



# Identification of He sources and estimation of He ages in groundwater of the North China Plain



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## ABSTRACT

Dissolved helium concentrations and  $^3\text{He}/^4\text{He}$  ratios were measured for 18 groundwater samples collected from the Quaternary confined aquifers in the North China Plain (NCP). The dissolved helium concentrations ranged from  $1 \times 10^{-7}$  to  $1 \times 10^{-6}$   $\text{cm}^3\text{STP}\cdot\text{g}^{-1}$  in the 14 samples from the central plain, but was approximately two orders of magnitude higher, between  $6 \times 10^{-6}$  and  $9 \times 10^{-5}$   $\text{cm}^3\text{STP}\cdot\text{g}^{-1}$ , in 4 samples from the coastal plain. Based on these concentrations and the corresponding  $^3\text{He}/^4\text{He}$  ratios varying from 0.09 to 0.55  $R_a$  (where  $R_a$  is the  $^3\text{He}/^4\text{He}$  ratio of air), the dissolved helium in groundwater in the central plain was identified to be primarily a mixture of atmospheric helium with radiogenic helium and a representative radiogenic helium ratio was estimated to be 0.035  $R_a$ . Despite the high fraction of terrigenous  $^4\text{He}$  in the samples from the coastal plain, their  $^3\text{He}/^4\text{He}$  ratios were found to be significantly above this radiogenic value, ranging between 0.20 and 0.37  $R_a$ , indicating the presence of a mantle-derived He component in this area. About 2–4% mantle helium was estimated to be present in the groundwater of the coastal plain, which probably is associated with the regional Cangdong fault and tectonic activities. Based on the radiogenic He component,  $^4\text{He}$  ages of the groundwater in the central plain were calculated by assuming either pure in situ production or an external helium flux  $J_0$  of  $4.7 \times 10^{-8}$   $\text{cm}^3\text{STPcm}^{-2}\text{a}^{-1}$ . The estimated  $^4\text{He}$  ages fall between 9.5 and 51.4 ka and are comparable to the  $^{14}\text{C}$  ages, suggesting that the results of  $^4\text{He}$  dating are reasonable and can be an effective tool to estimate groundwater residence times under suitable conditions.

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## 1. Introduction

Helium-4 is a stable isotope and a decay product of naturally occurring actinides, primarily uranium and thorium that are present in variable concentrations in all rock types (Mamyrin and Tolstikhin, 1984; Ozima and Podosek, 2002). Helium-4 enters groundwater from different sources including atmosphere, in situ production, inflow from the mantle and release from the aquifer sediments (Kazemi et al., 2006). Groundwater dissolves atmospheric He as a consequence of air-equilibration during recharge and thereafter accumulates radiogenic He which is generated within the aquifer and from adjacent layers of aquitards and/or an external He flux (Andrews and Lee, 1979; Lehmann et al., 2003; Tolstikhin et al., 2011). This process induces changes in the  $^3\text{He}/^4\text{He}$  ratio and the concentration of dissolved He, which may be

used to estimate the mixing proportions of atmospheric and radiogenic He in the groundwater.

The radiogenic He that gradually supplements the atmosphere-derived He can be applied to estimate groundwater residence time in confined aquifers (e.g., Savchenko, 1935; Andrews, 1985; Aeschbach-Hertig et al., 2002; Plummer et al., 2012). It has been shown that radiogenic  $^4\text{He}$  is able to provide groundwater residence time estimates that are comparable with  $^{14}\text{C}$  ages in simple aquifer systems (Castro et al., 2000). An advantage of helium dating compared with the traditional method of  $^{14}\text{C}$  dating is that it can be used for estimating very old ages because He is stable and thus its applicability is not limited in time.  $^4\text{He}$  can be used to estimate groundwater mean residence times ranging from 100 up to  $1 \times 10^8$  a (Rübel et al., 2002; Tolstikhin et al., 2011), whereas  $^{14}\text{C}$  dating is limited to about 5–6 half-lives corresponding to 30–35 ka. However, considerable scientific questions still remain concerning the applicability of  $^4\text{He}$ , such as the separation of the individual He components and determination the external He flux from the crust and mantle.

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Although the radiogenic or crustal He is often the only non-atmospheric He component in groundwater, in some cases significant contributions of He from the Earth's mantle have been found in aquifers (e.g., Stute et al., 1992; Kulongoski et al., 2005). These two terrigenous components can be distinguished based on their  $^3\text{He}/^4\text{He}$  ratios, about three orders of magnitude higher in the mantle than in the crust (Mamyrin and Tolstikhin, 1984). The presence of mantle He in aquifers in shallow layers of the crust implies that routes for the migration of mantle fluids to the surface exist and is often associated with tectonic or volcanic activity. Local high  $^3\text{He}/^4\text{He}$  anomalies may be related to fracture zones with locally enhanced permeability and have been used to identify zones with high potential for geothermal energy development (Kennedy and van Soest, 2007).

The purposes of this paper are to identify the sources of helium components in groundwater of the North China Plain (NCP) as well as to evaluate their contributions to the total He inventory, and thus to estimate groundwater age in the deep confined aquifers of the NCP, which is significant for the assessing groundwater resources renewability and therefore making measures for water resources management under the extensive exploitation in NCP.

## 2. Hydrogeological setting

The NCP is situated in the eastern part of China, it extends from the Taihang mountains in the west to the Bohai sea in the east and from the Yanshan Fold in the north toward the Yellow River in the south (Chen et al., 2003; von Rohden et al., 2010). It is one of the major food producing areas of China and is densely populated with more than 100 million inhabitants. The majority of water resources consumed for domestic, industrial and agricultural purposes are supported by groundwater, and this has resulted in a rapid decline of water levels in recent decades and the development of several big depression cones (Zhang et al., 2000).

The NCP is a thick Cenozoic sedimentary basin and it can be separated into three subsystems as the piedmont fluvial plain, the central alluvial and flood plain, and the coastal delta plain on the basis of topography and aquifer system characteristics (Fig. 1). There is great difference spatially among the hydraulic characteristics of the Quaternary aquifer in the NCP. The Quaternary sediments are 150–600 m thick and consist of unconsolidated deposits with clay, silty clay, sand and sandy gravel layers, where the clay and silty clay constitute relatively impermeable layers as aquitards.

The NCP hydrogeological framework has been extensively studied and consists of 4 water-bearing formations in vertical direction based on lithological and hydrodynamic properties, corresponding to the Holocene formation ( $Q_4$ ), the upper Pleistocene ( $Q_3$ ) formation, the middle Pleistocene formation ( $Q_2$ ) and the lower Pleistocene formation ( $Q_1$ ), respectively (Chen et al., 2003; Zhang et al., 2009).

This study focuses on the two important confined aquifers  $Q_2$  and  $Q_1$  located in the central and coastal plain of the NCP, which two aquifers are in hydraulic continuity and were strictly controlled for the groundwater exploitation. Groundwater flow in the confined aquifers is generally from the west to east (Zhang et al., 2009). Most recharge is from infiltration of precipitation near the outcrop area. Detailed descriptions of the aquifer system in the NCP have been provided (c.f. Zhang et al., 2000, 2009; Chen et al., 2003; Kreuzer et al., 2009).

## 3. Sampling and measurement

A total of 52 groundwater samples were collected along the piedmont to the east coastal plain during two campaigns that took place in 2004 and 2005. This project was carried out by Chinese

researchers (IHEG) in cooperation with German researchers (IUP). Some data have been reported before in a paleoclimate study (Kreuzer et al., 2009) and a study on the recharge regime (von Rohden et al., 2010). This paper focuses on the 18 noble gas samples which were collected from the deep confined aquifers along the central to the coastal plain, and aims to identify the sources of helium dissolved in groundwater as well as to estimate mean residence time with radiogenic  $^4\text{He}$ .

All samples were collected after three to five well-bore volumes had been purged, and after Eh, pH, and temperature readings had reached constant values. The samples could be characterized into 5 groups listed in Table 1 on the basis of hydrogeological setting and their respective  $^3\text{He}/^4\text{He}$  ratios. In particular, water samples for noble gases analysis were directly transferred and sealed off in copper tubes, and analyzed at the Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, using mass spectrometry with typical precisions of  $\pm 0.7\%$  for He,  $\pm 1.1\%$  for Ne,  $\pm 0.8\%$  for Ar,  $\pm 1.2\%$  for Kr,  $\pm 1.6\%$  for Xe, and  $\pm 0.7\%$  for the  $^3\text{He}/^4\text{He}$  ratio.

## 4. Methods

### 4.1. Sources of helium in the groundwater

The concentrations of He isotopes ( $^3\text{He}$ ,  $^4\text{He}$ ) in groundwater usually are in excess of those expected for water in solubility equilibrium with the atmosphere (Heaton and Vogel, 1981; Stute et al., 1992; Wilson and McNeill, 1997; Castro et al., 2000). These excesses can result from 5 different sources: (1) an excess air component (Heaton and Vogel, 1981); (2) tritiogenic  $^3\text{He}$ , the  $\beta$ -decay product of natural and bomb-produced  $^3\text{H}$ , which can provide age information on relatively young groundwater systems (Schlosser et al., 1988; Visser et al., 2014); (3) nucleogenic  $^3\text{He}$ , originating from the  $^6\text{Li}(n, \alpha)^3\text{H}(^3\text{He})$  reaction; (4) radiogenic  $^4\text{He}$ , the result of  $\alpha$ -decay of the natural U and Th decay series isotopes in common rocks; and (5) mantle contributions to both  $^3\text{He}$  and  $^4\text{He}$ . Therefore, the measured helium concentrations in groundwater samples can be interpreted as the sum of these components (Torgersen, 1980; Weise and Moser, 1987). Each component has a characteristic  $^3\text{He}/^4\text{He}$  ratio, for example, the Earth's atmospheric air ratio  $R_a$  of  $1.384 \times 10^{-6}$  (Clarke et al., 1976), the typical crustal (radiogenic and nucleogenic) helium isotope ratio of  $2.0 \times 10^{-8}$  or 0.02  $R_a$  (Mamyrin and Tolstikhin, 1984), and the typical mantle-derived helium isotope ratio of  $1.2 \times 10^{-5}$  or 8  $R_a$  (Craig and Lupton, 1981; Ozima and Podosek, 2002; Kazemi et al., 2006).

### 4.2. Modeling of excess air

In most natural groundwater, the concentration of dissolved noble gases is significantly higher than expected from equilibrium with atmospheric air. This phenomenon has been termed "excess air" and interpreted as the result of dissolution of small air bubbles trapped in groundwater by fluctuations of the groundwater table (Heaton and Vogel, 1981; Kipfer et al., 2002). Several models such as the total dissolution or unfractionated air (TD or UA) model, the partial diffusive re-equilibration (PR) model, and the closed-system re-equilibration (CE) model have been developed to explain and quantitatively describe this excess air component (Aeschbach-Hertig et al., 2000; Aeschbach-Hertig and Solomon, 2013). Inverse modeling algorithms have been developed to estimate the model parameters and study the ability of the different models to fit observed data (Aeschbach-Hertig et al., 1999). Among the mentioned models, the CE model was recognized to be physically realistic and to provide the best fit for interpreting the noble gas data in many case studies (Aeschbach-Hertig et al., 2000; Klump et al., 2007). The basic assumption of the CE model is that

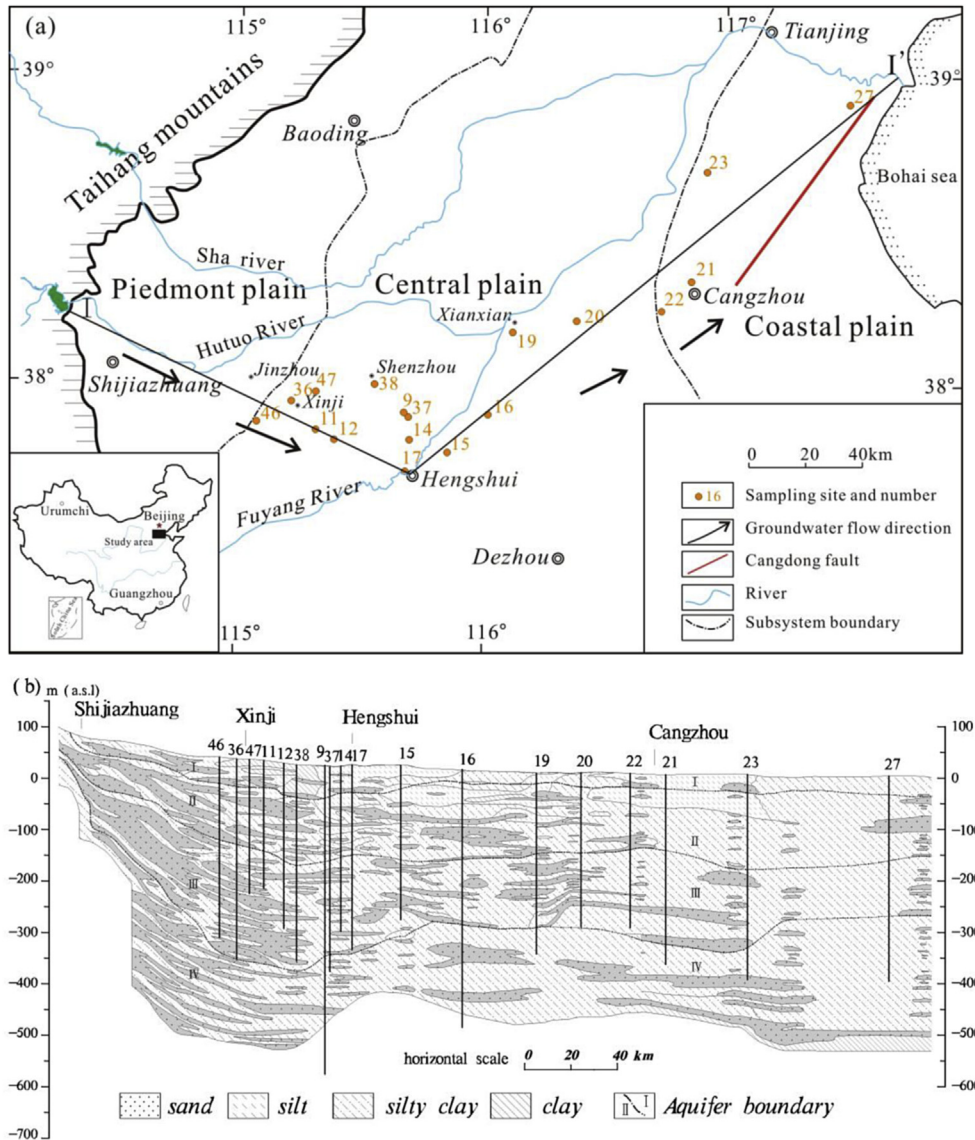


Fig. 1. (a) Map of study area with sampling sites in the North China Plain. (b) Schematic hydrogeological cross-section map along the expected groundwater flow path.

solubility equilibrium is attained in a closed system of initially air-saturated water and a finite volume of entrapped air under a constant hydrostatic pressure. The equation can be expressed as (Aeschbach-Hertig et al., 2000):

$$C_i(T, S, P, A, F) = C_i^{eq}(T, S, P) + \frac{(1 - F)A \cdot Z_i}{1 + A \cdot F \cdot Z_i / C_i^{eq}} \quad (1)$$

where  $C_i^q(T, S, P)$  are the moist-air solubility equilibrium concentrations as functions of temperature, salinity, and atmospheric pressure,  $A$  is the initial amount of entrapped air per unit mass of water,  $Z_i$  are the volume fractions of the individual gases in dry air, and  $F$  is the fractionation parameter.

#### 4.3. Separation of helium components

The measured  $^3\text{He}/^4\text{He}$  ratio of helium dissolved in groundwater can be written as (Stute et al., 1992; Castro et al., 2000):

$$R_s = \frac{^3\text{He}_s}{^4\text{He}_s} = \frac{^3\text{He}_{eq} + ^3\text{He}_{ea} + ^3\text{He}_{terr} + ^3\text{He}_{tri}}{^4\text{He}_{eq} + ^4\text{He}_{ea} + ^4\text{He}_{terr}} \quad (2)$$

where  $R_s$ ,  $^3\text{He}_s$ , and  $^4\text{He}_s$  represent the measured  $^3\text{He}/^4\text{He}$  ratio and the measured  $^3\text{He}$  and  $^4\text{He}$  concentrations, respectively;  $^3\text{He}_{eq}$  and  $^4\text{He}_{eq}$  represent the  $^3\text{He}$  and  $^4\text{He}$  concentrations in solubility equilibrium with the atmosphere at the water table and are related by  $^3\text{He}_{eq} = 0.983R_a \times ^4\text{He}_{eq}$  (Benson and Krause, 1980);  $^3\text{He}_{ea}$  and  $^4\text{He}_{ea}$  represent the  $^3\text{He}$  and  $^4\text{He}$  concentrations resulting from excess air;  $^3\text{He}_{terr}$  and  $^4\text{He}_{terr}$  represent the  $^3\text{He}$  and  $^4\text{He}$  concentrations of terrigenous origin, including in situ and externally produced crustal He as well as He of mantle origin; and  $^3\text{He}_{tri}$  represents  $^3\text{He}$  resulting from tritium decay. The He components of atmospheric origin, i.e., the equilibrium and excess air components, were determined by fitting the CE model to the concentrations of the other noble gases Ne, Ar, Kr, and Xe, which usually are of purely atmospheric origin in shallow groundwater (Kreuzer et al., 2006; Kreuzer, 2007).

**Table 1**  
Results of helium components and  $^4\text{He}$  ages.

Group	Sample	Location	Well depth (m)	Distance (km)	$^{14}\text{C}$ age <sup>a</sup> (ka)	$\text{He}_s^a$ ( $\text{cm}^3\text{STP g}^{-1}$ )	$^3\text{He}/^4\text{He}$ [ $R_a$ ]	$\text{He}_{ea}^a$ ( $\text{cm}^3\text{STP g}^{-1}$ )	$\text{He}_{terr}^a$ ( $\text{cm}^3\text{STP g}^{-1}$ )	$^4\text{He}$ age <sup>b</sup> (ka)	$^4\text{He}$ age <sup>c</sup> (ka)
I	46	Jinzhou	350	75.5	$7.7 \pm 1.4$	$1.34\text{E-}7$	0.51	$1.65\text{E-}8$	$7.29 \pm 0.09\text{E-}8$	$12.6 \pm 0.7$	$3.9 \pm 0.1$
	36	Xinji	390	83.6	$7.7 \pm 1.8$	$1.30\text{E-}7$	0.50	$1.10\text{E-}8$	$7.43 \pm 0.11\text{E-}8$	$12.8 \pm 0.8$	$4.0 \pm 0.1$
	47	Xinji	260	89.9	$10.7 \pm 1.8$	$1.08\text{E-}7$	0.55	$0.77\text{E-}8$	$5.48 \pm 0.09\text{E-}8$	$9.5 \pm 0.6$	$2.9 \pm 0.1$
II	11	Xinji	250	95.5	$21.8 \pm 1.3$	$2.10\text{E-}7$	0.45	$3.28\text{E-}8$	$1.31 \pm 0.02\text{E-}7$	$22.6 \pm 1.4$	$7.0 \pm 0.2$
	12	Shenzhou	320	103.4	$27.1 \pm 1.1$	$2.20\text{E-}7$	0.31	$1.19\text{E-}8$	$1.61 \pm 0.02\text{E-}7$	$27.9 \pm 2.6$	$8.6 \pm 0.2$
	38	Shenzhou	380	108.1	$29.9 \pm 1.5$	$1.94\text{E-}7$	0.36	$1.05\text{E-}8$	$1.38 \pm 0.02\text{E-}7$	$23.8 \pm 1.4$	$7.3 \pm 0.2$
III	9	Shenzhou	600	122.5	$30.2 \pm 1.6$	$4.45\text{E-}7$	0.18	$0.79\text{E-}8$	$3.91 \pm 0.03\text{E-}7$	$67.4 \pm 3.9$	$20.8 \pm 0.4$
	37	Shenzhou	400	123.6	$30.1 \pm 2.0$	$2.71\text{E-}7$	0.26	$0.92\text{E-}8$	$2.17 \pm 0.03\text{E-}7$	$37.5 \pm 2.2$	$11.5 \pm 0.2$
	14	Shenzhou	320	128.0	$28.0 \pm 2.0$	$2.88\text{E-}7$	0.24	$0.63\text{E-}8$	$2.35 \pm 0.03\text{E-}7$	$40.6 \pm 2.4$	$12.5 \pm 0.3$
IV	17	Hengshui	360	132.2	$35.2 \pm 1.9$	$7.48\text{E-}7$	0.14	$0.85\text{E-}8$	$6.93 \pm 0.07\text{E-}7$	$119.7 \pm 6.9$	$36.9 \pm 0.7$
	15	Hengshui	300	147.9	$21.2 \pm 2.2$	$4.51\text{E-}7$	0.16	$0.84\text{E-}8$	$3.97 \pm 0.04\text{E-}7$	$68.6 \pm 4.0$	$21.1 \pm 0.4$
	16	Wuyi	500	167.7	n.m.	$4.56\text{E-}7$	0.16	$0.76\text{E-}8$	$4.02 \pm 0.04\text{E-}7$	$69.4 \pm 4.0$	$21.4 \pm 0.4$
	19	Xianxian	350	193.6	$28.9 \pm 3.8$	$6.04\text{E-}7$	0.13	$0.93\text{E-}8$	$5.48 \pm 0.06\text{E-}7$	$94.6 \pm 5.5$	$29.1 \pm 0.6$
V	20	Xianxian	300	213.2	$31.6 \pm 2.8$	$1.03\text{E-}6$	0.09	$1.32\text{E-}8$	$9.66 \pm 0.09\text{E-}7$	$166.9 \pm 9.6$	$51.4 \pm 1.0$
	22	Cangzhou	300	239.7	35.6	$6.38\text{E-}6$	0.20	$1.21\text{E-}8$	$6.32\text{E-}6$	n.e.	n.e.
	21	Cangzhou	370	254.5	38.1	$2.67\text{E-}5$	0.29	$1.51\text{E-}8$	$2.67\text{E-}5$	n.e.	n.e.
	23	Tianjin	400	284.0	37.8	$9.00\text{E-}5$	0.37	$1.87\text{E-}8$	$8.99\text{E-}5$	n.e.	n.e.
	27	Tianjin	400	339.0	n.m.	$5.38\text{E-}5$	0.36	$1.85\text{E-}8$	$5.37\text{E-}5$	n.e.	n.e.

n.m. not measured. n.e. not estimated (the samples contain mantle-derived helium).

<sup>a</sup> Data after Kreuzer et al., 2009.

<sup>b</sup> He ages calculated with helium flux  $J_0 = 0$  and  $A_{\text{He}} = 5.79 \pm 0.33 \times 10^{-12} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1} \cdot \text{a}^{-1}$ .

<sup>c</sup> He ages calculated with helium flux  $J_0 = 4.7 \times 10^{-8} \text{ cm}^3 \text{STPcm}^{-2} \cdot \text{a}^{-1}$ ,  $Z_0 = 180 \text{ m}$  and  $\phi = 0.2$ .

$^3\text{He}/^4\text{He}$  ratios and noble gas concentrations are used to separate helium components originating from the atmosphere, tritium decay, crustal production, and mantle degassing (Stute et al., 1992). Under certain assumptions, some of the non-atmospheric components can be separated from each other. One way to separate the He components of a groundwater sample is to plot (Weise and Moser, 1987; Stute et al., 1992; Castro et al., 2000):

$$\underbrace{\frac{{}^3\text{He}_s - {}^3\text{He}_{ea}}{{}^4\text{He}_s - {}^4\text{He}_{ea}}}_Y = \underbrace{\left( R_{eq} - R_{terr} + \frac{{}^3\text{He}_{tri}}{{}^4\text{He}_{eq}} \right)}_m \underbrace{\frac{{}^4\text{He}_{eq}}{{}^4\text{He}_s - {}^4\text{He}_{ea}}}_X + \underbrace{R_{terr}}_b \quad (3)$$

where  $R_{terr}$  represents the  $^3\text{He}/^4\text{He}$  ratio originating from terrigenous sources (radiogenic  $^4\text{He}$ , nucleogenic  $^3\text{He}$  and mantle-derived He) and  $R_{eq} = 0.983R_a$  (Benson and Krause, 1980) is the  $^3\text{He}/^4\text{He}$  ratio in solubility equilibrium. Equation (3) describes a straight line, where Y is the measured  $^3\text{He}/^4\text{He}$  ratio corrected for excess air, and X is the contribution of the  $^4\text{He}$  dissolved in water in equilibrium with the atmosphere with respect to the total  $^4\text{He}$ , corrected for excess air. The values of X and Y are directly derived from measured noble gas concentrations using the atmospheric He components estimated from the CE model.

## 5. Results and discussion

### 5.1. Characteristics of dissolved helium in groundwater

The dissolved helium concentrations in the groundwater of the NCP used in this study are listed together with well information in Table 1. Parts of these data, along with results from wells further upstream, had been already published by Kreuzer et al. (2009). The dissolved helium concentrations range from  $1.08 \times 10^{-7}$  to  $1.03 \times 10^{-6} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1}$  in the central plain and  $6.38 \times 10^{-6}$  to  $9.00 \times 10^{-5} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1}$  in the coastal plain, respectively. These helium concentrations are significantly higher than the expected concentrations for atmospheric equilibrium ( $\text{He}_{eq}$ ) and excess air ( $\text{He}_{ea}$ ) listed in Table 1. This shows that there are important contributions of non-atmospheric helium dissolved in groundwater.

Corresponding  $^3\text{He}/^4\text{He}$  ratios of the samples normalized to the atmospheric  $^3\text{He}/^4\text{He}$  ratio range from 0.09 to 0.55  $R_a$  and 0.20 to 0.37  $R_a$ , respectively (Table 1). In view of the lower than atmospheric observed He isotope ratios, it can be seen that the non-atmospheric helium in the study area primarily consists of radiogenic helium, which may contain in situ produced and other sources of helium flux components, and/or a smaller contribution of mantle-derived helium. Since terrigenous He is expected to accumulate in the groundwater along flowpath and in addition to possibly reflect an upward flux from below, it is interesting to study the relationship of He concentrations and isotope ratios with flow distance and depth.

The dissolved helium concentrations increase systematically with the distance from the recharge area for all the groundwater samples (Fig. 2a), with corresponding  $^3\text{He}/^4\text{He}$  ratios decreasing along the distance in the central plain (up to a distance of about 200 km) but increasing in the coastal plain (Fig. 2b). The evolution of He concentrations and isotope ratios in the central plain is typical for many aquifers and reflects the continuous accumulation of radiogenic He with a low  $^3\text{He}/^4\text{He}$  ratio. The disproportional (note the logarithmic concentration scale in Fig. 2a) increase of He concentrations in the coastal plain indicates an additional strong source of terrigenous He in this region, which, however, has a higher  $^3\text{He}/^4\text{He}$  ratio, maybe indicating the presence of mantle component.

The relationships of measured He concentrations and  $^3\text{He}/^4\text{He}$  ratios in the groundwater with well depth are shown in Fig. 3. In contrast to distance (Fig. 2), no clear trends with depth are obvious. The lack of depth-dependence becomes particularly apparent if groups of wells at similar flow distances but with different depths are considered. Five groups are showed in Fig. 3 by connected symbols. For the groundwaters of group I to IV in the central plain, no systematic intra-group changes in dissolved helium concentrations with depth are observed. In contrast, for the groundwater of group V in the coastal plain a strong increase is present with respect to well depth (Fig. 3a). Also the  $^3\text{He}/^4\text{He}$  does not show much change within each of the groups I to IV, while generally decreasing as the He concentration increases from one group to the next. Within group V, i.e., the coastal plain, the  $^3\text{He}/^4\text{He}$  ratio increases with depth as the He concentration increases (Fig. 3b).



helium isotope ratio). The intercept  $b$  ( $R_{terr}$ ) was calculated to be  $4.78 \times 10^{-8}$ , which under the assumption that mantle contributions are negligible in this end-member can be interpreted as the representative radiogenic helium isotopic ratio in the NCP.

A  $R_{terr}$  was determined ( $6.10 \times 10^{-8}$ ) with the samples (46, 36, 47, 11, 12, 38, 9, 37, 14, 17, 15, 16, 19) in the central plain in NCP (Line B). And thus we may conclude that the radiogenic component is predominantly contributing to the total He in the central plain on the basis of assuming that a binary end-member mixing between a radiogenic He ratio of  $4.78 \times 10^{-8}$  and mantle-derived helium ratio of  $1.2 \times 10^{-5}$ . The slope  $m$  (equation (3)) was estimated to be  $14.69 \times 10^{-7}$ , which means that about  $3.13 \pm 0.03$  TU of  $^3\text{H}$  was completely decayed to  $^3\text{He}_{tri}$  ( $7.82 \times 10^{-15} \text{ cm}^3\text{STP} \cdot \text{g}^{-1}$ ) under an average value of  $4.60 \pm 0.05 \times 10^{-8} \text{ cm}^3\text{STP} \cdot \text{g}^{-1}$  for  $\text{He}_{eq}$ . This probably represents the natural level for tritium in paleowaters in the NCP.

Line C was inferred from line B by assuming that an addition of mantle-derived helium of 4% was present in the groundwater. Fig. 4 clearly shows that the groundwater samples in the coastal plain (22, 21, 23, 27) fall between Line B and Line C. The mantle-derived helium contributions to the total helium of these samples were estimated to be in the range of 1.82–3.82% resulting from a binary end-member mixing between a radiogenic and a mantle-derived component as above.

### 5.3. Estimation of $^4\text{He}$ ages

After separation of the individual He components, the radiogenic  $^4\text{He}$  can be used at least as a qualitative age tracer based on its accumulation in groundwater over time. He accumulation ages may in some cases provide an independent way to check the results derived from radiocarbon dating, on the other hand  $^{14}\text{C}$  ages can be used to calibrate the He age scale. The  $^4\text{He}$  age can be calculated from the following equation (Weise and Moser, 1987; Stute et al., 1992; Kulongoski et al., 2003):

$$\tau_{\text{corr}} = \frac{{}^4\text{He}_{\text{ex}}}{\left(\frac{J_0}{\phi Z_0 \rho_w} + A_{\text{He}}\right)} \quad (4)$$

Herein,  ${}^4\text{He}_{\text{ex}}$  is the total (both in situ produced and originating from an external flux) radiogenic He excess ( $\text{cm}^3\text{STP} \cdot \text{g}^{-1}$ ),  $J_0$  is the external  $^4\text{He}$  flux entering the aquifer ( $\text{cm}^3\text{STP} \cdot \text{cm}^{-2} \cdot \text{a}^{-1}$ );  $\phi$  is the effective porosity of the aquifer;  $Z_0$  is the aquifer thickness (cm);  $\rho_w$  is the density of water ( $\text{g} \cdot \text{cm}^{-3}$ ); and  $A_{\text{He}}$  is the  $^4\text{He}$  accumulation rate in the groundwater due to in situ production ( $\text{cm}^3\text{STP} \cdot \text{g}^{-1} \cdot \text{a}^{-1}$ ) (Kulongoski et al., 2003). This latter rate can be calculated by the following equation, which combines the radioelement content of the aquifer with its physical properties (e.g. Andrews and Lee, 1979):

$$A_{\text{He}} = \rho_{\text{rock}} \cdot \lambda \cdot \left\{ 1.19 \times 10^{-13} \cdot [U] + 2.88 \times 10^{-14} \cdot [Th] \right\} \cdot \frac{1-\phi}{\phi} \quad (5)$$

where [U] and [Th] are the uranium and thorium concentrations in the aquifer rock (ppm);  $\rho_{\text{rock}}$  is the bulk density of the aquifer rock ( $\text{g} \cdot \text{cm}^{-3}$ ), and the release rate  $\lambda$  is the fraction of helium produced in the rock that is released into the water, often assumed to be unity (Kulongoski et al., 2003).

On the basis of the statistical characteristics of samples collected from two boreholes in NCP (Table 2), the average values of U and Th concentrations were  $2.45 \pm 0.29$  ppm and  $11.37 \pm 0.99$  ppm in Hengshui,  $2.51 \pm 0.28$  ppm and  $11.86 \pm 1.57$  ppm in Cangzhou, respectively. The corresponding accumulation rates of He are

$5.69 \pm 0.41 \times 10^{-12} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1} \cdot \text{a}^{-1}$  and  $5.89 \pm 0.52 \times 10^{-12} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1} \cdot \text{a}^{-1}$  with a porosity of 0.2 and a rock density of  $2.3 \text{ g} \cdot \text{cm}^{-3}$  (Zhang et al., 2000). An average value of  $5.79 \pm 0.33 \times 10^{-12} \text{ cm}^3 \cdot \text{STP} \cdot \text{g}^{-1} \cdot \text{a}^{-1}$  ( $A_{\text{He}}$ ) was determined for the central-coastal plain in this study.

Because according to equation (5) the He accumulation rate resulting from in situ production can be calculated based on measured quantities, quantitative He dating may be possible if the generally unknown external flux  $J_0$  can be assumed to be negligible (Kipfer et al., 2002; Aeschbach-Hertig et al., 2002). In the central part of NCP, this assumption appears reasonable based on the lack of a vertical gradient in radiogenic He concentrations (Fig. 3). Using the accumulation rate and assuming that no external He flux exists ( $J_0 = 0$ ), a rough quantification of  $^4\text{He}$  ages in the range of 9.5–166.9 ka resulted for the groundwater samples in the central plain. For most of the groundwater samples of groups I to III (No. 46, 36, 47, 11, 12, 38, 37, 14), the estimated  $^4\text{He}$  ages in the range of 9.5–40.6 ka are close to the  $^{14}\text{C}$  ages (Fig. 5a), supporting the assumption that the in situ produced  $^4\text{He}$  is the predominant contribution to the total radiogenic  $^4\text{He}$  for these samples. The only exception in this part of the study region is well 9, where the He accumulation estimated from pure in situ production is more than twice the  $^{14}\text{C}$  age (67.4 vs. 30.2 ka, Table 1, Fig. 5a). The comparatively high radiogenic  $^4\text{He}$  content of well 9 may be explained by the fact that this well with a depth of 600 m and lower porosity due to the deepest well in this study, or probably some other external sources of helium emerged at this great depth.

Similar to well 9, the He age estimates based on in situ production only are significantly higher than the ages derived from  $^{14}\text{C}$  for all remaining wells from the central plain (group IV, wells 17, 15, 19, 20, in Fig. 5a), which may suggest that an upward helium flux was present through the bottom of the aquifer in this downstream part of the central plain. Such a transition from pure in situ production to the presence of an extraneous flux in downstream wells with older water has also been observed in other aquifers (Kulongoski et al., 2003). It thus seems reasonable to estimate He accumulation ages for the wells from group IV (and well 9) including the term with  $J_0$  in equation (3). However, since this term is not known, independent quantitative He dating is not possible in this region. Instead, a helium flux  $J_0$  of  $4.7 \times 10^{-8} \text{ cm}^3\text{STP} \cdot \text{cm}^{-2} \cdot \text{a}^{-1}$  was determined as suitable in order to achieve a good agreement between estimated  $^4\text{He}$  ages of the groundwater samples from wells 17, 15, and 19 with the corresponding  $^{14}\text{C}$  ages (Fig. 5b). Assuming this flux yields a somewhat too low estimated  $^4\text{He}$  age for well 9 and a considerably too high age for sample 20 in comparison with the respective  $^{14}\text{C}$  ages (Table 1, Fig. 5b). The high  $^4\text{He}$  age of 51.4 ka of well 20, which is about 60% higher than the corresponding  $^{14}\text{C}$  age, may be explained by a greater helium flux in this most distant part of the central plain. Obviously, a still much higher He flux is present a bit further downstream in the coastal plain, where the He concentrations increase strongly (Fig. 2a). However, as the He flux in the coastal plain is influenced by a mantle component and possibly originates from localized sources related to deep faults, no attempt of He dating was made for the coastal part of the NCP aquifer system.

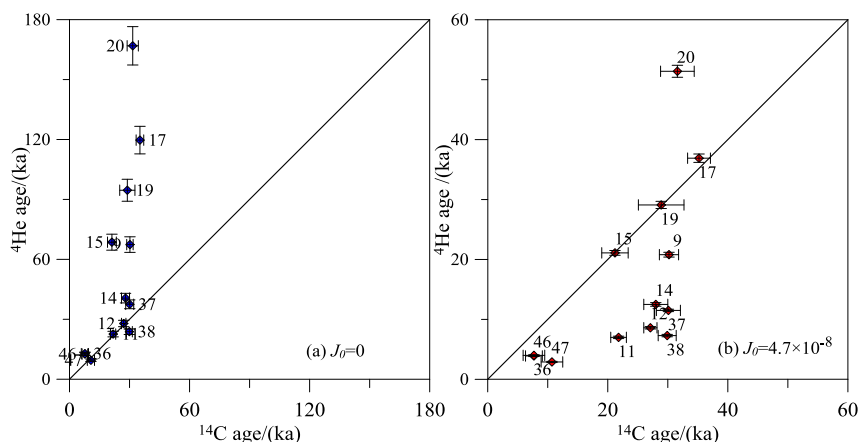
On the whole, the  $^4\text{He}$  ages assuming only in situ production within the deep NCP aquifers are comparable to the  $^{14}\text{C}$  ages for the groundwater in the upper half of central plain (groups I to III). This finding confirms that in situations with negligible external He source,  $^4\text{He}$  can be employed to derive quantitative estimates of the mean residence time of groundwater. Furthermore, a single value for the external He flux of  $J_0 = 4.7 \times 10^{-8} \text{ cm}^3\text{STP} \cdot \text{cm}^{-2} \cdot \text{a}^{-1}$  works reasonably well for the wells in the lower part of the central plain (group IV), indicating that semi-quantitative He dating is possible if the He flux can be determined, e.g. by calibration with  $^{14}\text{C}$  ages, and

**Table 2**  
[U] and [Th] concentrations of sediment samples from two cores in NCP.

Location	Depth [m]	N	Range U [ppm]	Range Th [ppm]	Average U [ppm]	Average Th [ppm]	$A_{\text{He}}$ [ $10^{-12}$ cm <sup>3</sup> ·STP·g <sup>-1</sup> ·a <sup>-1</sup> ]
Hengshui	0–111.6	31	1.49–3.18	9.25–14.80	2.45 ± 0.29	11.37 ± 0.99	5.69 ± 0.41
Cangzhou	0–76.6	40	1.97–3.40	9.26–18.50	2.51 ± 0.28	11.86 ± 1.57	5.89 ± 0.52
Average							5.79 ± 0.33

N, numbers of samples.

$A_{\text{He}}$  calculated with  $\rho_{\text{rock}} = 2.3$  g cm<sup>-3</sup> and  $\phi = 0.2$ .



**Fig. 5.** Corrected <sup>4</sup>He age vs <sup>14</sup>C age under the assumption of no external flux (left panel, a) and with a helium flux of  $4.7 \times 10^{-8}$  cm<sup>3</sup>·STP·cm<sup>-2</sup>·a<sup>-1</sup> (right panel, b).

can be assumed to be reasonably uniform in a certain area. However, it should be noted that the <sup>4</sup>He ages are prone to considerable uncertainties if the in-situ accumulation rate varies widely and/or the additional sources of radiogenic <sup>4</sup>He are not quantified, especially if no other environmental tracers for age dating are available. The <sup>4</sup>He flux estimated for the downstream part of the central plain ( $4.7 \times 10^{-8}$  cm<sup>3</sup>STP·cm<sup>-2</sup>·a<sup>-1</sup> =  $2.1 \times 10^{-8}$  mol m<sup>-2</sup>·a<sup>-1</sup> =  $4.0 \times 10^8$  atoms·m<sup>-2</sup>·a<sup>-1</sup>) is lower than the lower bound of flux values found in the GHP (Stute et al., 1992) and very low compared to crustal He fluxes found in other aquifers (Ballentine et al., 2002) and lakes (Kipfer et al., 2002), which are typically two orders of magnitude higher.

#### 5.4. Implications for groundwater resources management

The NCP is a semi-arid region that ongoing stringent water resources scarcity in China. The deep confined aquifers of NCP have been extensively exploited for water supplying and agriculture irrigation since the 1970s, which resulted in numerous environmental problems, e.g. groundwater depression cones emerged in large cities, land subsidence, seawater intrusion in the coastal area, etc.. The groundwater ages interpreted here confirm that the groundwaters in the deep confined aquifers are very old, some were up to several decades of thousands of years old, which could be thought as non-renewable on human timescales. The results of this study will aid in making reasonable exploitation and utilization strategies for the future sustainability of groundwater resources management.

## 6. Conclusions

Large amounts of non-atmospheric helium dissolved in the groundwater were identified by a detailed separation of the He components in the confined aquifers of the NCP. The results indicate that the terrigenous <sup>4</sup>He concentrations vary over three orders of magnitude from about  $5 \times 10^{-8}$  to  $9 \times 10^{-5}$  cm<sup>3</sup>STP·g<sup>-1</sup>. In the

central plain, the terrigenous <sup>4</sup>He component is comparatively small ( $<10^{-6}$  cm<sup>3</sup>STP·g<sup>-1</sup>) and shows a clear radiogenic signature. A typical radiogenic helium isotopic ratio of  $4.78 \times 10^{-8}$  (0.035 R<sub>a</sub>) was obtained for this part of the NCP, which is similar to the isotope ratio of radiogenic helium reported for other groundwater systems such as the GHP (Stute et al., 1992). As a further result of the He component separation for the wells in the central plain, a natural tritium level of about 3 TU was for the first time derived for the paleowaters in NCP.

The wells located in the coastal plain exhibited a much higher terrigenous helium component ranging between  $6 \times 10^{-6}$  and  $9 \times 10^{-5}$  cm<sup>3</sup>STP·g<sup>-1</sup>, which is characterized by elevated <sup>3</sup>He/<sup>4</sup>He ratios of up to 0.37 R<sub>a</sub>. It was estimated that about 1.82%–3.82% of mantle-derived helium were present in the groundwater of the coastal plain. Previous studies on the oil and natural gas reservoirs in this area are in agreement with this finding, which is supposed to be related to the regional faults and tectonic activities.

For the wells in the central plain, <sup>4</sup>He ages were estimated based on the accumulation of radiogenic He. In the upper half of the central plain, <sup>4</sup>He ages calculated assuming only in situ He production in the aquifer were comparable to the <sup>14</sup>C ages. In the lower part of the central plain, an additional but weak He flux of  $4.7 \times 10^{-8}$  cm<sup>3</sup>STP·cm<sup>-2</sup>·a<sup>-1</sup> had to be assumed in order to obtain agreement of <sup>4</sup>He and <sup>14</sup>C ages. These results show that <sup>4</sup>He can be employed to estimate the mean residence time of groundwater if some information on the He flux is available or can be derived from comparison with <sup>14</sup>C ages.

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