

Groundwater Residence Time Estimates Obscured by Anthropogenic Carbonate

(Short Title: Agricultural Lime Impacts Groundwater Dating)

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Abstract

Groundwater is an important source of drinking and irrigation water. Dating groundwater informs its vulnerability to contamination and aids in calibrating flow models. Here, we report measurements of multiple age tracers (^{14}C , ^3H , ^{39}Ar , ^{85}Kr) and parameters relevant to dissolved inorganic carbon (DIC) from 17 wells in California's San Joaquin Valley (SJV), an agricultural region that is heavily reliant on groundwater. We find evidence for a major mid-20th century shift in groundwater DIC input from mostly closed- to mostly open-system carbonate dissolution, which we suggest is driven by input of anthropogenic carbonate soil amendments. Crucially, enhanced open-system dissolution, in which DIC equilibrates with soil CO_2 , fundamentally impacts the initial ^{14}C activity of recently recharged groundwater. Conventional ^{14}C -dating of deeper SJV groundwater, assuming an open system, significantly overestimates residence time and thereby underestimates susceptibility to modern contamination. Because carbonate soil amendments are ubiquitous, other groundwater-reliant agricultural regions may be similarly affected.

INTRODUCTION

Billions of people are reliant upon groundwater as a source of drinking water (1, 2) and for irrigating nearly half of all global agriculture (3). Although the vast majority of Earth's groundwater is ancient, having been recharged centuries to millennia ago (4, 5), it remains vulnerable to anthropogenic contamination (6) and depletion (7–10) due to increasing groundwater extraction. Accurately determining groundwater residence times is important for understanding groundwater contaminant sources and transport pathways, calibrating models of groundwater flow that aid in sustainable management, and contextualizing human impacts on groundwater systems (11).

Here we investigate groundwater residence time distributions in the central-eastern San Joaquin Valley using a combination of geochemical modeling and analytical constraints informed by multiple independent age tracers. We measured radiocarbon (^{14}C), tritium (^3H), and a comprehensive suite of groundwater geochemical parameters from a network of 17 wells (36.65–36.75 °N, 117.55–117.85 °W) south of Fresno, California, which are or have been surrounded by irrigated farmland over the past 50 years (Figure S1). We also measured noble gas age tracers ^{39}Ar ($n=3$) and ^{85}Kr ($n=4$), which have historically been underutilized for groundwater dating (12, 13), in a subset of wells to independently explore potential chemical controls on ^{14}C . The SJV is California's largest and most productive agricultural region, and it is particularly vulnerable to contamination and long-term declines in groundwater reserves due to drought, increased rates of extraction, and seepage from irrigation (10, 14–16). The natural groundwater system in the SJV has been fundamentally altered by agricultural activities over the past several decades including both enhanced discharge and recharge due to groundwater pumping and irrigation seepage, respectively (10, 16–19). Given the influence of modern agriculture on groundwater in the SJV, this region serves as an ideal field-scale laboratory to assess the impact of anthropogenic perturbations to groundwater chemistry on residence time estimates.

The primary aim of this study is to understand natural and anthropogenic controls on the radiocarbon content of dissolved inorganic carbon (DIC), which is the most widely used groundwater age tracer (20). Measured trends in inorganic carbon chemistry in the SJV are modeled and interpreted in combination with multiple independent age tracers, from a subset of wells, to precisely isolate geochemical controls on ^{14}C activity. The use of multiple age tracers that are sensitive across a range of timescales, including inert dating tools like ^{39}Ar , provides key constraints for disentangling the impacts of groundwater mixing and DIC chemistry on ^{14}C . Using these data, we model the extent to which agricultural perturbations have impacted ^{14}C of DIC and, in turn, affected ^{14}C -based groundwater dating. Our results have broad implications for the susceptibility of deep groundwater to modern contamination.

Radiocarbon Dating of Groundwater

Radiocarbon activity of DIC is a ubiquitous groundwater dating tool because of its relative ease of sampling, inexpensive analytical cost, and applicability across a wide temporal range. ^{14}C has a 5,730-year half-life ($T_{1/2}$) but also a modern atmospheric excess from 20th century bomb testing (21), rendering it dually sensitive on time scales of both thousands of years and recent decades. However, the direct translation of measured ^{14}C activity to groundwater residence time is frequently complicated by ^{14}C -free inputs of DIC (22), isotopic exchange of DIC with soil CO_2 (23, 24), and by the mixing of groundwater water parcels of different age (25–27). Using ^{14}C to estimate groundwater residence times therefore requires conceptual models both for DIC chemistry and for groundwater flow and mixing.

The application of ^{14}C of DIC as a groundwater dating tool requires precise knowledge of the initial ^{14}C activity of DIC ($^{14}\text{C}_0$) at the time of recharge. The measured ^{14}C activity ($^{14}\text{C}_m$) in

groundwater (in the absence of mixing between different-aged waters) is linked to residence time (τ) by the decay equation:

$$^{14}C_m = ^{14}C_0 e^{-\lambda\tau} = \Gamma ^{14}C_{atm} e^{-\lambda\tau} \quad (1)$$

where λ is the decay constant (0.121 ka^{-1}), $^{14}C_{atm}$ is the atmospheric ^{14}C activity at the time of recharge, and Γ is a scalar that relates $^{14}C_0$ to $^{14}C_{atm}$ such that $^{14}C_0 = \Gamma ^{14}C_{atm}$. While the history of $^{14}C_{atm}$ over the relevant time range for groundwater dating is well constrained (21, 28), input of ^{14}C -free DIC sources to groundwater can dilute the overall ^{14}C concentration in DIC (by lowering the $^{14}C/^{12}C$ ratio) to values considerably lower than $^{14}C_{atm}$. In this sense, Γ represents the effective lowering of groundwater $^{14}C_0$ from the contemporary atmospheric value (~ 100 pmc prior to the 1950s and >100 pmc since then), which is essential for separating signals controlled by DIC chemistry from decay-related ^{14}C signals and thereby accurately quantifying residence times.

Groundwater DIC is intrinsically linked to exchange between dissolved and gaseous soil CO_2 . The respiration of soil organic carbon generates steady-state CO_2 partial pressures (pCO_2) above the water table that often exceed pCO_2 in the atmosphere by an order of magnitude or more (22). This large reservoir of soil CO_2 contributes to groundwater DIC both directly, by dissolving in water, and indirectly, through the generation of acidity that leads to weathering of minerals present in soil and aquifer rocks. Differences in isotopic composition between these sources of DIC partially govern both the stable (^{13}C , ^{12}C) and radioactive (^{14}C) carbon isotopic compositions of DIC. However, (i) gas exchange between DIC and CO_2 and (ii) equilibrium fractionation among DIC species further modify the isotopic composition of DIC. Where carbonate minerals are present in soils and rocks, it is commonly assumed that DIC in groundwater is derived from two primary sources: ^{14}C -rich soil CO_2 and ^{14}C -free carbonate minerals. Soil CO_2 is characteristically depleted in ^{13}C ($\delta^{13}C$ between -15 and -30 ‰_{VPDB} (22)) and is typically assumed to have a roughly atmospheric ^{14}C activity arising from the respiration of recently formed organic matter. The ^{14}C activity of CO_2 and DIC in the vadose zone can be somewhat lower due to the production of CO_2 from deeper and older organic material (29) and from drought-related impacts on water-sediment interaction (30). Conversely, carbonate minerals are generally ^{14}C -free, with $\delta^{13}C$ near 0‰_{VPDB} (20, 22). For a closed system in which carbonate dissolution occurs beneath the water table in isolation from soil CO_2 , the dissolution of carbonates tends to increase DIC concentrations and $\delta^{13}C$ while decreasing ^{14}C activity by adding ^{14}C -free DIC with $\delta^{13}C$ of ~ 0 ‰ to the DIC pool (31, 32). Thus, relatively young groundwater that has experienced closed-system carbonate dissolution may have lower ^{14}C activity and higher $\delta^{13}C$ than DIC acquired purely from dissolution of soil CO_2 . This assumption forms the basis of conventional closed-system dissolution models for groundwater ^{14}C dating that are constrained by observed values of $\delta^{13}C$ (31, 32) or DIC (33). For an open system in which carbonate dissolution occurs in the presence of soil CO_2 , isotopic equilibration between soil CO_2 and DIC leads to a near atmospheric ^{14}C activity of recently recharged groundwater (22). More complex models that involve complete or partial equilibrium isotope exchange and fractionation (23, 24, 34) and account for multiple reactions and processes (35) that alter ^{14}C have also been developed. In each conceptual model, the nature of interaction between soil CO_2 , groundwater DIC, and mineral weathering collectively determine the isotopic composition of DIC, pH and total DIC content.

RESULTS

Systematic Controls on Radiocarbon Activity

Across the 17 SJV wells sampled in this study, we observe surprising, yet coherent, relationships between groundwater ^{14}C , DIC, and pH (Figure 1). Specifically, ^{14}C activity increases with DIC, from ~ 40 pmc (percent modern carbon) at $\sim 2 \text{ mmol L}^{-1}$ DIC to ~ 120 pmc at

~10 mmol L⁻¹ DIC, in direct contrast to the common inverse relationship expected for closed-system dissolution of ¹⁴C-free carbonates (33), in which the progressive dissolution of carbonates in isolation from soil CO₂ yields an anticorrelation between ¹⁴C activity and DIC, pH, and δ¹³C (36). In the SJV samples, ¹⁴C activity consistently decreases with increasing pH, and DIC is positively correlated with Mg, Ca, and Sr concentrations (Figures 1 and S8), consistent with the general expectation for carbonate dissolution. Mean ³H activities (T_{1/2} = 12.5 years) indicate the presence of predominantly decades-old water (³H activity > 1 TU; where 1 TU = 1 tritium unit = 0.118 Bq L⁻¹) in wells where high DIC and low pH (<7.5) are observed. Despite the close correspondence between ¹⁴C, DIC, and pH, we observe no coherent relationship between any of these parameters and the stable carbon isotopic composition of DIC (δ¹³C). Taken together, closed-system dilution of DIC by ¹⁴C-free carbonate dissolution – the common expectation for natural systematic ¹⁴C variability in many global aquifers (37) – cannot explain these observed trends in the SJV.

The highest observed ¹⁴C activities (~120 pmc) in tritiated modern samples clearly indicate that DIC of recently recharged groundwaters experienced near-complete isotopic equilibration with soil CO₂, as the mean northern hemisphere atmospheric ¹⁴C activity between 1955 and 2010 was ~125 pmc (21). The δ¹³C values associated with high-¹⁴C (>100 pmc) samples fall within a -16.5 to -13.5‰ range, also consistent with open-system equilibrium exchange between DIC and biogenic soil CO₂ after accounting for equilibrium isotopic fractionation between DIC and CO₂ (Appendix S2). While δ¹³C values in lower-¹⁴C samples are slightly below those of the higher-¹⁴C samples, we note that the predicted sensitivity of δ¹³C to open- and closed-system dissolution is small relative to potential end-member variability (Appendix S2; Figure S5). Given the high potential for major changes in carbonate and soil CO₂ end-member δ¹³C changes driven by fundamental reconfiguration of the SJV groundwater system due to irrigation-derived recharge over the past century, we suggest that shifts in end-member δ¹³C have likely overprinted meaningful signals related to open- or closed-system dissolution. However, the conspicuous relationships between ¹⁴C and DIC, and ¹⁴C and pH, with marked concave-down curvatures, strongly indicates that a systematic process besides progressive closed-system carbonate dissolution – and not radioactive decay – controls much of the observed ¹⁴C variability in this system. Here, we investigate whether DIC chemistry and physical transport and mixing processes can account for the observed relationships between ¹⁴C, DIC, and pH, and evaluate the implications for the reliability of ¹⁴C-based groundwater residence times.

Typically, initial ¹⁴C activity (¹⁴C₀ in equation 1) is inferred from various combinations of measured DIC, δ¹³C, and major and trace ion concentrations by using models of varying complexity (24, 31, 32, 34, 38). Among existing single-sample models used to estimate ¹⁴C₀ (38), carbonate dissolution is assumed to occur under either entirely open- or closed-system conditions, whereby a portion of DIC isotopically exchanges with soil CO₂ (23, 24, 34) or carbonate minerals (23, 24) while the remainder of DIC does not. Conventionally, an appropriate model is chosen and validated based on observed trends in ¹⁴C, δ¹³C, and DIC in modern groundwater with high ³H activity (39). However, if fundamental changes to the DIC system have occurred over recent decades due to human activity, observed trends in modern groundwater (e.g., increases in ¹⁴C activity with DIC) may not be representative of the preceding natural processes in older groundwater. In the specific context of SJV measurements (Figure 1), it is therefore critical to understand if the inference of near-atmospheric ¹⁴C₀ for modern groundwater (*I*~1 based on the >100 pmc ¹⁴C activities of tritiated samples) is representative of natural, pre-development ¹⁴C₀. In other words, if it is assumed that the ¹⁴C₀ of deeper, ³H-free groundwater is similarly near-atmospheric (*I*~1), then the lowest observed ¹⁴C activities imply mean residence times of thousands of years; but if this assumption is invalid (e.g., *I*<1), then ¹⁴C measurements would imply considerably shorter residence times.

Insights from multiple age tracers

Radioactive noble gas isotopes such as ^{39}Ar ($T_{1/2} = 269$ yr) and ^{85}Kr ($T_{1/2} = 10.8$ yr) are inert and thus insensitive to any chemical process linking ^{14}C , DIC, and pH, making them ideal for understanding groundwater flow and mixing processes (13). While ^{85}Kr is sensitive on the same decadal time scale as tritium, ^{39}Ar is a unique intermediate age tracer, filling a gap between tritium and ^{14}C (40). Because of their conceptual simplicity as monatomic, unreactive dissolved gas tracers with well constrained input functions (40, 41), ^{85}Kr and ^{39}Ar offer valuable physical constraints but have remained underutilized due to analytical challenges (12, 13), with only a handful of studies having employed this set of age tracers in the same groundwater samples (e.g., 40, 41). In our SJV study area, these noble gas age tracers constitute a powerful tool to independently evaluate whether the observed low ^{14}C activities in low-DIC, high-pH, ^3H -free groundwaters (Figure 1) arise from systematic chemical processes that lowered $^{14}\text{C}_0$. In this study, we sampled a subset of six wells for analysis of inert age tracers in addition to ^{14}C and ^3H to test for consistency among independent age tracers under physically realistic mixing scenarios.

Prior work in the eastern SJV has demonstrated that the unconfined hydrogeologic setting is well-characterized by two distinct regimes: (i) a deeper (^3H free) portion of the aquifer recharged naturally by precipitation and river runoff before major agricultural and urban development, and (ii) a shallower, mostly tritiated (i.e., non-zero ^3H activity) portion recharged over the past 50-100 years at substantially higher rates by local irrigation seepage (16). We refer to these regimes as pre-development and post-development respectively. Notably, the modern rates of irrigation-derived recharge in the SJV are known to exceed natural recharge by roughly seven-fold (10, 18). This substantial influx of agriculturally impacted water also flows laterally (19), therefore influencing groundwater chemistry in more urban regions near irrigated farmland (17). Based on ^3H , the interface between these two regimes in the study area appears to fall between 50 and 100 meters below the land surface (Figure S2b), similar to previous findings to the north (16). Here, we first focus on three wells for which ^{39}Ar was measured, which are screened entirely in the pre-development regime and thus provide the simplest opportunity to compare inert tracers with ^{14}C without needing to account for mixing between pre- and post-development groundwater.

Direct comparison of ^{14}C -derived and ^{39}Ar -derived age estimates requires physical assumptions about mixing of different aged groundwaters in each well (Appendix S1). All three deep wells are ^3H -free, with ^{39}Ar in the range ~ 23 -50 pmAr (percent of modern atmospheric ^{39}Ar activity) and ^{14}C in the range ~ 43 -69 pmc (Table S1). It is readily apparent that residence time estimates based on ^{39}Ar and ^{14}C that neglect mixing (i.e., Eq. 1) are incompatible with a ^{14}C scaling factor Γ of 1, as both ^{39}Ar and ^{14}C observations across each well fall in the range of $\sim 50\%$ modern activity although the half-lives of the two tracers differ by an order of magnitude. However, even when groundwater mixing is rigorously accounted for by using a physical model, Γ must be well below unity in each well in order to reconcile ^{14}C with ^{39}Ar (Figure 2). During pumping, water is drawn into each well through a screened interval, inducing mixing that leads to a distribution of groundwater ages in the sample. In the deeper pre-development portion of the aquifer, an exponential age-depth profile is expected based on the unconfined nature of the aquifer (16, 44, 45). Our parameterization of mixing assumes a partial-exponential distribution of groundwater ages (e.g., panel b in Figure 2) that represents the fraction of each water mass sampled by a given well. We then (i) convolve this distribution with the ^{39}Ar and $^{14}\text{C}_{atm}$ (21, 28) atmospheric histories (e.g., panel a in figure 2), using different scaling factors for $^{14}\text{C}_0$, and (ii) account for radioactive decay to predict present-day measured ^{39}Ar and ^{14}C activities in these wells. We constrain the age distributions based on known well geometry and for maximum agreement between simulated and measured ^{39}Ar , such that an optimal ^{14}C scaling factor Γ can then be independently determined by comparing simulated ^{14}C with observations for each well (Appendix S1). Figure 2 shows the results of this analysis for well 180-1, as an example. For all deep wells (Figures S7, S10-11), we find that all optimal scaling factors Γ are substantially below unity (0.44-0.73). Critically, we find

that the assumption of no ^{14}C dilution ($F=1$) yields mean residence times between 3,200-8,300 years for these wells, whereas ^{39}Ar -optimized F values ($F<1$) yield smaller mean residence times of 240-840 years (Table S2).

Two shallower wells with screened intervals from 49-95 and 66-69 meters below the surface were found to have detectable ^{85}Kr activity and ^3H above 1 TU, indicating substantial contributions from modern recharge (Figures S8-9). Therefore these wells likely represent more complicated bimodal distributions of waters from both pre-development and post-development regimes (16), and a single-distribution modeling approach is thus overly simplified. However, comparison of ^{85}Kr with ^{14}C provides qualitative insights into potential temporal changes in F factors. Following the same partial exponential mixing (PEM) modeling approach for the deeper wells, but using ^{85}Kr instead of ^{39}Ar to tune age distributions, we find considerably higher F factors for these wells (0.85 and 0.91). Therefore, our inert tracer- ^{14}C age comparison case study points towards a shift from low $^{14}\text{C}_0$ to higher $^{14}\text{C}_0$ in both shallow and deep wells. This is interpreted to be associated with the transition from the natural, pre-development to modern recharge systems. Because a failure to account for this modern shift (i.e., by assuming $F=1$) would yield ^{14}C -derived residence times in the deeper wells that are thousands of years older than those independently implied by ^{39}Ar , it is essential to understand the underlying mechanisms.

DISCUSSION

Mid-century shift to open system dissolution

To explain the apparent shift in $^{14}\text{C}_0$ in groundwater over recent decades, we propose a simple conceptual DIC model that largely reproduces observed trends in ^{14}C , DIC, and pH, as well the findings of low ^{14}C scaling factors F in deeper wells. The model assumes that groundwater DIC is acquired through varying proportions of open-system (i.e., in the vadose zone, exposed to soil CO_2) and closed-system (i.e., below the water table) carbonate mineral dissolution (Appendix S2). The model also assumes that when carbonate minerals dissolve in the vadose zone, the isotopic composition of resultant carbonate-derived DIC is nearly atmospheric ($F\sim 1$) due to rapid isotopic equilibration with soil CO_2 via gas exchange (22, Appendix S3). Conversely, when carbonate dissolution occurs in isolation from soil CO_2 under closed-system conditions (i.e., beneath the water table), the resultant ^{14}C -free carbonate-derived DIC dilutes the ^{14}C activity of the DIC pool, thereby driving down $^{14}\text{C}_0$.

In the DIC model, the extent of “system openness” is parameterized based on the total DIC content of a groundwater parcel at the water table (DIC_{iso}), acquired under open-system conditions, before it is isolated from soil CO_2 by displacement beneath the water table due to subsequent recharge. Prior to any carbonate dissolution, the equilibrium dissolution of soil CO_2 in water provides a minimum DIC (DIC_0) in solubility equilibrium with soil CO_2 . If carbonate dissolution occurs rapidly enough to achieve equilibrium at or above the water table, before isolation, then groundwater will obtain a maximum open-system DIC ($\text{DIC}_{eq,open}$) in isotopic equilibrium with soil CO_2 . However, if groundwater is isolated from soil CO_2 before reaching $\text{DIC}_{eq,open}$, additional closed-system carbonate dissolution below the water table will consume acidity and dilute the DIC pool with ^{14}C -free input without replenishment by soil CO_2 , thereby limiting the equilibrium DIC ($\text{DIC} < \text{DIC}_{eq,open}$) and raising the equilibrium pH. Here, we define a system openness parameter (f) as the fraction of DIC that is acquired under open-system conditions before isolation from overlying soil CO_2 :

$$f \equiv \frac{\text{DIC}_{iso} - \text{DIC}_0}{\text{DIC}_{eq,open} - \text{DIC}_0} \quad (2)$$

The openness parameter (f) ranges from 0 (fully closed system) to 1 (fully open system). Figure 3 shows measured groundwater data alongside the modeled relationship between ^{14}C activity and pH, for varying system openness (f). At greater f , ^{14}C is higher, a larger fraction of

DIC exists as $\text{CO}_{2(\text{aq})}$, and, correspondingly, the pH is lower. In Figure 3, we demonstrate that this direct relationship between f and pH – rather than radioactive decay – can account for the inverse relationship between ^{14}C and pH observed in Figure 1. Notably, our idealized carbon model predicts a positive, concave-down curved relationship between ^{14}C and DIC, similar to the data plotted in Figure 1 (Figure S4) with a small range of variability in $\delta^{13}\text{C}$ relative to source endmember uncertainties (Figure S5). Importantly, f is quasi-conservative with respect to mixing, such that the DIC and ^{14}C activity of an admixture of waters with different f values will closely approximate the model-predicted DIC and ^{14}C activity for their average f (Figure S7). In Figure 3, comparison of measured data with the model curves suggests a shift at $f \sim 0.5$, such that groundwaters with substantial modern recharge fractions ($^3\text{H} > 1 \text{ TU}$) are best explained by mostly open-system dissolution ($f > 0.5$) with near-modern atmospheric ^{14}C of soil CO_2 (120 pmc). In contrast, older samples ($^3\text{H} < 1 \text{ TU}$) are best explained by mostly closed-system dissolution ($f < 0.5$) with a pre-development ^{14}C of soil CO_2 (100 pmc).

We hypothesize that the central-eastern SJV experienced a shift from mostly closed-system to mostly open-system carbonate dissolution regimes after the mid-1950s (Figure 4). This conceptual framework suggests a major shift in $^{14}\text{C}_0$ from as low as 50% atmospheric ($f \sim 0.5$) before the 1950s to nearly 100% atmospheric ($f \sim 1$) since the 1950s. Thus, for observed pre-development (deeper) groundwater ^{14}C activities between ~ 40 and 70 pmc, the contribution of radioactive decay to lowering ^{14}C is estimated to only be ~ 1 -10 pmc, resulting in ^{14}C -derived age estimates that are closer to those implied by ^{39}Ar (Table S2).

We caution, however, that while this idealized carbon model predicts coherent trends that are consistent with system-wide observations, it neglects processes that may be important for individual wells. For example, (i) silicate weathering likely accounts for some portion of DIC, (ii) observations of low modern pH imply heterogeneity in modern soil pCO_2 such that some locations exceed the uniform value (2.1%) prescribed in the model, (iii) enhanced open-system dissolution of natural carbonates driven by acidic agricultural infiltration could lead to excess DIC with modern atmospheric ^{14}C activity, and (iv) soil ^{14}C activities may have been somewhat lower than the atmosphere in the pre-development system, since modern irrigation seepage likely more efficiently delivers modern organic carbon to the vadose zone. For example, a greater contribution of soil CO_2 produced from respiration of older organic matter deeper in the vadose zone may have further lowered pre-development $^{14}\text{C}_0$ (29).

Our model is similar to several existing models for partially open-system dissolution of carbonate minerals (23, 24, 34), but differs in a subtle but important way. These existing models assume that DIC is comprised of (i) dissolved CO_2 in isotopic equilibrium with soil CO_2 , and bicarbonate derived from carbonate mineral dissolution that is either (ii) in isotopic equilibrium with CO_2 or (ii) isolated from CO_2 (thereby retaining the carbon isotopic composition of the carbonate minerals). These models parameterize an absolute concentration (q) of bicarbonate in equilibrium with soil CO_2 . Unlike these models, our approach defines a fraction (i.e., f) of the maximum equilibrium concentration of DIC that can be acquired via open-system carbonate dissolution ($\text{DIC}_{\text{eq,open}}$) relative to the minimum concentration of DIC in which only soil CO_2 , but no carbonate minerals, dissolve in the unsaturated zone. Our approach hence enables prediction of the evolution of carbon isotopic composition and total DIC as a function of f (i.e., system openness), whereas previous models do not directly parameterize total DIC as a function of q . The curved relationship between ^{14}C and DIC that our model predicts is an important clue in interpreting these groundwater data. However, it is crucial to note that, like previous models, our idealized approach accounts for just one of many potentially important processes. We suggest that idealized models and simple graphical approaches (e.g., 39) are helpful in identifying dominant processes and complement more complex geochemical models (e.g., 35) that include multiple mechanisms, but are often under-constrained.

Importantly, the indication of a general modern shift towards greater system openness points to an anthropogenic influence on groundwater chemistry, which we suspect is linked to irrigation seepage into shallow groundwater. While such a shift from closed- to open-system conditions directly affects the DIC of wells that draw mixtures of pre- and post-development groundwater (i.e., wells screened throughout the ~50-100 m interface between these two regimes; Figure S2), it also substantially impacts the interpretation of ^{14}C in deep wells that are unaffected by direct mixing with modern groundwater. That is, conventionally inferring that a near-atmospheric $^{14}\text{C}_0$ ($\Gamma \sim 1$), consistent with observations of high ^{14}C in shallow modern wells, applies to deeper wells, would yield erroneously long residence times. In this sense, this modern shift to system openness masks the closed-system nature of deeper, pre-development groundwater and thereby obfuscates ^{14}C dating of these wells without the additional insight from inert age tracers and consideration of broader trends in parameters related to DIC chemistry.

Like many other major agricultural regions worldwide (46, 47), human activities have substantially influenced groundwater in the SJV since the mid-20th century. Groundwater overdraft has induced meters of land subsidence (15), and land-use changes have both increased groundwater salinity (14) and led to contamination by agriculture (48, 49). Here we propose that irrigation seepage has directly influenced groundwater DIC in the SJV through the delivery of carbonate soil amendments, known as agricultural lime, to shallow groundwater. Agricultural lime (finely ground calcite, dolomite, and/or magnesite; hereafter AL) is ubiquitously used as a buffer for acidic soils on farmlands in the SJV (50) and globally. Inefficient tillage and limited depth mobility of AL in crop soils (51) can lead to surface excesses of these particulate carbonate minerals, which can be advected by precipitation or irrigation seepage into the subsurface. Crucially, the availability of easily dissolvable carbonate in the vadose zone, where pCO_2 is far higher than the atmosphere even at shallow depths, is key to raising the equilibrium groundwater DIC content via open-system dissolution. The prevalence of farmland throughout the study area (Figure S1) raises the possibility that the spatial distribution of recharge may have changed over recent decades, providing widespread pathways for alteration of groundwater chemistry and delivery of AL to the vadose zone. Previous work has identified prominent geochemical signals associated with AL dissolution in groundwater recharged by irrigation seepage (52). Because AL is designed to dissolve rapidly, due to its high surface area, transport of this particulate carbonate through the vadose zone would result in enhanced rates of open-system carbonate dissolution relative to the natural pre-development system, in which carbonate dissolution in subsurface rocks and soils was slower and thus occurred predominately beneath the water table. Although the ^{14}C activity of AL (sourced from old, naturally occurring, ^{14}C -free carbonate minerals) is negligible, rapid isotopic equilibration of DIC with the large reservoir of soil CO_2 via gas exchange would efficiently reset the ^{14}C activity of DIC to a near-atmospheric value over a timescale of weeks to months (Appendix S3). Figure 4 presents a schematic of pre-1950s closed-system and post-1950s open-system carbonate dissolution, where the mid-20th century shift is driven by anthropogenic carbonate input to groundwater.

The hypothesized agricultural influence on modern groundwater chemistry is further supported by measurements of elevated Sr^{2+} , NO_3^- , and SO_4^{2-} accompanying high DIC, Mg^{2+} , and Ca^{2+} in low-pH, tritiated groundwaters (Figure S8). While NO_3^- and SO_4^{2-} are common indicators of agricultural seepage (49, 53), Sr^{2+} is associated with AL dissolution due to its compatible valence and thus frequent incorporation into carbonate minerals (52). Irrigation seepage carrying particulate agricultural carbonates to the vadose zone thus provides a compelling mechanism for a modern shift toward greater open-system carbonate dissolution, leading to near atmospheric ^{14}C activities and higher DIC in modern tritiated groundwaters (Figure 1). Critically, if this widely used soil amendment (i.e., AL) has led to masking of natural closed-system dilution of ^{14}C throughout the SJV, corresponding to thousands-of-year overestimations of groundwater age, it

likely affects the use of ^{14}C as an age tracer in other global aquifers that are relied upon for major agricultural production worldwide.

Implications for groundwater dating

In this study, we observe two independent lines of evidence indicating a major mid-20th century shift in groundwater DIC in the central-eastern SJV: a residence-time modeling case study constrained by inert age tracers, and a wider consideration of geochemical trends corroborated by an idealized DIC model. These two approaches point to a transition from mostly closed-system to mostly open-system dissolution of carbonates, which we hypothesize is due to anthropogenic input of AL. This modern shift in DIC chemistry has masked underlying natural closed-system carbonate dissolution, which led to low $^{14}\text{C}_0$ under pre-development conditions. A key consequence of this finding is that without multiple age tracers and a mechanistic consideration of regional controls on inorganic carbon chemistry, apparent ^{14}C -based groundwater residence times in the deeper, pre-development portion of the aquifer (under the assumption that $f=1$, as suggested by modern tritiated water), would in fact be overestimated by hundreds to thousands of years. Specifically, we find that inert ^{39}Ar -derived mean age estimates in deeper wells, which range from ~240-840 years, are an order of magnitude younger than those implied by ^{14}C (if $f=1$), which range from ~3,200-8,300 years.

Erroneously long estimates of recharge timescales would invariably lead to underestimation of the susceptibility of deeper groundwater to modern contamination and can impact calibration of groundwater flow models that are important for sustainable management. Indeed, a new understanding that the deeper wells considered in this study have mean residence times of centuries, rather than millennia, raises the concern that continued groundwater withdrawal in the SJV and depression of the regional water table may soon allow modern irrigation-derived recharge to reach the depths of these wells. These findings have broad relevance to other global aquifers that have experienced fundamental changes from predominantly natural to anthropogenic recharge over the past century, driven by large-scale agricultural development (46, 47). We therefore suggest that a combined inert-gas and inorganic carbon-system modeling approach represents the best means of improving estimates of groundwater residence times in groundwater systems susceptible to DIC perturbations by recent agricultural activity, without the added uncertainties introduced by more complex models. Additionally, we emphasize that the agricultural regions most prone to masking of natural dilution of $^{14}\text{C}_0$ by irrigation seepage are often those most heavily reliant on groundwater, and therefore most vulnerable to declines in groundwater quality and quantity.

MATERIALS AND METHODS

Groundwater measurements:

The wells selected for this study were sampled either as a part of this work or in previous USGS groundwater measurement programs (54). Groundwater samples were collected following standard USGS protocols and analyzed at U.S. Geological Survey (USGS) and other laboratories using established analytical methods (55) as part of the USGS National Water-Quality Assessment (NAWQA) Enhanced Trends Network (ETN) program (54). The carbon isotopic composition of DIC was analyzed at the Woods Hole Oceanographic Institution National Ocean Sciences Accelerator Mass Spectrometry lab (56); major and trace elements were measured via ICPMS/AES, AAS, and ion chromatography at the USGS National Water Quality lab (57, 58); water isotopes at the USGS Reston Stable Isotope Lab (59); tritium at the USGS Menlo Park Tritium Lab (60); and noble gases at USGS Denver Noble Gas Laboratory (61). Measurements of ^{39}Ar in three deep wells were made at Pacific Northwest National Laboratory via ultra-low-background proportional counting (62). Radioactive Kr isotopes (^{85}Kr and ^{81}Kr) were measured in

four wells spanning multiple depth intervals at the same site (wells 180-1 through 180-4) at Argonne National Laboratory via Atom Trap Trace Analysis (ATTA) (13). DIC concentrations and speciation were determined from measured pH and alkalinity using inorganic carbon system equilibrium constants presented in Appendix S2.

Lumped parameter modeling:

Residence time distributions and associated tracer simulations were carried out in MATLAB using multiple age distribution models presented in TracerLPM (45). Atmospheric histories of ^{14}C activity (21, 28), ^3H activity (45), and ^{85}Kr activity (41) were prescribed, and atmospheric ^{39}Ar activity was assumed to be constant over the 3 ka time period considered in this study. For each of the five wells analyzed for inert age tracers (^{39}Ar and ^{85}Kr) in the case study (Appendix S1), the PEM model was used to estimate residence time distributions. Perforated depth intervals (Table S1) were used to constrain the PEM model, reducing the residence time distribution to a function only of mean residence time (τ). For each well, τ was first estimated by maximizing agreement between simulated and measured inert age tracer activities (^{39}Ar or ^{85}K). Next, using inter-tracer constrained PEM model was used to simulate ^{14}C activity and Γ was optimized to minimize disagreement between measured and simulated ^{14}C activities. Because all deep wells were ^3H free (indicating predominance of pre-1950s water), it was assumed that DIC was invariable across the age mixture for each well. Finally, Γ values were compared with τ and pH, indicating a consistent shift towards lower Γ with increasing τ and pH. Appendix S1 provides additional details on lumped parameter modeling.

Carbonate dissolution model:

The idealized inorganic carbon model used in this study solves for ^{14}C activity and $\delta^{13}\text{C}$ of DIC and for concentrations of $\text{CO}_{2(\text{aq})}$, CO_3^- , and HCO_3^- , pH, and Me^{2+} (where $\text{Me}^{2+} = \text{Mg}^{2+} + \text{Ca}^{2+}$) as a function of system openness, f , based on prescribed values of soil pCO_2 , soil and carbonate mineral ^{14}C and $\delta^{13}\text{C}$, and temperature. CO_2 solubility, reaction constants, and carbon equilibrium isotopic fractionation factors were prescribed based on literature values (22). The model solves for system parameters at three conceptual stages: (1) dissolution of CO_2 before carbonate dissolution occurs, (2) progressive carbonate dissolution under open-system conditions until the point of isolation of groundwater from overlying soil CO_2 , and (3) subsequent carbonate dissolution in the saturated zone under closed-system conditions. The model assumes equilibrium between DIC species at each stage and isotopic equilibrium between soil CO_2 and DIC for stages (1) and (2). Appendix S2 provides additional details on the idealized carbonate dissolution model, including example simulations under varying conditions.

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Author contributions: JTK and AMS designed the study and collected groundwater samples; AMS, JTK, DVB, PHB, KED, and BJ interpreted the data; AMS carried out data analysis and modeling with input from JTK and BJ; EKM and CEA measured ^{39}Ar ; JCZ and PM measured ^{85}Kr and ^{81}Kr ; AMS wrote the manuscript with edits from all authors.

Competing interests: The authors report no conflicts of interest.

Data and materials availability: All measurements and model output in this study are included as a supplementary data set and can be publicly accessed online through the USGS National Water Information System (NWIS, <https://waterdata.usgs.gov/nwis>) using the well station identification numbers provided in the supplementary data set.

Supplementary materials: The following documents are included with this manuscript.

- Supplementary Appendices S1-S3
- Supplementary Tables S1-S2
- Supplementary Figures S1-S8
- Supplementary data set (Excel spreadsheet)

FIGURE LEGENDS

Figure 1. SJV groundwater ^{14}C activity **(a)** increases as a function of DIC and $\text{Mg}^{2+} + \text{Ca}^{2+}$ concentrations, and **(b)** decreases with pH, such that tritiated samples (^3H activity > 1 TU) tend to have pH lower than 7.5 and ^{14}C greater than 100 pmc, while **(c)** shows no coherent relationship with $\delta^{13}\text{C}$. Note the linear and log scales of color bars in (a) and (b), respectively. (Note: DIC data are unavailable for well 180-4). The gray arrows indicate the conventional expected direction of change for each variable shown in these panels due to closed-system carbonate dissolution, which is clearly inconsistent with the data in **(a)** and **(c)**.

Figure 2. Multiple tracer age comparison for Well 180-1. **(a)** Initial groundwater ^{14}C activity histories for differing ^{14}C dilution factors (I , Eq. 1) values are convolved with **(b)** a modeled distribution of groundwater ages, constrained by ^{39}Ar , to **(c)** simulate tracer activities for direct comparison with measurements. Tracer activities are shown in units of pmc, pmAr, dpm cc^{-1} , and TU for ^{14}C , ^{39}Ar , ^{85}Kr , and ^3H , respectively. Open and closed circles show simulated ^{14}C activities associated with atmospheric ($I=1$) and sub-atmospheric ($I<1$) $^{14}\text{C}_0$, respectively.

Figure 3. Measured groundwater ^{14}C activity and modeled ^{14}C activity curves, versus pH (or $\text{CO}_{2(\text{aq})}/\text{DIC}$) for a soil pCO_2 of 21000 μatm . Most tritiated samples (< 50 years mean recharge age) fall on the modeled curve for high values of f (> 0.5) and an initial ^{14}C of mean modern atmospheric ^{14}C (120 pmc). Most ^3H -free samples fall onto or below the modeled curve, indicating greater degrees of closed-system equilibration and contributions from radioactive decay. Tritiated samples with high DIC and low pH are interpreted to result from modern open-system equilibrium at higher soil pCO_2 .

Figure 4. Illustration of hypothesized shift from natural carbonate dissolution (left panel) within the saturated zone (predominantly closed-system DIC exchange) to modern conditions where agricultural-lime influenced dissolution leads to predominantly open-system DIC exchange (right panel) through the vadose zone. In both panels, red arrows indicate the flux of soil CO_2 to groundwater DIC, gray arrows indicate the flux of carbonate dissolution (natural or anthropogenic) to the DIC pool, and the dashed arrows indicate the direction(s) of isotope exchange. Under closed system conditions, there is no isotopic exchange between DIC and soil CO_2 during carbonate dissolution, hence this arrow is unidirectional on the left, but bidirectional on the right. Dots on the right panel represent finely ground agricultural carbonate particles that dissolve throughout the unsaturated zone and at the water table in the presence of CO_2 .