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Dissolved organic matter in the subterranean estuary of a volcanic island, Jeju: Importance of dissolved organic nitrogen fluxes to the ocean

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ABSTRACT

We observed the origin, behavior, and flux of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), colored dissolved organic matter (CDOM), and dissolved inorganic nitrogen (DIN) in the subterranean estuary of a volcanic island, Jeju, Korea. The sampling of surface seawater and coastal groundwater was conducted in Hwasun Bay, Jeju, in three sampling campaigns (October 2010, January 2011, and June 2011). We observed conservative mixing of these components in this subterranean environment for a salinity range from 0 to 32. The fresh groundwater was characterized by relatively high DON, DIN, and CDOM, while the marine groundwater showed relatively high DOC. The DON and DIN fluxes through submarine groundwater discharge (SGD) in the groundwater of Hwasun Bay were estimated to be 1.3×10^5 and 2.9×10^5 mol d^{-1}, respectively. In the seawater of Hwasun Bay, the groundwater-origin DON was almost conservative while about 91% of the groundwater-origin DIN was removed perhaps due to biological production. The DON flux from the entire Jeju was estimated to be 7.9×10^8 mol yr^{-1}, which is comparable to some of the world's large rivers. Thus, our study highlights that DON flux through SGD is potentially important for delivery of organic nitrogen to further offshore while DIN is readily utilized by marine plankton in near-shore waters under N-limited conditions.

1. Introduction

Submarine discharge of fresh and saline groundwater has been recognized as an important pathway for transporting organic matter, nutrients, and trace elements to the coastal ocean (Burnett et al., 2003; Kim et al., 2011; Moore, 1996; Santos et al., 2009). The fluxes of nutrients through submarine groundwater discharge (SGD) rival or were often much higher than those through rivers into the coastal ocean (Burnett et al., 2003, 2007; Corbett et al., 1999; Slomp and Van Cappellen, 2004). Thus, nutrient inputs through SGD into the coastal ocean showed significant effects on coastal primary production (Hwang et al., 2005a; Slomp and Van Cappellen, 2004), eutrophication including outbreak of red tides (Lee and Kim, 2007; Lee et al., 2010), and benthic production (Hwang et al., 2005b; Waska and Kim, 2010).

The magnitude of SGD-driven fluxes of chemical constituents is in general regulated by the amount of SGD and the concentrations of solutes in seeping groundwater. Thus, the chemical reactions in the subterranean estuary (STE), a coastal mixing zone between fresh groundwater and recirculating seawater in the permeable aquifer (Moore, 1999), are important processes that should be understood (Charette and Sholkovitz, 2002; Slomp and Van Cappellen, 2004; Windom and Niencheski, 2003). However, there have been only a few studies on the characteristics and behaviors of inorganic nutrients in the STE. For example, dissolved inorganic nitrogen (DIN) flux through the STE of Waquoit Bay was found to be entirely composed of regenerated ammonium (Talbot et al., 2003), with a loss of DIN in the STE as evidenced by stable nitrogen isotope ($\delta^{15}N$) ratios (Kroeger and Charette, 2008). Similarly, Addy et al. (2005) showed that the STE of a Rhode Island fringing salt marsh has a high potential to remove a considerable amount of nitrogen. Beck et al. (2007) reported that nitrate and phosphate had also undergone non-conservative removal from a STE in West Neck Bay, USA. Relevant biogeochemical and physical processes removing nutrients from STEs may include denitrification (Addy et al., 2005; An and Joye, 2001), calcium phosphate precipitation (Cable et al., 2002; Slomp and Van Cappellen, 2004), and sorption of P to Fe-oxides (Charette and Sholkovitz, 2002).

Since dissolved organic matter (DOM) plays significant roles in biological productivity, penetration of lights, and exchange of gases in the sea surface, it is important to investigate the behavior of DOM in the STE (Azam et al., 1983; Pomeroy, 1974; Post, 1990). Santos et al. (2009) reported that DOM is produced in the STE in the Gulf of Mexico, and land-derived fresh DOM makes up 34% of the dissolved organic carbon (DOC) and 52% of the dissolved organic nitrogen (DON) in the total SGD flux. In contrast, the concentrations of DOC were lower in groundwater than the adjacent ocean in West Neck Bay, USA (Beck et al., 2007). Therefore, in this study, we aim (1) to determine the behavior of DOM in the STE of a volcanic island where the discharge of groundwater is fast, (2) to evaluate the sources of DOM using colored dissolved organic

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matter (CDOM), (3) to compare the behavior of SGD-driven DON versus DIN in a coastal bay using a mass balance model, and (4) to estimate the flux of DOM (DOC and DON) through SGD.

2. Materials and Methods

2.1. Study area

Jeju Island, located in the southern sea of Korea (Fig. 1), is a volcanic island with an area of ~1830 km^2. The island is composed mainly of porous basaltic rocks. The annual average temperature of Jeju is ~16 °C, and the annual rainfall is 1440–1690 mm. The island is formed by numerous volcanic activities, and there are considerable differences between the western and eastern part in geological structures and hydrogeology (Hahn et al., 1997). The fresh groundwater contributed about 20% of the SGD on the western part of Jeju, while recirculating seawater contributed almost the entire SGD on the eastern part of Jeju (Kim et al., 2003). The seepage rates were in the range 14–82 cm d^{-1} along the sandy coast on both western and eastern coasts of Jeju (Kim et al., 2003). The island has little sustained river flow, thus, abundant groundwater discharge has been recognized as a remarkable source of trace elements and nutrients in the coastal zone (Hwang et al., 2005a; Jeong et al., 2012; Kim et al., 2011; Won et al., 2005).

2.2. Sampling

Samplings of spring water, groundwater, and coastal seawater were conducted on 15th October, 2010, 13th January, 2011, and 9th June, 2011 in Hwasun Bay for the analyses of CDOM, DOC, total dissolved nitrogen (TDN), and inorganic nutrients. This bay is located in the southwestern parts of Jeju Island, with an area of ~19 km^2 and a mean depth of ~13 m (Fig. 1). In addition, archived seawater samples from Hwasun bay in 23th August, 2009 (Fig. 1, Kim et al., 2011) were analyzed for DON. Samplings of groundwater were also conducted on 9th June, 2011 in Samyang and Gimnyeong beaches, located in the northeastern parts of Jeju Island (Fig. 1). The seeping groundwater samples were collected from shallow wells in near-shore sandy sediments. The sampling depths were confined to a sandy layer positioned above porous basaltic rocks. Both confined and unconfined aquifers are connected to the mixing zone of the sandy layer. The wells were about 50 cm below the surface, with the water depths of about 20 cm. Groundwater seepage is clearly visible and seepage rate is fast enough to collect freshly recharging groundwater within 1–2 min. The sampling was conducted at low tide after the first 2–3 fills were discarded. Seawater samples were collected in the low-tide line using a plastic beaker.

Samples for the analyses of CDOM, DOC, TDN, and nutrients were collected using a syringe, and passed through a Whatman 0.7 μm disposable syringe filter. CDOM samples were stored in pre-combusted amber glass vials and kept below 4 °C in a refrigerator before analysis.

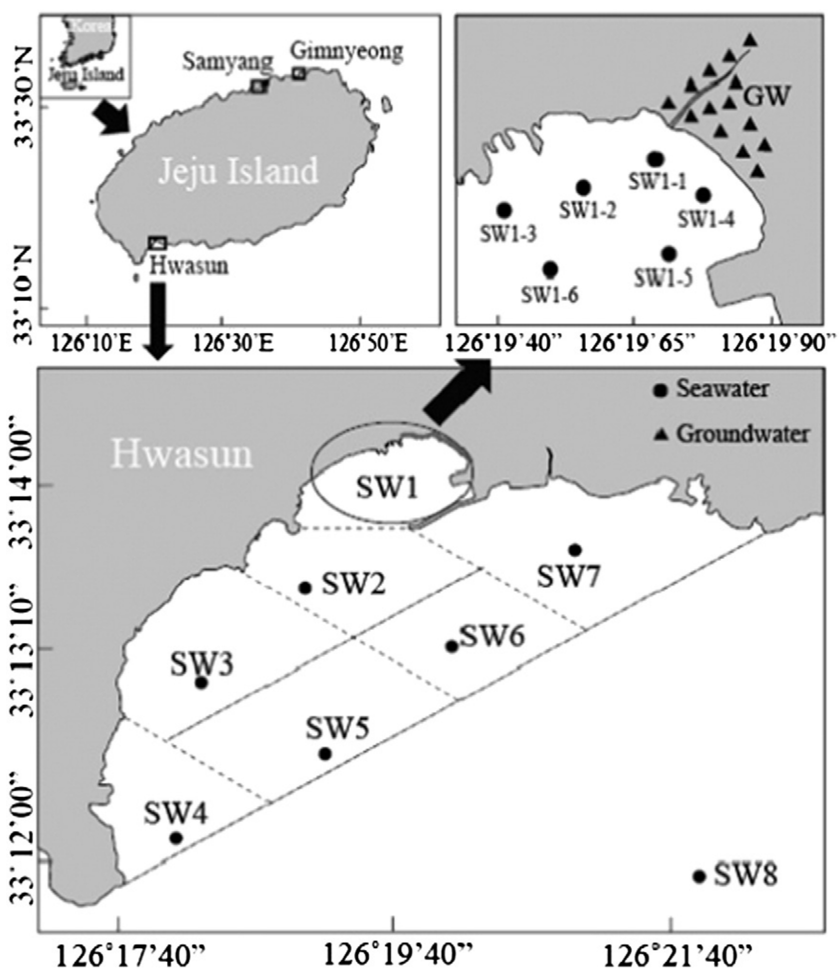

Fig. 1. The location of the sampling sites in Jeju Island. The sampling area is divided into 7 boxes (as indicated by the gridded lines) in order to obtain an area-weighted average concentration of DON in the inner bay.

DOC and TDN samples were acidified to pH ~2 with 6 M HCl and stored in fire-sealed pre-combusted glass ampoules. Nutrient samples were stored in a HDPE bottle (Nalgene) and kept frozen until analysis. All the glass vials and ampoules were pre-combusted in the furnace at 500 °C for 4 h.

2.3. Analytical methods

Salinity was measured in situ using a YSI Pro Series conductivity probe. CDOM fluorescence was determined in a scan mode using a spectrofluorometer (SCINCO FluoroMate FS-2). Emission (Em) spectra were collected from 250 to 500 nm at 2 nm intervals at excitation (Ex) wavelengths from 250 nm to 360 nm at 5 nm intervals. The sample data were subtracted for daily fresh distilled water signals in order to eliminate Raman scatter peaks. All data were obtained in counts per second (cps), converted to ppb quinine sulfate equivalents (ppb QSE), using the fluorescence spectra of quinine sulfate standard solution in 0.1 N sulfuric acid at Ex/Em of 350/450 nm. Finally, the collected data were smoothed with a Savitsky–Goray filter using MATLAB and then described as Excitation-emission matrices (EEMs).

We observed four peaks in the fluorescence spectra (EEMs) for all samples. We designated these major peaks as peak C for $Ex_{max}/Em_{max} = 342 \pm 6/427 \pm 7$ nm, peak M for $Ex_{max}/Em_{max} = 318 \pm 6/406 \pm 10$ nm, peak B for $Ex_{max}/Em_{max} = 273 \pm 3/309 \pm 4$ nm, and peak T for $Ex_{max}/Em_{max} = 282 \pm 9/343 \pm 6$ nm (Table 1) as determined by Coble (1996, 2007). Coble (2007) identified peak C with humic-like DOM, peak B (tyrosine-like) and peak T (tryptophan-like) with protein-like DOM, and peak M with marine humic-like DOM (Table 1).

Inorganic nutrients were analyzed using nutrient auto-analyzers (Alliance Instruments, FUTURA +) based on the continuous flow analysis in the laboratory after the samples were thawed. The procedures for determining NO_x (NO_3^- and NO_2^-) and NH_4 utilized the cadmium reduction and indophenol blue methods. Artificial seawater was used as matrix for the standard and blank. In this study, DIN is defined as the sum of NO_3^-, NO_2^-, and NH_4^+. The concentrations of DOC and TDN were measured with a TOC-V_{CPH} analyzer (Shimadzu, Japan). The standardization was based on the calibration curve of acetanilide. Certified reference materials (MOOS-1 from National Research Council, Canada and DSR from University of Miami, USA) were measured to check the validity of our method. The measured values were compared with a certified seawater sample for NO_x (23.7 ± 0.9 μmol L^{-1}), DOC (44–46 μmol L^{-1}), and TDN (32–34 μmol L^{-1}). Our results were 23.2 ± 0.5 μmol L^{-1} for NO_x (n = 4), 44 ± 1 μmol L^{-1} for DOC (n = 6), and 32 ± 1 μmol L^{-1} for TDN (n = 6), which agreed with the certified values within 5%. The analytical uncertainties for inorganic and organic nutrients were <2%. Concentrations of DON were quantified as the difference between DIN and TDN concentrations.

3. Results

The concentrations of DOC in the groundwater of Hwasun Bay ranged from 49 to 65 μmol L^{-1} in October 2010 (avg.: 56 ± 5 μmol L^{-1}), 24 to 47 μmol L^{-1} in January 2011 (avg.: 36 ± 8 μmol L^{-1}), and 20 to 69 μmol L^{-1} in June 2011 (avg.: 42 ± 13 μmol L^{-1}) for a salinity range from 0 to 32 (Fig. 2). While the concentrations of DOC in the seawater were almost constant during different sampling periods (avg.: 59 ± 5 μmol L^{-1}), the concentrations of DOC in fresh groundwater were higher in October 2010 (54 μmol L^{-1}) than those in January 2011 (29 μmol L^{-1}) and June 2011 (21 μmol L^{-1}). The concentrations of DON in the groundwater of Hwasun Bay ranged from 9 to 91 μmol L^{-1} in October 2010 (avg.: 54 ± 23 μmol L^{-1}), 15 to 85 μmol L^{-1} in January 2011 (avg.: 47 ± 22 μmol L^{-1}), and 37 to 115 μmol L^{-1} in June 2011 (avg.: 73 ± 22 μmol L^{-1}), which were relatively higher than those in seawater (avg.: 25 ± 15 μmol L^{-1}) (Fig. 2).

EEMs for groundwater in the STE of Hwasun Bay showed four major peaks, named C, T, M, and B, with similar EEM shapes diminishing from low to high salinity waters (Fig. 3). Peaks C and M were observed in all samples while peaks B and T were shown in just 10% of samples. In surface seawater, peak C concentrations were as low as the detection limit (0.9 ppb QSE) and only peak T was observed (avg.: 3.8 ± 3.2 ppb QSE). Since the peaks C and M showed distinct positive correlation ($r^2 = 0.99$), we use only peak C in this study. The humic-like peak C in the groundwater of Hwasun Bay ranged from 2.8 to 6.7 ppb QSE in October 2010 (avg.: 4.2 ± 1.1 ppb QSE), 1.7 to 2.8 ppb QSE in January 2011 (avg.: 2.2 ± 0.3 ppb QSE), and 1.9 to 2.8 ppb QSE in June 2011 (avg.: 2.2 ± 0.3 ppb QSE). The concentrations of peak C in fresh groundwater were higher in October 2010 (6.7 ppb QSE) than those in January 2011 (2.8 ppb QSE) and June 2011 (1.9 ppb QSE) (Fig. 2). This pattern was similar to that of DOC.

The concentrations of DIN in the groundwater of Hwasun Bay ranged from 37 to 136 μmol L^{-1} in October 2010 (avg.: 107 ± 27 μmol L^{-1}), 130 to 245 μmol L^{-1} in January 2011 (avg.: 171 ± 36 μmol L^{-1}), and 0.4 to 250 μmol L^{-1} in June 2011 (avg.: 128 ± 92 μmol L^{-1}), which were significantly higher than those in seawater (avg.: 39 ± 15 μmol L^{-1}) (Fig. 2). The concentrations of DIN in fresh groundwater were lower in October 2010 (133 μmol L^{-1}) than those in January 2011 (246 μmol L^{-1}) and June 2011 (224 μmol L^{-1}).

4. Discussion

4.1. Origin and behavior of DOM and DIN in the subterranean estuary

The plots of DOC, DON, and DIN concentrations versus salinity showed conservative mixing for salinity ranging from 0 to 32 in Hwasun Bay (Fig. 2). These results indicate that the sink and source of DOM are negligible in this STE perhaps due to rapid SGD rates (50–300 m yr^{-1}) (Kim et al., 2003). The concentrations of DON and DIN were relatively higher in the fresh groundwater than in the seawater, while those of DOC were relatively lower in the fresh groundwater. Similarly, peak C, well known to indicate humic sources (i.e., terrestrial, anthropogenic, and agriculture, Coble, 2007), decreased with increasing salinity in all seasons (Fig. 2). Peak C normalized with DOC (Fig. 2E) also showed a clear decreasing pattern against salinity. Thus, these STE samples showed a good positive correlation between peak C and DON, as opposed to a negative correlation between peak C and DOC (Fig. 2). The peak C pattern is similar to humic-like CDOM which usually decreases toward the ocean in estuaries (Conmy et al., 2004; Guéguen et al., 2005), but the DOC trend

Table 1
The properties and locations in the EEMs of major fluorescence components.

Component	Peak name	Ex/Em		Source
		Previous study (Coble, 2007)	This study	
Protein-like (tyrosine-like)	B	275/305	273 ± 3/309 ± 4	Autochthonous
Protein-like (tryptophan-like)	T	275/340	282 ± 9/343 ± 6	Autochthonous
UVA marine humic-like	M	290–310/370–410	318 ± 6/406 ± 10	Anthropogenic from wastewater and agriculture
UVA humic-like	C	320–360/420–460	342 ± 6/427 ± 7	Terrestrial, anthropogenic, agriculture

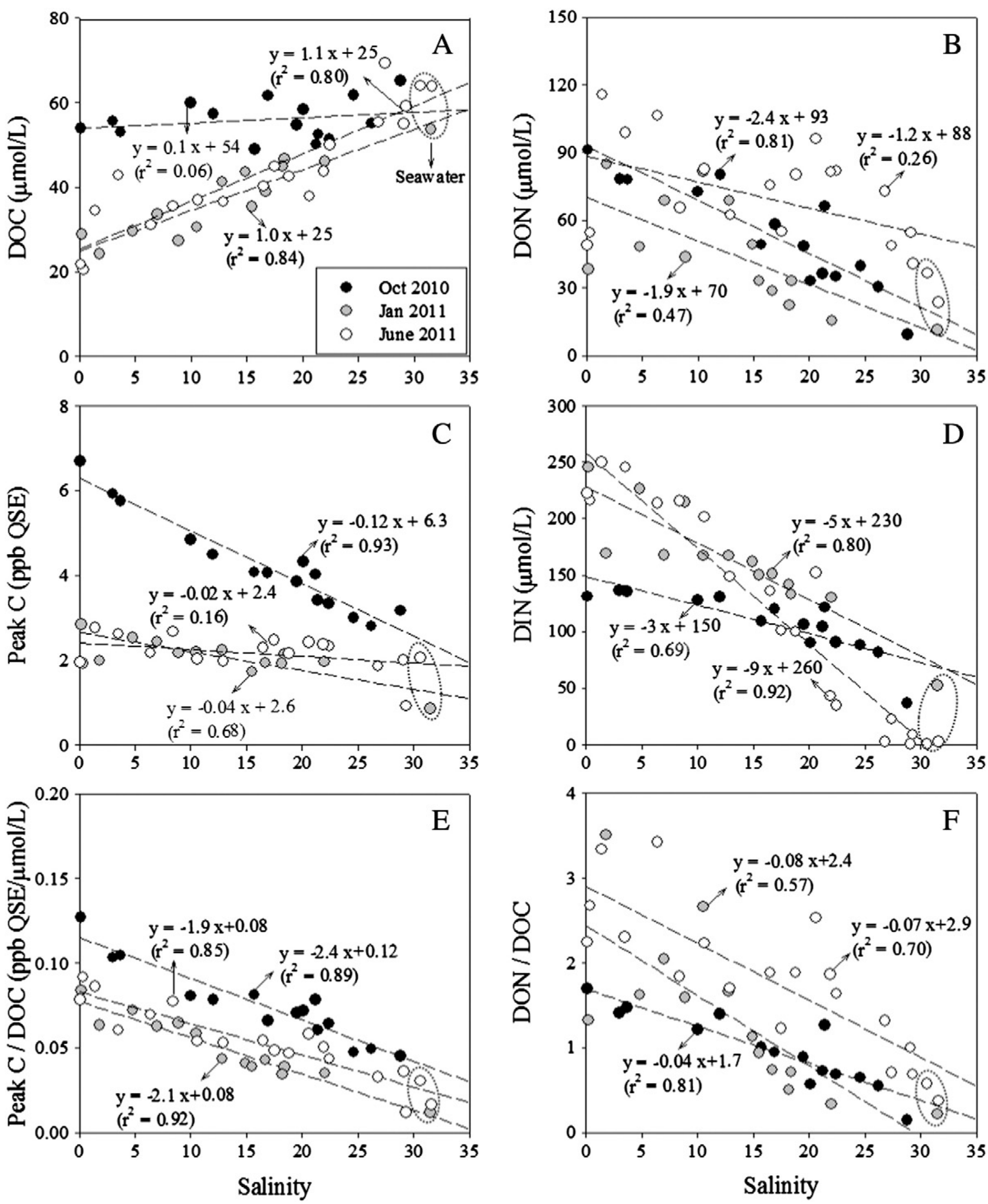

Fig. 2. Plots of salinity versus the concentrations of (A) DOC, (B) DON, (C) peak C, (D), DIN, (E) the ratio of peak C to DOC, and (F) the ratio of DON to DOC in ground water and seawater (the dotted circle) samples of Hwasun Bay.

is opposite to that generally found in coastal waters, showing positive correlations with peak C and DON (Ferris and Lehman, 2008; Kallio, 1999). Therefore, DON and DIN seem to be mainly from terrestrial sources while DOC is mainly from marine sources. The DON:DOC ratios also showed a clear decreasing pattern against salinity. In fresh groundwater, the DON:DOC ratios ranged from 1.3 to 2.7. Such high DON:DOC ratios near "one" have been often observed in soil waters of the catchment (Saunders et al., 2006) and in wastewater treatment plant effluents (Pagilla et al., 2008), while DON:DOC ratios range from 0.02 to 0.2 in fresh groundwater of more pristine environments (Inamdar et al., 2009; Kim et al., 2012; van Verseveld et al., 2009). Thus, we suggest that the higher DON in fresh groundwater in this subterranean estuary could be likely from pollution (i.e., agricultural fertilizers or domestic sewage) although we cannot clearly discount natural sources in this study.

Although the distribution patterns of DOC, DON, DIN, and peak C against salinity were similar for January and June 2011, those in October 2010 showed relatively much higher DOC and peak C but much lower DIN in fresh groundwater water sources. The different sources of fresh groundwater in October 2010 were also clearly shown in plots between peak C versus DOC and DON (Fig. 2). The entire shapes of the EEMs do not display any differences for October 2010 from the other two seasons. Therefore, the lower DON/DOC ratios (~1.7), lower DIN concentrations, but higher DOC and peak C values in

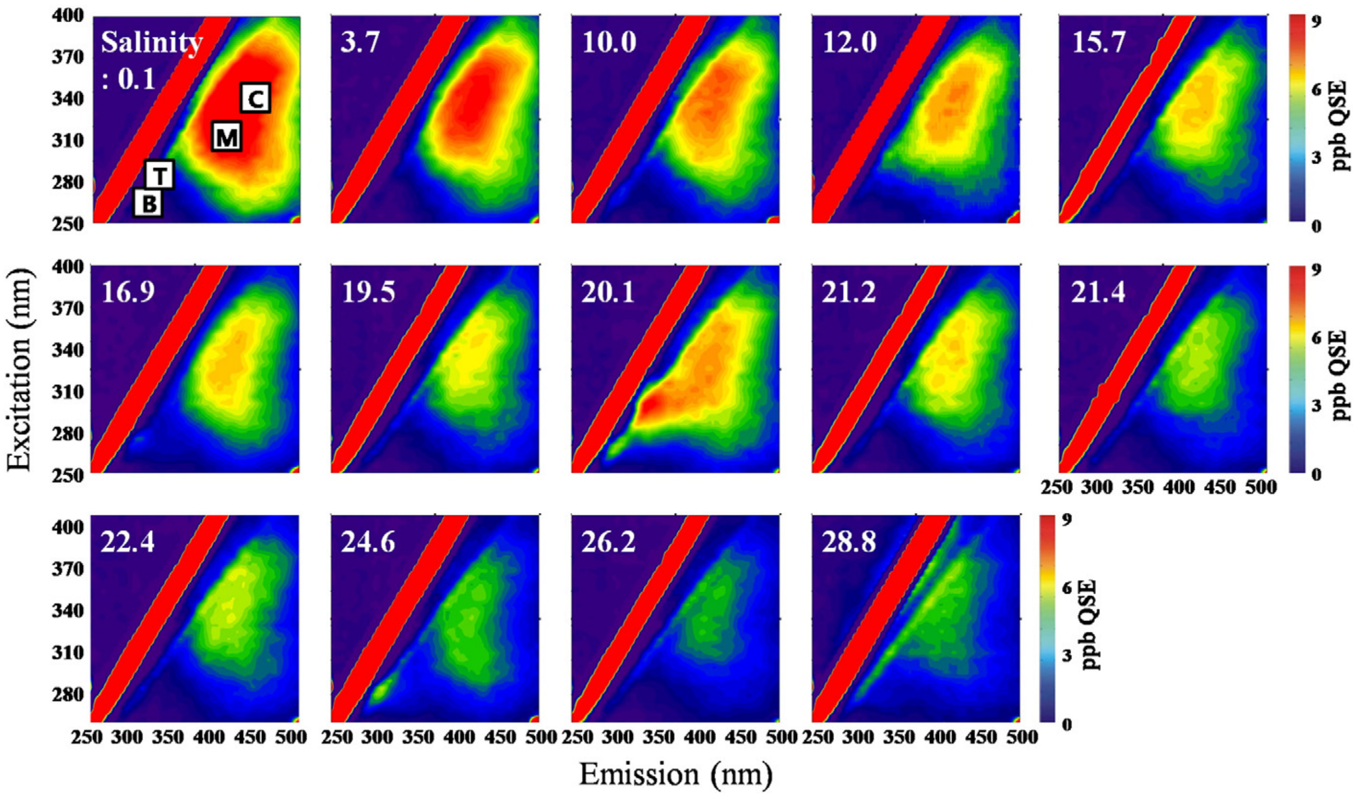

Fig. 3. The excitation–emission matrices (EEMs) for groundwater samples of Hwasun Bay in October 2010. Red bands in all spectra indicate Rayleigh scattering.

fresh groundwater in October 2010, seem to be associated with seasonal changes in the fresh groundwater-borne DOM supply to this STE. Alternatively, higher peak C and DOC could be associated with leaf litter in deciduous forests in fall (Dowell, 1985; Qualls et al., 1991).

4.2. Fluxes and behavior of DON versus DIN in Hwasun bay water

Jeju Island provides a good opportunity for studying the biogeochemical responses of SGD-driven fluxes of chemical constituents in the coastal waters since it has oligotrophic coastal waters, high seepage rates, no influence of rivers, and relatively small influence of bottom sediments (Kim et al., 2003; Lee and Kim, 2007). To evaluate the behavior of DON in comparison to DIN in Hwasun Bay, we constructed a mass balance model for DON using equation:

$$\frac{dN}{dt} = C_{GW} \times \psi_{SGD} + F_{Diff} - (C_{inner} - C_{outer}) \times V_S \times \lambda_{Mix} - F_{Missing}$$

where C_{GW} is the endmember concentrations in groundwater (μmol L^{-1}) for DON; ψ_{SGD} is the SGD flux ($m^3 d^{-1}$); C_{inner} and C_{outer} are the average concentrations of DON in the inner and outer bay (μmol L^{-1}), respectively; V_S is the volume of the bay (m^3); and λ_{Mix} is the water exchange rate between the inner and outer bay (d^{-1}). The first term on the right-hand side of the equation represents the input flux of DON from SGD, the second term (F_{Diff}) represents the input fluxes by diffusion from bottom sediments, the third term represents the output flux from mixing with outer-bay seawater, and the final term ($F_{Missing}$) represents the unidentified removal of DON (i.e., by particle scavenging or biological uptake).

The C_{inner} and C_{outer} values of DON obtained from inner bay samples and an outer bay sample in August 2009 were 5.0 ± 1.2 and 3.8 μmol L^{-1}, respectively. The average concentrations of DON in the inner bay water were calculated by dividing the entire bay water into 7 boxes in order to obtain an area-weighted average (Fig. 1). The SGD flux (ψ_{SGD}) into Hwasun Bay was 2.2×10^6 $m^3 d^{-1}$ (0.12 m^3 $m^{-2} d^{-1}$) based on the ^{222}Rn tracer (Kim et al., 2011). Since diffusive DON fluxes from bottom sediments are not available for this bay, we assumed an average value (0.2 mmol $m^{-2} d^{-1}$) of DON fluxes from muddy sediments of various coastal environments (Burdige and Zheng, 1998; Nixon and Pilson, 1983; Tyler et al., 2001). This diffusive flux value may be a maximum value since the diffusive fluxes of DON are much lower in the sandy zone relative to those in the muddy zone (Tyler et al., 2001). The λ_{Mix} value is the reciprocal of the water residence time (2.5 d) in this bay (Kim et al., 2011). We assume that the DON fluxes through the atmosphere were negligible. Then, at steady state, the unidentified loss term, $F_{Missing}$, can be calculated.

The result of DIN mass-balance modeling for Hwasun Bay in August 2009 was already reported by Kim et al. (2011) using the same equation as the DON. They showed that 93% of the SGD-driven DIN was removed from the bay water by biological production in this extremely N-limited environment. Since we do not have DON data for groundwater endmember (C_{GW}) in August 2009, we assume that the C_{GW} value of DON is 60 μmol L^{-1}, which is the average DON value in groundwater in October 2010, January 2011, and June 2011. Thus, we use groundwater endmember values for DON and DIN for the same periods (average values in samples obtained in October 2010, January 2011, and June 2011) in order to compare the flux and behavior of DON versus DIN in this study. On the basis of these assumptions, SGD-driven fluxes of DON and DIN to Hwasun Bay were estimated to be 1.3×10^5 mol d^{-1} and 2.9×10^5 mol d^{-1}, respectively, which were 1–2 orders of magnitude greater than those by diffusion from bottom sediments (Table 2). In this comparison, the seasonal decoupling of DIN and DON will result in insignificant problem since the average value of DIN obtained in October 2010, January 2011, and June 2011 (133 μmol L^{-1}, $n = 46$), agreed well with that obtained in August 2009 (125 μmol L^{-1}, $n = 32$).

F_{Diff} value in this study area is calculated to be $< 0.03 \times 10^5$ mol d^{-1}. Thus, the unidentified loss term, $F_{Missing}$, for DON in bay water was 8–10% of the SGD-driven flux (Table 2). This suggests that SGD-driven

Table 2
The comparison of input and output fluxes of DON and DIN ($\times 10^3$ mol d^{-1}) in Hwasun Bay, Jeju Island, Korea.

	Endmember (μmol L^{-1})	Source		Sink	
		F_{SGD}	F_{Diff}	F_{Mix}	$F_{Missing}$
DON	60 (n = 46)	130	<3	120	10–30
DIN	133 (n = 46)	290	<25	50	240–265

F_{SGD}, F_{Diff}, F_{Mix}, and $F_{Missing}$ denote the flux of DON and DIN by SGD, the diffusion from bottom sediments, mixing with the outer-bay seawater, and unidentified removal.

DON is quite conservative in this bay water. This trend is very different from the SGD-driven DIN, which showed 83–91% removal in this bay water for the same periods (Table 2). DON can play an important role in supplying N nutrition directly or indirectly to phytoplankton and bacteria and may influence the species composition of the ambient microbial assemblage (Berman and Bronk, 2003; Jackson and Williams, 1985). Therefore, our result suggests that SGD-driven DON is quantitatively significant and can be transported further offshore, relative to SGD-driven DIN, in a N-limited environment, playing an important role in open-ocean biogeochemistry.

4.3. The SGD-driven flux of DOM and DIN from the entire island

The SGD-driven fluxes of DOC, DON, and DIN over the entire island were calculated by multiplying the average concentrations in groundwater (49 ± 18 μmol L^{-1} for DOC, 50 ± 27 μmol L^{-1} for DON, and 109 ± 70 μmol L^{-1} for DIN, n = 65) measured in Hwasun Bay, Samyang beach, and Gimnyeong beach (Fig. 1) by the average SGD rate in Jeju (4.5×10^7 $m^3 d^{-1}$) (Kim et al., 2003). The concentrations of DOC in the groundwater of Jeju were similar to those (<50 μmol L^{-1}) in the groundwater of West Neck Bay, USA (Sañudo-Wilhelmy et al., 2002) but were lower than those in the groundwater of the Gulf of Mexico (>300 μmol L^{-1}) and Tempa Bay (30–670 μmol L^{-1}), USA (Chen et al., 2007; Santos et al., 2009). The concentrations of DON in the groundwater of Jeju were similar to those in the groundwater of Tempa Bay (41–87 μmol L^{-1}), USA (Kroeger et al., 2007). The concentrations of DIN in the groundwater of Jeju were lower than those (180–380 μmol L^{-1}) in West Neck Bay, USA (Sañudo-Wilhelmy et al., 2002) but were higher than those in the Gulf of Mexico (20 μmol L^{-1}) and Tempa Bay (40–80 μmol L^{-1}), USA (Kroeger et al., 2007; Santos et al., 2009). In general, the concentrations of DOC in groundwater samples were much lower than those in river waters, while the concentrations of DON and DIN in groundwater samples were much higher than those in river waters (Table 3).

Table 3
DOC, DON, and DIN fluxes from Jeju Island via SGD in comparison with those from large rivers across the world (Berman and Bronk, 2003; Gao et al., 2002; Ludwig et al., 1996; Meybeck, 1982).

River	Water discharge ($m^3 d^{-1}$)	Concentrations (mg L^{-1})			Fluxes (Gg yr^{-1})		
		DOC	DON	DIN	DOC	DON	DIN
Jeju Is. SGD	4.5×10^7	0.7	0.7	1.5	9.8	11	25
Colorado	5.5×10^7	2.8	0.2	0.02	56	3.2	0.36
Delaware	3.3×10^7	–	0.4	0.9	–	5.0	10
Stikine	1.4×10^8	–	0.2	0.1	–	8.3	4.3
Negro	7.8×10^7	6.3	0.3	0.1	180	8.5	1.4
Fraser	3.1×10^8	–	0.1	0.1	–	15	8.0
Churchill	1.1×10^8	–	0.6	0.1	–	24	2.8
Rhone	1.9×10^8	–	0.5	0.6	–	33	41
Yukon	1.9×10^8	–	0.6	0.1	–	42	9.0
Nelson	2.4×10^8	8.0	0.6	0.1	710	54	11
Mississippi	1.3×10^9	8.8	0.2	1.1	4200	79	520
Changjiang	2.5×10^9	12.4	0.2	1.0	11,000	140	970
Hudson	1.6×10^9	–	0.5	0.7	–	280	400
Amazon	1.5×10^{10}	4.5	0.2	0.2	25,000	1100	1300

The fluxes of DOC, DON, and DIN through the SGD from the entire Jeju Island were 9.8×10^9, 1.1×10^{10}, and 2.5×10^{10} g yr^{-1}, respectively. Although this DOC flux is orders of magnitude lower than that for large rivers (Table 3), these DON and DIN fluxes were larger than those for some large rivers, such as the Colorado, Delaware, and Stikine. However, these DON and DIN fluxes were still an order of magnitude lower than those obtained for the world's major rivers (Table 3). The SGD-driven DIN flux in this study was similar to the previous result (2.9×10^{10} g yr^{-1}) in this island reported by Kim et al. (2011). Since Jeju Island accounts for only <1% of the total land mass of volcanic islands, we expect that DON and DIN inputs from all volcanic islands standing in the world's oceans combined would be globally significant if such high fluxes are consistent.

5. Conclusions

In the subterranean estuary of Jeju Island, the fresh groundwater showed relatively high DON, CDOM, and DIN concentrations, but the marine groundwater showed relatively high DOC concentrations. The mixing patterns of DON, CDOM, and DIN in this subterranean estuary were conservative, indicating insignificant inputs and removals of these components in the mixing processes. In a semi-enclosed bay, Hwasun Bay, DON removal by biological utilization was ineffective (~10%), while DIN removal was very effective (~90%). The DON flux from the entire Jeju was comparable to some of the world's large rivers. Thus, the SGD-driven DON in Jeju Island seems to be an important nutrient source in offshore waters, while the SGD-driven DIN is readily utilized by phytoplankton in near-shore waters. In order to understand the sources and behavior of DOM in the STE of a volcanic island, extensive studies are necessary in the future over larger area- and time-scales by including various isotopic tracers, such as $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$.

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