Using multiple tracers to quantify groundwater discharge to Yellow river in Weining plain

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Abstract. It is important to quantify the hydraulic relationship between surface water and groundwater for developing water resources sustainably. In this study, thirty-six samples were taken and the interaction between river water and groundwater was analyzed on the basis of hydrogeochemical characteristics. Environment tracers such as EC and Cl were used to calculate groundwater inflows along river flow path by the mass balance method, then it provided a detailed longitudinal profile of groundwater discharge rates. The results show that groundwater discharged to Yellow River mainly in dry season and varied spatially along river length with larger rates in two areas. The groundwater inflows calculated by Cl- and EC mass balances differentiated with each other, which indicated potential uncertainties. Thus, it was necessary to use multiple tracers to quantify groundwater discharge in order to improve accuracy. The representation of the groundwater end-member for environment tracers, the completeness of water balance items and sample resolution were shown to be of vital importance for calculating groundwater inflows using environmental trace method.

1. Introduction
In arid and semi-arid areas, groundwater discharge as essential components of river baseflow is important not only in the hydrological cycle [1], but also from an ecological perspectives, especially for the river ecosystems dependent on groundwater [2]. It is basis work to determine groundwater discharge quantitively for the evaluation and sustainable development of water resources in a basin. In recent years, a number of studies have evaluated groundwater discharge rates to rivers by longitudinal river chemistry surveys and lots of environment tracers such as Cl, \(^{18}\)O, \(^{222}\)Rn and EC had been used to establish end-member model for theirs water cycle significances. The Weining plain is located in the western of Ningxia province in the Yellow river valley, in where, the industrial and agriculture production mainly depend on surface water. For a long period of irrigation, the interaction between groundwater and surface water is so complex to identify. In this study, geochemistry of groundwater and surface water were analyzed during dry season and Cl' and EC were used to calculate groundwater discharge inflows using mass balance method with regards of evaporation rates. The potential uncertainties were discussed as well as the factors affecting evaluation.

2. Study area and Methodology

2.1. Study area
Weining basin is a faulted basin developed in Cenozoic, to the north and south of which are Xiang mountain and North Weining mountain. Mean annual rainfall for the study area is 273.5 mm and
1888.4 mm for evapotranspiration. The study focus on a segment of Yellow river in Weining plain, with average width of 600 m, depth of 2 to 4 m and discharge of 1039.8 m$^3$/s. A tributary named Qingshui river is located in the Eastern of basin.

The Quaternary groundwater systems can be divided into 2 groups: upper phreatic aquifer and lower confined aquifer. The vertical extent of upper aquifer consisting of fine sand, coarse and thin silt clay is from 6 to 48 m, in which the buried depth of groundwater is less than 5 m. The vertical extent of lower confined aquifer is from 40 to 150 m, consisting of coarse and silt sand. Groundwater is mainly recharged by leaked water from channels, irrigation return flow, infiltrating meteoric water and laterally penetrating fracture water from rocks along mountain front. It is mainly discharged via vertical evapotranspiration, artificial abstract and inflows to Yellow river. Naturally, groundwater flows from two sides to the middle of the basin.

### 2.2. Sampling and analytical methods

Thirty-six samples including 24 groundwater samples plus 12 river water samples were taken along 69.7 Km length of Yellow river from Xiaheyan Hydrologic Station to Mingsha Village in 26 March, 2014 (Fig 1). River water were sampled at the depth more than 0.5 m to insure that groundwater and surface water had mixed fully. Water samples were filtered through 0.45 um membranes after pumping more than 10 minutes. Electrical conductivity was measured field when sampling and major elements were determined using ion chromatograph.

![Fig.1 Location map of study area and sampling sites](image)

### 2.3. Methodology

The end-member model is established on the basis of mass balance that takes account into groundwater discharge to river, evaporation and upstream flow. The change in flow with distance and tracer concentration change along Yellow river that receives groundwater discharge are given as below [3].

$$\frac{\partial Q}{\partial x} = l(C_i - C) + wEC$$

$$Q = Q_0 + lx - wEx$$

Where $Q$ is river discharge (m$^3$/d), $C$ is the concentration of a given tracer in river (mg/L), $x$ is the distance in river flow direction (m), $I$ is groundwater discharge rates (m$^3$/d), $C_i$ is the concentration of a given tracer in groundwater (mg/L), $w$ is width of a river (m), $E$ is the evaporation rate (m/d), $Q_0$ is river discharge at the beginning (m$^3$/d).

### 3. Results and discussion

#### 3.1. Hydrogeochemistry

The main ions in upper phreatic aquifer were Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$ and SO$_4^{2-}$ with the concentration of 76.4-148.1 mg/L, 36.1-77.28 mg/L, 340.9-568.2 mg/L, 112.7-288.4 mg/L respectively and water types
of $\text{HCO}_3\cdot \text{SO}_4$—Ca·Mg mainly, $\text{HCO}_3\cdot \text{SO}_4$—Mg·Ca and $\text{HCO}_3\cdot \text{SO}_4\cdot \text{Cl}$—Ca·Mg secondly (Fig 2). TDS was 596.5-1162.6 mg/L with a mean of 867.7 mg/L. Water types in lower confined aquifer were similar to that in upper aquifer and TDS was 338.6-928.0 mg/L with a mean of 725.9 mg/L. River water had complex water types of $\text{HCO}_3\cdot \text{SO}_4$—Ca·Mg, $\text{HCO}_3$—Ca·Mg and $\text{HCO}_3$—Ca·Na. TDS was 321.5-375.9 mg/L with a mean of 341.9 mg/L, which was lower than that in groundwater.

The electrical conductivity (EC) reflects the total contents of all dissolved ions, which can be an effective indicator of flow paths and duration in water cycle. As a conservative ion, chloride is almost impossible to involve with precipitation, ion exchange and biological processes, while its concentration is only affected by mixing and halite weathering [4]. Thus, EC and Cl$^-$ were used to trace terrestrial water cycle in a number of studies. The interaction between groundwater and surface water can be determined effectively by a detailed understanding of spatial distribution and variation of EC and Cl$^-$ in different types of water (Fig 3). The concentration of Cl$^-$ in phreatic groundwater, confined groundwater and surface water were 91.2-178.9 mg/L, 73.5-162.7 mg/L and 39.0-42.2 mg/L respectively, and EC were 1269.2-2469.6 us/cm, 741.7-1974.58 us/cm and 685.6-735.9 us/cm respectively. It was obvious that the concentration of EC and Cl$^-$ were lower in confined water than that in phreatic water, arose from more evaporation, while lowest in river water among three types of water. Along Yellow river, tracer concentration changed irregularly in groundwater, it was that samples were all located in discharge area and experienced different flow paths and water-rock interactions. Tracer concentration had an increasing trend downstream in river water, which identified that surface water had been recharged by groundwater with higher concentration of EC and Cl$^-$ from two sides continuously. Especially, groundwater discharged to the river more strongly in two areas suggested by a rapid increase of Cl$^-$ concentration in river water.

3.2. Groundwater inflows

It can be seen that groundwater discharged to Yellow river and had higher concentration of EC and Cl$^-$ than river water. In general, environmental tracer method will be more accurate when the tracer concentration in groundwater is more distinct from that in river water. Environment tracers such as EC and Cl$^-$ were used to calculate groundwater inflows along river flow path by the mass balance method in this study. A hypothesis was given that tracer concentration and groundwater discharge rates remained constantly during two sample sites and tracer concentration in groundwater averaged that in phreatic water and confined water nearby. The parameters were given as below: $Q_0$ is 316 m$^3$/s monitored in Xiaheyan Hydrological Station in 26 March, 2014, river evaporation rate is 5 mm/d, the average width of Yellow river is 600 m and the initial values of EC and Cl$^-$ concentration in river water are 39.0 mg/L and 687.6 uS/cm respectively.

![Fig.2 Piper diagram for groundwater and surface water](image)
The results inferred from EC and Cl\(^-\) mass balance show that groundwater discharge rates varied spatially along river length with greater rates in two areas (Fig 4). In the length of 14.6-19.9 Km, it had a rate more than 10 m\(^2\)/d, more than 15 m\(^2\)/d in the length of 56.2-61.8 Km, and 0-0.4 m\(^2\)/d in the length of 42.4 Km which showed a lower discharge rate here. Despite of continuous evaporation, river discharge mainly increased along flow path except in the areas where it received minor groundwater discharge.

The groundwater inflows calculated by Cl\(^-\) and EC mass balances differentiated with each other. For example, in the length of 14.6 Km, groundwater inflows derived from two methods were 37.6 m\(^2\)/d and 22.4 m\(^2\)/d respectively and in the length of 51.3 Km, 24.9 m\(^2\)/d and 1.1 m\(^2\)/d respectively. Using Cl\(^-\) mass balance, the evaluated river discharge at the end of length was 327.7 m\(^3\)/s and 0-37.6 m\(^2\)/d for groundwater discharge rates with cumulative flows of 14.1 m\(^3\)/s which account for 4.3 percent of river discharge, while the respective values were 322.9 m\(^3\)/s, 1.1-29.4 m\(^2\)/d, 9.3 m\(^3\)/s and 2.9 percent when using EC mass balance. It was obvious that there was an over estimation of groundwater inflow using Cl\(^-\) mass balance than EC mass balance.

3.3. Uncertainties
It is credible for the cumulative groundwater discharge inferred from this study in contrast with the inflow of 6.7m\(^3\)/s using base flow separation method in previous study. The wide spatial variation of groundwater discharge was controlled by the hydrogeological settings in the study area. The quaternary aquifer had a narrow distribution toward west and east. Groundwater flowed from two sides to the middle of plain and discharged to Yellow river. The aquifer thickness and the spatial scale were bigger to benefit for groundwater discharge where there groundwater inflow was higher. The environmental tracer method to quantify groundwater inflow from longitudinal groundwater and
surface water samples is attractive in remote areas where hydrological stations are limited. When correctly applied, it is able to provide information on the spatial distribution of groundwater discharge at a scale and accuracy that is impossible with most of other methods. It may mislead estimates when using a single tracer method indicated by the large differences of groundwater inflows derived from two methods. The method on the basis of mass balance assumes the knowledge of groundwater end-member chemistry [5]. However, the assumption is always invalid that groundwater sampled some distances from the river represents the groundwater discharged to river, which may lead potential uncertainties. For the difficulty of accurate determination of groundwater end-member chemistry, it is necessary to use multiple tracers to quantify groundwater discharge in order to improve accuracy. Secondly, the uncertainties of mass balance items involved with artificial activities can cause large uncertainties in groundwater inflows. For the lack of information of surface water abstraction for industry and domestic needs, these items were without considered in this study. Another factor limiting the method is sampling resolution. Despite of wide spatial variation of groundwater tracer concentration, there was an assumption that groundwater chemistry in one sampling point represented that in entire flow path between two sampling locations in brief. In theory, the more the water samples, the higher the accuracy of groundwater inflows evaluation. In this study, a small resolution of one sample per 6 Km was taken, thus reducing the accuracy of the method.

4. Conclusions
When correctly applied, environmental tracer method is able to provide information on the spatial distribution of groundwater discharge at a scale and accuracy that is impossible with most of other methods. The assumption that tracer concentration in groundwater sampled some distances from the river represented that in the groundwater discharged to river may lead potential uncertainties, thus it is necessary to use multiple tracers to quantify groundwater discharge in order to improve accuracy. The representation of the groundwater end-member, the completeness of water balance items and sample resolution are shown to be important for evaluating groundwater inflows using this method.

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