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Porewater-derived dissolved inorganic carbon and nutrient fluxes in a saltmarsh of the Changjiang River Estuary

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Abstract

Saltmarshes are one of the most productive ecosystems, which contribute significantly to coastal nutrient and carbon budgets. However, limited information is available on soil nutrient and carbon losses via porewater exchange in saltmarshes. Here, porewater exchange and associated fluxes of nutrients and dissolved inorganic carbon (DIC) in the largest saltmarsh wetland (Chongming Dongtan) in the Changjiang River Estuary were quantified. Porewater exchange rate was estimated to be (37±35) cm/d during December 2017 using a radon (^{222}Rn) mass balance model. The porewater exchange delivered 67 mmol/(m^2·d), 38 mmol/(m^2·d) and 2 690 mmol/(m^2·d) of dissolved inorganic nitrogen (DIN), dissolved silicon (DSi) and DIC into the coastal waters, respectively. The dominant species of porewater DIN was NH_4^+ (>99% of DIN). However, different with those in other ecosystems, the dissolved inorganic phosphorus (DIP) concentration in saltmarsh porewater was significantly lower than that in surface water, indicating that saltmarshes seem to be a DIP sink in Chongming Dongtan. The porewater-derived DIN, DSi and DIC accounted for 12%, 5% and 18% of the riverine inputs, which are important components of coastal nutrient and carbon budgets. Furthermore, porewater-drived nutrients had obviously high N/P ratios (160–3 995), indicating that the porewater exchange process may change the nutrient characteristics of the Changjiang River Estuary and further alter the coastal ecological environment.

Key words: porewater exchange, coastal wetlands, saltwater intrusion, nitrogen cycle, blue carbon, Changjiang River Estuary

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1 Introduction

Saltmarshes are one of the highest productive ecosystems on the earth, which have been considered to be important sources/sinks, and/or transformers of important compounds such as carbon and nutrients in the coastal landscape (Tobias and Neubauer, 2019). Atmospheric CO_2 is assimilated into organic compounds (i.e., carbohydrates) by saltmarshes. Meanwhile, the carbohydrates are utilized by respiration for plant growth and reproduction (Liang et al., 2017; Tang et al., 2018). The dead plants of saltmarsh are decomposed into CO_2, and other organic and inorganic matter by microorganisms, with the release of nutrients, and the remaining organic carbon is buried in the sediments (Mcleod et al., 2011; Tang et al., 2018). Some of the carbon and nutrients are then released to the coastal waters through submarine groundwater discharge (SGD) and/or porewater exchange (Charette, 2007; Santos et al., 2019; Liu et al., 2021).

SGD is defined as “all the fluid flow on continental margins from the seabed to the coastal ocean, with scale lengths of meters to kilometers, regardless of fluid composition and driving force” (Burnett et al., 2003). Some small scale processes with scale lengths of millimeters to meters such as flow- and topography-induced advection, wave pumping, ripple migration, shear flow and shallow bio-irrigation are collectively referred to as porewater exchange (Santos et al., 2012b; Hong et al., 2017). Although SGD or porewater exchange in coastal regions has received the increasing attention in recent decades (Burnett et al., 2001; Taniguchi et al., 2019), determining that the porewater exchange in coastal wetlands, especially in saltmarshes, is challenging and rarely reported because of complex and heterogeneous sediments, variability in tidal water flows and burrowing crab effects (Tait et al., 2016; Gutiérrez et al., 2018).

Over the past decades there have been significant advances in quantifying SGD or porewater exchange using natural geochemical tracers (Taniguchi et al., 2019; Santos et al., 2021). In particular, tracing SGD or porewater exchange with radon and/or radium radioisotopes has been widely applied to most coastal systems, such as estuaries (Xu et al., 2014; Correa et al., 2020; Guo et al., 2020), bays or lagoons (Su et al., 2014; Yi et al., 2016; Sugimoto et al., 2016), mangroves (Maher et al., 2013; Tait et al., 2016; Chen et al., 2021; Wang et al., 2021), coral reefs (Wang et al.,

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2014; Oehler et al., 2019), sandy beaches (Tamborski et al., 2017; Chen et al., 2019), karst systems (Rodellas et al., 2017; Chen et al., 2020a), marginal seas and shelves (Gu et al., 2012; Liu et al., 2017; Tan et al., 2018). Recently, a novel method, termed “the ^{224}Ra/^{228}Th disequilibrium approach”, was developed to quantify benthic solute fluxes from coastal sediments (Cai et al., 2014, 2015, 2020; Hong et al., 2017; Shi et al., 2019). Up to now, the estimates of porewater exchange and associated biogenic elemtnts such as carbon and nutrient fluxes in saltmarshes is limited (Cai et al., 2003; Charette, 2007; Krest et al., 2000; Santos et al., 2019). Although these studies estimated the porewater exchange and associated carbon and nutrient fluxes in saltmarshes using radon or radium tracers, they only calculated the fluxes of dissolved inorganic nitrogen (DIN, the sum of NO_2^-, NO_3^- and NH_4^+) without distinguishing the main component of DIN.

Chongming Dongtan, located in the center of the Changjiang River Estuary, is a Ramsar Wetland of International Importance and National Nature Reserve (Li et al., 2014). Recent studies of Chongming Dongtan have primarily focused on biodiversity conservation, carbon sequestration capability and carbon storage capacity of wetland vegetation (e.g., *Spartina alterniflora*), as well as soil organic carbon content (Gan et al., 2009; Guo et al., 2009; Li et al., 2010). However, the carbon and nutrient fluxes via porewater exchange in Chongming Dongtan have not yet been estimated.

In this study, hypothesizing that porewater exchange will be a significant pathway for carbon and nutrients exported to the coastal waters. This hypothesis was tested by performing radon (^{222}Rn, a natural groundwater tracer) time series observation in surface waters of Chongming Dongtan wetland and focusing on both dissolved inorganic carbon (DIC) and nutrient fluxes via porewater exchange.

2 Materials and methods

2.1 *Study area*

Chongming Dongtan is the largest and youngest saltmarsh in the Changjiang River Estuary, located at the eastern end of Chongming Island, China (Fig. 1a). The climate of this region is classified as a subtropical ocean climate with a mean annual temperature of 15.3°C. The mean annual precipitation is 1 120 mm, with 60% of rainfall occurring from May to September (Hu et al., 2012). Tides in this region are irregular and semidiurnal, with a range of 2.0–3.1 m (Yang, 1999). The tidal flat has a large vegetation area (27.5 km^2) dominated by native *Phragmites australis*, and *S. alterniflora* (Ge et al., 2015). Chongming Dongtan was designated a national nature reserve in 2005 because of its importance for bird conservation (Ma et al., 2009). More recently, Chongming Island has been strategically positioned by the Shanghai Overall Planning Office to be developed into a world-class eco-island and has received great attention and cooperation and involvement from international organizations (e.g., the United Nations Environmental Programs) (Luo et al., 2018).

2.2 *Experimental design and laboratory analysis*

Field investigations were performed in Chongming Dongtan wetland in December 2017. To assess how tidal fluctuations drive porewater exchange, a time series station was deployed for 24 h (two complete tidal cycles) at the surface waters of Chongming Dongtan wetland (Fig. 1b). Continuous ^{222}Rn monitoring in coastal waters was conducted using a RAD7 detector connected with an air-water exchanger. Salinity, temperature, and dissolved oxygen (DO) were measured in the surface water every hour (Multi 3 430 WTW, Weilheim, Germany).

Discrete samples for DIC, nutrients and ^{226}Ra were collected every 3 h. DIC and nutrient samples were filtered through the 0.45 μm cellulose acetate filters into polyethylene bottles. Then the water samples were poisoned with saturated $HgCl_2$ and kept away from light. DIC samples were analyzed using the CM140 Total Inorganic Carbon Analyzer (UIC Inc., Rockdale, IL, USA). Nutrient samples were analyzed using an auto-analyzer (Model: Skalar SAN^{plus}) (Liu et al., 2009). DIN represents the sum of NO_2^-, NO_3^- and NH_4^+. Dissolved inorganic phosphorus (DIP) and dissolved silicon (DSi) are the concentrations of PO_4^{3-} and $Si(OH)_4$, respectively. ^{226}Ra samples were collected by filtering surface water through MnO_2-impregnated acrylic fiber (Moore and Arnold, 1996). The fibers were then analyzed using a RAD7 detector (Kim et al., 2001).

Porewater samples in the saltmarsh intertidal zone were collected from a push-point piezometer using a peristaltic pump (Fig. 1b). Crab burrows can strongly enhance porewater exchange in coastal wetlands (e.g., saltmarshes and mangroves) (Xin et al., 2009; Tait et al., 2016; Xiao et al., 2021). Based on the possible depths of crab burrows, the porewater depths (i.e., porewater end-member) were 0.4–1.5 m in this study. These depths are consistent with previous studies (0.3–1.5 m) (Maher et al., 2013; Tait et al., 2016). Temperature, salinity and DO were measured directly in the field using a digital multi parameter meter (Multi 3 430 WTW, Weilheim, Germany). ^{222}Rn samples were collected in 250 mL glass bottles using the overflow method and

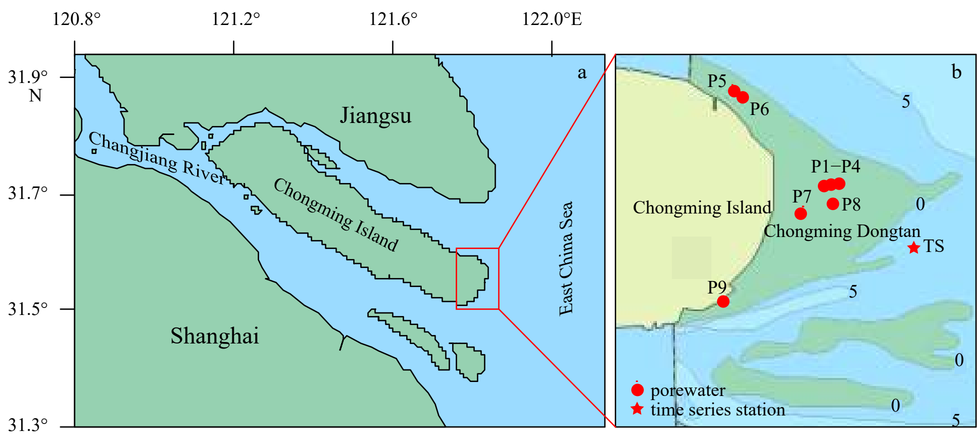

Fig. 1. Study site location (a) and sampling stations (b) in Chongming Dongtan. Zero and five indicate water depths of 0 m and 5 m.

were immediately analyzed using a RAD7 detector (Chen et al., 2018a, 2018b). DIC and nutrient samples were stored and analyzed as described above.

To determine the diffusive flux of ^{222}Rn from sediments, triplicate about 100 g sediments were collected at the time series station and incubated with 400–500 mL of radium-free water for 30 days. The ^{222}Rn activities in equilibrated water were then analyzed using a RAD7 detector (Corbett et al., 1998).

2.3 ^{222}Rn mass balance model

A ^{222}Rn mass balance model originally developed by Burnett and Dulaiova (2003) is used to quantify porewater exchange. This model has been widely applied to coastal systems (Tse and Jiao, 2008; Zhang et al., 2016; Chen et al., 2018a, 2018b; Wang et al., 2019). Based on this model, the ^{222}Rn flux via porewater exchange (F_{PWE}) is estimated after all other ^{222}Rn sources and sinks are estimated. The other ^{222}Rn sources include incoming surface water during flood tide (F_{in}), ^{226}Ra decay ($F_{Ra\text{-}226}$) and ^{222}Rn diffusion from sediments (F_{sed}), while the ^{222}Rn sinks include outgoing surface waters during ebb tide (F_{out}), atmospheric evasion (F_{atm}), ^{222}Rn decay (F_{dec}) and mixing loss with offshore waters (F_{mix}). Thus, the ^{222}Rn mass balance model in the water column can be written as follows (unit of each item in equation is Bq/(m^2·h)):

$$\Delta F = F_{PWE} + F_{in} + F_{Ra\text{-}226} + F_{sed} - F_{out} - F_{atm} - F_{dec} - F_{mix}, \quad (1)$$

in which,

$$\Delta F = \frac{I_{t+\Delta t} - I_t}{\Delta t}, \quad (2)$$

where ΔF is the variation of the excess ^{222}Rn inventory between two successive periods; I is the ^{222}Rn inventory (Bq/m^2) defined as the product of ^{222}Rn activity in the water (C_w, Bq/m^3) and water depth; and Δt is the time interval (1 h in this study).

2.3.1 *Tidal effects*

Tidal effects on the variation of ^{222}Rn activity in coastal water cannot be ignored (Tse and Jiao, 2008; Chen et al., 2018a, 2018b), which can be described by the following equations (Zhang et al., 2016):

$$F_{in} = \frac{h_{t+\Delta t} - h_t}{\Delta t}\left[b\overline{C_w} + (1-b)C_{off}\right], \quad (3)$$

$$F_{out} = \frac{h_t - h_{t+\Delta t}}{\Delta t} C_w, \quad (4)$$

where h_t is the water depth (h, m) at time t; $\overline{C_w}$ and C_{off} are the mean ^{222}Rn activity (Bq/m^3) in surface water and offshore water; C_w is the ^{222}Rn activity (Bq/m^3) over a time interval at time series station; b is the return flow factor, which can be determined based on a radium mixing model (Moore et al., 2006). The raw data of radium are from Zhang (2007) and Gu et al. (2012).

2.3.2 *Atmospheric evasion*

Atmospheric evasion of ^{222}Rn can be calculated by the following equation (Maclntryee et al., 1995):

$$F_{atm} = k(C_w - \alpha C_{air}), \quad (5)$$

where C_{air} and C_w are the ^{222}Rn activities in the air and surface water, respectively; α is partition coefficient, which is described by the Fritz Weigel equation (Burnett and Dulaiova, 2003); Gas transfer velocity (k) is calculated as follows (Maclntryee et al., 1995):

$$k_{600} = \begin{cases} 0.45\mu^{1.6}\left(\dfrac{S_c}{600}\right)^{-0.5} & (\mu > 3.6\ \text{m/s}) \\ 0.45\mu^{1.6}\left(\dfrac{S_c}{600}\right)^{-0.666\,7} & (\mu \leqslant 3.6\ \text{m/s}) \end{cases}, \quad (6)$$

where μ is the wind speed; S_c is Schmidt number and calculated based on the formulations given by Pilson (1998).

2.3.3 *Diffusion from sediments*

The diffusive flux of ^{222}Rn from sediments can be determined based on the following equation (Peng et al., 1974; Martens et al., 1980):

$$F_{sed} = (\lambda_{Rn\text{-}222} \times \varphi \times D_m)^{0.5}(C_{eq} - C_o), \quad (7)$$

where $\lambda_{Rn\text{-}222}$ is the decay constant of ^{222}Rn (0.181 d^{-1}); φ is porosity of sediment; D_m is a function of temperature described by Peng et al. (1974); C_{eq} is the ^{222}Rn activity (Bq/m^3) in porewater that is equilibrium with that in sediment; C_o is ^{222}Rn activity (Bq/m^3) in overlying water.

2.3.4 *Decay loss of ^{222}Rn and production from ^{226}Ra*

The ^{222}Rn flux from the ^{226}Ra decay and the ^{222}Rn decay loss can be calculated by the following equations (Chen et al., 2018a):

$$F_{Ra\text{-}226} = \lambda_{Rn\text{-}222} \times C_{Ra\text{-}226} \times h, \quad (8)$$

$$F_{dec} = \lambda_{Rn\text{-}222} \times C_w \times (1 - e^{-\lambda_{Rn\text{-}222}\Delta t}) \times h, \quad (9)$$

where $C_{Ra\text{-}226}$ is the dissolved ^{226}Ra activity in the surface waters (Bq/m^3). Other items are described as above.

2.3.5 *Mixing loss and porewater exchange*

Net ^{222}Rn flux (F_{net}) can be evaluated by taking the change in inventories over time after correcting for atmospheric evasion, tidal effect, ^{226}Ra support, ^{222}Rn decay, and sediment diffusion (Zhang et al., 2016):

$$F_{net} = \Delta F - F_{in} - F_{Ra\text{-}226} - F_{sed} + F_{out} + F_{atm} + F_{dec}. \quad (10)$$

Based on the Eqs (8) and (9), F_{net} should be a balance between the F_{PWE} and F_{mix}. To evaluate the conservative estimates of the F_{mix}, the maximum negative F_{net} are selected as F_{mix} in adjacent periods because the conservative estimates of the mixing loss provide estimations of the minimum porewater exchange flux (Burnett and Dulaiova, 2003). Then the ^{222}Rn fluxes via porewater exchange can be determined based on Eqs (1) and (2). And the porewater exchange rates (PW, cm/d) can be obtained by dividing the ^{222}Rn fluxes via porewater exchange by the ^{222}Rn activity of porewater end-member (C_{PW}, Bq/m^3):

$$PW = \frac{F_{PWE}}{C_{PW}}. \quad (11)$$

3 Results and discussion

3.1 *Time series observation*

All measured parameters such as salinity, DO, ^{222}Rn, nutrients and DIC fluctuated during time series observation without an obvious tidal pattern except the temperature (Figs 2 and 3). Salinity, temperature and DO ranged from 2.3 to 10.7, 10.5°C to 11.5°C and 10.8 mg/L to 11.4 mg/L, with averages of 6.3±2.4, (10.9±0.3)°C and (11.1±0.2) mg/L, respectively. ^{222}Rn activity ranged from 10.6 Bq/m^3 to 42.7 Bq/m^3 with an average of (26.2±9.5) Bq/m^3. Concentrations of DIN, DIP, DSi, and DIC ranged from 91.5 μmol/L to 112 μmol/L, 1.24 μmol/L to 1.76 μmol/L, 87.8 μmol/L to 115 μmol/L, and 1.68×10^3 μmol/L to 2.03×10^3 μmol/L, with averages of (102±6) μmol/L, (1.68±0.16) μmol/L, (104±7) μmol/L, and (1.85±0.09)×10^3 μmol/L, respectively.

3.2 *Porewater observation*

Salinity, temperature and DO of porewater in Chongming Dongtan wetland changed from 1.4 to 20.5, 9.8°C to 12.3°C and 0.35 mg/L to 3.32 mg/L, with averages of 12.6±5.1, (10.9±0.7)°C and (1.06±0.88) mg/L, respectively. ^{222}Rn activity of porewater varied from 1.59×10^3 Bq/m^3 to 4.35×10^3 Bq/m^3 with an average of (2.87±0.97)×10^3 Bq/m^3 (Table 1), which was about 110 fold higher than that in surface water.

Nutrients and DIC displayed considerable variability in intertidal porewater (Table 1). DIN (range: 12–840 μmol/L; mean: (283±251) μmol/L), DSi (range: 181–249 μmol/L; mean: (206±23) μmol/L) and DIC (range: (7.09×10^3–12.0×10^3) μmol/L; mean: (9.12±1.65)×10^3 μmol/L) concentrations were significantly higher than those in surface water. However, DIP concentration ranged from 0.03 μmol/L to 1.25 μmol/L with an average of (0.42±0.48) μmol/L, which was significantly lower than that in surface water.

3.3 *^{222}Rn mass balance and porewater exchange*

According to Eqs (1)–(5), all ^{222}Rn sources and sinks were estimated (Table 2). Based on ^{222}Rn mass balance, porewater-derived ^{222}Rn fluxes were calculated to be 0–138 Bq/(m^2·h), mean: (43.8±42.4) Bq/(m^2·h). In terms of the ^{222}Rn sources in Chongming Dongtan wetland, porewater exchange flux, incoming surface water during flood tide, ^{222}Rn diffusion from sediments and ^{226}Ra decay accounted for 88.0%, 11.2%, 0.6% and 0.2% of the ^{222}Rn sources, respectively. In terms of the ^{222}Rn sinks, mixing loss with offshore waters, outgoing surface waters during ebb tide, atmospheric evasion and ^{222}Rn decay accounted for 83.0%, 14.4%, 2.6% and <0.1% of the ^{222}Rn sinks, respectively. ^{222}Rn diffusion from sediments, ^{226}Ra decay and ^{222}Rn decay were minor components of the ^{222}Rn mass balance and can be negligible as these items were <1% of the ^{222}Rn sources or sinks. Similar results were found in other coastal areas (Burnett and Dulaiova, 2006; Chen et al., 2018a, 2018b; Sadat-Noori et al., 2018).

Defining the porewater end-member is a crucial step in the estimates of porewater exchange and associated nutrient or carbon flux calculations, which has been recognized as a major source of uncertainty (Santos et al., 2012a; Cook et al., 2018; Chen

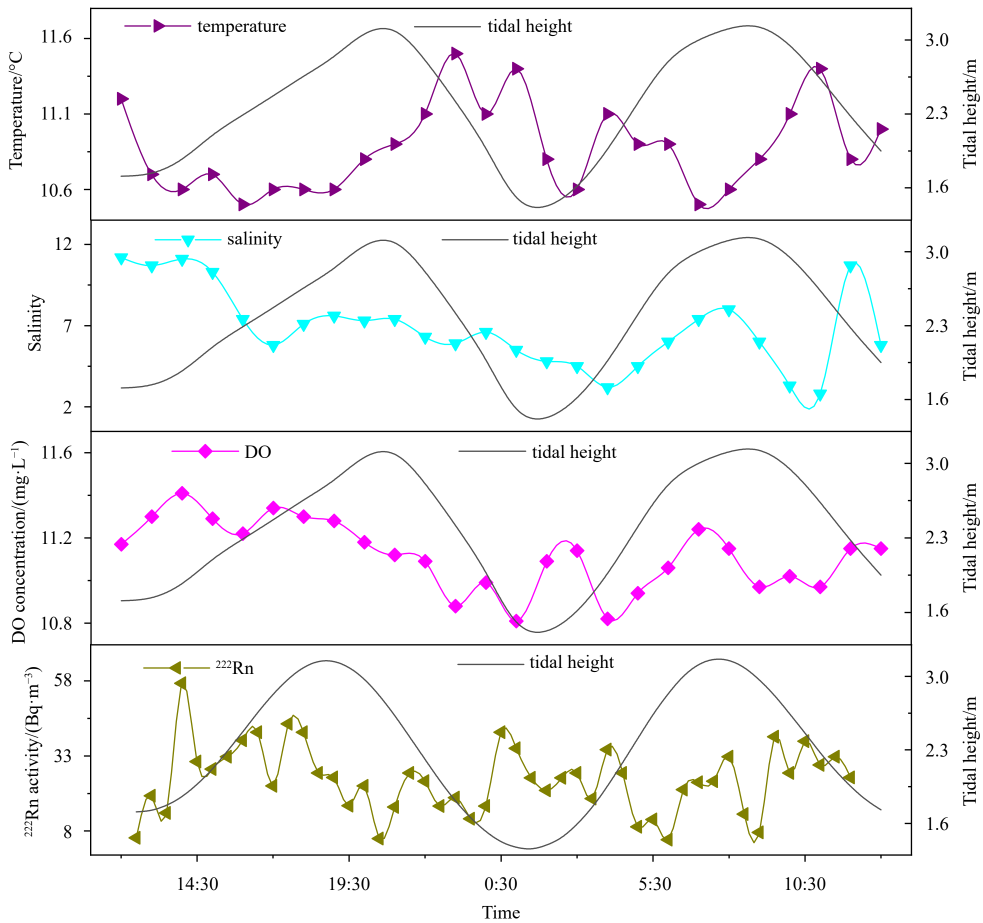

Fig. 2. Variations of tidal height, temperature, salinity, DO concentration, and ^{222}Rn activity during the time series observation.

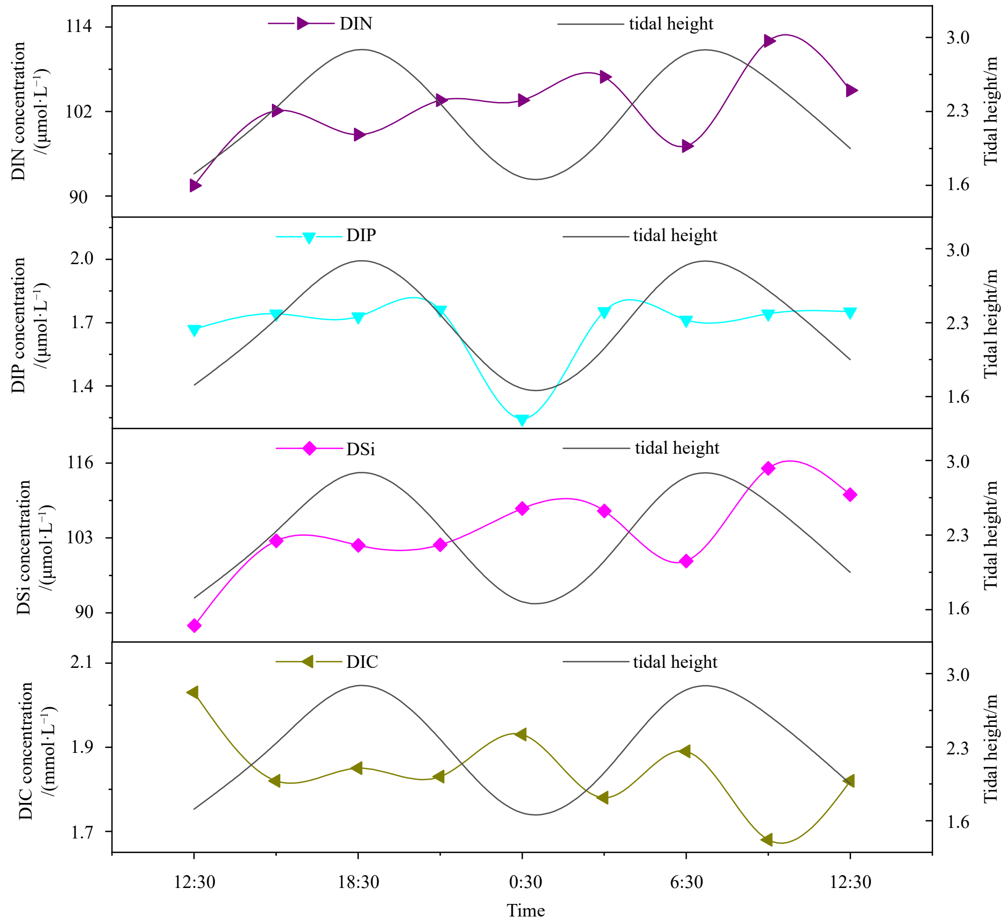

Fig. 3. Variations between tidal height and nutrients, and DIC during the time series observation.

Table 1. Summary of sampling stations, ^{222}Rn activities, temperature, salinity, DO, nutrient (DIN, DIP and DSi) and DIC concentrations of porewater samples in the Chongming Dongtan

Station	^{222}Rn activity/ (Bq·m^{-3})	Temperature/ °C	Salinity	DO concentration/ (mg·L^{-1})	DIN concentration/ (μmol·L^{-1})	DIP concentration/ (μmol·L^{-1})	DSi concentration/ (μmol·L^{-1})	DIC concentration/ (μmol·L^{-1})
P1	1.69×10^3	11.4	12.8	0.70	339	0.42	216	7.71×10^3
P2	3.09×10^3	10.7	12.3	0.65	386	0.21	233	9.20×10^3
P3	2.63×10^3	10.7	13.2	0.55	339	1.18	203	9.06×10^3
P4	1.59×10^3	10.8	12.2	0.50	840	1.25	181	8.12×10^3
P5	3.67×10^3	10.3	19.0	0.35	208	0.09	249	12.0×10^3
P6	4.20×10^3	10.4	20.5	1.05	–	–	–	–
P7	4.35×10^3	11.4	9.9	1.66	12	0.07	184	11.5×10^3
P8	2.24×10^3	9.8	12.1	3.32	130	0.03	185	7.09×10^3
P9	2.35×10^3	12.3	1.4	0.73	13	0.08	194	8.27×10^3
Average	(2.87±0.97)×10^3	10.9±0.7	12.6±5.1	1.06±0.88	283±251	0.42±0.48	206±23	(9.12±1.65)×10^3

et al., 2020b). In this study, a spatial porewater survey were conducted in Chongming Dongtan wetland (Fig. 1). The mean ^{222}Rn value ((2.87±0.97)×10^3 Bq/m^3) in the spatial porewater survey was selected as the most representative groundwater end-member. Hence, the porewater exchange rate was calculated to be (37±35) cm/d by using porewater exchange flux divided by this groundwater end-member value.

3.4 *Porewater-derived nutrient and DIC fluxes*

Previous studies have confirmed that porewater exchange plays an important even decisive role in coastal ecosystems (Cai et al., 2014, 2015; Tait et al., 2016; Chen et al., 2019). However, there are limited studies on nutrient and carbon fluxes through porewater exchange in saltmarsh ecosystem (Charette, 2007; Santos et al., 2019) due to the heterogenic geological matrix and highly dynamic aquifer system. Therefore, based on the porewater exchange rates calculated by ^{222}Rn mass balance, the porewater-derived nutrient and DIC fluxes in Chongming Dongtan saltmarshes were estimated.

3.4.1 *Porewater-derived nutrient fluxes*

DIN and DSi had high porewater/surface water ratios while

Table 2. ^{222}Rn budget during December 2017 in the Chongming Dongtan

Sources and sinks	^{222}Rn fluxes /(Bq·m^{-2}·h^{-1})	Percentage to total ^{222}Rn sources and sinks/%
Sources		
^{226}Ra contribution	0.13±0.02	0.2
Sediment diffusion	0.30±0.02	0.6
Influx during flood tide	5.56±3.74	11.2
Porewater exchange flux	43.8±42.4	88.0
Sinks		
^{222}Rn decay	0.007±0.003	0.01
Atmospheric evasion	1.25±0.67	2.6
Outflux during ebb tide	6.90±2.89	14.4
Mixing loss	39.9±36.9	83.0

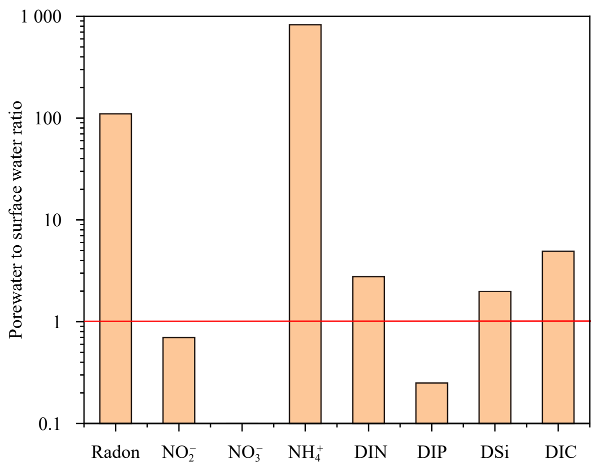

Fig. 4. Ratios of measured ^{222}Rn, nutrients and DIC for porewater to surface water.

porewater DIP was significantly lower than that in surface water (Fig. 4). The low porewater/surface water ratio of DIP is due to mineralization (Slomp and Van Cappellen, 2004) and utilization of phosphate by saltmarshes (Patrick and Delaune, 1976), indicating that porewater exchange in Chongming Dongtan was not DIP source to coastal waters. Therefore, multiplying the porewater exchange rate by the corresponding concentration differences of DIN and DSi in porewater and overlying seawater yields porewater-derived DIN and DSi fluxes of 67 mmol/(m^2·d) and 38 mmol/(m^2·d), respectively, which are within the wide ranges (DIN: 0.1–680 mmol/(m^2·d); DSi: 0.04×10^3–1.40×10^3 mmol/(m^2·d)) of other coastal ecosystems (summarized in Chen et al. (2018a, 2020a) and Wang et al. (2018b)). Similarly, by multiplying the radon-derived porewater exchange by the concentration differences of NO_2^-, NO_3^- and NH_4^+ in porewater and overlying seawater, the NO_2^-, NO_3^- and NH_4^+ fluxes via porewater exchange were estimated to be −0.05 mmol/(m^2·d), −37 mmol/(m^2·d) and 104 mmol/(m^2·d), respectively.

Based on the analysis of different inorganic nitrogen species, the concentrations of NO_2^-, NO_3^- and NH_4^+ in the porewater of Chongming Dongtan ranged from 0.08 μmol/L to 0.41 μmol/L, 0.28 μmol/L to 3.87 μmol/L, and 9 μmol/L to 838 μmol/L, respectively. Almost all of the DIN in porewater of Chongming Dongtan was NH_4^+ (>99% of total inorganic nitrogen species) (Table 3, Fig. 5). The concentrations of NO_2^-, NO_3^- and NH_4^+ in groundwater/porewater of other ecosystems were summarized in Table 3. Whether compared with small-scale bays, lagoons and seagrass beds, or large-scale estuaries, continental shelves and marginal seas, the NO_3^- concentration in porewater of Chongming Dongtan ((1.48±0.98) μmol/L) was significantly lower than that in other ecosystems (range: 19.6–1 460 μmol/L; mean: (342±431) μmol/L), while NH_4^+ in porewater of Chongming Dongtan ((282±251) μmol/L) was much higher than that in others (range: 0.38–38.1 μmol/L). Compare with other ecosys-

Table 3. The concentrations of different inorganic nitrogen species in groundwater of different marine ecosystems

Study area	Ecosystem type	NO_2^- concentration /(μmol·L^{-1})	NH_4^+ concentration /(μmol·L^{-1})	NO_3^- concentration /(μmol·L^{-1})	DIN concentration /(μmol·L^{-1})	Reference
Yucatan Coast, Mexico	seagrass bed	0.42	10.4	19.6	30.4	Kantún-Manzano et al. (2018)
Laoye Lagoon, China	lagoon	0.84	5.36	212	218	Ji et al. (2013)
Sanggou Bay, China	bay	0.73	1.17	1.64×10^3	1.64×10^3	Wen (2013)
Shipu Bay, China	bay	0.13	1.66	395	397	Ji (2013)
La Paz, Mexico	bay	0.47	4.80	122	127	Urquidi-Gaume et al. (2016)
Sansha Bay, China	bay	1.73	13.8	889	905	Wang et al. (2018a)
Maowei Sea, China	bay/mangrove	0.76	27.5	196	224	Chen et al. (2018a)
Shengsi, China	sandy beach	0.99	38.1	89.9	129	Chen et al. (2019)
Yucatan Peninsula, Mexico	beach	5.53	8.22	132	146	Null et al. (2014)
Kinvara Bay, Ireland	bay/karst aquifer	0.24	0.38	79.4	80.0	Rocha et al. (2015)
Zaton Bay, Croatia	bay/anchialine cave	0.09	0.89	164	165	Chen et al. (2020a)
Yellow Sea, China	continental shelf/marginal sea	0.42	7.72	182	190	Ye et al. (2016)
Xiangshan, China	coastal aquifer	0.24	2.18	325	327	Wen (2013)
Chongming Dongtan, China	saltmarsh	0.31	282	1.48	283	this study

tems (Fig. 5), the high NH_4^+ concentration and NH_4^+/DIN ratio of porewater are mainly due to the degradation of organic matter (White and Howes, 1994; Tobias and Neubauer, 2019).

3.4.2 *Porewater-derived DIC flux*

The DIC concentration in coastal groundwater is usually higher than that in surface waters (Maher et al., 2013; Tan et al., 2018; Reithmaier et al., 2021). The porewater DIC concentration in Chongming Dongtan ((9.12±1.65)×10³ μmol/L) was also significantly higher than that in surface waters ((1.85±0.09)×10³ μmol/L). In addition, the porewater DIC concentration in Chongming Dongtan was higher than that in other ecosystems such as bays, coral reefs, estuaries, continental shelves and marginal seas (range: 0–5.38 mmol/L; mean: 2.63 mmol/L), except for the Zhujiang River Estuary (1.2–19.5 mmol/L) (Table 4). Multiplying the porewater exchange rate by the corresponding concentration differences of DIC in porewater and overlying seawater yields porewater-derived DIC flux of 2.69×10³ mmol/(m²·d), which is higher than that in other coastal ecosystems (1.6×10³–1.96×10³ mmol/(m²·d), summarized in Sadat-Noori et al. (2016) and Chen et al. (2018b)). Therefore, the DIC flux into coastal waters via porewater exchange in saltmarsh wetlands may be an important DIC source, which may have an important contribution to the coastal carbon budget.

3.5 *Implications of porewater exchange in saltmarshes on nutrient and DIC fluxes into the Changjiang River Estuary*

The concentrations of NO_2^-, NO_3^- and DIP in the porewater of Chongming Dongtan were significantly lower than those in surface waters, while the NH_4^+ concentration in the porewater was much higher than that in surface waters. Because the NO_3^- concentration in porewater of Chongming Dongtan was much lower than that in other ecosystems while the NH_4^+ concentration was significantly higher than that in other ecosystems (Table 3), the DIN concentration in porewater of Chongming Dongtan (range: 12–840 μmol/L; mean: (283±251) μmol/L) has the same order of magnitude as other coastal ecosystems (range: 30–1 640 μmol/L;

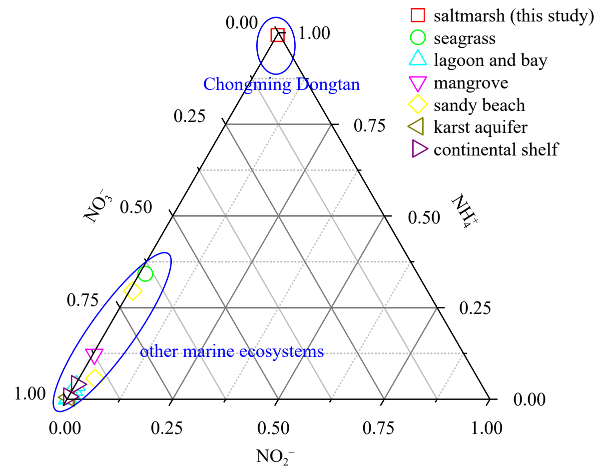

Fig. 5. Ternary diagram illustrating the percentage of different inorganic nitrogen species in groundwater of different ecosystems. The concentrations of different inorganic nitrogen species in groundwater of other marine ecosystems are summarized in Table 3.

Table 4. A summary of the DIC concentrations in different subterranean estuaries

Study area	Ecosystem type	DIC concentration/(mmol·L⁻¹)	Reference
Western Port Bay, Australia	mangrove	11.4	Lee et al. (2016)
Watson Inlet, Australia	mangrove	2.6	Faber et al. (2014)
Chinaman Inlet, Australia	mangrove	2.7	Faber et al. (2014)
Blackwater River estuary, USA	mangrove	4.62	Atekwana et al. (2003)
Mangrove tidal creek, Australia	mangrove	5.15	Maher et al. (2013)
Haughton River Estuary, Australia	mangrove	13.8	Kristensen and Alongi (2006)
Ras Dege, Tanzania	mangrove	2.82	Bouillon et al. (2007)
Can Gio Mangrove Biosphere Reserve, Vietnam	mangrove	4.86	Taillardat et al. (2018)
Twin Cays, Belize	mangrove	about 12.5	Lee et al. (2008)
Celestun Lagoon, Mexico	mangrove	0.74–1.53	Young et al. (2005)
Indian Sundarbans, India	mangrove	2.18	Ray et al. (2018)
Maowei Sea, China	mangrove	1.6	Chen et al. (2018b)
Rarotonga, Australia	coral reef	0–3.06	Cyronak et al. (2013)
Sanya Bay, China	coral reef	1.44–2.54	Wang et al. (2014)
Northern South China Sea	marginal sea	4	Liu et al. (2012)
Northern South China Sea	marginal sea	4.71	Tan et al. (2018)
East China Sea	marginal sea	4.65	Tan et al. (2018)
Waquoit Bay, USA	bay	0.7–1.9	Liu et al. (2017)
Sanggou Bay, China	bay	0.07–0.12	Jiang et al. (2015)
Bay of Puck, Poland	Bay	5.38	Szymczycha et al. (2014)
Had Head, Australia	estuary	1.46	Sadat-Noori et al. (2016)
Jiulong River Estuary, China	estuary	0.5–1.4	Wang et al. (2015)
Zhujiang River Estuary	estuary	1.2–19.5	Cai et al. (2015)
Weitou Bay, China	sandy beach	2.2–3.1	Cai et al. (2020)
Okatee, USA	saltmarsh	3.51–22.7	Moore et al. (2006)
North Inlet, USA	saltmarsh	2–12	Cai et al. (2003)
Chongming Dongtan, China	saltmarsh	8.65	this study

Table 5. Nutrient and DIC fluxes via porewater exchange or SGD versus local riverine input for estuarine systems worldwide

Study area	SGD/(10^6 mol·d^{-1})			River/(10^6 mol·d^{-1})			Ratio of SGD or porewater exchange to river			Reference
	DIN	DSi	DIC	DIN	DSi	DIC	DIN	DSi	DIC	
Chao Phraya River Estuary, Thailand	0.19–0.48	0.11–0.65	–	0.49–2.3	0.26–4.3	–	0.21–0.40	0.15–0.44	–	Burnett et al. (2007)
Yarra River Estuary, Australia	0.01	–	0.23	0.04	–	0.41	0.25	–	0.55	Santos et al. (2012a)
Caloosahatchee River Estuary, USA	0.017	–	–	0.05	–	–	0.35	–	–	Charette et al. (2013)
Tuckean Swamp, Australia	0.005	–	–	0.013	–	–	0.41	–	–	Santos et al. (2013)
Jiulong River Estuary, China	0.88–4.8	1.5–7.9	13–72	11–20	10–22	35–58	0.14–0.32	0.07–0.19	0.24–1.1	Wang et al. (2015)
Krka River Estuary, Croatia	0.05–0.33	0.05–0.27	3.7–22	0.02	0.15	65.9	2.3–16.3	0.31–2.8	0.06–0.33	Liu et al. (2019)
Urbanized Estuary, China	0.18	0.069	–	0.61	0.093	–	0.3	0.7	–	Xiao et al. (2019)
Zhujiang River Estuary, China	8.2	–	115	33.4	–	649	0.25	–	0.18	Cai et al. (2015)
Jiulong River Estuary, China[a]	–	1.4–1.5	34.6–85.4	–	6.2–12.6	28.1–39.5	–	0.11–0.23	1.2–2.4	Hong et al. (2017)
Jiulong River Estuary, China[b]	–	2.7–14.4	20.7–118	–	6.2–12.6	28.1–39.5	–	0.44–1.1	0.74–2.4	Hong et al. (2017)
Chongming Dongtan, China	9.72	5.56	390	83	118	2 190	0.12	0.05	0.18	this study

Note: [a]porewater exchange; [b]SGD.

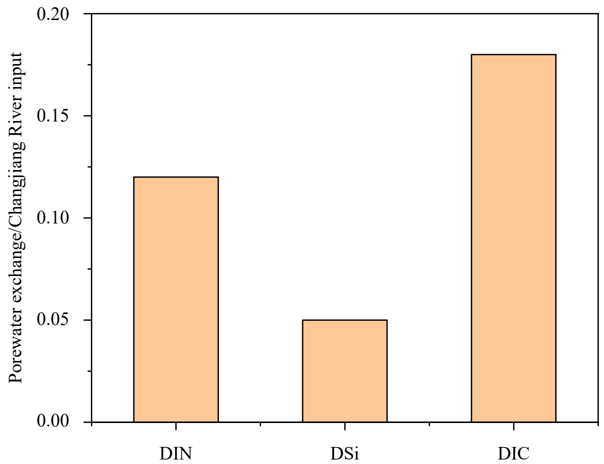

Fig. 6. A comparison of DIN, DSi and DIC to the Changjiang River Estuary via porewater exchange of saltmarshes and surface runoff of the Changjiang River in the dry season.

mean: (352±429) μmol/L) when compared with other ecosystems. However, due to the low DIP concentration in porewater, the N/P ratios (range: 160–4.0×10^3; mean: 681) in porewater of Chongming Dongtan were much higher than those in surface waters (61) and Redfield ratio (N: P=16: 1). Based on the porewater-derived DIN and DSi flux per unit area and the area of this study site (145 km^2), the DIN and DSi fluxes through porewater exchange in the dry season of Chongming Dongtan were estimated to be 9.72×10^6 mol/d and 5.46×10^6 mol/d, respectively, which accounted for 12% and 5% of DIN and DSi fluxes in the Changjiang River (Zhang et al., 2007) (Fig. 6). These ratios of porewater exchange to river are within the broad range (DIN: 0.14–16.3; DSi: 0.07–2.8) observed in other estuarine systems worldwide (Table 5). Therefore, the nutrient fluxes with high N/P ratio via porewater exchange in Chongming Dongtan may change the nutrient components and the phytoplankton community structure in surface waters, thereby affect the nutrient cycles and the marine ecological environment of coastal waters.

The DIC flux via porewater exchange in Chongming Dongtan was significantly higher than that in other ecosystems as described above, which indicates that porewater exchange has an important contribution to coastal DIC budget. Similar with those of nutrients, the DIC flux via porewater exchange in the dry season of Chongming Dongtan was estimated to be 3.90×10^8 mol/d, which accounted for 18% of DIC flux in the Changjiang River (Zhang et al., 2014) (Fig. 6). The ratio of porewater exchange to river for DIC are also within the range (0.06–2.4) observed in other estuarine systems worldwide (Table 5). Therefore, the high porewater-derived DIC flux may have a buffering effect on the decreased DIC concentration/flux in the Changjiang River Estuary due to upstream dam construction (Zhang et al., 2014).

4 Conclusions

Chongming Dongtan, the largest and youngest saltmarsh in the Changjiang River Estuary, is a typical subtropical saltmarsh ecosystem in China. In the present study, porewater and surface water (time series observation) data sets were collected from the Chongming Dongtan during December 2017. Based on the distribution patterns of the ^{222}Rn, nutrients and DIC in porewater and surface water, the following conclusions have been drawn:

(1) Porewater exchange rate in Chongming Dongtan was estimated to be (37±35) cm/d during December 2017 using a ^{222}Rn mass balance model. The estimated DIN, DSi and DIC fluxes via porewater exchange were 67 mmol/(m^2·d), 38 mmol/(m^2·d) and 2.69×10^3 mmol/(m^2·d), respectively. Porewater-derived NO_2^-, NO_3^- and NH_4^+ fluxes were –0.05 mmol/(m^2·d), –37 mmol/(m^2·d) and 104 mmol/(m^2·d), respectively.

(2) Compared with the nutrient and carbon fluxes through the Changjiang River, porewater-derived DIN, DSi and DIC fluxes in Chongming Dongtan was equivalent to 12%, 5% and 18% of the riverine inputs during December 2017.

(3) Even though there is large riverine inputs, saltmarsh porewater exchange seems to be important sources of biogenic elements such as DIN and DIC into estuary or coastal area. This suggests that saltmarsh porewater exchange should be included in

carbon and nutrient assessments in the Changjiang River Estuary.

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