

## Large submarine groundwater discharge and benthic eutrophication in Bangdu Bay on volcanic Jeju Island, Korea

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### Abstract

We estimated the submarine discharge of groundwater (SGD) and associated nutrients into the semienclosed Bangdu Bay on a volcanic island, Jeju, Korea, by analyzing <sup>222</sup>Rn, Ra isotopes (<sup>224</sup>Ra and <sup>226</sup>Ra), and nutrients in seawater, pore water, and coastal groundwater. The submarine inputs of groundwater into Bangdu Bay of 120–180 m<sup>3</sup> m<sup>-2</sup> yr<sup>-1</sup> (on the basis of <sup>222</sup>Rn, <sup>224</sup>Ra, <sup>226</sup>Ra, and Si mass balances) were much higher than those reported from typical continental margins. The nutrient fluxes from SGD were about 90%, 20%, and 80% of the total input (except from open ocean waters) for dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved inorganic silicate (DSi), respectively. These excess nutrient inputs from SGD are the major sources of “new nutrients” in this bay. On the basis of photosynthetic pigments and benthic algal distributions, we suggest that the large fluxes of excess nutrients from SGD can cause benthic eutrophication in a semienclosed bay on this highly permeable volcanic island.

Submarine groundwater discharge (SGD) has been recognized as an important pathway for chemical constituents, such as Ra, Rn, CH<sub>4</sub>, and nutrients, from continents to the ocean (Moore 1996; Burnett et al. 2003; Hwang et al. 2005). Although only fresh groundwater input is quantified as submarine discharge for water balance purposes, brackish groundwater, including recirculating seawater, is an equally or often more important route for transporting continental materials into the ocean (Church 1996; Moore 1997; Kim et al. 2003a). Using a <sup>226</sup>Ra tracer, it was estimated that the volume of groundwater could be as great as 40% of the total river flow for the South Atlantic Bight (Moore 1996). However, Younger (1996) argued that the volume of groundwater recharge was only 1.7% of the freshwater discharge from rivers in the same region. On the basis of a theoretical calculation, Li et al. (1999) showed that groundwater circulation and oscillation flow, caused by wave setup and tidal actions, may constitute up to 96% of the SGD in the South Atlantic Bight. More recently, Kim and Hwang (2002) suggested that recirculation of seawater through the ground is even more largely controlled by spring and neap tide fluctuations.

The magnitudes and mechanisms of SGD are indeed poorly understood, since there is no accurate tool for measuring SGD because this source is invisible, slow, and spatially and temporally variable. To tackle this, recent studies have used various geochemical tracers such as <sup>226</sup>Ra (t<sub>1/2</sub> = 1,620 yr), <sup>222</sup>Rn (t<sub>1/2</sub> = 3.83 d), CH<sub>4</sub>, and Si, which are much more highly enriched in groundwater relative to seawater, for tracing SGD on a large space and time scale (Bugna et al. 1996;

Corbett et al. 1997; Hwang et al. 2005). The fluxes of nutrients from SGD were estimated in several coastal environments by correlating the average concentrations of nutrients in pore water or groundwater to the volume of SGD (Krest et al. 2000; Charette et al. 2001; Kelly and Moran 2002).

Thus, the objective of this study was to estimate the input of submarine groundwater and nutrients into a small coastal bay on a volcanic island, Jeju, using <sup>222</sup>Rn, <sup>224</sup>Ra, <sup>226</sup>Ra, and Si mass balances. This bay of Jeju is known to have high seepage rates due to the high permeability of the rocks (Kim et al. 2003a). Pigment signatures were also measured to investigate the community compositions of phytoplankton in the water column in response to the nutrient supply from SGD. In addition, benthic eutrophication was examined visually at near-shore areas. Here, we chose Bangdu Bay since it serves as a unique natural SGD chamber on Jeju.

### Study area and analytical methods

*Study area*—Jeju Island is located in the South Sea of Korea, with an area of ~1,830 km<sup>2</sup> (Fig. 1). Jeju is a shield volcano that is composed mainly of basaltic lava flows and a subordinate amount of pyroclastic and sedimentary rocks. In the central part of the island Mt. Hanla (height, ~1,950 m) is located with a gentle slope from the peak to the east and the west. There is a large difference in geological structures between the western and eastern parts of Jeju. A low-permeability sedimentary formation, the Seogwipo formation, underlies high-permeability volcanic rocks in western Jeju, while an unconsolidated fine-sand layer underlies the thick high-permeability basaltic layer in eastern Jeju (Koh 1997; Kim et al. 2003b). Therefore, there are a number of artesian springs and wells on the western coast, while the groundwater below a few meters is composed almost entirely of recirculated seawater on the eastern coast of Jeju (Kim et al. 2003b).

Since most of the precipitation infiltrates the geologic structures rapidly, there is little sustained stream flow on the

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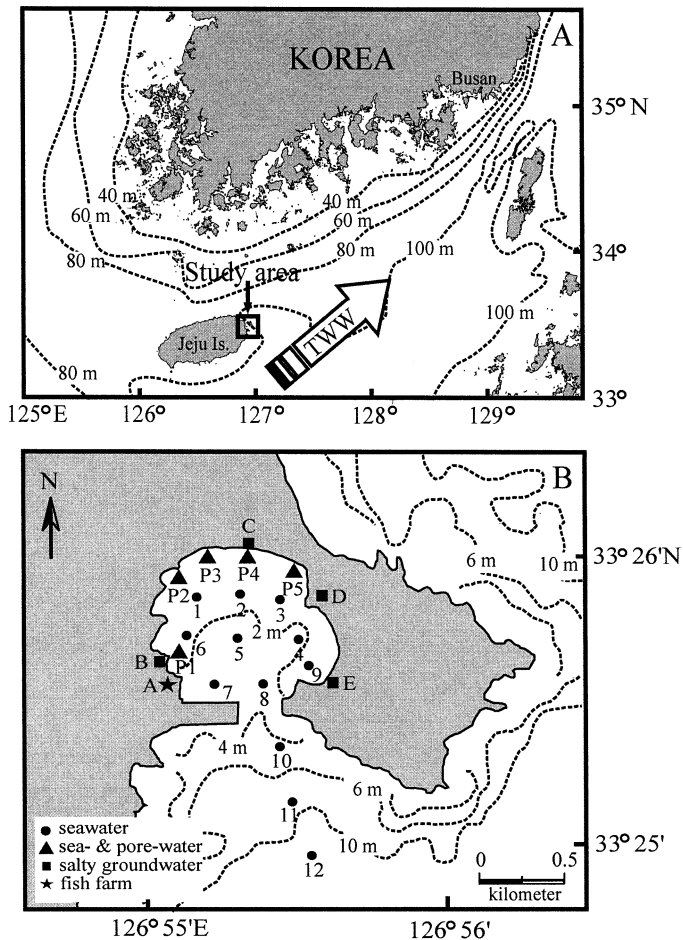


Fig. 1. The maps showing (A) the location of the study area and (B) the sampling sites in May 2004. The arrow represents the flow of the Tsushima Warm Water (TWW). Most of the coastal waters in eastern Jeju Island were highly influenced by the TWW during all seasons.

island, despite heavy rainfall ( $\sim 1,900 \text{ mm yr}^{-1}$ ) in the summer and the torrential runoffs that occur during and immediately after large rain events. Because of the high permeability of the geologic structures, the seepage rates measured along the sandy coast were in the range of  $50\text{--}300 \text{ m yr}^{-1}$  ( $14\text{--}82 \text{ cm d}^{-1}$ ) (Kim et al. 2003a), which is much higher than for those reported for typical continental coasts (Bugna et al. 1996; Corbett et al. 1997; Charette et al. 2001; Kelly and Moran 2002).

The study area, Bangdu Bay, is a semienclosed bay located in the eastern part of Jeju (Fig. 1). This bay is relatively small and shallow, with an area of about  $0.8 \text{ km}^2$  and a mean depth of  $\sim 3 \text{ m}$ . Although there is no continuous river discharge, there is a temporary inflow of freshwater from an intermittent stream during the summer monsoon season. On the western part of the bay, there is a fish farm (Fig. 1) that uses groundwater (entirely recirculating seawater) with a temperature of  $\sim 16^\circ\text{C}$  to facilitate the maintenance of a constant temperature of the farm's seawater during all seasons. Since this farm discharges the seawater used directly into the bay, there are environmental concerns in

terms of the occurrence of excess nutrient loadings and other contaminants during farming processes.

**Sampling and analytical method**—Water samples were taken to analyze for nutrients, pigments, Rn, and Ra isotopes from Bangdu Bay and adjacent groundwater wells in May 2004 (Fig. 1). The seawater samples were collected from the surface ( $\sim 1 \text{ m}$ ) and bottom ( $\sim 3 \text{ m}$ ) layers using a submersible pump with a flow rate of  $15\text{--}20 \text{ L min}^{-1}$  on shipboard. The brackish groundwater samples were obtained from wells (70 m) and boreholes ( $<1 \text{ m}$ ) using an electric pump. In addition, pore-water samples were collected to determine the vertical distributions of nutrients between 0 and 15 cm using 5-cm intervals with a multilevel sampler coupled to a 10-mL polyethylene syringe.

The activity of  $^{222}\text{Rn}$  in seawater and coastal groundwater was determined in the field with an automated system using a RAD7 (radon-in-air monitor, Durrige) recently developed by Burnett et al. (2001). This system determines the activity of  $^{222}\text{Rn}$  released from a constant flow of seawater (driven by a submersible pump) passing through an air-water exchanger to a closed air loop. The air in the closed air loop was continuously circulated with a built-in air pump in the RAD7. The RAD7 determines the activity of  $^{222}\text{Rn}$  by the collection and measurement of the alpha emitting daughter particles,  $^{218}\text{Po}$  and  $^{214}\text{Po}$ , using a charged semiconductor detector in the radon chamber.

To measure  $^{224}\text{Ra}$  and  $^{226}\text{Ra}$ , about 60 liters of seawater ( $n = 13$ ) and coastal groundwater ( $n = 5$ ) samples were collected in polypropylene cubitainers and, while in the field, directly passed through an acrylic column (4.5 cm in diameter, 20 cm in length) filled with  $\text{MnO}_2$ -impregnated acrylic fiber ( $\sim 60 \text{ g-wet}$  with a flow rate of  $<1 \text{ L min}^{-1}$ ). This procedure is a quantitative method for extracting Ra isotopes from seawater and groundwater to Mn fiber (Kim et al. 2001). In the laboratory, the water content of the Mn fibers was adjusted (Kim et al. 2001), and then the fibers were placed in a delayed coincidence counter for measuring  $^{224}\text{Ra}$  (Moore and Arnold 1996). About 20 d after sampling, the activities of  $^{228}\text{Th}$  were measured via  $^{224}\text{Ra}$  using a delayed coincidence counter, but they were mostly lower than the detection limit. The 60-liter sample volume was insufficient to obtain statistically meaningful counts for  $^{223}\text{Ra}$  within the 12-h counting time. A delayed coincidence counter for  $^{224}\text{Ra}$  was calibrated using  $^{228}\text{Th}/^{232}\text{U}$  standards.  $^{226}\text{Ra}$  was measured by alpha counting the  $^{222}\text{Rn}$  daughter ( $^{218}\text{Po}$ ), which is in equilibrium with  $^{226}\text{Ra}$ , using the RAD7 (Kim et al. 2001). The RAD7 was calibrated for measuring  $^{226}\text{Ra}$  by counting a  $^{226}\text{Ra}$  standard that had been adsorbed on an equivalent weight of Mn fiber.

About 1-liter seawater samples were used to measure the concentrations of photosynthetic pigments. The seawater samples were filtered through a GF/F filter (47 mm in diameter) in the field, and then the filters were immediately stored in a deep freezer ( $-80^\circ\text{C}$ ). The concentrations of photosynthetic pigments were determined using the modified method described by Wright et al. (1991). First, photosynthetic pigments were extracted using 100% acetone (5 mL) at  $-20^\circ\text{C}$  for 24 h in the dark. After sonification and centrifugation, the supernatant (1 mL) was mixed with 0.3 mL

of deionized water. The mixed solution (0.1 mL) was measured by reverse-phase high-performance liquid chromatography (Waters system). The pigments were identified and quantified with authentic standards obtained from Sigma Chemical and DHI.

Temperature and salinity were measured in the field using a portable salinometer (model LF340, WTW). Nutrient ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{Si}(\text{OH})_4$ ) samples were collected in polyethylene bottles (~100 mL) and frozen until analysis; they were then determined using an Auto-Analyzer (TRAACS 2000, Bran+Lubbe K.K) in the laboratory. In this study, we define DIN as the sum of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ , DIP as  $\text{PO}_4^{3-}$ , and DSi as  $\text{Si}(\text{OH})_4$ .

## Results and discussion

*Distribution of salinity, nutrients,  $^{222}\text{Rn}$ , and Ra isotopes*—The measured results for salinity, nutrients, and radionuclide tracers in pore water, coastal groundwater, and seawater are shown in Tables 1, 2. Salinity in pore water and coastal groundwater ranged from 29.6 to 33.7 (mean = 31.4,  $n = 5$ ) and from 30.5 to 35.9 (mean = 33.2,  $n = 5$ ), respectively, which was lower than the salinity of the seawater in the bay. The concentrations of nutrients,  $^{222}\text{Rn}$ , and Ra isotopes in pore water and coastal groundwater were a factor of two to three times higher than those in seawater.

The shallow coastal waters in the northwestern part of this bay showed particularly low salinity but high concentrations of nutrients,  $^{222}\text{Rn}$ , and Ra isotopes (Fig. 2). Such a trend could have resulted from a relatively large discharge of coastal groundwater, since there were no visible streams during the sampling period. Salinity and DSi concentrations showed a good negative correlation ( $r^2 = 0.80$ ), indicating a conservative behavior of Si in the bay (Fig. 3). We used Si as an SGD tracer (Hwang et al. 2005), together with  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{222}\text{Rn}$ , since the concentrations of Si were a factor of two to three times higher in coastal groundwater than in seawater. Therefore, we evaluated the magnitude of SGD and the associated nutrient fluxes in the next section using various mass balance models for chemical tracers.

*Estimating seepage rates and water residence times using mass balances for  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi*—To establish mass balance models for  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi, we must consider all source and sink terms for each chemical species. A simple schematic for this model is shown in Fig. 4A. The input sources of DSi and Ra isotopes in Bangdu Bay include (1) discharge of the fish farm water, (2) diffusion from bottom sediments, and (3) SGD and pore water, while output sources include (1) decay of short-lived Ra isotopes and (2) tidal exchange between bay seawater and open ocean water. The changes in the concentrations of  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi in the water column of the bay may be expressed as follows (Eqs. 1–3):

Table 1. Concentrations of nutrients, Rn, and Ra isotopes in the coastal groundwater and pore water in Bangdu Bay in May 2004.

Station	Location		Temp. (°C)	Nutrients ( $\mu\text{mol L}^{-1}$ )					$^{222}\text{Rn}$ (dpm $\text{L}^{-1}$ )		Ra activity (dpm 100 $\text{L}^{-1}$ )	
	Latitude	Longitude		Salinity	DIN	DIP	DSi	$^{222}\text{Rn}$	$^{226}\text{Ra}$	$^{224}\text{Ra}$		
A	33°25'37"N	126°55'05"E	16.6	39.4	0.44	242	18.6 ± 10.8	42.6 ± 1.5	17.2 ± 1.4			
B	33°25'32"N	126°55'03"E	16.7	85.3	0.50	187	71.7 ± 14.5	40.7 ± 2.6	17.0 ± 1.1			
C	33°25'55"N	126°55'24"E	19.0	69.4	0.20	146	76.9 ± 15.9	70.4 ± 2.4	13.6 ± 1.5			
D	33°25'48"N	126°55'33"E	18.7	38.8	0.20	103	14.5 ± 7.7	61.4 ± 2.4	13.8 ± 1.4			
E	33°25'32"N	126°55'37"E	20.0	33.7	0.10	40	64.2 ± 13.3	36.2 ± 3.4	16.2 ± 1.0			
P 1	33°25'43"N	126°55'06"E	22.2	45.1	0.25	89	—	—	—			
P 2	33°25'52"N	126°55'06"E	23.8	—	1.54	130	—	—	—			
P 3	33°25'54"N	126°55'12"E	19.5	25.5	0.30	81	—	—	—			
P 4	33°25'55"N	126°55'24"E	23.4	64.4	0.10	93	—	—	—			
P 5	33°25'49"N	126°55'32"E	22.3	32.9	0.10	69	—	—	—			

Table 2. The concentrations of nutrients, Rn, and Ra isotopes in the seawater of Bangdu Bay in May 2004.

Station	Location			Temp. (°C)	Nutrients ( $\mu\text{mol L}^{-1}$ )					Ra activity (dpm 100 L $^{-1}$ )		
	Latitude	Longitude			Salinity	DIN	DIP	DSi	$^{222}\text{Rn}$ (dpm L $^{-1}$ )	$^{226}\text{Ra}$	$^{226}\text{Ra}$	
Bay water												
P1S	33°25'43"N	126°55'06"E		18.1	28.3	36.9	0.10	144	—	—	—	
P2S	33°25'52"N	126°55'06"E		18.8	31.6	27.8	0.10	117	—	—	—	
P3S	33°25'54"N	126°55'12"E		18.7	33.3	20.3	0.10	62	—	—	—	
P4S	33°25'55"N	126°55'24"E		19.9	30.8	27.7	0.10	73	—	—	—	
P5S	33°25'49"N	126°55'32"E		—	—	47.7	0.10	96	—	—	—	
1S	33°25'73"N	126°55'24"E		16.5	32.7	19.7	0.68	74	9.5±2.7	24.7±1.2	9.8±0.8	
2S	33°25'74"N	126°55'30"E		16.7	33.4	13.9	0.55	58	11.6±2.6	13.4±0.9	10.3±0.8	
3S	33°25'74"N	126°55'42"E		16.3	33.9	15.1	0.48	56	9.8±2.5	9.3±0.7	8.2±0.8	
4S	33°25'63"N	126°55'44"E		16.8	34.4	8.4	0.59	20	6.1±2.1	12.4±0.9	9.9±0.9	
5S	33°25'63"N	126°55'26"E		17.3	32.7	28.1	0.76	73	8.9±2.4	13.2±2.0	10.5±1.0	
6S	33°25'64"N	126°55'21"E		17.7	33.9	12.5	0.54	57	7.9±2.2	25.2±2.8	8.9±0.9	
7S	33°25'56"N	126°55'19"E		18.3	34.4	9.4	0.57	26	6.8±2.3	8.4±1.3	10.8±1.0	
7B				16.2	34.5	7.2	0.13	18	4.2±1.9	12.3±1.7	24.9±0.9	
8S	33°25'57"N	126°55'31"E		17.9	33.1	20.1	0.42	69	13.0±2.7	16.1±2.6	9.9±0.7	
8B				17.9	33.6	6.7	0.25	27	11.9±2.6	24.6±1.7	11.8±0.8	
9S	33°25'58"N	126°55'51"E		17.0	34.2	8.0	0.05	19	4.1±1.8	8.2±0.7	12.3±0.5	
Offshore water												
10S	33°25'41"N	126°55'37"E		17.5	33.3	13.7	0.80	60	—	—	—	
10B				17.0	34.2	6.6	0.45	21	—	—	—	
11S	33°25'30"N	126°55'37"E		17.3	33.9	13.7	0.35	31	—	—	—	
11B				16.7	33.5	8.7	0.25	19	—	—	—	
12S	33°25'18"N	126°55'56"E		16.9	34.0	13.9	0.25	32	2.8±1.6	6.4±1.1	13.5±0.9	
12B1				16.9	34.5	9.9	0.25	17	4.9±1.9	3.2±0.8	9.9±0.8	
12B2				16.3	34.7	8.7	0.25	8	—	—	—	

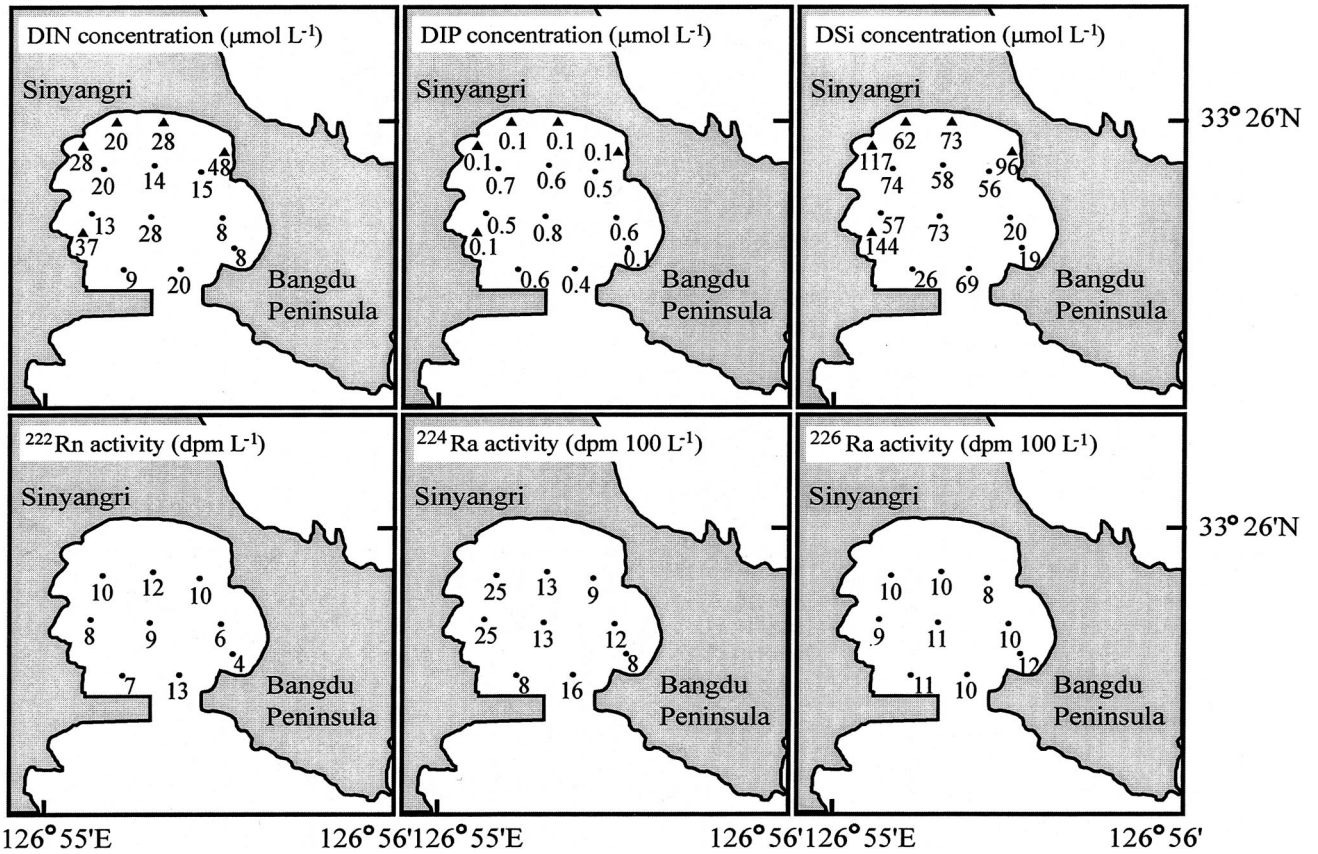


Fig. 2. The horizontal distributions of nutrients, <sup>222</sup>Rn, and Ra isotopes in the surface seawater of Bangdu Bay in May 2004.

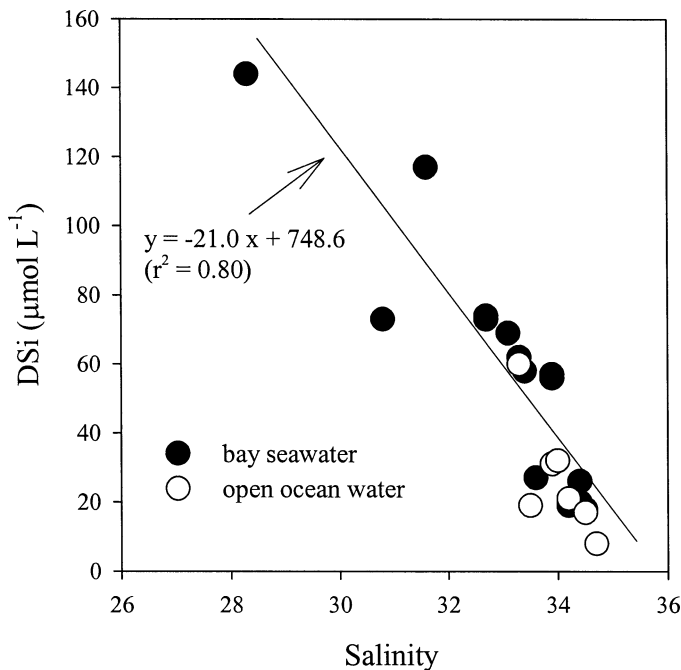


Fig. 3. Plot of salinity versus DSi in seawater of the study region in May 2004.

$$\frac{d^{226}\text{Ra}}{dt} = F_{\text{Fish}}^{\text{Ra-226}} + F_{\text{Diff}}^{\text{Ra-226}} + C_{\text{GW}}^{\text{Ra-226}} \times A_{\text{Bott}} \times \psi_{\text{SGD}} - I_{\text{SW}}^{\text{Ra-226}} \times \lambda_{\text{Ra-226}} - C_{\text{EX}}^{\text{Ra-226}} \times V_{\text{S}} \times \lambda_{\text{Mix}} \quad (1)$$

$$\frac{d^{224}\text{Ra}}{dt} = F_{\text{Fish}}^{\text{Ra-224}} + F_{\text{Diff}}^{\text{Ra-224}} + C_{\text{GW}}^{\text{Ra-224}} \times A_{\text{Bott}} \times \psi_{\text{SGD}} - I_{\text{SW}}^{\text{Ra-224}} \times \lambda_{\text{Ra-224}} - C_{\text{EX}}^{\text{Ra-224}} \times V_{\text{S}} \times \lambda_{\text{Mix}} \quad (2)$$

$$\frac{d\text{Si}}{dt} = F_{\text{Fish}}^{\text{Si}} + F_{\text{Diff}}^{\text{Si}} + C_{\text{GW}}^{\text{Si}} \times A_{\text{Bott}} \times \psi_{\text{SGD}} - C_{\text{EX}}^{\text{Si}} \times V_{\text{S}} \times \lambda_{\text{Mix}} \quad (3)$$

where the terms on the right side of the equations represent input fluxes from the fish farm water (the first term), diffusion from sediments (the second term), submarine groundwater flow (the third term), and output fluxes from radioactive decay and mixing with open ocean water (the final term). The definitions and values of each term are shown in Table 3. The ingrowth term for <sup>224</sup>Ra and <sup>226</sup>Ra in seawater was neglected, since the activities of <sup>228</sup>Th and <sup>230</sup>Th in seawater were relatively negligible. At steady state, we can determine two unknown terms,  $\lambda_{\text{Mix}}$  and  $\psi_{\text{SGD}}$ , using any pair of three simultaneous equations.

Here, the fluxes of each species from the fish farm (which uses recirculating ground seawater) were estimated on the basis of the fluxes of the daily discharge of fish farm water and the concentration in the fish farm water. The diffusive

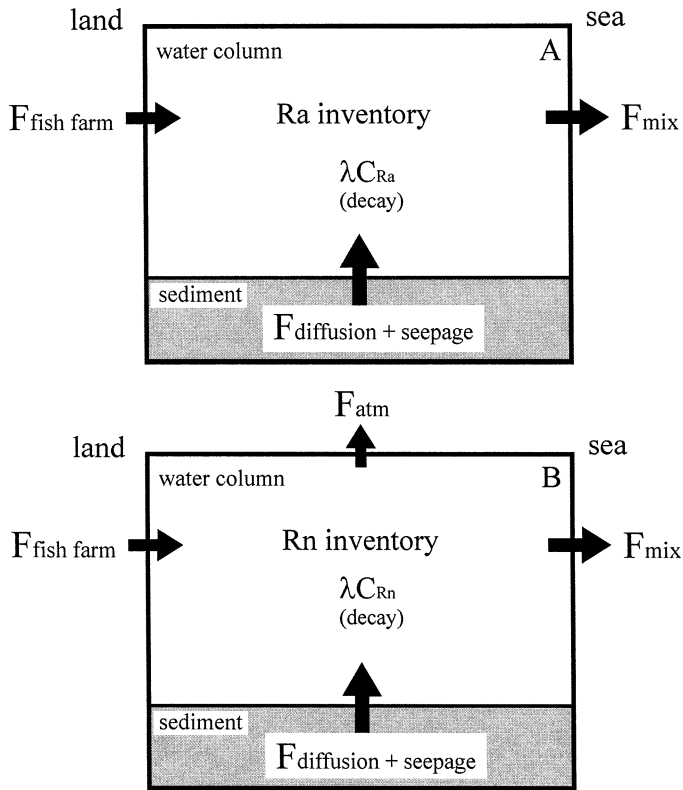


Fig. 4. Box model showing the sources and sinks of (A) Ra isotopes and (B) Rn in the water column of Bangdu Bay.

fluxes of  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi from the bottom sediment were based on estimations of diffusive fluxes from coastal sediments from Charette et al. (2001), Bird et al. (1999), and Jung and Cho (2003), respectively, multiplied by the areas of this bay. Although there are large uncertainties in these assumptions, the errors of calculated SGD arising from them appear to be small, since the maximum assumed values of diffusive fluxes are much smaller than the advective fluxes (Table 3). Furthermore, the diffusive fluxes of  $^{224}\text{Ra}$  from different sediment facies were similar (Bird et al. 1999). In the case of long-lived  $^{226}\text{Ra}$ , the production rate from  $^{230}\text{Th}$  is very slow in sediments (Rama and Moore 1996; Charette et al. 2003; Hwang et al. 2005).

The end-member concentrations of each species in coastal groundwater were from the average of four brackish groundwater samples. The end-member concentrations of  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi in open ocean waters were assumed to be approximately  $7.2 \text{ dpm } 100 \text{ L}^{-1}$  (Nozaki et al. 1991),  $1.5 \text{ dpm } 100 \text{ L}^{-1}$  (Hwang et al. 2003), and  $8 \mu\text{mol L}^{-1}$  (NFRDI 2003), respectively. The average concentrations of  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi in bay water were calculated by dividing the entire bay water into 15 boxes in order to obtain a volume-weighted average. The average concentrations were calculated to be about  $12.2 \text{ dpm } 100 \text{ L}^{-1}$ ,  $14.3 \text{ dpm } 100 \text{ L}^{-1}$ , and  $52 \mu\text{mol L}^{-1}$  for  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and DSi, respectively.

The residence times of bay water ( $1/\lambda_{\text{mix}}$ ), based on  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  mass balances (Eqs. 1, 2),  $^{226}\text{Ra}$  and DSi mass balances (Eqs. 1, 3), and  $^{224}\text{Ra}$  and DSi mass balances (Eqs. 2, 3), were determined to be approximately 2.0, 2.1, and 2.0

d, respectively. The seepage rates ( $\psi_{\text{SGD}}$ ) estimated from these mass balance models ranged from  $45$  to  $48 \text{ cm d}^{-1}$  (mean =  $47 \text{ cm d}^{-1}$ ) in the entire bay.

On the other hand, Kim et al. (2003a) previously measured the seepage rates of coastal groundwater along the shore of Jeju by using manual seepage meters (modified from the Lee-type seepage meter) from April 2002 to August 2002. The seepage rates in eastern Jeju were in the range of  $14$ – $82 \text{ cm d}^{-1}$ , with a relatively small spatial and temporal variation. The seepage rates estimated in this study from Bangdu Bay (a natural chamber) fall within the range of the seepage rates measured by manual seepage meters (Kim et al. 2003a), showing consistency between various years and methods.

*Estimating SGD using a  $^{222}\text{Rn}$  mass balance model*—Since  $^{222}\text{Rn}$  is highly enriched in both fresh and brackish groundwater, the estimated seepage rate, based on a  $^{222}\text{Rn}$  mass balance, can be decoupled from that based on the mass balances of  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ , which are more enriched in brackish groundwater relative to fresh groundwater in Jeju Island (Kim et al. 2003a). Thus, in this study, we calculated SGD independently using a  $^{222}\text{Rn}$  tracer for comparison. For the mass balance of excess  $^{222}\text{Rn}$  ( $^{222}\text{Rn}$ – $^{226}\text{Ra}$ ) in bay water, we have to add a gas exchange term to the previous mass balances for  $^{226}\text{Ra}$  or  $^{224}\text{Ra}$  (Eqs. 1, 2) (Fig. 4B). At steady state, the mass balance of  $^{222}\text{Rn}$  may be expressed as follows (Eq. 4):

$$F_{\text{Fish}}^{\text{Rn-222}} + F_{\text{Diff}}^{\text{Rn-222}} + C_{\text{GW}}^{\text{Rn-222}} \times A_{\text{Bott}} \times \psi_{\text{SGD}} - I_{\text{SW}}^{\text{Rn-222}} \times \lambda_{\text{Rn-222}} - C_{\text{EX}}^{\text{Rn-222}} \times V_s \times \lambda_{\text{Mix}} - F_{\text{Atm}}^{\text{Rn-222}} = 0 \quad (4)$$

where the terms on the left side of the equation represent input fluxes from fish farm 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 open ocean water (the fifth term), and evasion flux to the atmosphere (the final term).

The calculations of each term are similar to those for  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$ . The input fluxes from fish farm water and diffusion from sediments were about  $3.7 \times 10^8$  and  $8.1 \times 10^7 \text{ dpm d}^{-1}$ , respectively. The output fluxes from radioactive decay and mixing with the open ocean water were about  $3.8 \times 10^9$  and  $1.0 \times 10^{10} \text{ dpm d}^{-1}$ , respectively. Here, we calculated the water mixing fluxes on the basis of the water residence time (average from the  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ , and Si methods) and the difference in  $^{222}\text{Rn}$  activities between open ocean water and the average of bay water.

The gas exchange across the air–water interface is a significant sink for dissolved radon in coastal waters (Corbett 1999). The total flux of dissolved gases escaping from the seawater to the atmosphere depends on the molecular diffusion resulting from the concentration gradient across the air–water interface and turbulent transfer by physical processes such as wind speed. In this study, the atmospheric loss of radon ( $F_{\text{Atm}}$ ) was calculated from the following equation suggested by Macintyre et al. (1995):

$$F_{\text{Atm}} = k(C_{\text{Bw}} - \alpha C_{\text{Atm}}) \times A \quad (5)$$

Table 3. The definition and values used in the simultaneous equations for  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $\text{DSi}$ , and  $^{222}\text{Rn}$  mass balances for calculating the residence time of seawater and seepage rates in Bangdu Bay, Jeju Island.

	Definition	Value				Unit
		$^{226}\text{Ra}$	$^{224}\text{Ra}$	$\text{DSi}$	$^{222}\text{Rn}$	
$A_{\text{Bot}}$	Bottom area of bay	$8.10 \times 10^5$	$8.10 \times 10^5$	$8.10 \times 10^5$	$8.10 \times 10^5$	$\text{m}^2$
$V_s$	Water volume of bay	$2.50 \times 10^6$	$2.50 \times 10^6$	$2.50 \times 10^6$	$2.50 \times 10^6$	$\text{m}^3$
$\lambda_{\text{Ra}}$	Decay constant: $\lambda_{\text{Ra},^{226}}$ , $\lambda_{\text{Ra},^{224}}$ , and $\lambda_{\text{Ra},^{222}}$	$1.17 \times 10^{-6}$	0.1904	—	0.1809	$\text{d}^{-1}$
$F_{\text{Fish}}$	Input flux through fish farm water ( $F_D \times C_{\text{FW}}$ ) for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	$3.44 \times 10^6$	$8.52 \times 10^6$	$4.84 \times 10^6$	$3.72 \times 10^8$	$\text{dpm (or mmol) d}^{-1}$
	$F_D$ : Discharge of fish farm water	$2.00 \times 10^4$	$2.00 \times 10^4$	$2.00 \times 10^4$	$2.00 \times 10^4$	$\text{m}^3 \text{d}^{-1}$
	$C_{\text{FW}}$ : Concentrations in fish farm water for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	172	426	242	18,600	$\text{dpm (or mmol) m}^{-3}$
$F_{\text{Diff}}$	Diffusive flux from bottom sediment ( $R_G \times A_{\text{Bot}}$ ) for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	$3.56 \times 10^4$	$1.70 \times 10^7$	$4.05 \times 10^6$	$8.10 \times 10^7$	$\text{dpm (or mmol) d}^{-1}$
	$R_G$ : Regeneration rate of $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	0.044	21	5	100	$\text{dpm (or mmol) m}^{-2} \text{d}^{-1}$
$C_{\text{GW}}$	Concentration in groundwater for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	152	522	119	56,800	$\text{dpm (or mmol) m}^{-3}$
$\psi_{\text{SGD}}$	Seepage rate of submarine groundwater	?	?	?	?	$\text{m d}^{-1}$
$I_{\text{SW}}$	Inventory in bay water for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , and $^{222}\text{Rn}$	$3.05 \times 10^8$	$3.58 \times 10^8$	—	$2.07 \times 10^{10}$	$\text{dpm}$
$C_{\text{EX}}$	Difference in activity between bay water and open ocean water ( $C_B - C_o$ ) for $^{226}\text{Ra}$ , $^{224}\text{Ra}$ , $\text{Si}$ , and $^{222}\text{Rn}$	50	128	44	8,200	$\text{dpm (or mmol) m}^{-3}$
$\lambda_{\text{Mix}}$	Exchange rate between bay water and open ocean water	?	?	?	?	$\text{d}^{-1}$
$F_{\text{Atm}}$	Output flux of radon ( $F_R \times A_{\text{Bot}}$ ) across air–sea interface $F_R$ : Average flux of radon out of the surface of each box by aerial evasion	—	—	—	$2.02 \times 10^9$	$\text{dpm d}^{-1}$
					2,499	$\text{dpm m}^{-2} \text{d}^{-1}$

where  $C_{Bw}$  represents the  $^{222}\text{Rn}$  activity in surface water (within  $\sim 2$  m of depth),  $C_{\text{Atm}}$  represents the mean  $^{222}\text{Rn}$  activity in the air during the sampling period,  $A$  is the area of each box ( $\sim 9.0 \times 10^4 \text{ m}^2$ ),  $\alpha$  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; Macintyre et al. 1995; Corbett et al. 1997) and can be calculated from the following equation:

$$k = 0.45 \times W_s^{1.6} \times (\text{Sc}/600)^{-0.66667} \quad (6)$$

where  $W_s$  is the wind speed, and  $\text{Sc}$  represents the Schmidt number ( $=V:\text{Dm}$ ), which is the ratio of the kinematic viscosity ( $V = -0.0003t + 0.0169$ ;  $\text{cm}^2 \text{ s}^{-1}$ ;  $t$  is water temperature) to the molecular diffusion coefficient ( $\text{Dm} = 10^{-(0.980/(t+273))+1.59)}$ ;  $\text{cm}^2 \text{ s}^{-1}$ ) (Macintyre et al. 1995). The solubility coefficient ( $\alpha$ ) can be calculated by the following equation:

$$\alpha = \beta \times T/273 \quad (7)$$

where  $\beta$  represents the Bunsen coefficient ( $=e^{(-11.95+(31.66 \times (100/T)))}$ ), and  $T$  represents the absolute temperature.

Given the measured water temperature (16.3–18.3°C), the measured  $^{222}\text{Rn}$  activity in water and air ( $\sim 190 \text{ dpm m}^{-3}$ ) from Kosan, Jeju Island, and the wind speed ( $\sim 2.4 \text{ m s}^{-1}$ ) during the sampling period, the evasion flux of  $^{222}\text{Rn}$  to the atmosphere is estimated to be  $2.0 \times 10^9 \text{ dpm d}^{-1}$ . Thus, the seepage rate is calculated to be approximately  $34 \text{ cm d}^{-1}$ , which is slightly lower than that from the  $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$ , and  $\text{Si}$  methods. However, this value is in the range (14–82  $\text{cm d}^{-1}$ ) of the seepage rates obtained from the eastern coast of Jeju Island using a manual seepage meter. Thus, we used the average of the seepage rates obtained from all methods using  $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$ ,  $\text{Si}$ , and  $^{222}\text{Rn}$  for calculating the nutrient fluxes from SGD in the next section. In this comparison of SGD, which is based on different methods, it is important to bear in mind that the uncertainties arising from chemical analysis and, more significantly, from the measurement of end-member samples of groundwater and open ocean water could be large, although we cannot determine these uncertainties because of natural variability.

**Fluxes of DIN, DIP, and DSi from SGD**—To determine the main source of excess nutrients in bay water, we evaluated the supply of nutrients from all sources such as fish farm water, diffusion from bottom sediment, and SGD. The nutrient fluxes via fish farm water were determined by multiplying the discharge of fish farm water ( $\sim 2.0 \times 10^4 \text{ m}^3 \text{ d}^{-1}$ ) by the concentrations of nutrients in the fish farm water samples (39, 0.44, and  $242 \mu\text{mol L}^{-1}$  for DIN, DIP, and DSi, respectively), yielding fluxes of  $0.78 \times 10^3$ ,  $0.009 \times 10^3$ , and  $4.8 \times 10^3 \text{ mol d}^{-1}$  for DIN, DIP, and DSi, respectively. The nutrient fluxes due to the regeneration of bottom sediments were calculated by multiplying the area of the bay ( $\sim 8.0 \times 10^5 \text{ m}^2$ ) by the regeneration rates of nutrients measured by Kim and Park (1998) and Jung and Cho (2003) in coastal bays and estuaries of Korea (1.3, 0.6, and  $5.0 \text{ mmol m}^{-2} \text{ d}^{-1}$  for DIN, DIP, and DSi, respectively). The fluxes of DIN, DIP, and DSi by diffusion from bottom sediment were

Table 4. The comparison of nutrient fluxes through fish farm water, bottom sediment, and submarine groundwater discharge in Bangdu Bay, Jeju Island.

Pathway	Nutrients ( $\times 10^3 \text{ mol d}^{-1}$ )		
	DIN	DIP	DSi
Fish farm water*	0.78	0.009	4.8
Diffusion from bottom sediments†	1.1	0.5	4.1
Submarine groundwater discharge‡	17	0.13	37

\* Based on the discharge of fish farm water multiplied by the concentrations of nutrients in the fish farm water samples.

† Calculated by multiplying the area by the regeneration rates of nutrients measured by Kim and Park (1998) and Jung and Cho (2003) in coastal bays and estuaries of Korea.

‡ Based on the average concentrations of nutrients in potential groundwater (including the pore water) multiplied by the estimated SGD.

estimated to be  $1.1 \times 10^3$ ,  $0.5 \times 10^3$ , and  $4.1 \times 10^3 \text{ mol d}^{-1}$ , respectively.

On the basis of the average concentrations of nutrients in coastal salty groundwater and pore water (49, 0.36, and  $104 \mu\text{mol L}^{-1}$  for DIN, DIP, and DSi, respectively) and the estimated average of SGD, the fluxes of DIN, DIP, and DSi from SGD are calculated to be approximately  $1.7 \times 10^4$ ,  $1.3 \times 10^2$ , and  $3.7 \times 10^4 \text{ mol d}^{-1}$ , respectively. Here, we assumed no loss of DIN by denitrification during the transport of groundwater within the sediment, since intrinsic nitrate removal by denitrification is often slow relative to the groundwater flow rate (Smith et al. 1996), and the denitrification process in coastal aquifers is mostly limited by the absence of electron donors (e.g., organic C, Fe(II),  $\text{S}^{2-}$ ) (Starr and Gillham 1993; Devlin et al. 2000). These fluxes of DIN, DIP, and DSi from SGD contribute approximately 90%, 20%, and 80% of the total DIN, DIP, and DSi fluxes in the seawater of Bangdu Bay, respectively (Table 4). Therefore, SGD is the dominant source of new DIN and DSi in Bangdu Bay, although diffusion from bottom sediment is also important for regenerated DIP in the water column (Table 4).

The estimated DIN flux from SGD in this bay is much higher than that observed in the eastern part of the United States, such as the North Inlet, Waquoit Bay, Rhode Island, and the Pettaquamscutt estuary, and in the Yeolja Bay of Korea (references are in Table 5). The DIP flux in this bay is much higher than that observed in Rhode Island and the Pettaquamscutt estuary, while it is of the same order as that observed in the North Inlet and Yeolja Bay (Table 5). Nutrient fluxes into Bangdu Bay are characterized by high DIN:DIP ratios (96–193) relative to the Redfield ratio (16) in seawater and are probably under the influence of contaminated sources of DIN. Such a DIN:DIP imbalance can affect the ecosystem of coastal seawater (Smith 1984; Paerl 1988; Krom et al. 1991).

**Benthic eutrophication and the distributions of pigments in seawater**—The blooming of benthic green algae (*Ulva conglobata* and *Ulva pertusa*) is perennial in the shallow areas of this bay (Fig. 5). Because of this benthic eutrophication, tons of these benthic algae are removed daily from this bay. As shown from the budget of nutrients in this bay in the previous section, the large fluxes of excess nutrients

Table 5. A comparison of DIN and DIP fluxes through SGD in various coastal environments.

Region	SGD ( $\text{m}^3 \text{m}^{-2} \text{yr}^{-1}$ )	DIN flux ( $\text{mmol N m}^{-2} \text{d}^{-1}$ )	DIP flux ( $\text{mmol P m}^{-2} \text{d}^{-1}$ )	DIN/DIP	Reference
North Inlet, SC	11.5	2.42	0.91	2.7	Krest et al. (2000)
Waquoit Bay	3.6	0.57	—	—	Charette et al. (2001)
Rhode Island	2.5	1.84	0.003	613	Scott and Moran (2001)
Point Judith	6.7	4.88	0.007	697	
Potter	5.2	3.73	0.006	561	
Green Hill	2.6	1.91	0.003	636	
Ninigret	4.2	0.17–0.49	0.012–0.036	13.8	Kelly and Moran (2002)
Pettaquamscutt estuary	87	26	0.11	236	Hwang et al. (2005)
Yeoja Bay	159	21.4±3.2	0.16±0.02	134	This study



Fig. 5. Photographs of dense distribution of benthic green algae in the shallow zone of Bangdu Bay.

from SGD appear to cause this benthic eutrophication. To confirm our hypothesis, direct measurement of benthic production and geochemical signatures (i.e.,  $^{15}\text{N}$ ) will be necessary in the future.

On the other hand, measurement of photosynthetic pigments in overlying seawater was thought to be necessary, since a strong fluorescence signal was reported to be present toward the bottom in seawater off the South Carolina coast where subsurface fluid input is obvious (Moore and Shaw 1998). Chlorophyll *a* (Chl *a*) concentrations in bay seawater ranged from 120 to 1,100  $\text{ng L}^{-1}$  (mean = 450  $\text{ng L}^{-1}$ ,  $n = 14$ ), which was about a factor of five times higher than for sites out from the bay (Sta. 10–12) (Fig. 6). Similarly, the concentrations of carotenoid pigments, such as fucoxanthin, peridinin, and zeaxanthin, in bay seawater were a factor of two to three times higher than those in seawater out from the bay.

Distributions of Chl *a* and carotenoid pigments in surface seawater showed a large spatial variation (Fig. 6). Elevated concentrations of photosynthetic pigments were found in the shallow coastal waters (less than approximately 1 m) (particularly in the northern part of this bay). The dominant phytoplankton communities, calculated using the CHEMTAX

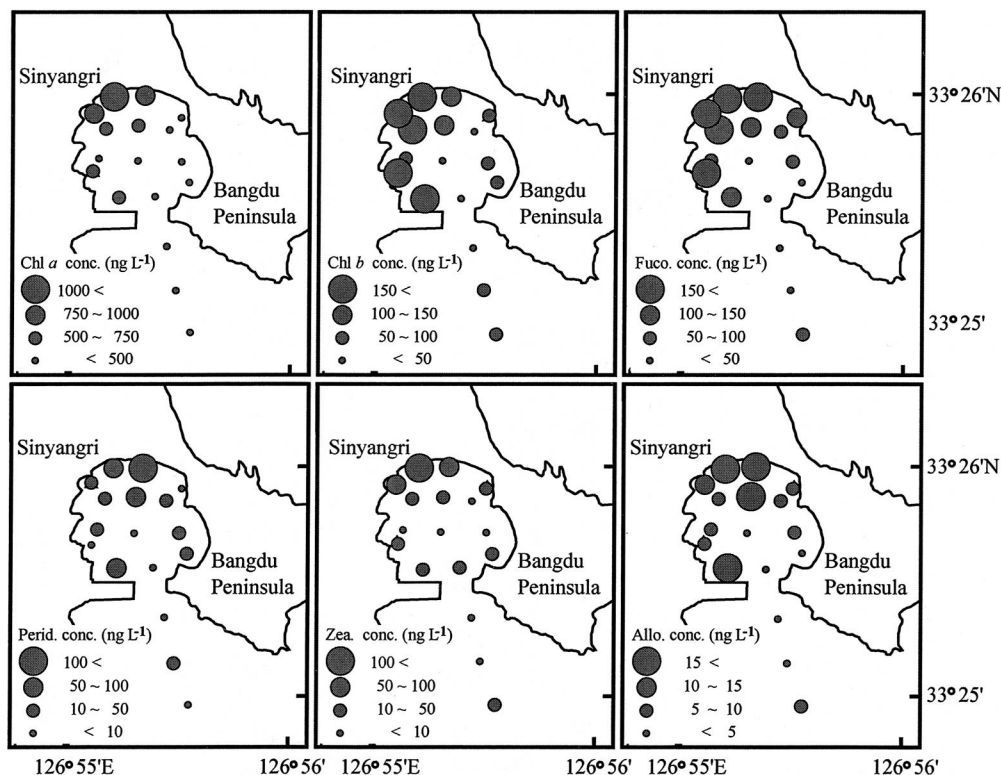


Fig. 6. Horizontal distributions of pigments for Chl *a*, Chl *b*, fucoxanthin, peridinin, zeaxanthin, and alloxanthin in Bangdu Bay.

program for pigments (Mackey et al. 1996), are chlorophytes (40%), diatoms (34%), cyanobacteria (9%), and dinoflagellates (7%). The higher proportion of chlorophytes could be largely attributed to the fragments of benthic green algae (*Ulva* sp.), which cover the upper or middle of the sandflat in the intertidal zone of this bay.

We cannot quantify the biological production of this bay, including benthic algal production, since the purpose of this study was to gauge SGD and associated nutrient fluxes. However, the community structure and abundance of phytoplankton and benthic eutrophication appear to be largely influenced by SGD, since SGD contributes the largest portion of nutrient inputs to this bay, and the distribution patterns of pigments are similar to the Rn distribution (an SGD tracer) away from the fish farm. To quantify the eutrophication of coastal bays due to SGD, more extensive interdisciplinary studies are necessary in the future.

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