

1 **Submitted manuscript entitled:** Global aquifers dominated by fossil groundwaters but
2 vulnerable to modern contamination

3 **Submitted to:** *Nature Geoscience* on 23 February 2017

4 **Authors:** Scott Jasechko^{1,*}, Debra Perrone^{2,3}, Kevin M. Befus⁴, M. Bayani Cardenas⁵, Grant
5 Ferguson⁶, Tom Gleeson⁷, Elco Luijendijk⁸, Jeffrey J. McDonnell^{9,10,11}, Richard G. Taylor¹²,
6 Yoshihide Wada^{13,14,15,16}, James W. Kirchner^{17,18,19}

7 **Author affiliations:**

8 ¹ Department of Geography, University of Calgary, Calgary, Alberta, T2N 4H7, Canada

9 ² Water in the West, Stanford University, Stanford, California, 94305, USA

10 ³ Civil and Environmental Engineering, Stanford University, Stanford, California, 94305, USA

11 ⁴ Civil and Architectural Engineering, University of Wyoming, Laramie, Wyoming, 82071, USA

12 ⁵ Department of Geological Sciences, The University of Texas at Austin, Austin, Texas, 78712,
13 USA

14 ⁶ Department of Civil and Geological Engineering, University of Saskatchewan, Saskatoon,
15 Saskatchewan, S7N 5A9, Canada

16 ⁷ Department of Civil Engineering and School of Earth and Ocean Sciences, University of
17 Victoria, Victoria, British Columbia, V8P 5C2, Canada

18 ⁸ Geoscience Centre, University of Göttingen, Göttingen, 37077, Germany⁹ Global Institute for
19 Water Security, and School of Environment and Sustainability, University of
20 Saskatchewan, Saskatoon, Saskatchewan, S7N 3H5, Canada

21 ¹⁰ School of Geosciences, University of Aberdeen, Aberdeen, Scotland, AB24 3FX UK

22 ¹¹ Department for Forest Engineering, Resources and Management, Oregon State University,
23 Corvallis, Oregon, 97330, USA

24 ¹² Department of Geography, University College London, London, WC1E 6BT, UK

25 ¹³ International Institute for Applied Systems Analysis, Schlossplatz 1, Laxenburg, A-2361,
26 Austria

27 ¹⁴ Department of Physical Geography, Utrecht University, Utrecht, 80115, The Netherlands

28 ¹⁵ NASA Goddard Institute for Space Studies, 2880 Broadway, New York, New York, 10025,
29 USA

30 ¹⁶ Center for Climate Systems Research, Columbia University, 2880 Broadway, New York, New
31 York, 10025, USA

32 ¹⁷ Department of Environmental System Sciences, ETH Zürich, Universitätstrasse 16, CH-8092,
33 Switzerland

34 ¹⁸ Swiss Federal Research Institute WSL, Birmensdorf, CH-8903, Switzerland

35 ¹⁹ Department of Earth and Planetary Science, University of California, Berkeley, California,
36 94720, USA

37 ***Corresponding author:**

38 Scott Jasechko

39 Department of Geography, University of Calgary

40 2500 University Drive, Calgary, AB, T2N 1N4

41 Telephone: +1 403 220 5584

42 Fax: +1 403 282 6561

43 Email: sjasechk@ucalgary.ca

Words (abstract): 194

Words (main text): 2323

Words (methods): 1118

Number of figures: 2

Number of tables: 1

45 **The vulnerability of groundwater supplies to contamination is closely related to their age.**
46 **Fossil groundwaters that infiltrated prior to the Holocene have been documented in**
47 **numerous aquifers and are widely assumed to be immune to modern contaminants.**
48 **However, the global prevalence and vulnerability of fossil groundwater to modern-era**
49 **pollutants have not been systematically studied. Here we analyse groundwater carbon**
50 **isotope data (^{12}C , ^{13}C , ^{14}C) from 6455 wells around the globe. We show that fossil**
51 **groundwaters comprise a large share (42-85%) of total aquifer storage in the upper 1 km**
52 **of the crust, and the majority of waters pumped from wells deeper than 250 m. Fossil**
53 **groundwater resources are often exploited unsustainably, but are thought to be unaffected**
54 **by current climate variability and modern-era pollutants. However, half of the wells in our**
55 **study that are dominated by fossil groundwater also contain detectable levels of tritium,**
56 **indicating the presence of much younger, decadal-age waters. The prevalence of decadal-**
57 **age waters in wells predominantly pumping fossil groundwater implies that contemporary**
58 **contaminants may be able to reach deep wells tapping fossil aquifers. Thus, the**
59 **management of fossil groundwater resources should also consider water quality risk along**
60 **with sustainable use.**

61 Global groundwater is an immense resource, storing ~100 times more water than all the
62 world's lakes^{1,2}, supplying ~40% of the water for global irrigated agriculture³, and providing
63 drinking water to billions of people around the world. Recent research has evaluated the global
64 depths of both the groundwater table⁴ and modern groundwater recharged within the past ~50
65 years¹, but the global prevalence and distribution of "fossil groundwater" remain unclear. Here
66 we define fossil groundwater as groundwater recharged by precipitation more than ~12,000 years
67 ago, prior to the beginning of the Holocene epoch; we define prevalence as the frequency with

68 which regional well waters contain fossil groundwater. Understanding the global extent and
69 depth of fossil groundwater resources is important because of their distinctive susceptibility to
70 overdraft⁵, presumed isolation from surface-borne pollutants^{6,7}, potential vulnerability to
71 geogenic contaminants⁸, and isolation from modern climate variability⁹.

72 To calculate the prevalence of fossil groundwater in well waters, we compiled a
73 groundwater carbon isotope (¹²C, ¹³C, ¹⁴C) database of 6455 well water samples from around the
74 globe. The continental USA and Europe are overrepresented in our compilation, which is also
75 inevitably biased towards sedimentary basins where groundwater use is common (Supplementary
76 Figs. S1 and S2; Methods). Radiocarbon (¹⁴C) has a half-life of 5730 years and has been widely
77 used to identify fossil groundwaters¹⁰⁻¹⁸. Stable carbon isotope (¹²C, ¹³C) data were used to
78 correct for the dissolution of carbonate rocks, which are devoid of radiocarbon¹⁹ and thus would
79 otherwise distort ¹⁴C-based fossil groundwater calculations. We estimated fossil groundwater
80 fractions in wells around the world using a recently developed radiocarbon end-member mixing
81 model, which accounts for both radioactive decay and carbonate dissolution for pre- and post-
82 Holocene recharge²⁰. Our approach, which estimates the fraction of fossil groundwater in a water
83 sample rather than the sample's average age, is designed to be less vulnerable to the aggregation
84 errors that are known to bias mean groundwater age calculations²¹⁻²³. We plotted depth profiles
85 of fossil groundwater for aquifers around the world, and calculated the depth below which fossil
86 groundwater becomes common (>50% of wells pump some fossil groundwater) or dominant
87 (>50% of wells pump >50% fossil groundwater; Methods). Where tritium (³H) data were
88 available (n=5661 well water samples), we determined the fraction of the groundwater sample
89 that recharged more recently than ~1953 by relating groundwater ³H concentrations to historical
90 precipitation ³H time-series²⁴ (Methods). The threshold year 1953 was selected because

91 widespread thermonuclear testing in subsequent years increased precipitation tritium levels by
92 ~5 to ~500 times above local natural background concentrations²⁴, providing a tracer of recently
93 recharged groundwater (e.g., Ref. 15). For samples with both radiocarbon and tritium data, we
94 calculated the fractions of water that (i) recharged more than ~12 thousand years ago (fossil
95 groundwater), (ii) recharged more recently than the year 1953 (post-1953 groundwater), and (iii)
96 was of an intermediate age, having recharged more recently than ~12 thousand years ago, but
97 before the year 1953.

98 **Fossil groundwater in global aquifers**

99 Our global compilation of radiocarbon data shows that fossil groundwater is not an
100 anomaly in the upper 1 km of the crust, but instead is common in wells drilled to depths of more
101 than ~250 m (Figs. 1, 2 and S3). Among all surveyed wells (n=6455; Fig. S3), we find that over
102 half of all wells deeper than 250 m yield groundwater that was mostly (>50%) replenished before
103 the Holocene (i.e., minimum fossil groundwater exceeds 50% for the majority of groundwater
104 samples pumped from wells deeper than 250 m). By contrast, post-1953 groundwater becomes
105 increasingly scarce with depth (Fig. 2). Half of all wells deeper than 40 m pump groundwater
106 that is comprised almost entirely (>90%) of groundwater recharged before 1953 (i.e., maximum
107 post-1953 groundwater is less than 10% for the majority of groundwater samples pumped from
108 deeper than 40 m).

109 Fossil groundwaters are found throughout several major aquifers that sustain modern
110 irrigated agriculture (Fig. 1), including the North China Plain (at depths >200 m), the Southern
111 Central Valley of California (at depths >260 m), the north, central and south High Plains aquifers
112 of the central USA (at depths >120-280 m), Italy's Emilia-Romagna Plain (at depths >100-300

113 m) and Hungary's Pannonian Basin (at depths >160-300 m). Among our 62 study aquifers (Fig.
114 1), we find the range of depths below which fossil groundwaters dominate well waters (i.e.,
115 fossil groundwaters comprise >50% of the water pumped from more than half of all deeper
116 samples) has a median of 200 m, an upper-lower quartile range of 115-290 m, and a 10th-90th
117 percentile range of 70-430 m.

118 *[Fig. 1 and Fig. 2 about here]*

119 Assuming that isotopes measured in well waters reflect the isotopic compositions of
120 groundwater stored in aquifers and are not the result of contamination by infiltrated surface water
121 or rainfall (e.g., Refs. 1,5,11-18), our data show that fossil groundwater likely comprises 42-85%
122 of total groundwater in the crust's uppermost 1 km, 31-79% in the uppermost 500 m, and 10-
123 63% in the uppermost 100 m (Fig. 2c). By contrast, post-1953 groundwater comprises only 5-
124 22% of total groundwater in the crust's uppermost 1 km, 6-27% in the uppermost 500 m, and 13-
125 51% in the uppermost 100 m (Fig. 2d). Fossil groundwater storage in the uppermost 1 km of the
126 crust is, therefore, ~1.9 to ~17 times larger than post-1953 groundwater stores. By combining our
127 new global fossil groundwater storage estimate with global porosity data¹, we calculate that of
128 the 12-22 million km³ of unfrozen water stored in the uppermost 1 km of the crust¹ (~85-152 m
129 equivalent depth of a column of water), approximately 5-18 million km³ is fossil groundwater
130 (36-130 m equivalent depth), 0.6-4.6 million km³ is post-1953 groundwater (4-33 m equivalent
131 depth), and less than 8000 km³ is recent rain and snow that becomes streamflow in less than
132 three months²⁵ (<0.055 m equivalent depth).

133 Figs. 1 and 2 show that the abundance of modern (post-1953) groundwater generally
134 decreases with depth and that the abundance of fossil groundwater generally increases with

135 depth. Topography-driven groundwater flow, geologic layering, and the decrease of permeability
136 with depth generally lead to well-flushed shallow zones overlying poorly-flushed deeper zones,
137 consistent with the occurrence of fossil groundwaters at depth. We conclude that a substantial
138 share (42-85%) of global groundwater in the upper 1 km of the crust is fossil in age. Further, our
139 analysis may even underestimate fossil groundwater abundance because of (a) possible sampling
140 biases towards more permeable basins, (b) contamination of samples by atmospheric $^{14}\text{CO}_2$ that
141 would bias our results to smaller fossil groundwater fractions²⁶, (c) preferential pumping from
142 more permeable strata that may be more likely to contain younger groundwaters (Supplementary
143 Information section S3), and (d) contamination of well waters by recent precipitation due to the
144 construction and use of the well itself (see subsequent section). Although our finding that old
145 water is more common at greater depths is highly intuitive, our analysis is the first global,
146 empirical assessment of the depths at which global aquifer systems transition to poorly-flushed
147 storage dominated by fossil groundwaters.

148 Global groundwater use is accelerating^{27,28}. Declining water tables, more intense
149 droughts, and improved well construction technologies may encourage deeper drilling and
150 increase society's reliance on fossil groundwaters. Assessing how much fossil groundwater is
151 pumped from aquifers requires records of well construction depths, which are available in the
152 western US (Supplementary Information section S4) but not available globally. We examined
153 how frequently fossil groundwaters are pumped in three western US groundwater aquifers by
154 relating constructed well depths to ^{14}C -based fossil groundwater abundances (Supplementary
155 Information section S4). In the northern High Plains, 99% of wells are shallower than the depth
156 at which fossil groundwaters become common (~170 m), implying that fossil groundwater
157 pumping here is relatively rare (Fig. 3). Similarly, in the San Joaquin Valley, the large majority

158 (98%) of wells are shallower than the depth at which fossil groundwater becomes common
159 (~240 m). In the Denver Basin, however, many (38%) groundwater wells have been constructed
160 to depths where fossil groundwater is either detectable or dominant (>125 m), implying that
161 fossil groundwater use in the Denver Basin is widespread. Further, fossil groundwater pumping
162 in the Denver Basin has likely increased over the past ~60 years because older wells drilled
163 between 1950 and 1970 were substantially shallower (median well depth of 27 m) than wells
164 constructed more recently than 2010 (median well depth of 126 m), and because total
165 groundwater pumping has more than quadrupled since 1970 (Ref. 29).

166 Our comparison of groundwater well depths and vertical distributions of fossil
167 groundwater emphasizes that both fossil and post-1953 groundwaters are withdrawn from US
168 aquifers. Pumping fossil groundwater may lead to aquifer depletion, and this risk is greater in
169 arid regions where groundwater tables are deeper and compensatory increases in recharge or
170 decreases in groundwater discharge are less likely (see Ref. 30). Water levels in deep wells have
171 declined across much of the US over the past six decades, likely due to changes in groundwater
172 pumping in response to climate variations³¹. Groundwater well construction is guided by
173 groundwater aquifer conditions (e.g., transmissivity) and quality (e.g., salinity) rather than
174 groundwater age. Nevertheless, we conclude that deep fossil groundwater is already used in
175 some parts of the US, and posit that reliance on fossil groundwaters is probably also widespread
176 in other regions, particularly in hyper-arid climates where modern recharge is negligible.

177 **Fossil well waters vulnerable to contamination**

178 Our compilation of radiocarbon and tritium data shows that roughly half of the well water
179 samples that are measurably depleted in carbonate-dissolution-corrected ¹⁴C (which is clear

180 evidence of fossil age) also contain measurable amounts of ^3H (which is unequivocal evidence of
181 recharge after the onset of thermonuclear bomb testing in the 1950s; Table 1). This observation
182 questions the common perception that fossil groundwaters are largely immune to modern
183 contamination (e.g., Refs. 6,7). Our finding that fossil well waters often contain a component of
184 much younger, decades-old groundwater means that fossil well waters—and, possibly, the
185 aquifers from which they derive—are more vulnerable to pollution from modern-era
186 contaminants than previously thought.

187 *[Table 1 about here]*

188 Several processes can mix decadal-age groundwater with fossil groundwater and thus
189 make fossil well waters vulnerable to modern contaminants. One plausible explanation is aquifer
190 heterogeneity, leading to preferential flow of younger groundwater through high-permeability
191 zones and slower flows of correspondingly older groundwater through less permeable parts of
192 the aquifer system, with mixing of these different-aged waters by dispersion or diffusion.
193 Topography-driven multi-scale groundwater flow can also result in adjacent groundwater flow
194 paths with very different ages, and thus there can be substantial mixing or dispersion of ages
195 where flow paths converge, such as low-lying discharge areas on the land surface^{32,33}. Induced
196 mixing of young and old waters could also occur in wells with open holes or long screens that
197 simultaneously capture young and old groundwater from shallow and deep layers of an
198 aquifer^{34,35}. Leaks in corroded or poorly sealed portions of a well may also contribute to mixing
199 of young and old waters in the well bore itself. Co-occurrences of fossil and post-1953
200 groundwater pumped from wells screened hundreds of meters below the land surface more likely
201 arise from the construction, presence and use of the well itself. For some hydrogeologic settings,

202 it is unlikely that natural flow paths transmit groundwater hundreds of meters below the land
203 surface within a few decades. We note that tritium occurs equally often in well waters containing
204 some fossil groundwater (tritium was detected in ~half of all samples with >0%) and in well
205 waters containing mostly fossil groundwater (tritium was detected in ~half of samples with
206 >50% fossil water). If natural flow paths were the primary cause of the widespread mixing of
207 fossil and post-1953 groundwater, we would expect that samples dominated by fossil
208 groundwater (>50%) would contain measurable tritium less frequently than samples that contain
209 some fossil groundwater (>0% but possibly <50% fossil water), which is not the case (Table 1).
210 Thus, tritium may co-occur with fossil groundwaters primarily as a result of pumping along
211 extensive well screens, up-coning and down-coning of groundwater due to pumping, and leaks
212 along well bores.

213 Regardless of how tritium has become mixed with much older groundwaters, the main
214 implication for drinking water supplies is clear: many (~50%) fossil well waters contain
215 detectable amounts of recently recharged groundwater (Table 1), rendering them potentially
216 vulnerable to modern anthropogenic contamination despite their great age. Because aquifers
217 bearing fossil groundwater require millennia to be flushed, their contamination may also persist
218 for millennia, causing effectively irreversible harm to these aquifers over human timescales.
219 However, it remains unclear how frequently tritium arises in fossil well waters as the result of
220 mixing within the aquifer itself, versus mixing induced by the construction and pumping of the
221 groundwater well.

222 **Concluding remarks**

223 Our analysis shows that fossil groundwater likely dominates global groundwater storage
224 in the uppermost 1 km of the crust (42-85%). This figure is likely to be a lower bound on the
225 global prevalence of groundwater, because the likely biases in our analysis (detailed above) serve
226 to minimize our calculated fossil groundwater fractions. Further, our analysis focuses solely on
227 the shallowest 1 km of the crust that is also the most rapidly flushed. Fractured rocks deeper than
228 1 km can host ancient fossil groundwaters that have been isolated for millions or even billions of
229 years³⁶⁻³⁷.

230 Improving access to freshwater for agriculture, households, and industry while sustaining
231 vital ecosystems in a changing global environment represents a critical scientific and political
232 challenge. Fossil groundwater resources likely comprise more than half of global unfrozen
233 freshwater (Figs. 1 and 2), and dependence upon fossil groundwater to meet water demands is
234 rising as a consequence of increasing groundwater withdrawals and deeper drilling in some
235 regions (e.g., Denver Basin, USA). Groundwater quality remains a critical concern in many parts
236 of the world³⁸⁻⁴¹, and our results highlight that even though deeper wells pump predominantly
237 fossil groundwater, they are not immune to modern contamination.

238 **Methods**

239 **Global groundwater isotope data.**

240 We analysed global groundwater isotope data compiled from hundreds of primary
241 literature sources and from the United States Geological Survey's Water Quality Portal (Tables
242 S1 and S2). About two-thirds (65%) of our global radiocarbon compilation comes from North
243 America, which represents only ~18% of the global landmass. By contrast, only 9% and 11% of
244 our compiled radiocarbon data come from Africa and Asia, which each comprise much larger

245 shares of global ice-free land areas (~22% and ~33% of the global landmass, respectively; Fig.
 246 S2). We analysed the compiled groundwater isotope data to partition the fraction of groundwater
 247 samples that recharged (i) before the Holocene-Pleistocene transition 11,700 years ago (“fossil
 248 groundwater”, based on ^{14}C with a half-life of 5730 years), and (ii) more recently than 1953,
 249 when the “hydrogen bomb peak” in meteoric tritium began (“post-1953 groundwater”, based on
 250 ^3H with a half-life of 12.3 years).

251 **Determining fossil groundwater fractions.**

252 We used stable ($\delta^{13}\text{C}$) and radioactive (^{14}C) carbon isotope data to calculate fossil
 253 groundwater fractions (F_{fossil}) following (Ref. 20):

$$254 \quad F_{\text{Fossil}} = 1 - \frac{{}^{14}\text{C}_{\text{sample}} - {}^{14}\text{C}_{\text{fossil}}}{{}^{14}\text{C}_{\text{Holocene}} - {}^{14}\text{C}_{\text{fossil}}} \quad \text{Equation 1}$$

255 where dissolved inorganic carbon concentrations are assumed to be roughly equal for the fossil
 256 and Holocene waters²⁰, and ^{14}C represents the radiocarbon activity of: the groundwater sample
 257 (subscript “sample”), Holocene groundwater recharged within the past 11,700 years (subscript
 258 “Holocene”), or fossil groundwater recharged more than 11,700 years ago (subscript “fossil”).
 259 Holocene and fossil ^{14}C inputs are based on late-Quaternary atmospheric ^{14}C time series^{42,43}
 260 corrected for radioactive decay following (Ref. 20):

$$261 \quad {}^{14}\text{C}_t = \left(q_t {}^{14}\text{C}_{\text{precip}(t)} e^{-0.693(t_{\text{sample}} - t)/(5730 \text{ years})} \right)_t \quad \text{Equation 2}$$

262 where ${}^{14}\text{C}_{\text{precip}(t)}$ represents precipitation ^{14}C at time t , and t_{sample} is the date that the groundwater
 263 sample was analysed. ${}^{14}\text{C}_{\text{Holocene}}$ is represented by ${}^{14}\text{C}_t$ evaluated for the time interval of $0 <$
 264 $\text{abs}(t_{\text{sample}} - t) < 11700$ years; ${}^{14}\text{C}_{\text{fossil}}$ is represented by ${}^{14}\text{C}_t$ evaluated prior to the Holocene (i.e.,
 265 $\text{abs}(t_{\text{sample}} - t) > 11700$ years). For years postdating thermonuclear-bomb testing, we apply a 10-

266 year running average to estimate the maximum possible $^{14}C_{Holocene}$ value (Supplementary Fig.
267 S5), effectively assuming some amount of dispersion has taken place in most aquifer systems
268 over the past 50 years. The factor q is used to correct for the dissolution of carbonate with zero
269 radiocarbon:

$$270 \quad q_t = \frac{\delta^{13}C_t - \delta^{13}C_{carbonate}}{\delta^{13}C_{recharge} - \delta^{13}C_{carbonate}} \quad \text{Equation 3}$$

271 where $\delta^{13}C_{recharge}$ and $\delta^{13}C_{carbonate}$ are the stable isotope compositions of recharge and carbonates.
272 We used $\delta^{13}C_{recharge}$ and $\delta^{13}C_{carbonate}$ values reported in the compiled studies when available, and
273 otherwise assumed $\delta^{13}C_{carbonate} = 0 \text{ ‰}$ and $\delta^{13}C_{recharge} = -14.3 \text{ ‰}$. Global $\delta^{13}C_{carbonate}$ and
274 $\delta^{13}C_{recharge}$ values vary around the globe²⁰ such that our assumption of $\delta^{13}C_{carbonate} = 0 \text{ ‰}$ and
275 $\delta^{13}C_{recharge} = -14.3 \text{ ‰}$ introduces uncertainty into our fossil groundwater calculations.

276 The range of $\delta^{13}C$ values ascribed to each time interval ($\delta^{13}C_t$) is assumed to be
277 constrained by $\delta^{13}C_{recharge} \leq \delta^{13}C_{Holocene} \leq \delta^{13}C_{sample} \leq \delta^{13}C_{fossil} \leq \delta^{13}C_{carbonate}$ (Ref. 20). Because
278 the possible ages of the Holocene and pre-Holocene end members vary widely, the ranges of
279 $^{14}C_{Holocene}$ and $^{14}C_{fossil}$ values are often large; we apply upper and lower limits of $^{14}C_{Holocene}$ and
280 $^{14}C_{fossil}$ in equation 1 to estimate minimum and maximum fossil groundwater fractions. $^{14}C_{Holocene}$
281 and $^{14}C_{fossil}$ share an identical end-member at the 11,700 year boundary. The shared 11.7 ka
282 endmember, and the large atmospheric radiocarbon variations over each end-member interval,
283 lead to highly uncertain F_{fossil} calculations for some samples.

284 In each aquifer, we pinpointed two depths where we observed transitions from Holocene
285 groundwater to pre-Holocene fossil groundwater, and used these depths as upper and lower
286 limits in the bar graphs shown in Fig. 1. The first (shallower) recorded transition depth specifies

287 a depth below which the majority (>50%) of well water samples from a given aquifer must
288 contain some fraction of fossil groundwater (i.e., over half the samples have a minimum fossil
289 groundwater fraction of greater than zero). The second (deeper) recorded transition depth
290 represents a depth below which the majority (>50%) of sampled well waters from a given aquifer
291 system must contain mostly fossil groundwater (i.e., over half of the samples deeper than the
292 depth have a minimum fossil groundwater fraction of greater than 50%).

293 Where oxygen stable isotope data are also available, we confirmed the depth to fossil
294 groundwater by comparing the $^{18}\text{O}/^{16}\text{O}$ ratio in groundwater to a new global map of $\delta^{18}\text{O}$ in late-
295 Pleistocene precipitation⁴⁴; where $\delta^{18}\text{O} = ([^{18}\text{O}/^{16}\text{O}]_{\text{sample}} / [^{18}\text{O}/^{16}\text{O}]_{\text{standard ocean water}} - 1) \times 10^3 \text{‰}$.
296 Late-Holocene and late-Pleistocene precipitation $\delta^{18}\text{O}$ values are detectably different (>1 ‰)
297 over the great majority (~87%) of the global landmass⁴⁴, enabling use of depth- $\delta^{18}\text{O}$ plots as a
298 qualitative secondary indicator of the depth to fossil groundwater.

299 **Determining post-1953 groundwater fractions.**

300 To calculate the fraction of modern, post-1953 groundwater in a sample we used
301 globally-interpolated precipitation tritium for years spanning the pre-bomb era (prior to 1950) to
302 2010 from Ref. 24. Global precipitation ^3H estimates derive from >60,000 monthly ^3H
303 measurements made at 738 globally distributed stations (data provided by the International
304 Atomic Energy Agency: iaea.org/water). We then weighted the monthly precipitation ^3H data
305 against the long-term average monthly precipitation rate⁴⁵ to estimate an annually integrated
306 precipitation ^3H value at each well site. Once a precipitation tritium record was developed for
307 each well location (from Ref. 24), we decay-corrected the precipitation tritium input curve to the
308 date that each sample was collected²⁰. As in our radiocarbon-based calculation, we assume that

309 some amount of dispersion takes place in the aquifer and apply a 10-year running average before
310 calculating maximum and minimum possible ${}^3H_{post-1953}$ values (Supplementary Fig. S5). We then
311 applied the range of possible decay-corrected, post-1953 precipitation 3H values as one end-
312 member in a two-component mixing model, and pre-1953 precipitation 3H as the other
313 component:

$$314 \quad F_{post-1953} = \frac{{}^3H_{sample} - {}^3H_{pre-1953}}{{}^3H_{post-1953} - {}^3H_{pre-1953}} \quad \text{Equation 4}$$

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

322 **Estimating groundwater age-storage volumes.**

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

330

331 **Data availability**

332 Compiled isotope data are available in the primary references listed in Tables S1 and S2 and in
333 tabulated form from www.isohydro.ca.

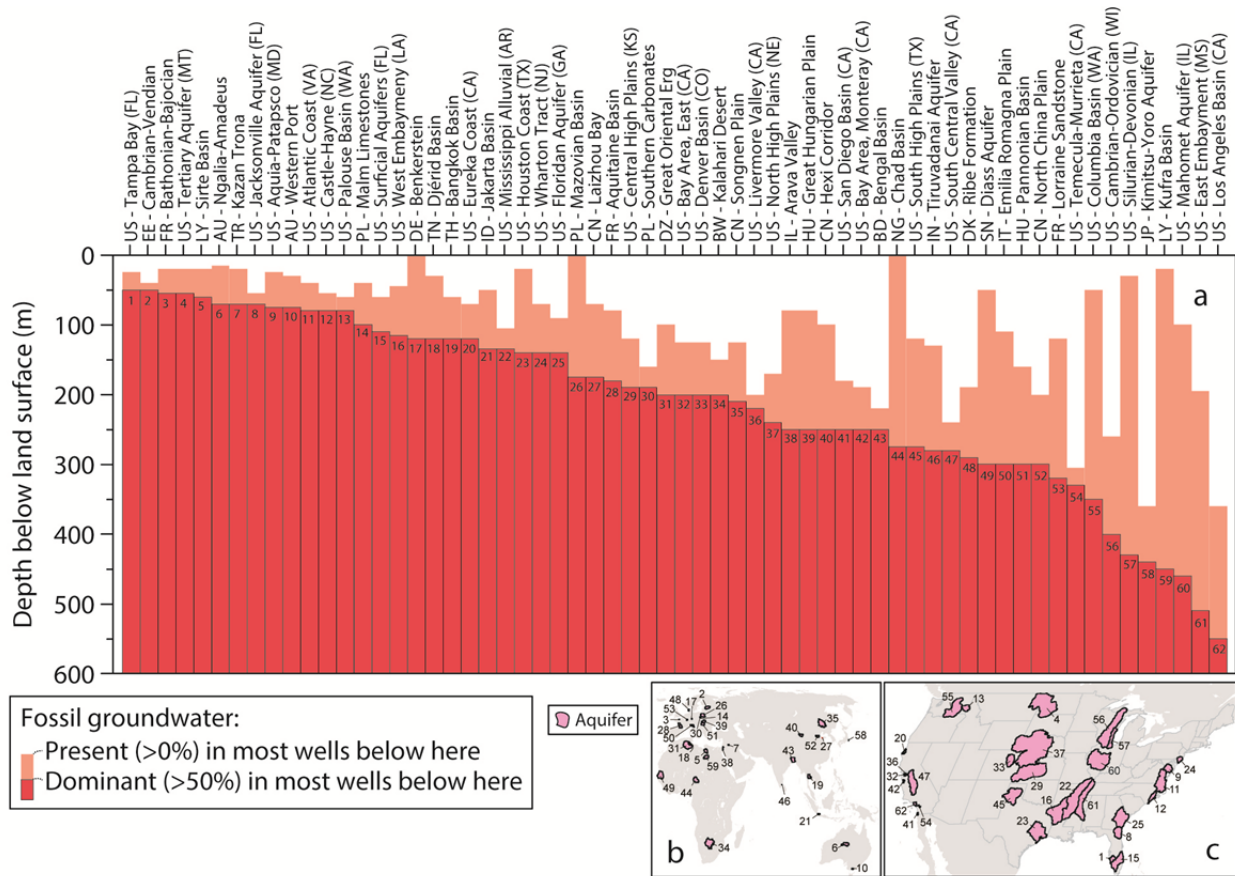
334 **Acknowledgements**

335 This project was supported by an NSERC Discovery Grant to S.J. (no. 5668).

336 **Contributions**

337 S.J. and J.W.K. analysed the compiled groundwater isotope data and wrote initial drafts of the
338 manuscript. S.J. and D.P. analysed the compiled groundwater well construction data. All authors
339 discussed results and edited the manuscript.

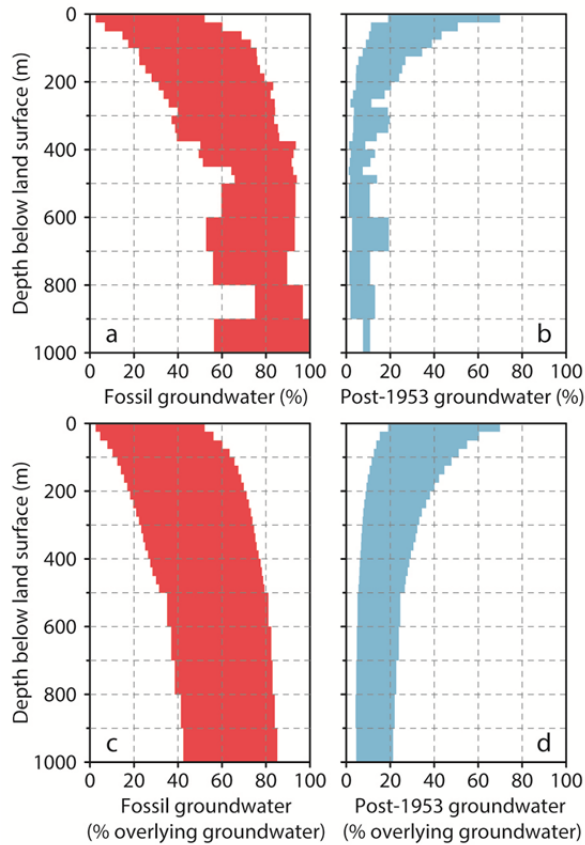
340



341

342 **Fig. 1.** Prevalence of fossil groundwater in global aquifers. (a) Depth to the fossil groundwater
 343 transition in 62 aquifers. The shallow depth (top of orange bar) represents a depth below which
 344 most wells (>50%) contain detectable fossil groundwater (minimum fossil groundwater fraction
 345 >0%). The deeper depth (top of red bar) represents a depth below which most wells (>50%) are
 346 dominated by fossil groundwater (minimum fossil groundwater fraction is >50%). Fossil
 347 groundwater becomes dominant at a median depth of 200 m, an upper-lower quartile range of
 348 depths of 115-290 m, and a 10th-90th percentile range of depths of 70-430 m. We note that the
 349 lower limit of our graph (600 m) does not necessarily represent the lower boundary for any of
 350 our 62 study aquifers, nor do the depths covered by red and orange bars imply that the
 351 groundwater quality is high or that the aquifer is productive at these depths.

352



353

354 **Fig. 2.** Variations of fossil (red) and post-1953 groundwater (blue) with depth. Panels a and b
 355 show statistical distributions of fossil and post-1953 groundwater binned at various depths.
 356 Panels c and d show the cumulative distribution with depth of stored fossil groundwater (pre-
 357 Holocene; red in panel a) and modern groundwater (post-1953; blue in panel b); that is, these
 358 panels represent the fraction of total groundwater overlying a given depth (data have been
 359 corrected for porosity changes with depth following Ref. 1). The coloured areas represent the
 360 estimated maximum and minimum range, calculated using all groundwater samples within a
 361 given depth bin (average of the maximum and minimum estimates of fossil groundwater and
 362 post-1953 groundwater for a given range of well depths).

363

364 **Table 1.** Radioisotope (^{14}C , ^3H) evidence for post-1953 and fossil groundwater mixing

Presence of fossil groundwater	Total ^{14}C samples with ^3H data	Presence of post-1953 groundwater	
		Present ($^3\text{H}>0$)	Absent ($^3\text{H}\approx 0$)
May contain no fossil water (possibly 0%)	n=984	74%	26%
Must contain fossil water (>0% and possibly <50%)	n=179	49%	51%
Must contain mostly fossil water (>50%)	n=365	50%	50%

365

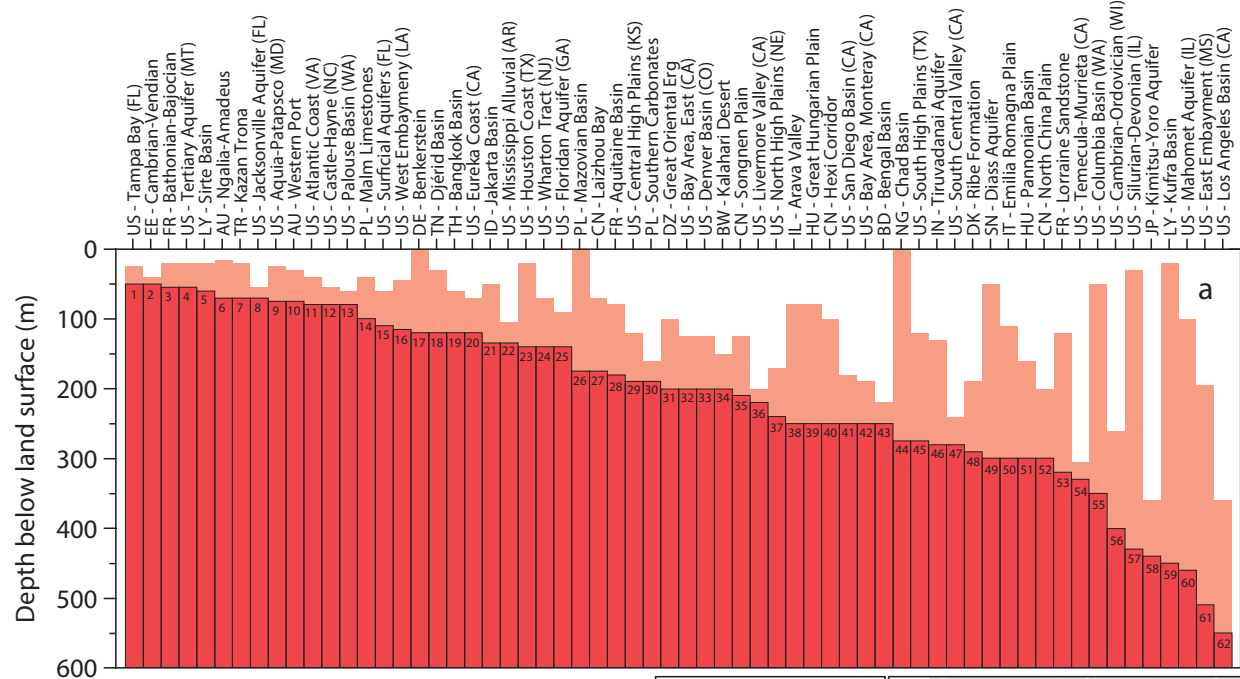
366 **References**

- 367 1. Gleeson, T., Befus, K. M., Jasechko, S., Luijendijk, E. & Cardenas, M. B. The global volume
368 and distribution of modern groundwater. *Nature Geoscience* **9**, 161–168 (2016).
- 369 2. Messenger, M. L., Lehner, B., Grill, G., Nedeva, I. & Schmitt, O. Estimating the volume and
370 age of water stored in global lakes using a geo-statistical approach. *Nature Communications*
371 **7**, 13603 (2016).
- 372 3. Siebert, S., Burke, J., Faures, J. M., Frenken, K., Hoogeveen, J., Döll, P., & Portmann, F. T.
373 Groundwater use for irrigation—a global inventory. *Hydrol. Earth Syst. Sci.* **14** 1863–1880
374 (2010).
- 375 4. Fan, Y., Li, H., & Miguez-Macho, G. Global patterns of groundwater table depth. *Science*
376 **339**, 940–943 (2013).
- 377 5. Chen, Z., Nie, Z., Zhang, Z., Qi, J. & Nan, Y. Isotopes and sustainability of ground water
378 resources, North China Plain. *Groundwater* **43**, 485–493 (2005).
- 379 6. Yamada, C. First report on shared natural resources, United Nations International Law
380 Commission, A/CN.4/533 + Add.1 (2003), access from:
381 legal.un.org/ilc/documentation/english/a_cn4_533.pdf
- 382 7. Buser, H. R. Atrazine and other s-triazine herbicides in lakes and in rain in Switzerland.
383 *Environ. Sci. Technol.* **24**, 1049–1058 (1990).
- 384 8. Burgess, W. G., Hoque, M. A., Michael, H. A., Voss, C. I., Breit, G. N. & Ahmed, K. M.
385 (2010). Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by
386 arsenic. *Nature Geoscience* **3**, 83–87 (2010).
- 387 9. Taylor, R. G. et al. Ground water and climate change. *Nat. Clim. Change* **3**, 322–329 (2013).
- 388 10. Thatcher, L., Rubin, M. & Brown, G. F. Dating desert groundwater. *Science* **134**, 105–106
389 (1961).
- 390 11. Edmunds, W. M. & Wright, E. P. Groundwater recharge and palaeoclimate in the Sirte and
391 Kufra basins, Libya. *J. Hydrol.* **40**, 215–241 (1979).
- 392 12. Phillips, F. M., Peeters, L. A., Tansey, M. K. & Davis, S. N. Paleoclimatic inferences from
393 an isotopic investigation of groundwater in the central San Juan Basin, New Mexico,
394 *Quatern. Res.* **26**, 179–193 (1986).

- 395 13. Weyhenmeyer, C. E., Burns, S. J., Waber, H. N., Aeschbach-Hertig, W., Kipfer, R., Loosli,
396 H. H. & Matter, A. Cool glacial temperatures and changes in moisture source recorded in
397 Oman groundwaters. *Science* **287**, 842–845 (2000).
- 398 14. Plummer, N. L. & Sprinkle, C. L. Radiocarbon dating of dissolved inorganic carbon in
399 groundwater from confined parts of the Upper Floridan aquifer, Florida, USA. *Hydrogeol. J.*
400 **9**, 127-150 (2001).
- 401 15. Vengosh, A., Gill, J., Davisson, M. L. & Hudson, G. B. A multi-isotope (B, Sr, O, H, and C)
402 and age dating (^3H - ^3He , and ^{14}C) study of groundwater from Salinas Valley, California:
403 Hydrochemistry, dynamics, and contamination processes. *Water Resour. Res.* **38**, 1008
404 (2002).
- 405 16. Brown, K. B., McIntosh, J. C., Baker, V. R. & Gosch, D. Isotopically-depleted late
406 Pleistocene groundwater in Columbia River Basalt aquifers: Evidence for recharge of glacial
407 Lake Missoula floodwaters? *Geophys. Res. Lett.* **37**, L21402 (2010).
- 408 17. Morrissey, S. K., Clark, J. F., Bennett, M., Richardson, E. & Stute, M. Groundwater
409 reorganization in the Floridan aquifer following Holocene sea-level rise. *Nature Geoscience*
410 **3**, 683–687 (2010).
- 411 18. Cartwright, I. & Weaver, T. R. Hydrogeochemistry of the Goulburn Valley region of the
412 Murray Basin, Australia: implications for flow paths and resource vulnerability. *Hydrogeol.*
413 *J.* **13**, 752-770 (2005).
- 414 19. Vogel, J. C. Carbon-14 dating of groundwater. Isotope Hydrology. International Atomic
415 Energy Agency STI/PUB/255, 225–239 (1970).
- 416 20. Jasechko, S. Partitioning young and old groundwater with geochemical tracers. *Chem. Geol.*
417 **427**, 35–42 (2016a).
- 418 21. Weissmann, G. S., Zhang, Y., LaBolle, E. M. & Fogg, G. E. Dispersion of groundwater age
419 in an alluvial aquifer system. *Water Resour. Res.* **38**, 1198 (2002).
- 420 22. Bethke, C.M. and Johnson, T.M., 2008. Groundwater age and groundwater age dating. *Annu.*
421 *Rev. Earth Planet. Sci.* **36**, 121–152.
- 422 23. Torgersen, T., Purtschert, R., Phillips, F. M., Plummer, L. N., Sanford, W. E. & Suckow, A.
423 Defining groundwater age. in: Isotope Methods for Dating Old Groundwater, International
424 Atomic Energy Agency, Vienna, Austria (2013).

- 425 24. Jasechko, S. & Taylor, R. G. Intensive rainfall recharges tropical groundwaters. *Environ.*
426 *Res. Lett.* **10**, 124015 (2015).
- 427 25. Jasechko, S., Kirchner, J. W., Welker, J. M. & McDonnell, J. J. Substantial proportion of
428 global streamflow less than three months old. *Nature Geoscience* **9**, 126–129 (2016).
- 429 26. Aggarwal, P. K., Araguas-Araguas, L., Choudhry, M., van Duren, M. & Froehlich, K. Lower
430 groundwater ¹⁴C age by atmospheric CO₂ uptake during sampling and analysis. *Groundwater*
431 **52**, 20–24 (2014).
- 432 27. Wada, Y., Wisser, D. & Bierkens, M. F. P. Global modeling of withdrawal, allocation and
433 consumptive use of surface water and groundwater resources. *Earth System Dynamics* **5**, 1-
434 15 (2014).
- 435 28. Famiglietti, J. S. The global groundwater crisis. *Nature Climate Change* **4**, 945-948 (2014).
- 436 29. Bauch, N. J., Musgrove, M., Mahler, B. J. & Paschke, S. S. Water Quality in the Denver
437 Basin Aquifer System, Colorado, 2003-05, pp. 113 (2014).
- 438 30. Theis, C. V. The source of water derived from wells. *Civil Eng.* **10**, 277–280 (1940).
- 439 31. Russo, T.A. & Lall, U. Depletion and response of deep groundwater to climate-induced
440 pumping variability. *Nature Geoscience*, doi:10.1038/ngeo2883 (2017).
- 441 32. Toth, J. A theoretical analysis of groundwater flow in small drainage basins. *J. Geophys. Res.*
442 **68**, 4795–4812 (1963).
- 443 33. Jiang, X. W., Wan, L., Cardenas, M. B., Ge, S. & Wang, X. S. Simultaneous rejuvenation
444 and aging of groundwater in basins due to depth-decaying hydraulic conductivity and
445 porosity. *Geophys. Res. Lett.* **37**, L05403 (2010).
- 446 34. Zinn, B. A., & Konikow, L. F. Effects of intraborehole flow on groundwater age distribution.
447 *Hydrogeol. J.* **15**, 633-643 (2007).
- 448 35. Ferguson, G. A., Betcher, R. N. and Grasby, S. E. Hydrogeology of the Winnipeg formation
449 in Manitoba, Canada. *Hydrogeol J.* **15**, 573–587 (2007).
- 450 36. Lin, L. H. et al. Long-term sustainability of a high-energy, low-diversity crustal biome.
451 *Science* **314**, 479-482 (2006).
- 452 37. Holland, G., Sherwood Lollar, B., Li, L., Lacrampe-Couloume, G., Slater, G. F. &
453 Ballentine, C. J. Deep fracture fluids isolated in the crust since the Precambrian. *Nature* **497**,
454 367-360 (2013).

- 455 38. Burow, K. R., Nolan, B. T., Rupert, M. G. & Dubrovsky, N. M. Nitrate in groundwater of the
456 United States, 1991–2003. *Environmental Science & Technology* **44**, 4988-4997 (2010).
- 457 39. Graham, J. P. & Polizzotto, M. L. Pit latrines and their impacts on groundwater quality: A
458 systematic review. *Environmental Health Perspectives* **121** (2013).
- 459 40. Sorensen, J. P. R. et al. Emerging contaminants in urban groundwater sources in Africa.
460 *Water Research* **72**, 51-63 (2015).
- 461 41. MacDonald, A. M. et al. Groundwater quality and depletion in the Indo-Gangetic Basin
462 mapped from in situ observations. *Nature Geoscience* **9**, 762–766 (2016).
- 463 42. Reimer, P. J. et al. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years
464 cal BP. *Radiocarbon* **55**, 1869–1887 (2013).
- 465 43. Hua, Q. & Barbetti, M. Review of tropospheric bomb ¹⁴C data for carbon cycle modeling and
466 age calibration purposes. *Radiocarbon* **46**, 1273–1298 (2004).
- 467 44. Jasechko, S. Late-Pleistocene precipitation $\delta^{18}\text{O}$ interpolated across the global landmass.
468 *Geochem. Geophys. Geosy.* **17**, 3274–3288 (2016b).
- 469 45. New, M., Lister, D., Hulme, M. & Makin, I. A high-resolution data set of surface climate
470 over global land areas. *Climate Research* **21**, 1–25 (2002).



Fossil groundwater:

- █ Present (>0%) in most wells below here
- █ Dominant (>50%) in most wells below here

 Aquifer

