Evaluation of submarine groundwater discharge into the northern Bohai Bay, China using $^{226}$Ra
Xuejing Wang, Hailong Li, Yan Zhang, Chaoyue Wang, Wenjing Qu and Qian Ma

ABSTRACT

Submarine groundwater discharge (SGD) has been widely recognized as a significant source of water and dissolved material transport from land to ocean. To quantify SGD into the northern Bohai Bay, China, naturally occurring radium isotope ($^{226}$Ra) was measured in water samples collected along two transects in September 2012. Based on a tidal prism model, two different flushing times of the coastal water were determined to be 9.1 d and 11.5 d with respect to the different return flow factor ($b$) obtained from a physical model and a mass balance model of $^{226}$Ra and salinity, respectively. Using the derived flushing time, we developed a $^{226}$Ra mass balance model to estimate the SGD into the bay, which includes mixing, sedimentary input and SGD. The $^{226}$Ra budget indicated the $^{226}$Ra input from SGD accounted for 99% of the total tracer input to the northern Bohai Bay. We arrived at an average flux from SGD of $4.83 \times 10^7$ m$^3$/d. The large volume of SGD confirms its importance in supplying a considerable quantity of nutrients to the bay.

Key words | $^{226}$Ra, Bohai Bay, flushing time, mass balance model, submarine groundwater discharge

INTRODUCTION

Interaction between fresh groundwater and coastal seawater in the aquifer results in two complementary processes: seawater intrusion and submarine groundwater discharge (SGD). The definition of SGD, defined by Burnett et al. (2003), is any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force. The driving forces of SGD are complicated, and include the hydraulic gradients, density gradients and a variety of oceanic processes such as waves and tidal pumping (Burnett et al. 2006; Geng & Boufadel 2015). As an important natural component of the hydrological cycle, SGD has been widely recognized as a significant source of water and an important pathway for nutrients and chemicals transport from land to the ocean (Burnett et al. 2006; Moore 2010).

Due to spatial and temporal variations in SGD, it is not easy to measure and evaluate its effect accurately. Currently, the main methods of measuring SGD include direct physical measurement (seepage meters), tracer techniques (radium isotopes, radon) and modelling methods. Among these methods, geochemical tracers are particularly useful for calculating SGD on large temporal and spatial scales (Kim et al. 2005). $^{226}$Ra, a naturally occurring isotope of the $^{238}$U-series with a half-life of 1,600 years, is a tracer of considerable interest in studies of SGD since it is conservative chemically and widely enriched in groundwater compared to surface waters (Moore 2003; Burnett et al. 2006).

Although the SGD has been quantified using radium and radon isotope methods in many coastal areas of China (Kim et al. 2005; Peterson et al. 2008; Wu et al. 2013; Xu et al. 2013; Wang et al. 2015), SGD in Bohai Bay is seldom estimated, particularly using geochemical tracers. Bohai Bay, surrounded by the Bohai Economic Ring, is considered to be one of the most polluted marine areas in China (Gao & Chen 2012). In recent years, Bohai Bay has encountered an increasing number of algal blooms due to its poor
physical self-clean capacity and the continuous increase of the pollution inputs (Feng et al. 2017). In order to promote sustainable development and management in the coastal regions, the research on groundwater–seawater circulation in Bohai Bay must be paid much attention. Thus, our study aimed to evaluate the dynamics of groundwater discharge and associated impacts on the coastal ecosystem in northern Bohai Bay. We used $^{226}$Ra to estimate SGD into Bohai Bay, Bohai Sea, China.

**METHODS**

**Field sampling**

Our field work was conducted on September 21–23, 2012 in northern Bohai Bay, China. We collected 6 coastal groundwater samples along the shoreline and 10 surface seawater samples (1–2 m below the seawater surface). Ten surface seawater stations were oriented along two shore-perpendicular transects within ~20 km distance offshore (Figure 1). $^{226}$Ra was collected from waters using the methods established by Moore (1976). Large volume water samples (~30 L for seawater, ~15 L for groundwater) were pumped and filtered through 1 µm filter for $^{226}$Ra extraction. $^{226}$Ra was extracted from the samples by passing the water slowly through a cartridge containing about 25 g of Mn-fibers (Moore 1976). The flow rate was controlled not to exceed 1.0 L min$^{-1}$ to ensure complete $^{226}$Ra adsorption on the Mn-fibers. The extracting efficiency of $^{226}$Ra determined by two Mn-fibers connected in series was found to be ~95.2%. The salinity, temperature, and pH of the water samples were measured *in situ* using a handheld HI9828 Model probe (HANNA).

$^{226}$Ra analysis

In the laboratory, $^{226}$Ra adsorbed on Mn-fibers was analyzed using a radon-in-air monitor (RAD7, Durridge Co., Inc., USA) proposed by Kim et al. (2001). The $^{226}$Ra activity for the portable system is determined based on the equilibrium between $^{226}$Ra and $^{222}$Rn. Our procedure for $^{226}$Ra analysis in water samples can be summarized into the following steps. (1) The fibers were sealed for 20 d to allow $^{222}$Rn and its daughter nuclides to equilibrate with $^{226}$Ra. The weight ratios of water/fiber may be maintained between 0.7 and 2.5, and in this case the escape efficiency of Rn from Mn-fiber is optimal (Sun & Torgersen 1992; Kim et al. 2001). (2) Before the measurement, helium was circulated for 5 min through the detector chamber to sweep the residual $^{222}$Rn ($^{218}$Po), creating a low background value and a dry environment. (3) The Mn-fiber column was connected to a desiccant column and a radon-in-air monitor through a closed loop. In order to quickly reach equilibration between $^{222}$Rn and $^{226}$Ra and reach the optimal detection efficiency, the system was allowed to run for 15 min before data collection. (4) To improve the accuracy of measurement, a long counting time of 8 h was set on every sample and the humidity in the closed loop was controlled not to exceed 10%.

**RESULTS AND DISCUSSION**

**Hydrographic distribution**

The results of $^{226}$Ra measurements are listed in Table 1, together with the latitude, longitude, pH, and salinity for all samples. $^{226}$Ra activity in coastal groundwater ranged from 8.38 to 79.07 dpm 100 L$^{-1}$ with a large spatial variation (dpm means disintegrations per minute). $^{226}$Ra activity in surface seawater varied from 32.97 to 69.43 dpm 100 L$^{-1}$, with
an average of 52.20 dpm 100 L⁻¹. Saline groundwater usually has high activities of Ra, because it contacts more sediment surfaces and gains large supply from decay of their insoluble parent isotopes in solid phase and desorption from the adsorbed phase (Moore et al. 2006; Luo et al. 2014). However, 226Ra activities in groundwater samples in this study were not high. In particular, some were lower than those in surface seawater. This is because the seawater samples were pumped at a depth of ∼2.5 m below the surface and they contained shallow groundwater from the surficial coastal aquifer. Surficial aquifers that are continuously flushed by seawater have low activities of 226Ra because there is not enough time for this isotope to regenerate from its parent (230Th).

Figure 2(a) and 2(b) show the variation in salinity and pH along the two transects, respectively. The surface water samples collected from transect I had salinity ranging from 24.6 to 28.3 with an average of 27, and the samples from transect II had salinity varying from 26.7 to 28.3 with an average of 28. The salinity of the surface seawater along two transects showed similar variation trend. The pH ranged from 7.89 to 8.01 with an average 7.95 for transect I and it varied from 8.04 to 8.14 with an average of 8.09 for transect II (Figure 2(b)). The pH in each transect was relatively stable and showed a lower value in Transect I compared with transect II. In general, both the salinity and pH of the samples from transect I were slightly lower than those collected from transect II. Based on the analysis of the two parameters, one can conclude that the freshwater discharge along transect I may be higher than that of transect II. This is likely because transect I includes longer shoreline.

### Determination of flushing time

To explore the dynamics of coastal water in the northern Bohai Bay, the flushing time related to the timescale of material transport is introduced. Flushing time is used to describe the general exchange characteristics of a water body and is defined as the ratio of the mass or volume of a constituent (V) to its renewal rate (Q), or $T_f = V/Q$ (Geyer 1997).
et al. 2000). One can estimate the flushing time based on the tidal prism method (Sanford et al. 1992):

\[ T_f = \frac{VT}{P(1-b)} \quad (1a) \]

\[ P = \int_0^H A \, dz \quad (1b) \]

where \( T_f \) is the flushing time; \( V \) is the volume of water in the system; \( T \) is the tidal period; \( P \) is the tidal prism (total volume of seawater entering the system during a rising tide); \( b \) is the return flow factor (percentage of the tidal prism that returns from outside of the bay during the flood tide); \( A \) is the water surface area of the region; \( z \) is the water depth over tidal range (\( H = 1.75 \, \text{m} \)).

The above equations are based on the following assumptions: (1) the influence of wind is neglected; (2) the system should be well mixed (Sanford et al. 1992); (3) flushing is related exclusively to the tidal prism; (4) river flow and groundwater discharge must be small compared to tidal flow; (5) the tidal prism must be large enough to dilute the water in the system so that offshore water quality does not change.

To calculate the flushing time, the tidal prism \( P \), water volume \( V \) and return flow factor \( b \) should be determined firstly. The water volume of the system was defined as the product of the average area and water depth, which turned out to be approximately \( 2.3 \times 10^9 \, \text{m}^3 \). The tidal prism was determined by multiplying the average surface area by the tidal range during the sampling period to be \( 3.3 \times 10^8 \, \text{m}^3 \). The tidal period was equal to 0.52 d in the study area. The return flow factor \( b \) is the most difficult parameter to obtain. Here we used two methods for estimating the return flow factor.

Van de Kreeke (1985) defined the return flow factor using the outflowing ebb velocity and the incoming flood velocity as:

\[ b = \frac{v - U}{v + U} \quad (2) \]

where \( v \) is the average value of the flood and ebb velocity; \( U \) is the net velocity (the difference between incoming flood velocity and the outflowing ebb velocity). The average velocities of the rising tide and falling tide are 28.3 cm s\(^{-1}\) and 25.0 cm s\(^{-1}\), respectively. Using the parameters above, we estimated \( v = 26.6 \, \text{cm s}^{-1} \) and \( U = 5.5 \, \text{cm s}^{-1} \). Solving this equation yields a return flow factor of \( b = 0.78 \).

To identify whether the return flow factor was applicable, we used another method to determine the flushing time in the region. Moore et al. (2006) developed a three-end-member mixing model for estimating the return flow factor. This mixing model was used to estimate the fraction of every end-member (groundwater, rivers, Bohai Sea):

\[ f_s + f_r + f_{gw} = 1 \quad (3a) \]

\[ ^{226}\text{Ra}_s f_s + ^{226}\text{Ra}_r f_r + ^{226}\text{Ra}_{gw} f_{gw} = ^{226}\text{Ra}_M \quad (3b) \]

\[ S_s f_s + S_r f_r + S_{gw} f_{gw} = S_M \quad (3c) \]

where \( f_s \), \( f_r \), and \( f_{gw} \) are the fractions of the open seawater (Bohai Sea), river and groundwater end-members, respectively; \( ^{226}\text{Ra}_s \), \( ^{226}\text{Ra}_r \), and \( ^{226}\text{Ra}_{gw} \) are the activities of \( ^{226}\text{Ra} \) in open seawater, river and groundwater end-members, respectively; \( S_s \), \( S_r \), and \( S_{gw} \) are the salinity in the open seawater, river and groundwater end-members, respectively; \( ^{226}\text{Ra}_M \) and \( S_M \) are the \( ^{226}\text{Ra} \) activity and salinity measured in surface seawater, respectively. The parameter \( f_r \) was equal to zero, because no river discharged into the study area during our sampling time. We used the sample S4 as the seawater end-member and used the sample GW-2 as the groundwater end-member. Based on Equation (3), the average fractions of water from the open sea and groundwater were 0.83 and 0.17, respectively. The model calculated the amount of water from the open sea, which is simply the return flow. Thus we can treat \( f_s \) as the return flow \( b \). This is comparable with the physical estimate of \( b = 0.78 \).

Based on Equation (1a), we can derive the flushing time of 9.1 d and 11.5 d with respect to the return flow factor 0.78 and 0.83. The derived flushing time will be used for estimating SGD in the \( ^{226}\text{Ra} \) mass balance model.

**SGD estimate based on \( ^{226}\text{Ra} \) mass balance model**

In order to quantify the fluxes of SGD into the northern Bohai Bay, a \( ^{226}\text{Ra} \) mass balance model was developed. The variation of \( ^{226}\text{Ra} \) in a coastal water body is a balance of inputs into the system and losses from the system. The sources of \( ^{226}\text{Ra} \) include SGD, rivers (dissolved \( ^{226}\text{Ra} \)), and desorption from suspended particulate matter (SPM),
diffusion from bottom sediments and ingrowth from parent isotopes. The loss of $^{226}\text{Ra}$ is primarily mixing with open sea, because the decay term of $^{226}\text{Ra}$ is not significant on the time scale of flushing time. We assumed that the water column was well mixed vertically; $^{226}\text{Ra}$ fluxes from rivers and desorption from suspended particles were neglected since the discharge of rivers was very low during the sampling period. In addition, the ingrowth for $^{226}\text{Ra}$ in seawater was neglected since the activity of $^{230}\text{Th}$ in seawater would be negligible. Thus, $^{226}\text{Ra}$ in this system was mainly influenced by SGD, diffusion from bottom sediments and mixing loss with the open sea, and the equation of $^{226}\text{Ra}$ mass balance model can be written as follows:

$$V_{\text{SGD}}^{^{226}\text{Ra}} + A_{\text{sed}}R^{^{226}\text{Ra}} = \frac{V^{^{226}\text{Ra}}_{\text{OS}} -^{^{226}\text{Ra}}_{\text{GW}}}{T_f}$$

where $V_{\text{SGD}}$ is the flux of groundwater (m$^3$ d$^{-1}$); $^{226}\text{Ra}_{\text{GW}}$, $^{226}\text{Ra}_{\text{OS}}$ and $^{226}\text{Ra}_{\text{GW}}$ are the $^{226}\text{Ra}$ activity in groundwater, surface seawater along two transects and offshore water (the background activity of $^{226}\text{Ra}$), respectively; $A_{\text{sed}}$ is the area of bottom sediments; $R^{^{226}\text{Ra}}$ is the regeneration rate of $^{226}\text{Ra}$ from sediments (dpm m$^{-2}$ d$^{-1}$); $T_f$ is the flushing time (d).

The average flux of $^{226}\text{Ra}$ from fine-grained sediments is very low compared with other three radium isotopes. Hancock et al. (2006) suggested the highest regeneration rate of $^{226}\text{Ra}$ from fine-grained sediments was 0.66 dpm m$^{-2}$ d$^{-1}$ in the Great Barrier Reef. The value of this rate used by Hancock et al. (2006) was applied approximately to estimate $^{226}\text{Ra}$ input from sediment diffusion. The area of the water-sediment interface of the study area ($A_{\text{sed}}$) is estimated to be $3.84 \times 10^6$ m$^2$, based on which a $^{226}\text{Ra}$ input from sediment diffusion of $2.53 \times 10^9$ dpm/d can be calculated (Table 2). To obtain the mixing loss, we used the lowest activity of $^{226}\text{Ra}$ measured at station S-4 as the seawater end-member, i.e. $^{226}\text{Ra}_{\text{GW}} = 32.97$ dpm 100 L$^{-1}$. Using the flushing time of 11.5 d, $^{226}\text{Ra}$ mixing loss was calculated to be $4.86 \times 10^{10}$ dpm d$^{-1}$. Given a representative value of 79.07 dpm 100 L$^{-1}$ for $^{226}\text{Ra}$ activity in coastal groundwater, we can determine a conservative SGD flux into the bay to be $4.83 \times 10^7$ m$^3$ d$^{-1}$ or $0.15$ m$^3$ m$^{-2}$ d$^{-1}$. All parameters needed in the model were listed in Table 2.

### Table 2: Parameter values used in SGD mass balance model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{226}\text{Ra}$ in groundwater end-member ($^{226}\text{Ra}_{\text{GW}}$)</td>
<td>79.07 dpm 100 L$^{-1}$</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$ in seawater end-member ($^{226}\text{Ra}_{\text{OS}}$)</td>
<td>32.97 dpm 100 L$^{-1}$</td>
</tr>
<tr>
<td>$^{226}\text{Ra}$ activity in surface seawater ($^{226}\text{Ra}_{\text{OS}}$)</td>
<td>52.20 dpm 100 L$^{-1}$</td>
</tr>
<tr>
<td>Area of bottom sediments</td>
<td>$3.84 \times 10^6$ m$^2$</td>
</tr>
<tr>
<td>The regeneration rate of $^{226}\text{Ra}$ ($R^{^{226}\text{Ra}}$)</td>
<td>0.66 dpm m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>Mean volume ($V$)</td>
<td>$2.30 \times 10^9$ m$^3$</td>
</tr>
<tr>
<td>Flushing time</td>
<td>11.5 d</td>
</tr>
<tr>
<td>SGD flux ($V_{\text{SGD}}$)</td>
<td>$4.83 \times 10^7$ m$^3$ d$^{-1}$</td>
</tr>
</tbody>
</table>

### Uncertainty analysis

Estimates of the SGD fluxes are always subject to inherent uncertainties associated with sampling and analytical measurements. In the $^{226}\text{Ra}$ model, the uncertainties of the SGD calculation mainly depend on the groundwater end-member and flushing time in the study area. Because the contribution of the diffusion from bottom sediments to the total $^{226}\text{Ra}$ flux was less than 1%, we can neglect the uncertainty caused by this term.

Defining the groundwater end-member activity is a crucial step in groundwater tracer studies and has been recognized as a major source of uncertainty (Peterson et al. 2008; Xu et al. 2015). The large groundwater end-member activity used in the model will cause a comparatively low SGD. Here, to assess the model uncertainty induced by this end-member selection, we conducted the model assuming 10% decrease of the end-member. In this case, the average SGD fluxes would increase by 11.1%.

The flushing time was based on the tidal prism mode via two independent estimates of the return flow factor. The short flushing time determined by scaling the water volume may result in high SGD rates. If a short flushing time was used (9.1 d) in our study, the corresponding modeled SGD flux would increase by 26.5%. Although there were large uncertainties in the groundwater end-member and flushing time, these values allowed us to estimate a conservative SGD flux into the bay. This value is comparable to the SGD fluxes in the regions of China’s northern coast (Table 3).
CONCLUSIONS

In this study, the flushing time and SGD flux in northern Bohai Bay were estimated for the first time using radium isotopes and salinity as geochemical tracers. We can draw the following conclusions. (1) The salinity and pH of the samples from transect I were slightly lower than those collected from transect II. This showed that freshwater discharge along transect I may be higher than that of transect II. (2) The estimated return flow factor (b) was 0.78 and 0.82 based on two independent methods. This yielded flushing times of 9.1 d and 11.5 d, respectively. (3) A SGD flux of $4.83 \times 10^7 \text{m}^3/\text{d}$ into northern Bohai Bay was obtained based on a $^{226}\text{Ra}$ mass balance model. It demonstrated that the primary input of radium to this system was SGD. The SGD, mentioned here, is a mixture of the terrestrial freshwater and the re-circulated seawater in the nearshore aquifer. The large volume of SGD confirms its importance in delivering nutrients to northern Bohai Bay. With new understanding of our assessment of SGD, the management of the bay related to water resources, ecology and environment in coastal and offshore areas should be reviewed. We hope that our results stimulate future work on these problems in this area.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (Grant No. 41025009 and 41272267). The authors thank Tao Zheng, Zhenfei Xu, Long Xi, Shengtao Zheng and Zhigang Cheng for their field laboratory work.

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Table 3 | Comparison of SGD fluxes with previous studies on the coast of China

<table>
<thead>
<tr>
<th>Sites</th>
<th>Methods</th>
<th>SGD (cm/d)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow Sea</td>
<td>$^{226}\text{Ra}$</td>
<td>0.3–1.7</td>
<td>Kim et al. (2005)</td>
</tr>
<tr>
<td>Yellow River Delta</td>
<td>$^{224,223,226}\text{Ra},^{222}\text{Rn}$</td>
<td>4.5–13.9</td>
<td>Peterson et al. (2008)</td>
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<td></td>
<td>Seepage meters</td>
<td>12.3–16.3</td>
<td>Taniguchi et al. (2008)</td>
</tr>
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<td>Changjiang effluent plume</td>
<td>$^{226}\text{Ra}$</td>
<td>3.1–14.6</td>
<td>Gu et al. (2012)</td>
</tr>
<tr>
<td>Dongshan Bay</td>
<td>$^{226}\text{Ra}$</td>
<td>24–230</td>
<td>Ji et al. (2012)</td>
</tr>
<tr>
<td>Jiaozhou Bay</td>
<td>$^{222}\text{Rn}$</td>
<td>6.4–8.3</td>
<td>Guo et al. (2013)</td>
</tr>
<tr>
<td>Xiangshan Bay, East China Sea</td>
<td>$^{222}\text{Rn}$</td>
<td>23–69</td>
<td>Wu et al. (2015)</td>
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<tr>
<td>Laizhou Bay</td>
<td>$^{226}\text{Ra}$</td>
<td>8.9–10.3</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>Northern Bohai Bay</td>
<td>$^{226}\text{Ra}$</td>
<td>13</td>
<td>This study</td>
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First received 13 July 2015; accepted in revised form 14 September 2015. Available online 25 September 2015.