Non-peer reviewed paper submitted to Nature Geoscience, August 24, 2022

Chloride fluxes show isolation of deep groundwaters from the global water cycle

Grant Ferguson[1,2,3,4], Jennifer C. McIntosh[1,2], Scott Jasechko[5], Ji-Hyun Kim[6], James S. Famiglietti[3,4] and Jeffrey J. McDonnell[3,4,7,8]

1. Department of Civil, Geological and Environmental Engineering, University of Saskatchewan
2. Hydrology and Atmospheric Sciences, University of Arizona
3. School of Environment and Sustainability, University of Saskatchewan
4. Global Institute for Water Security, University of Saskatchewan
5. Bren School of Environmental Science & Management, University of California, Santa Barbara
6. Department of Geoscience, University of Calgary
7. School of Resources and Environmental Engineering, Ludong University, Yantai, China.
8. School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, UK

Email addresses:

Grant Ferguson: grant.ferguson@usask.ca

Jennifer C. McIntosh: jenmc@arizona.edu

Scott Jasechko: jasechko@ucsb.edu

Ji-Hyun Kim: jihyun.kim1@ucalgary.ca

James S. Famiglietti: jay.famiglietti@usask.ca

Jeffrey J. McDonnell: jeffrey.mcdonnell@usask.ca

Abstract

Groundwater is one of the largest reservoirs of water on Earth but has relatively small fluxes compared to its volume. This behaviour is exaggerated with depth where the majority of groundwater exists at depths below 500 m and where residence times of millions to even a billion years have been documented. However, the extent of interactions between deep groundwater (>500 m) and the rest of the water cycle at a global scale is unclear because of challenges in detecting their contributions to streamflow. Here, we use a chloride mass balance approach to quantify the contribution of deep groundwater to global streamflow. We show that deep groundwater likely contributes less than 0.1% to global streamflow and is only weakly and sporadically connected to the rest of the water cycle on geological timescales. Despite this weak connection to streamflow, we found that deep groundwaters are important to the global Cl cycle, providing ~7% of the flux of Cl to the ocean.

Introduction

The terrestrial water cycle is fundamental to hydrology [1–3] and water-mediated cycles of labile solutes [4,5]. Since the first measurements of precipitation inputs and streamflow outputs and demonstration that precipitation alone could explain streamflow [6] the water balance equation (inputs – outputs = storage change) has been hydrology's most important equation [7]. Despite long-standing recognition that groundwater generates much, if not most, of global streamflow [8,9], the relative importance of deep groundwater (where much of the world's fresh water is stored) in generating streamflow remains relatively unexplored [10,11].

Recent work has suggested possible compartmentalization of the terrestrial water cycle [12] based on some global estimates of the age of groundwater, where 2/3 of groundwater below 250 m is >12,000 yr old [13] and streamflow transit times, where 1/3 of global streamflow is <3 mo old [14]. Documentation of a large volume of deep and saline groundwater with residence times of 10s of millions of years or more supports this idea of compartmentalization [15–18] (Figure 1). However, stable water isotopes show that groundwaters down to depths of a few km are commonly meteoric in origin, indicating at least some connection to the rest of the water cycle. What has not been yet done is to quantitatively link streamflow and the huge mass of deep groundwater to determine how much of this groundwater turns over or is effectively stuck in place until a geological event (e.g. continental-scale glaciation, downcutting by a large river) connects these deeper fluids with the surface. Understanding the links between deep groundwater and streamflow is fundamental to surface water hydrology and the field of critical zone science, which uses the bottom of groundwater as its lower limit [19,20] without a clear definition of how this depth relates to hydrological and biogeochemical cycles.

Here, we quantify the contribution of deep groundwater to global streamflow. We begin with the known volume of global groundwater on the order of ~44 million km^3 [21] and the understanding that groundwater recharge fluxes are small compared to the volume of groundwater reservoirs. Estimates of global recharge rates from large-scale hydrologic models range from 5,900 to 24,500 km^3/yr [22–27] (Figure 2). Discharge from groundwater as pumping (734 km^3/yr; Wada et al., 2010) and submarine groundwater discharge (78 km^3/yr; Luijendijk et al., 2020) are comparatively small and within the range of uncertainty of global recharge estimates. Ignoring the portion of pumping that is derived from depletion of groundwater storage, this suggests that groundwater discharge to streams should be equal to 86 to 97% of groundwater recharge.

Groundwater residence times on the order of a few millennia should be expected for these recharge rates and storage volumes [28]. However, residence times in groundwater are acutely unevenly distributed. Much groundwater in the upper 10 to 100 meters of the Earth's crust is no more than a few decades old [13], but groundwater can be millions to even as much as a billion years old at depths of several hundred meters [15,17,18,29]. This distribution of ages suggests that groundwaters at depths exceeding several 100 m are relatively isolated from shallow groundwaters and overlying surface waters.

We hypothesize that the terrestrial water cycle is not a continuous cycle for all water, but one where continuity of cycling is limited to a shallow groundwater involvement with returns to streamflow and the atmosphere of deeper water effectively cut off and isolated from rapid cycling. To date, there is no consensus on the depth at which groundwater contributions cease to be important to streamflow and hence the broader hydrologic cycle. Large-scale hydrologic models have used depths of 102 m [30], 50 to 500 m [31] and 200 m [32] as the base of the simulated portion of the groundwater system to estimate this, without a thorough exploration of the implications of those choices. Some have speculated on a piece of this question – getting to grips with where the bottom of a watershed may be located (Condon et al., 2020). Corroborating ideas on terrestrial water cycling at large scales—beyond small watersheds—remains challenging because of the dearth of residence time estimates of groundwater at depths [29] and little way of quantifying their contribution, if it exists, to streamflow. We have some nascent theories on why stream water is so young when groundwater is so old [33], supported by measurements [34] due to permeability contrasts in the subsurface. However, testing the completeness of terrestrial water cycling has not yet been attempted.

Approach

We use a geochemical transport approach to quantify how deep groundwater systems connect to shallower groundwaters and, in turn, streamflow. Much of the groundwater below 1 km has high salinity relative most surface waters [35–37]. Previous estimates of global riverine Cl fluxes range from 1.15×10^{11} to 3.1×10^{11} kg/yr [38–40]. These estimates relied on multiplying average Cl concentrations in global streams (7.8 mg/L [41] and 8.3 mg/L [4]) by streamflow (32,500 km^3/yr [42] and 37,500 km^3/yr [43]. Subsequent estimates of global streamflow have been higher, up to 38,500 km^3/yr [44], 44,200 km^3/yr [45], and 45,900 km^3/yr [3], which would increase the estimated global Cl fluxes to the ocean. Streamwater Cl has a variety of sources including wet and dry deposition, dissolution of soil and rock by streams, groundwater discharges, and anthropogenic sources such as road salt [40].

Using the coupling of Cl and groundwater fluxes to estimate groundwater recharge and discharge rates dates back to at least the 1960s [46]. Cl is a conservative solute and generally increases in concentration along a flowpath [47] due to water-rock interaction and evapotranspiration above the water table, although the latter does not directly affect the mass of Cl in groundwater (Scanlon et al., 2002). Increases in the flux of Cl along a flowpath within a groundwater system is caused by various mechanisms, including dispersive mixing with relict seawater and water-rock interaction. Dissolution of evaporites, especially halite, can be a major source of Cl to groundwater. Springs discharging waters that have dissolved evaporites can have Cl concentrations in excess of 20,000 mg/L [48] and even higher concentrations have been found in the subsurface [49–51].

We use the Cl tracing approach to estimate the proportion of streamflow that derives from deeper groundwaters before resurfacing at seeps and springs. We first divide groundwaters into deep and shallow components based on their Cl concentrations to explore their relative contributions of each to global riverine fluxes. We then consider the connectedness of shallow and deep groundwater to streamflow using Cl concentrations from groundwaters and estimated Cl fluxes for large rivers globally. Finally, we explore how these results impact our thinking on the global Cl cycle.

Results and Discussion

The entire Cl flux to the ocean via streams of 3.8 x 10^{11} kg/yr (see Methods) could be accounted for with observed Cl concentrations in shallow groundwater and groundwater recharge within the range of previous estimates (Figure 2; Figure 3). This suggests that deeper groundwater does not contribute measurably to streamflow generation globally. The median Cl concentration for both wells between 0 and 10 m deep and between 0 and 100 m deep in the United States (USGS, 2020) is 20 mg/L (Figure 1). A study of background groundwater chemistry in Europe arrived at a similar median value of 19 mg/L [52], although variations with depth were not accounted for in that study.

Using a Cl concentration of 20 mg/L and the range of groundwater recharge estimates presented in Figure 2, Cl fluxes from shallow (<100 m) groundwater varies from 1.2 x 10^{11} to 4.9 x 10^{11} kg/yr. Using the 25th percentile of Cl concentrations over this depth range (7.1 mg/L) resulted in Cl fluxes from 4.2 x 10^{10} to 1.7 x 10^{11} kg/yr. Using the 75th percentile of Cl concentrations over this depth range (80.7 mg/L) resulted in Cl fluxes from 4.8 x 10^{11} to 2.0 x 10^{12} kg/yr. Cl fluxes from shallow groundwater would exceed those for rivers for a Cl concentration of 20 mg/L if the global groundwater discharge exceeds 19,000 km^3/yr. Shallow groundwater Cl concentrations at the 75th percentile produced Cl flux estimates more than those observed in streams. This value is an upper bound given that a range of other sources of Cl will be present, including deeper (>100 m) groundwater with higher Cl concentrations. Using an estimated atmospheric deposition of 4.0 x 10^{10} to 2.4 x 10^{11} kg/yr [53], the discharge of shallow groundwater required to match the observed global riverine Cl flux would be reduced to a value between 7,000 and 17,000 km^3/yr. We note that because Cl concentrations have little variability with depth in the uppermost 100 m, our analysis cannot discern variations in contributions to streamflow from within this upper 100 m interval.

Groundwaters deeper than 100 m increase in salinity and Cl concentration (Figure 1). Between 100 and 500 m depth, the median Cl concentration increases slightly to 120 mg/L. Cl concentrations increase markedly at depths beneath 500 m, with a median value of 30,400 mg/L. Groundwaters between 100 and 500 m could make some contribution to stream discharge on the order of a few percent but groundwaters beneath 500 m do not make a measurable contribution to the global hydrologic cycle over human timescales. Only 13 km^3/yr of groundwater discharge with a concentration of 30,400 mg/L would be required to match the observed global riverine Cl flux. This discharge of water is less than 0.1% of previous global groundwater recharge estimates, although this percentage could be slightly higher if global recharge rates have been overestimated (Figure 2). We also note that pumping of deep groundwater may provide another pathway for deep groundwater to reconnect with the rest of the water cycle. Large volumes of groundwater have been removed for the subsurface [54,55] including a substantial portion of which has residence times exceeding 12,000 years [56].

While salinity in deep groundwater can be attributed to modification of ancient seawater by water-rock reaction and a range of other processes [37], dissolution of evaporites is most commonly associated with circulating meteoric water [16,49,51]. Meteoric waters are commonly found at depths of a thousand meters or more [57], indicating that while these waters contribute a negligible fraction of streamflow they are still participating in the global water and biogeochemical cycles. Examining the rate of evaporite dissolution by these deep groundwaters allows us to use the stratigraphic record to provide an additional constraint on the amount of Cl fluxes. By reconstructing the volumes of evaporites over geologic time, Hay et al. (2006) estimate that 2.68 x 10^{10} kg/year of Cl was dissolved during the Holocene Epoch. At the median Cl concentration beneath 500 m, this would require 0.89 km^3/yr of water. This suggests that deep groundwater discharge is on the order of 0.004 to 0.02% of previous estimates of global groundwater recharge rates. Based on a groundwater volume of 16.7 million km^3 in sediments below 500 m [21], this would result in an average residence time of ~20 Ma for deep sedimentary rocks. Residence times within deep groundwater systems can vary over several orders of magnitude but this flux-based estimate is in approximate agreement with a limited number of studies using noble gases (Figure 1c). Groundwater ages of as much as 30 Ma have been documented in the Paris Basin [15], while ages in the Williston Basin extend from a few Ma to several hundred Ma [58]. In the Paradox Basin, Kim et al. (2022a) noted some waters at these depths with residence times of several 100 ka using ^{81}Kr. However, other samples from the basin were too old to be dated with this technique (> 1 Ma). Groundwaters in cratonic rocks can be considerably older still [17,18,59–61] and groundwater discharge from these environments is expected to be smaller than those estimated for deep sedimentary rocks due to their lower permeabilities [62].

Over the past few decades, it has been emphasized that groundwater and surface water are one resource [63,64], leading to an explosion in groundwater-surface water interaction studies focused on the fluxes of water between these two reservoirs [65,66]. However, groundwater is not a well-mixed reservoir and the distribution of residence times in groundwater that discharges to streamflow is very different from the distribution of residence times of groundwater in the subsurface [33]. The sluggish nature of deeper groundwater systems due to regional flow patterns [67] and permeability contrasts [68] and their implications for regional groundwater flow systems are well understood and critical to producing models of groundwater systems. However, these details may not be necessary to understand the role of groundwater in streamflow generation in all cases. This is possible in part because of the different rates and timescales involved with the different compartments of the water cycle – the fluxes of deep groundwater are orders of magnitude smaller than those in other compartments.

Although the discharge of groundwater in deep strata is insignificant to the global hydrologic cycle, the fluxes of Cl are potentially important. The estimate of 2.68 x 10^{10} kg/yr of Cl from evaporite dissolution [40] is approximately 7% of global riverine Cl flux estimated here. These deep Cl fluxes are commonly associated in small areas of sedimentary basins containing evaporites. Surface waters draining the Williston, Alberta, Paradox and Permian basins are thought to have a combined Cl flux of 5.0 x 10^9 kg/yr (Table 1), which accounts for 18.7% of the annual mass of Cl from evaporite dissolution and 1.3 % of the estimated global riverine Cl flux. The Dolores River, UT, USA, which is a tributary of the Colorado River, is particularly notable. It has an average Cl flux of 1.3 x 10^9 kg/yr [69], which accounts for 0.38% of the global Cl flux, from a catchment with 0.0013% of global discharge [70]. These hot spots of Cl fluxes tend to occur in areas that have recently experienced a perturbation that promoted deeper circulation of fresh meteoric recharge and salt dissolution. The Alberta and Williston basins were both glaciated during the Pleistocene and there is abundant evidence that subglacial recharge displaced connate brines and dissolved evaporites [49,71–73]. The southwestern United States has experienced denudation during the past few Ma, resulting in the creation of greater hydraulic gradients and drains that have promoted the dissolution of evaporites [74]. Conversely, brines at depths of a few km that have not been subjected to perturbations such as large-scale denudation or glaciation typically have marine origins and do not actively participate in regional groundwater flow systems [16]. Contributions of Cl from deep groundwaters to streams are punctuated both in space and time.

Table 1: Cl fluxes from selected sedimentary basins containing evaporites in North America.

Sedimentary Basin	**Cl Flux (kg/yr)**	**Reference**
Williston (Manitoba, Canada)	1.0 x 10^9	[75]
Paradox (Utah/Colorado,USA)	1.3 x 10^8	[69]
Alberta (Alberta, Canada)	7.0 x 10^7	[76]
Permian (Texas, USA)	3.8 x 10^9	[77]
Total	**5.0 x 10^9**	

Conclusions

Our work shows clear evidence of the compartmentalization of the terrestrial water cycle where deep groundwater (below ~500 m) does not contribute measurably to global streamflow. This boundary is shallower than the transition between that of meteoric waters and those with other origins (McIntosh and Ferguson, 2021), indicating that the groundwater flow extends beyond this depth but at very low rates. These findings are important since the volume of groundwater below 500 m represents ~40% of global liquid fresh water and ~80% of all groundwater [21]—effectively cut off from the terrestrial water cycle.

While accounting for ~7% of the global Cl flux to the oceans, deep groundwater contributes less than 0.1% to streamflow. This deep reservoir is slow to turnover, with estimated mean residence times of ~20 Ma.-Some groundwater may never turn over, unless activated by a geological event. This lack of turnover is supported by the widespread occurrence of stable isotopes of H and O that do not plot on the global meteoric water line in deep groundwater [57], suggesting that at least some of these waters have an origin other than infiltration of rain or snowmelt. This early emplacement of deep groundwater and then effective stagnation and isolation on geological time scales demands a re-conceptualization of the terrestrial water cycle. A cycle denotes a continuous rotation, revolution and rhythm. Our new calculations regarding deep groundwater show that the vast majority of groundwater that sits below 500 m exists outside of the classic view of the water cycle. This large, cryptic reservoir of deep groundwater is essentially non-participatory – a terrestrial water messiness and disorderliness that we must confront.

Methods

Cl fluxes were calculated by multiplying river discharge by Cl concentrations from the GEMS-GLORI world river discharge database [78]. These data were compiled at the mouths of major rivers entering the ocean with a total annual discharge of 24,500 km^3/yr, about two-thirds of global river discharge (Clark et al., 2015) and encompassing a combined catchment area of 67.4 million km^2 (about half of global ice-free lands). These large rivers integrate Cl fluxes throughout their watersheds, likely representing the most liberal estimate of cycling from groundwater. The values in the GEMS-GLORI dataset are from different studies covering individual years between 1960 and 1996. As a result, the analysis presented here does not account for any trends in streamflow [79,80] or groundwater fluxes [23] that may be occurring due to changes in climate or other factors.

We estimate total Cl flux of 2.1×10^{11} kg/yr for the 249 rivers with both discharge and Cl concentrations in the GEMS-GLORI database. Scaling this Cl flux, which had a corresponding discharge rate of 24,500 km^3/yr, by the estimated global stream discharge of 44,200 km^3/yr (Clark et al., 2015) results in a total Cl flux of 3.8×10^{11} kg/yr.

The contribution of groundwater to streamflow was estimated using the method given by Pinder and Jones (1969):

$$Q_{gw} = \frac{C_{tr}Q_{tr} - C_{dr}Q_{dr}}{C_{gw}} \quad \textbf{[1]}$$

where Q_{gw} is groundwater discharge, C_{tr} is the concentration of Cl in total runoff, Q_{tr} is the volume of total runoff, C_{dr} is the concentration of Cl in direct runoff, Q_{dr} is the volume of direct runoff and C_{gw} is the concentration of Cl in groundwater discharging to the stream. While this approach has commonly been applied to separate storm hydrographs (Klaus & McDonnell, 2013), here we use it to estimate contributions of groundwater to large streams globally, assuming conditions are near steady state over time periods of decades.

We estimate C_{gw} using the NAWQA dataset (USGS, 2020) and the USGS Produced Waters Database [81] to constrain the possible inputs of deep and shallow groundwater. The possibility of shallow and deep components of groundwater contributing to the overall Cl flux from groundwater to streams is described by:

$$C_{gw}Q_{gw} = C_sQ_s + C_dQ_d \qquad [2]$$

where subscripts *s* and *d* refer to shallow and deep groundwater components. Without additional information, it is not possible to determine unique values for the shallow and deep fluxes of water. However, equation [2] does allow for examination of how an increasing amount of deep groundwater with higher Cl concentrations would reduce the overall groundwater flux.

References

1. Bierkens, M. F. Global hydrology 2015: State, trends, and directions. *Water Resour. Res.* **51**, 4923–4947 (2015).
2. Eagleson, P. S. The emergence of global-scale hydrology. *Water Resour. Res.* **22**, 6S-14S (1986).
3. Rodell, M. *et al.* The observed state of the water cycle in the early twenty-first century. *J. Clim.* **28**, 8289–8318 (2015).
4. Meybeck, M. Concentration des eaux fluviales en éléments majeurs et apports en solution aux océans. *Rev. Géologie Dyn. Géographie Phys. Paris* **21**, 215–246 (1979).
5. Vance, D., Teagle, D. A. & Foster, G. L. Variable Quaternary chemical weathering fluxes and imbalances in marine geochemical budgets. *Nature* **458**, 493–496 (2009).
6. Perrault, P. *De l'origine des fontaines*. (chez Jean de la Caille, ruë S. Jacques, à la Prudence, 1678).
7. Rodriguez-Iturbe, I. Ecohydrology: A hydrologic perspective of climate-soil-vegetation dynamies. *Water Resour. Res.* **36**, 3–9 (2000).
8. Horton, R. E. The role of infiltration in the hydrologic cycle. *Eos Trans. Am. Geophys. Union* **14**, 446–460 (1933).
9. Meyboom, P. Estimating ground-water recharge from stream hydrographs. *J. Geophys. Res.* **66**, 1203–1214 (1961).
10. Condon, L. E. *et al.* Where is the bottom of a watershed? *Water Resour. Res.* **56**, (2020).
11. Hare, D. K., Helton, A. M., Johnson, Z. C., Lane, J. W. & Briggs, M. A. Continental-scale analysis of shallow and deep groundwater contributions to streams. *Nat. Commun.* **12**, 1–10 (2021).
12. McDonnell, J. J. Beyond the water balance. *Nat. Geosci.* **10**, 396–396 (2017).
13. Jasechko, S. *et al.* Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. *Nat. Geosci.* **10**, 425–429 (2017).

14. Jasechko, S., Kirchner, J. W., Welker, J. M. & McDonnell, J. J. Substantial proportion of global streamflow less than three months old. *Nat. Geosci.* **9**, 126–129 (2016).

15. Castro, M. C., Jambon, A., De Marsily, G. & Schlosser, P. Noble gases as natural tracers of water circulation in the Paris Basin: 1. Measurements and discussion of their origin and mechanisms of vertical transport in the basin. *Water Resour. Res.* **34**, 2443–2466 (1998).

16. Ferguson, G. *et al.* The Persistence of Brines in Sedimentary Basins. *Geophys. Res. Lett.* **45**, 4851–4858 (2018).

17. Holland, G. *et al.* Deep fracture fluids isolated in the crust since the Precambrian era. *Nature* **497**, 357 (2013).

18. Warr, O. *et al.* Tracing ancient hydrogeological fracture network age and compartmentalisation using noble gases. *Geochim. Cosmochim. Acta* **222**, 340–362 (2018).

19. Grant, G. E. & Dietrich, W. E. The frontier beneath our feet. *Water Resour. Res.* **53**, 2605–2609 (2017).

20. Singha, K. & Navarre-Sitchler, A. The importance of groundwater in critical zone science. *Groundwater* **60**, 27–34 (2022).

21. Ferguson, G. *et al.* Crustal Groundwater Volumes Greater than Previously Thought. *Geophys. Res. Lett.* e2021GL093549 (2021).

22. Bodnar, R. J. *et al.* Whole Earth geohydrologic cycle, from the clouds to the core: The distribution of water in the dynamic Earth system. (2013).

23. Döll, P. & Fiedler, K. Global-scale modeling of groundwater recharge. *Hydrol. Earth Syst. Sci. Discuss. Discuss.* **4**, 4069–4124 (2007).

24. Fan, Y., Li, H. & Miguez-Macho, G. Global patterns of groundwater table depth. *Science* **339**, 940–943 (2013).

25. Gleeson, T., Befus, K. M., Jasechko, S., Luijendijk, E. & Cardenas, M. B. The global volume and

distribution of modern groundwater. *Nat. Geosci.* **9**, 161–167 (2016).

26. Mohan, C., Western, A. W., Wei, Y. & Saft, M. Predicting groundwater recharge for varying land cover and climate conditions–a global meta-study. *Hydrol. Earth Syst. Sci.* **22**, 2689–2703 (2018).
27. Wada, Y. *et al.* Global depletion of groundwater resources. *Geophys. Res. Lett.* **37**, (2010).
28. Befus, K. M., Jasechko, S., Luijendijk, E., Gleeson, T. & Cardenas, M. B. The rapid yet uneven turnover of Earth's groundwater. *Geophys. Res. Lett.* (2017).
29. Warr, O. *et al.* The role of low-temperature ^{18}O exchange in the isotopic evolution of deep subsurface fluids. *Chem. Geol.* **561**, 120027 (2021).
30. Maxwell, R. M., Condon, L. E. & Kollet, S. J. A high-resolution simulation of groundwater and surface water over most of the continental US with the integrated hydrologic model ParFlow v3. *Geosci. Model Dev.* **8**, 923–937 (2015).
31. de Graaf, I. de, Sutanudjaja, E. H., Van Beek, L. P. H. & Bierkens, M. F. P. A high-resolution global-scale groundwater model. *Hydrol. Earth Syst. Sci.* **19**, 823–837 (2015).
32. Reinecke, R. *et al.* Challenges in developing a global gradient-based groundwater model (G 3 M v1. 0) for the integration into a global hydrological model. *Geosci. Model Dev.* **12**, 2401–2418 (2019).
33. Berghuijs, W. R. & Kirchner, J. W. The relationship between contrasting ages of groundwater and streamflow. *Geophys. Res. Lett.* **44**, 8925–8935 (2017).
34. Gabrielli, C. P., Morgenstern, U., Stewart, M. K. & McDonnell, J. J. Contrasting groundwater and streamflow ages at the Maimai watershed. *Water Resour. Res.* **54**, 3937–3957 (2018).
35. Ferguson, G., McIntosh, J. C., Perrone, D. & Jasechko, S. Competition for shrinking window of low salinity groundwater. *Environ. Res. Lett.* **13**, 114013 (2018).
36. Fritz, P. & Frape, S. K. Saline groundwaters in the Canadian Shield—a first overview. *Chem. Geol.* **36**, 179–190 (1982).

37. Hanor, J. S. Origin of saline fluids in sedimentary basins. *Geol. Soc. Lond. Spec. Publ.* **78**, 151–174 (1994).

38. Berner, E. K. & Berner, R. A. *The global water cycle: geochemistry environment.* (1987).

39. Drever, J. I. *The geochemistry of natural waters.* vol. 437 (prentice Hall Englewood Cliffs, 1988).

40. Hay, W. W. *et al.* Evaporites and the salinity of the ocean during the Phanerozoic: Implications for climate, ocean circulation and life. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **240**, 3–46 (2006).

41. Livingston, D. A. Chemical composition of rivers and lakes, Chapter G. *Data Geochem. US Geol. Surv. Prof. Pap.* **440**, (1963).

42. Mackenzie, F. T. & Garrels, R. M. *Evolution of sedimentary rocks.* (Norton New York, 1971).

43. Marcinek, J. & Rosenkranz, E. *Das Wasser der Erde: Lehrbuch der geographischen Meeres-und Gewässerkunde.* (H. Deutsch, 1989).

44. Chandanpurkar, H. A., Reager, J. T., Famiglietti, J. S. & Syed, T. H. Satellite-and reanalysis-based mass balance estimates of global continental discharge (1993–2015). *J. Clim.* **30**, 8481–8495 (2017).

45. Clark, E. A., Sheffield, J., van Vliet, M. T., Nijssen, B. & Lettenmaier, D. P. Continental runoff into the oceans (1950–2008). *J. Hydrometeorol.* **16**, 1502–1520 (2015).

46. Pinder, G. F. & Jones, J. F. Determination of the ground-water component of peak discharge from the chemistry of total runoff. *Water Resour. Res.* **5**, 438–445 (1969).

47. Palmer, C. D. & Cherry, J. A. Geochemical evolution of groundwater in sequences of sedimentary rocks. *J. Hydrol.* **75**, 27–65 (1984).

48. Grasby, S. E. & Betcher, R. N. Regional hydrogeochemistry of the carbonate rock aquifer, southern Manitoba. *Can. J. Earth Sci.* **39**, 1053–1063 (2002).

49. Grasby, S. E. & Chen, Z. Subglacial recharge into the Western Canada Sedimentary Basin—Impact of Pleistocene glaciation on basin hydrodynamics. *Geol. Soc. Am. Bull.* **117**, 500–514

(2005).

50. Kim, J.-H. *et al.* Hydrogeochemical evolution of formation waters responsible for sandstone bleaching and ore mineralization in the Paradox Basin, Colorado Plateau, USA. *GSA Bull.* (2022).
51. McIntosh, J. C., Walter, L. M. & Martini, A. M. Pleistocene recharge to midcontinent basins: effects on salinity structure and microbial gas generation. *Geochim. Cosmochim. Acta* **66**, 1681–1700 (2002).
52. Shand, P. & Edmunds, W. M. The baseline inorganic chemistry of European groundwaters. *Nat. Groundw. Qual.* 22–58 (2008).
53. Möller, D. The Na/Cl ratio in rainwater and the seasalt chloride cycle. *Tellus B* **42**, 254–262 (1990).
54. Konikow, L. F. Contribution of global groundwater depletion since 1900 to sea-level rise. *Geophys. Res. Lett.* **38**, (2011).
55. Rodell, M. *et al.* Emerging trends in global freshwater availability. *Nature* **557**, 651–659 (2018).
56. GebreEgziabher, M., Jasechko, S. & Perrone, D. Widespread and increased drilling of wells into fossil aquifers in the USA. *Nat. Commun.* **13**, 1–12 (2022).
57. McIntosh, J. C. & Ferguson, G. Deep Meteoric Water Circulation in Earth's Crust. *Geophys. Res. Lett.* **48**, e2020GL090461 (2021).
58. Cheng, A. *et al.* Determining the role of diffusion and basement flux in controlling 4He distribution in sedimentary basin fluids. *Earth Planet. Sci. Lett.* **574**, 117175 (2021).
59. Heard, A. W. *et al.* South African crustal fracture fluids preserve paleometeoric water signatures for up to tens of millions of years. *Chem. Geol.* **493**, 379–395 (2018).
60. Kietäväinen, R. Deep groundwater evolution at Outokumpu, Eastern Finland: from meteoric water to saline gas-rich fluid. *Faculty of Science, Department of Geosciences and Geography, Division of*

Geology and Geochemistry vol. Ph.D. (University of Helsinki, 2017).

61. Lippmann-Pipke, J. *et al.* Neon identifies two billion year old fluid component in Kaapvaal Craton. *Chem. Geol.* **283**, 287–296 (2011).
62. Achtziger-Zupančič, P., Loew, S. & Mariethoz, G. A new global database to improve predictions of permeability distribution in crystalline rocks at site scale. *J. Geophys. Res. Solid Earth* **122**, 3513–3539 (2017).
63. Winter, T. C. Recent advances in understanding the interaction of groundwater and surface water. *Rev. Geophys.* **33**, 985–994 (1995).
64. Winter, T. C., Harvey, J. W., Franke, O. L. & Alley, W. M. *Ground water and surface water: A single resource.* http://pubs.er.usgs.gov/publication/cir1139 (1998) doi:10.3133/cir1139.
65. Fleckenstein, J. H., Krause, S., Hannah, D. M. & Boano, F. Groundwater-surface water interactions: New methods and models to improve understanding of processes and dynamics. *Adv. Water Resour.* **33**, 1291–1295 (2010).
66. Lewandowski, J., Meinikmann, K. & Krause, S. Groundwater–surface water interactions: Recent advances and interdisciplinary challenges. *Water* **12**, 296 (2020).
67. Toth, J. A theoretical analysis of groundwater flow in small drainage basins. *J. Geophys. Res.* **68**, 4795–4812 (1963).
68. Freeze, R. A. & Witherspoon, P. Theoretical analysis of regional groundwater flow: 2. Effect of water-table configuration and subsurface permeability variation. *Water Resour. Res.* **3**, 623–634 (1967).
69. Hite, R. J. & Lohman, S. W. *Geologic appraisal of Paradox basin salt deposits for water emplacement.* (1973).
70. USGS. USGS Water Data for the Nation. https://waterdata.usgs.gov/usa/nwis (2021).
71. Ferguson, G., Betcher, R. N. & Grasby, S. E. Hydrogeology of the Winnipeg Formation in

Manitoba, Canada. *Hydrogeol. J.* **15**, 573–587 (2007).

72. Grasby, S. E., Osadetz, K., Betcher, R. N. & Render, F. Reversal of the regional-scale flow system of the Williston Basin in response to Pleistocene glaciation. *Geology* **28**, 635–638 (2000).
73. Mowat, A. C., Francis, D. J., McIntosh, J. C., Lindsay, M. B. & Ferguson, G. A. Variability in timing and transport of Pleistocene meltwater recharge to regional aquifers. *Geophys. Res. Lett.* **48**, e2021GL094285 (2021).
74. Kim, J.-H. *et al.* Krypton-81 dating constrains timing of deep groundwater flow activation. *Geophys. Res. Lett.* e2021GL097618 (2022).
75. Underwood, E. C., Ferguson, G. & Grasby, S. E. Estimating basin brine fluxes to Lake Winnipegosis. in *Proceedings of GeoEdmonton 2008 : the 61. Canadian geotechnical conference and 9. joint CGS/IAH-CNC groundwater conference : a heritage of innovation* (2008).
76. Gue, A. E., Mayer, B. & Grasby, S. E. Origin and geochemistry of saline spring waters in the Athabasca oil sands region, Alberta, Canada. *Appl. Geochem.* **61**, 132–145 (2015).
77. Bachman, G. O. & Johnson, R. B. *Stability of salt in the Permian salt basin of Kansas, Oklahoma, Texas, and New Mexico, with a section on dissolved salts in surface water.* (1973).
78. Meybeck, M. & Ragu, A. GEMS-GLORI world river discharge database. *Laboratoire de Geologie Applique, Universite Pierre et Marie Curie, Paris, France* (2012) doi:10.1594/PANGAEA.804574.
79. Do, H. X., Westra, S. & Leonard, M. A global-scale investigation of trends in annual maximum streamflow. *J. Hydrol.* **552**, 28–43 (2017).
80. Gudmundsson, L., Leonard, M., Do, H. X., Westra, S. & Seneviratne, S. I. Observed trends in global indicators of mean and extreme streamflow. *Geophys. Res. Lett.* **46**, 756–766 (2019).
81. Blondes, M. S. *et al.* US Geological Survey National Produced Waters Geochemical Database v2. 3 (PROVISIONAL). *U. S. Geol. Surv.* (2016).
82. USGS. National Water-Quality Assessment (NAWQA). https://www.usgs.gov/mission-

areas/water-resources/science/national-water-quality-assessment-nawqa (2020).

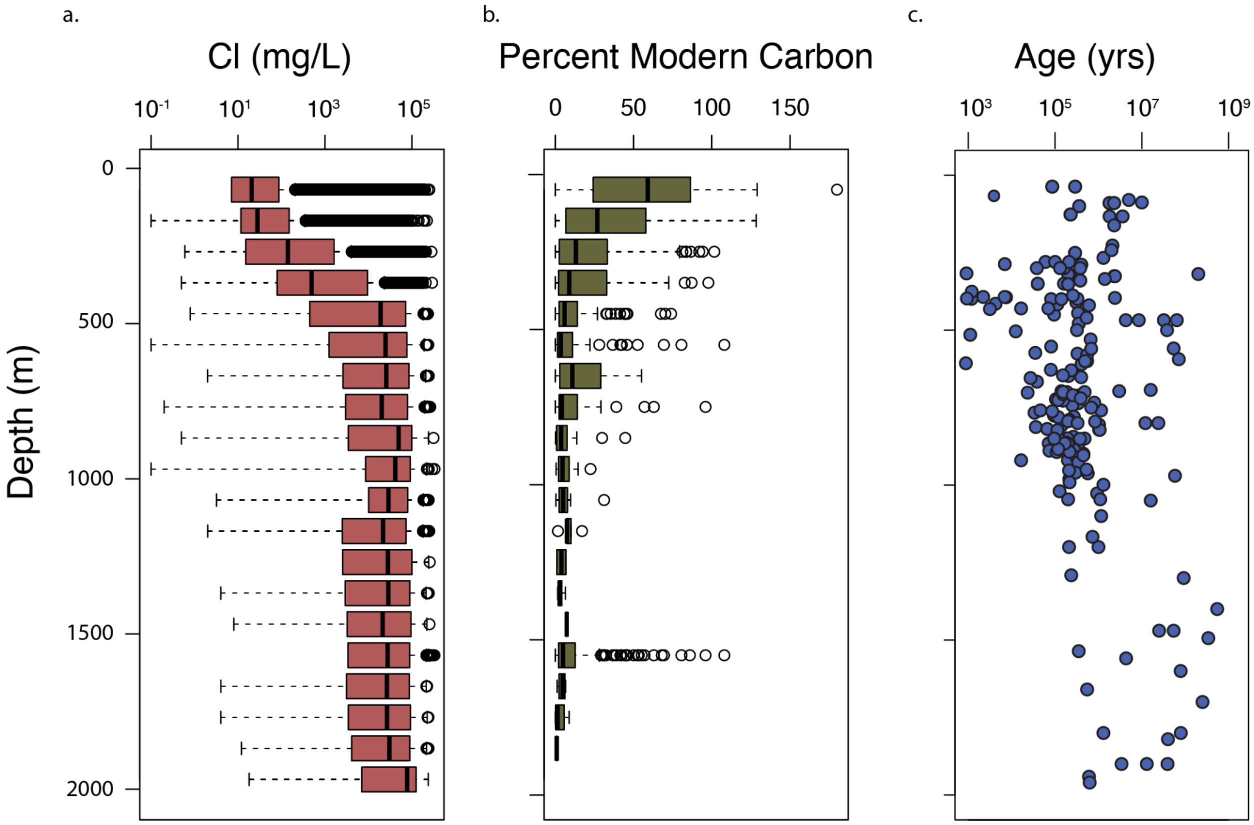

Figure 1: Distribution of a) Cl, b) percent modern carbon and c) groundwater age with depth. Cl concentrations are derived from the USGS NAWQA Database [82] and USGS Produced Waters Database [81]. Percent modern carbon data was compiled by Jasechko et al. (2017). Residence time estimates are from a range of sources (see SI).

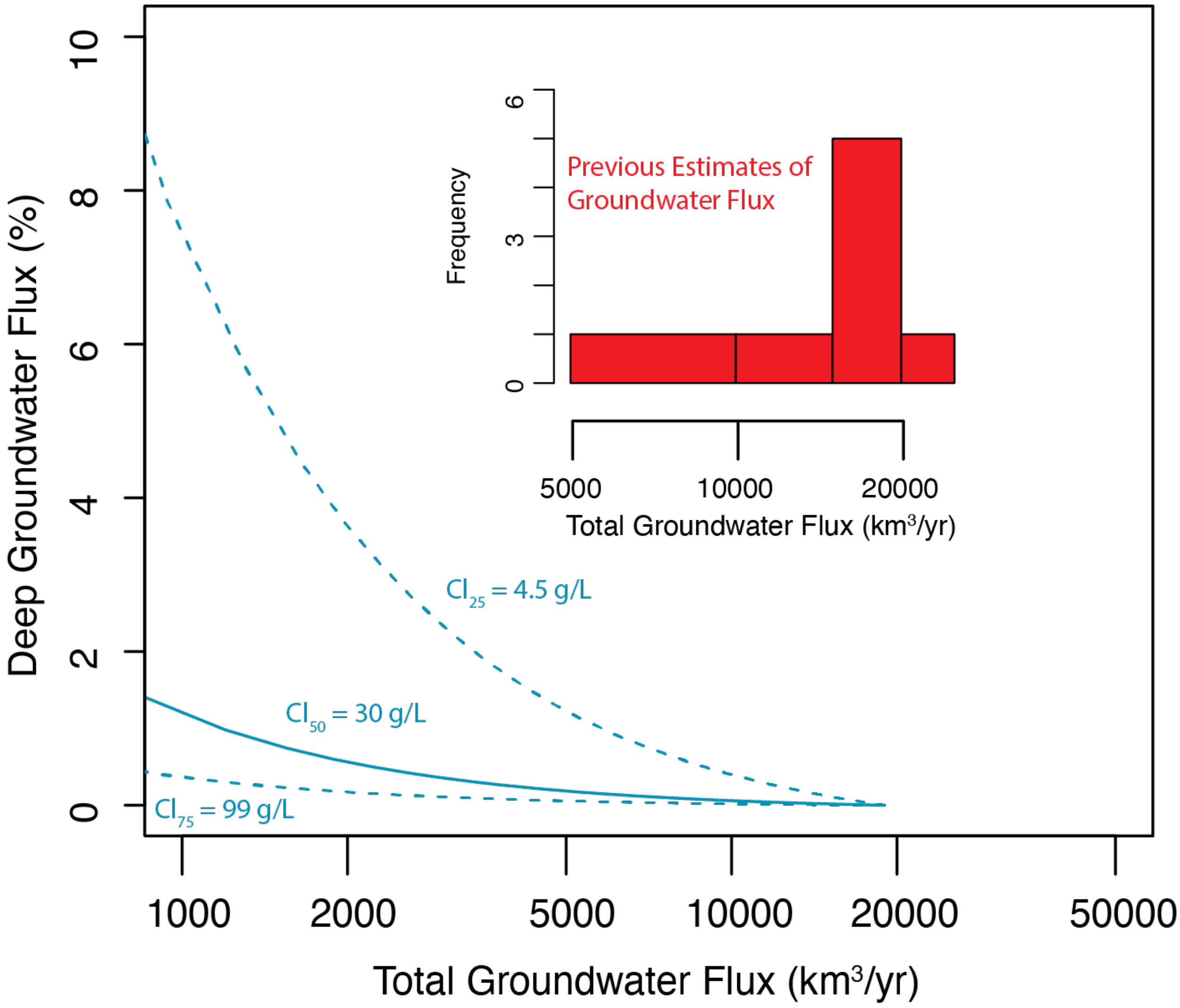

Figure 2: Global groundwater fluxes estimated using the Cl concentration of 20 mg/L for shallow groundwaters and the 25th (4.5 g/L), 50th (30 g/L) and 75th (99 g/L) percentiles for groundwater Cl concentrations beneath 500 m, assuming all Cl in the world's streams is from groundwater. At a contribution of less than 2%, the contributions of deep groundwater would result in a total groundwater flux less than previous estimates, indicating that deep groundwater does not make a substantial contribution to fluxes of water globally.

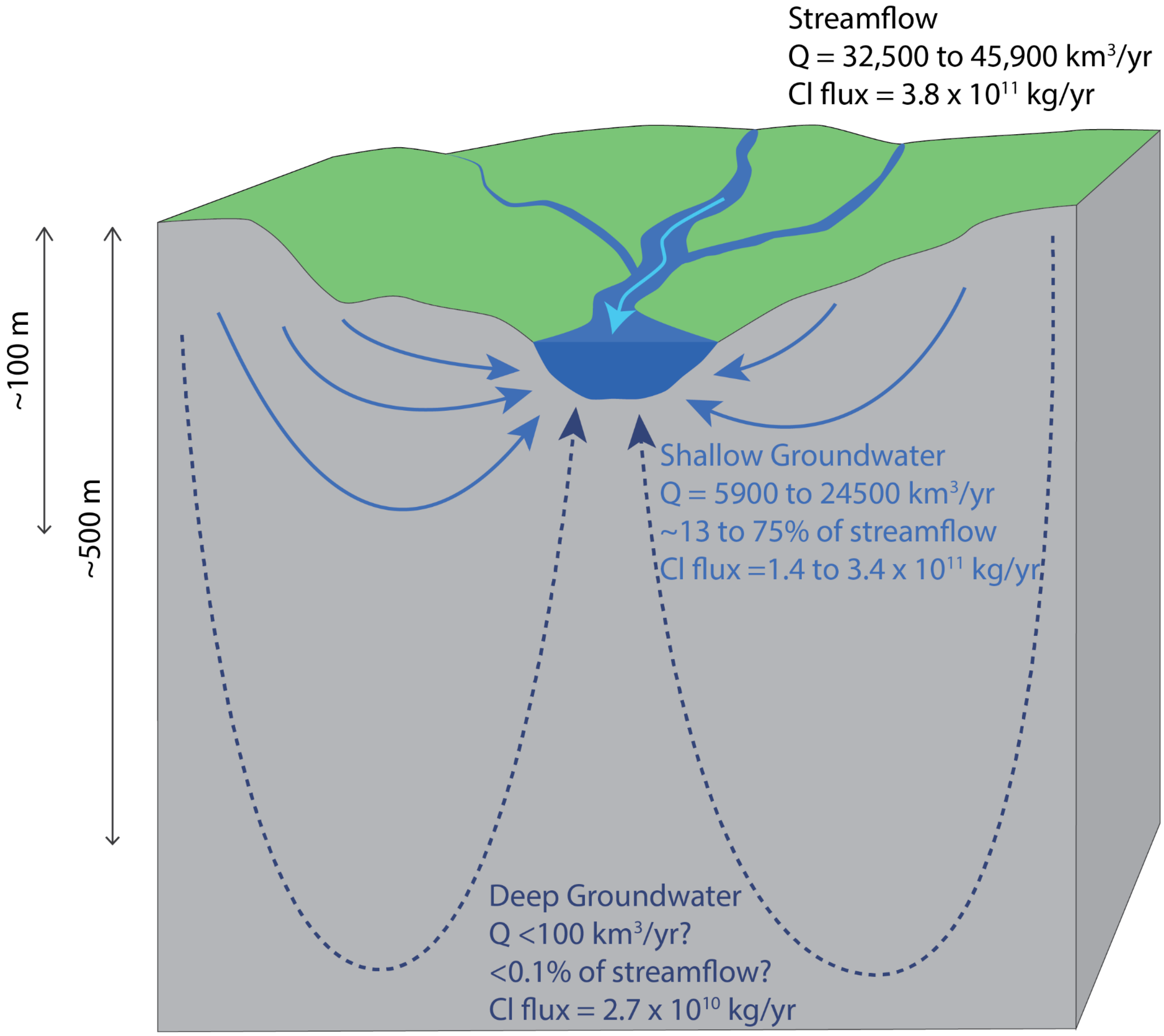

Figure 3: Shallow groundwater fluxes dominate the contribution of groundwater to streamflow. Deep groundwaters are largely isolated from the rest of the water cycle but still contribute a sizeable fraction of Cl found in streams.