid $[\text{H}_2\text{CO}_3]$ that dissociates to

Table 2 Radiokrypton and ¹⁴C isotopic abundances of gaseous CO₂ and DIC. Numbers listed in the “UGA” columns are the analytical IDs of the AMS facility at University of Georgia (UGA). References are as follows: [1] Carmi 1987; [2] Kronfeld et al. 1993; [3] Vengosh et al. 2007; [4] Burg et al. 2013; [5] Adar unpublished data. The ⁸¹Kr age of Paran 20 and Tamar 11 samples were corrected for mixing of young component using ⁸⁵Kr abundance. The ¹⁴C data are corrected for the blank of 0.195 ±0.06 pMC, and data within 2σ of this value were reported as <0.195 pMC. The uncertainty of the blank was estimated based on the long-term reproducibility of ±30% reported for geologic graphite, coal, and calcite blanks in Cherkinsky et al. (2013), which reflects the reproducibilities of both the background and the measurement.

Name	Aquifer	⁸⁵ Kr dpm/cc	⁸¹ Kr R/Ra	⁸¹ Kr Age kyr	CO ₂ - ¹⁴ C pMC	CO ₂ - ¹⁴ C age kyr	UGA	DIC- ¹⁴ C pMC	DIC- ¹⁴ C age kyr	Ref/UGA
Revivim 2	Judea	<0.35	1.05 ± 0.05	-16.1 ± 15.8	0.71 ± 0.06	40.9 ± 0.7	21754	1.8 ± 0.1	33.2 ± 0.5	[2]
Nitzana 1	Judea	<0.39	0.92 ± 0.05	27.5 ± 18.0	0.94 ± 0.06	38.6 ± 0.6	21758	6.5 ± 0.3	22.6 ± 0.4	[2]
Qetora 115	Judea	<0.27	0.9 ± 0.05	34.8 ± 18.4	0.5 ± 0.06	43.8 ± 1.0	21772	1.3 ± 0.5	35.9 ± 3.2	[4]
Yorke'am 1	Kurnub	<0.30	0.82 ± 0.04	65.6 ± 16.4	0.28 ± 0.06	48.6 ± 1.8	21720	0.8 ± 0.5	39.9 ± 5.2	[4]
								0.4 ± 0.1	45.6 ± 2.1	[3]
Ein Ofarim 5	Kurnub	<0.40	0.63 ± 0.03	152.6 ± 17.4	<0.195	>51.6	21760	2.8 ± 0.2	29.6 ± 0.6	[1]
Ein Yahav 6	Kurnub	<0.25	0.7 ± 0.03	117.8 ± 15.2	0.35 ± 0.06	46.7 ± 1.4	21753	1.9 ± 0.5	32.8 ± 2.2	[4]
Paran 20	Kurnub	5.5 ± 0.46	0.56 ± 0.03	>212.8	<0.195	>51.6	21769	2.2 ± 0.5	31.6 ± 0.2	[4]
Tamar 11	Kurnub	1.16 ± 0.58	0.49 ± 0.04	>241.8	<0.195	>51.6	21762	0.2 ± 0.2	51.4 ± 8.3	[1]
Ein Ofarim 6	Kurnub	<0.32	0.63 ± 0.04	152.6 ± 22.2	<0.195	>51.6	21761	0.2	51.4	[5]
OKF105-upper	Floridan	0.44 ± 0.1	1.02 ± 0.04	-6.5 ± 13.0	2.3 ± 0.06	31.2 ± 0.2	22211	0.33 ± 0.06	47.2 ± 1.5	21183
OKF105-middle	Floridan	0.14 ± 0.09	0.95 ± 0.03	16.9 ± 10.5	1.0 ± 0.06	38.1 ± 0.5	22212	1.42 ± 0.06	35.2 ± 0.4	21184
LAB-PW2	Floridan	0.16 ± 0.1	0.90 ± 0.03	34.8 ± 11.1	1.8 ± 0.06	33.2 ± 0.3	22213	0.40 ± 0.06	45.6 ± 1.3	21185
I75-MZ3	Floridan	<0.34	0.90 ± 0.03	34.8 ± 11.1	18.1 ± 0.09	14.1 ± 0.05	22210	19.0 ± 0.09	13.7 ± 0.04	21182

Table 3 The results of modeled carbon isotopic fractionation and relevant parameters. $F_{H_2CO_3^*}$, $\delta^{13}C_{DIC,Model}$, and $\Delta^{13}C$ are the fraction of $H_2CO_3^*$ among total DIC species, the $\delta^{13}C$ of DIC modeled from the $\delta^{13}C$ measured in CO_2 gas, and the deviation of the modeled value from the actual DIC composition ($\Delta^{13}C = \delta^{13}C_{DIC} - \delta^{13}C_{DIC,Model}$). This correction does not include any isotopic modifications caused by chemical reactions in the subsurface. *This sample did not contain sufficient CO_2 or DIC for ^{14}C analysis.

Name	pH	S‰	T°C	F_{CO_2}	$\delta^{13}C_{CO_2}$ ‰	$\delta^{13}C_{DIC}$ ‰	$\delta^{13}C_{Corr}$ ‰	$\Delta^{13}C$ ‰
Revivim 2	7.5	2.1	40.5	0.037	-16.3	-9.9	-9.2	0.7
Nitzana 1	7.2	3.5	37.8	0.065	-19.9	-11	-12.8	-1.8
Qetora 115	7.6	0.9	31.7	0.037	-13.5	-5.7	-5.8	-0.1
Yorke'am 1	7.5	1.4	37.6	0.041	-16.3	-8.4	-8.8	-0.4
				0.041	-16.3	-7.26	-8.8	-1.5
Ein Ofarim 5	7.5	1.2	35.6	0.042	-15.6	-9.9	-8.2	1.7
Ein Yahav 6	7.3	1.1	43.3	0.063	-14.8	-8.9	-8.1	0.8
Paran 20	7.1	1.2	57.0	0.091	-13.7	-7.8	-8.0	-0.2
Tamar 11	7.4	1.4	42.4	0.049	-13.4	-9.3	-6.5	2.8
Ein Ofarim 6	7.4	1.2	43.3	0.050	-15.4			
Shunit*	9.7	0.1	29.4	0.00028				
OKF105-upper	8.2	0.4	24.0	0.011	-14.6	-6.5	-6.1	0.4
OKF105-middle	7.9	1.5	28.6	0.018	-13.6	-6.5	-5.5	1.0
LAB-PW2	7.3	18.0	32.7	0.038	-10.7	-2.9	-3.0	-0.1
175-MZ3	7.3	36.0	30.0	0.040	-9.4	-2.5	-1.5	1.0

bicarbonate [HCO^-] and carbonate [CO^{2-}] ions. These four chemical species all together are considered DIC and are used for the analyses of conventional ^{14}C analyses in water. The former two species are expressed together as $H_2CO_3^*$. The relative abundances of the carbon species in water are thermodynamically constrained (e.g. Millero et al. 2006), depending primarily on pH and also on temperature (T) and salinity (S). Salinity was calculated based on the Cl concentration. In typical groundwater ($6.5 < pH < 8.5$, $0 < T < 50^\circ C$ and $0 < S < 45$ ‰), the fraction of dissolved CO_2 constitutes between 0.1% and 54% of total DIC (Figure 3a).

Ideally, AMS analyses of ^{14}C require 2 cm³STP of CO_2 . Provided that 5–10 L STP of bulk gas is usually collected for the analyses of Kr radioisotopes, CO_2 concentration of $>0.04\%$ in the extracted gas phase is required. Because N_2 is the major constituent of dissolved atmospheric gas in groundwater, the CO_2/N_2 ratio serves as a good proxy for CO_2 concentration in extracted gas. Carbon dioxide and molecular nitrogen solubility was calculated based on Ozima and Podosek (2002) and Weiss (1974). For a range of possible recharge conditions ($7.0 < pH < 7.5$, $0 < T < 50^\circ C$ with low salinity) and P_{CO_2} in soil gas (Brook et al. 1983), the DIC/ N_2 molar ratio varies between 0.12 and 35.5, significantly higher than the atmospheric CO_2/N_2 ratio (0.0005). Water–rock interactions may cause changes in pH and salinity, which determine the $H_2CO_3^*/DIC$ ratio. The anticipated $H_2CO_3^*/N_2$ ratio in groundwater for a range of subsurface conditions ($6.5 < pH < 8.5$, $0 < T < 50^\circ C$ and $0 < S < 45$ ‰, assuming no significant gain or loss of C) is plotted in Figure 3b; In most cases, the gas sample will contain a sufficient concentration ($>0.04\%$) of CO_2 for ^{14}C analyses. The gases extracted from groundwater often have $>1\%$ CO_2 .

Figure 3c depicts the $H_2CO_3^*/Kr$ ratio in groundwater for the same conditions. Most groundwater samples have higher $H_2CO_3^*/Kr$ ratios compared with atmospheric CO_2/Kr ratio, often by orders of magnitude, due to the high CO_2 solubility in water and elevated P_{CO_2} in soil gas. This makes ^{85}Kr a very sensitive indicator of atmospheric contamination for ^{14}C in gaseous

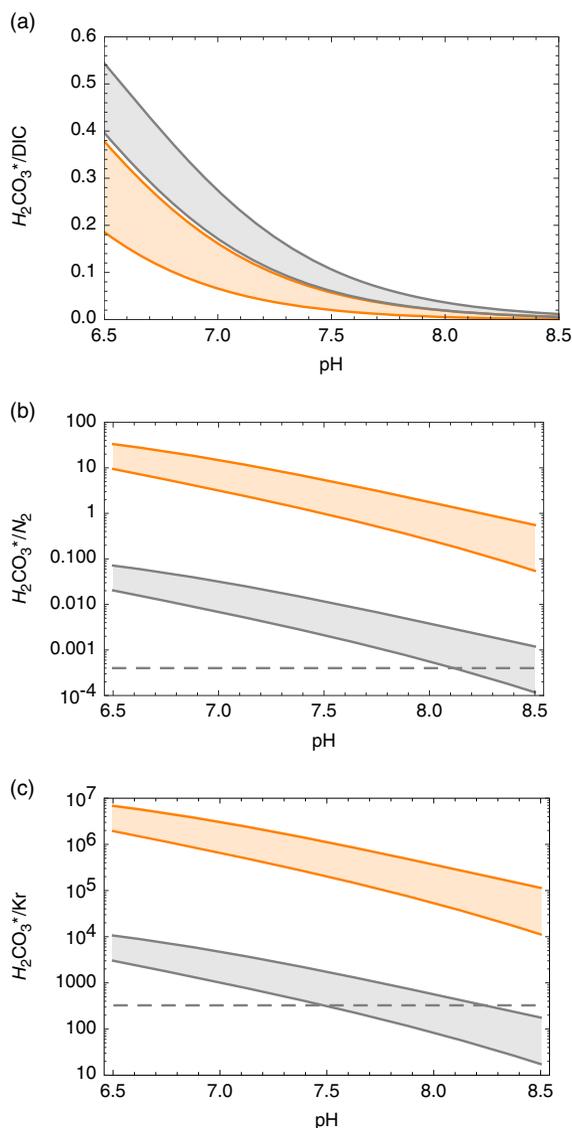


Figure 3 Carbon dioxide abundance relative to other species in groundwater as a function of pH: (a) fractional abundance of $H_2CO_3^*$ among dissolved inorganic carbon (DIC). Gray and orange zones represent 0–50°C, respectively, for the salinity range of 0–45‰, calculated based on Millero et al. (2006). Salinity was calculated based on the Cl concentration. (b) Expected $H_2CO_3^*/N_2$ ratio of dissolved gas in groundwater assuming near neutral pH, zero salinity conditions for soil gas CO_2 -enrichment factors of 1 (orange zone) and 105 (gray zone) (Brook et al. 1983) at recharge temperatures range between 0 and 50°C (see “Methods” section). The dashed line represents a desired minimum $H_2CO_3^*$ concentration of 0.04% among dissolved gases assuming N_2 -dominant chemistry. (c) Expected $H_2CO_3^*/Kr$ ratio of dissolved gas in groundwater using the same method described above for N_2 . The dashed line represents modern atmospheric CO_2/Kr ratio. (Colors refer to online version.)

CO₂ samples because the most liable source of atmospheric contamination is via gaseous atmospheric air leaks during the operation of the field gas extraction device. As shown in Figure 4, the ⁸⁵Kr isotope signal is >10 fold more sensitive than ¹⁴C to a mixing of modern atmospheric component with old (zero-activity) groundwater. It is a remarkable advantage of the newly developed method that we can (semi-)quantitatively evaluate the potential impact of atmospheric contamination on ¹⁴C abundance during sample collection.

One bulk gas sample, Shunit (Table 3), extracted from groundwater with a high pH of 9.7 had low CO₂ concentration (71 ± 15 ppm), confirming a low H₂CO₃*/DIC ratio as expected. This sample did not contain sufficient CO₂ or DIC for the analysis of ¹⁴C activity. The low CO₂ concentration in the gas phase also implies that background CO₂ contribution from the sample container and sampling device (e.g. degassing from the membrane contactor and leakage) is below this level. For samples with high pH (thus low CO₂ concentrations), the procedural background needs to be more thoroughly tested for both modern and dead C contributions.

Two samples characterized with significant (>1% modern) ⁸⁵Kr activities probably experienced either atmospheric air contamination during sampling or the admixture of young groundwater components, which would affect both ¹⁴C and ⁸¹Kr abundances: samples from Paran 20 and Tamar 11 wells had ⁸⁵Kr activities of 5.5 and 1.2 dpm/cm³_{Kr}, respectively, corresponding to

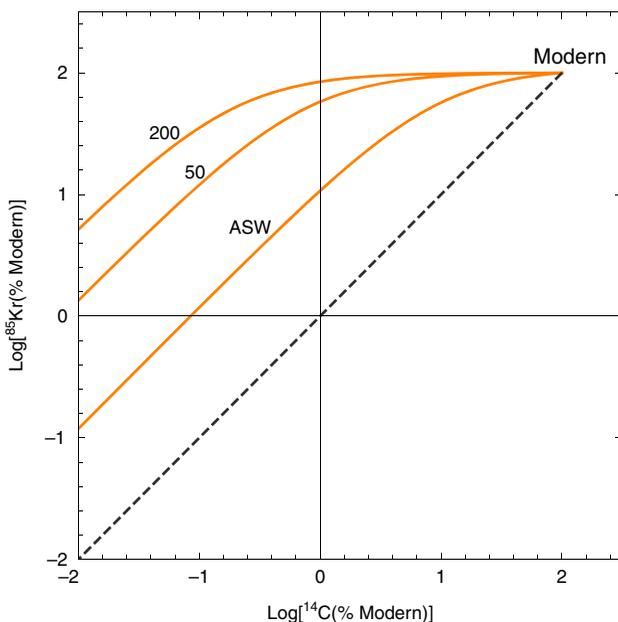


Figure 4 Modeled covariation of ¹⁴C-⁸⁵Kr isotopic abundances in response to a mixing of modern atmosphere air into dissolved gas in old (¹⁴C-dead) groundwater with various DIC concentrations. The numbers correspond to the concentration of total DIC (mg/L) in groundwater under 25°C at zero salinity. The line marked “ASW” represents mixing of modern atmospheric air with water in equilibrium with air. In all cases, the effect of modern air mixing is more significant for ⁸⁵Kr. The dashed line is shown as a reference of mixing between modern and zero-activity components with identical C/Kr ratios.

7.3% and 1.6% modern atmospheric Kr contribution assuming 75 dpm/cm³ ⁸⁵Kr in atmospheric air (Winger et al. 2005; Ahlswede et al. 2013). The contributing fraction of ⁸¹Kr is equal to that of ⁸⁵Kr in the case of modern atmospheric contamination, or larger in case of the admixture of sub-modern young groundwater which contains lower ⁸⁵Kr activities than modern atmosphere. Assuming modern ⁸⁵Kr activity concentration for the young mixing component, ⁸¹Kr abundances of Tamar 11 is corrected from 0.49 to 0.48. That of Paran 20 is corrected from 0.56 to 0.53. These values are upper limits, and they can be lower if the ⁸⁵Kr carrier has a sub-modern ⁸⁵Kr activity. Although a similar situation applies to ¹⁴C, the ¹⁴C activities of these two samples are still at baseline values, probably due to the high H₂CO₃*/Kr in the samples. Therefore, no correction was applied in these cases.

Carbon Isotope Fractionation and Mixing

Carbon isotopic composition of DIC is often used for evaluating the degree of water–rock interaction and isotope exchange that disturb the ¹⁴C chronometer by the addition of dead carbon (Plummer and Glynn 2013 and references therein). Equilibrium isotope fractionation factors α among different chemical species x and y are defined as $[\alpha]_{xy}(T) = (^{13}\text{C}/^{12}\text{C})_x / (^{13}\text{C}/^{12}\text{C})_y$, also expressed as $\delta^{13}\text{C}_y = (\delta^{13}\text{C}_x + 1000)\alpha_{xy} - 1000$. Using the fractional abundance of each species discussed above, the equilibrium fractionation factor between DIC and H₂CO₃* over the range of T, S, and pH conditions can be estimated as shown in Figure 5. In typical groundwater (6.5 < pH < 8.5), it is expected that the $\delta^{13}\text{C}$ value in H₂CO₃* is lower than $\delta^{13}\text{C}$ value of total DIC by 6–10‰. If the field gas extraction device is only extracting the fraction of DIC that was in the state of H₂CO₃* prior to degassing, it is therefore expected that the $\delta^{13}\text{C}$ composition of total DIC (TDIC) is heavier than the measured $\delta^{13}\text{C}_{\text{CO}_2}$ value by several ‰.

Assuming extraction of only H₂CO₃* fraction ($= F_{\text{H}_2\text{CO}_3^*}$) and isotope equilibrium among DIC species, the ¹³C isotopic abundances of total DIC were estimated ($\delta^{13}\text{C}_{\text{DIC,Model}}$) from the measured value of each CO₂ sample collected by the field degassing method ($\delta^{13}\text{C}_{\text{CO}_2}$). The modeled compositions ($\delta^{13}\text{C}_{\text{DIC,Model}}$) are compared with the actual DIC data ($\delta^{13}\text{C}_{\text{DIC}}$) to examine whether the DIC species are in chemical and isotopic equilibrium (Figure 6; Table 3). The $F_{\text{H}_2\text{CO}_3^*}$ ranged between 1.1% and 9.1%, resulting in $\Delta^{13}\text{C}$ ($= \delta^{13}\text{C}_{\text{DIC,Model}} - \delta^{13}\text{C}_{\text{CO}_2}$) between 5.7 and 8.5‰ for the measured temperature range of 24.0–57.0°C. The $\delta^{13}\text{C}_{\text{DIC}}$ of water samples agree, within a few ‰, with $\delta^{13}\text{C}_{\text{DIC,Model}}$ (solid symbols in Figure 6). The general agreement between $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{DIC,Model}}$ indicates that the model assumptions well represent the actual degassing environment, and other effects that modifies carbon isotopic compositions such as diffusion and dehydration of bicarbonate ions appears minor (see Appendix for details).

As mentioned above, the impact of atmospheric contamination is proven to be insignificant for most ¹⁴C data of CO₂ samples based on the low ⁸⁵Kr activities. Had there been no chemical processes that modify isotopic compositions inside the DIC sample container, ¹⁴C activity of DIC samples would be identical to that of CO₂ or possibly higher if there was any atmospheric contamination. However, ¹⁴C activities for two of the DIC samples from Florida were lower than in the CO₂ gas. In the gas phase acquired from the OKF105-Upper well, the concentration of CH₄ and CO₂ in the collected bulk gas were approximately 10% and 1%, respectively. Because no inhibitor of microbial activities was added in the DIC samples, it is possible that anaerobic oxidation of ¹⁴C-dead CH₄ and possibly other organic carbon could have taken place. Inorganic dissolution of carbonate particles could lead to the same consequence, given that the water sample was not filtered. In either case, the data imply a possibility that there may

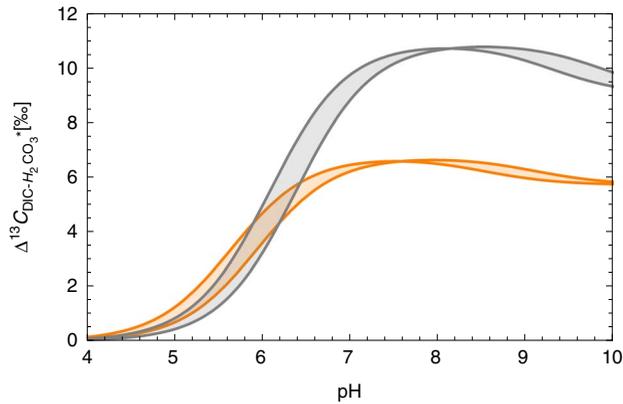


Figure 5 Carbon isotope fractionation between total DIC and H_2CO_3^* . Equilibrium isotope fractionation factors are from Deines et al. (1974), and the fractions of DIC species were calculated as in Figure 3a. The range of salinity is between 0 and 45‰ and the colors represent different temperatures, gray for 0°C and orange for 50°C. (Colors refer to online version.)

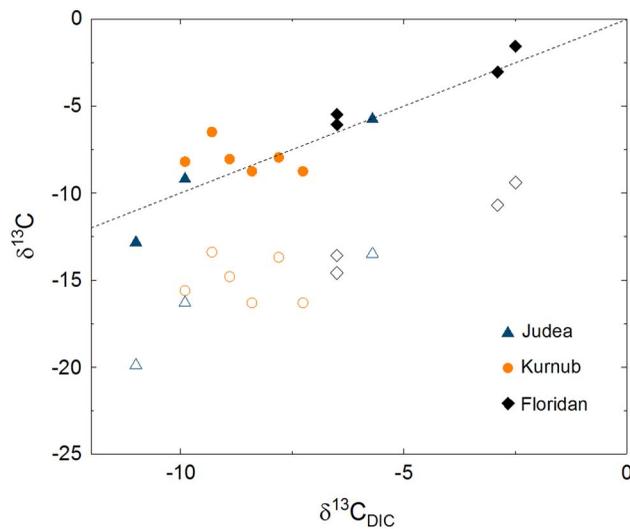


Figure 6 Carbon isotope compositions of CO_2 gas (open symbols, $\delta^{13}\text{C}_{\text{CO}_2}$) and theoretically expected DIC (solid symbols, $\delta^{13}\text{C}_{\text{DIC,Model}}$) are plotted against measured $\delta^{13}\text{C}_{\text{DIC}}$. The dashed line represents the case where measured and theoretical DIC values are identical, showing that they are in good agreement.

have been a process that lowered ^{14}C activity in water inside the DIC sample container. Although it is beyond the scope of this study, a large-scale, systematic study is desirable for ascertaining a reliable sampling method for DIC- ^{14}C . None of the above-mentioned processes can take place in an aluminum compressed gas cylinder when CO_2 gas is collected and stored for ^{14}C analyses.

Tracer Age Comparison and Implications

The groundwater ages calculated from ⁸¹Kr are listed in Table 2 and plotted in Figure 7 against apparent ¹⁴C ages (Table 2). For comparison with ⁸¹Kr age, ¹⁴C ages are calculated assuming simple decay with a half-life of 5730 yr, with an initial ¹⁴C activity of 100 pMC. No correction for dead C contribution was applied since it only affects in favor of our conclusion that previous DIC-¹⁴C ages may be underestimated by atmospheric contamination. Four CO₂ gas samples from Israel had ¹⁴C abundances at background level (≤ 0.195 pMC), in agreement with ⁸¹Kr ages of >150 kyr (Figure 7a). The ¹⁴C abundances of DIC in these samples were somewhat higher, resulting in the apparent age range of 30–51 kyr (Figure 7 b). The difference in ¹⁴C abundances between DIC and gaseous CO₂ is attributed to modern ¹⁴C contamination of DIC samples during the sampling and chemical preparation procedure in laboratories performed in previous studies. Krypton-81 age generally agrees better with ¹⁴C in CO₂ gas from this study than ¹⁴C of DIC reported in the literature. Krypton-81 ages of three samples (Nitzana1, Qetora115, and LAB-PW2) agree with both CO₂-¹⁴C and DIC-¹⁴C ages within relatively large uncertainty. Two samples collected near the recharge area of the Floridan aquifer and Revivim2 from Israel are characterized by younger ⁸¹Kr age than both CO₂- and DIC-¹⁴C age. A plausible explanation for the apparently discordant ages is a contribution of dead C from the interaction with reservoir carbonate rocks (Plummer and Sprinkle 2001; Vengosh et al. 2007). Two samples, I75-MZ3 from Florida and Ein Yahav 6 from Israel, which showed measurable ¹⁴C and older ⁸¹Kr-ages can probably be explained by mixing of multiple water bodies with distinct ages.

The newly developed CO₂-¹⁴C analyses of the groundwater with very long (>150 kyr) residence time proved that this method can provide ¹⁴C activities of groundwater devoid of modern atmospheric contamination. The sampling protocol can be conducted for the analyses of ¹⁴C using a relatively simple device at smaller scale (e.g. see Device A in Yokochi 2016). It will significantly simplify the interpretation of ¹⁴C age of old groundwater by excluding any ambiguity on whether a measured low activity is due to contamination or the real presence of ¹⁴C-bearing groundwater components. Old samples give old age rather than a few pMC that corresponds to the Last Glacial Period, and therefore extends the reliable age range of ¹⁴C from 30 kyr to 50 kyr. Detectable ¹⁴C activity with a discordant ⁸¹Kr age serves as a proxy for mixing of water body with different ages.

The presented field gas extraction method can be used for collecting CO₂-¹⁴C samples without radiokrypton analyses. Single-ended gas tight containers may be used with the configuration of Device A in Yokochi (2016), whereas the configuration for double ended sample containers proposed in Figure 1 allows simpler sample collection procedures. The sealed Pyrex tube containing CO₂ sample gas is adaptable to an ampoule cracker type inlet of a gas source AMS (Ruff et al. 2007, 2010) as well as to the emerging optical radiocarbon detection method, saturated-absorption cavity ring-down (SCAR; Galli et al. 2013), for which the graphitization of carbon is not necessary, and consequently lower blank and higher sample throughput may be achieved. There are ways of determining sample contamination or young groundwater contribution using alternative tracers to radiokrypton isotopes. Because relatively old groundwater is usually anoxic, modern atmospheric contamination during sampling may be quantified by measuring O₂ concentration in the bulk gas phase collected (e.g. Yokochi et al. 2013). Mixing with young groundwater component can be identified with other commonly used anthropogenic tracers such as tritium (⁻³He), CFCs, and SF₆ (e.g. Corcho Alvarado et al. 2007). Compared to other membrane-based gas samplers in the literatures (Loose et al. 2010; Garnett et al. 2012; Matsumoto et al. 2013), this method does not wait for the gas–water solubility equilibrium to be attained. It enables rapid collection of large size samples, but chemical and isotope fractionations

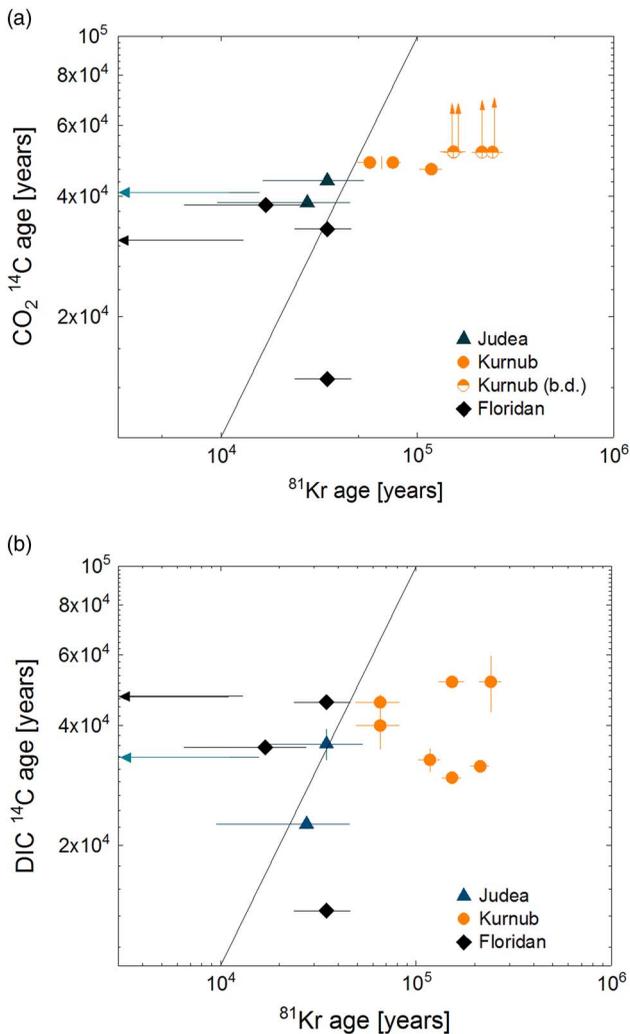


Figure 7 Comparison of ^{81}Kr age against (a) $\text{CO}_2\text{-}^{14}\text{C}$ age and (b) $\text{DIC-}^{14}\text{C}$ age. For comparison with ^{81}Kr age, ^{14}C ages are calculated assuming simple decay with a half-life of 5730 yr, with an initial ^{14}C activity of 100 pMC. ^{14}C ages are uncorrected for the effects of chemical reactions in the subsurface. The solid line represents equal ages for the two tracers. The arrows represent cases where ^{81}Kr ages were modern or where ^{14}C activities were blank level.

are anticipated. Whenever precise $\delta^{13}\text{C}$ data is required, correction for such fractionations is essential. Alternatively, small-size sample for $\delta^{13}\text{C}$ analyses may be collected separately.

The traditional $\text{DIC-}^{14}\text{C}$ method implied the recharge period around 30 kyr for groundwater from the Judea and Kurnub aquifers in Israel. The revised much older groundwater ages based on ^{81}Kr brought new insights into the hydrology of the Negev Nubian aquifer. The ^{81}Kr abundance of samples from the Floridan Aquifer confirmed the relatively young groundwater age anticipated from some of the corrected ^{14}C abundances. Hydrological implications will be discussed in separate papers.

CONCLUSION

This study demonstrates that the field-degassing method used for the studies of noble gas radionuclides provides reliable samples for the analyses of ¹⁴C in the form of CO₂ gas. Although dissolved CO₂ gas is not usually the major species among DIC, sufficient quantities of gaseous CO₂ can be acquired during most standard sampling procedures of noble gas radionuclides (Kr and Ar) because the analyses of rare noble gas radionuclides currently require comparably large amounts of gas to be extracted from the groundwater. The δ¹³C compositions of gaseous CO₂ were significantly lighter than that of DIC samples but the degree of isotope fractionation is, in most cases, in good agreement with the theoretically expected value and therefore δ¹³C is still useful for evaluating exchange with ¹⁴C dead carbon sources. An obvious advantage of using field-degassed CO₂ instead of DIC from a separate aliquot of water is that the gases are collected in a way that has proven to be highly immune against atmospheric contamination, and any potential atmospheric contamination occurring during sampling can be rigorously traced by the analyses of ⁸⁵Kr. An additional advantage is that it is improbable that any biological activity would take place in compressed gas cylinders where the only liquid water inside the gas cylinders is condensate of water vapor that traveled through the hydrophobic membrane contactor. The field data presented here confirmed the reliability of the newly developed method and the significant role of radiokrypton isotopes as hydrological tracers.

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APPENDIX

Dissolved inorganic carbon (DIC) in water consists of dissolved CO₂ [CO₂]_{aq}, carbonic acid [H₂CO₃], bicarbonate ion [HCO₃⁻] and carbonate ion [CO₃²⁻]. The former two species cannot be analytically distinguished and are thus treated together as [H₂CO₃*]. The relative abundances of these species are thermodynamically constrained as a function of temperature and salinity as (for more detailed discussion, see Zeebe and Wolf-Gladrow 2001):

$$K_0 = \frac{[H_2CO_3^*]}{P_{CO_2}}; K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}; K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (1)$$

Total DIC concentration is defined as

$$TDIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (2)$$

The four equations can be solved for the four chemical species, and we obtain

$$[H^+] = \frac{K_0 \cdot K_1 \cdot P_{CO_2}}{[HCO_3^-]} = \frac{2K_2}{\sqrt{1 - 4\frac{K_2}{K_1} + 4\frac{K_2}{K_0 \cdot K_1} \frac{TDIC}{P_{CO_2}} - 1}} \quad (3)$$

When these reactions are primary controls of pH,

$$pH = -\text{Log}_{10} \left[\frac{2K_2}{\sqrt{1 - 4\frac{K_2}{K_1} + 4\frac{K_2}{K_0 \cdot K_1} \frac{TDIC}{P_{CO_2}} - 1}} \right] \quad (4)$$

The fraction of carbonic acid over TDIC is expressed as

$$F_{H_2CO_3^*} = \frac{K_0 \cdot P_{CO_2}}{TDIC} \quad (5)$$

As water flows through the membrane contactor in steady state, $H_2CO_3^*$ is rapidly extracted via pumping so that TDIC decreases. The initial (prior to degassing) fraction $F_{H_2CO_3^*}$ of TDIC is subject to this process, which constitute <10% for studied samples. Typical P_{CO_2} drop of about 90% is anticipated based on the membrane gas phase pressure around 0.1 bar during sample collection. As the CO_2 gas is drawn off, the $[H_2CO_3^*]$ will decrease, driving the reaction $HCO_3^- + H^+ \rightarrow H_2CO_3^*$. This raises the pH and decreases the $P_{CO_2}/TDIC$ at equilibrium by about a factor of 10. The newly equilibrating (and still degassing) water has an equilibrium $F_{H_2CO_3^*}$ values lowered approximately by a factor of 10. The fraction of CO_2 gas formed via dehydration of bicarbonate ion will constitute <10% of total CO_2 gas extracted.

The residence time of water in the membrane contactor is relatively short, on the order of 5–10 s. This is comparable to the relaxation time scale (5–20 s; Zeebe and Wolf-Gladrow 2001) of the $H_2CO_3^*$ equilibration in aqueous system. An incomplete dehydration of bicarbonate ion may occur, during which kinetic isotope fractionation is anticipated with a relatively large fractionation factor $\Delta^{13}C \sim -15\%$ at 24°C (Marlier and O’Leary 1984). Because the contribution of $H_2CO_3^*$ formed via this dehydration reaction is estimated to be minor (<10%), the effect on $\delta^{13}C_{CO_2}$ is also relatively small, <–1.5% compared to the $\delta^{13}C_{CO_2} - \delta^{13}C_{DIC, Model}$ of several % (see subsection “Carbon Isotope Fractionation and Mixing”). The relatively good agreement between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DIC, Model}$ (Figure 6) confirms that the effect of this kinetic isotope fractionation is minor for the purpose of the presented method.

The apparatus effectively extracts inert gases with low diffusivity in water, which indicates that the degassing process is not diffusion-limited. We therefore do not consider isotopic fractionation by diffusion.