Study on groundwater recharge based on chloride mass balance and hydrochemistry in the irrigated agricultural area, North China Plain

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Abstract
In the North China Plain, water shortage seriously restricts economic development, and agricultural irrigation depends heavily on groundwater extraction. Irrigation water and precipitation may directly recharge groundwater in the irrigated agricultural region. Therefore, calculating the recharge of precipitation and irrigation to groundwater is essential for the sustainable utilization of water resources. Furthermore, determining the transformation relationship of precipitation-soil water-groundwater is helpful to understand the hydrological cycle process better. The average groundwater recharge calculated by the chloride mass balance method is between 66 and 144 mm/year, accounting for only 7–17% of the total precipitation and irrigation water. The hydrogen (2H) and oxygen (18O) isotopes reveal that precipitation only affects soil water in topsoil, and soil water in deep soil is recharged upward by groundwater. The hydrochemical composition of soil water shows high concentrations of salt in unsaturated zones. Infiltration water dissolves salt through the unsaturated zone and carries them into the shallow groundwater, causing the deterioration of shallow groundwater quality. These results contribute to the effective management of groundwater resources and the control of agricultural pollution in groundwater.

Keywords North China Plain · Unsaturated zone · Hydrochemistry · Stable isotopes · Chloride mass balance

Introduction
The North China Plain is one of the most densely populated economic belts and the most developed industrial and agricultural production area. However, water resources are scarce, and the per capita water is only 335 m³/year, far below the baseline of global water pressure (1700 m³/year) (Zhang et al. 2020). Therefore, industrial, agricultural and urban water demand largely depends on groundwater exploitation. In recent years, with the development of urbanization and improved living standards, groundwater extraction has increased sharply and this has caused problems such as declining groundwater levels and ground subsidence. Therefore, it is essential to study the groundwater recharge process in the North China Plain, which is beneficial to quantify the allowable groundwater exploitation and sustainably utilize water resources.

Previous studies held a view that the recharge sources of groundwater systems in the North China Plain are mainly vertical infiltration of precipitation and irrigation water, and lateral runoff from the Taihang Mountains in the west (Cao et al. 2013; Wang et al. 2008; Kendy et al. 2004; Foster et al. 2004; Yang et al. 2002; Chen et al. 2003a). Using water balance, chloride mass balance, geochemistry, and isotopic tracers, several researchers calculated the average annual recharge of groundwater by precipitation and irrigation water to be 3.8–383 mm/year (Chen et al. 2003b; Kendy et al. 2004; Wang et al. 2008; Min et al. 2018). However, studies of vertical infiltration ignored the effect of salts leached by infiltrating water in the unsaturated zone on groundwater quality. The long-term precipitation–evaporation process causes the accumulation of salts in the unsaturated zone. When precipitation and irrigation penetrate through the unsaturated zone, infiltration water leaches salts...
and carries them into the groundwater and thus leading to the deterioration of groundwater quality. Therefore, calculating groundwater recharge by precipitation and irrigation and analyzing salt transport in the unsaturated zone can help to control the pollution of groundwater.

The methods of evaluating groundwater recharge include the groundwater level fluctuation method (Healy and Cook et al. 2002), the water balance method (Chen et al. 2003b), the soil water flux method (Kendy et al. 2003; Kendy et al. 2004), and the numerical simulation method (Min et al. 2015). Most of these methods require many or long sequences of hydrogeological parameters (precipitation, evaporation, runoff, and groundwater level), which are highly variable and difficult to obtain. The tracer method generally only requires a short sequence of data (Yuan et al. 2012; Wang et al. 2006). When calculating the recharge of groundwater, tracer (Cl) is mainly input by atmospheric precipitation and dry deposition in the natural state. In contrast, the input of the irrigation water should be considered under irrigation conditions. The chloride mass balance (CMB) method can estimate the groundwater recharge rate in arid and semi-arid areas. Therefore, the CMB method is used to estimate the recharge of groundwater by irrigation water and precipitation. With strong mobility along the flow path, chloride can be used to trace and analyze the solute input by infiltrating water into groundwater.

The unique isotopic composition of different water bodies is widely used to determine the various components in groundwater systems. Generally, water maintains its characteristics of stable isotopes without being diluted and mixed with other water sources. The stable isotopic composition can identify the recharge area of groundwater and water circulation in groundwater systems, which have been successfully used in arid and semi-arid regions (Payne et al. 1978; Weyhenmeyer et al. 2002; Currell et al. 2015). Since the 1980s, many sampling campaigns have been conducted in the North China Plain to study the chemistry and isotopes of the groundwater system (Zhang et al. 1987; Chen et al. 2003a; Rohden et al. 2010; Yuan et al. 2012; Zhai et al. 2013; Wang et al. 2017; Qin et al. 2017). The research mainly collected groundwater, rivers, soil, and precipitation in a short period (Yuan et al. 2012; Qin et al. 2017).

The current research has several limitations. The important reference line, the local meteoric water line (LMWL), generally comes from the line fitting of δ²H and δ¹⁸O in local precipitation. The conversion of precipitation to different water bodies can be analyzed according to the relative positions of different water bodies and LMWL. The average values of δ²H and δ¹⁸O in precipitation can be used to calculate the mixing ratio of different water end members in the groundwater system. Therefore, the study has two problems. One is that the precipitation collection campaigns are intermittent, and the accuracy of LMWL is limited by the number of samples and sampling time. The other is that the arithmetic means in the end-member mixing calculation are likely to increase the uncertainty because of the prominent isotopic dispersive characteristics of precipitation (Zhai et al. 2013). Previous studies have shown that the δ²H and δ¹⁸O of deep groundwater are far more depleted than that of local precipitation. It is suggested that the groundwater with a depleted signature is recharged by precipitation in the late Pleistocene (Chen et al. 2003a). Jasechko (2016) interpolated the global δ¹⁸O value in the late Pleistocene with the difference of late-Pleistocene minus late-Holocene precipitation δ¹⁸O less than − 6‰ in the global and − 1 to − 2‰ in North China Plain. However, the δ¹⁸O value of groundwater collected in the North China Plain (Hengshui) is − 3.4‰ lower than Holocene precipitation, with the range exceeding precipitation in the late Pleistocene. The groundwater recharged by precipitation in the late Pleistocene is fossil water with no renewal capacity. Contradictorily, the latest study found that the groundwater level declined because of groundwater exploitation during the irrigation period and steadily rose during the non-irrigation period (Long et al. 2020). It shows that groundwater is rapidly recharged by modern water. These two conclusions about groundwater with a depleted signature are contradictory. Thus, the transformation process and the sources of groundwater with depleted signatures need further research.

Based on the sediment samples in the unsaturated zone, water chemistry and stable isotopes are used to (1) estimate the groundwater recharge from precipitation and irrigation calculated by the CMB, (2) analyze the transformation process of precipitation-soil water-groundwater, and (3) understand the transport of water and solute in the unsaturated zone. This study contributes to the sustainable utilization of groundwater and the control of groundwater pollution in the North China Plain.

Materials and methods

Study area

The North China Plain (32° ~ 40° N, 114° ~ 121° E) is a semi-arid and semi-humid area dominated by monsoons. The annual average precipitation of Shijiazhuang Station from 1985 to 2003 was 554 mm (IAEA: https://www.iaea.org), of which summer precipitation (June–August) accounted for approximately 63% of the total annual precipitation. The annual average temperature is 14 °C, and the potential evaporation within the year is 1100–2000 mm.

The land-use types of the North China Plain are mainly farmland and woodland. The woodland includes coniferous forests, broad-leaved forests, and shrubland. The farmland is primarily wheat, corn, vegetables, and cotton (Min et al.
Given that the distribution of precipitation during the year is inconsistent with the water demand period of crops, irrigation is used to meet the water demand for crop growth. Agricultural irrigation water mainly comes from the extraction of groundwater. The average annual irrigation water for winter wheat and summer maize is 317 mm (Hu et al. 2016).

The North China Plain is an alluvial plain formed by sediments carried by rivers, such as the Yellow River, the Haihe River, and the Luan River. The distribution of the soil texture of the plain is related to the source of the sediment. Loam, loamy sand, and clay account for 90% of the plain area. The North China Plain is divided into piedmont plains (I), central plains (II), and coastal plains (III) from west to east (Fig. 1). The groundwater level of the piedmont plain is generally between 10 and 40 m, and the unsaturated zone is mainly silt and fine sand. The groundwater depth of the central plain is 1–20 m, and the unsaturated zone is mainly divided into clay and silt. The groundwater depth in the coastal plain is generally between 1 and 4 m, and the unsaturated zone is mostly clay.

With the long-term exploitation of groundwater, the groundwater level in the North China Plain has generally declined and a large depression cone of groundwater has formed. According to the National Groundwater Pollution Prevention Plan (2011–2020), released by the Ministry of Ecology and Environment of the People’s Republic of China, the area of the depression cone of deep confined groundwater in the North China Plain was up to 70,000 km² by 2011. Therefore, it is essential to estimate groundwater recharge by precipitation and irrigation to help assess the allowable groundwater extraction.

**Sampling and laboratory analyses**

Considering the infiltration of precipitation and irrigation, four soil profiles were collected in a typical irrigation area in May 2018 to consider the influence of irrigation water on infiltration (Fig. 1). Each time after sampling soil, the cores were filled tightly. Bulk soil samples of approximately 250 g were collected at intervals of 10 cm in topsoil (<20 cm) and 20 cm in deep soil (>20 cm) for stable isotope analysis. Samples were immediately sealed in airtight polyethylene bottles to prevent evaporation or atmospheric moisture pollution in the field. 21, 21, 21 and 26 soil samples were collected in profiles A, B, C, and D, respectively, and one groundwater sample was also performed in the vicinity of each profile at the same time.

Soil moisture content is analyzed with the oven drying method with an analytical precision of better than 1%. To measure Cl⁻ concentration in soil water, the soil sample was
dried at 110 °C for 12 h, and then 50 g of the dried soil was mixed with 100 ml of deionized water. The mixture was allowed to equilibrate for 48 h and periodically stirred (Scanlon et al. 2009). After equilibration, the leachate was filtered with medium-speed quantitative filter paper for anions measurement. Solutes and groundwater samples were then analyzed by ion chromatography. Then the anions (Cl\(^-\)) concentrations in soil water were converted according to soil moisture content.

Water for stable isotope analysis was extracted from the bulk soil samples using azeotropic distillation at 105 °C. For stable isotope composition analysis of the extracted water samples, the water was directly introduced into a Flash EA sample injection system attached via a micro pump to a MAT 253 mass spectrometer. All measurements were performed at the State Key Laboratory of Hydrology Water Resources and Hydraulic Engineering, Hohai University, China. The results are reported relative to V-SMOW, with uncertainties of ± 1‰ in δ\(^2\)H and ± 0.20‰ in δ\(^18\)O.

**Data analysis**

Chloride hardly participates in geochemical processes in the hydrological cycle. It is a stable environmental tracer and has a strong ability to migrate with water. Thus, it is used to estimate the average groundwater recharge. In semi-arid zones, the sources of chloride in soil water in the natural state include mainly wet atmospheric deposition (precipitation) and dry atmospheric deposition. In irrigated agricultural areas, the sources of chloride also include irrigation water. Chloride accumulation in the unsaturated zone is mainly due to the evaporative concentration of chloride in precipitation and irrigation water. The source of chloride in groundwater is related to the recharge source and process, which probably come from vertical downward infiltration and lateral runoff.

Groundwater recharge rates were calculated using the CMB method (Eq. (1)). The assumptions of the CMB method (Allison and Hughes 1978; Min et al. 2018) are as follows: (1) The sources of chloride are precipitation and irrigation water in an agricultural area; (2) lateral flow and surface runoff are negligible, and infiltration is the one-dimensional downward vertical water flow; and (3) chloride transport reaches a steady state.

Based on the above assumptions, the chloride input from precipitation (P, mm/year) and irrigation (I, mm/year) balance the chloride output in the recharge (R, mm/year) as follows:

\[
P \times Cl_p + I \times Cl_I = R \times Cl_s, \tag{1}
\]

where Cl\(_p\) (mg/L) and Cl\(_I\) (mg/L) are the average chloride concentration in the precipitation and irrigation water, respectively, and Cl\(_s\) (mg/L) is the average chloride concentration of the soil water below the root zone. The average precipitation values at Shijiazhuang, Hengshui, and Cangzhou are 534, 497 and 542 mm, respectively. The soil texture of the four profiles (A, B, C, D) is sand, clay, sandy/ clay, and sandy, respectively. The bulk density of sand and clay is 1.5 and 1.3 g/cm\(^3\), respectively.

Records of solute concentrations in precipitation are sparse for much of China. The chloride concentration of precipitation in Shijiazhuang varies from 1.8 to 2.9 mg/L according to the acid precipitation monitoring data (Hong et al. 2014). The monthly weighted mean chloride concentration of precipitation in Cangzhou is from the precipitation sample from April to November 2009 (Wang et al. 2014). The summer oceanic monsoon mainly influences precipitation in the study area, and the concentration is strongly controlled by the distance to its oceanic source. Hengshui is midway between the monsoon paths of Cangzhou and Shijiazhuang. Therefore, the chloride concentration of precipitation in Hengshui can be replaced by the average value in Shijiazhuang and Cangzhou.

Winter wheat and summer corn was planted by rotation in the North China Plain. Irrigation water was the sum of irrigation of winter wheat (320 mm/year) and summer corn (50 mm/year) (Min et al. 2018). The agricultural irrigation water consumption in Shijiazhuang (A) and Hengshui (B, C) is derived from the deep groundwater extracted. The chloride concentration of irrigation water can be represented by that of nearby groundwater. Furthermore, given the over-exploitation of groundwater, extracted deep groundwater in Cangzhou (D) is only used for drinking water, and agricultural water is mainly from reservoirs. The concentration of samples in the Huangbizhuang reservoir is used in the calculation collected in 2012. The depth of the root-affected area is mainly controlled by root depth and plant evapotranspiration. The vegetation coverage in sites A, B, C, and D was winter wheat, and the root influence depth was generally 1–1.5 m (Min et al. 2018).

**Results**

**Groundwater recharge estimated by CMB**

The calculation of CMB shows that the average groundwater recharge at sites A, B, and C are 66, 95 and 144 mm/year (Table 1), accounting for 7, 11 and 17% of precipitation and irrigation water, respectively. Chloride concentrations in groundwater near profiles A, B, and C are 20.7, 84.1 and 83.3 mg/L, respectively, which are much lower than the chloride concentrations in soil water (Fig. 5), thus the calculation results are credible. The average groundwater recharge at site D is 307 mm/year, but the chloride concentration of
groundwater (115.9 mg/L) near site D is much higher than that of soil water (38.5 mg/L). Since profile D is close to the coastal area and the groundwater level is high, the soil water may be affected by chloride in seawater. The premise of CMB is broken that the sources of chloride are only precipitation and irrigation, and hence the calculation in profile D is not credible.

The vegetation conditions in sites A, B, and C are the same, but there are differences in the average groundwater recharge, which may be related to the groundwater level depth and soil texture. The groundwater recharge in profile A is lower than that in profiles B and C, which may be related to the greater depth of groundwater level near profile A. Comparing profiles B and C in Hengshui, the soil texture in profile B is homogeneous clay, while the upper layer is fine sand and the lower layer is homogeneous clay in profile C. The presence of the sand layer is favorable for infiltration, and therefore the groundwater recharge in profile C is higher.

### Isotopic characteristics

#### Hydrogen and oxygen isotopes in precipitation

Stable isotope data of precipitation at the Shijiazhuang station were downloaded from GNIP (IAEA: [https://www.iaea.org]). Figure 2a shows that the $\delta^2$H and $\delta^{18}$O values of precipitation range from $-16$ to $-0.3\%e$ and $-111.3$ to $0.7\%e$, and the average values are $-7.6$ and $-51.9\%e$.

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**Table 1** Site descriptions, chloride concentration in precipitation and recharge rate in four sites

| Setting borehole | Location  | Groundwater depth (m) | Land use | Number of samples | Maximum depth (m) | Bulk density (g/m$^3$) |
|------------------|-----------|-----------------------|----------|-------------------|-------------------|-----------------------|
| A                | Shijiazhuang | 30~50                 | Wheat    | 21                | 4                 | 1.5                   |
| B                | Hengshui   | 4~8                   | Wheat    | 21                | 4                 | 1.3                   |
| C                | Hengshui   | 4~8                   | Wheat    | 21                | 4                 | 1.5*/1.3*             |
| D                | Cangzhou   | 2~4                   | Wheat    | 26                | 5                 | 1.5                   |

| Setting borehole | $P_a$ (mm) | $I_a$ (mm) | $[\text{Cl}]_P$ (mg/L) | $[\text{Cl}]_I$ (mg/L) | Depth (m) | $R$ (mm/year) |
|------------------|------------|------------|------------------------|------------------------|-----------|---------------|
| A                | 534        | 370        | 2.5                    | 20.7                   | 1.6       | 66            |
| B                | 497        | 370        | 1.9                    | 84.1                   | 1.4       | 95            |
| C                | 497        | 370        | 1.9                    | 84.1                   | 1.6       | 144           |
| D                | 542        | 370        | 1.4                    | 27.3                   | 1.6       | 307           |

$P_a$ represents annual mean precipitation from China Meteorological Data Service Center (http://data.cma.cn/en)  
$I_a$ represents the average irrigation water for winter wheat and summer corn rotation (Min, 2018)  
Depth represents the depth of root  
* indicates that the bulk density of soil profile B is 1.5 g/m$^3$ for 0–120 cm and 1.3 g/m$^3$ for 120–400 cm, respectively.
respectively. The weighted average of \( ^2\text{H} \) and \( ^18\text{O} \) is \(-7.3\) and \(-51.9\%\text{e}, \) respectively. Local Meteoric Water Line (LMWL: \( \delta^2\text{H} = 6.07 + 0.9 \delta^{18}\text{O} - 5.76, \ R^2 = 0.86 \)) is obtained by fitting precipitation points. The slope and intercept of LMWL are affected by the local climate, and thus are slightly different from Global Meteoric Water Line (GMWL: \( \delta^2\text{H} = 8 + 10 \delta^{18}\text{O} + 10 \)) (Craig 1961). Compared with GMWL, the lower slope of LMWL may be related to the secondary evaporation of precipitation. The study area is located in a semi-arid area with strong evaporation. After the water vapor condenses, the secondary evaporation of precipitation may occur when it descends through dry air. Secondary evaporation significantly reduces the value of excess deuterium (d-excess). d-excess is defined as follows: \( \text{d-excess} = \delta^2\text{H} - 8 \delta^{18}\text{O} \). The average value of d-excess of precipitation is \(6\%\text{e}, \) which is less than the average value of GMWL (10\%\text{e}).

In the region, the characteristics of \( ^2\text{H} \) and \( ^18\text{O} \) precipitation are mainly affected by the effects of latitude, elevation, temperature, and precipitation. Temperature controls the fractionation processes of hydrogen and oxygen isotopes in evaporation and condensation, generally resulting in the enrichment of \( ^2\text{H} \) and \( ^18\text{O} \) in summer and depletion of \( ^2\text{H} \) and \( ^18\text{O} \) in winter (Clark and Fritz, 1997). The \( ^2\text{H} \) and \( ^18\text{O} \) in precipitation change significantly, with maximum values reaching \(-3.7\) and \(-27.5\%\text{e}, \) and minimum values being \(-11.4\) and \(-78.8\%\text{e}, \) respectively (Fig. 2b), showing obvious dispersion during the year. From October to April, the changes of \( ^2\text{H} \) and \( ^18\text{O} \) in precipitation are positively correlated with temperature (Fig. 2c). As the temperature decreases, \( ^2\text{H} \) and \( ^18\text{O} \) in precipitation deplete, which is controlled by the effect of the temperature. From May to September, the changes of \( ^2\text{H} \) and \( ^18\text{O} \) are affected by precipitation amount, which causes the values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) to decrease with the increase in precipitation amount. Therefore, characteristics of \( ^2\text{H} \) and \( ^18\text{O} \) in precipitation are simultaneously affected by temperature and precipitation, and the highest values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) do not appear in summer and winter, but in April.

**Hydrogen and oxygen isotopes in soil water and groundwater**

The vertical distribution of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) of soil water in sites A, B, C, and D is shown in Fig. 3. As the depth increases, \( ^2\text{H} \) and \( ^18\text{O} \) are gradually depleted with slight fluctuations. The fluctuation may be related to the evaporation and condensation of water vapor in the soil. The \( ^2\text{H} \) and \( ^18\text{O} \) in the topsoil (0–20 cm) are significantly enriched, and the values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) are \(-8.8 \text{ to } -60.2\%\text{e}, \(-1.2 \text{ to } -7.3\%\text{e} \) (Fig. 3), indicating that the topsoil water is strongly affected by evaporation. Below 20 cm, the average values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) at sites A, B, C, and D are \(-69.9\) and \(-8.8\%\text{e}, \(-65.2\) and \(-8.6\%\text{e}, \(-69.2\) and \(-9.1\%\text{e}, \) and \(-73.4\) and \(-9.9\%\text{e}, \) respectively. The effect of evaporation is reduced. The soil texture at sites A and D is sandy. The isotopic characteristics of the deep soil water and nearby groundwater indicate that the groundwater replenishes the deep soil from bottom to top through the capillary in the sand. The soil texture at sites B and C is clay. The \( ^2\text{H} \) and \( ^18\text{O} \) of the deep soil water are significantly more enriched than that of the groundwater, indicating that soil seepage water accounts for little proportion of groundwater with a depleted signature.

In Fig. 4, the soil water evaporation line (SWL: \( \delta^2\text{H} = 6.55 + 0.9 \delta^{18}\text{O} - 9.67, \ R^2 = 0.94 \)) is fitted by the points of soil water. Compared with GMWL, the lower slope of SWL and the points of soil water below GMWL indicate that soil water is significantly affected by evaporation. The intersection values of SWL and GMWL are \(-98.8\) and \(-13.6\%\text{e}, \) which represent the initial values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) in soil water without evaporation. The initial values of \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) are lower than the average weighted values of precipitation by \(-6.3 \text{ and } -46.9\%\text{e}, \) indicating that precipitation is not the source of the initial water of deep soil water before evaporation. The \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \) of groundwater and soil water fall within the same range, and \( ^2\text{H} \) and \( ^18\text{O} \) groundwater is relatively more depleted. The initial value is close to the groundwater point, indicating that groundwater recharges the deep soil water. The direction of water transmission is from the groundwater to the unsaturated zone.

**Hydrochemistry in the soil profile**

When precipitation infiltrates through the unsaturated zone to recharge groundwater, salt in the surface and the unsaturated zone are leached into the groundwater. The water chemistry of the infiltration water should have continuity in the flow path. Therefore, the movement of soluble ions can trace the movement process of the infiltration water.

Figure 5 shows that the average soil moisture content of sites A, B, C, and D is 9.8, 30.0, 26.7 and 26.2\%\text{e, respectively. The moisture content varies greatly with depth and has no apparent correlation with the vertical distribution of chloride concentration. The low chloride concentration in the topsoil is related to the dilution of soil water by precipitation. As the depth increases, the chloride concentration of the soil water increases significantly. At sites A, B, C and D, the average chloride concentration of soil water is 106.3, 232.1, 512.7 and 38.5 mg/L, respectively, and the chloride concentration of nearby groundwater is 20.7, 82.9, 512.7 and 38.5 mg/L, respectively. Except for site D, the chloride concentration of soil water is much higher than that of groundwater, and the hydrochemical characteristics of soil water and groundwater are not continuous, indicating that precipitation cannot infiltrate to recharge groundwater through the unsaturated zone. The
A high concentration of chloride has not yet penetrated the groundwater and caused groundwater pollution. The chloride concentration of groundwater should be equivalent to the concentration of deep soil water.

The distance between profiles B and C is 3.7 km, and the vertical distributions of $^2$H and $^{18}$O in both profiles are similar to exponential distributions. However, the vertical distributions of chloride in profiles B and C show a significant difference, which is related to soil texture. Profile B is homogeneous clay and the peak of chloride occurs at 2.2 m, which indicates the maximum infiltration depth of historical precipitation events. Soil texture of profile C changes from fine sand to clay at 1.2 m, and the permeability coefficient decreases. In this layer, infiltration water is intercepted and subsequent evaporation leads to a concentrated accumulation of chloride so that the chloride concentration of the soil water increases significantly at a depth of 1.0 − 1.2 m in profile C. In connection with this, the $^2$H and $^{18}$O are slightly enriched at depth of 1 m.
Discussion

Uncertainty of CMB calculation

The sources of chloride in the CMB calculation do not take into account the input of dry atmospheric deposition, which may overestimate groundwater recharge. In addition, the chloride concentration data of precipitation and irrigation are only available for a few years or months, long-term monitoring data are lacking. Therefore, the uncertainty of chloride concentration of precipitation and irrigation causes the uncertainty of the calculated groundwater recharge. The chloride concentrations in precipitation do not vary significantly over a long time. Irrigation water comes from extracted deep groundwater with stable hydrochemical characteristics and little changes in chloride concentrations over time. Considering the influence of the above factors, the uncertainty of 10% is set for chloride concentrations in precipitation and irrigation water respectively in the calculation, and eventually, uncertainties of groundwater recharge are < 1 and < 10%, respectively. Therefore, the errors in groundwater recharge are acceptable despite the uncertainties of the chloride concentrations in precipitation and irrigation water.

Fig. 5 Chloride concentration and soil water content versus depth (Shijiazhuang: (a), Hengshui: (b, c), Cangzhou (d)). A (a-1, a-2), B (b-1, b-2), C (c-1, c-2), D (d-1, d-2)
Transformation process of precipitation-soil water-groundwater

Affected by temperature and precipitation, the $^2$H and $^{18}$O of the precipitation in the study area show evident dispersion during the year. Research in Beijing has found that the dispersion of $^2$H and $^{18}$O occurs annually and interannually (Zhai et al. 2013). This dispersive characteristic has also been observed in Hong Kong and Guangzhou (Zhang et al. 2009; Xie et al. 2011). Although the reason and mechanism of this phenomenon are not apparent, values of $^2$H and $^{18}$O in single or seasonal precipitation cannot be used to analyze the evolution process and calculate groundwater recharge and end-member mixing. The weighted average of precipitation over a long time series should be used to eliminate the dispersive characteristics and the influence of precipitation. Based on the monitoring data of $^2$H and $^{18}$O in precipitation from 1985 to 2003, the average weighted precipitation calculated is $-7.3$ and $-51.9\%$. 

In arid or semi-arid regions, the $^2$H and $^{18}$O of topsoil water are significantly enriched by evapotranspiration. With the occurrence of subsequent precipitation events, the enriched $^2$H and $^{18}$O move downward with the infiltration. A recharge rate up to 200 mm/year generally causes periodic changes of $^2$H and $^{18}$O in the vertical. Preferential flow can make the soil water with the enriched signature flow down quickly, forming other peaks of $^2$H and $^{18}$O in the soil profile. The $^2$H and $^{18}$O of the four soil profiles in this study only have a peak in the topsoil respectively. The vertical distributions of $^2$H and $^{18}$O in four profiles are similar to exponential distributions, and this indicates that the seepage mode in the soil profile is mainly piston flow instead of preferential flow, which satisfies the assumption of piston flow in the CMB method. No periodic change is observed in the vertical distributions of $^2$H and $^{18}$O in four profiles, indicating that the lower recharge causes the peak and trough to be close. The subsequent diffusion smoothens the difference between the peak and trough. Thus, the periodicity disappeared. Site D is located in Cangzhou in the coastal plain. The chloride background value in the aquifer is up to 115.9 mg/L, which may be related to the seawater intrusion in the geological history period. Therefore, it breaks the assumption that the source of chloride is only precipitation and irrigation, and the CMB method is not applicable in this area.

Stable isotope analysis reveals that the initial values of $^2$H and $^{18}$O in deep soil water before evaporation fall within the range of groundwater, indicating the recharge from groundwater to deep soil water. $^2$H and $^{18}$O of groundwater are significantly more depleted than that of local precipitation, and it implies that precipitation accounts for a small proportion of groundwater recharge. In the groundwater system, there is no process to make $^2$H and $^{18}$O in groundwater evolve toward depletion. The groundwater with a depleted signature was recharged by precipitation in the cold late Pleistocene (Chen et al. 2003a). Jasechko (2016) interpolated the global $\delta^{18}$O value in the late Pleistocene with the difference of late-Pleistocene minus late-Holocene precipitation $\delta^{18}$O less than $-6\%$ globally and $-1$ to $-2\%$ in the North China Plain. However, the $\delta^{18}$O value of groundwater collected in the North China Plain (Hengshui) is $-3.4\%$ lower than Holocene precipitation with a range exceeding precipitation in the late Pleistocene. The groundwater recharged by precipitation in the late Pleistocene is fossil water with no renewal capacity. Contradictorily, the latest study found that the groundwater level declined because of groundwater exploitation during the irrigation period and steadily rose during the non-irrigation period (Long et al. 2020). Therefore, modern water can quickly recharge groundwater. The values of $\delta^2$H and $\delta^{18}$O in precipitation significantly reduce affected by the altitude; thus, groundwater may be recharged by leakage of water from high-altitude areas.

Mechanisms of increasing recharge related to irrigation

From 2000 to 2018, the average agricultural area in the North China Plain is $9.27 \times 10^3$ ha (National Bureau of Statistics: http://data.stats.gov.cn). The crops are mainly wheat, corn, cotton, and vegetables, and wheat and corn account for more than 60%. Therefore, the literature on the groundwater recharge for wheat and corn in irrigated areas is compiled. Groundwater recharge in literature is shown in Table 2. In the irrigated areas in the piedmont plain and the central plain, the groundwater recharge calculated by several methods ranges from 38 to 300 mm/year, which is similar to the calculations of profiles A, B and C in this study (78–158 mm/year). In contrast, the calculations of groundwater recharge in the coastal plain range from 50 to 1090 mm/year, which are significantly higher than those in the piedmont plain and the central plain. This is related to the higher groundwater level in the coastal plain that facilitates groundwater recharge. In the piedmont plain, the groundwater recharge in the non-irrigated area is only 3.8 mm/year, which is significantly lower than that in the irrigated area. It may be related to the increase in water input and the decrease of evapotranspiration and runoff in irrigated areas.

In the irrigated and non-irrigated area, the soil water balance equation in the unsaturated zone is as follows:

$$R = T - ET - R_0,$$  \hspace{1cm} (2)

where $R$ is the average groundwater recharge; $T$ is the total amount of input water, including precipitation and irrigation; $ET$ is evapotranspiration; $R_0$ is surface runoff. Compared with non-irrigated areas, the higher groundwater recharge
in irrigated areas is related to increased water input and decreased evapotranspiration. The water input of the irrigation area includes precipitation and irrigation, and the irrigation is the short-duration and high-intensity pulse input. The deep leakage below the root zone in the irrigation area is significantly higher than that in the non-irrigated area, thus increasing groundwater recharge in the irrigated area. Given the centralized groundwater extraction to meet irrigation needs, the groundwater level drops and surface evapotranspiration reduces (Condon and Maxwell 2019).

The higher groundwater recharge in the irrigated area is also related to the root depth of the vegetation. The vegetation in the non-irrigated area is mainly woods, which are perennial plants with a developed root system. After a heavy precipitation event, deep seepage occurs, and soil moisture is redistributed. The root of perennial vegetation can absorb and reuse the deep leakage water, which is consistent with the monitoring results of the matric potential in the unsaturated zone that the matrix potential changes little with a depth greater than 5 m (Scanlon et al. 2007). The crops in the irrigation area are mostly annual plants, the root depth of which is only approximately 1.5 m, such as wheat, corn, and cotton (Min et al. 2018). After heavy precipitation or irrigation, deep seepage occurs, the root system only absorbs seepage water in the topsoil, and the deep seepage water is easily recharged to the groundwater. Therefore, the depth of the root system causes the difference in groundwater recharge between irrigated and non-irrigated areas. The type of irrigation is mainly flood irrigation in the North China Plain, which is a short-duration and high-intensity water input. The infiltration mechanism is similar to that of a heavy precipitation event. Deep seepage water is more likely to reach and recharge shallow groundwater.

### Movement of water and salt in the unsaturated zone

The movement of chloride can represent the transport process of salts, and salts leached by infiltration water into groundwater can affect the quality of groundwater. In the semi-arid zone, high concentrations of chloride and salts accumulate in the unsaturated zone due to long-term evaporation (Fig. 5). When precipitation and irrigation penetrate through the unsaturated zone, the salts and chloride are leached and carried into the groundwater. During the initial precipitation and irrigation, the precipitation is mainly used to make up for the water deficit in the unsaturated zone, and after the soil water content reaches the field moisture capacity, the water infiltrates into the deep soil as gravity water. After precipitation ends, the infiltration of gravity water soon stops without continuous water input. When the depth of infiltration of gravity water does not reach that of the groundwater level, the salts and chloride leached out are transported downward and preserved in the deep soil with a low concentration of chloride and salts in the groundwater (Fig. 6a). When the depth of infiltration of gravity water can reach that of the groundwater level, infiltration water leaches salts and carries them into the groundwater and thus leading to the deterioration of groundwater quality. In this situation, the chloride and salts in the groundwater significantly increase (Fig. 6b). For example, in the part of Hengshui with high permeability, precipitation and irrigation water can infiltrate fast, resulting in the TDS of shallow groundwater being monitored to be as high as 9 g/L (Shi et al. 2010). The recharge of groundwater by infiltration is affected by groundwater level and the intensity of precipitation and irrigation. Controlling the intensity of single irrigation is recommended to minimize the impact of infiltration with salt and chloride on groundwater quality.

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**Table 2** Groundwater recharge calculated by different methods in North China Plain

| Input type | Location          | R (mm/year) | Method                                      | Reference         |
|------------|-------------------|-------------|---------------------------------------------|-------------------|
| With irrigation | Piedmont plain | 169–180 | Hydrus-1D | Lu 2011                                    |
|            |                   | 36–209      | One-dimensional soil–water-balance model   | Kendy et al. 2003 |
|            |                   | 38          | Water balance and $^3$H tracers            | Chen et al. 2003b |
|            |                   | 300         | $^3$H–$^3$He tracers; water balance        | Rohden et al. 2010|
|            |                   | 78          | CMB                                         | This study        |
| Central plain    | 140–155 | Hydrus-1D | Lu 2011                                    |
| Coastal plain    | 102–158 | CMB       | This study                                 |
| Coastal plain    | 102          | Hydrus-1D | Lu 2011                                    |
| Coastal plain    | 153–211      | Tritium and Bromide tracers                 | Wang et al. 2008  |
| Coastal plain    | 50–1090      | Soil–water balance                          | Kendy et al. 2004 |
| Coastal plain    | 233          | Transient matric flow model                  | Min et al. 2015  |
| Without irrigation | Piedmont plain | 3.8      | CMB                                         | Yuan et al. 2012  |
After precipitation and irrigation stop, soil evaporation turns to be dominant. At the beginning of evaporation, soil water content is close to saturation, and evaporation intensity is high. Deep soil water and groundwater transport water upward as liquid water through capillary water and film water. As evaporation continues and the water content decreases, deep soil water and groundwater transport water upward as water vapor. Chloride can only be transported in liquid water, while $^2$H and $^{18}$O can be transported in both water vapor and liquid water. Hence, the accumulation of Cl$^-$ is mainly related to the surface evapotranspiration, while the enrichment of $^{18}$O is related to not only the surface evapotranspiration, but also the transport of water vapor in the unsaturated zone, so there is no correlation between Cl$^-$ and $^{18}$O in the profiles of this study.

$^2$H and $^{18}$O in topsoil water are continuously enriched under the influence of evapotranspiration and peaks of $^2$H and $^{18}$O occur in the surface layer. However, the peak of Cl$^-$ can be transported to deeper soils with infiltration in wet years, so the peak of Cl$^-$ is usually deeper than that of $^2$H and $^{18}$O in the vertical profile. As shown in Fig. 3 and Fig. 5, the depth of the peak of Cl$^-$ occurs between 1 and 2.5 m, while the peaks of $^2$H and $^{18}$O all occur at 0.2 m. In addition, the vertical distributions of Cl$^-$, $^2$H and $^{18}$O are also related to the time scale and aridity, but due to the lack of relevant detailed data, further discussion is not carried out in this study, which will be continued in future work.

**Conclusion**

The $^2$H and $^{18}$O in deep soil water slightly vary vertically with no periodic variation. The infiltration mode is dominated by piston flow in the unsaturated zone, which meets the premise hypothesis of the chloride mass balance method. Based on the CMB method, the average groundwater recharge in irrigation areas of Hengshui and Shijiazhuang is 66–95 mm/year and 144 mm/year, respectively, accounting for 7–11% and 17% of precipitation and irrigation water, respectively. The background value of chloride in the stratum is as high as 115.9 mg/L in Cangzhou, which breaks the assumption that the source of chloride is only precipitation and irrigation. Therefore, the calculation results are unreliable, and the CMB method is unsuitable for coastal plains.

The analysis of $^2$H and $^{18}$O in precipitation, groundwater, and soil water reveals that the $^2$H and $^{18}$O in soil water in topsoil are enriched because of the strong influence of evaporation. The initial values of $\delta^2$H and $\delta^{18}$O are much lower than the average weighted values of precipitation, and it indicates that precipitation only affects soil water in the topsoil, and deep soil water is mainly recharged upward by groundwater.

The long-term precipitation–evaporation process causes the accumulation of salts in the unsaturated zone. When precipitation and irrigation penetrate through the unsaturated zone, infiltration water leaches salts and carries them into the groundwater and thus leading to the deterioration of groundwater quality. Compared with non-irrigated areas, the higher groundwater recharge in irrigated areas is related to increased water input and decreased evapotranspiration. In addition, irrigation is the short-duration and high-intensity pulse water input, thus salt in the unsaturated zone is easier to pollute groundwater in the irrigation area than in the non-irrigated area. These results contribute to the effective management of groundwater resources and the control of agricultural pollution in groundwater.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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