



Contribution of groundwater carbon pools to atmospheric carbon sinks: A case study of the Yinchuan Basin, Northwest China

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ABSTRACT

Addressing global warming, a common change today, requires achieving peak carbon dioxide emissions and carbon neutrality (also referred to as the dual carbon goals). Enhancing research on the carbon cycle is urgently needed as the foundation. Water, a key carrier in the carbon cycle, necessitates investigation into groundwater carbon pools' contribution to atmospheric carbon sinks. This study assessed carbon stocks in the Yinchuan Basin's soil and groundwater carbon pools. Findings indicate the basin's surface soils contain approximately 24.16 Tg of organic carbon and a total of 60.01 Tg of carbon. In contrast, the basin's groundwater holds around 4.90 Tg of carbon, roughly one-fifth of the organic carbon in surface soils. Thus, groundwater and soil carbon pools possess comparable carbon stocks, underscoring the importance of the groundwater carbon pool. Studies on terrestrial carbon balance should incorporate groundwater carbon pools, which deserve increased focus. Evaluating groundwater carbon pools' contributions is vital for achieving the dual carbon goals.

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1. Introduction

To proactively address global climate change and mitigate natural disasters like extreme weather, China has initiated the dual carbon goals and has been actively engaged in research on the carbon cycle. Such research highlights the investigation of the dynamics of the carbon cycle and carbon budget of terrestrial ecosystems, as minor alterations in these ecosystems' carbon pools can cause considerable shifts in atmospheric CO₂ concentration (Piao SL et al., 2019; Wang K et al., 2023).

Terrestrial ecosystem carbon primarily resides in two pools: Biomass and surface soils (Elana LL et al., 2016; TAM Pugh et al., 2016). Surface soil carbon, derived from plant debris and roots, extends the biomass carbon pool. However, both types of carbon pools have a finite capacity for storage and cannot expand indefinitely (Fang JY, 2021; Piao SL et al.,

2022; Zhao HX et al., 2024).

The soil carbon pool, the largest within a terrestrial ecosystem, holds 2–3 times more carbon than the biomass pool and thrice the carbon stored in the atmosphere (Tan ZX et al., 2004; Wang HY et al., 2023). Soil respiration releases CO₂, accounting for approximately two-thirds of the total carbon exchange between terrestrial ecosystems and the atmosphere, making the soil carbon pool a crucial component and carrier of the carbon cycle (Wang YX et al., 1999). Consequently, the soil carbon pool's balance is intrinsically linked to atmospheric CO₂ concentration changes, significantly influencing global climate change (Anil CS et al., 2023; Zhang YX et al., 2022).

In addition to emitting CO₂ into the atmosphere, a soil carbon pool serves as a primary carbon source for groundwater (Kartik J et al., 2022; Li L et al., 2022). In other words, groundwater acts as a significant repository for soil carbon, especially the organic carbon from surface soils. Under biochemical reactions, this organic carbon readily transforms into soluble humic acids like humic acid, fulvic acid, and humin (Li YM et al., 2017; Liu YT et al., 2017). These humic acids from the surface soils infiltrate into groundwater in substantial amounts via processes such as

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atmospheric precipitation and irrigation, thus becoming the primary carbon source in groundwater. Consequently, the groundwater carbon cycle represents a crucial extension of soil carbon migration.

The questions then arise: What is the share of the groundwater carbon cycle, and does it have the capacity to influence soil carbon storage? In other words, could the groundwater carbon pool act as an adjunct to the soil carbon pool? These aspects warrant further investigation and clarification.

This study, focusing on the Yinchuan Basin, quantified the organic and total carbon in the surface soil pool, examined the groundwater carbon cycle process, identified the carbon sources in groundwater flow, explored the bases for the evaluation of the groundwater carbon pool, and ultimately juxtaposed the storage of the groundwater carbon pool with that of the soil carbon pool. This study aims to shed light on the impact of the groundwater carbon cycle on the overall

atmospheric carbon cycle.

2. Methods

2.1. Study area

The Yinchuan Basin is situated between longitudes $105^{\circ}45'$ and $106^{\circ}56'$ E and latitudes $37^{\circ}46'$ and $39^{\circ}23'$ N. It stretches along the Yellow River, extending 165 km from north to south and spanning 42 km to 60 km from east to west, covering an area of roughly 6138 km². The basin is flanked by the Ordos Block to the east and the Alashan Block to the west, occurring within a subsided depression at the junction of these two blocks (Huang XF et al., 2016). Its terrain is predominantly flat, with elevations ranging from 1100 m to 1200 m (Fig. 1b).

Characterized by an inland arid climate, the Yinchuan Basin experiences a typical continental climate with long,

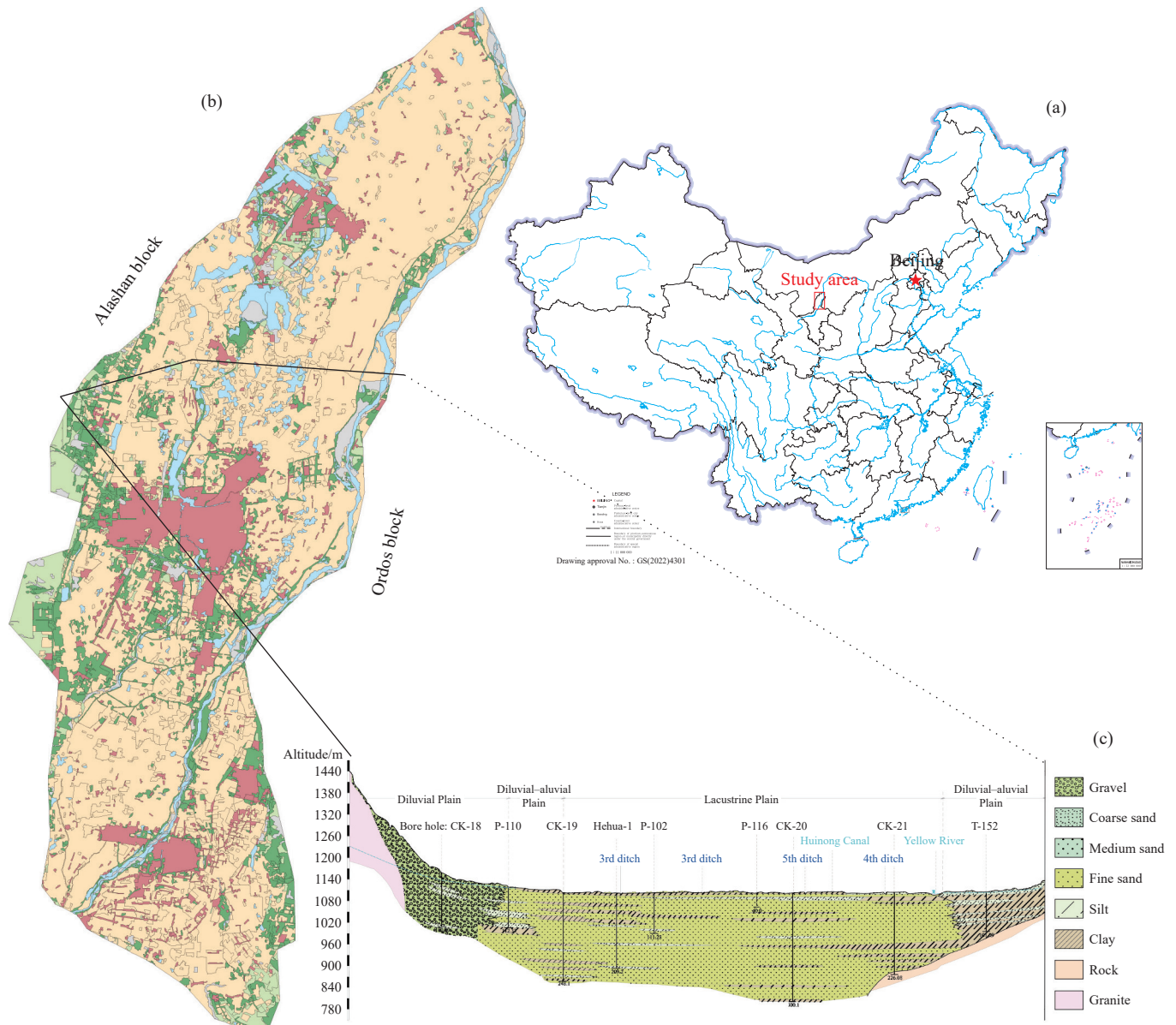


Fig. 1. Location of the Yinchuan Basin.

among their samples. More detailed information is available in the National Geological Archives of China.

The land use data for the Yinchuan Basin were sourced from China's Third National Land Survey (Fig. 1b), covering a total area of 6138 km², including 654 km² of construction land, 3913 km² of farmland (the largest category), 306 km² of grassland, 710 km² of various forestland, 159 km² of barren land (the smallest category), and 397 km² of water area (Table 1). The water area was excluded from the calculation of the surface soil carbon pool.

Calculating the carbon amount involved in the carbon cycle in a groundwater system necessitates the use of groundwater geochemical data of shallow layers. The groundwater geochemical data for the Yinchuan Basin were sourced from projects entitled *A Comprehensive Geological Survey of the Ningxia Yanhuang Economic Zone* and *A Comprehensive Geological Survey of the Ningxia Yanhuang Ecological Economic Zone*, conducted by the Xi'an Center of the China Geological Survey (CGS) from 2016 to 2018 and from 2019 to 2021, respectively. A total of 452 pieces of geochemical data from shallow groundwater (less than 50 m deep) were chosen for analysis.

3. Results and discussion

3.1. Storage assessment of surface soil carbon pools

The soil carbon pool consists of two components: The organic carbon pool and the inorganic carbon pool. Organic carbon in the surface soil primarily originates from plant litter and root systems, with its accumulation in the soils being influenced by the rates of organic matter input, as well as the decomposition and migration rates of soil organic matter (Bao LR et al., 2023). In contrast, inorganic carbon predominantly comprises carbonate minerals like CaCO₃, along with dissolved inorganic carbon (HCO₃⁻) in soil moisture and carbon dioxide (CO₂) gas.

Compared to inorganic carbon, organic carbon is more susceptible to microbial breakdown, a complex process that yields various humic acids and eventually releases CO₂. This CO₂ often readily escapes back into the atmosphere, making the link between the organic carbon pool and the atmospheric carbon pool a focal point of concern. Inorganic carbon, however, tends to be more stable.

Since the 1950s, efforts have been made to gauge the carbon stocks of global soil organic carbon pools (Jia YP, 2004). The estimations largely rely on the organic carbon concentration at depths less than 1 m, as soil organic carbon is predominantly found within this top layer. In reality, the concentration of soil organic carbon is especially high in the upper 50 cm, with many soil geochemical surveys concentrating on the top 20 cm. Therefore, a 50 cm depth was chosen as the representative thickness for surface soils in this study.

The soil bulk density in the Yinchuan Basin generally ranges from 1.2 g/L to 1.8 g/L, with an average of 1.5 g/L, which was applied in the assessment of this study.

This study employed the mean contents of organic carbon and total carbon content in samples of each land use to represent the averages of total organic carbon (TOC) and total carbon (TC) in the surface soils of the land type. These values were then multiplied by the total soil mass for a 50 cm depth per unit area and by the total area of the land type. Consequently, the storage of the Yinchuan Basin's surface soil organic carbon pool was estimated at 24.16 Tg and the basin's total carbon storage in surface soil at 61.07 Tg. Detailed calculations are presented in Table 2.

3.2. Analysis of carbon sources in groundwater

Groundwater, as a solution, typically contains seven primary solutes, consisting of four key cations, i.e., Na⁺, K⁺, Ca²⁺, and Mg²⁺, and three principal anions, i.e., Cl⁻, SO₄²⁻, and HCO₃⁻. In contrast, other elements in the solute composition generally exhibit minor concentrations. These components primarily enter the groundwater system through dissolution, except for HCO₃⁻. Analyses indicate that the major anions and cations in groundwater gradually dissolve into it during the groundwater runoff. However, carbon often comes from the soil layer and has already reached a saturation or near-saturation state at the onset of groundwater formation. The subsequent entry of carbon into the groundwater in the runoff process is minimal.

As shown in Fig. 2, the correlation between the total anions (Te⁻) and total cations (Te⁺) was depicted through a fitted line with a slope of 0.99, demonstrating a strong linear relationship. Excluding SO₄²⁻ and Cl⁻ separately from the total anions would significantly alter the slopes of the fitted lines displaying the correlation between the remaining anions and the total cations, dropping from 0.99 to 0.62 and 0.40, respectively. The standard deviation (*R*²) for the comparative data in each dataset exceeded 0.9, indicating a robust correlation between the data. The changes in these anion content positively correlated with a shift in the total solute concentration in groundwater, suggesting that SO₄²⁻ and Cl⁻ progressively enter the groundwater system through dissolution as groundwater flows.

Similarly, when comparing total cations to total anions in groundwater (Fig. 3), removing Ca²⁺ and Mg²⁺ or Na⁺ and K⁺ from the cations and then comparing with the total anions revealed a significant decline in the slopes of the fitted lines, from 1 to 0.69 or 0.31, respectively. This suggests that all

Table 2. Calculated organic carbon and total carbon storage in the various land use types of Yinchuan Basin.

Land use type	Area	TOC content	TC content	TOC	TC
	km ²	%	%	Tg	Tg
Construction land	654	0.71	1.88	3.49	14.54
Farmland	3913	0.60	1.99	17.70	38.34
Grassland	306	0.30	1.07	0.69	2.96
Forestland	710	0.39	1.41	2.05	4.47
Barren land	159	0.19	0.67	0.23	0.76
Water area	397	–	–	–	–
Total	6138	–	–	24.16	61.07

major cations, sulfate ions, and chloride ions exhibited similar trends and positively correlated with the total concentration of groundwater, meaning that they all gradually dissolve into the groundwater during the groundwater runoff.

However, the HCO_3^- concentration changed in a significantly different way from those of other ions. As shown in Fig. 2, excluding HCO_3^- led to insignificant shifts in the slope of the fitted line representing the relationship between remaining anions and total cations, only reducing from 0.99 to 0.95. This implies that the HCO_3^- concentration roughly follows the same trend as the total concentration increases. Rather than gradually dissolving into groundwater during the groundwater runoff, carbon has already attained a certain concentration during groundwater formation, with no substantial changes thereafter.

Fig. 4 illustrates the comparison between the total anions and total dissolved carbon in groundwater, which included carbon in various hydrochemical forms such as HCO_3^- ,

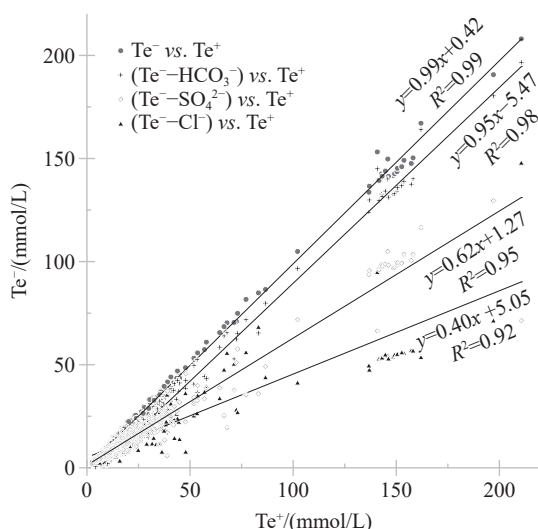


Fig. 2. Anion concentration vs. total cation concentration in groundwater.

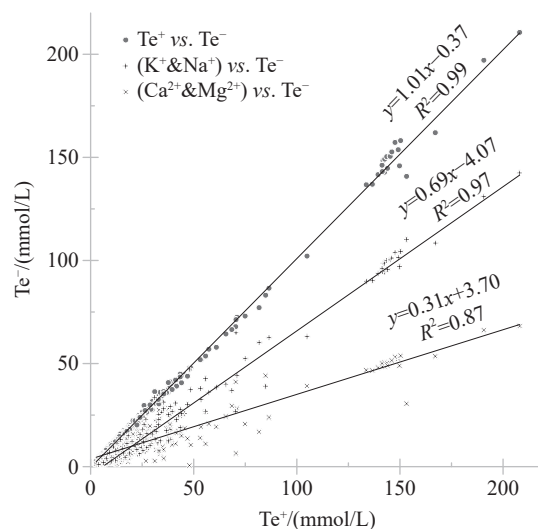


Fig. 3. Cation concentration vs. total anion concentration in groundwater.

CO_3^{2-} , and free CO_2 . The total dissolved carbon concentration and the total anion concentration exhibited a weak correlation, as evidenced by an R^2 value of 0.36.

As depicted in Fig. 5, the ratio of total dissolved carbon to total anions (TC/Te^-) declined with an increase in the total anion concentration. This trend suggests that the dissolution of Cl^- and SO_4^{2-} during the groundwater runoff progressively diminishes the proportion of carbon ions to total anions. In conclusion, carbon does not gradually dissolve and enter the groundwater during the groundwater runoff, making a minimal contribution to the increasing total anion concentration.

Theoretically, given that HCO_3^- represents the primary form of carbon in groundwater, its concentration should align with that of Ca^{2+} if the carbon present in groundwater primarily results from the dissolution of CaCO_3 .

Nevertheless, a comparison between the Ca^{2+} concentration and the total dissolved carbon concentration in groundwater (Fig. 6) revealed a relatively weak positive correlation, evidenced by a modest slope of 0.26 and an R^2 value of only 0.35. This suggests that the carbon found in the Yinchuan Basin’s groundwater might not predominantly originate from CaCO_3 dissolution. Instead, it is more likely that the carbon derives from the infiltration of soluble humic acids formed by organic carbon decomposition, though

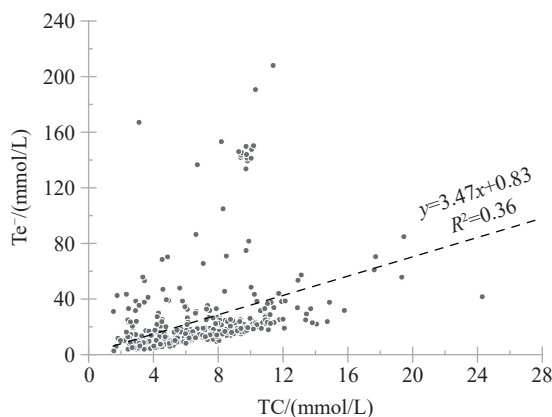


Fig. 4. Total anion concentration vs. total dissolved carbon concentration in groundwater.

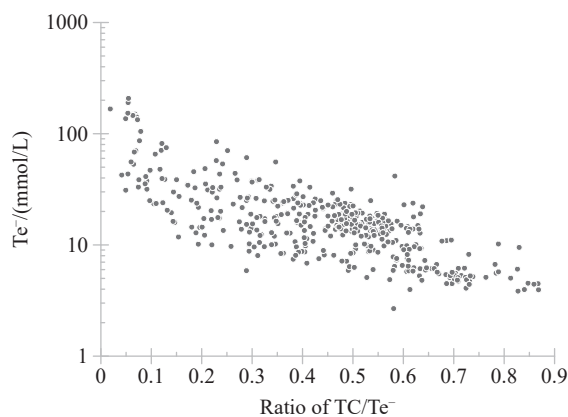


Fig. 5. Total anion concentration vs. ratio of total dissolved carbon to total anions in groundwater.

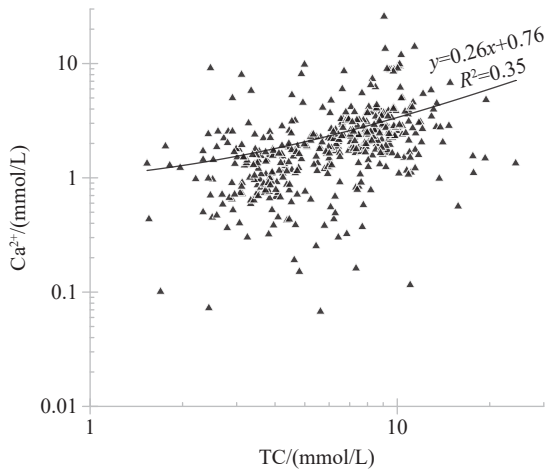


Fig. 6. Calcium concentration vs. total dissolved carbon concentration in groundwater.

conclusive evidence for this is lacking.

In conclusion, the presence of carbon in groundwater is primarily attributed to infiltration from the surface soil carbon pools rather than from a gradual dissolution during groundwater runoff. Thus, groundwater serves as a significant outlet for the surface soil carbon pool.

Further exploration is required to determine the reasonable range for the groundwater carbon pool as a downstream recipient of the surface soil carbon pool.

3.3. Storage assessment of groundwater carbon pool

The Yinchuan Basin boasts an extensive groundwater system, with the Quaternary aquifer's thickness generally ranging from 400 m to 1600 m, supporting various levels of groundwater circulation. The shallow groundwater circulates at depths up to 50 m, with a cycle lasting several decades, whereas deep groundwater circulation extends down to 300 m, with cycles spanning thousands or even tens of thousands of years.

Strictly speaking, all carbon present in groundwater should be considered part of the groundwater carbon pool, which may be extremely large (Zhang SJ et al., 2022; Zhu LL et al., 2022). However, quantifying this is arguably impractical since most groundwater carbon serves merely as a reserve, not interacting with the atmosphere over relevant timescales (beyond a century). The focus should instead be on the portion of groundwater carbon storage that maintains a close connection with the surface soil carbon pool or the atmospheric carbon pool. This portion should have the potential to return to the surface within a specific timeframe and engage in carbon exchange with the atmosphere.

The Yinchuan Basin possesses a comprehensive drainage and irrigation network, with drainage ditches serving as the primary outlet for shallow groundwater. The volume of water discharged through these ditches is substantial, amounting to $18 \times 10^8 \text{ m}^3/\text{a}$. This volume significantly surpasses other forms of groundwater discharge, such as manual extraction and runoff to the Yellow River, which are 2 to 3 orders of magnitude smaller and thus negligible for this discussion.

Furthermore, the majority of the water in the drainage ditches originates from shallow groundwater discharge. In contrast, contributions from other sources like precipitation, urban domestic drainage, and lake runoff are 2 to 3 orders of magnitude smaller, thereby not influencing the ditches' water volume. Consequently, the water volume in the drainage ditches remains relatively constant over the years, making it a reliable indicator of the active groundwater circulation volume in the Yinchuan Basin.

The active groundwater circulation cycle, also reflected in the drainage water age within the ditches, was assessed using the tritium abundance in various water bodies across the basin (Fig. 7; Ma HY et al., 2019). The cycle period of shallow groundwater was determined based on the average tritium abundance ($^3\text{H} = 53.67 \text{ TU}$) in the basin's main water supply (the Yellow River) and that in the primary discharge (drainage water for irrigation), which averages $^3\text{H} = 7.89 \text{ TU}$, yielding a calculated cycle period of 33.6 years. The total active groundwater circulation volume was estimated at approximately $604.8 \times 10^8 \text{ m}^3$, derived by multiplying the average annual drainage water volume ($18 \times 10^8 \text{ m}^3/\text{a}$) by the cycle period (33.6 years).

The average cyclic volume, calculated by dividing the total active groundwater circulation volume ($604.8 \times 10^8 \text{ m}^3$) by the total area of the Yinchuan Basin (6138 km^2), is $0.985 \times 10^6 \text{ m}^3/\text{km}^2$. The cyclic depth, derived from the average cyclic volume and the average porosity of the shallow aquifer (0.23), is 42.8 m. When considering aquitards, which may act as impermeable barriers within the shallow aquifer and thus do not contribute to active groundwater circulation, the cyclic depth is highly consistent with the commonly accepted shallow groundwater circulation depth of approximately 50 m in the region.

Considering the active groundwater circulation volume in the Yinchuan Basin, which is $604.8 \times 10^8 \text{ m}^3$, and the average total dissolved carbon in the shallow groundwater, measured at 81.01 mg/L derived from 452 samples, the carbon storage in the groundwater pool was estimated at approximately 4.90 Tg (expressed as carbon). This represents 20.27% of the total organic carbon in the surface soils (24.16 Tg) and 8.02% of the total carbon in the surface soils (61.07 Tg). Compared to

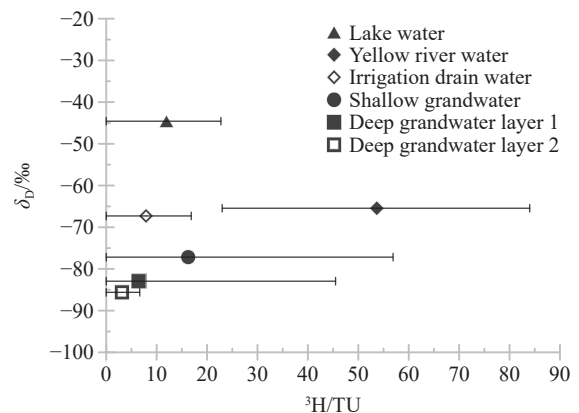


Fig. 7. Tritium abundance in different water bodies across the Yinchuan Basin (error lines denoting the distribution ranges of tritium).

the surface soil carbon pool, the carbon storage in the shallow groundwater pool of the Yinchuan Basin is significant and should not be overlooked.

3.4. Doubtful issues deserving discussion

Evaluating the storage of the surface soil carbon pool entails some uncertainties. The first uncertainty is the soil layer thickness of the Yinchuan Basin, which varies significantly across different regions, ranging from 10 cm to 70–90 cm, making it challenging to adjust the assessment on a basin-wide scale to the specific depth of each soil layer. Furthermore, sampling and testing targeted the layers at depths ranging from 0 cm to 20 cm or from 0 cm to 50 cm, with fewer samples taken from depths greater than 50 cm. However, the carbon content is not uniform across depths, tending to decrease sharply with increasing soil depth. Consequently, sample results may not accurately reflect the carbon content across various soil layers, introducing potential errors in the assessment. Some evaluations of surface soil carbon pools' storage consider a depth of 1 m. However, the lack of data on soil layers in this study has hampered a detailed understanding of the vertical distribution of organic carbon in the Yinchuan Basin. Given this, a 50 cm depth was adopted for this assessment. The organic carbon storage in the surface soils of the Ningxia irrigation area with water diverted from the Yellow River, as calculated by the Institute of Soil Science, Chinese Academy of Sciences, is approximately 17.65 Tg (Dong LL et al., 2015), closely aligning with the current estimate of 17.70 Tg. This congruence suggests that the chosen assessment depth is appropriate.

The second uncertainty centers on defining the extent of the groundwater carbon pool. In this study, attention was directed toward shallow groundwater, the most dynamically circulating water in the Yinchuan Basin, while the contributions of middle and deep groundwater were overlooked. This approach is justified by the lengthy cycle periods of deeper groundwater layers, whose carbon content is minimally connected to the atmospheric and surface soil carbon pools. Consequently, the authors agree to primarily consider the actively circulating groundwater for assessments of the groundwater carbon pool, with the definition of actively circulating groundwater being subject to the unique conditions of different watersheds. In this study, the annual discharge from drainage ditches was used to represent active groundwater circulation, deemed to be a suitable metric for evaluation.

The study area's distinct characteristics, particularly its reliance on flood irrigation for agriculture, resulting in substantial irrigation and drainage volumes, significantly enhance the circulation rate of shallow groundwater. This, in turn, contributes to the notable size of the groundwater carbon pool.

When these aspects are set aside and the volumes are compared, the storage estimations of the groundwater carbon

pool and the surface soil organic carbon pool are found to have similar orders of magnitude. Thus, the groundwater carbon pool is substantial and warrants increased attention.

4. Conclusions

Evaluations and comparisons between the surface soil carbon pool and the groundwater carbon pool in the Yinchuan Basin lead to several conclusions:

(i) At a 50 cm depth, the surface soils in the Yinchuan Basin hold an organic carbon storage of 24.16 Tg and a total carbon storage of 60.01 Tg.

(ii) Groundwater geochemical characteristics suggest that carbon in groundwater predominantly originates from the infiltration process. Thus, the migration of groundwater carbon represents a significant outflow from the surface soil carbon pool.

(iii) The most dynamically active groundwater in the Yinchuan Basin is the shallow groundwater (less than 50 m deep), which can be considered representative of the groundwater carbon pool's storage. This storage amounts to 4.90 Tg, a substantial figure that cannot be overlooked when compared to the surface soil organic carbon pool, accounting for 20.3%.

Accordingly, it is recommended that the groundwater carbon pool be regarded as an ancillary carbon pool to the surface soils, warranting concurrent evaluation and considerable focus. This approach will enhance the precision of terrestrial carbon balance studies and provide a robust scientific foundation for more effectively meeting the dual carbon goals.

CRedit authorship contribution statement

Hong-yun Ma conceived of the presented idea and performed the computations. Hong-na Ma assisted in plotting the maps. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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