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# Groundwater deeper than 500 m contributes less than 0.1% of global river discharge

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Groundwater is one of the largest reservoirs of water on Earth but has relatively small fluxes compared to its volume. This behavior is exaggerated at depths below 500 m, where the majority of groundwater exists 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 terrestrial water cycle at a global scale are 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. Deep groundwater likely contributes <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 chloride cycle, providing ~7% of the flux of chloride to the ocean.

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

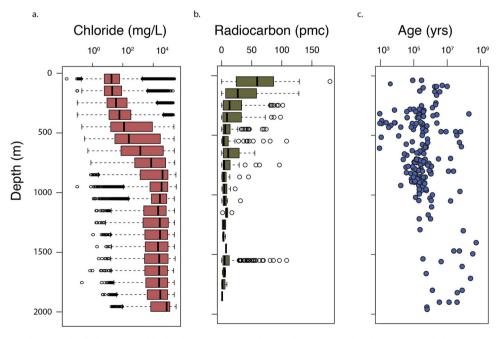
Recent work has suggested possible compartmentalization of the terrestrial water cycle<sup>12</sup> based on some global estimates of the age of groundwater, where 2/3 of groundwater below 250 m is >12,000 year old<sup>13</sup> and streamflow transit times, where 1/3 of global streamflow is <3 months old<sup>14</sup>. Fresh groundwater typically extends down to depths of 500 to 1,000 m<sup>15</sup>. Beneath this zone, a large volume of deep saline groundwater with residence times of 10 s of millions of years or more has been documented, supporting the idea of compartmentalization  $^{16-19}$  (Fig. 1). However, stable water isotopes show that groundwaters down to a depth of at least 1 km are typically meteoric in origin<sup>20</sup>, indicating at least some connection -past or present-to the rest of the water cycle. What has not yet been done is to quantitatively link streamflow and the huge mass of deep groundwater to determine how much of this deep groundwater turns over and contributes to streamflow or if it 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 a key missing piece of surface water hydrology and the field of critical zone science, which uses the bottom of groundwater as its lower limit<sup>21,22</sup> 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 estimated volume of global groundwater on the order of  $\sim\!44$  million km<sup>3</sup>  $^{23}$  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 km³/yr²⁴-²² (Fig. 2). An analysis examining a global compilation of field estimates of recharge suggested a value near the upper end of this range³0. Discharge from groundwater as pumping (734 km³/yr²²) and submarine groundwater discharge (78 km³/yr³¹) 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 and any fluxes associated with evapotranspiration, 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<sup>32</sup>. However, residence times in groundwater are unevenly distributed. Much groundwater in the upper 10 to 100 meters of the Earth's crust is no more than a few decades old<sup>13</sup>, but groundwater can be millions to even as much as a billion years old at depths of several hundred meters to a few kilometers<sup>16,18,19,33</sup>. This distribution of ages suggests that there is minimal exchange of water between groundwaters at depths exceeding several 100 m and shallow groundwaters and overlying surface waters.

We hypothesize that the bulk of groundwater that is actively involved in the water cycle occurs at shallow depths, with deeper groundwater making only a small contribution to the global water cycle. 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 over human timescales. Large-scale hydrologic models have used depths of 102 m<sup>34</sup>, 50 to 500 m<sup>35</sup> and 200 m<sup>36</sup> as the base of the simulated portion of the active 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 <sup>10</sup>. Corroborating



**Fig. 1 Groundwater CI and age typically increase with depth.** This is shown by the distribution of **a** chloride (mg/L), **b** radiocarbon (percent modern carbon (pmc)) and **c** groundwater age with depth from noble gas measurements. CI concentrations are derived from the USGS NAWQA Database<sup>93</sup> and USGS National Produced Waters Geochemical Database<sup>61</sup>. Percent modern carbon data was compiled by Jasechko et al. (2017). Residence time estimates are compiled from a range of sources (Supplementary Data 1). Boxes extend to 25<sup>th</sup> and 75<sup>th</sup> percentiles and whiskers represent the extreme values or ±1.5 times the interquartile range.

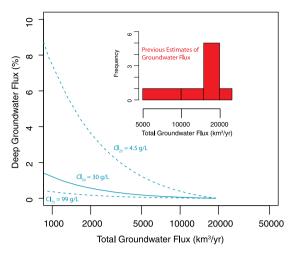


Fig. 2 Global groundwater fluxes estimated using the CI concentration of 18 mg/L for shallow groundwaters and the 25th (4.5 g/L), 50th (30 g/L) and 75th (99 g/L) percentiles for groundwater CI concentrations beneath 500 m, assuming all CI in the world's streams is from groundwater. At a contribution of less than 2%, the contributions of deep groundwater would result in a total groundwater flux less than previous estimates<sup>24-29</sup>, indicating that deep groundwater does not make a substantial contribution to fluxes of water globally on human timescales.

ideas on terrestrial water cycling at large scales—beyond small watersheds—remains challenging because of the dearth of residence time estimates of groundwater at depth<sup>33</sup> 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<sup>37</sup>, supported by measurements<sup>38</sup>, related to permeability contrasts in the subsurface. However, testing the completeness of terrestrial water cycling has not yet been attempted.

## **Approach**

Delineating the contribution of deep groundwater to streamflow is challenging in part because studies of these two systems typically use different residence time tracers. Transit time distributions in streams are commonly based on  $\delta^{18}$ O,  $\delta^{2}$ H and  $^{3}$ H, whereas the residence times of deep groundwaters are typically estimated using noble gases,  $^{14}$ C and  $^{36}$ Cl $^{39}$ , which will be close to atmospheric values in surface water systems $^{40,41}$  and require streambed sampling for detection $^{42,43}$ . Here, we use a geochemical transport approach using Cl 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 to most surface waters  $^{15,44,45}$ . Previous estimates of global riverine Cl fluxes range from  $1.15\times10^{11}$  to  $3.1\times10^{11}\,\mathrm{kg/yr^{46-48}}$ . These estimates relied on multiplying average Cl concentrations in global streams (7.8 mg/L $^{49}$  and 8.3 mg/L $^{4}$ ) by streamflow (32,500 km $^3/\mathrm{yr^{50}}$  and 37,500 km $^3/\mathrm{yr^{51}}$ ). Subsequent estimates of global streamflow have been higher, up to 38,500 km $^3/\mathrm{yr^{52}}$ , 44,200 km $^3/\mathrm{yr^{53}}$ , and 45,900 km $^3/\mathrm{yr^{3}}$ , which would increase the estimated global Cl fluxes to the ocean.

Streamwater Cl has a variety of sources including wet and dry atmospheric deposition, mineral dissolution in streambed or riparian areas, groundwater discharge, and anthropogenic sources, such as road salt<sup>48</sup>. Previous estimates of atmospheric deposition of Cl range from  $4.0\times10^{10}$  to  $2.4\times10^{11}\,\mathrm{kg/yr^{48,54}}$ . Global salt mining removes  $2.9\times10^{11}\,\mathrm{kg/yr}$  of NaCl suggesting that as much as  $1.7\times10^{11}\,\mathrm{kg/yr}$  of Cl could be returned to the world's rivers<sup>55</sup>. Dissolution of evaporites is thought to contribute

 $\sim$ 2.0 × 10<sup>11</sup> kg/yr<sup>46,56</sup>. The sum of these estimates is greater than the observed riverine Cl flux, highlighting their uncertainty.

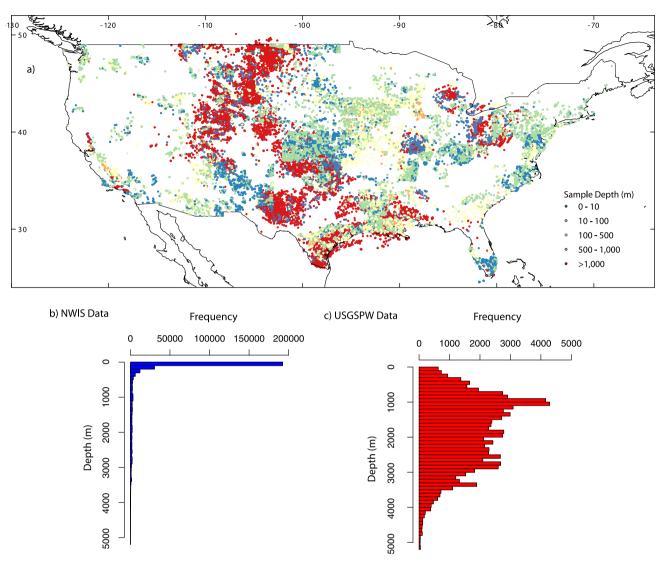
Using the coupling of Cl and groundwater fluxes to estimate groundwater recharge and discharge rates dates back to at least the 1960s<sup>57</sup>. Cl is a conservative solute and generally increases in concentration along a flowpath<sup>58</sup> due to water-rock interaction and evapotranspiration above the water table, although the latter does not directly affect the mass of Cl in groundwater<sup>59</sup>. 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<sup>60</sup> and even higher concentrations have been found in the subsurface<sup>61</sup>.

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 to global riverine fluxes. We then consider the connectedness of shallow and deep groundwater to streamflow using Cl concentrations from over 300,000 analyses covering depths from the ground surface to over 5,000 m below ground surface in the United States<sup>61,62</sup> (Fig. 3) and Cl concentrations and discharge rates for large rivers globally<sup>63</sup>. The interval of depths considered is within the upper 10 km of the Earth's brittle crust, where bulk permeabilities are thought to be sufficiently high to support advection<sup>64</sup>. 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  $3.8 \times 10^{11}$  kg/yr (see Methods) could be accounted for with observed Cl concentrations in shallow groundwater and groundwater recharge within the range of previous estimates (Figs. 2 and 4). Atmospheric and anthropogenic sources could account for more than 50% of the overall Cl flux, indicating that groundwater fluxes are lower than previously estimated or that discharging groundwaters have lower Cl concentrations than the median values for shallow groundwater used here. This also suggests that deeper groundwater does not contribute measurably to streamflow generation globally. The median Cl concentration for wells between 0 and 100 m deep in the United States is 18 mg/L (Fig. 1). At depths of less than 10 m, this value is 24 mg/L. A study of background groundwater chemistry in Europe arrived at a similar median value of 19 mg/ L<sup>65</sup>, although variations with depth were not accounted for in that study. We also note there are spatial biases in the data (Fig. 3) that may not account for areas where Cl levels are lower and circulation of meteoric water occurs to depths greater than the global average, such as orogenic belts where high hydraulic gradients and large-scale faults are common<sup>20</sup>.

Using a Cl concentration of 18 mg/L and the range of groundwater recharge estimates presented in Fig. 2, Cl fluxes from shallow (<100 m) groundwater vary from  $1.1\times10^{11}$  to  $4.4\times10^{11}\,\mathrm{kg/yr}$ . Using the 25th percentile of Cl concentrations over this depth range (7.1 mg/L) resulted in Cl fluxes from  $3.5\times10^{10}$  to  $1.5\times10^{11}\,\mathrm{kg/yr}$ . Using the 75th percentile of Cl concentrations over this depth range (61 mg/L) resulted in Cl fluxes from  $3.6\times10^{11}$  to  $1.5\times10^{12}\,\mathrm{kg/yr}$ . Cl fluxes from shallow groundwater would exceed those for rivers for a Cl concentration of 18 mg/L if the global groundwater discharge exceeds 21,000 km³/yr. Shallow groundwater Cl concentrations at the 75th percentile produced Cl flux estimates in excess of those observed in streams. This value is an upper bound given that a range of



**Fig. 3 CI data from a range of geographic settings to depths >5,000 m were considered in this study.** Groundwater analyses were from **a** various regions in the United States and various depths from **b** NWIS data from groundwater wells<sup>62</sup> and **c** from produced waters from the oil and gas industry<sup>61</sup>.

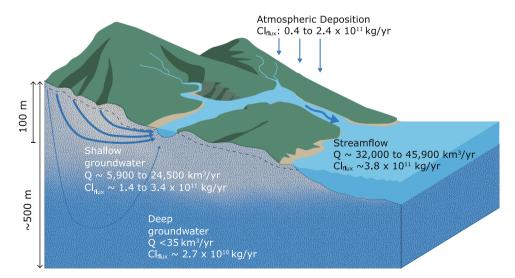


Fig. 4 Deep groundwater contributes less than 0.6% of global streamflow but is responsible for ~7% of the CI flux. The transition between shallow groundwater (gray blue) and deep groundwater (dark blue) will be controlled by some combination of permeability and negative buoyancy and will be gradual rather than sharp in most settings. Deeper circulation of meteoric water will likely be common in orogenic belts, especially those with large-scale faults.

other sources of Cl will be present, including deeper (>100 m) groundwater with higher Cl concentrations. Using an estimated atmospheric deposition of  $4.0\times10^{10}$  to  $2.4\times10^{11}\,\text{kg/yr}^{54}$ , the discharge of shallow groundwater required to match the observed global riverine Cl flux would be reduced to a value between 7,800 and 18,900 km³/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 (Fig. 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 25,500 mg/L for all samples beyond this depth. 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<sup>3</sup>/yr of groundwater discharge with a concentration of 25,500 mg/L would be required to match the observed global riverine Cl flux. This discharge of water is less than 0.01% of previous global groundwater recharge estimates. Using the median Cl concentration value of 10,900 mg/L, found between depths of 500 and 1000 m, would require a discharge volume of less than 0.6% of global recharge<sup>24–29</sup>. These percentages could be slightly higher if global recharge rates have been overestimated (Fig. 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<sup>66,67</sup> including a substantial portion of which has residence times exceeding 12,000 years<sup>68</sup>.

Salinity in deep groundwater can often be attributed to the chemical composition of the original fluids and water-rock reaction<sup>45</sup>; elevated salinity in meteoric waters is commonly associated with dissolution of evaporites<sup>17,69–71</sup>. Meteoric waters are commonly found at depths of a thousand meters or more<sup>20</sup>, 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.<sup>48</sup> estimate that  $2.68 \times 10^{10}$  kg/year of Cl was dissolved during the Holocene Epoch. At the median Cl concentration beneath 500 m, this would require 1.1 km<sup>3</sup>/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<sup>24–29</sup>. Based on a groundwater volume of 16.7 million km<sup>3</sup> in sediments below 500 m<sup>23</sup>, this would result in an average residence time of ~20 Ma for deep sedimentary rocks. Residence times within deep regional groundwater flow 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 (Fig. 1c). Groundwater ages of as much as 30 Ma have been documented in the Paris Basin 16, while ages in the Williston Basin extend from a few Ma to several hundred Ma<sup>72</sup>. In the Paradox Basin, waters at these depths have residence times of several 100 ka using 81Kr<sup>73</sup>. However, other groundwaters in the basin were too old to be dated with this technique (>1 Ma).

Groundwaters in cratonic rocks can be considerably older still  $^{18,19,74-76}$  and groundwater discharge from these environments is expected to be smaller than those estimated for deep sedimentary rocks due to their lower permeabilities  $^{77}$ . Waters in cratons at depths of a few km commonly have  $\delta^2H$  and  $\delta^{18}O$  values that plot to the left of the global meteoric water line and a

lack of differential losses of noble gases<sup>33</sup>, which indicate the presence of isolated fracture networks. These groundwaters in deep cratonic environments, which appear to be isolated from the rest of the hydrologic cycle over time periods of 10 s to 100 s of Ma, may consist of approximately 25% of the global groundwater volume<sup>23</sup>.

Over the past few decades, it has been emphasized that groundwater and surface water are one resource<sup>78,79</sup>, leading to an explosion in groundwater-surface water interaction studies focused on the fluxes of water between these two reservoirs<sup>80,81</sup>. 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 deep subsurface<sup>37</sup>. The sluggish nature of deeper groundwater systems due to regional flow patterns<sup>82</sup> and permeability contrasts<sup>83</sup> and their implications for regional groundwater flow systems are well understood and critical to producing models of groundwater systems. However, these concepts have not been fully integrated into our conceptual understanding of deep groundwater systems, where the sharp impermeable bottom boundary invoked by Toth<sup>82,84</sup> is likely a more gradual transition associated with negative buoyancy<sup>20</sup> and decreasing permeability<sup>64,77</sup> (Fig. 4). 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 shallower 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  $2.68 \times 10^{10}$  kg/yr of Cl from evaporite dissolution<sup>48</sup> is approximately 7% of global riverine Cl flux estimated here. This ignores the Cl flux associated submarine groundwater discharge but we expect this flux to be small given that direct discharge to the ocean accounts for only a fraction of a percent of overall groundwater discharge (0.3 to 1.3%)31. These deep Cl fluxes to rivers are commonly associated with sedimentary basins containing evaporites. Surface waters draining the Williston, Alberta, Paradox and Permian basins are thought to have a combined Cl flux of  $5.0 \times 10^9$  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  $1.3 \times 10^8$  kg/yr<sup>85</sup>, which accounts for 0.038% of the global Cl flux, from a catchment with 0.0013% of global discharge<sup>86</sup>. 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<sup>69,87–89</sup>. The southwestern United States has experienced denudation during the past few

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 × 10 <sup>9</sup>	94
Paradox (Utah/Colorado, USA)	1.3 × 10 <sup>8</sup>	85
Alberta (Alberta, Canada)	$7.0 \times 10^{7}$	95
Permian (Texas, USA)	$3.8 \times 10^9$	96
Total	5.0 × 10 <sup>9</sup>	

Ma, resulting in the creation of greater hydraulic gradients and drains that have promoted circulation of meteoric water to depths of up to 3 km and the dissolution of evaporites<sup>73</sup>. Conversely, sedimentary basin 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<sup>17</sup>. Contributions of Cl from deep groundwaters to streams are punctuated both in space and time.

### **Conclusions**

Our work shows clear evidence of the compartmentalization of the terrestrial water cycle where deep groundwater (below  $\sim\!500$  m) does not contribute substantially to global streamflow. This depth is shallower than the transition between that of meteoric waters and those with other origins  $^{20}$ , indicating that the groundwater flow extends beyond this depth but at very slow rates. These findings are important since the volume of groundwater below 500 m—representing  $\sim\!40\%$  of global liquid fresh water and  $\sim\!80\%$  of all groundwater  $^{23}$ —is effectively cut off from the terrestrial water cycle on human timescales.

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<sup>20,33</sup>, 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 disconnection on geological time scales demands a reconceptualization 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  $^{63}$ . These data were compiled at the mouths of major rivers entering the ocean with a total annual discharge of  $24,500~\rm km^3/\rm yr,^{53}$  and encompassing a combined catchment area of  $67.4~\rm million~\rm km^2$  (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  $^{90.91}$  or groundwater fluxes  $^{25}$  that may be occurring due to changes in climate or other factors.

We estimate total Cl flux of  $2.1 \times 10^{11}$  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 km³/yr, by the estimated global stream discharge of 44,200 km³/yr.  $^{53}$  results in a total Cl flux of  $3.8 \times 10^{11}$  kg/yr.

The contribution of groundwater to streamflow was estimated with the following equation  $^{57}$ :

$$Q_{gw} = \frac{C_{tr}Q_{tr} - C_{dr}Q_{dr}}{C_{gw}}$$
 (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  $^{92}$ , 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 >254,000 analyses from NWIS Dataset  $^{62}$  and >65,000 analyses from the the USGS National Produced Waters Geochemical Database  $^{61}$  covering depths from ground surface down to >5,000 m (Fig. 3) 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:

$$C_{gw}Q_{gw} = C_sQ_s + C_dQ_d \tag{2}$$

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.

## **Data availability**

Noble gas data compiled in this study are available in Supplementary Data 1 and can be accessed at https://doi.org/10.6084/m9.figshare.21869367.v1. Cl data used in this study can be accessed at https://waterdata.usgs.gov/usa/nwis and https://www.usgs.gov/data/us-geological-survey-national-produced-waters-geochemical-database-v23. River chemistry data is available at https://www.usgs.gov/data/us-geological-survey-national-produced-waters-geochemical-database-v23.

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## **Author contributions**

G.F. and J.C.M. conceived of this study and led the writing of this paper. Methodology was developed by G.F., S.J., and J.C.M. Calculations were performed G.F. and data was compiled by G.F., J.C.M., S.J., and J.H.-K. G.F., J.C.M., S.J., J.-H.K., J.F., and J.J.M. contributed to writing and editing.

#### **Competing interests**

The authors declare no competing interests.

#### Additional information

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