

Quantification of the water age and submarine groundwater discharge in a typical semi-enclosed bay: Using stable oxygen (^{18}O) and radioactive radium (^{228}Ra) isotopes

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Abstract

Nutrient inputs through submarine groundwater discharge (SGD) play a significant role in sustaining primary productivity and nutrient cycling in coastal areas. Currently, various geochemical isotopes are used to trace the SGD processes. However, mass balance models of stable water isotopes (^2H and ^{18}O) are seldom used in SGD estimating. In this study, mass balance models of ^{18}O and radium isotopes were used to estimate the water age and SGD in Laizhou Bay, China based on the isotope data sampled in August 2017. The water age ranged from 23.5 to 50.0 days with an average of 32.1 ± 16.3 days. The SGD flux ranged from $1.29 \times 10^8 \text{ m}^3 \text{ d}^{-1}$ to $2.84 \times 10^8 \text{ m}^3 \text{ d}^{-1}$ with an average of $(2.07 \pm 1.04) \times 10^8 \text{ m}^3 \text{ d}^{-1}$. The sensitivity analysis revealed that estimated results of the water age and SGD are very sensitive to the ^{18}O value in evaporation, as well as ^{18}O and ^{228}Ra values in groundwater end-members. Based on the isotope method, the proportion of the Yellow River discharging into Laizhou Bay was estimated to be less than 27% of the total discharge. Furthermore, combining water and salt mass balance models, the submarine fresh groundwater discharge (SFGD) flux ranged from $0.54 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ to $1.31 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ with an average of $(0.93 \pm 0.46) \times 10^7 \text{ m}^3 \text{ d}^{-1}$. This study reveals that stable and radium isotopes can be effectively combined to estimate the water age and SGD, which may be applied to coastal areas elsewhere.

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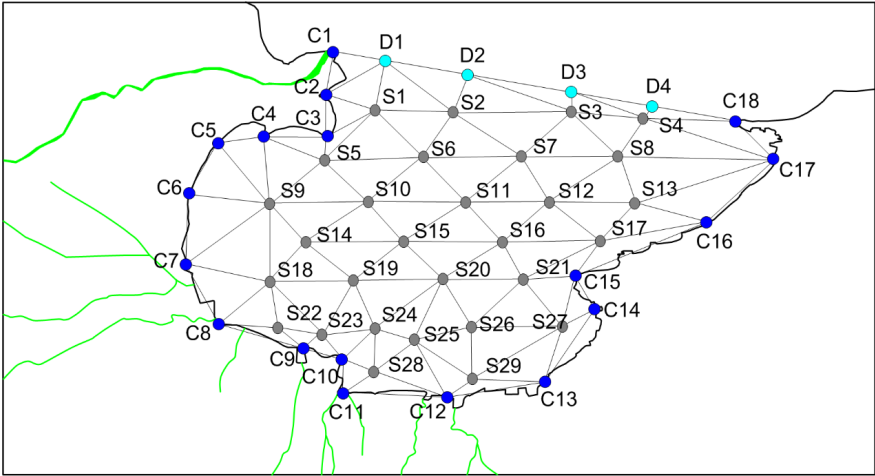


Figure S1. Triangle elements for calculations of the area, water volume, salt, ^{18}O and ^{228}Ra inventories in Laizhou Bay. The parameters of each triangle node are listed in Table S4.

Table S1. The location, water depth, salinity, ^{228}Ra activities, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and nutrient concentrations in seawater of Laizhou Bay in July 2017.

Sample	Longitude	Latitude	Depth (m)	Salinity PSU	^{228}Ra (dpm 100 L^{-1})	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (	TDN (μmol L^{-1})	TDP (μmol L^{-1})
S1	119.38	37.71	9.0	27.21	305.57 $\pm$ 21.39	-12.62	-1.18	NA	NA
S2	119.56	37.71	14.0	30.64	179.00 $\pm$ 12.53	-12.42	-1.28	26.99	6.90
S3	119.84	37.71	15.0	31.28	154.73 $\pm$ 10.83	-12.57	-1.11	21.14	3.10
S4	120.01	37.70	13.0	31.51	120.54 $\pm$ 8.44	-8.68	-0.95	22.41	4.86
S5	119.26	37.61	3.0	27.49	302.52 $\pm$ 21.18	-14.16	-1.52	30.49	8.53
S6	119.49	37.62	12.0	30.72	222.52 $\pm$ 15.58	-13.32	-1.24	107.07	40.23
S7	119.73	37.62	14.0	31.92	123.44 $\pm$ 8.64	-12.10	-1.22	331.64	6.94

Sample	Longitude	Latitude	Depth (m)	Salinity PSU	^{228}Ra (dpm 100 L^{-1})	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (	TDN (μmol L^{-1})	TDP (μmol L^{-1})
S8	119.95	37.62	13.0	31.91	148.75 $\pm$ 10.41	-9.63	-1.09	10.81	0.61
S9	119.13	37.52	3.0	25.21	161.38 $\pm$ 11.30	-16.36	-1.73	NA	NA
S10	119.36	37.53	9.0	29.28	191.45 $\pm$ 13.40	-13.04	-1.08	29.46	8.69
S11	119.59	37.52	12.0	31.21	171.19 $\pm$ 11.98	-11.60	-0.71	46.81	12.08
S12	119.79	37.52	13.0	30.89	170.65 $\pm$ 11.95	-11.64	-0.82	57.91	19.40
S13	119.99	37.52	13.0	30.52	127.91 $\pm$ 8.95	-6.44	-0.82	7.26	0.27
S14	119.22	37.44	7.0	30.14	202.46 $\pm$ 14.17	-18.12	-2.25	69.44	22.90
S15	119.45	37.44	10.0	31.34	222.60 $\pm$ 15.58	-14.16	-1.40	38.94	4.61
S16	119.68	37.44	11.7	31.34	215.36 $\pm$ 15.07	-12.59	-1.25	22.84	3.87
S17	119.91	37.44	10.0	31.65	136.57 $\pm$ 9.56	-11.32	-1.00	NA	NA
S18	119.13	37.36	5.0	27.83	171.39 $\pm$ 12.00	-17.68	-1.88	61.41	11.76
S19	119.33	37.36	10.0	28.86	285.02 $\pm$ 19.95	-14.66	-1.48	46.89	7.01
S20	119.54	37.38	10.0	30.26	279.05 $\pm$ 19.53	-15.14	-1.54	62.26	19.81
S21	119.73	37.37	8.4	30.55	225.61 $\pm$ 15.79	-12.85	-1.54	18.73	1.12
S22	119.15	37.27	4.0	26.97	238.92 $\pm$ 16.72	-22.16	-2.09	NA	NA
S23	119.26	37.25	4.0	30.15	295.57 $\pm$ 20.69	-16.02	-1.60	30.39	3.81

Sample	Longitude	Latitude	Depth (m)	Salinity PSU	^{228}Ra (dpm 100 L^{-1})	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (	TDN (μmol L^{-1})	TDP (μmol L^{-1})
S24	119.38	37.27	5.7	31.19	225.05 $\pm$ 15.75	-16.50	-1.45	28.28	3.12
S25	119.47	37.24	6.3	30.88	210.79 $\pm$ 14.76	-11.60	-1.25	15.60	0.33
S26	119.61	37.27	7.0	31.25	204.05 $\pm$ 14.28	-13.63	-1.31	25.28	3.87
S27	119.82	37.27	4.0	30.92	164.96 $\pm$ 11.55	-11.26	-1.15	13.74	0.13
S28	119.38	37.18	4.0	29.74	215.19 $\pm$ 15.06	-17.17	-1.92	32.49	0.20
S29	119.61	37.16	4.0	29.90	259.77 $\pm$ 18.18	-13.76	-1.79	31.46	4.19

NA: not available.

Table S2. The location, salinity, ^{228}Ra activities, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values and nutrient concentrations in groundwater in July 2017.

Sample	Longitude	Latitude	Salinity PSU	^{228}Ra (dpm 100 L^{-1})	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (	TDN ($\mu\text{mol L}^{-1}$)	TDP ($\mu\text{mol L}^{-1}$)	Si L^{-1}
GW01-L	119.55	37.12	30.00	700.14 $\pm$ 49.01	-13.35	-0.88	239.71	0.59	22
GW01-U	119.55	37.12	40.00	796.69 $\pm$ 55.77	-15.61	-1.08	330.36	5.54	51
GW02	119.78	37.16	27.34	643.71 $\pm$ 45.06	-19.14	-2.37	36.11	5.94	13
GW03-L	119.92	37.38	22.16	141.37 $\pm$ 9.90	-24.87	-3.52	316.36	4.99	93
GW03-U	119.92	37.38	25.30	235.05 $\pm$ 16.45	-24.59	-3.59	135.79	2.81	96
GW04-L	119.87	37.23	29.03	168.32 $\pm$ 11.78	-15.27	-1.21	185.00	1.52	41
GW04-U	119.87	37.23	26.18	808.24 $\pm$ 56.58	-19.77	-2.23	1078.57	111.48	53

Sample	Longitude	Latitude	Salinity PSU	^{228}Ra (dpm 100 L^{-1})	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (	TDN ($\mu\text{mol L}^{-1}$)	TDP ($\mu\text{mol L}^{-1}$)	Si L^{-1}
GW05-L	120.16	37.48	28.84	225.75 $\pm$ 15.80	-13.34	-1.64	NA	NA	NA
GW05-U	120.16	37.48	26.24	284.14 $\pm$ 19.89	-17.09	-2.05	249.07	9.50	15
GW06-L	120.25	37.67	30.18	461.50 $\pm$ 32.30	-11.94	-1.49	201.57	1.52	29
GW06-U	120.25	37.67	30.50	956.83 $\pm$ 66.98	-12.46	-1.07	279.93	68.32	33
GW08-L	120.75	37.82	27.20	157.27 $\pm$ 11.01	-15.26	-1.64	162.57	7.45	17
GW08-U	120.75	37.82	29.57	157.75 $\pm$ 11.04	-10.59	-1.09	115.71	10.93	13
GW07-L	120.44	37.74	24.98	460.38 $\pm$ 32.23	-19.86	-2.47	132.36	1.82	15
GW09	119.37	37.11	10.00	164.25 $\pm$ 11.50	-52.43	-7.05	80.43	1.44	13
GW10	119.21	37.22	25.00	270.92 $\pm$ 18.96	-22.28	-2.44	76.93	1.14	63
GW11-L	119.01	37.27	24.50	1112.17 $\pm$ 77.85	-17.54	-0.99	99.14	0.65	27
GW11-U	119.01	37.27	21.00	523.29 $\pm$ 36.63	-26.50	-3.24	780.71	88.13	75
GW13	118.91	37.43	>35	1396.77 $\pm$ 97.77	-30.21	-2.66	118.71	3.83	36
GW14	118.96	37.62	32.39	331.23 $\pm$ 23.19	-26.48	-3.10	75.29	2.06	22

NA: not available. The “-U” denotes samples taken from the high tide location. The “-L” denotes samples taken from the low tide location.

Table S3. The location, salinity, ^{228}Ra activities, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in river water in July 2017.

Sample	Longitude	Latitude	Salinity PSU	^{228}Ra (dpm 100 L ⁻¹)	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (
Sample	Longitude	Latitude	Salinity PSU	^{228}Ra (dpm 100 L ⁻¹)	$\delta^2\text{H}$ (	$\delta^{18}\text{O}$ (
R1	119.15	37.76	0.60	50.92 $\pm$ 3.56	-50.88	-6.61
R2	118.67	37.30	1.80	45.37 $\pm$ 3.18	-51.60	-6.74
R3	118.87	37.27	5.00	47.50 $\pm$ 3.32	-50.65	-6.56
R4	119.15	37.04	4.00	102.75 $\pm$ 7.19	-54.09	-6.95
R5	119.54	37.06	40.00	206.09 $\pm$ 14.43	-39.75	-4.63
R6	119.24	36.98	2.00	51.17 $\pm$ 3.58	-46.59	-6.12

Table S4. Triangle nodes for calculations of the area, water volume, salt, ^{18}O and ^{228}Ra inventories in Laizhou Bay.

Stations	Longitude	Latitude	Water depth	Salinity PSU	^{228}Ra (dpm 100 L ⁻¹)	$\delta^{18}\text{O}$ (
S1	119.38	37.71	9.0	27.21	305.57 $\pm$ 21.39	-1.18
S2	119.56	37.71	14.0	30.64	179.00 $\pm$ 12.53	-1.28
S3	119.84	37.71	15.0	31.28	154.73 $\pm$ 10.83	-1.11
S4	120.01	37.70	13.0	31.51	120.54 $\pm$ 8.44	-0.95
S5	119.26	37.61	3.0	27.49	302.52 $\pm$ 21.18	-1.52
S6	119.49	37.62	12.0	30.72	222.52 $\pm$ 15.58	-1.24
S7	119.73	37.62	14.0	31.92	123.44 $\pm$ 8.64	-1.22
S8	119.95	37.62	13.0	31.91	148.75 $\pm$ 10.41	-1.09
S9	119.13	37.52	3.0	25.21	161.38 $\pm$ 11.30	-1.73
S10	119.36	37.52	9.0	29.28	191.45 $\pm$ 13.40	-1.08
S11	119.59	37.52	12.0	31.21	171.19 $\pm$ 11.98	-0.71
S12	119.79	37.52	13.0	30.89	170.65 $\pm$ 11.95	-0.82
S13	119.99	37.52	13.0	30.52	127.91 $\pm$ 8.95	-0.82
S14	119.22	37.44	7.0	30.14	202.46 $\pm$ 14.17	-2.25
S15	119.45	37.44	10.0	31.34	222.60 $\pm$ 15.58	-1.40

Stations	Longitude	Latitude	Water depth	Salinity PSU	^{228}Ra (dpm 100 L ⁻¹)	$\delta^{18}\text{O}$ (
S16	119.68	37.44	11.7	31.34	215.36 ± 15.07	-1.25
S17	119.91	37.44	10.0	31.65	136.57 ± 9.56	-1.00
S18	119.13	37.36	5.0	27.83	171.39 ± 12.00	-1.88
S19	119.33	37.36	10.0	28.86	285.02 ± 19.95	-1.48
S20	119.54	37.37	10.0	30.26	279.05 ± 19.53	-1.54
S21	119.73	37.37	8.4	30.55	225.61 ± 15.79	-1.54
S22	119.15	37.27	4.0	26.97	238.92 ± 16.72	-2.09
S23	119.26	37.25	4.0	30.15	295.57 ± 20.69	-1.60
S24	119.38	37.26	5.7	31.19	225.05 ± 15.75	-1.45
S25	119.47	37.24	6.3	30.88	210.79 ± 14.76	-1.25
S26	119.61	37.27	7.0	31.25	204.05 ± 14.28	-1.31
S27	119.82	37.27	4.0	30.92	164.96 ± 11.55	-1.15
S28	119.38	37.18	4.0	29.74	215.19 ± 15.06	-1.92
S29	119.61	37.16	4.0	29.90	259.77 ± 18.18	-1.79
C1	119.28	37.83	0	27.21	305.57 ± 21.39	-1.18
C2	119.26	37.75	0	27.21	305.57 ± 21.39	-1.18
C3	119.27	37.66	0	27.49	302.52 ± 21.18	-1.52
C4	119.12	37.66	0	27.49	302.52 ± 21.18	-1.52
C5	119.01	37.65	0	25.21	161.38 ± 11.30	-1.73
C6	118.94	37.54	0	25.21	161.38 ± 11.30	-1.73
C7	118.94	37.40	0	25.21	161.38 ± 11.30	-1.73
C8	119.01	37.28	0	27.83	171.39 ± 12.00	-1.88
C9	119.21	37.23	0	26.97	238.92 ± 16.72	-2.09
C10	119.30	37.20	0	30.15	295.57 ± 20.69	-1.60

Stations	Longitude	Latitude	Water depth	Salinity PSU	^{228}Ra (dpm 100 L ⁻¹)	$\delta^{18}\text{O}$ (
C11	119.31	37.14	0	29.74	215.19 ± 15.06	-1.92
C12	119.55	37.13	0	29.90	259.77 ± 18.18	-1.79
C13	119.78	37.16	0	29.90	259.77 ± 18.18	-1.79
C14	119.90	37.31	0	30.92	164.96 ± 11.55	-1.15
C15	119.85	37.37	0	30.55	225.61 ± 15.79	-1.54
C16	120.16	37.48	0	30.52	127.91 ± 8.95	-0.82
C17	120.32	37.61	0	30.52	127.91 ± 8.95	-0.82
C18	120.23	37.69	0	31.51	120.54 ± 8.44	-0.95
D1	119.40	37.82	9.0	27.21	305.57 ± 21.39	-1.18
D2	119.60	37.79	14.0	30.64	179.00 ± 12.53	-1.28
D3	119.84	37.75	15.0	31.28	154.73 ± 10.83	-1.11
D4	120.03	37.72	13.0	31.51	120.54 ± 8.44	-0.95

“C” and “D” means a triangle node on the coastline corresponding to Fig. S1.

For stations C1-C18, the radium activities and salinity at each triangle node on the coastline were approximated by those at the nearest seawater station and the water depths at these nodes are set to be zero.

For stations D1-D4, ^{18}O value, ^{228}Ra activity, salinity and depth of these triangle nodes were calculated based on the distance-weighted method. The distance is between the triangle node and corresponding two or three near seawater stations.

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Abstract

Nutrient inputs through submarine groundwater discharge (SGD) play a significant role in sustaining primary productivity and nutrient cycling in coastal areas. Currently, various geochemical isotopes are used to trace the SGD processes. However, mass balance models of stable water isotopes (^2H and ^{18}O) are seldom used in SGD estimating. In this study, mass balance models of ^{18}O and radium isotopes were used to estimate the water age and SGD in Laizhou Bay, China based on the isotope data sampled in August 2017. The water age ranged from 23.5 to 50.0 days with an average of 32.1 ± 16.3 days. The SGD flux ranged from $1.29 \times 10^8 \text{ m}^3 \text{ d}^{-1}$ to $2.84 \times 10^8 \text{ m}^3 \text{ d}^{-1}$ with an average of $(2.07 \pm 1.04) \times 10^8 \text{ m}^3 \text{ d}^{-1}$. The sensitivity analysis revealed that estimated results of the water age and SGD are very sensitive to the ^{18}O value in evaporation, as well as ^{18}O and ^{228}Ra values in groundwater end-members. Based on the isotope method, the proportion of the Yellow River discharging into Laizhou Bay was estimated to be less than 27% of the total discharge. Furthermore, combining water and salt mass balance models, the submarine fresh groundwater discharge (SFGD) flux ranged from $0.54 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ to $1.31 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ with an average of $(0.93 \pm 0.46) \times 10^7 \text{ m}^3 \text{ d}^{-1}$. This study reveals that stable and radium isotopes can be effectively combined to estimate the water age and SGD, which may be applied to coastal areas elsewhere.

Keywords: Coastal groundwater; Hydrogen and oxygen isotopes; Radium isotopes; Submarine fresh groundwater discharge; Nutrient loading; Laizhou Bay

1. Introduction

Submarine groundwater discharge (SGD) has been recognized as an important component of the global water cycle, and it is a significant pathway for delivering terrestrial substances to the ocean (Moore, 1996; Burnett et al., 2003; Michael et al., 2016; Santos et al., 2021). The studies on SGD are increasingly carried out in different regions and countries around the world (Cho & Kim, 2016; Moosdorf & Oehler, 2017; Zhang et al., 2020). SGD typically comprises submarine fresh groundwater discharge (SFGD) and recirculated saline groundwater discharge (RSGD). Increasing studies have revealed that various environmental problems such as harmful algal blooms in coastal waters are closely related to SGD-associated nutrients (Lee & Kim, 2007; Luo & Jiao, 2016; Chen et al., 2020). Therefore, evaluating the magnitude of SGD and associated nutrient fluxes is vital for protecting and managing marine ecological environments in the coastal area.

The water age is essential to understanding the hydrodynamic processes, and it is also a key parameter in the calculation process of SGD. Radium isotopes have been widely used to estimate water age and SGD at different spatial and temporal scales (Moore et al., 2006; Rodellas et al., 2017; Wang et al., 2019). The radium-derived water ages represent the time it took for radium isotopes to enter into the system via their sources (Zhang et al., 2020). Moore (2000) built a simple but sagacious model based on radium isotopes to derive the water age of continental shelf. Moore et al. (2006) proposed another mass model of radium isotope by considering all sources and sinks to estimate the water age. The two models have been widely used to estimate the water age in coastal regions worldwide (Xu et al., 2013; Sadat-Noori et al., 2015; Petermann et al., 2018). However, different models have site-specific assumptions. For example, the model from Moore (2000) is not applicable to estuaries and salt marshes where radium additions from sediments and groundwater are continuous. The model of Moore et al. (2006) may be misused by quite a few successive investigators without checking all the site-specific conditions in their case study sites (Zhang et al., 2020). Therefore, evaluating the water age is still challenging because all the site-specific conditions need to consider in the coastal area.

Radium (Ra) isotopes are significantly enriched in both brackish groundwater and nearshore pore water, making Ra an ideal tool for tracing SGD processes in the coastal area (Garcia-Orellana et al., 2014; Tamborski et al., 2017; Nakajima et al., 2021). Stable hydrogen (^2H) and oxygen (^{18}O) isotopes are useful conservative tracers for the mixing processes at the groundwater-seawater interface because they clearly distinguish between terrestrial groundwater and seawater (Povinec et al., 2008). They have been increasingly used to construct an end-member mixing model to distinguish the source of groundwater discharge (Povinec et al., 2008; Chaillou et al., 2018; Wang et al., 2021). For example, Petermann et al. (2018) built four end-member mixing model of stable and

radioactivity isotopes to estimate fractions of seawater. Debnath et al. (2019) used two end-member mixing model of ^{18}O to distinguish groundwater from SGD. However, there are few studies to estimate SGD flux using mass balance models of stable isotopes in the coastal area.

The current study was conducted to estimate the water age and SGD by combining stable water and radium isotope mass balance models. This study was conducted in Laizhou Bay (China), a vertically well mixed semi-enclosed embayment. The SFGD flux was also estimated by combining water and salt mass balance models. Nutrient fluxes from SGD were estimated based on the estimated SGD flux,

1. Materials and methods

(a) Study area

Laizhou Bay (37.05° - 37.80°N , 118.90° - 120.35°E), one of three major bays of Bohai Sea, is located in the north of the Shandong peninsula in China (Fig. 1). Laizhou Bay has an overall surface area of $\sim 6000 \text{ km}^2$, and it is a typical semi-enclosed bay with an average water depth of 8 m and a maximum water depth of $\sim 15 \text{ m}$ at the east mouth of the bay (Wang et al., 2020a). The natural coastline of Laizhou Bay, with a length of $\sim 320 \text{ km}$, extends from the Qimu Cape to the Yellow River estuary. Seawater in the bay is vertically well mixed and can be treated as a single layer (Wang et al., 2015b; Wang et al., 2020a). The Yellow River, as the fifth largest river in the world, is the largest one discharging into Laizhou Bay. It carries large amounts of sediments, forming a cluster of sand bars at the river mouth (Xu et al., 2013; Wang et al., 2019). The mouth of the Yellow River is located between Bohai Bay and Laizhou Bay.

The tides in the region are composed of a mixture of semidiurnal and diurnal components, which are also affected by the natural development of the Yellow River delta and the coastline changes resulting from large-scale anthropogenic land reclamation and fishing farms (Pelling et al., 2013).

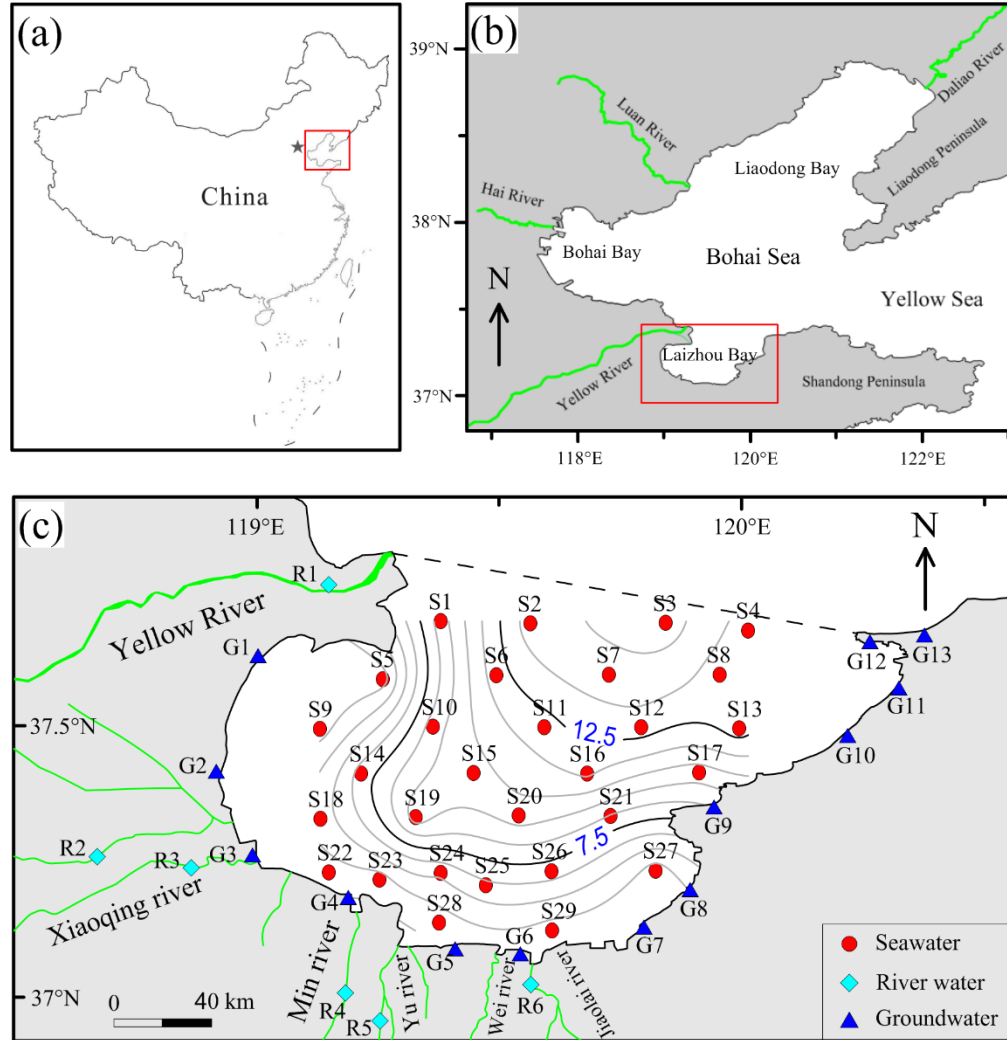


Fig. 1. Map of study area: (a) the relative locations of Bohai Sea to Mainland China; (b) the specific location of Laizhou Bay in Bohai Sea; (c) the spatial distribution of sampling locations. The lines with marked numbers 7.5 and 12.5 are water depth (m) contours with respect to mean sea level. The red circles, blue triangle and green diamond indicate the sampling locations of seawater, groundwater and river water, respectively.

1. Sampling and analytical methods

The sampling campaign was conducted in August 2017. The sampling stations are shown in Fig.1. Samples of Ra isotopes were collected from the methods proposed by Moore & Reid (1973). Seawater samples (60 L) for Ra isotopes were collected at depths of 2 m below the water surface. River water samples

(30 L) for Ra isotopes were collected at a depth of 1 m below the water surface. Groundwater samples (2-10 L) for Ra isotopes were taken using a push-point sampler at the depths ranging from 0.5 m to 1.5 m in the intertidal zone. Water samples for Ra isotopes were filtered through ~25 g of manganese-coated acrylic fiber (Mn-fibers) at a flow rate of less than 1 L min⁻¹ to absorb dissolved Ra (Moore & Reid, 1973). These Mn-fibers were then washed thoroughly using distilled water to remove any particles and salts.

Water samples for stable isotopes (¹⁸O and ²H) at each station were filtered through a 0.45- μ m membrane filter. Samples for stable isotopes were collected in 15-mL polyethylene bottles with no headspace. Nutrient samples were also filtered through a 0.45- μ m membrane filter. All samples were stored at 4-6°C until laboratory measurements. In addition, water samples for salinity and temperature at each station were measured in situ using a handheld HI9828 multi-parameter water quality meter (HANNA).

The activity of ²²⁸Ra was measured by Radium Delayed Coincidence Counter (RaDeCC) using the method proposed by Moore & Arnold (1996). The activity of ²²⁸Ra was determined by measuring ²²⁸Th ingrown from ²²⁸Ra and calculating the initial ²²⁸Ra (Moore et al., 2008; Charette et al., 2008). The uncertainty of ²²⁸Ra in the lab system was ~7%. The values of stable water isotopes were determined by off-axis integrated cavity output spectroscopy (OA-ICOS) (LGR, DLC-100). The ¹⁸O and ²H measurements were reported relative to the Vienna Standard Mean Ocean Water (VSMOW). The ¹⁸O and ²H values were reported in the conventional delta (‰) notation and in per mil (‰). The analytical precisions were 0.1‰ for ¹⁸O and 0.3‰ for ²H.

1. Theoretical models

2.3.1 Stable isotope mass balance

Under steady-state conditions, water inputs in the system were mainly from precipitation, river and submarine fresh groundwater discharge. Water outputs in the system included mixing with open sea water and evaporation. Stable isotope mass balance model was based on water mass balance model (Petermann et al., 2018). The ²H was not used here because it is relatively high sensitivity in temperature and humidity (Stalker et al., 2009) and it was well correlated with ¹⁸O ($R^2=0.99$, $n=54$). Therefore, ¹⁸O mass balance model can be expressed as equation (1).

(1)

where Q_{SGD} is SGD flux; Q_{river} is river discharge; Q_{in} and Q_{out} are input and output of water from precipitation and evaporation; δ_{SGD} , δ_{river} and δ_{sea} are ¹⁸O values in SGD, river water and open sea water, respectively. δ_{precip} and δ_{evap} are ¹⁸O values in precipitation and evaporation, respectively. V_{bay} is the inventory of ¹⁸O in the bay; V_{total} is the total water volume in the bay; τ is water age of the bay. Here, δ values are defined as isotopic ratios reflecting deviation in per mil from Vienna-SMOW (Standard Mean Ocean Water) (Gibson et al., 2016).

In equation (1), δ , ϵ , α , and β can be directly measured. Direct observation of the isotopic composition of evaporating water, δ , is not technically feasible, but can be estimated using the linear resistance model proposed by Craig & Gordon (1965):

$$(2)$$

where h is the relative humidity normalized to surface water temperature (decimal fraction), α is the total fractionation factor (; Krabbenhoft, 1990; Stets et al., 2010); ϵ is the diffusion controlled or the kinetic fractionation factor (; Krabbenhoft, 1990); β is an empirical constant relating to the kinetic fractionation factor and relative humidity and it was 14.3 (Gibson and Reid, 2010); α is the equilibrium isotopic fractionation factor at the temperature of the air-water interface, which is related to temperature (T) as (Stets et al., 2010); δ is the isotopic composition of atmospheric moisture, which can be estimated by (Stets et al., 2010).

2.3.2 Radium mass balance

Ra sources in the system were mainly from SGD, rivers, diffusion from bottom sediments and atmospheric dust. River inputs include the dissolved portion and desorbed portion from suspended particulate matter (SPM). In this study, we only considered SPM in the Yellow River, which accounted for >90% of total SPM flux in Laizhou bay. Ra sinks in the system generally included radioactive decay and mixing loss with open sea water. Especially, in the approach proposed by Peterson et al. (2008), the average of two low-activity values of Ra in the bay water is used as an indicator of the background activity. These background activities can be regarded as containing the contributions from bottom sediments and atmospheric dust. Here, ^{228}Ra was selected to build a mass balance model because it has a long-life and low uncertainty; the decay loss of ^{228}Ra can be neglected. Therefore, ^{228}Ra mass balance model in the system can be expressed as equation (2).

$$(5)$$

Where A , B , and C are ^{228}Ra activity in SGD, river water and open sea water, respectively; I is the inventory of ^{228}Ra in the bay; λ is the decay constant of ^{228}Ra .

2.3.3 Calculations of the water age and SGD

All the parameters in equations (1) and (3) can be derived or estimated from the data collected and the literature. The only exceptions are the water age and SGD flux. We thus combined equations (1) and (3) to solve the unknown parameters (i.e., the water age and SGD flux).

2.3.4 Calculation of SFGD

From the method proposed by Wang et al. (2015b), SFGD flux can be estimated by combining water mass balance and salt mass balance:

$$(6)$$

where S is the inventory of salt in the bay; σ is the salinity in open sea water.

1. Results

(a) Salinity, ^{228}Ra and stable isotope distributions

Data for salinity, ^{228}Ra and stable (^2H and ^{18}O) isotopes in seawater are shown in Supporting Table S1. During the sampling period, the salinity of seawater ranged from 25.21 to 31.92 with an average value of 30.10. The salinity generally increased from the nearshore areas to the mouth of the bay (Fig. 2a). The salinity was distinctly higher in the east than that in the west (Fig. 2a), which may be related to the freshwater from the Yellow River.

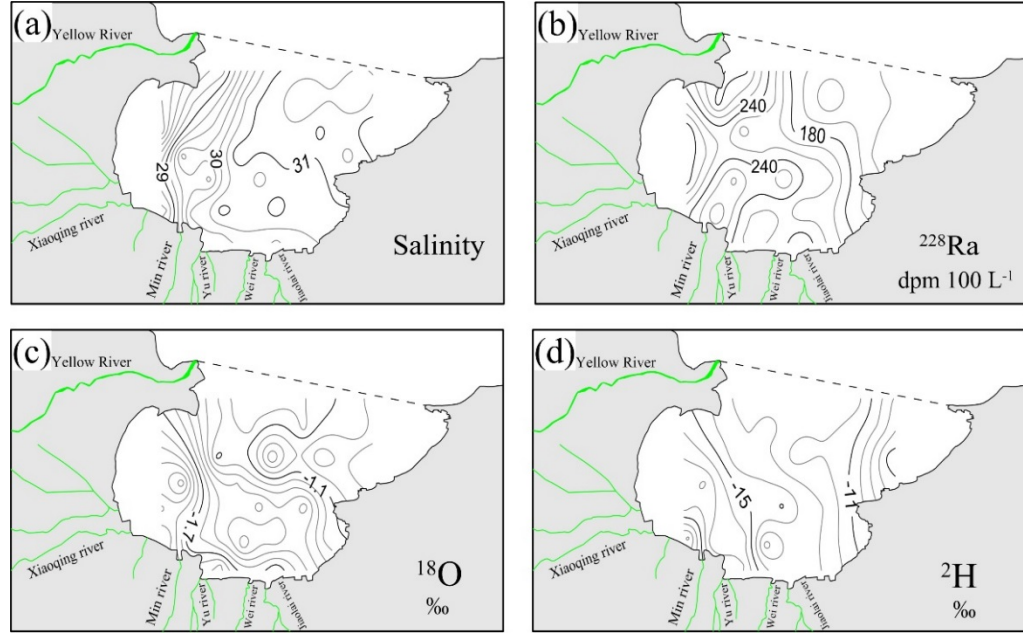


Fig. 2. Spatial distributions of salinity, ^{228}Ra and stable isotopes (^2H and ^{18}O) in seawater

Activities of ^{228}Ra in seawater ranged from 120.54 to 305.57 dpm 100 L⁻¹ with an average value of 204.55 dpm 100 L⁻¹. Activities of ^{228}Ra generally decreased from the nearshore areas to the mouth of the bay (Fig. 2b). The elevated activities of ^{228}Ra were located near the southern coast and the mouth of the Yellow River.

The values of ^2H in seawater ranged from -22.16 to -6.44 ‰ with an average value of -13.49 ‰. The value of ^{18}O in seawater ranged from -2.25 to -0.71 ‰ with an average value of -1.36 ‰. The ^2H and ^{18}O had the similar distributions with salinity.

Data for salinity, ^{228}Ra and stable (^2H and ^{18}O) isotopes in groundwater and river water are shown in Supporting Table S2 and S3. Figs 3a-3c show the relationships between ^{228}Ra and stable isotopes versus salinity in all samples.

Activities of ^{228}Ra in groundwater were higher than those in seawater and river water, suggesting that the groundwater discharge may be a major source of ^{228}Ra in the bay. On the other hand, values of ^2H and ^{18}O in river water were significantly lower than those in groundwater and seawater. The high depletion of ^2H and ^{18}O in river water suggests significantly evaporation rates in river water. Values of ^2H and ^{18}O in all samples ($^2\text{H}=6.9593 \times ^{18}\text{O}-4.3432$, $R^2=0.9668$) deviated from the global meteoric water line (GMWL) and the local meteoric water line (LMWL), also suggesting the influence of evaporation.

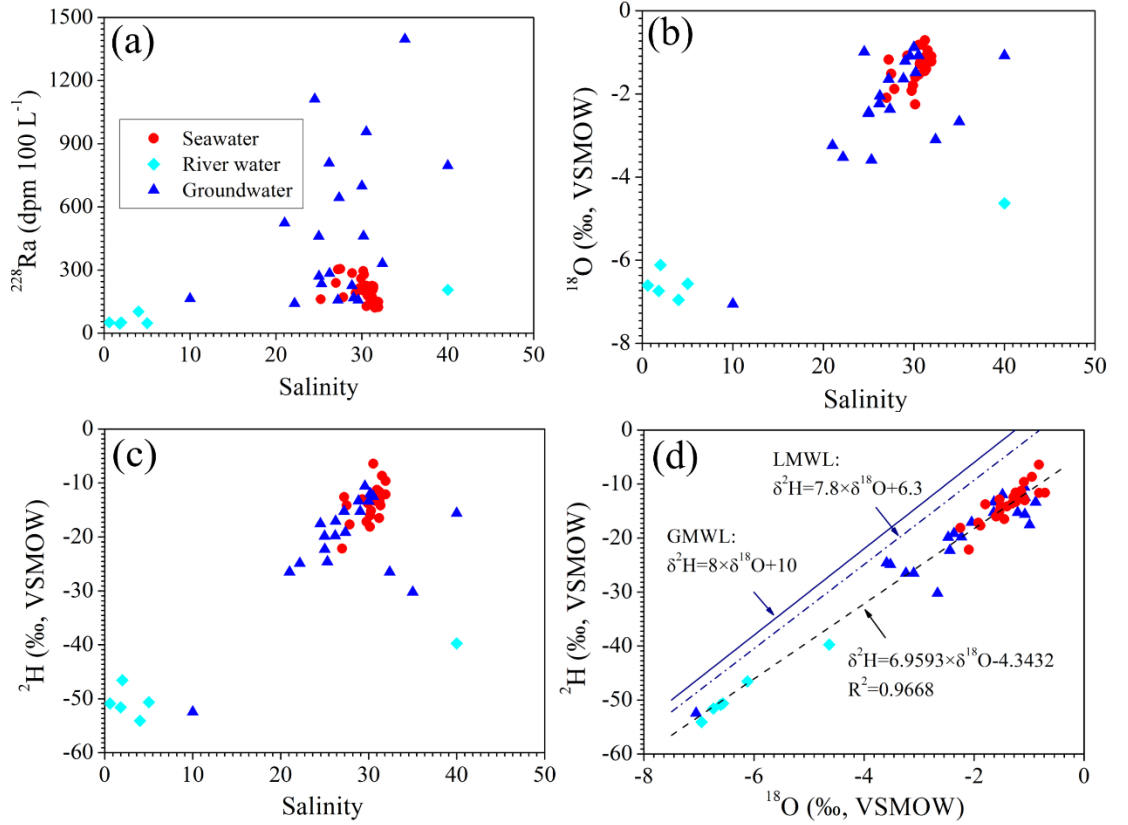


Fig. 3. Salinity, ^{228}Ra and stable isotopes in all samples (a) ^{228}Ra versus salinity; (b) ^{18}O versus salinity; (c) ^2H versus salinity; (d) ^2H versus ^{18}O . The global meteoric water line (GMWL) was from Craig (1961) and the local meteoric water line (LMWL) was from Han et al. (2011).

3.2 Fluxes of ^{228}Ra and ^{18}O from rivers

The flux of ^{228}Ra from the river generally consists of the dissolved portion and desorption portion from suspended sediments. The Yellow River delivers large amounts of water and suspended sediments to the Bohai Sea (Yang et al., 2019). The discharge of the Yellow River in August 2017 was $8.48 \times 10^8 \text{ m}^3 \text{ d}^{-1}$. The

flux of SPM from the Yellow River in August 2017 was $2.07 \times 10^7 \text{ kg d}^{-1}$. These data of the Yellow River was obtained from the Yellow River Water Resources Bulletin published by the Yellow River conservancy commission of the Ministry of Water Resources of China in 2017. Combining the desorption rate of 2000 dpm kg^{-1} for ^{228}Ra from SPM (Moore et al., 2008; Wang et al., 2019), the total flux of ^{228}Ra from the Yellow River was estimated to be $(5.58 \pm 0.62) \times 10^{10} \text{ dpm d}^{-1}$. The discharge of rivers other than the Yellow River during the corresponding sampling period was $2.70 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. The flux of ^{228}Ra from rivers other than the Yellow River was estimated to be $(2.14 \pm 0.62) \times 10^9 \text{ dpm d}^{-1}$.

The flux of ^{18}O from the Yellow River was estimated to be $-1.87 \times 10^8 \text{ ‰}$. The flux of ^{18}O from rivers other than the Yellow River during the sampling period was estimated to be $-1.70 \times 10^7 \text{ ‰}$.

3.3 Inventories of ^{228}Ra and ^{18}O

The evaluation of ^{228}Ra (or ^{18}O) inventory is key to estimate SGD when using the mass balance model because it directly significantly affects the mixing loss with open sea water (Savatier & Rocha, 2021). In this study, the study area was divided into 78 sections (triangular elements) so that each of the sampling stations is a vertex of a triangular element (Supporting Fig. S1). The inventory of ^{228}Ra (or ^{18}O) in the total study area was calculated as the sum of ^{228}Ra (or ^{18}O) inventory in each triangular element. The ^{228}Ra (or ^{18}O) inventory in each triangular element was calculated as the product of the volume of the seawater and the average activities of ^{228}Ra (or ^{18}O) at three vertices of the triangular element. The volume of the seawater in each triangular element was calculated as the product of the area of the corresponding triangular element and the averaged seawater depths at the three vertices of the element.

The total seawater area and volume of Laizhou Bay were estimated to be $6.87 \times 10^9 \text{ m}^2$ and $4.62 \times 10^{10} \text{ m}^3$, respectively. Inventories of ^{228}Ra and ^{18}O were estimated to be $(8.87 \pm 0.62) \times 10^{13} \text{ dpm}$ and $-5.72 \times 10^{10} \text{ ‰}$, respectively.

3.4 Values of ^{18}O in the evaporation and precipitation

Samples of ^{18}O in seawater deviated significantly from the LMWL as a consequence of isotopic enrichment of seawater due to evaporate (Fig. 3d). Here, the value of ^{18}O in the evaporation was estimated from equation (2). Parameter values in equation (2) are shown in Table 1. The value of ^{18}O in the evaporation in Laizhou Bay was then estimated to be -23.47 ‰ . Gibson et al. (2016) estimated the value of ^{18}O in the evaporation ranging from -20.00 ‰ to -54.15 ‰ in coastal and continental areas. Our estimated result was within the ranges of their results.

The value of ^{18}O in the precipitation was -7.0 ‰ from the direct measurement based on the rainfall monitored at Yantai stations in Shandong province, China (Han et al., 2011).

3.5 Values of ^{228}Ra and ^{18}O in the open sea water

The activity of ^{228}Ra in the open sea water was determined using the lowest-activity ^{228}Ra at station S4. Similarly, the value of ^{18}O in the open sea water is determined using the value of ^{18}O at station S4. The station S4 was closest to the open sea and farthest from the coastline among all the offshore stations (Fig. 1). Therefore, the activity of ^{228}Ra in the open sea water was 120.54 dpm 100 L^{-1} , and the value of ^{18}O in the open sea water was -0.95 ‰.

1. Discussion

4.1 Water age and SGD estimations

The parameter values in equations (1) and (3) are listed in Table 2. Fig. 4a shows how the water age changes with the proportion of the Yellow River input into Laizhou Bay (β). One can see that the water age increases as β increases. When $\beta = 0$, the water age was estimated to be 23.5 ± 11.8 d. Hainbucher et al. (2004) modeled seawater circulation in the Bohai Sea and determined the water age (defined as “turnover time”) in different areas of the Bohai Sea. Their results suggest that Laizhou Bay’s water age is in the range of 15-40 d. Based on the radium isotope model and the tidal prism method, Wang et al. (2015b) obtained a water age estimation of 36.6 ± 5.3 d of Laizhou Bay. Wang et al. (2020a) estimated the water age of Laizhou Bay ranging from 15 to 50 d using radium quartet mass balance models. From above-mentioned estimated water age of Laizhou Bay, it is reasonable to assume that the water age of Laizhou Bay is less than 50 d. Combining our estimated water age, therefore, we can conclude the water age of Laizhou Bay ranging from 23.5 to 50.0 d with an average of 32.1 ± 16.3 d. Thus, we can obtain the reasonable value of β ranging from 0 to 0.27 with an average of 0.14. Namely, the proportion of the Yellow River discharging into Laizhou Bay was less than 27% of the total discharge during the sampling period. The Yellow River mouth is northerly-oriented, which may limit the input of the Yellow River into Laizhou Bay (Xu et al., 2013). Wang et al. (2015b) also reported the value of β was less than 0.14 in August 2012 from the radium isotope method.

Fig. 4b shows how the SGD flux changes with the proportion of the Yellow River input into Laizhou Bay (β). One can see that the SGD flux decreases as β increases. When $\beta = 0$, the SGD flux was estimated to be $(2.84 \pm 1.42) \times 10^8\text{ m}^3\text{ d}^{-1}$. Based on the above estimated ranging from 0 to 0.27, the SGD flux ranged from $2.84 \times 10^8\text{ m}^3\text{ d}^{-1}$ to $1.29 \times 10^8\text{ m}^3\text{ d}^{-1}$ with an average of $(2.07 \pm 1.04) \times 10^8\text{ m}^3\text{ d}^{-1}$. The estimated SGD flux was an order of magnitude larger than the discharge of the Yellow River during the sampling period.

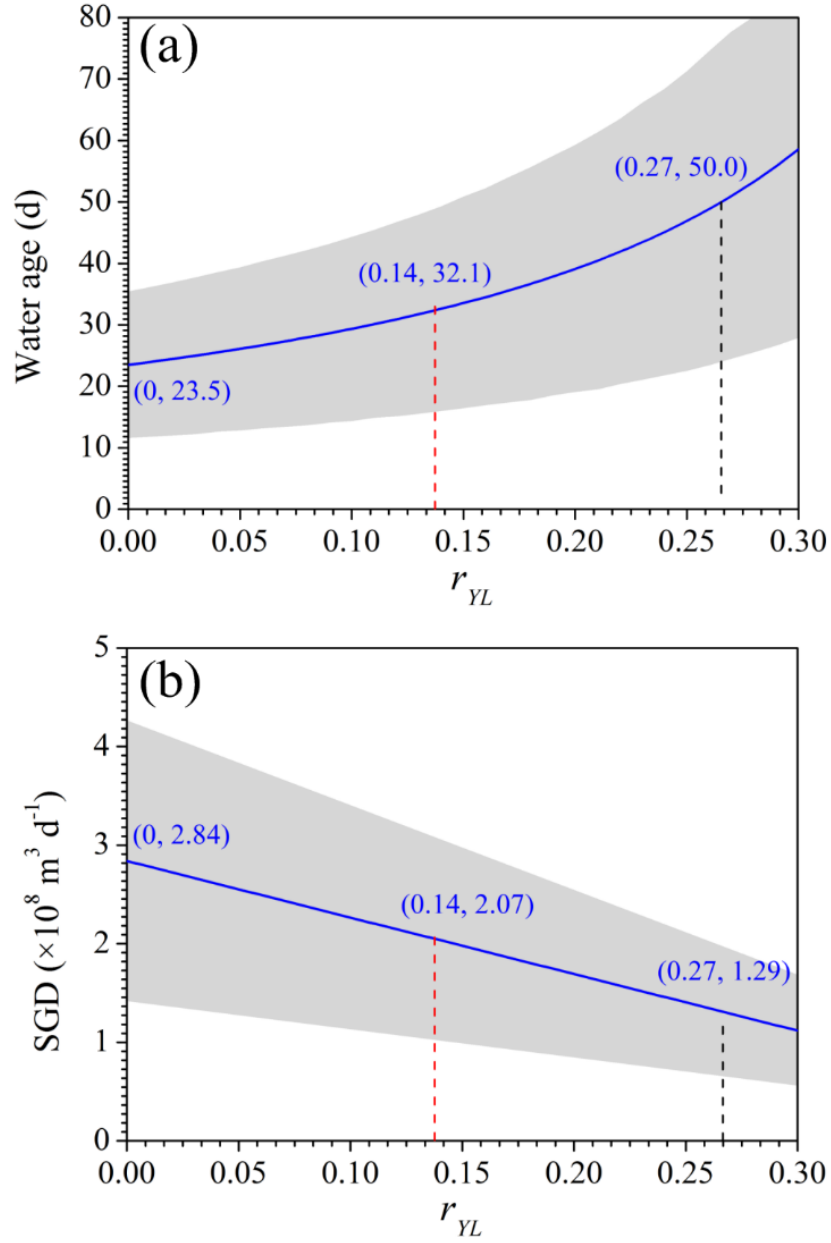


Fig. 4. Changes of water age (a) and SGD (b) with the proportion of the Yellow River input into Laizhou Bay. The value of ranged from 0 to 0.27. The red vertical dashed line represents the average value of . The blue bands bounded by the pair of dotted-lines represent the error ranges.

4.2 SFGD estimation

Fig. 5 shows how the SFGD flux changes with the proportion of the Yellow River input into Laizhou Bay (r_{YL}). One can see that the SFGD flux decreases as r_{YL} increases. When $r_{YL} = 0$, the SGD flux was estimated to be $(1.31 \pm 0.65) \times 10^7 \text{ m}^3 \text{ d}^{-1}$. Based on the above estimated ranging from 0 to 0.27, the SFGD flux ranged from $0.54 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ to $1.31 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ with an average of $(0.93 \pm 0.46) \times 10^7 \text{ m}^3 \text{ d}^{-1}$. Compared with the estimated SGD, the value of r_{YL} had a significant influence on the estimated SFGD. The estimated SFGD flux was 0.19-0.45 times the discharge of the Yellow River during the sampling period. From Fig. 5, one can also see that the value of r_{YL} was less than 0.46, which suggests that it is reasonable to assume the water age of Laizhou Bay ranging from 0 to 0.27.

In addition, the ratio of SFGD to SGD ranged from 4.3% to 4.6% with an average of 4.5%. On the other hand, RSGD is the main component of SGD. Previous regional investigations also reported that SFGD typically represents less than 10% of the total SGD at several sites worldwide (Beck et al., 2008; Tanuguchi et al., 2008; Santos et al., 2011).

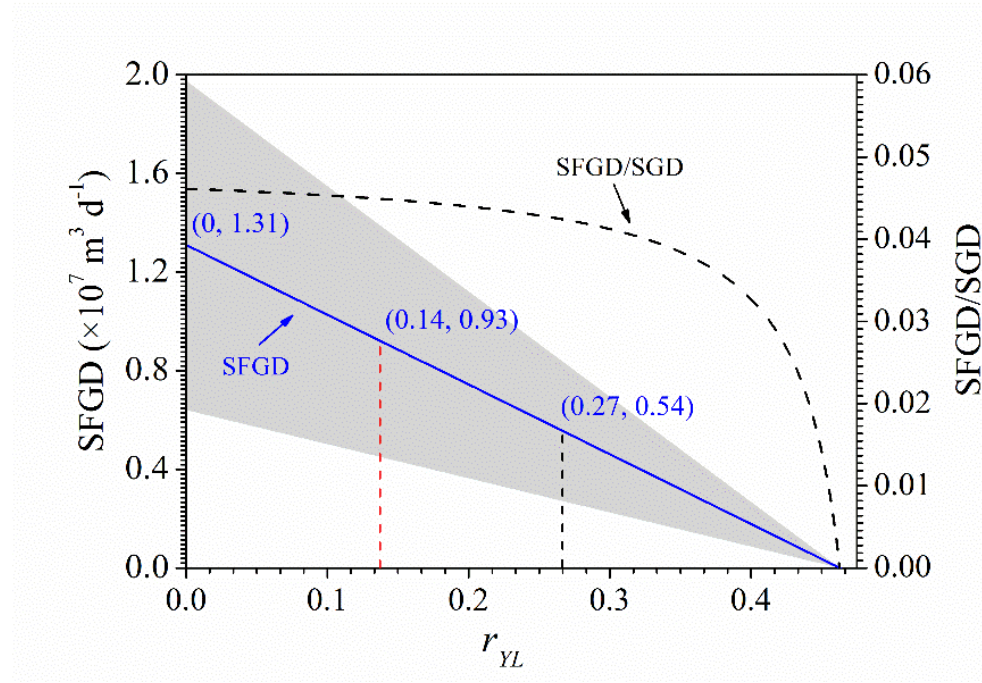


Fig. 5. Changes of SFGD and SFGD/SGD with the proportion of the Yellow River input into Laizhou Bay. The ratio of SFGD to SGD is shown on the right-axis. The value of r_{YL} ranged from 0 to 0.27. The red vertical dashed lines represent the average value of r_{YL} . The red vertical dashed line represents the average value of r_{YL} .

4.3. Comparisons with previous studies

Table 3 shows the estimated SGD flux in Laizhou Bay in several previous studies during different periods. Our results, if using the same unit, ranged from 2.2 to 4.7 cm d⁻¹. The differences among these reported results mainly may be attributed to different tracers and methods as well as the sampling periods. For example, in general, the relatively high SGD flux estimated by ²²²Rn mass balance is because ²²²Rn traces the total SGD including fresh and brackish groundwater (Luo & Jiao, 2016). Radium isotopes mainly trace the brackish groundwater discharge. On the other hand, previous studies have revealed seasonal variations of SGD (e.g., Moore et al., 2006; Wang et al., 2015a). These variations may be related to precipitation and sea level change (Wang et al., 2015a; Chen et al., 2017). Overall, our results were within the ranges of the results reported by previous studies.

Wang et al. (2019) used radium isotopes to estimate SGD flux in Bohai Bay, China. They estimated that SGD flux of Bohai Bay ranged 2.0 to 4.8 cm d⁻¹. Our result was similar to the SGD flux of Bohai Bay, where the hydrological conditions are similar to those of Laizhou Bay. In addition, the coastline length of Laizhou Bay was 320 km (Wang et al., 2020a). When scaled to the coastline length, the SGD flux ranged from 4.0×10^7 m³ m⁻¹ d⁻¹ to 8.9×10^7 m³ m⁻¹ d⁻¹. Our result was at the same order of magnitude of the global average SGD flux (Kwon et al., 2014). These would provide additional confidence in the result estimated by combining stable water and radium isotope mass balances models.

4.4 Uncertainty and sensitivity analysis

Selecting representative end-members of ¹⁸O and ²²⁸Ra in mass balance models is of great importance to estimate the water age and SGD. In this study, we used sensitivity analysis to discuss the impact of different end-members on the estimated results. Since the value of was unknown, both the minimum value =0 and maximum value =0.27 were used in the following discussion.

Sensitivity analysis was performed to examine the contribution of single parameter to the water age and SGD by increasing and decreasing the parameter by 10% without changing the other parameters. In this study, end-members of ¹⁸O and ²²⁸Ra in precipitation, evaporation, river and groundwater were selected for the sensitivity analysis. Table 4 and Table 5 show sensitivity analysis of the calculated water age and SGD, respectively. Sensitivity analysis shows that ¹⁸O in precipitation, evaporation and groundwater end-members, as well as ²²⁸Ra in groundwater end-member have a large influence on both the water age and SGD. In general, ¹⁸O in precipitation can be directly measured, while direct observation of ¹⁸O in evaporation is not technically feasible (Gibson et al., 2016). The value of ¹⁸O in evaporation can be estimated using the theoretical model. Therefore, determining ¹⁸O value in the evaporation is crucial for estimating the water age and SGD.

On the other hand, ²²⁸Ra is continuously produced by the decay of uranium and thorium parents in aquifers. ²²⁸Ra is generally adsorbed onto the particle surface

in freshwater. When exposed to brackish or saline water, ^{228}Ra rapidly desorbs from the particle surface (Webster et al., 1995; Gonneea et al., 2008). Due to heterogeneity in sediment composition and salinity distribution, the activity of ^{228}Ra in coastal groundwater could show several orders of magnitude variability (Michael et al., 2011; Duque et al., 2019). In this study, the highest activity of ^{228}Ra was an order of magnitude higher than the lowest one. The value of ^{18}O in groundwater at different depths were mainly affected by evaporation. Therefore, the value of ^{18}O in groundwater can vary widely at the regional scale. Overall, both determining ^{18}O value in evaporation and selecting ^{18}O and ^{228}Ra in groundwater end-members are crucial for estimating the water age and SGD.

4.5 Nutrient fluxes from SGD

Many studies showed that SGD can transport large fluxes of nutrient from land to ocean (Sadat-Noori et al., 2015; Wang et al., 2020b; Selvam et al., 2021). Given that the estimated SGD flux was an order of magnitude larger than the discharge of the local largest river, the Yellow River, SGD may have the significant influence on delivering nutrients to the ocean. In this study, to obtain a conservative estimate of SGD associated nutrient fluxes, the average SGD flux of $(2.07 \pm 1.04) \times 10^8 \text{ m}^3 \text{ d}^{-1}$ was used to calculate. The nutrient fluxes from SGD were calculated as the product of SGD flux and the difference of nutrient concentrations between groundwater and seawater (Wang et al., 2017).

Average nutrient concentrations of TDN, TDP and Si in groundwater were $2.5 \times 10^{-4} \text{ mol L}^{-1}$, $1.7 \times 10^{-5} \text{ mol L}^{-1}$ and $2.5 \times 10^{-4} \text{ mol L}^{-1}$, respectively. Average nutrient concentrations of TDN, TDP and Si in seawater were $4.6 \times 10^{-5} \text{ mol L}^{-1}$, $5.4 \times 10^{-5} \text{ mol L}^{-1}$ and $7.9 \times 10^{-6} \text{ mol L}^{-1}$, respectively. Thus, nutrient fluxes through SGD can be estimated to be $(4.1 \pm 2.1) \times 10^7 \text{ mol d}^{-1}$ for TDN, $(2.0 \pm 1.0) \times 10^6 \text{ mol d}^{-1}$ for TDP and $(4.0 \pm 2.0) \times 10^7 \text{ mol d}^{-1}$ for Si. In general, nutrient is non-conservative behavior due to complex biogeochemical processes and water-rock interactions in groundwater, such as mineralization, nitrification, denitrification and redox reaction (Zhang et al., 2016). Therefore, nutrient fluxes using this method only serve as a rough estimate of input, not absolute input.

The nutrient fluxes from the Yellow River were estimated by multiplying the nutrient concentrations in the Yellow River and the corresponding discharge. Average concentrations of TDN, TDP and Si in the Yellow River were $1.7 \times 10^{-4} \text{ mol L}^{-1}$, $0.5 \times 10^{-6} \text{ mol L}^{-1}$ and $5.5 \times 10^{-5} \text{ mol L}^{-1}$. Thus, nutrient fluxes from Yellow River were $4.7 \times 10^6 \text{ mol L}^{-1}$ for TDN, $1.5 \times 10^4 \text{ mol L}^{-1}$ for TDP, and $1.5 \times 10^6 \text{ mol L}^{-1}$ for Si. In this study, nutrient fluxes from SGD were higher than those from the Yellow River. Therefore, SGD is recognized as a significant pathway for delivering solute materials from land into the ocean and it may have important effects on the ecosystem environments.

1. Conclusions

This study demonstrated a method for estimating the water age and SGD by

combining stable and radium isotope mass balance models. The method was applied in Laizhou Bay, China. The estimated water age ranged from 23.5 to 50.0 days, and the estimated SGD flux ranged from $1.29 \times 10^8 \text{ m}^3 \text{ d}^{-1}$ to $2.84 \times 10^8 \text{ m}^3 \text{ d}^{-1}$. When using this method, both the ^{18}O value in evaporation, and ^{18}O and ^{228}Ra values in groundwater end-members were crucial for estimating the water age and SGD. The geochemical behaviors of stable water and radium isotopes are typically different in groundwater. For a comprehensive understanding of SGD processes, multiple isotope integrated studies is greatly need. By combining water and salt mass balance models, we also estimated SFGD flux in Laizhou Bay. The estimated SFGD flux ranged from $0.54 \times 10^7 \text{ m}^3 \text{ d}^{-1}$ to $1.31 \times 10^7 \text{ m}^3 \text{ d}^{-1}$. The SFGD flux was 0.19-0.45 times the discharge of the Yellow River during the sampling period. Nutrient fluxes from SGD were shown to be significantly higher than those from the Yellow River, which may have important effects on the ecosystem environments.

In addition, based on the isotope method, we estimated the proportion of the Yellow River input into Laizhou Bay. The estimated proportion ranged from 0 to 27%. The proportion would offer instructional information in the management of water resources and sediments in the Yellow River estuary in the future study.

Data Availability Statement

The data used to produce the results of this study are available online (https://zenodo.org/record/4902941#.YLso_7czapo).

Acknowledgments

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Table 1 Definitions of parameters and values used in equation (2) to estimate the isotopic composition of evaporating water

Parameter	Definition	Value
T	the surface water temperature	22
h	the relative humidity	0.78
K	an empirical constant relating the kinetic fractionation factor and relative humidity ^a	14.3

Parameter	Definition	Value
Δ	the kinetic fractionation factor	3.15
	the total fractionation factor	12.85
*	the equilibrium isotopic fractionation factor at the temperature of the air-water interface	0.99
A	the isotopic composition of atmospheric moisture	-5.45
E	the isotopic composition of evaporating water	-24.4

^a referring to data from Stets et al. (2010).

Table 2 Parameters and values used in ^{228}Ra and ^{18}O mass balance models.

Parameter	Value	Definition
V_{bay}	4.62×10^{10}	Water volume in the bay (m^3)
P_T	5.72×10^7 ^a	Precipitation ($\text{m}^3 \text{d}^{-1}$)
E_T	2.27×10^7 ^a	Evaporation ($\text{m}^3 \text{d}^{-1}$)
I_{Ra}	8.87×10^{13}	Inventory of ^{228}Ra in the bay (dpm)
I_O	-5.72×10^{10}	Inventory of ^{18}O in the bay (‰)
Q_{YL}	2.83×10^7	Discharge of the Yellow River ($\text{m}^3 \text{d}^{-1}$)
Q_r	2.70×10^6	Total discharge of other rivers ($\text{m}^3 \text{d}^{-1}$)
M_{sus}	2.38×10^7	Flux of the SPM from the Yellow River (kg d^{-1})
des	2000	^{228}Ra desorption rate (dpm kg^{-1})
$^{228}\lambda$	3.27×10^{-4}	Decay coefficient of ^{228}Ra (d^{-1})
P	-8.0	Value of ^{18}O in precipitation (‰)
T	-24.4	Value of ^{18}O in evaporation (‰)
O	-0.95	Value of ^{18}O in open sea water (‰)
YL	-6.61	Value of ^{18}O in the Yellow River (‰)
r	-6.30	Average value of ^{18}O in other rivers (‰)
SGD	-2.29	Value of ^{18}O in groundwater (‰)
$^{228}Ra_O$	120.54	Activity of ^{228}Ra in open sea water (dpm 100 L^{-1})
$^{228}Ra_{YL}$	50.92	Activity of ^{228}Ra in the Yellow River (dpm 100 L^{-1})
$^{228}Ra_r$	79.28	Average activity of ^{228}Ra in other rivers (dpm 100 L^{-1})
$^{228}Ra_{SGD}$	499.79	Value of ^{18}O in groundwater (dpm 100 L^{-1})

^a The precipitation and evaporation can be calculated as the sum of the total area of study region and average daily precipitation and evaporation occurred during August 2017.

Table 3 Comparison of SGD with previous studies in Laizhou Bay.

Laizhou Bay, China	Method	Sampling period
The Yellow River delta	Radium and radon isotopes Seepage meters	May in 2005, September in 2004 and 2005
A tidal flat of Laizhou Bay (Haimiao)	Darcy's law	September in 2014

Laizhou Bay, China	Method	Sampling period
The eastern Laizhou Bay	^{222}Rn	September in 2014
The entire Laizhou Bay	$^{223}, ^{226}\text{Ra}$	August in 2012
	^{224}Ra	August in 2012
	$^{223}, ^{224}, ^{226}, ^{228}\text{Ra}$	July-August in 2012 (wet)
		March-April in 2014 (dry)
	O^{18} and ^{228}Ra	August in 2017

Table 4 Sensitivity analysis of the water age. For this analysis, the value of each list below was increased (+) and decreased (-) by 10%, while the other parameters remained unchanged.

Term (end-member)	% change in the water age with a:	
	% increase in term value	% decrease in term value
Y_L	+16	
r	+5	
p	+549	-55
T	-60	+308
SGD	+77	-81
$^{228}\text{Ra}_{Y_L}$		
$^{228}\text{Ra}_r$		
$^{228}\text{Ra}_{SGD}$	-73	+86
r	+2	
p	+133	-36
T	-41	+224
SGD	+81	-81
$^{228}\text{Ra}_r$		
$^{228}\text{Ra}_{SGD}$	-74	+90

Table 5 Sensitivity analysis of the SGD. For this analysis, the value of each list below was increased (+) and decreased (-) by 10%, while the other parameters remained unchanged.

Term (end-member)	% change in SGD flux with a:	
	% increase in term value	% decrease in term value

Term (end-member)	% change in SGD flux with a:	
YL		+14
r		+5
p	-126	+126
T	+152	-152
$^{SGD}_{228}Ra_{YL}$	-45	+435
$^{228}Ra_r$		
$^{228}Ra_{SGD}$	+249	-42
r		+2
p	-57	+57
T	+69	-69
$^{SGD}_{228}Ra_r$	-45	+435
$^{228}Ra_{SGD}$	+249	-42