Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination

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The vulnerability of groundwater to contamination is closely related to its age. Groundwaters that infiltrated prior to the Holocene have been documented in many aquifers and are widely assumed to be unaffected by modern contamination. However, the global prevalence of these ‘fossil’ groundwaters and their vulnerability to modern-era pollutants remain unclear. Here we analyse groundwater carbon isotope data (13C, 14C) from 6,455 wells around the globe. We show that fossil groundwaters comprise a large share (42–85%) of total aquifer storage in the upper 1 km of the crust, and the majority of waters pumped from wells deeper than 250 m. However, half of the wells in our study that are dominated by fossil groundwater also contain detectable levels of tritium, indicating the presence of much younger, decadal-age waters and suggesting that contemporary contaminants may be able to reach deep wells that tap fossil aquifers. We conclude that water quality risk should be considered along with sustainable use when managing fossil groundwater resources.

Gl obal groundwater is an immense resource, storing ~100 times more water than all the world’s lakes1,2, supplying ~40% of the water for global irrigated agriculture3, and providing drinking water to billions of people around the world. Recent research has evaluated the global depths of both the groundwater table1 and modern groundwater recharged within the past ~50 years4, but the global prevalence and distribution of ‘fossil groundwater’ remain unclear. Here we define fossil groundwater as groundwater recharged by precipitation more than ~12,000 years ago, prior to the beginning of the Holocene epoch; we define prevalence as the frequency with which regional well waters contain fossil groundwater. Understanding the global extent and depth of fossil groundwater resources is important because of their distinctive susceptibility to overdraft5, presumed isolation from surface-borne pollutants6,7, potential vulnerability to geogenic contaminants8, and isolation from modern climate variability9.

To calculate the prevalence of fossil groundwater in well waters, we compiled a groundwater carbon isotope (13C, 14C) database of 6,455 well water samples from around the globe. The continental USA and Europe are over-represented in our compilation, which is also inevitably biased towards sedimentary basins where groundwater use is common (Supplementary Figs 1.2 and Methods). Radiocarbon (~14C) has a half-life of 5,730 years and has been widely used to identify fossil groundwaters10–14. Stable carbon isotope (13C, 14C) data were used to correct for the dissolution of carbonate rocks, which are devoid of radiocarbon15 and thus would otherwise distort 14C-based fossil groundwater calculations. We estimated fossil groundwater fractions in wells around the world using a recently developed radiocarbon endmember mixing model, which accounts for both radioactive decay and carbonate dissolution for pre- and post-Holocene recharge16. Our approach, which estimates the fraction of fossil groundwater in a water sample rather than the sample’s average age, is designed to be less vulnerable to the aggregation errors that are known to bias mean groundwater age calculations17–20. We plotted depth profiles of fossil groundwater for aquifers around the world and calculated the depth below which fossil groundwater becomes common (>50% of wells pump some fossil groundwater) or dominant (>50% of wells pump >50% fossil groundwater; Methods). Where tritium (~3H) data were available (n = 5,661 well water samples), we determined the fraction of the groundwater sample that recharged more recently than around 1953 by relating groundwater ~3H concentrations to historical precipitation ~3H time series15 (Methods). The threshold year 1953 was selected because widespread thermonuclear testing in subsequent years increased precipitation tritium levels by ~5 to ~500 times above local natural background concentrations4, providing a tracer of recently recharged groundwater (for example, ref. 15). For samples with both radiocarbon and tritium data, we
calculated the three fractions of groundwater that recharged more than ~12 thousand years ago (fossil groundwater); recharged more recently than the year 1953 (post-1953 groundwater); and is of an intermediate age, having recharged more recently than ~12 thousand years ago, but before the year 1953.

**Fossil groundwater in global aquifers**

Our global compilation of radiocarbon data shows that fossil groundwater is not an anomaly in the upper 1 km of the crust, but instead is common in wells drilled to depths of more than 250 m (Figs 1, 2 and Supplementary Fig. 3). Among all surveyed wells \( n = 6,455 \) (Supplementary Fig. 3), we find that more than half of all wells deeper than 250 m yield groundwater that was mostly (>50%) replenished before the Holocene (that is, minimum fossil groundwater exceeds 50% for the majority of groundwater samples pumped from wells deeper than 250 m). By contrast, post-1953 groundwater becomes increasingly scarce with depth (Fig. 2). Half of all wells deeper than 40 m pump groundwater that is comprised almost entirely (>90%) of groundwater recharged before 1953 (that is, maximum post-1953 groundwater is less than 10% for the majority of groundwater samples pumped from deeper than 40 m).

Fossil groundwater is found throughout several major aquifers that sustain modern irrigated agriculture (Fig. 1), including the North China Plain (at depths >200 m), the southern Central Valley of California (at depths >260 m), the north, central and south High Plains aquifers of the central USA (at depths >120–280 m), Italy’s Emilia–Romagna Plain (at depths >100–300 m) and Hungary’s Pannonian Basin (at depths >160–300 m). Among our 62 study aquifers (Fig. 1), we find the range of depths below which fossil groundwater domine wells water (that is, fossil groundwater comprise >50% of the water pumped from more than half of all deeper samples) has a median of 200 m, a lower–upper quartile range of 115–290 m, and a 10th–90th percentile range of 70–430 m.

Assuming that isotopes measured in well waters reflect the isotope compositions of groundwater stored in aquifers and are not the result of contamination by infiltrated surface water or rainfall (for example, refs 1,5,11–18), our data show that fossil groundwater likely comprises 42–85% of total groundwater in the crust’s uppermost 1 km, 31–79% in the uppermost 500 m, and 10–63% in the uppermost 100 m (Fig. 2c). By contrast, post-1953 groundwater comprises only 5–22% of total groundwater in the crust’s uppermost 1 km, 6–27% in the uppermost 500 m, and 13–51% in the uppermost 100 m (Fig. 2d). Fossil groundwater storage in the uppermost 1 km of the crust is, therefore, ~1.9 to ~17 times larger than post-1953 groundwater stores. By combining our new global fossil groundwater storage estimate with global porosity data, we calculate that of the 12–22 million km³ of unfrozen water stored.
in the uppermost 1 km of the crust (\( \sim 85–152 \text{ m equivalent depth} \)) of a column of water, approximately 5–18 million km\(^3\) is fossil groundwater (36–130 m equivalent depth), 0.6–4.6 million km\(^3\) is post-1953 groundwater (4–33 m equivalent depth), and less than 8,000 km\(^3\) is recent rain and snow that becomes streamflow in less than three months\(^{25}\) (<0.055 m equivalent depth).

Figures 1 and 2 show that the abundance of modern (post-1953) groundwater generally decreases with depth and that the abundance of fossil groundwater generally increases with depth. Topography-driven groundwater flow, geologic layering, and the decrease of permeability with depth generally lead to well-flushed shallow zones overlying poorly flushed deeper zones, consistent with the occurrence of fossil groundwaters at depth. We conclude that a substantial share (42–85\%) of global groundwater is fossil in age. Further, our analysis may even imply that fossil groundwater pumping here is relatively rare (Supplementary Fig. 6). Similarly, in the San Joaquin Valley, the large majority (98\%) of wells are shallower than the depth below which fossil groundwater becomes common (\( \sim 240 \text{ m} \)). In the Denver Basin, however, many (38\%) groundwater wells have been constructed to depths where fossil groundwater is either detectable or dominant (\( > 125 \text{ m} \)), implying that fossil groundwater use in the Denver Basin is widespread (Supplementary Fig. 6). Further, fossil groundwater pumping in the Denver Basin has probably increased over the past \( \sim 60 \) years because older wells drilled between 1950 and 1970 were substantially shallower (median well depth of 27 m) than wells constructed more recently than 2010 (median well depth of 126 m), and because total groundwater pumping has more than quadrupled since 1970 (ref. 29).

Our comparison of groundwater well depths and vertical distributions of fossil groundwater emphasizes that both fossil and post-1953 groundwaters are withdrawn from US aquifers. Pumping fossil groundwater may lead to aquifer depletion, and this risk is greater in arid regions where groundwater tables are deeper and compensatory increases in recharge or decreases in groundwater discharge are less likely (see ref. 30). Water levels in deep wells have declined across much of the US over the past six decades, probably due to changes in groundwater pumping in response to climate variations\(^{31}\). Groundwater well construction is guided by aquifer properties (for example, transmissivity) and groundwater quality (for example, salinity) rather than groundwater age. Nevertheless, we conclude that deep fossil groundwater is already used in some parts of the US, and posit that reliance on fossil groundwaters is probably also widespread in other regions, particularly in hyper-arid climates where modern recharge is negligible.

**Fossil well waters vulnerable to contamination**

Our compilation of radiocarbon and tritium data shows that roughly half of the well water samples that are measurably depleted in carbonate-dissolution-corrected \(^{14}\text{C}\) (which is clear evidence of fossil age) also contain measurable amounts of \(^{3}\text{H}\) (which is unequivocal evidence of recharge after the onset of thermonuclear-bomb testing in the 1950s; Table 1). This observation questions the common perception that fossil groundwaters are largely immune to modern contamination (for example, refs 6,7). Our finding that fossil well waters often contain a component of much younger, decades-old groundwater means that fossil well waters—and, possibly, the aquifers from which they derive—are more vulnerable to pollution from modern-era contaminants than previously thought.

Several processes can mix decadal-age groundwater with fossil groundwater and thus make fossil well waters vulnerable to modern contaminants. One plausible explanation is aquifer heterogeneity, leading to preferential flow of younger groundwater through...
widespread mixing of fossil and post-1953 groundwater, we would find fossil water). If natural flow paths were the primary cause of the mixing, tritium would also be detected in approximately half of samples with tritium evidence (Table 1), rendering them immune to modern contamination. Thus, tritium may co-occur with some fossil groundwater (>0% but possibly <50% fossil water), which is not the case (Table 1). Consequently, tritium can occur in wells with open holes or long screens that simultaneously capture young and old groundwater from shallow and deep layers of an aquifer. Leaks in corroded or poorly sealed portions of a well may also contribute to mixing of young and old waters in the well bore itself. Co-occurrences of fossil and post-1953 groundwater pumped from wells perforated hundreds of metres below the land surface more likely arise from the construction, presence and use of the well itself. For some hydrogeologic settings, it is unlikely that natural flow paths transmit groundwater hundreds of metres below the land surface within a few decades. We note that tritium occurs equally often in well waters containing some fossil groundwater (tritium was detected in approximately half of all samples with >0% and in well waters containing mostly fossil groundwater). If natural flow paths were the primary cause of the widespread mixing of fossil and post-1953 groundwater, we would expect that samples dominated by fossil groundwater (>50%) would contain measurable tritium less frequently than samples that contain some fossil groundwater (>0% but possibly <50% fossil water), which is not the case (Table 1). Thus, tritium may co-occur with fossil groundwater primarily as a result of pumping along extensive well screens, up-coning and down-coning of groundwater due to pumping, and leaks along well bores. Regardless of how tritium has become mixed with much older groundwater, the main implication for drinking water supplies is clear: many (~50%) fossil well waters contain detectable amounts of recently recharged groundwater (Table 1), rendering them potentially vulnerable to modern anthropogenic contamination despite their great age. Because aquifers bearing fossil groundwater require millennia to be flushed, their contamination may also persist for millennia, causing effectively irreversible harm to these aquifers over human timescales. However, it remains unclear how frequently tritium arises in fossil well waters as the result of mixing within the aquifer itself, versus mixing induced by the construction and pumping of the groundwater well. Fossil groundwater resources Our analysis shows that fossil groundwater probably dominates global groundwater storage in the uppermost 1 km of the crust (42–85%). This figure is likely to be a lower bound on the global prevalence of fossil groundwater, because the probable biases in our analysis (detailed above) serve to minimize our calculated fossil groundwater fractions. Further, our analysis focuses solely on the shallowest 1 km of the crust that is also the most rapidly flushed. Fractured rocks deeper than 1 km can host ancient fossil groundwater that have been isolated for millions or even billions of years.

Improving access to freshwater for agriculture, households, and industry while sustaining vital ecosystems in a changing global environment represents a critical scientific and political challenge. Fossil groundwater resources probably comprise more than half of global unfrozen freshwater (Figs 1 and 2), and dependence upon fossil groundwater to meet water demands is rising as a consequence of increasing groundwater withdrawals and deeper drilling in some regions. Groundwater quality remains a critical concern in many parts of the world, and our results highlight that even though deeper wells pump predominantly fossil groundwater, they are not immune to modern contamination.

### Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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### References


### Table 1 | Radioisotope (14C, 3H) evidence for post-1953 and fossil groundwater mixing.

<table>
<thead>
<tr>
<th>Presence of fossil groundwater</th>
<th>Total 14C samples with 3H data</th>
<th>Presence of post-1953 groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present (3H &gt; 0)</td>
<td>Absent (3H ≈ 0)</td>
</tr>
<tr>
<td>May contain no fossil water (possibly 0%)</td>
<td>n = 984</td>
<td>74%</td>
</tr>
<tr>
<td>Contains fossil water (&gt;0%), but possibly &lt;50%</td>
<td>n = 179</td>
<td>49%</td>
</tr>
<tr>
<td>Contains mostly fossil water (&gt;50%)</td>
<td>n = 365</td>
<td>50%</td>
</tr>
</tbody>
</table>

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**Author contributions**
S.I. and J.W.K. analysed the compiled groundwater isotope data and wrote initial drafts of the manuscript. S.I. and D.P. analysed the compiled groundwater well construction data. All authors discussed results and edited the manuscript.

**Additional information**
Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Springer's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Correspondence and requests for materials should be addressed to S.J.

**Competing financial interests**
The authors declare no competing financial interests.
Methods

Global groundwater isotope data. We analysed global groundwater isotope data compiled from hundreds of primary literature sources and from the United States Geological Survey’s Water Quality Portal (Supplementary Tables 1 and 2). About two-thirds (65%) of our global radiocarbon compilation comes from North America, which represents only ~18% of global ice-free lands. By contrast, only 9% and 11% of our compiled radiocarbon data come from Africa and Asia, which each comprise much larger shares of the global landmass (~22% and ~33% of global ice-free lands, respectively; Supplementary Fig. 2). We analysed the compiled groundwater isotope data to partition the fraction of groundwater samples that recharged before the Holocene–Pleistocene transition 11,700 years ago (‘fossil groundwater’, based on 14C with a half-life of 5,730 years), and more recently than 1953, when the ‘hydrogen bomb peak’ in meteoric tritium began (‘post-1953 groundwater’, based on 1H with a half-life of 12.3 years).

Determining fossil groundwater fractions. We used stable (δ13C) and radioactive (14C) carbon isotope data to calculate fossil groundwater fractions (F_fossil) following (ref. 20):

\[ F_{fossil} = 1 - \frac{\delta^{14}C_{sample} - \delta^{14}C_{fossil}}{\delta^{14}C_{Holocene} - \delta^{14}C_{fossil}} \]  

(1)

where dissolved inorganic carbon concentrations are assumed to be roughly equal for the fossil and Holocene waters18, and 14C represents the radiocarbon activity of the groundwater sample (subscript ‘sample’), Holocene groundwater recharged within the past 11,700 years (subscript ‘Holocene’), or fossil groundwater recharged more than 11,700 years ago (subscript ‘fossil’). Holocene and fossil 14C inputs are based on late-Quaternary atmospheric 14C time series20.22 corrected for radioactive decay following (ref. 20):

\[ \delta^{14}C = (\delta^{14}C_{precip}(t) - 0.693(\text{atm-age})14/12)(5730\text{ years}) ] \]  

(2)

where 14C_{precip}(t) represents precipitation 14C at time t, and atm-age is the date that the groundwater sample was analysed. 14C_{atm}-14C_{fossil}, evaluated for the time interval of 0 < atm-age < 11,700 years: 14C_{fossil} is represented by 14C_{fossil} evaluated prior to the Holocene (that is, atm-age > 11,700 years). For years postdating thermonuclear-bomb testing, we apply a 10-year running average to estimate the maximum possible 14C_{atm}-14C_{fossil} value (Supplementary Fig. 5), effectively assuming some amount of dispersion has taken place in most aquifer systems over the past 50 years. The factor 0.693 is used to correct for the dissolution of carbonate with zero radiocarbon:

\[ \delta^{13}C = \delta^{13}C_{carbonate} - \delta^{13}C_{rock} \]  

(3)

where 13C_{carbonate} and 13C_{rock} are the stable isotope compositions of recharge and carbonates. We used 13C_{rock} and 13C_{carbonate} values reported in the compiled studies when available, and otherwise assumed 13C_{carbonate} = 0‰ and 13C_{rock} = -14‰. PDB (Pee Dee Belemnite). Global 13C_{carbonate} and 13C_{rock} values vary around the globe29 such that our assumption of 13C_{carbonate} = 0‰ is 13C_{rock} = -14‰ introduces uncertainty into our fossil groundwater calculations.

The range of 14C values ascribed to each time interval (δ14C) is assumed to be constrained by 14C_{rock} ≤ δ14C ≤ 14C_{Holocene} ≤ δ14C ≤ 14C_{carbonate} (ref. 20). Because the possible ages of the Holocene and pre-Holocene endmembers vary widely, the ranges of 14C_{Holocene} and 14C_{carbonate} are often large; we apply upper and lower limits of 14C_{Holocene} and 14C_{carbonate} in equation (1) to estimate minimum and maximum fossil groundwater fractions. 14C_{Holocene} and 14C_{carbonate} share an identical endmember at the 11,700-year boundary. The shared 11,700-year endmember, and the large atmospheric radiocarbon variations over each endmember interval, lead to highly uncertain F_{fossil} calculations for some samples.

In each aquifer, we pinpointed two depths where observed transitions from Holocene groundwater to pre-Holocene fossil groundwater, and used these depths as upper and lower limits in the bar graphs shown in Fig. 1. The first (shallower) recorded transition depth specifies a depth below which the majority (> 50%) of well water samples from a given aquifer must contain some fraction of fossil groundwater (that is, over half the samples have a minimum fossil groundwater fraction of greater than zero). The second (deeper) recorded transition depth represents a depth below which the majority (> 50%) of sampled well waters from a given aquifer system contain mostly fossil groundwater (that is, over half of the samples deeper than the depth have a minimum fossil groundwater fraction exceeding 50%).

Where oxygen stable isotope data are also available, we confirmed the depth to fossil groundwater by comparing the 18O/16O ratio in groundwater to a new global map of 18O in late-Pleistocene precipitation17; where δ18O = ([18O/16O]_{sample} - [18O/16O]_{modern ocean water}) × 10^3/18O. Late-Holocene and late-Pleistocene precipitation δ18O values are detectably different (> 1‰) over the great majority (~87%) of the global landmass18, enabling use of depth-δ18O plots as a qualitative secondary indicator of the depth to fossil groundwater.

Determining post-1953 groundwater fractions. To calculate the fraction of modern, post-1953 groundwater in a sample we used globally interpolated precipitation tritium for years spanning the pre-bomb era (prior to 1950) to 2010 from ref. 24. Global precipitation 3H estimates derive from > 60,000 monthly 3H measurements made at 738 globally distributed stations (data provided by the International Atomic Energy Agency: iaea.org/water). We then weighted the monthly precipitation 3H data against the long-term average monthly precipitation rate24 to estimate an annually integrated precipitation 3H value at each well site. Once a precipitation tritium record was developed for each well location (from ref. 24), we decay-corrected the precipitation tritium input curve to the date that each sample was collected20. As in our radiocarbon-based calculation, we assume that some amount of dispersion takes place in the aquifer and apply a 10-year running average before calculating maximum and minimum possible 3H_{post-1953} values (Supplementary Fig. 5). We then applied the range of possible decay-corrected, post-1953 precipitation 3H values as one endmember in a two-component mixing model, and pre-1953 precipitation 3H as the other component:

\[ F_{post-1953} = \frac{3H_{sample} - 3H_{pre-1953}}{3H_{post-1953} - 3H_{pre-1953}} \]  

(4)

where 3H_{pre-1953} is the measured 3H in the groundwater sample, and 3H_{post-1953} and 3H_{pre-1953} are the local meteoric water tritium activities that have been decay-corrected to the time of sampling for either prior to 1953 (3H_{pre-1953}), or years after 1953 (3H_{post-1953}). The year 1953 was selected as a threshold20 so that the overwhelming majority of possible 3H_{post-1953} values fall below analytical detection limits, leading us to assume 3H_{post-1953} = 0. We assume subterranean tritium production leads to secular equilibrium tritium contents that do not exceed the common analytical detection limit of 0.8 tritium units.

Estimating groundwater age-storage volumes. In Fig. 2 of the main text, we present ranges of fossil and post-1953 groundwater with depth. The ranges shown represent averages of the minimum and maximum fossil groundwater (or post-1953 groundwater) fractions at each depth interval. For example, the range of fossil groundwater from 0 m to 25 m depth shown in Fig. 2a is 3%–52%, where 3% is the average minimum fossil groundwater fractions among all n = 627 wells perforated in the uppermost 25 m of the crust, and 52% is the average maximum fossil groundwater fraction for these n = 627 well waters.

Data availability. Compiled groundwater isotope data are available in the primary references listed in Supplementary Tables 1 and 2 and in tabulated form in the Supplementary Information. Additional groundwater isotope data for the USA used in this analysis can be downloaded from https://www.waterqualitydata.us.

References