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Estimating the input of submarine groundwater discharge (SGD) and SGD-derived nutrients in Geoje Bay, Korea using ^{222}Rn-Si mass balance model

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ABSTRACT

In order to evaluate the main source of nutrients for maintaining the high production in shellfish farming bay, we have measured ^{222}Rn activities and the concentrations of nutrients in stream water, seawater, and coastal groundwater around Geoje Bay, one of the largest cultivation areas of oyster in the southern sea of Korea in April 2013. Using the ^{222}Rn and Si mass balance model, the residence time of bay seawater was about 5 days and the submarine groundwater discharge (SGD) into the bay was estimated to be approximately 1.8×10^6 m^3 d^{-1}. The SGD-derived nutrient fluxes contributed approximately 54% for DIN, 5% for DIP, and 50% for DSi of total nutrient input entering into the bay. Thus, our results suggest that SGD is the major source of nutrients in Geoje Bay, and SGD-derived nutrients are very important to support the biological production of this shellfish farming bay.

1. Introduction

The direct discharge of submarine groundwater (SGD) including terrestrially-derived fresh groundwater and saline re-circulated seawater has been recently recognized as a potentially important pathway for the transport of terrestrial materials including nutrients and trace elements to the coastal ocean (Moore, 1996; Taniguchi et al., 2002; Burnett et al., 2003; Santos et al., 2009; Kim et al., 2012, Beusen et al., 2013, Rodellas et al., 2015). Especially, the concentrations of dissolved inorganic nutrients in coastal groundwater are one or two order of magnitude higher than those in seawater, and the input fluxes of nutrients through SGD have a significant impact on nutrient budgets and biogeochemical change, such as primary production, eutrophication, and red tide outbreak, in coastal ocean (Slomp and Cappellen, 2004; Hwang et al., 2005a, 2005b; Street et al., 2008; Lee et al., 2009, 2010; Kim et al., 2013; Wang et al., 2014).

In general, nutrients in the marine environment are one of significant parameter controlling the abundance of phytoplankton in water column, while the high nutrient concentrations can often be a negative impact on cultivation environments for fish and shellfish by causing the red-tide, eutrophication, and hypoxia (Treasurer et al., 2003; Dalsgaard and Krause-Jensen, 2006; Hwang et al., 2010). To maintain the proper nutrient concentration in the fish and shellfish cultivation is of great important in order to enhance their production (Lee, 1993; Kang and Kim, 2006).

The semi-enclosed bay is appropriate marine environment for the fish and shellfish cultivation since the risks of environmental factors such as wave, tidal current, and storm are not a threat, and the primary production is much higher relative to general coastal zone due to the continuous input of nutrient through stream and ditch from land and the restricted exchange with the open ocean (Hwang et al., 2015). Especially, the semi-enclosed bay is easy to install and manage the cultivation facility because of the high accessibility by short distance from land and shallow depth (Lee et al., 2011). Therefore, the cultivation of fish and shellfish in Korea has expanded rapidly around a semi-enclosed bay over the last few decades.

Thus, in this study, we estimated the magnitude of SGD in semi-enclosed oyster farming bay of Korea using ^{222}Rn and Si mass balance model as a tracer of SGD and evaluated the contribution of SGD to total nutrient input entering into the bay. Here, we chose Geoje Bay as a study region since this Bay is one of the largest cultivation areas of the Pacific Oyster (*Crassostrea gigas*) in the southern sea of Korea and has been designated as shellfish production area for export after 1970′s.

2. Materials and methods

2.1. Study area

Geoje Bay is a semi-enclosed bay located at Geoje Island in the southeastern sea of Korea (Fig. 1). The bay extends roughly over 7.8 km from north to south and 5.9 km from east to west (Kim and

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Chang, 1985). The water depth of this bay is relatively shallow in the innermost bay (<3 m depth) and increasing to ~30 m outside the mouth of the bay (mean depth: ~8 m). The area and water volume of this bay are approximately 41 km^2 and 3.3×10^8 m^3, respectively.

Based on climate data during the last 10 years (2004–2013) reported by the Korea Meteorological Administration (http://www.kma.go.kr), the average annual precipitation of this region is about 1700 mm, with most of this falling during the heavy rainy season (from June to August). The total amount of freshwater entering into this bay through streams and ditches ranges from $0.01–61 \times 10^3$ m^3 d^{-1} (average 7.3×10^3 m^3 d^{-1}), with a large seasonal variation (NFRDI, 2014).

The tide is semidiurnal and tidal fluctuation is quite large, with minimum and maximum tidal amplitude of ~0.5 m and ~2.5 m during the neap and spring tides, respectively (http://www.khoa.go.kr). The bottom sediments in bay consist mainly of finer sediments with >90% of silt and clay content (mean grain size: >7.5 Ø), whereas coarse sediments predominate in the peripheral areas (Hwang et al., 2015).

2.2. Sampling and analytical methods

Samplings of the coastal seawater ($n = 15$), stream water ($n = 4$), and groundwater ($n = 6$) were conducted from Geoje Bay and adjacent groundwater wells in April 22–25, 2013 for the analyses of temperature, salinity, nutrients (NO_3^-, NO_2^-, NH_4^+, $Si(OH)_4$, and PO_4^{3-}), and ^{222}Rn (Fig. 1). The seawater samples were collected from the surface (1–2 m depth) and bottom (5–6 m depth) layers using a submersible pump with a flow rate of 5–10 L min^{-1}. The stream water samples were collected directly using a sampling bottle. The coastal groundwater samples were obtained from shallow pits (depth: 30–50 cm) dug into sandy sediments in the intertidal zone near shoreline (<50 m) layer using a portable peristaltic pump.

The activity of ^{222}Rn in seawater, stream water, and coastal groundwater was determined with the radon measurement system using a grab water sample and a radon-in-air monitor (RAD-7, Durridge *Co.*) recently developed by Lee and Kim (2006). The grab water sample is carefully collected in 4 L glass bottle using a submersible pump. Briefly, the water outlet of a submersible pump is placed inside the sample bottle, letting the water sample overflow, and capping the bottle without any air inside. About 1 L of the water sample is discarded carefully, and the sample bottle is connected to RAD-7 in a closed air-loop mode with a desiccant column. By purging air through the water sample using an internal air pump in the RAD-7 (flow rate: ~1 L min^{-1}), radon is emanated from the water and is circulated continuously in a closed air-loop system. When a chemical equilibration of radon is obtained between water and air, the activity of the ^{222}Rn is determined by counting its alpha-emitting daughters (^{214}Po and ^{218}Po).

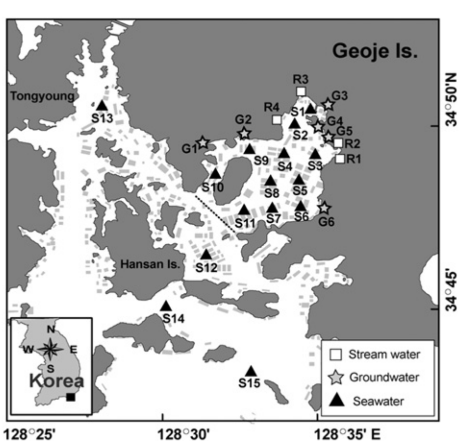

Fig. 1. A map showing the sampling sites in the study region during April 22–25, 2013. The gray squares in Geoje Bay represent fish and shellfish farming areas. The stream water, seawater, and coastal groundwater were collected from the sampling stations marked with blanked squares (Sts. R1–*R*3), filled triangle (Sts. S1–S15), and gray stars (Sts. G1–G6), respectively. The dotted line defines the boundary of the inner bay in order to estimate the input of submarine groundwater.

The ^{222}Rn activities in the water samples were calculated by the following Eq. (1) reported by Lee and Kim (2006).

$$C_{water} = \frac{C_{air} \times V_{air} \; + k \times C_{air} \times V_{water}}{V_{water}} \quad (1)$$

Where C_{air} is the activity of ^{222}Rn in the air loop, V_{water} and V_{air} are the water volume and the air volume in the loop, respectively, and k is the radon distribution coefficient between water and air. Here, the water/air distribution coefficient of radon were calculated from the relationship among water temperature (T, unit: K), salinity (S), and the Bunsen coefficient (β) (Schubert et al., 2012).

The temperature and salinity in water were measured in situ using a portable salinometer (Professional, YSI). The nutrient samples were collected in polyethylene bottles (~100 mL) and then filtered using Whathman GF/F filters (25 mm in diameter, 0.7 μm in pore size) in the field. They were stored in a conical tube (~50 mL) and frozen until analysis. Nutrient concentrations were measured using a Nutrient Auto-Analyzer (Seal analytical GmbH, Model QUAATRO) in the laboratory after the samples had been thawed. Here, we define DIN as the sum of NO_3^-, NO_2^-, and NH_4^+, DIP as PO_4^{3-}, and DSi as $Si(OH)_4$.

3. Results and discussion

3.1. Distributions of salinity, nutrients, and ^{222}Rn in water

The measured results for temperature, salinity, ^{222}Rn activity, and nutrients in the stream water, seawater, and coastal groundwater around the Geoje Bay are shown in Figs. 2 and 3. The temperature and salinity ranged from 12.1 to 16.7 °C (avg.: 13.8 ± 2.0 °C) and 0.1 to 0.2 ppt (avg.: 0.13 ± 0.05 ppt) in the stream water, from 12.9 to 14.6 °C (avg.: 13.6 ± 0.4 °C) and 32.0 to 34.0 ppt (avg.: 32.8 ± 0.4 ppt) in the seawater, and from 14.2 to 21.1 °C (avg.: 17.3 ± 2.9 °C) and 1.4 to 29.4 ppt (avg.: 14.7 ± 11.5 ppt) in the coastal groundwater, respectively (Fig. 2). Salinity in bay seawater increased gradually from innermost bay to the mouth of the bay and was relatively lower than that in the open ocean water. The temperature and salinity in the groundwater showed large spatial variation relative to those in the stream water and seawater. Especially, the salinity in coastal groundwater was significantly lower than that in the seawater around this bay (Fig. 4A).

The activities of ^{222}Rn ranged from 33 to 152 dpm L^{-1} (avg.: 76 ± 52 dpm L^{-1}) in the stream water, from 2.2 to 6.6 dpm L^{-1} (avg.: 4.0 ± 1.3 dpm L^{-1}) in the seawater, and from 46 to 385 dpm L^{-1} (avg.: 204 ± 138 dpm L^{-1}) in the coastal groundwater, respectively (Fig. 2). The ^{222}Rn activity in bay seawater decreased gradually from innermost bay to the mouth of the bay and was relatively higher than that in the open ocean water unlike salinity. The ^{222}Rn activities in the stream water and coastal groundwater showed large spatial variation. The average of ^{222}Rn activities in the coastal groundwater were the highest and were one or two orders of magnitudes higher than those in the seawater (Fig. 4B). Generally, ^{222}Rn is much more highly enriched in the coastal groundwater relative to seawater due to the effective recoil of the noble gas ^{222}Rn in the sediment (Kim et al., 2003, 2011).

The concentrations of DIN, DIP, and DSi ranged from 49 to 114 μM (avg.: 85 ± 28 μM), 0.05 to 0.64 μM (avg.: 0.24 ± 0.28 μM), and 130 to 348 μM (avg.: 208 ± 99 μM) in the stream water, from 2.1 to 19.6 μM (avg.: 7.8 ± 4.9 μM), 0.02 to 0.26 μM (avg.: 0.10 ± 0.06 μM), and 4.4 to 20.5 μM (avg.: 12.7 ± 5.1 μM) in the seawater, and from 6.8 to 162 μM (avg.: 44 ± 59 μM), 0.05 to 1.53 μM (avg.: 0.63 ± 0.54 μM), and 24 to 299 μM (avg.: 130 ± 100 μM) in the groundwater, respectively (Fig. 3). The average concentrations of DIN and DIP in bay seawater were relatively lower than those in the open ocean water, whereas the average DSi concentration in bay seawater was a factor of two to three times higher than that in the open ocean water. This implies

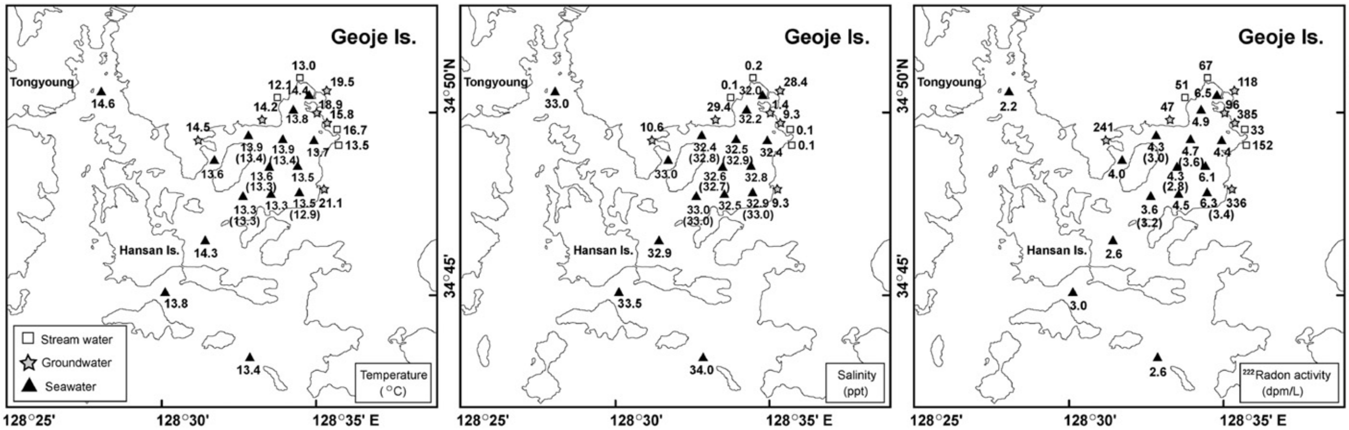

Fig. 2. The horizontal distributions of temperature, salinity and ^{222}Rn activity in stream water, seawater, and coastal groundwater of the study region observed during April 22–25, 2013. The values in parenthesis represent the temperature, salinity and ^{222}Rn activity in bottom seawater.

that DIN and DIP were effectively consumed in the bay due to rapid biological uptake relative to DSi in bay seawater. The nutrient concentrations in the stream water and coastal groundwater showed large spatial variation and were a factor of three to ten times higher than those in the seawater of the study region (Fig. 4C–E).

The ^{222}Rn activity and DSi concentrations in the seawater showed a widely scattered variation against salinity (Fig. 5A and B). Nevertheless, these two species were conservative and showed a negative correlation against salinity ($R^2 = 0.32$–0.34, $P < 0.01$). In addition, these two species had a good positive correlation each other ($R^2 = 0.70$, $P < 0.01$; Fig. 5C). This indicates that there are the substantial sources for ^{222}Rn and DSi in the bay, such as the input of stream water, diffusion from bottom sediments, and SGD.

3.2. Estimating SGD using ^{222}Rn and DSi mass balance

Generally, it is well known that ^{222}Rn is an useful geochemical tracer for estimating SGD on a large space and time scale although ^{222}Rn mass balance method has a largely uncertainty due to the natural variability of ^{222}Rn in the groundwater endmember and the mixing losses to offshore water in coastal environments (Kim et al., 2003, 2010; Santos et al., 2009). Si can be also used as SGD tracer to determine the magnitude of SGD if Si shows a conservative behavior in the seawater, and the difference of DSi concentrations between groundwater and seawater is much high (Hwang et al., 2005b, Kim and Swarzenski, 2010). Recently, Kim et al. (2011) estimated the input of SGD using ^{222}Rn and Si mass balance model in the coastal bays of Jeju Island, Korea. Therefore, in this study, we also calculated the input of SGD and SGD-derived nutrient fluxes using a ^{222}Rn and Si mass balance since ^{222}Rn activity and DSi concentrations were found to be conservative against salinity in Geoje Bay.

To calculate the magnitude of SGD using ^{222}Rn concentrations, the measured ^{222}Rn activities in the water column should be converted to excess (unsupported by ^{226}Ra, parent radionuclide of ^{222}Rn) ^{222}Rn (Burnett and Dulaiova, 2003; Lambert and Burnett, 2003). For the mass balance of excess ^{222}Rn (^{222}Rn—^{226}Ra) in bay water, we used ^{226}Ra data in bay seawater (avg.: 145 dpm m^{-3}) and open ocean water (avg.: 88 dpm m^{-3}) around Masan Bay, located near to Geoje Bay, reported by Lee et al. (2009) since ^{226}Ra did not determined in this study. Hereafter, radon activities of seawater presented in ^{222}Rn mass balance model are excess radon values. At steady state, the mass balance of ^{222}Rn and Si may be expressed as follows:

$$F_{Stm}^{Rn-222} + F_{Diff}^{Rn-222} + C_{GW}^{Rn-222} \times A_{Bott} \times \psi_{SGD} - I_{SW}^{Rn-222} \times \lambda_{Rn-222} - C_{EX}^{Rn-222} \times V_S \times \delta_{Mix} - F_{Atm}^{Rn-222} = 0 \quad (1)$$

$$F_{Stm}^{Si} + F_{Diff}^{Si} + C_{GW}^{Si} \times A_{Bott} \times \psi_{SGD} - C_{EX}^{Si} \times V_S \times \delta_{Mix} = 0 \quad (2)$$

where the terms on the left side of the equation represent input fluxes from stream water (the first term), diffusion from sediments (the second term), submarine groundwater flow (the third term), and output fluxes from radioactive decay (the fourth term), mixing with

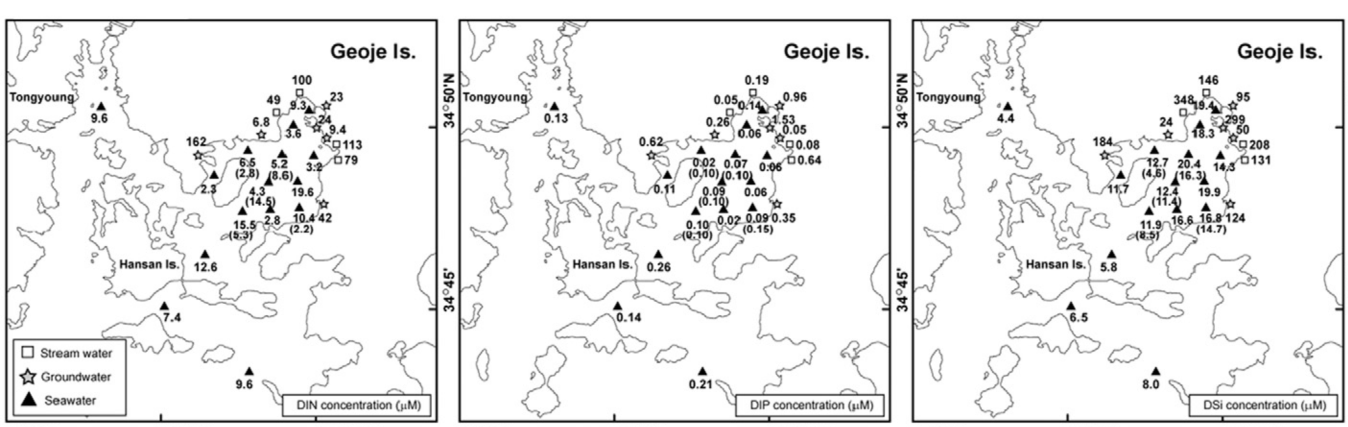

Fig. 3. The horizontal distributions of DIN, DIP, and DSi concentrations in stream water, seawater, and coastal groundwater of the study region observed during April 22–25, 2013. The values in parenthesis represent the nutrient concentrations in bottom seawater.

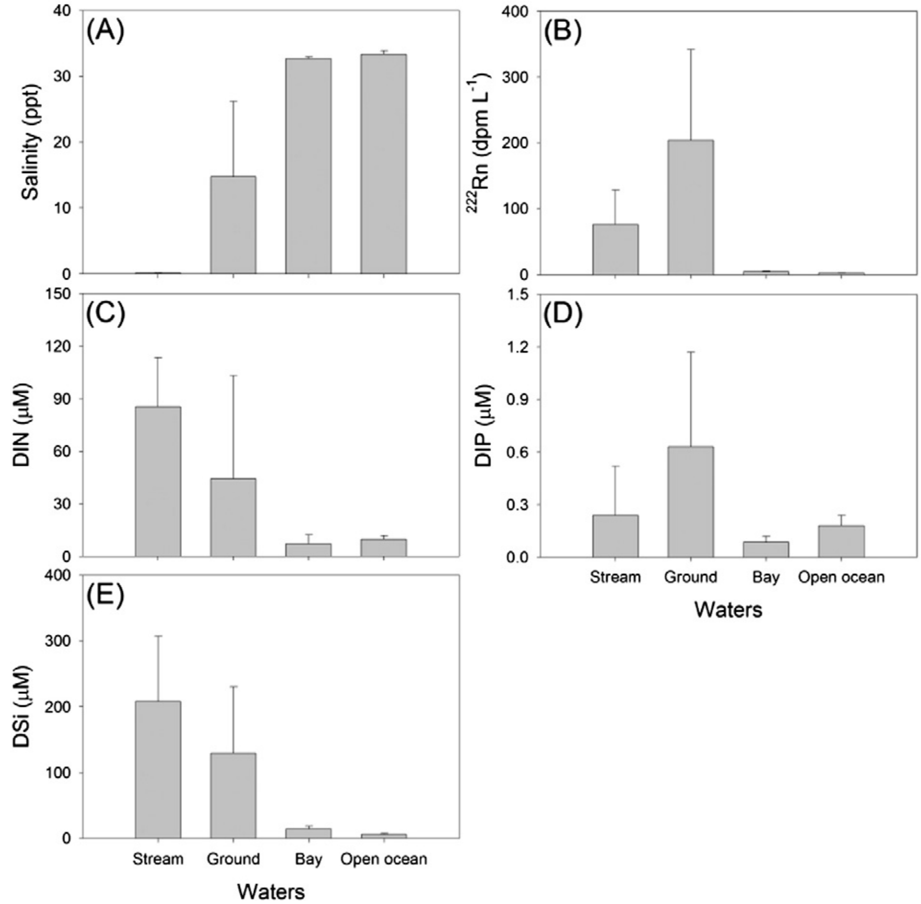

Fig. 4. The average and standard deviations of salinity (A), ^{222}Rn activity (B), DIN (C), DIP (D), and DSi (E) concentrations in stream water, coastal groundwater, bay seawater, and open ocean water of the study region in April 22–25, 2013.

open ocean water (the fifth term; the fourth term in case of Si), and evasion flux to the atmosphere (the final term). The definitions and values of each term in Eqs. (1) and (2) are shown in Table 1. Here, if this system is under a steady state, we can determine two unknown terms (Ψ_{SGD} and δ_{Mix}) from two simultaneous equations.

Firstly, the input fluxes of ^{222}Rn and Si through stream water were calculated by using the average concentrations of ^{222}Rn (75,700 dpm m^{-3}) and DSi (208 mmol m^{-3}) in four stream water samples and daily discharge of stream water (1.88×10^5 m^3 d^{-1}) during the sampling period (NFRDI, 2014). The diffusive fluxes of ^{222}Rn and DSi from bottom sediments were calculated by using the area (4.06×10^7 m^2) in Geoje Bay and the regeneration rates for ^{222}Rn (100 dpm m^{-2} d^{-1}) and Si (5 mmol m^{-2} d^{-1}) assumed from other studies in Korea (Jung and Cho, 2003; Hwang et al., 2005b). The input fluxes through SGD were estimated from the average concentrations of ^{222}Rn (2.04×10^5 dpm m^{-3}) and DSi (130 mmol m^{-3}) in six coastal groundwater samples, an area of bay, and the unknown seepage rate of groundwater (m d^{-1}).

The output flux from ^{222}Rn decay was calculated by the average concentration of ^{222}Rn (3880 dpm m^{-3}) in bay seawater, the water volume of the bay (3.25×10^8 m^3), and the decay constant of ^{222}Rn (0.181 d^{-1}). The mixing fluxes with the open ocean water were calculated by the differences in average concentration between bay water and open ocean water for ^{222}Rn (1420 dpm m^{-3}) and DSi (7.37 mmol m^{-3}), the water volume of the bay, and the unknown exchange rate between

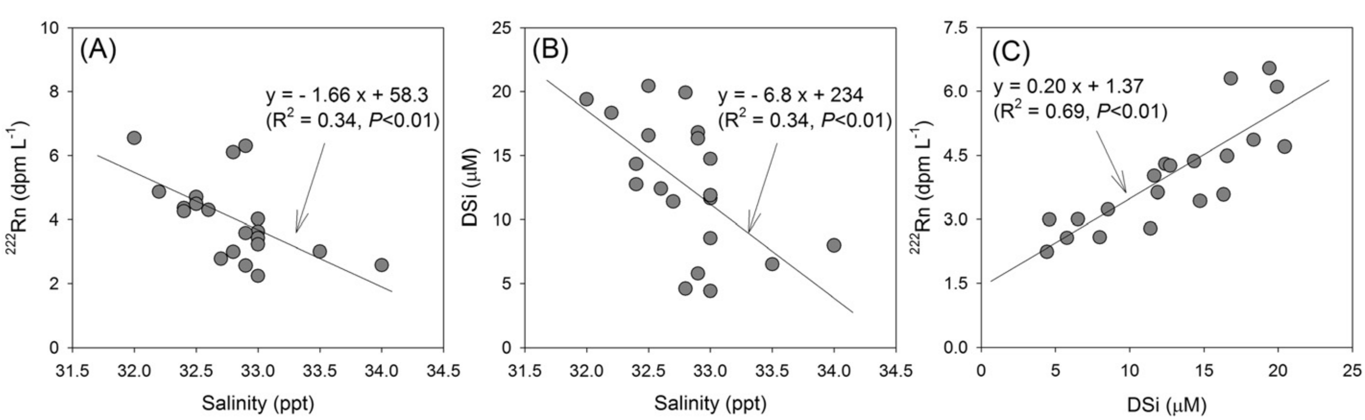

Fig. 5. Plots of salinity versus ^{222}Rn activity (A) and DSi (B) and DSi versus ^{222}Rn activity (C) in seawater of the study region in April 22–25, 2103.

Table 1
The definition and values used in ^{222}Rn- Si mass balances for calculating the input of submarine groundwater in Geoje Bay during April 22–25, 2013.

Definition		Value		Unit
		^{222}Rn	DSi	
A_{Bott}	Bottom area of bay	4.06×10^7	4.06×10^7	m^2
V_S	Water volume of bay	3.25×10^8	3.25×10^8	m^3
F_{Stm}	Input flux through stream water ($F_D \times C_{Stm}$) for ^{222}Rn and Si	1.42×10^{10}	3.91×10^7	dpm (or mmol) d^{-1}
	F_D: Discharge of stream water	1.88×10^5	1.88×10^5	$m^3\ d^{-1}$
	C_{Stm}: Average concentrations in stream water for ^{222}Rn and Si	7.57×10^4	208	dpm (or mmol) m^{-3}
F_{Diff}	Diffusive flux from bottom sediment ($R_G \times A_{Bott}$) for ^{222}Rn and Si	4.06×10^9	2.03×10^8	dpm (or mmol) d^{-1}
	R_G: Regeneration rate of ^{222}Rn and Si	100	5	dpm $m^{-2}\ d^{-1}$
C_{GW}	Average concentration in groundwater for ^{222}Rn and Si	2.04×10^5	130	dpm (or mmol) m^{-3}
Ψ_{SGD}	Seepage rate of submarine groundwater	?	?	m d^{-1}
I_{SW}	Inventory in bay seawater ($V_S \times C_{BW}$) for ^{222}Rn	1.26×10^{12}	–	dpm
	C_{BW}: Volume weighted average concentrations in bay seawater for ^{222}Rn and Si	3.88×10^3	13.55	dpm (or mmol) m^{-3}
$\lambda_{Rn\text{-}222}$	Decay constant for ^{222}Rn	0.181	–	d^{-1}
C_{EX}	Difference in concentrations between bay seawater and open ocean water (C_{BW}-C_O) for ^{222}Rn and Si	1.37×10^3	7.37	dpm (or mmol) m^{-3}
	C_O: Average concentrations in open ocean water for ^{222}Rn and Si	2.51×10^3	6.18	
δ_{Mix}	Exchange rate between bay seawater and open ocean water	?	?	d^{-1}
F_{Atm}	Output flux of ^{222}Rn ($F_R \times A_{Bott}$) across air-sea interface	7.51×10^{10}	–	dpm d^{-1}
	F_R: Flux of ^{222}Rn out of the surface by aerial evasion	1.85×10^3	–	dpm $m^{-2}\ d^{-1}$

bay water and open ocean water. Here, the average concentrations of ^{222}Rn and DSi in bay seawater were calculated by dividing the entire bay water into 20 boxes to obtain a volume weighted average concentrations. The volume weighted average values of ^{222}Rn and DSi were calculated to be about 4025 dpm m^{-3} and 13.55 μM, respectively. The average concentrations of ^{222}Rn (2500 dpm m^{-3}) and DSi (6.18 mmol m^{-3}) in open ocean water were obtained from four seawater samples out of bay.

Finally, the atmospheric loss of ^{222}Rn (F_{Atm}) across the air-water interface was calculated from the following equation suggested by Macintyre et al. (1995):

$$F_{Atm} = k\,(C_{bw} - \alpha\, C_{Atm}) \times A \tag{3}$$

where C_{bw} represents the average of ^{222}Rn activity in the surface bay seawater, C_{Atm} represents the ^{222}Rn activity in the atmosphere, A is the area of Geoje Bay, α is the Ostwald's solubility coefficient (dimensionless), and k is the gas transfer velocity (also referred to as the piston velocity). This gas transfer velocity (k) is dependent on the wind speed (Jahne et al., 1987; Corbett et al., 1997) and can be calculated from the following equation:

$$k = 0.45 \times Ws^{(1.6)} \times (S_C/600)^{(-0.66667)} \tag{4}$$

where W_S is the wind speed, and Sc represents the Schmidt number (=V/Dm), which is the ratio of the kinematic viscosity ($V = 0.0003\ t + 0.0169$; $cm^2\ s^{-1}$; t is water temperature) to the molecular diffusion coefficient ($Dm = 10^{(-((980/(t+273))+1.59))}$; $cm^2\ s^{-1}$) (Macintyre et al., 1995). The solubility coefficient (α) can be calculated by the following equation:

$$\alpha = \beta \times T/273.13 \tag{5}$$

where β represents the Bunsen coefficient ($\ln\beta = -76.15 + 120.63\ (100/T) + 31.26\ \ln\ (T/100) + S\ [-0.2631 + 0.1673\ (T/100) + (-0.027)\ (T/100)^2]$; S is salinity) (Schubert et al., 2012), and T represents the absolute temperature ($T = 273 + t$, unit: K).

Considering the volume weighted average of temperature (13.7 °C), salinity (32.6 ppt) and ^{222}Rn activity (4650 dpm m^{-3}) in the surface seawater of Geoje Bay, the wind speed (4.2 m s^{-1}) during the sampling times of bay seawater, and ^{222}Rn activity in the atmosphere (190 dpm m^{-3}) used data suggested by Hwang et al. (2005b), the evasion flux of ^{222}Rn to the atmosphere is estimated to be 7.52×10^{10} dpm d^{-1}.

Based on the above mentioned values (Table 1), we calculated the residence time of bay water and seepage rate of groundwater in Geoje Bay from the pairs of simultaneous Eqs. (1) and (2). As a result, the residence time of bay water ($1/\ \delta_{Mix}$) and the seepage rate of coastal groundwater (Ψ_{SGD}) were determined to be approximately 5.0 days and 0.05 m d^{-1} ($= 1.8 \times 10^6\ m^3\ d^{-1}$) in the entire bay, respectively. These results have 80–100% of large uncertainties from chemical analysis, the groundwater and stream water endmembers, the diffusion values from sediment, atmospheric evasion, and mixing losses for ^{222}Rn (Hwang et al., 2005b; Burnett et al., 2007). Among the uncertainties in Rn-derived SGD estimate, the endmember concentration in coastal groundwater is the greatest uncertainty (approximately 70–80%). Nevertheless, the residence time of bay water calculated in this study was similar with that (~4.2 days) estimated using a residual current model at the neap tide agree with the tidal difference (<2 m) during the sampling periods of this study (Kim and Chang, 1985), and the estimated seepage rate of groundwater was much higher than that found in the eastern coast of United States although the seepage rate of groundwater in this bay was relatively lower than that previously reported in the coastal zone of Korea and China (Table 2). In addition, SGD in Geoje Bay was about ten times of magnitude higher than the total stream water discharge ($1.88 \times 10^5\ m^3\ d^{-1}$) during the sampling period.

3.3. Evaluation of SGD contribution for excess nutrient fluxes

As the mentioned earlier, the oyster cultivating activities have been developed in Goeje Bay and the nutrient concentrations in bay seawater are very important to maintain the high oyster production continuously. Therefore, in this study, we evaluated the relative contribution for all nutrient sources in this bay such as stream, diffusion from bottom sediment, and SGD in order to determine the main source of nutrients in bay water. Here, we neglected atmospheric deposition of nutrients since the scale of this bay is very small and the atmospheric nutrient fluxes through dry and wet deposition reported in the northeastern Asia including Yellow Sea and East China Sea are about one or two orders of magnitudes lower than the regeneration rates of the nutrients from the sediment reported in the southern coast of Korea (Zhang et al., 2011; Shi et al., 2013; Zhu et al., 2013).

The nutrient fluxes from the stream were determined by multiplying the discharge rate of stream water during the sampling period by the average concentration of nutrients in the stream water samples (85, 0.2, and 208 μM for DIN, DIP, and DSi, respectively). The nutrient fluxes due to diffusion from bottom sediments were determined by multiplying the total area of bay by the regeneration rates of the

Table 2
A comparison of DIN, DIP, and DSi fluxes through SGD in various coastal ocean of the whole world.

Region	SGD ($m^3/m^2/d$)	DIN flux (mmol $N/m^2/d$)	DIP flux (mmol $P/m^2/d$)	DSi flux (mmol $Si/m^2/d$)	DIN/DIP	Reference
USA						
North Inlet, SC	0.03	2.42	0.91	–	3	Krest et al. (2000)
Salt pond, RI	0.006–0.02	1.84–4.88	0.003–0.007		561–697	Scott and Moran (2001)
Pettaquamscutt, RI	0.002–0.02	0.17–0.49	0.01–0.04	–	~ 14	Kelly and Moran (2002)
Huntington Beach, CA	0.06–0.92	0.7–12	0.04–0.54	–	~ 20	Boehm et al. (2004)
Tampa Bay, FL	0.002–0.01	0.19–1.36	0.01–0.14	0.08–0.61	10	Swarzenski et al. (2007)
Hawai'ian Island, HW	0.02–0.65	0.04–40	0.01–1.60	–	4–25	Street et al. (2008)
China						
Tolo Harbour, HK	0.17	21	0.28	28	75	Lee et al. (2012a)
Laoye Lagoon, Hainan	0.15	9.4	0.03	2.9	~ 330	Ji et al. (2013)
Sanggou Bay, YS	0.13–0.15	19–23	0.07–0.09	1.0–1.3	~ 280	Wang et al. (2014)
Other country						
Gulf of Aquaba, Israel	0.06–0.26	2.9–10	0.02–2.0	–	5–100	Shellenbarger et al. (2006)
Falma Beach, Balearic	0.01	0.97	0.008	–	~ 120	Rodellas et al. (2014)
Korea						
Yeoja Bay	0.24	26	0.11	26	~ 230	Hwang et al. (2005a)
Masan Bay	0.06–0.07	6.01–7.79	0.14–0.19	3.8–5.0	~ 42	Lee et al. (2009)
Gamak Bay	0.08–0.11	8.8–12.1	0.10–0.23	–	40–88	Hwang et al. (2010)
Geoje Bay	0.05	2.0	0.03	5.9	71	This study

nutrients from the sediment reported by Kim and Park (1998) and Jung and Cho (2003) in the southern coast of Korea (1.3, 0.6, and 5.0 mmol m^{-2} d^{-1} for DIN, DIP, and DSi, respectively). The nutrient fluxes through SGD were determined by multiplying the estimated discharge rate of submarine groundwater during the sampling period by the average concentration of nutrients in the coastal groundwater samples (44.5, 0.6, and 130 μM for DIN, DIP, and DSi, respectively). The nutrient fluxes estimated from each source are shown in Table 3.

The DIN and DSi fluxes from stream, bottom sediment, and SGD were calculated to be 1.61×10^4 and 3.91×10^4 mol d^{-1}, 5.28×10^4 and 20.3×10^4 mol d^{-1}, and 8.18×10^4 and 23.8×10^4 mol d^{-1}, respectively (Table 3). The estimated DIN and DSi fluxes through SGD are much higher than those from stream and bottom sediment and contribute approximately 54% and 50% of the total DIN and DSi fluxes in the seawater of Geoje Bay, respectively. In contrast, DIP flux from stream, bottom sediment, and SGD were calculated to be 0.005×10^4 mol d^{-1}, 2.44×10^4 mol d^{-1}, and 0.12×10^4 mol d^{-1}, respectively (Table 3). The estimated DIP flux through diffusion from bottom sediment is much higher than those from the stream and SGD and contributes approximately 95% of the total DIP flux in bay seawater. Therefore, SGD appears to be the dominant source of DIN and DSi, while the diffusion from bottom sediment is the main source of DIP in the seawater of Geoje Bay.

Table 3
The comparison of nutrients fluxes through stream water, bottom sediment, and SGD in Geoje Bay.

	Nutrient Flux ($\times 10^4$ mol/day)		
	DIN	DIP	DSi
Stream [1]	1.61	0.005	3.91
Diffusion from bottom sediment [2]	5.28	2.44	20.3
SGD [2]	8.18	0.12	23.8

1. Based on the concentration of nutrients in the stream water and the input of stream water which is measured during the from sampling data.
2. Calculated by multiplying the area of defined SGD by the regeneration rates of nutrients measured by Kim and Park (1998) and Jung and Cho (2003) in coastal bay and estuary of Korea.
3. Based on the average concentrations of nutrients in potential groundwater and the estimated SGD.

The SGD-derived DIN and DIP fluxes in this bay are higher than or similar to those observed from estuary system in the eastern part of the United States, such as North Inlet, Pettaquamscutt, and Tampa Bay, and while they are significantly lower than those observed in China, such as Tolo harbour, Laoye lagoon, and Sanggou Bay with low tidal difference (< 1.5 m) compared to this study region. In addition, they are much lower than those observed from semi-enclosed bays (i.e. Gamak, Masan, and Yeoja Bays) with similar marine environment in southern sea of Korea (references are in Table 2). The SGD-derived DSi flux in this bay is higher than that observed in Tampa Bay of the United States, Laoye lagoon and Sanggou Bay of China, and Masan Bay of Korea, while it is much lower than that observed in Tolo harbour of China and Yeoja Bay of Korea (Table 2).

On the other hand, the nutrient fluxes into Goeje Bay were characterized by higher DIN/DIP ratios (~70) relative to the Redfield ratio (~16) like other SGD study sites, such as salt pond in Rhode Island of the United States, Tolo harbour, Laoye Lagoon, and Sanggou Bay of China, and Yeoja Bay and Gamak Bay of Korea. Recently, Lee et al. (2010) reported that there are close relationship between the magnitude of SGD-derived nutrients and the intensity of dinoflagellate (*Cochlodinium polykrikoides*) red-tides occurring in the southern sea of Korea. Lee et al. (2012b) revealed that brackish groundwater along Tongyoung coast neighboring this study region have a trigger elements occurring *C. polykrikoides* red-tides. Thus, the input of coastal groundwater in Geoje Bay is likely to have a significant influence on the phytoplankton biomass in the bay.

Based on the overall distribution patterns of DIN, DIP, and salinity in seawater, the concentrations of DIN and DIP show a widely scattered variation and are not conservative against salinity. In addition, these two species are almost depleted in bay water with salinity range between 32 and 33 ppt, which might be due to active biological uptake. If DIN and DIP fluxes from stream, bottom sediment, and SGD are fully utilized to support the net primary production in Geoje Bay, the potential carbon productions in bay water are calculated to be 0.29–0.81 g C m^{-2} d^{-1} by applying the Redfield ratio ($C:N:P = 106:16:1$) in general seawater. The estimated values are within a range of the total primary production (0.19–1.27 g C m^{-2} d^{-1}) estimated by using an eco-hydrodynamic model in oyster farming areas of Geoje-Hansan Bay including this bay (Park et al., 2002). Thus, new DIN and DIP fluxes from stream, bottom sediment, and SGD are almost fully utilized by the biological activity in this bay before they reach the open ocean, and the SGD-derived DIN flux appear to play an important role for nutrient budget required to support the high oyster farming production in the bay.

4. Conclusions

The SGD in Geoje Bay, an oyster farming bay, of Korea was determined using the ^{222}Rn and Si mass balance model. The estimated SGD (approximately 1.8×10^6 m^3 d^{-1}) was about ten times of magnitude higher than the total stream water discharge during the sampling period. The DIN and DSi fluxes through SGD were much higher than those through the stream water and diffusion from bottom sediment. Especially, the input of coastal groundwater with DIN/DIP imbalance (~70) and trigger elements around this study region could have a significant impact on oyster farming production as well as phytoplankton biomass in the bay. More intensive studies for the relationship between SGD and production or growth rate of farmed oyster in the future in order to sustain the high oyster production in this bay.

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