



Importance of dissolved organic carbon flux through submarine groundwater discharge to the coastal ocean: Results from Masan Bay, the southern coast of Korea



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ABSTRACT

In order to estimate the fluxes of dissolved organic carbon (DOC) through submarine groundwater discharge (SGD), salinity and DOC concentrations in groundwater, stream water, and seawater were investigated in May 2006 and 2007 (dry season) and August 2006 (wet season) in Masan Bay, Korea. In both seasons, the average concentrations of DOC in groundwater ($139 \pm 23 \mu\text{M}$ in May and $113 \pm 18 \mu\text{M}$ in August) were relatively lower than those in stream water ($284 \pm 104 \mu\text{M}$ in May and $150 \pm 36 \mu\text{M}$ in August) but similar to those of the bay water ($149 \pm 17 \mu\text{M}$ in May and $117 \pm 13 \mu\text{M}$ in August). The DOC concentrations in groundwater, stream water, and seawater showed negative relationships with salinity, but those in the surface bay water were observed above the theoretical mixing line, indicating that DOC may be produced by *in situ* primary production in this bay. Based on a simple DOC mass balance model, SGD-derived DOC fluxes in Masan Bay were estimated to be $6.7 \times 10^5 \text{ mol d}^{-1}$ in the dry season and $6.4 \times 10^5 \text{ mol d}^{-1}$ in the wet season, showing no remarkable seasonal variation. The DOC fluxes through SGD in Masan Bay accounted for approximately 65% of the total input fluxes. This result suggests that the DOC flux through SGD can be the most important source of DOC in this bay, and SGD may play an important role in carbon budget and biogeochemistry in coastal areas.

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1. Introduction

Submarine groundwater discharge (SGD) has been recognized as an important pathway for transporting organic matter, nutrients, and trace elements to the coastal area comparable to river discharge (Burnett et al., 2003; Moore, 1996; Kim et al., 2012; Kim et al., 2013). SGD is described as any water flow which passes through the sediment into the coastal ocean regardless of composition or driving force (Moore, 2010) and consists of terrestrially derived fresh groundwater and re-circulated saline groundwater (Burnett et al., 2003; Moore et al., 2008). The driving forces of SGD in coastal zones are tidal pumping, wave set-up, terrestrial hydraulic gradients, fluid shearing, density-driven convection, sediment compaction, and bio-irrigation (Santos et al., 2012). Moore (1999) reported that the subterranean estuary (STE), where groundwater passes through with various biogeochemical reactions, is a coastal mixing zone between fresh groundwater and seawater invading through a permeable aquifer. Biogeochemical reactions occurring in STE combined with SGD are known to have a large impact on

coastal budgets of various chemical constituents (Charette and Sholkovitz, 2002; Windom and Niencheski, 2003; Slomp and Cappellen, 2004).

Dissolved organic carbon (DOC), the largest organic carbon reservoirs in the ocean, accounts for an important component of the global carbon cycle (Williams and Druffel, 1987; Hansell and Carlson, 1998; Hansell et al., 2009). Since DOC in coastal zones mainly originates from terrestrial sources such as groundwater or river water and enters the oceans, it is important to investigate origins and fates of DOC for better understanding the carbon cycle. However, there have only been a few studies dealing with its behavior in STEs (Beck et al., 2007; Santos et al., 2009; Kim et al., 2013).

Groundwater-derived DOC flux was underestimated as an important source to investigate the carbon cycle in estuarine systems but has been recognized as an important coastal DOC input source. For example, Kim et al. (2012) reported that DOC flux through SGD in Hampyeong Bay, located on the southern coast of Korea, accounted for 24% of the total SGD-driven dissolved organic matter (DOM) flux into this bay. Sadat-Noori et al. (2016) reported that SGD-derived DOC contributed 41% of carbon exports from a subtropical estuary (New South Wales, Australia). Furthermore, Stewart et al. (2015) reported that

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SGD-derived DOC flux was equivalent to ~38 times the annual delivery via all rivers into Moreton Bay (Queensland, Australia), suggesting that SGD is a major component of hydrological and biogeochemical cycles in the bay. However, the behavior and cycling of DOC in STE were not fully explored, as behavior of DOC shows a large difference in various environments depending on hydrological and climatic conditions.

Masan Bay (Gyeongsangnam-do, Korea) has suffered from domestic and industrial effluents and SGD, resulting in complicated problems including outbreaks of harmful algal blooms (Lim et al., 2006; Kim et al., 2007; Lee et al., 2009). Lee et al. (2009) reported that SGD could play an important role in sources of nutrients and factors controlling the outbreak of phytoplankton blooms, resulting from proportions of dissolved inorganic nitrogen (42–45%) and phosphorus (42–51%) through SGD of the total fluxes in Masan Bay. However, very limited investigation has been conducted on the DOC behavior in STE and SGD-derived DOC flux in this bay. Therefore, the aims of this study were (1) to investigate DOC distribution in different types of water samples (seawater, groundwater, and bay water) in Masan Bay where the discharge of groundwater is an order of magnitude higher than the discharge of stream water and (2) to estimate SGD-derived DOC flux using a mass balance model in different climatic and hydrological conditions (dry and wet seasons).

2. Materials and methods

2.1. Study area

Masan Bay, located on the southeast coast of Korea, is surrounded by industrial complexes and megacities and is semi-enclosed. The previous studies reported that Masan bay was one of the most contaminated

regions in Korea due to sewage and wastewater discharged into the bay (Li et al., 2008; Choi et al., 2009). The annual precipitation of this region is 1560 mm. Three streams (Nam, Changwon, and Samho streams) enter the bay, with a large seasonal variation due to a monsoon climate (KIOST, 2002). The surface sediment of this bay consists mainly of silt and clay (>90%) with small portion of sand (Woo et al., 2003). There are two wastewater treatment plants which treat about 370,000 ton/day and discharge the effluents into Masan Bay (MOE, 2012).

2.2. Sampling

Stream water, groundwater, and seawater samples were collected in May and August 2006 and May 2007 in Masan Bay for the analyses of DOC (Fig. 1). Stream water samples ($n = 2$ in May and $n = 3$ in August) were obtained using a submersible pump (a flow rate of 15–20 L min⁻¹). The groundwater samples ($n = 20$ in May and $n = 7$ in August) were collected from various shallow (<0.5 m) and deeper (<10 m) wells from the shore (<20 m). Bay water ($n = 11$ in May and $n = 10$ in August) and seawater ($n = 1$ in May and August) samples were obtained from the surface (~1 m below the surface) using a submersible pump on shipboard. Samples for the analyses of DOC were filtered using Whatman GF/F filters (0.7 μm) and stored in fire-sealed glass ampoules after acidifying the samples to pH 2 using 6 M HCl. All filters and ampoules were pre-combusted at 500 °C for 5 h (Kim and Kim, 2010). Groundwater level, precipitation rate, and stream water discharge rate were obtained from National Groundwater Information Center (www.gims.go.kr), Korea Meteorological Administration (www.kma.go.kr), and the previous study (Lee et al., 2009), respectively.

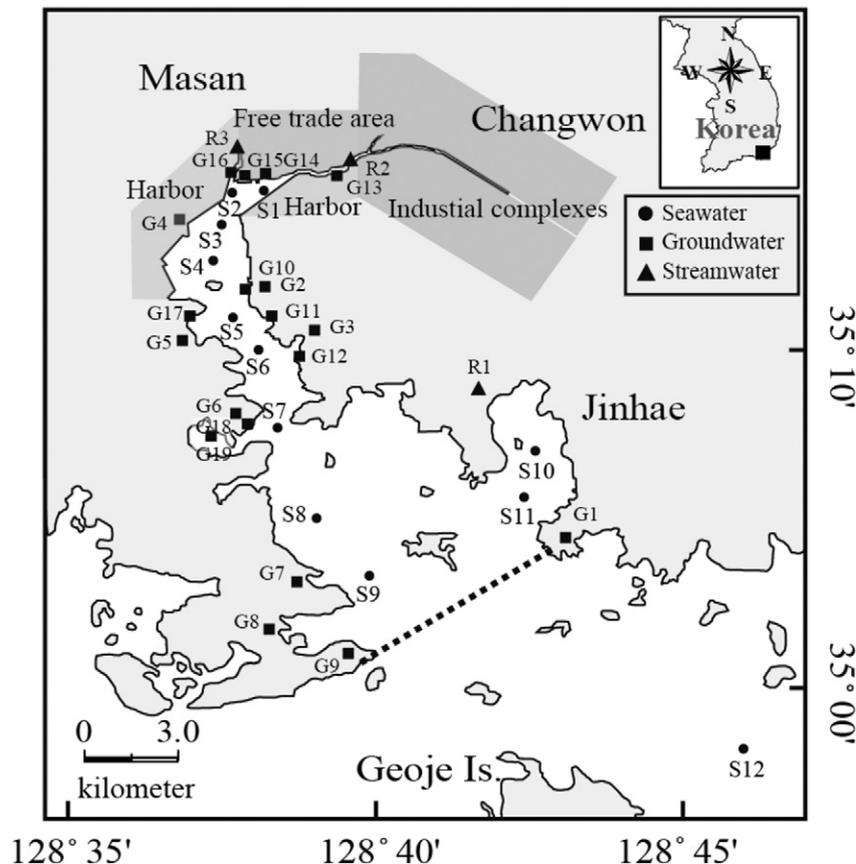


Fig. 1. A map showing groundwater and seawater sampling stations for dissolved organic carbon (DOC) in Masan Bay. Circle, square, and triangle represent sampling stations for seawater, groundwater, and stream water in the bay, respectively.

2.3. Analytical methods

Temperature and salinity were measured directly in the field using a portable salinometer (Model 340C, Isteck, Korea) for stream water and coastal groundwater and using a portable CTD (SBE 25, Seabird Electronics, USA) for seawater. DOC samples were analyzed using a TOC-V_{CPH} (Shimadzu, Japan) and five-point standard curves of acetanilide were used to standardize DOC measurements. The acidified seawater samples in the injection system were bubbled with high-purity air gas (99.999%) to completely remove inorganic carbon species. Carrier gas was passed at a controlled flow rate of 150 mL min⁻¹ through a combustion tube that was filled with Pt-coated Al catalyst and heated to 720 °C. The samples of DOC were oxidized to form CO₂ which was detected by a non-dispersive infrared sensor. The reliability of measurements was checked on a daily basis by comparison with a DOC certified seawater sample (Deep Sea Reference, University of Miami: 44–46 μM for DOC) and with procedural blanks. The result agreed within 5% of the certified value of the reference materials. Uncertainty in this study was calculated based on uncertainty propagation.

3. Results

3.1. Hydrologic and climatic conditions

Sampling campaigns were conducted in May 2006 and 2007 and August 2006 to compare DOC concentration and SGD-derived DOC flux in Masan Bay during contrasting hydrological conditions. The hydrological data (groundwater level, precipitation rate, and stream water discharge rate) were averaged during 3-months prior to each sampling periods considering the residence time of the bay water. The precipitation rate in the wet season (10.9 mm day⁻¹) was 2-fold higher than that in the dry season (3.7 mm day⁻¹). As a result, groundwater levels were 100 cm higher in the wet season (12.26 m) than in the dry seasons (11.24 m). Based on these differences and for simplicity, we described the sampling campaign conducted in May and August as the dry and wet seasons, respectively. The stream water discharge rate in the wet season (10.5 × 10⁵ m³ d⁻¹) was approximately 2-time higher than in the dry season (5.7 × 10⁵ m³ d⁻¹). We expected these contrasting conditions of sampling periods to have an influence on DOC concentration and SGD-derived DOC flux in this bay.

3.2. Salinity and DOC concentration

Salinities and DOC concentrations in the stream water, bay water, groundwater, and open ocean seawater during the dry and wet seasons are described in Table 1. Salinity in the groundwater relative to the stream and bay water showed large variations. While salinity in the stream water approached almost zero in both seasons, salinity in the groundwater ranged from 10.0 to 30.9 (mean: 22.6 ± 5.1, *n* = 20) in the dry season and from 7.9 to 25.7 (mean: 21.6 ± 6.2, *n* = 7) in the wet season, reflecting a high precipitation rate in the wet season. The lowest salinity in the bay water was observed in the innermost bay area, increasing with distance from the bay head. The averages of salinity in the bay water were relatively higher than those in the groundwater and lower than those in the stream water in both dry and wet seasons.

In the dry season, the concentrations of DOC ranged from 104 to 170 μM (mean: 149 ± 17 μM, *n* = 11) in the surface bay water, from 98 to 177 μM (mean: 139 ± 23 μM, *n* = 20) in the groundwater, and from 210 to 357 μM (mean: 284 ± 104 μM, *n* = 2) in the stream water. In the wet season, the concentrations of DOC ranged from 100 to 148 μM (mean: 117 ± 13 μM, *n* = 10) in the surface bay water, from 95 to 143 μM (mean: 113 ± 18 μM, *n* = 7) in the groundwater, and from 117 to 189 μM (mean: 150 ± 36 μM, *n* = 3) in the stream water. The concentrations of DOC in the offshore seawater were relatively lower than those in the bay water, with values of 123 and 90 μM in the dry

and wet seasons, respectively. The averages of DOC concentration in the bay water, groundwater, and stream water were slightly higher in the dry season than in the wet season.

4. Discussion

4.1. DOC dynamics

The concentrations of DOC in the groundwater of Masan Bay were higher than those in the groundwater of Jeju Island (49 ± 18 μM), Korea (Kim et al., 2013) and West Neck Bay (<50 μM), USA (Sañudo-Wilhelmy et al., 2002) but were lower than those in the groundwater of Hampyeong Bay (185 ± 52 μM), Korea (Kim et al., 2012), Tempa Bay (30–670 μM), USA (Chen et al., 2007), and the Gulf of Mexico (>300 μM), USA (Santos et al., 2009).

The plots of DOC concentrations versus salinity in the STE showed conservative mixing for salinity ranging from 10.0 to 30.9 in the dry season and 7.9 to 25.7 in the wet season (Fig. 2). These results were similar to those of the STE of Hwasun Bay, Korea (Kim et al., 2013), indicating that DOC source and sink in STE of Masan Bay could be negligible owing to rapid SGD rates. The DOC concentration, except for the bay water, was negatively correlated with salinity in both dry (*r* = -0.86, *n* = 11, *p* < 0.005) and wet (*r* = -0.78, *n* = 22, *p* < 0.001) seasons (Fig. 2). These results indicate that DOC seems to be from terrestrial sources.

On the contrary, the excess DOC concentrations in the bay waters were observed in the dry season (38 ± 19 μM) and in the wet season (21 ± 14 μM) on the basis of conservative mixing lines. This result indicates that DOC in the bay water may be influenced by other factors rather than a simple stream water-bay water-seawater mixing process. In the bay water, the average excess DOC concentration in the dry season was 1.8 times higher than that in the wet season, perhaps due to a higher primary production rate in the dry season. This hypothesis may be supported by the fact that most of the DOC production in the ocean is closely linked to the magnitude of primary production (Carlson and Hansell, 2014) and by higher chlorophyll *a* concentration in the dry season (15.9 ± 7.0 μg L⁻¹) than in the wet season (9.7 ± 2.3 μg L⁻¹) (Lee et al., 2009).

4.2. DOC mass balance model

To evaluate SGD-derived DOC flux in Masan Bay, the equation presented in Kim et al. (2013) was modified for DOC:

$$\frac{dDOC}{dt} = C_{Stm} \times Q_{Stm} + C_{GW} \times Q_{SGD} + \psi_{Ben} \times A - (C_{Inn} - C_{Out}) \times V \times (1/\tau) + F_{Net}$$

$$F_{Net} = F_{Pro} - F_{Rem}$$

where *C*_{Stm} and *C*_{GW} are the DOC endmember concentrations in stream water and groundwater (μM); *Q*_{Stm} and *Q*_{SGD} are the discharge rates of stream water and groundwater (m³ day⁻¹); *ψ*_{Ben} is the diffusive rate from the bottom sediment; *A* is the area of the bay (m²); *C*_{Inn} and *C*_{Out} are the average concentrations of DOC in the inner and outer bay (μM), respectively; *V* is the volume of the bay (m³); and *τ* is the residence time of Masan Bay (day). The first term on the right-hand side of the equation represents the input flux of DOC from discharge of stream water, and the second term represents the input flux of SGD-derived DOC. The third term represents the input fluxes by diffusion from bottom sediments, and the fourth term represents the output flux by mixing with outer-bay seawater. The final term (*F*_{Net}) represents an unidentified DOC flux. *F*_{Pro} means production flux by phytoplankton, and *F*_{Rem} means removal flux by particle scavenging or bacterial degradation in the bay during the residence time.

Table 1
Temperature, salinity, and the concentrations of dissolved organic carbon (DOC) in bay water, offshore water, groundwater, and stream waters around Masan Bay in May and August 2006 and May 2007.

	Station	Temp. (°C)	Sal.	DOC (μM)		Station	Temp. (°C)	Sal.	DOC (μM)
May 2006	Bay water				Aug. 2006	Bay water			
	S 1	19.5	29.5	162		S 1	25.8	28	119
	S 2	18.9	29.9	149		S 2	21.4	29.4	111
	S 3	19.7	29.5	140		S 3	26.1	28.2	119
	S 4	18.3	31.1	143		S 4	22.7	29.3	116
	S 5	17.9	31.2	104		S 6	24.8	29.2	119
	S 6	19.3	30.4	150		S 7	23.6	29.2	107
	S 7	17.7	32.1	155		S 8	25.7	29.8	106
	S 8	19.9	31.8	150		S 9	23.5	30.2	122
	S 9	18.1	33.3	154		S 10	23.4	30.0	100
	S 10	18.6	33.5	170		S 11	23.7	31.4	148
Average	19.0	31.3	149	Average	24.1	29.5	117		
St. deviation	0.9	1.4	17	St. deviation	1.5	1.0	13		
	Offshore water				Offshore water				
	S12	19.2	31.5	123	S12	29.0	29.8	90	
May 2006	Groundwater				Groundwater				
	G1	17.5	28.3	98	G1	23.5	23.7	108	
May 2007	G3	17.1	22.2	112	G2	22.8	25.6	98	
	G2	14.6	24.0	133	G4	17.0	25.7	95	
	G3	14.7	30.0	132	G5	23.4	21.4	131	
	G4	16.7	23.0	152	G6	25.4	24.0	101	
	G5	16.2	18.1	166	G7	23.2	22.6	114	
	G6	17.3	26.0	144	G8	20.5	7.9	143	
	G7	14.0	19.3	162	Average	22.3	21.6	113	
	G8	17.1	18.4	161	St. deviation	2.7	6.2	18	
	G9	16.9	30.9	107					
	G10	–	26.3	120					
	G11	15.3	27.0	120					
	G12	–	20.2	134					
	G13	–	23.8	154					
	G14	15.7	21.8	134					
	G15	–	14.5	167					
	G16	16.3	23.0	155					
	G17	24.6	25.8	112					
	G18	20.7	10.0	177					
	G19	–	20.0	133					
Average	17.0	22.6	139						
St. deviation	2.6	5.1	23						
May 2007	Stream water				Stream water				
	R1	17.1	0	210	R1	28.2	0	145	
	R2	17.2	0	357	R2	28.0	0	189	
	Average	17.2	0	284	R3	27.6	0	117	
	St. deviation	0.1	0	73	Average	27.9	0	150	
				St. deviation	0.3	0	21		

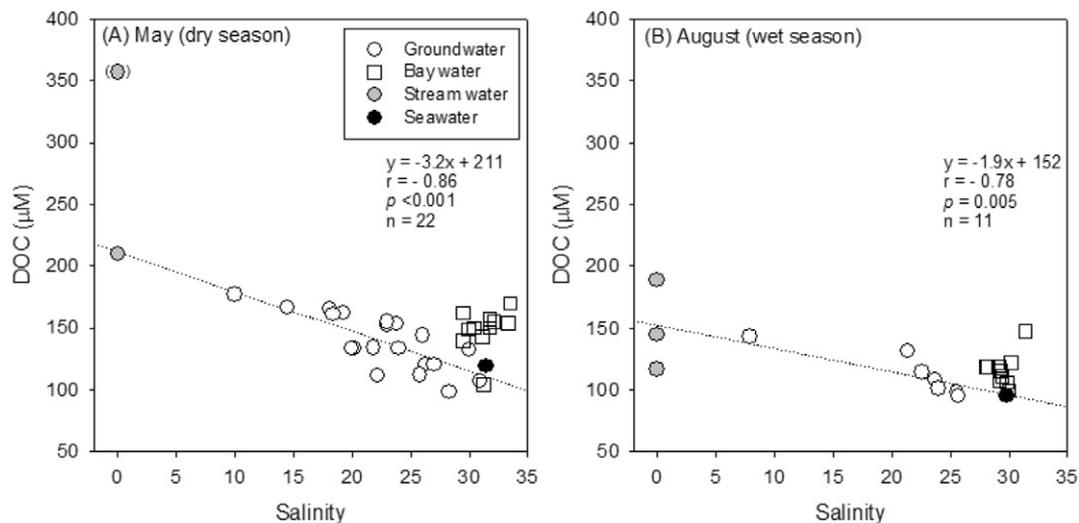


Fig. 2. Plots of DOC concentration versus salinity in (A) May and (B) August. The dotted line indicates a regression line based on DOC data of stream water, groundwater, and seawater (open ocean water). The stream water DOC data in parenthesis in (A) is excluded for the regression line.

Since DOC concentration of the stream water endmember was not obtained in May 2006, we used an average DOC concentration of the stream water samples obtained in May 2007. For the groundwater DOC endmember concentration in “dry season”, we averaged all groundwater DOC concentrations in May 2006 and 2007 as we have only two groundwater samples in May 2006. Q_{Stm} and Q_{SGD} estimated from Ra mass balance model into Masan Bay were obtained from the previous study conducted in Masan Bay (Lee et al., 2009). Since we did not directly measure the diffusive DOC flux from the bottom sediments and the sediment of Masan Bay consists mainly of silt and clay (>90%) (Woo et al., 2003), an average value ($2.3 \text{ mmol m}^{-2} \text{ d}^{-1}$) of DOC flux from muddy sediments of various estuarine (Maher and Eyre, 2010) was used for the diffusive rate (ψ_{Ben}) from the bottom sediment. The area of Masan Bay is assumed to be $8.0 \times 10^7 \text{ m}^2$ and V is $7.5 \times 10^8 \text{ m}^3$ (Lee et al., 2009). C_{mn} in the dry and wet were $149 \pm 17 \text{ }\mu\text{M}$ and $117 \pm 13 \text{ }\mu\text{M}$, respectively. Since DOC showed a significant correlation with salinity as described above, we used the DOC concentration in the obtained seawater samples in this study as the DOC seawater endmember concentrations (C_{Out} , 123 μM for dry season and 90 μM for wet season) regardless of only one open ocean water sample. The assumed residence time (τ) of the bay water in our mass balance model is 23.2 days which was reported in the previous study (Ryu et al., 1998) for the average residence time for the whole bay.

4.3. SGD-derived and unidentified DOC fluxes

Naturally occurred tracers (radium, radon, and silicate) to estimate SGD in coastal zones have been used for the last few decades, but there were large uncertainties associated with SGD estimation in the previous studies (Peterson et al., 2008; Burnett et al., 2008; Tait et al., 2013). For example, Burnett et al. (2008) reported that the uncertainty of SGD estimated in the Flamengo Bay was about 50% using radon mass balance model. Su et al. (2011) reported >100% uncertainties of SGD in estuaries of eastern Hainan Island, China using the ^{226}Ra mass balance model. Similarly, there are large uncertainties in our DOC mass balance model although the calculations used in the model is thought to be reasonable. For the uncertainty calculation, Maher and Eyre (2010) reported 100% uncertainty of DOC flux from bottom sediment. The important sources of uncertainties in the mass balance model were the SGD flux obtained from the previous study (Lee et al., 2009) and the water residence time. The roughly calculated SGD fluxes into this bay based on the terms reported in Lee et al. (2009) have ~60% uncertainty ($5.7 \times 10^6 \pm 3.0 \times 10^6$ in the dry season and $4.8 \times 10^6 \pm 2.5 \times 10^6$ in the wet season). These uncertainties are mainly related to the water residence time and the radium endmember concentrations of the groundwater.

We assigned a 50% uncertainty of the residence time, reflecting the reported residence times (approximately 40 day) based on the particle transport model and water-salt budget in more recent studies (KIOST, 2002; Park et al., 2011) in this bay, although the residence time of Masan bay was assumed to be 23.2 days in the previous studies (Ryu et al., 1998; Lee et al., 2009). The DOC loss flux by water mixing between the bay and open ocean waters has approximately 60% uncertainty.

Table 2

The comparison of input and output fluxes of DOC ($\times 10^5 \text{ mol d}^{-1}$) in Masan Bay in May and August 2006 and May 2007.

	Endmember (μM)		Source			Sink	
	SGD	Stream water	F_{SGD}	F_{Stm}	F_{Dif}	F_{Mix}	F_{Net}
May	139 ($n = 20$) ^a	284 ($n = 2$) ^b	6.7	1.6	1.8	8.3	1.8
August	113 ($n = 7$)	150 ($n = 3$)	6.4	1.6	1.8	8.6	1.2

F_{SGD} , F_{Stm} , F_{Dif} , F_{Mix} , and F_{Net} denote the flux of DOC by SGD, by stream water, by the diffusion from bottom sediments, by mixing with the outer-bay seawater, and by the unidentified processes, respectively.

^a The value is the average of endmember obtained in May 2006 and 2007.

^b The value is the average of endmember obtained in May 2007.

Table 3

DOC from Masan Bay via SGD in comparison with those from other areas.

Location	SGD ($\text{m}^3 \text{ m}^{-2} \text{ d}^{-1}$)	Fluxes ($\text{mmol m}^{-2} \text{ d}^{-1}$)	References
Masan Bay (May)	0.06	8.4	This study
Masan Bay (Aug.)	0.07	7.9	This study
Hwasun Bay, Jeju Island	0.12	5.4	Kim et al. (2013)
Hampyeong Bay	0.25	46	Kim et al. (2012)
Gulf of Mexico	0.11	34	Santos et al. (2008)
North Inlet, South Carolina	0.03	50	Goñi and Gardner (2003)
West Neck Bay, New York	0.12	0.6	Beck et al. (2007)

Based on the uncertainty propagation, this uncertainty of DOC loss flux by water mixing was calculated using a standard error of bay water DOC concentration ($149 \pm 5 \text{ }\mu\text{M}$) and the assumed uncertainty of the bay water residence time (23.2 ± 11.6 days). The calculated SGD-derived DOC fluxes have ~65% uncertainties. The calculated uncertainties of the unidentified DOC fluxes based on the uncertainty propagation calculation ranged from 280 to 540%. To reduce uncertainties associated with SGD and SGD-derived DOC flux, a more intensive investigation needs to be conducted for determination of temporal and spatial SGD-derived DOC flux and the DOC production and removal fluxes in the bay. Furthermore, considering seasonal and spatial variations in ^{226}Ra groundwater endmember concentrations in each season, the maximum portions of SGD-derived DOC fluxes account for 91 and 69% and the minimum portions for 52 and 37% of total input flux in the dry and wet season, respectively. These results imply that changes in the groundwater endmember concentration used in the mass balance model have a significant influence on the final estimate of SGD.

At steady state, the SGD-derived fluxes of DOC in the dry and wet seasons were calculated by multiplying the average DOC concentrations in groundwater ($139 \pm 23 \text{ }\mu\text{M}$ in the dry and $113 \pm 18 \text{ }\mu\text{M}$ in the wet) by the SGD rate in Masan Bay ($0.06 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ in May and $0.07 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ in August) (Lee et al., 2009). SGD-driven fluxes of DOC to Masan Bay were estimated to be $8.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($6.7 \times 10^5 \text{ mol d}^{-1}$) in the dry season and $7.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($6.4 \times 10^5 \text{ mol d}^{-1}$) in the wet season (Table 2). These DOC fluxes are 4–6 times smaller than those in the Gulf of Mexico ($34 \text{ mmol m}^{-2} \text{ d}^{-1}$), USA (Santos et al., 2008), Hampyeong Bay ($46 \text{ mmol m}^{-2} \text{ d}^{-1}$), Korea (Kim et al., 2012), and North Inlet ($50 \text{ mmol m}^{-2} \text{ d}^{-1}$), USA (Goñi and Gardner, 2003) (Table 3). However, these values are larger than those in Hwasun Bay ($5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$), Korea (Kim et al., 2013) and West Neck Bay ($0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$), USA (Beck et al., 2007) despite relatively lower SGD fluxes (Table 3). The calculated F_{Net} had negative values in both May ($1.8 \times 10^5 \pm 6.1 \times 10^5 \text{ mol d}^{-1}$) and August ($1.2 \times 10^5 \pm 6.0 \times 10^5 \text{ mol d}^{-1}$), indicating that removal rate by particle scavenging or bacterial degradation in this bay is relatively higher than *in situ* production rate by phytoplankton during the residence time. F_{Net} accounts for 18% of total DOC input flux in bay water in the dry season and 12% in the wet season (Table 2). Thus, although DOC concentrations in the groundwater were relatively lower than those in the stream water, the DOC fluxes associated with the stream water, diffusion from the bottom sediment, and SGD account for approximately 15, 20, and 65% of total DOC input flux in both seasons, indicating that SGD-derived DOC is the most important source of DOC in this bay.

5. Conclusions

SGD-derived DOC fluxes were estimated on the basis of DOC mass balance in an estuarine system, Masan Bay, during contrasting hydrological and climatic conditions (dry and wet seasons). Except for the bay water, DOC concentration showed significant correlations with salinity, indicating that there is no DOC input or removal throughout the

flow path. In contrast, the excess DOC concentrations in this bay water seem to be due to effective production by phytoplankton during the bay water residence time. The DOC fluxes through SGD in this bay were $6.7 \times 10^5 \text{ mol d}^{-1}$ in the dry season and $6.4 \times 10^5 \text{ mol d}^{-1}$ in the wet season although there were large uncertainties. These DOC fluxes accounted for 65% of total DOC input flux and were approximately 4 times higher than those from stream water and by diffusion from bottom sediments, suggesting that SGD-derived DOC is the most important source of DOC in this bay and SGD may play an important role in carbon budget and biogeochemistry in coastal areas.

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References

- Beck, A.J., Tsukamoto, Y., Tovar-Sanchez, A., Huberta-Diaz, M., Bokuniewicz, H.J., Sañudo-Wilhelmy, S.A., 2007. Importance of geochemical transformations in determining submarine groundwater discharge-derived trace metal and nutrient fluxes. *Appl. Geochem.* 22, 477–490.
- Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W.S., Taniguchi, M., 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* 66, 3–33.
- Burnett, W.C., Peterson, R., Moore, W.S., Oliveira, J., 2008. Radon and radium isotopes as tracers of submarine groundwater discharge—results from the Ubatuba, Brazil SGD assessment intercomparison. *Estuar. Coast. Shelf Sci.* 76, 501–511.
- Carlson, C.A., Hansell, D.A., 2014. DOM source, sinks, reactivity, and budgets. In: Hansell, D.A., Carlson, C.A. (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*. Academic Press, San Diego, CA, pp. 65–126.
- Charette, M.A., Sholkovitz, E.R., 2002. Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophys. Res. Lett.* 29. <http://dx.doi.org/10.1029/2001GL014512>.
- Chen, Z., Hu, C., Conmy, R.N., Muller-Karger, F., Swarzenski, P., 2007. Colored dissolved organic matter in Tampa Bay, Florida. *Mar. Chem.* 104, 98–109.
- Choi, M., Moon, H.B., Yu, J., Kim, S.S., Pait, A.S., Choi, H.G., 2009. Nationwide monitoring of nonylphenolic compounds and coprostanol in sediments from Korean coastal waters. *Mar. Pollut. Bull.* 58, 1086–1092.
- Goñi, M.A., Gardner, L.R., 2003. Seasonal dynamics in dissolved organic carbon concentrations in a coastal water-table aquifer at the forest-marsh interface. *Aquat. Geochem.* 9, 209–232.
- Hansell, D.A., Carlson, C.A., 1998. Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature* 395, 263–266.
- Hansell, D.A., Carlson, C.A., Repeta, D.J., Schlitzer, R., 2009. Dissolved organic matter in the ocean: a controversy stimulates new insights. *Oceanography* 22 (4), 202–221.
- Kim, T.H., Kim, G., 2010. Distribution of dissolved organic carbon (DOC) in the southwestern East Sea in summer. *Ocean Polar Res.* 32 (3), 291–297.
- Kim, J.D., Kim, B., Lee, C.G., 2007. Alga-lytic activity of *Pseudomonas fluorescens* against the red tide causing marine alga *Heterosigma akashiwo* (Raphidophyceae). *Biol. Control* 41, 296–303.
- Kim, T.H., Waska, H., Kwon, E., Suryaputra, I.G.N., Kim, G., 2012. Production, degradation and flux of dissolved organic matter in the subterranean estuary of a large tidal flat. *Mar. Chem.* 142–144, 1–10.
- Kim, T.H., Kwon, E., Kim, I., Lee, S.A., Kim, G., 2013. Dissolved organic matter in the subterranean estuary of a volcanic island Jeju: importance of dissolved organic nitrogen fluxes to the ocean. *J. Sea Res.* 78, 18–24.
- KIOST, 2002. *Land–Ocean Interactions in the Coastal Zone*. Korea Institute of Ocean Science & Technology (in Korean).
- Lee, Y.W., Hwang, D.W., Kim, G., Lee, W.C., Oh, H.T., 2009. Nutrient inputs from submarine groundwater discharge (SGD) in Masan Bay, an embayment surrounded by heavily industrialized cities, Korea. *Sci. Total Environ.* 407, 3181–3188.
- Li, D., Dong, M., Shim, W.J., Yim, U.H., Hong, S.H., Kannan, N., 2008. Distribution characteristics of nonylphenolic chemicals in Masan Bay environments, Korea. *Chemosphere* 71, 1162–1172.
- Lim, H.S., Diaz, R.J., Hong, J.S., Schaffner, L.C., 2006. Hypoxia and benthic community recovery in Korean coastal waters. *Mar. Pollut. Bull.* 52, 1517–1526.
- Maher, D.T., Eyre, B.D., 2010. Benthic fluxes of dissolved organic carbon in three temperate Australian estuaries: implications for global estimates of benthic DOC fluxes. *J. Geophys. Res.* 115. <http://dx.doi.org/10.1029/2010JG001433>.
- MOE, 2012. *Statistics of Sewerage in 2011*. Ministry of Environment (in Korean).
- Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* 380, 612–614.
- Moore, W.S., 1999. The subterranean estuary: a reaction zone of ground water and sea water. *Mar. Chem.* 65, 111–125.
- Moore, W.S., 2010. The effect of submarine groundwater discharge on the ocean. *Annu. Rev. Mar. Sci.* 2, 59–88.
- Moore, W.S., Sarmiento, J.L., Key, R.M., 2008. Submarine groundwater discharge revealed by ^{228}Ra distribution in the upper Atlantic Ocean. *Nat. Geosci.* 1, 309–311.
- Park, S.-E., Lee, W.C., Hong, S.J., Kim, H.-C., Kim, J.-H., 2011. Variation in residence time and water exchange rate by release time of pollutants over a tidal cycle in Masan Bay. *Korean Soc. Mar. Environ. Eng.* 14 (4), 249–256.
- Peterson, R.N., Burnett, W.C., Taniguchi, M., Chen, J., Santos, I.R., Ishitobi, T., 2008. Radon and radium isotope assessment of submarine groundwater discharge in the Yellow River delta, China. *J. Geophys. Res.* 113:C09021. <http://dx.doi.org/10.1029/2008JC004776>.
- Ryu, C.-R., Kim, J.-K., Seol, D.-G., 1998. The tidal water-exchange estimation method based on particle tracking model. *J. Korean Soc. Coast. Ocean Eng.* 12 (4), 76–82.
- Sadat-Noori, M., Maher, D., Santos, I., 2016. Groundwater discharge as a source of dissolved carbon and greenhouse gases in a subtropical estuary. *Estuar. Coasts* 39 (3), 639–656.
- Santos, I.R., Burnett, W.C., Chanton, J., Mwashote, B., Suryaputra, I.G.N.A., Dittmar, T., 2008. Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. *Limnol. Oceanogr.* 53 (2), 705–718.
- Santos, I.R., Burnett, W.C., Dittmar, T., Suryaputra, I.G.N.A., Chanton, J., 2009. Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary. *Geochim. Cosmochim. Acta* 73, 1325–1339.
- Santos, I.R., Eyre, B.D., Huettel, M., 2012. The driving forces of porewater and groundwater flow in permeable coastal sediments: a review. *Estuar. Coast. Shelf Sci.* 98, 1–15.
- Sañudo-Wilhelmy, S.A., Rossi, F.K., Bokuniewicz, H., Paulsen, R.J., 2002. Trace metal levels in uncontaminated groundwater of a coastal watershed: importance of colloidal forms. *Environ. Sci. Technol.* 36, 1435–1441.
- Slopp, C.P., Cappellen, P.V., 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *J. Hydrol.* 295:64–86. <http://dx.doi.org/10.1016/j.jhydrol.2004.02.018>.
- Stewart, B.T., Santos, I.R., Tait, D.R., Macklin, P.A., Maher, D.T., 2015. Submarine groundwater discharge and associated fluxes of alkalinity and dissolved carbon into Moreton Bay (Australia) estimated via radium isotopes. *Mar. Chem.* 174 (20), 1–12.
- Su, N., Du, J., Moore, W.S., Liu, S., Zhang, J., 2011. An examination of groundwater discharge and the associated nutrient fluxes into the estuaries of eastern Hainan Island, China using ^{226}Ra . *Sci. Total Environ.* 409 (19), 3909–3918.
- Tait, D.R., Santos, I.R., Erler, D.V., Befus, K.M., Cardenas, M.B., Eyre, B.D., 2013. Estimating submarine groundwater discharge in a South Pacific coral reef lagoon using different radioisotope and geophysical approaches. *Mar. Chem.* 156, 49–60.
- Williams, P.M., Druffel, E.R.M., 1987. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature* 330, 246–248.
- Windom, H., Niencheski, F., 2003. Biogeochemical processes in a freshwater-seawater mixing zone in permeable sediments along the coast of southern Brazil. *Mar. Chem.* 83, 121–130.
- Woo, H.-J., Cho, J.-H., Jeong, K.-S., Chung, C.-S., Kwon, S.-J., Park, S.-M., 2003. Pollution history of the Masan Bay, southeast Korea, from heavy metals and foraminifera in the subsurface sediments. *J. Korean Earth Sci. Soc.* 24, 635–649.