

Unexpectedly high dissolved ^{210}Pb in coastal groundwaters: Is submarine groundwater discharge important in coastal sea?

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ABSTRACT

Estimating ^{210}Pb sources/sinks is significant for understanding the transport processes and chronology of sediment in coastal seas. Although submarine groundwater discharge (SGD) has been recognized as an important pathway for the transport of terrestrial chemical components, the ^{210}Pb source in coastal seas from SGD is generally ignored. In the present work, we built the ^{210}Pb budget by analyzing the ^{210}Pb activity concentrations in submarine groundwater (i.e., coastal well water and pore water), river water, and seawater in a typical aquaculture bay along the Chinese coast in the Beibu Gulf (Qinzhou Bay). The results showed that the ^{210}Pb activity concentrations (Bq/m^3) in well water, porewater, seawater and river water were 6.0 ± 3.6 ($n = 13$), 3.8 ± 0.4 ($n = 2$), 1.2 ± 0.3 ($n = 4$), and 1.9 ± 0.6 ($n = 3$), respectively. The SGD-derived ^{210}Pb flux was calculated to be $(3.3 \pm 0.4) \times 10^{10} \text{ Bq}/\text{yr}$ (approximately 1.4 times the river input flux), which accounted for $\sim 18\%$ of the total ^{210}Pb sources in Qinzhou Bay. Although most of the ^{210}Pb ($>66\%$) would be buried into the sediment of this coastal bay, SGD-discharged dissolved ^{210}Pb can account for approximately half of the ocean mixing, which is the second most important ^{210}Pb sink in Qinzhou Bay. Therefore, based on these estimates, we have shown that the ^{210}Pb input from SGD can be an important source at the coastal sea scale and needs to be accounted for in coastal sea areas.

1. Introduction

Coastal seas act as major barriers retaining large amounts of terrestrial material, particularly reactive species such as suspended solids, trace metals or nutrients, from continents before reaching the open oceans (Benninger, 1978). To establish the solute fluxes between the coastal zone and the open ocean, it is necessary to construct appropriate balances. ^{210}Pb and its daughters (naturally occurring ^{238}U decay series) are widely used in estimating particulate organic carbon flux (Anand et al., 2018; Su et al., 2017; Tang et al., 2019), sediment dating (Rubin et al., 1994; Sha et al., 2017), drainage basin erosion (Battarbee et al., 1985; Matisoff, 2014), and sediment budget and transport (Du et al.,

2016; Gao et al., 2017; Qiao et al., 2017; Su and Huh, 2002; Wang et al., 2018), for which the quantitative evaluation of ^{210}Pb sources and sinks becomes challenging but indispensable work.

Previously, when using ^{210}Pb to trace sediment sources and to construct sediment budgets, most researchers focused on three important ^{210}Pb inputs: (1) atmospheric, (2) riverine and (3) offshore transport (Du et al., 2016; Gao et al., 2017; Qiao et al., 2017; Su and Huh, 2002; Wang et al., 2018). Some other sources are often considered to be negligible, including release from sediments, in situ ^{210}Pb production from ^{226}Ra and shoreline erosion (Benninger, 1978). However, submarine groundwater discharge (SGD) has been recognized as an important factor in land-sea material exchange (e.g., nutrients, carbon, and

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radionuclides) (Cho et al., 2018; Santos et al., 2019; Chen et al., 2020), and it may have a magnitude comparable to or exceeding those of river-water driven fluxes (Moore, 1996; Burnett et al., 2003; Kim et al., 2005a; Rodellas et al., 2015; Taniguchi et al., 2019). Therefore, SGD may be a considerable source of ^{210}Pb into coastal seawater, although it has been historically disregarded (e.g., Du et al., 2016; Gao et al., 2017; Qiao et al., 2017; Su and Huh, 2002; Wang et al., 2018).

A few studies have focused on the SGD-driven ^{210}Pb source. An example is Benninger (1978), who evaluated fresh groundwater inflow to Long Island Sound, although in that study area, the input from submarine fresh groundwater discharge (SFGD) appeared to be negligible compared to the riverine supply, but the other recirculated saline groundwater discharge (RSGD) was ignored. In a Mediterranean wetland (Peníscola marsh, Spain), SGD represented the major source of ^{210}Pb in wetland waters, and SGD was responsible for the significant increases in ^{210}Po and ^{210}Pb contents in both fishes and plants from the studied wetland (García-Orellana et al., 2013).

In this study, the relevance of SGD as a source of ^{210}Pb in Qinzhou Bay is evaluated using the concentrations of ^{210}Pb in groundwater (including coastal well water and pore water), river water, seawater, and previously estimated SGD water flows.

2. Materials and methods

2.1. Study area

The study area, Qinzhou Bay, is located in the north of the Beibu Gulf and was selected because it provides excellent geographic and geomorphic conditions (e.g., the calabash-shaped structure, the low hill coastal platform, the north high south low topography), and there are detailed hydrological data. The Qinzhou Bay coast is an alluvial plain with loose rock porewater as the groundwater type, and the occurrence form of porewater in loose rocks is mainly phreatic water. The lithology of the aquifer solid in Qinzhou Bay coastal areas is mainly Quaternary clay, subclay, subsandy soil, sand and sand gravel layers (Chen et al., 2016). Additionally, the SGD rate has been well investigated and has been previously reported (Luo, 2018; Chen et al., 2018a, 2018b). The semiclosed inner part of Qinzhou Bay is the Maowei Sea, which is

connected with the outer part of the bay through a narrow channel (Fig. 1). The channel sustains the exchange of tidal water and suspended particles between these two parts. Counteracted by its neck-like inlet, the velocity of the tides in the Maowei Sea is much lower than that in the outer part of Qinzhou Bay, resulting in alluvial deposition of river input and formation of coasts (Meng et al., 2016). The tides in Qinzhou Bay are irregular diurnal tides, with an average tidal range of 2.5 m and a maximum tidal range of 5.5 m (Chen et al., 2018a; Meng et al., 2016). The nearshore regions of Qinzhou Bay are relatively shallow, with an average water depth of 10 m (Guo et al., 2020). There are two major rivers in Qinzhou Bay (Maolingjiang River and Qinjiang River), which deliver approximately $4.6 \times 10^9 \text{ m}^3/\text{yr}$ of fresh water and $7.4 \times 10^8 \text{ kg/yr}$ of suspended sediment (Kang et al., 2017; Li and Haung, 2018) into the inner bay (Maowei Sea). The average annual rainfall is 1900 mm (Tian and Liang, 2016), and 80–85% of the annual precipitation falls in the wet season (April–September) (Meng et al., 2016). There are some earlier investigations in this bay that focused on SGD flux and SGD-associated nutrient (Chen et al., 2018a; Luo, 2018) and carbon fluxes (Chen et al., 2018b), nutrient biogeochemical cycling (Yang et al., 2019; Zhang et al., 2019), and bacterial and archaeal assemblages in SGD (Chen et al., 2019).

2.2. Sampling

Coastal groundwater samples were collected along Qinzhou Bay from wells and mudflats near the sea during May and June 2019, respectively (Fig. 1). Porewater samples (PW) were collected near the shore (~40 cm below the sediment-water interface, ~10 L), and well water samples (GW) (~10 L) were filled into clean and acid-treated polyethylene drums. Before sampling, porewaters and well waters were purged to ensure that we could collect the fresh groundwaters. River water samples (~10 L) were collected using a clean plastic bucket in the upstream regions (Fig. 1). pH, dissolved oxygen (DO) and salinity were measured with a WTW Multi 3630 (WTW, Germany) in the field. After collection, samples were immediately transported to the Marine Laboratory of Beibu Gulf University for subsequent processing and radionuclide (i.e., ^{210}Po , ^{210}Pb , ^{222}Rn , and radium isotopes) analyses.

Twenty liter of seawater samples (SW) were collected using a

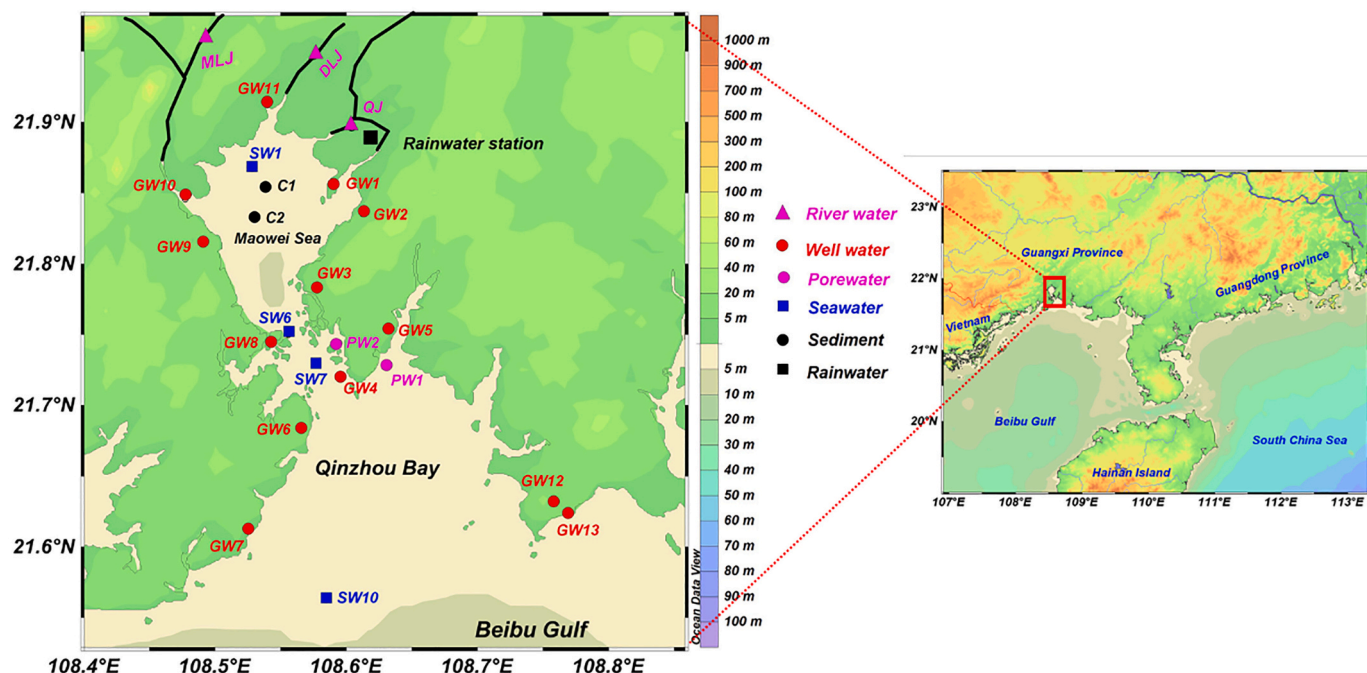


Fig. 1. Map of the study area and sampling stations. Note that MLJ, DLJ, and QJ denote the Maolingjiang River, Dalanjiang River and Qinjiang River, respectively.

submerged pump from 1 to 2 m depth below the surface. Two surface (0–3 cm) sediment samples (C1 and C2) were collected with a Van Veen grab sampler using a small vessel in the Maowei Sea. A suspended particulate matter (SPM) sample was collected from the Qinjiang River in June 2016 (see sampling details in Luo et al. (2019)).

2.3. ^{210}Pb analysis

The analytical methods for ^{210}Pb analyses are described in Zhong et al. (2020). The water samples were immediately filtered through 0.45 μm membrane filters and bubbled vigorously for half an hour to remove the residual ^{222}Rn gas. The filtered samples were acidified immediately to pH 1–2 with HNO_3 and soon after spiking with ~ 2 dpm of ^{209}Po (1526-81-1, Eckert & Ziegler Isotope Products) and Pb^{2+} (20 mg). Fe^{3+} (200 mg) was added, and after letting the samples equilibrate for a few hours, Po and Pb were coprecipitated with $\text{Fe}(\text{OH})_3$ by raising the pH to 8 with NH_4OH . After settling and centrifugation, the supernatant was discarded, and the precipitate was dissolved within 60 mL of 0.5 M HCl. ^{210}Po and ^{209}Po in dilute HCl solution were autoplated onto a silver disc immersed in the solution. Then, the disc was removed from the solution, rinsed gently with Milli-Q water and ethanol and air dried. ^{210}Po and ^{209}Po on the disc were measured by using ultralow background α -spectrometers with 12 PIPS detectors (Alpha Analyst, Canberra 7200, Canberra Industries, USA). After analysis for ^{210}Po , the remaining ^{210}Po and ^{209}Po in the solutions were cleaned by suspending another new silver disc, and the solution was stored for 6 months to allow for ^{210}Po ingrowth. After storage, another 2 dpm ^{209}Po was added to the solution, and the newly produced ^{210}Po isotope was autodeposited onto a third new silver disc, similar to the first autodeposition. The ^{209}Po and ^{210}Po activities were also measured by using the same ultralow background α -spectrometer. Pb^{2+} recoveries were determined by using ICP-OES (iCAP 7400). Based on these two autoplating for Po isotopes and ingrowth and decay corrections, the in situ ^{210}Pb activities in

groundwaters and seawaters were obtained at the time of sampling (Baskaran et al., 2013; Rigaud et al., 2013).

The treatment and analysis method of ^{210}Pb on sediment and SPM samples were described in detail in Du et al. (2016) and Wang et al. (2018). In short, dried sediments and river SPM samples were ground and sealed for at least 3 weeks in a closed plastic box, and the concentrations of total ^{210}Pb (46.5 keV) and ^{226}Ra (351.9 keV and 609.1 keV) were measured by HPGe γ -spectrometry (Canberra Be3830). Excess ^{210}Pb (i.e., not supported by the ^{226}Ra present in the sediment; $^{210}\text{Pb}_{\text{ex}}$) was obtained by subtracting the measured ^{226}Ra activity from the total ^{210}Pb activity. The IAEA-385 standard sediment was used to calibrate the efficiency of the γ -spectrometry at regular intervals of every three months.

3. Results

Salinity, dissolved oxygen (DO), pH and ^{210}Pb concentrations are shown in Table 1. The salinities of well water samples along the Qinzhou Bay coast were <0.3 (Table 1). Seawater salinity ranged from 9.5 to 29.5 from the inner bay to the outer bay. Salinities in porewaters in the intertidal zone (23.5–29.6) were close to those in seawater samples (20.2–29.5, except station SW1, which had a salinity of 9.5). The pH of well water samples ranged from 5.00 to 6.74 (mean: 6.07 ± 0.64 , $n = 13$), while the pH of rainwater was 7.20, similar to the pH of river water (mean: 7.20 ± 0.07 , $n = 3$) and porewater (mean: 7.10 ± 0.10 , $n = 2$). The DO concentrations (mg/L) in groundwater samples (range: 0.50–7.74, mean: 3.20 ± 1.53 , $n = 14$) were much lower than those in seawater (range: 8.70–8.72, mean: 8.71 ± 0.01 , $n = 4$) and river water (range: 6.11–7.15, mean: 6.66 ± 0.43 , $n = 3$). The much lower DO concentration in the groundwater indicated that the groundwater along Qinzhou Bay was in a reducing environment.

The ^{210}Pb concentrations in well water, porewater, seawater and river water ranged from 0.8 to 13.5 Bq/m^3 (mean: $6.0 \pm 3.6 \text{ Bq/m}^3$, $n =$

Table 1
 ^{210}Pb concentrations in well water, porewater, seawater and river water.

Station	Sampling Date	Longitude °E	Latitude °N	DO mg/L	pH	Salinity	$^{210}\text{Pb} \text{ Bq/m}^3$
Well water (GW)							
GW1	2019/5/20	108.589	21.855	7.74	6.74	0	0.8 ± 0.1
GW2	2019/5/20	108.612	21.835	3.90	6.62	0	2.2 ± 0.1
GW3	2019/5/20	108.577	21.782	2.22	5.25	0	4.6 ± 0.2
GW4	2019/5/20	108.595	21.720	3.81	6.49	0.2	4.7 ± 0.2
GW5	2019/5/20	108.632	21.754	2.90	5.25	0	12.3 ± 0.5
GW6	2019/5/21	108.565	21.684	2.91	5.94	0	9.2 ± 0.4
GW7	2019/5/21	108.526	21.612	3.33	6.71	0.3	2.3 ± 0.1
GW8	2019/5/21	108.544	21.744	3.48	6.44	0.1	5.1 ± 0.3
GW9	2019/5/21	108.491	21.815	2.67	6.72	0.1	6.3 ± 0.3
GW10	2019/5/23	108.477	21.845	2.44	5.27	0	13.5 ± 0.5
GW11	2019/5/23	108.540	21.912	0.50	6.53	0	5.1 ± 0.3
GW12	2019/6/20	108.759	21.631	3.79	5.90	0.2	4.0 ± 0.3
GW13	2019/6/20	108.767	21.623	3.15	5.00	0	7.3 ± 0.4
Porewater (PW)							
PW1	2019/5/20	108.629	21.727	2.00	7.00	29.6	3.4 ± 0.2
PW2	2019/5/21	108.591	21.744	NA	7.20	23.5	4.2 ± 0.2
Seawater (SW)							
SW1	2019/5/22	108.528	21.867	8.70	7.55	9.5	1.6 ± 0.1
SW6	2019/5/22	108.556	21.750	8.71	7.69	20.2	1.0 ± 0.1
SW7	2019/5/22	108.577	21.731	8.71	7.81	24.6	0.9 ± 0.1
SW10	2019/5/22	108.584	21.563	8.72	8.04	29.5	1.1 ± 0.1
River water (RW)							
DLJ	2019/5/23	108.576	21.946	6.73	7.22	0.2	2.7 ± 0.1
MLJ	2019/5/23	108.493	21.959	7.15	7.28	0.1	1.2 ± 0.1
QJ	2019/5/20	108.604	21.896	6.11	7.10	2.9	1.6 ± 0.1

Note: DLJ = Dalanjiang River; MLJ = Maolingjiang River; QJ = Qinjiang River; NA = not available.

13), 3.4 to 4.2 Bq/m³ (mean: 3.8 ± 0.4 Bq/m³, $n = 2$), 0.9 to 1.6 Bq/m³ (mean: 1.2 ± 0.3 Bq/m³, $n = 4$), and 1.2 to 2.7 Bq/m³ (mean: 1.9 ± 0.6 Bq/m³, $n = 3$), respectively (Table 1 and Fig. 2a). The order of ²¹⁰Pb concentrations in these water samples is well groundwater > porewater > river water > seawater (Fig. 2b), suggesting that a potential source of ²¹⁰Pb in the bay could be groundwater discharge and that SGD may have a great influence on ²¹⁰Pb budgets in Qinzhou Bay.

Total ²¹⁰Pb (²¹⁰Pb_{tot}) and ²²⁶Ra activities in sediments and SPM samples are shown in Table 2. ²²⁶Ra activity in both sediment samples was similar: C1 = 31.2 ± 0.7 Bq/kg and C2 = 28.3 ± 1.0 Bq/kg. The concentration of ²²⁶Ra (50.9 ± 1.8 Bq/kg) in the SPM sample reported by Luo et al. (2019) was approximately two times higher than that in sediments. The ²¹⁰Pb_{ex} activity of seaward sediment (C2: 121.3 ± 4.1 Bq/kg) was much higher than that of nearshore sediment (C1: 62.9 ± 2.4 Bq/kg) and SPM (22.2 ± 6.2 Bq/kg) in the river, as expected.

4. Discussion

4.1. Geochemical behavior of ²¹⁰Pb in waters of Qinzhou Bay

SGD comprises SFGD and RSGD (Burnett et al., 2003; Li et al., 1999). SGD-driven fluxes of elements of interest can be obtained by multiplying the Ra-derived SGD rate and the concentrations of those elements in the SGD endmember (Beck et al., 2009; Jeong et al., 2012; Rodellas et al., 2014). Selecting suitable endmember values is often the main uncertainty in estimating SGD-derived solute fluxes (Chen et al., 2018a, 2018b; Cook et al., 2018). The heterogeneous nature of the spatial and temporal distribution of SGD and the variability of the element concentrations in the aquifers make it difficult to identify a representative SGD endmember (Santos et al., 2008; Wang et al., 2019).

When SGD carries elevated concentrations of terrestrial radionuclides, nutrients, and heavy metals to the coastal sea, especially at the salinity transition zone of an intertidal aquifer, geochemical processes occurring in the mixing zone can affect groundwater composition (Trezzi et al., 2016; Liu et al., 2019). Variations in redox condition and pH values can play an important role in heavy metal cycling (element concentration change or species transformation) in groundwater (Beck et al., 2010; Liu et al., 2019; Wang et al., 2019). To define the SGD endmember, Wang et al. (2019) and Rodellas et al. (2014) used the average metal concentrations in coastal groundwaters after subtracting the contribution from seawater. Beck et al. (2009) proposed that for

some metals, the “effective zero-salinity endmember” can be estimated from the linear distribution between metal concentration and salinity. Some studies have suggested that the average concentrations of trace elements in porewater or fresh groundwater can be directly used as SGD endmembers to conservatively estimate the SGD-driven metal fluxes (Beck et al., 2009; Jeong et al., 2012; Windom et al., 2006), while others have identified representative endmembers for fresh groundwater and recirculated porewater to account for the differences in concentrations between both SGD components (Alorda-Kleinglass et al., 2019). In any case, the selection of the ²¹⁰Pb endmember should be determined by considering the behavior of ²¹⁰Pb in coastal aquifers and the dominant SGD processes occurring in the study site.

In this study, we examined the distributions of ²¹⁰Pb relative to pH, DO and salinity (Fig. 3) to obtain some insights relative to its geochemical behavior. The ²¹⁰Pb concentration decreased significantly with increasing pH from terrestrial groundwater (pH: 5.0–7.0) to seawater (pH: 7.5–8.0) (Fig. 3a), similar to the observations for Pb by Rodellas et al. (2014), suggesting that pH controls the scavenging behavior of ²¹⁰Pb. When ²¹⁰Pb is transported from coastal aquifers (fresh groundwater, pH < 6.7) to porewater (pH ~7.2), ²¹⁰Pb is potentially scavenged and deposited in the subterranean estuary (where porewater is sampled) (Beck et al., 2009; Zhong et al., 2020). Therefore, if we define the intertidal salinity transition zone as the boundary for heavy metal (Wang et al., 2019) or ²¹⁰Pb budget evaluation, then the ²¹⁰Pb concentration in porewater samples can be considered the SGD endmember to derive the SGD-driven ²¹⁰Pb flux. For surface waters, from the river to the offshore seawater, the ²¹⁰Pb activity concentration decreased with salinity, which indicated that ²¹⁰Pb shows quasi-conservative geochemical behavior (conservative mixing line: $R = 0.67$, $P < 0.05$) (Fig. 3d). Therefore, it is suitable to choose river samples with low salinity (nearly 0) as endmembers when calculating the river discharged ²¹⁰Pb flux.

4.2. Sources of ²¹⁰Pb in Qinzhou Bay

Potential sources of ²¹⁰Pb to coastal seawater include (1) SGD, (2) riverine discharge, and (3) atmospheric deposition. Additional sources of ²¹⁰Pb, such as in situ production from the mother nuclide ²²²Rn, direct sewage discharge, release of dissolved ²¹⁰Pb from sediments, and ocean mixing, are also discussed in the following sections.

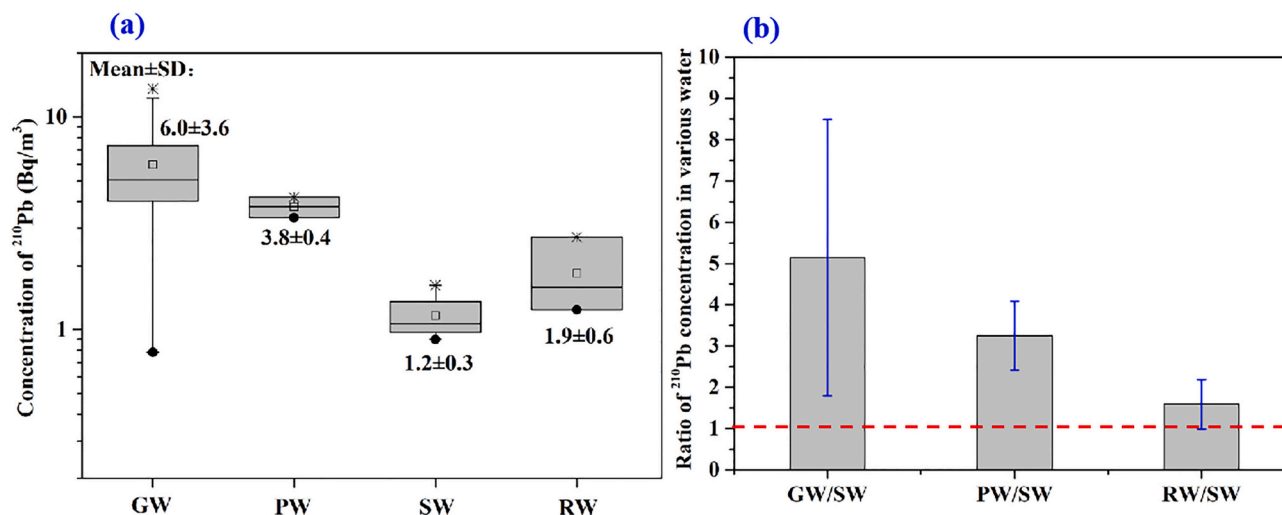


Fig. 2. (a) Concentrations of ²¹⁰Pb in well water, porewater, seawater and river water. The box plots report the median (see values reported) and the 1st and 3rd quartiles. The “*” and the black dots represent the 99% and 1% of the range, respectively, the empty squares represent the mean values and T-shape bars represent the minimum and maximum values. (b) ²¹⁰Pb concentration ratios of well water to seawater (GW/SW), porewater to seawater (PW/SW) and river water to seawater (RW/SW).

Table 2
Activities of $^{210}\text{Pb}_{\text{total}}$, ^{226}Ra and $^{210}\text{Pb}_{\text{ex}}$ in surface sediments and SPM samples.

Station	Date	Longitude °E	Latitude °N	$^{210}\text{Pb}_{\text{total}}$	^{226}Ra	$^{210}\text{Pb}_{\text{ex}}$	References
				Bq/kg			
SPM	2016/6/16	108.605	21.864	73.1 ± 5.9	50.9 ± 1.8	22.2 ± 6.2	Luo et al., 2019 This study
C1	2019/5/22	108.537	21.854	94.1 ± 2.3	31.2 ± 0.7	62.9 ± 2.4	
C2	2019/5/22	108.531	21.832	149.6 ± 3.9	28.3 ± 1.0	121.3 ± 4.1	

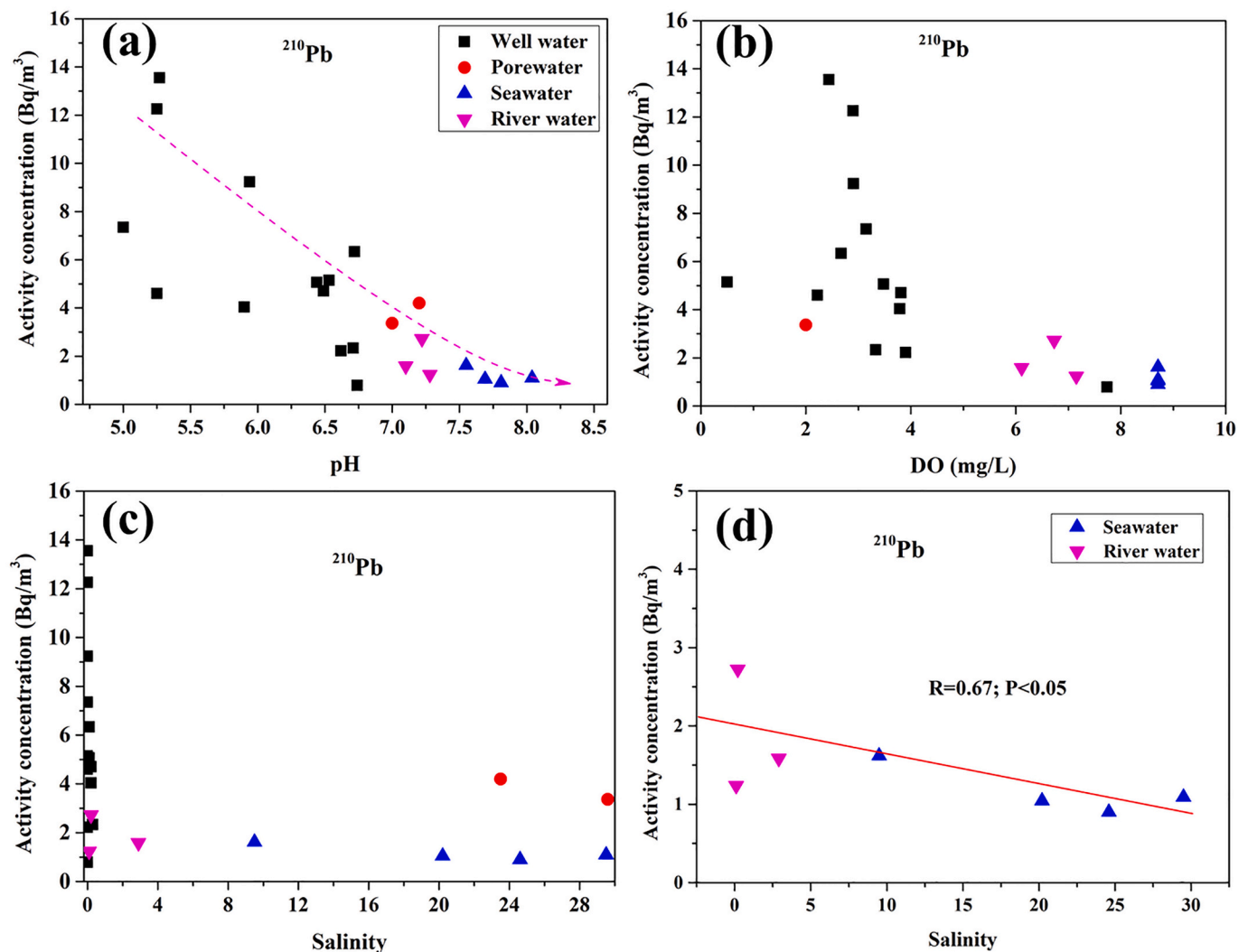


Fig. 3. Relationship between ^{210}Pb activity concentration and pH (a), dissolved oxygen (b) and salinity (c and d).

4.2.1. SGD input

Based on a mass balance model of Ra isotopes (^{224}Ra , ^{228}Ra and ^{226}Ra), Luo (2018) estimated that the Ra-estimated SGD fluxes in the wet and dry seasons in Qinzhou Bay were $(2.5 \pm 1.3) \times 10^7 \text{ m}^3/\text{d}$ and $(3.7 \pm 1.3) \times 10^7 \text{ m}^3/\text{d}$, respectively. However, based on a ^{222}Rn mass balance model, Chen et al. (2018b) reported that the SGD fluxes in that area were 4.9×10^7 and $2.6 \times 10^7 \text{ m}^3/\text{d}$ for the wet and dry seasons, respectively. The different radionuclide tracing methods used by Luo (2018) and Chen et al. (2018b) lead to different SGD flux estimates. We recalculated the mean SGD flux in the wet and dry season combined with the Ra and Rn tracing methods. The SGD flux in the wet season was calculated to be $(3.7 \pm 1.2) \times 10^7 \text{ m}^3/\text{d}$, and the SGD flux in the dry season was $(3.2 \pm 0.6) \times 10^7 \text{ m}^3/\text{d}$. Interestingly, the SGD results in the wet and dry seasons were surprisingly close. Hence, we infer that the SGD- ^{210}Pb flux does not change significantly due to the wet/dry season

SGD dynamics. To assess the ^{210}Pb SGD input, we used the average SGD flux of $(3.4 \pm 1.1) \times 10^7 \text{ m}^3/\text{d}$ obtained from both SGD estimation studies to estimate the annual SGD-derived ^{210}Pb flux, assuming that the magnitude of SGD in the wet season was the same as that in the dry season over a time scale of a year for the ^{210}Pb budget in Qinzhou Bay. Generally, SGD denotes all direct discharges of subsurface fluids across the land-ocean interface, which can be composed of SFGD and RSGD (Baudron et al., 2015; Burnett et al., 2003; Moore, 1996; Taniguchi et al., 2002). Considering that ^{210}Pb concentrations are considerably different in SFGD and RSGD, identifying the relative contribution of each SGD component is crucial to accurately estimate SGD-derived solute fluxes (Rodellas et al., 2018). Since we have no information on which is the dominant component of SGD in Qinzhou Bay, the SGD-driven ^{210}Pb flux can be constrained by minimum and maximum values using two extreme cases with SGD being only RSGD and being

SFGD. Assuming that RSGD is the main component, the averaged porewater ^{210}Pb activity concentration ($3.78 \pm 0.42 \text{ Bq/m}^3$) minus the averaged overlying seawater ^{210}Pb activity concentration ($1.16 \pm 0.27 \text{ Bq/m}^3$) can be used as the ^{210}Pb concentration in the SGD endmember ($2.62 \pm 0.50 \text{ Bq/m}^3$). This would result in an SGD-derived ^{210}Pb flux of $(3.3 \pm 0.4) \times 10^{10} \text{ Bq/yr}$. When SFGD is considered the main component, SGD-derived ^{210}Pb fluxes would be $(7.4 \pm 3.5) \times 10^{10} \text{ Bq/yr}$ (using the average ^{210}Pb activity concentration in fresh groundwater ($5.97 \pm 3.64 \text{ Bq/m}^3$) as the SGD endmember). Given that RSGD is often the dominant component of SGD (accounting for 90% of total SGD) in many regions (Hussain et al., 1999; Liu et al., 2017; Moore, 1996; Santos et al., 2009), it is likely that the real SGD-driven ^{210}Pb flux is similar to the estimated flux using the RSGD endmember. We thus use an SGD-derived ^{210}Pb flux of $(3.3 \pm 0.4) \times 10^{10} \text{ Bq/yr}$, which represents a conservative estimate that assumes that SGD is dominated by RSGD.

4.2.2. Riverine supply

Rivers supply ^{210}Pb to Qinzhou Bay through dissolved and adsorbed forms in suspended particles in river estuaries. To quantify the dissolved fraction of riverine inputs, we analyzed the ^{210}Pb activity concentration in the Qinjiang River, $1.6 \pm 0.1 \text{ Bq/m}^3$, which was similar to that measured in the Maolingjiang River ($1.2 \pm 0.1 \text{ Bq/m}^3$) but significantly lower than the activity concentration measured in the Dalanjiang River ($2.7 \pm 0.1 \text{ Bq/m}^3$). Multiplying the ^{210}Pb activity concentration by the annual river runoff for each river (Qinjiang River, Luwu Station: $2.0 \times 10^9 \text{ m}^3/\text{yr}$ (Li and Huang, 2018); Maolingjiang River, Huangwutun Station: $2.6 \times 10^9 \text{ m}^3/\text{yr}$ (Kang et al., 2017)), we obtain a total river-discharged dissolved ^{210}Pb flux of $(7.6 \pm 0.4) \times 10^9 \text{ Bq/yr}$ in Qinzhou Bay.

The riverine flux of ^{210}Pb adsorbed onto suspended particulate matter was calculated by multiplying the $^{210}\text{Pb}_{\text{ex}}$ activity measured in SPM by the annual average sediment transport flux of these rivers. The perennial average sediment transport flux for the Maolingjiang River is $5.5 \times 10^8 \text{ kg/yr}$ (Kang et al., 2017), and based on a 50-year statistical average, the Qinjiang River (including the tributary Dalanjiang River) discharges $1.9 \times 10^8 \text{ kg}$ sediments per year to the sea (Li and Haung, 2018). The activity of $^{210}\text{Pb}_{\text{ex}}$ in suspended riverine particles in the Qinjiang River reported by Luo et al. (2019) is $22.2 \pm 6.2 \text{ Bq/kg}$. Assuming similar activities in SPM for the Maolingjiang and Dalanjiang Rivers, we scaled this value by the total sediment delivery from these rivers yielding a river particle discharged $^{210}\text{Pb}_{\text{ex}}$ flux of $(1.6 \pm 0.5) \times 10^{10} \text{ Bq/yr}$. Thus, the total (dissolved + particulate) riverine source of ^{210}Pb to Qinzhou Bay is estimated to be $(2.4 \pm 0.5) \times 10^{10} \text{ Bq/yr}$. Based on this model, 68.4% of the ^{210}Pb flux was carried on suspended solids, which was similar to the ratio of 70.6% reported in Long Island Sound (Benninger, 1978). However, there were significant seasonal variations in dissolved and particulate ^{210}Pb fluxes due to the seasonal variations in river sediment and water discharge fluxes. Therefore, the total riverine ^{210}Pb flux here was a conservative estimate.

4.2.3. Atmospheric deposition

^{210}Pb in the atmosphere is produced by decay of ^{222}Rn after its emanation from the Earth's surface. The decay of ^{222}Rn in the atmosphere proceeds through a series of very short-lived, involatile daughter radionuclides to ^{210}Pb . The decay half-lives of the intermediate nuclides are short relative to the mean residence time of the atmospheric aerosol, so that almost all the atoms emitted as ^{222}Rn are redeposited as ^{210}Pb adsorbed onto atmospheric particles (Benninger, 1978). Due to the very strong particle affinity of ^{210}Pb , a significant positive correlation between the atmospheric deposition flux of ^{210}Pb and rainfall has been reported (Du et al., 2015; Mohan et al., 2019; Peng et al., 2019; Wang et al., 2014). Consequently, direct atmospheric deposition is frequently the main source of excess ^{210}Pb (nearly 90% of the total in the dissolved phase) to coastal waters among all sources (Baskaran, 2011).

The most representative approach to obtain the atmospheric ^{210}Pb deposition flux was to continuously collect atmospheric bulk deposition

(dry + wet) samples for an annual cycle (>12 months). This flux was taken as equal to the flux of $^{210}\text{Pb}_{\text{ex}}$ because ^{226}Ra -supported atmospheric ^{210}Pb is assumed to be negligible. A previous study reported that the global atmospheric depositional flux of ^{210}Pb at $20\text{--}30^\circ$ in the Northern Hemisphere was $200 \text{ Bq/m}^2/\text{yr}$ (Baskaran, 2011). Wang and Su (2019) reported that the monthly atmospheric bulk deposition flux of ^{210}Pb in Qinzhou city varied from 3.6 to $63 \text{ Bq/m}^2/\text{month}$ and that the annual atmospheric deposition flux of ^{210}Pb was $331 \pm 17 \text{ Bq/m}^2/\text{yr}$ in 2018. Similar results have been reported in a series of observation sites close to our study area ($266 \text{ Bq/m}^2/\text{yr}$ in Shenzhen city, Liu et al., 2020; $275 \text{ Bq/m}^2/\text{yr}$ in Hengyang city, Peng et al., 2019). To conservatively constrain the SGD-derived ^{210}Pb flux estimation, the highest atmospheric ^{210}Pb flux of Wang and Su (2019) was used. Multiplying the atmospheric ^{210}Pb deposition flux ($331 \pm 17 \text{ Bq/m}^2/\text{yr}$) by the area of Qinzhou Bay (380 km^2) yields a total atmospheric input of $(12.6 \pm 0.6) \times 10^{10} \text{ Bq/yr}$.

4.2.4. Other sources

Other possible sources of ^{210}Pb into Qinzhou Bay are i) in situ production from dissolved ^{222}Rn , ii) direct sewage discharge, and iii) potential release of dissolved ^{210}Pb from sediments. For the ^{210}Pb supply (ocean mixing) from the Beibu Gulf or open sea (the South China Sea), thus far, we were not sure whether it might be a sink or a source, which will be further discussed in the following section.

Chen et al. (2018a) found a mean ^{222}Rn concentration of $75.1 \pm 24.5 \text{ Bq/m}^3$ in 53 seawater samples from Qinzhou Bay from the Maowei Sea to the outer bay area; hence, the annual ^{210}Pb production from this quantity of ^{222}Rn (assuming no losses) is $2.3 \pm 0.8 \text{ Bq/m}^3/\text{yr}$. He (2015) estimated that the seawater volume in Qinzhou Bay under static water depth is $2.4 \times 10^9 \text{ m}^3$. Therefore, the in situ production of ^{210}Pb from ^{222}Rn is only approximately $(5.5 \pm 1.8) \times 10^9 \text{ Bq/yr}$, clearly lower than the direct atmospheric deposition and riverine discharge.

Benninger (1978) reported that ^{210}Pb in sewage from an urbanized environment could also be a potential source of ^{210}Pb . The sewage described by Benninger (1978) consists of three components: domestic wastes, industrial wastes, and storm runoff. Benninger (1976) suggested that these components were a minor source of ^{210}Pb for the Long Island Sound (<10% of the in situ production flux of mother nuclides), which is an estuary surrounded by large urban areas (e.g., New York city). We think the ^{210}Pb input flux from sewage discharge can be neglected in Qinzhou Bay because the cities and towns around Qinzhou Bay are small and mainly engaged in agriculture and aquaculture, and the sewage should have a low discharge amount.

^{210}Pb is a particle reactive nuclide with high distribution coefficients (K_d values) ranging from 10^3 to 10^7 mL/g in coastal seas and open seas (Zhong et al., 2019). Generally, ^{210}Pb would not be easily released from sediments unless the redox conditions change. Benoit and Hemond (1990) observed that ^{210}Pb was found to be significantly remobilized from sediments into stratified and anoxic water columns and estimated a ^{210}Pb release flux of up to $117 \text{ Bq/m}^2/\text{yr}$ in the Bickford Reservoir, and this ^{210}Pb remobilization from sediments was closely linked with the cycling of iron and manganese. However, dissolved ^{210}Pb remobilization from sediments is not ubiquitous, and this phenomenon tends to be present as hot spots (Benoit and Hemond, 1990; Kim et al., 2005b; Jones et al., 2015). In Qinzhou Bay, there is no report of ^{210}Pb release from sediments, and the water column is shallow (water depth < 15 m in our study area during sampling). In addition, stratification in the water column can generally be conducive to anoxic conditions. Qinzhou Bay has strong hydrodynamic mixing conditions (the tide range can reach up to 5.5 m), and stratification is not observed during sampling. Based on a study in Qinzhou Bay, it was found that the DO concentrations in seawater were stable at $5.83\text{--}10.66 \text{ mg/L}$ during a 20-year investigation (Wei and He, 2009). Therefore, we judge that the anoxic conditions in Qinzhou Bay were not valid. In other words, the prerequisite for ^{210}Pb remobilization from sediments does not hold. However, due to the high turbidity of coastal seas, if ^{210}Pb was remobilized, then this particle-

reactive ^{210}Pb tends to be bound to the sinking particles, and therefore, this ^{210}Pb remobilization flux would be insignificant. Based on all the mentioned reasons, we think that the release flux of dissolved ^{210}Pb from sediments can be neglected in Qinzhou Bay.

4.3. Sinks of ^{210}Pb in Qinzhou Bay

Removal processes for ^{210}Pb include loss via radioactive decay and deposition to the seabed after scavenging by SPM and sediment particles. The decay constant of ^{210}Pb is $3.1 \times 10^{-2} \text{ yr}^{-1}$. The inventory of ^{210}Pb , $(2.7 \pm 0.6) \times 10^9 \text{ Bq}$, was obtained by multiplying the seawater ^{210}Pb concentration ($1.2 \pm 0.3 \text{ Bq/m}^3$) by the seawater volume of Qinzhou Bay ($2.4 \times 10^9 \text{ m}^3$, He, 2015). Combining its decay rate with the seawater inventory of ^{210}Pb results in a loss due to radioactive decay of $(8.5 \pm 1.9) \times 10^7 \text{ Bq/yr}$.

^{210}Pb has a high particle affinity and is efficiently scavenged by sinking particles, ending in the seabed where ^{210}Pb will be buried and kept relatively stable in the seabed for many years (Gao et al., 2017; Qiao et al., 2017). When quantifying the removal flux of ^{210}Pb , it is usually assumed that (1) the $^{210}\text{Pb}_{\text{ex}}$ deposited is distributed uniformly, without regard to lithology, and (2) ^{210}Pb accumulates exclusively in the silt and clay of the sea-bottom mud (Benninger, 1978; Qiao et al., 2017). Due to a lack of information about the surface sediment type and grain size properties of sediments in Qinzhou Bay, we assumed that $^{210}\text{Pb}_{\text{ex}}$ is distributed uniformly in the total bottom area of the bay.

Two surficial sediments were collected in this investigation (Table 1, samples C1 and C2); however, they are both in the inner part of the bay (Maowei Sea), and they probably do not represent the outer bay appropriately; thus, the representation derived from these two samples may not be sufficient for the whole Qinzhou Bay. To improve the accuracy and representation for this evaluation, we compiled all the available $^{210}\text{Pb}_{\text{ex}}$ data for the study area. The distribution of $^{210}\text{Pb}_{\text{ex}}$ activities in surficial sediments of Qinzhou Bay is shown in Fig. 4a, and Fig. 4b displays the ^{210}Pb -derived sedimentation rates. Due to the significantly different sedimentation rates ($p = 0.05$) in the inner and outer bays, the whole bay can be divided into two regions for calculation. Region I represents the whole part of the Maowei Sea and the inlet

area and has an average sedimentation rate of $0.75 \pm 0.44 \text{ cm/yr}$ ($n = 6$, Fig. 4b). Region II represents the outer bay of Qinzhou Bay, and the average sedimentation rate is $0.50 \pm 0.14 \text{ cm/yr}$ ($n = 6$, Fig. 4b). As expected, the $^{210}\text{Pb}_{\text{ex}}$ activity is higher in the inner bay and lower in the outer bay, with average $^{210}\text{Pb}_{\text{ex}}$ activities in the surficial sediments of Region I and Region II being 80 ± 40 ($n = 10$) Bq/kg and 66 ± 13 ($n = 7$) Bq/kg, respectively (Fig. 4a). To obtain the annual deposition of $^{210}\text{Pb}_{\text{ex}}$, we used Eq. (1) (Gao et al., 2017):

$$F_{\text{buried}} = \sum \rho_{\text{dry}} \times S_r \times C_s \times A_i \quad (1)$$

where F_{buried} is the $^{210}\text{Pb}_{\text{ex}}$ burial flux (Bq/yr), ρ_{dry} is the dry density of sediment (kg/m^3), S_r is the sedimentation rate (m/yr), C_s is the $^{210}\text{Pb}_{\text{ex}}$ activity in units of sediment mass (Bq/kg), and A_i is the area (m^2) of different parts of Qinzhou Bay. ρ_{dry} in this study was 711 kg/m^3 obtained from the two surface sediment samples (C1 and C2). Therefore, the average annual burial flux of $^{210}\text{Pb}_{\text{ex}}$ in Qinzhou Bay was $(11.5 \pm 4.8) \times 10^{10} \text{ Bq/yr}$.

Another sink term for ^{210}Pb is mixing with offshore seawaters, since open ocean waters are expected to have lower concentrations of ^{210}Pb than bay waters (Ma, 2013; Marsan et al., 2014). If we assume that Qinzhou Bay is in steady state in relation to ^{210}Pb (i.e., total ^{210}Pb losses are balanced by total inputs), the flux of ^{210}Pb exported offshore can be inferred from the difference between the contribution from all ^{210}Pb sources ($(18.8 \pm 0.9) \times 10^{10} \text{ Bq/yr}$) and all ^{210}Pb sinks except mixing offshore ($(11.5 \pm 4.8) \times 10^{10} \text{ Bq/yr}$). Therefore, the flux of ^{210}Pb lost by ocean mixing in Qinzhou Bay should account for $(7.3 \pm 4.9) \times 10^{10} \text{ Bq/yr}$ (Fig. 5a).

SGD-derived ^{210}Pb inputs have not been considered when assessing sediment budgets in coastal seas (Du et al., 2016; Gao et al., 2017; Qiao et al., 2017; Su and Huh, 2002; Wang et al., 2018). From Fig. 5a and b, the SGD-derived ^{210}Pb flux is 1.4 times higher than those from local rivers, accounting for $\sim 18\%$ of the total sources. The SGD-derived ^{210}Pb flux represents the second most important source of all ^{210}Pb sources to Qinzhou Bay (Fig. 5b). Additionally, as we can see from Fig. 5a, most of the ^{210}Pb ($11.5/(11.5 + 7.3) > 66\%$) would be buried in the sediments of Qinzhou Bay.

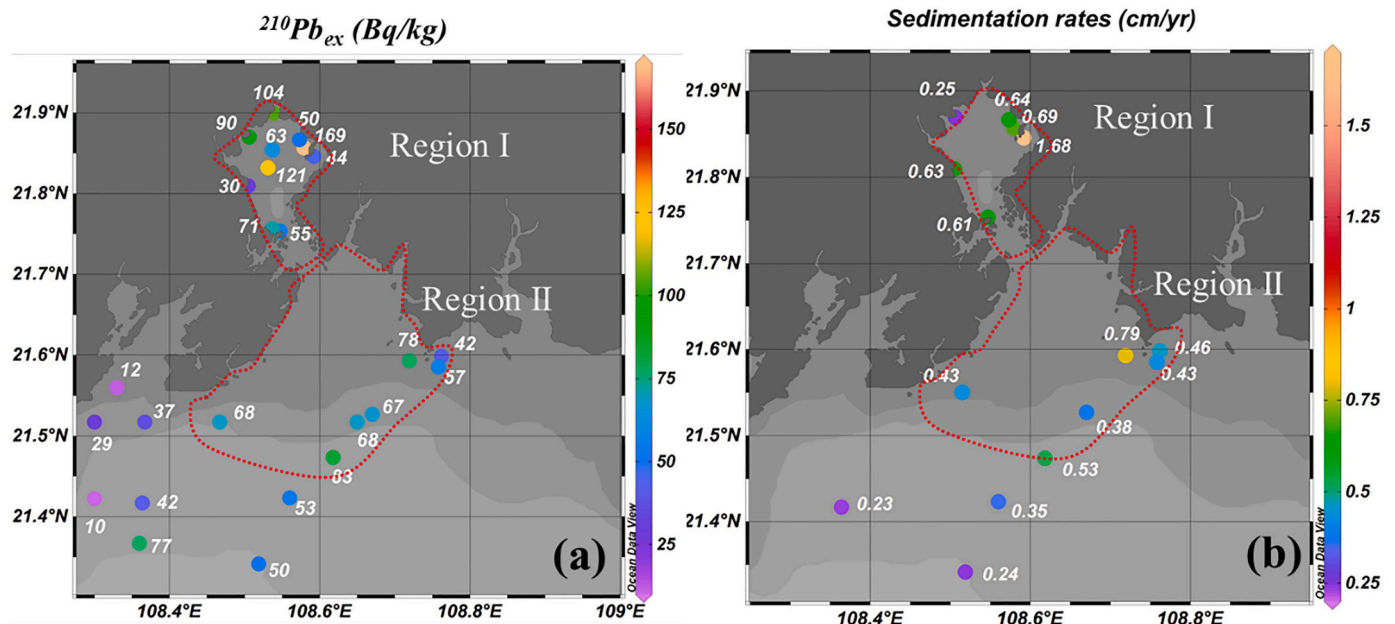


Fig. 4. Distribution of $^{210}\text{Pb}_{\text{ex}}$ concentrations in surficial sediments (a) and ^{210}Pb -derived sedimentation rates (b) in Qinzhou Bay. The $^{210}\text{Pb}_{\text{ex}}$ data shown in Panel (a) were obtained from Gan et al. (2015), Guo et al. (2020), Li et al. (2010), Li et al. (2014), Liao et al. (2020), Mao et al. (2018), Wang et al. (2017), Xu et al. (2012), and this study. The data shown in Panel (b) have been reported in Li et al. (2010), Li et al. (2014), Liao et al. (2020), Gan et al. (2015), Guo et al. (2020), Wang et al. (2017), and Xu et al. (2012). The numbers on the graphs represent the specific activity values and sedimentation rates for each location.

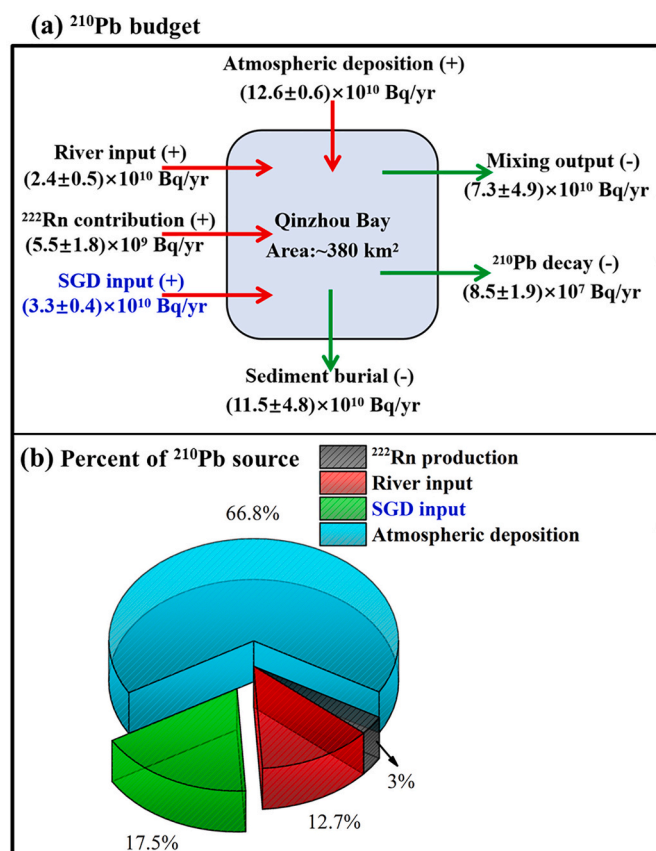


Fig. 5. ^{210}Pb budget (a) and the percentage of ^{210}Pb sources in Qinzhou Bay (b).

4.4. Environmental impacts of SGD-derived ^{210}Pb in the coastal seas

In the above, we reported a case study in a typical embayment, and the SGD-derived ^{210}Pb could account for a relatively high proportion of the total ^{210}Pb (here, 17.5%, Fig. 5) in general coastal seas. In other words, this SGD-derived ^{210}Pb would be ubiquitous in the global coastal seas, although the order of magnitude of SGD-derived ^{210}Pb and its relative contribution proportion may be different in different coastal regions.

The potential environmental impacts of SGD-derived ^{210}Pb on coastal seas are displayed in these three aspects. The first is to increase the radioactivity level in offshore seawaters and even in fishes. Garcia-Orellana et al. (2013) reported that the SGD derived ^{210}Pb flux was $6 \times 10^5 \text{ Bq/d}$, which increased the concentration of ^{210}Pb in marsh waters of Península in the Mediterranean Sea, and this SGD should be responsible for the obvious increase in ^{210}Po and ^{210}Pb activities in both fishes and plants in the salt marsh wetland (Garcia-Orellana et al., 2016). The second one is to result in anomalies of excess ^{210}Pb activity in certain layers of sediment columns. There is a large amount of SGD-derived water to the coastal areas, which would not only deliver nutrients but also Ra isotopes, Rn isotopes, ^{210}Pb , ^{210}Po , and other radionuclides. Discharge of ^{210}Pb and subsequent removal onto the freshwater end of the coastal zone will result in excess ^{210}Pb to the sediments, which will subsequently result in difficulties in ^{210}Pb dating in the nearshore regions. Another potential environmental impact is related to the application of ^{210}Po – ^{210}Pb disequilibrium in particle cycling and evaluation of particulate organic carbon export flux in the marginal seas. Our previous observations in the Changjiang Estuary and its adjacent sea areas of the East China Sea found that abnormally high dissolved ^{210}Pb concentrations in the bottom waters of nearshore stations might be caused by release from bottom sediments or SGD (Zhong et al., 2022).

This additional input of dissolved ^{210}Pb from SGD would enlarge the disequilibrium between ^{210}Po and ^{210}Pb in the seawater column, which would further lead to an overestimate of evaluation results based on the ^{210}Po – ^{210}Pb method.

5. Conclusion

The activity concentrations of ^{210}Pb in submarine groundwater (well water and pore water), river water, and seawater were measured and applied to construct a ^{210}Pb budget in Qinzhou Bay. Activity concentrations of ^{210}Pb in Qinzhou Bay's water systems ranked by the order of well water > pore water > river water > seawater. The SGD-derived ^{210}Pb flux $((3.3 \pm 0.4) \times 10^{10} \text{ Bq/yr})$ accounted for $\sim 18\%$ of the total sources to Qinzhou Bay. SGD might play a critical role as a ^{210}Pb source in coastal seas and should not be neglected when assessing ^{210}Pb budgets in coastal areas for sediment transport studies.

Research data

Relevant research data are in attached spreadsheet.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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