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Article

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Large Temporal Changes in Contributions of Groundwater-borne Nutrients to Coastal Waters off a Volcanic Island

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Abstract – We examined the contribution of submarine groundwater discharge (SGD) to nutrient budgets in Hwasun Bay, Jeju Island, Korea in August 2009, October 2014, and May 2015. The concentrations of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in fresh groundwater were in the range of 285−716 μM and 2.3−3.2 μM, respectively, which were each 1−2 orders of magnitude higher than those in the bay seawater. The outer-bay seawater flowing into the bay was oligotrophic (2.9 ± 1.9 μM for DIN and 0.2 ± 0.3 μM for DIP). Nutrient budget calculations were performed for each season by accounting for submarine fresh groundwater discharge (SFGD) and water residence times. In August 2009 (DIN = 1.8 μM and DIN:DIP ratio = 4.6 for the outer-bay water), DIN inputs from SFGD accounted for approximately 40% of the DIN inventory in the bay seawater. In October 2014 (DIN = 1.1 μM and DIP < 0.05 μM for the outer-bay water), DIP from SFGD accounted for approximately 100% of the DIP inventory in the bay seawater. In May 2015, mean concentrations of DIN and DIP in the bay seawater were 8.6 ± 12 μM and 0.11 ± 0.04 μM, respectively, with conservative behaviors in the bay seawater in association with excessive groundwater inputs. These results imply that SGD plays a critical but different role in nutrient budgets and stoichiometry in coastal waters off a volcanic island depending on open-ocean nutrient conditions.

Keywords – submarine groundwater discharge, nutrients, N:P ratio, coastal ocean, Jeju Island

1. Introduction

Submarine groundwater discharge (SGD), including both submarine fresh groundwater discharge (SFGD) and saline groundwater (recirculated seawater), is an important nutrient transport pathway from land to the coastal ocean (Taniguchi et al. 2002; Sawyer et al. 2016). Submarine groundwater discharge is particularly important on tropical islands (e.g., Jeju Island, Hawaii, Balearic Islands, Mauritius, and etc.), where precipitation is large and rocks are highly permeable (Kim et al. 2003; Garcia-Solsona et al. 2010; Knee et al. 2010; Kim et al. 2011; Povinec et al. 2012; Moosdorf et al. 2015). In this connection, nutrient fluxes through SGD are very important in coastal waters off islands standing in oligotrophic oceans.

In Flic-en-Flac lagoon, Mauritius Island, the concentrations of dissolved nitrate in wells were one order of magnitude greater than those in the lagoon and offshore waters (Povinec et al. 2012). In this region, the fluxes of SGD-derived dissolved inorganic nitrogen (DIN) were estimated to be approximately 0.3 × 10^4 mmol m^{-1} day^{-1} along a shoreline. In Palma Bay of the island of Majorca, in the Mediterranean Sea, the fluxes of DIN via SGD were in the range of 0.01−1 × 10^4 mmol m^{-1} day^{-1}. In this bay, the amount of DIN supplied by SGD accounted fully for the excess nutrients (Rodellas et al. 2014). In Hawaii, nitrogen inputs through SGD were 2−100 times higher than N-fixation in coral reefs (Street et al. 2008). On Jeju Island, SGD-derived DIN fluxes were found to be approximately 2 × 10^4 mmol m^{-1} day^{-1} in association with groundwater contamination (Kim et al. 2011).

Such a large input of nutrients through SGD could play a critical role in primary production in the coastal ocean. In the Balearic Islands, phytoplankton biomass in coastal waters seems to be sustained by consuming nutrients supplied from SGD (Garcia-Solsona et al. 2010). As such, SGD from the highly permeability volcanic island, Jeju, is critical for feeding nutrients to coastal organisms (Kim et al. 2011). Nitrogen inputs through SGD also contribute significantly to the biomass and succession of aquatic vegetation of reefs (Ishigaki Island,

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Japan, Umezawa et al. 2002). In the coral reefs of Hawaii, the SGD-derived DIN fluxes may support up to 100% of primary production (Street et al. 2008). However, too much nutrient loading via SGD often adversely affects coastal waters. For example, excess nutrient inputs from SGD resulted in benthic eutrophication in a semi-enclosed bay (Bangdu Bay) on Jeju Island (Hwang et al. 2005). As such, enhanced nutrient loading by human activity via SGD can lead to reef degradation (Paytan et al. 2006).

In general, there are large variations in SGD magnitudes and groundwater quality depending on the precipitation and hydrogeological conditions of islands. In addition, nutrient conditions of open-ocean waters passing alongside the islands are dynamic and dependent on oceanographic conditions. However, the role of SGD in different seasons with regard to changes in open-ocean water conditions is poorly understood. Thus, in this study, we observed temporal changes in SGD and SGD-derived nutrient fluxes and budgets in Hwasun Bay of Jeju Island. This island has high groundwater seepage rates, and the outer-bay water is upstream of the Kuroshio Current, which is very oligotrophic. Based on seasonal sampling campaigns, we present the relative contribution of SFGD and the outer-bay seawater to the nutrient loading and stoichiometry of Hwasun Bay.

2. Materials and Methods

Study area

Jeju Island is located within approximately 140 km of the Korean Peninsula (Fig. 1). This volcanic island has few streams in spite of high precipitation (1140–1960 mm yr^{-1}) because the island mostly consists of porous basalt (Hahn et al. 1997). Hydrologic budget analyses show that approximately half of the total amount of rainfall contributes to groundwater recharge (1.7×10^9 m^3 yr^{-1}, Won et al. 2006). The SFGD flux calculated from the water mass balance on the island was 4.5×10^6 m^3 day^{-1} (Lee and Kim 2007).

The study site, Hwasun Bay (1.4 km^2), is located in the

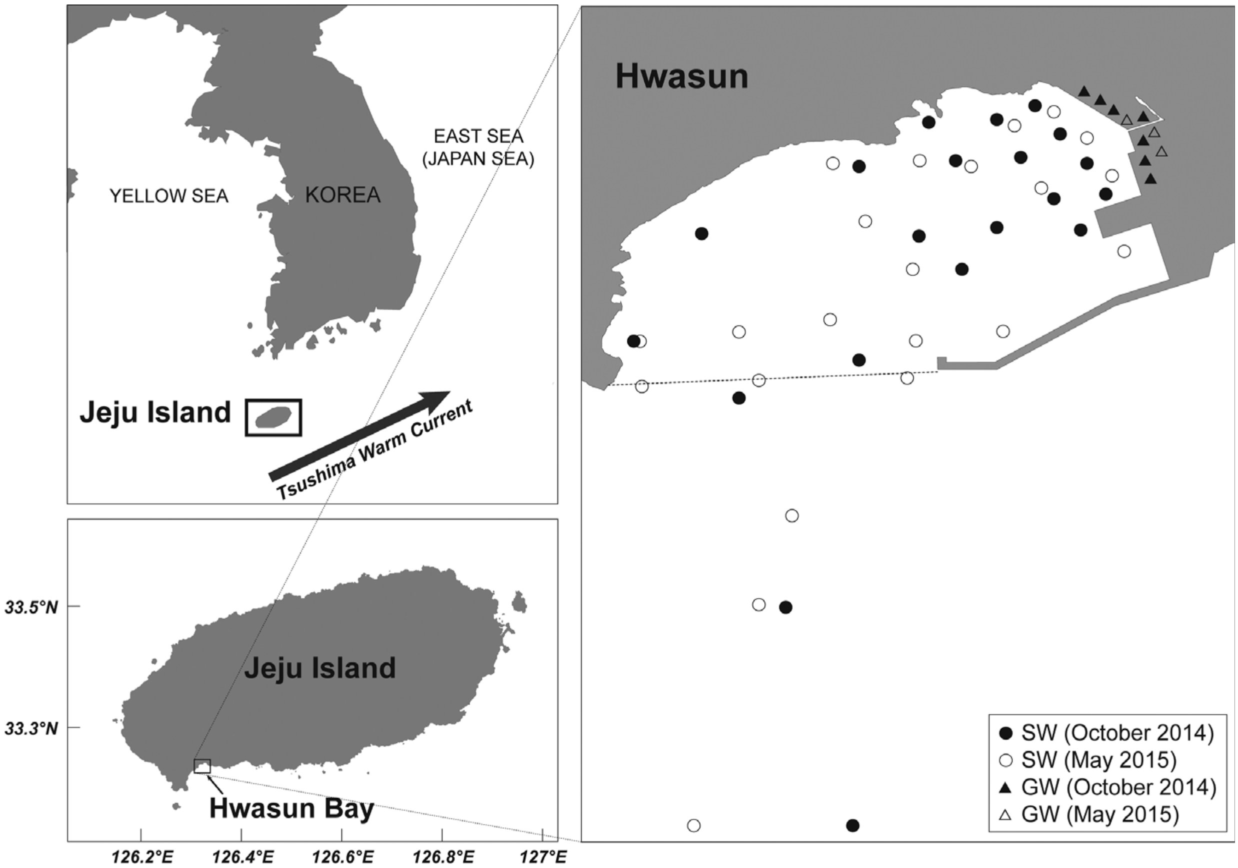

Fig. 1. A map showing the sampling stations of coastal seawater (circle) and groundwater (triangle) in October 2014 and May 2015 in Hwasun Bay, Jeju Island. Sampling locations for groundwater and seawater from Hwasun Bay in August 2009 are shown in Fig. 1 in Kim et al. (2011)

southwestern part of the island (Fig. 1). Since the low-permeability Seogwipo Formation is widely distributed under the thick basaltic layer in this region (Hahn et al. 1997; Koh et al. 2005), there are plenty of fresh groundwater springs that emerge from the aquifer. There is no continuous stream flow or river discharge into the bay. The total submarine groundwater (fresh and saline) inputs into the bay were estimated to be approximately 0.12 m^3 m^{-2} day^{-1} (Kim et al. 2011). The average depth of the bay is approximately 7 m (maximum ~15 m depth).

The coastal seawater near the bay is the Tsushima Current, which has high salinity (> 35) and low nitrate concentrations (< 1 μM) and originates from the north-flowing oligotrophic Kuroshio Current (Chang et al. 2000). The Tsushima Current is diluted by Changjiang River diluted water (CDW), which has low salinity (< 32), in summer and fall (Lie 1984; Park 1986; Chang and Isobe 2003). The CDW has relatively high DIN concentrations relative to the dissolved inorganic phosphorus (DIP) concentrations, with N:P ratios exceeding 100 (Tang et al. 1990; Wong et al. 1998).

Sampling and analyses

Bay seawater and coastal groundwater samples were collected for DIN, DIP, and dissolved silicate (DSi) analyses. Seawater samples were collected in the bay from 20 and 22 stations in October 2014 and May 2015, respectively (Fig. 1). The 2–4 seawater samples were collected for different depths at each site depending on water depths. The temperature and salinity of the seawater samples were measured onboard a ship using a conductivity-temperature-depth (CTD) instrument (Ocean Seven 304, IDRONAUT). Coastal groundwater samples (n = 7 and n = 3 in October 2014 and May 2015, respectively) were collected from beach wells along the shoreline. The temperature and salinity of groundwater samples were measured using a portable multi-parameter sensor (Orion star A329, Thermo Scientific).

Nutrient samples were collected in 50 mL conical tubes and filtered through 0.7-μm GF/F filters (Whatman, 45-mm diameter). The samples were frozen until the analysis was conducted. Dissolved inorganic nitrogen ($NO_3^- + NO_2^- + NH_4^+$), DIP (PO_4^{3-}), and DSi ($Si(OH)_4^-$) were analyzed using nutrient auto-analyzers (FUTURA PLUS, Alliance and New QuAAtro39, SEAL).

In this study, we also used data from Kim et al. (2011) (August 2009) together with our data (October 2014 and May 2015) in order to examine the seasonal variations.

3. Results and Discussion

Concentrations of nutrients in groundwater, outer-bay seawater, and bay seawater

In fresh groundwater, the mean concentrations of DIN were quite constant over the three periods (463 ± 275, 416 ± 142, and 551 ± 232 μM in August 2009, October 2014, and May 2015, respectively) (Fig. 2a). The mean concentrations of DIP in the fresh groundwater samples in August 2009 (3.8 ± 1.8 μM) were approximately 1.5-fold higher than those in October 2014 (2.7 ± 0.5 μM) and May 2015 (2.7 ± 0.4 μM; (Fig. 2b). The mean concentrations of DSi in fresh groundwater samples in October 2014 (513 ± 4 μM) and May 2015 (456 ± 56 μM) showed similar values, which were approximately four times lower than the value (2173 ± 1346 μM) in August 2009 (Fig. 2c). This difference seems to be due to two extremely high values (SPL2, SPL3) in August 2009. The DIN:DIP (N:P) ratios were similar for the three periods (158 ± 147, 162 ± 83, and 213 ± 106 μM in August 2009, October 2014, and May 2015, respectively; Fig. 2d). The higher N:P ratios in groundwater suggest that SGD has a larger impact in N-limited water conditions. The temporal variations of nutrient concentrations in fresh groundwater were insignificant relative to spatial variations.

In the outer-bay seawater, the concentrations of DIN in May 2015 (3.6 ± 1.9 μM) were 2–3 times the values in August 2009 (1.8 ± 1.0 μM) and October 2014 (1.1 ± 0.1 μM; Fig. 2a). Dissolved inorganic phosphorus in the outer-bay seawater in October 2014 was depleted, lower than the detection limit (< 0.05 μM), which was much lower than DIP concentrations in August 2009 (0.6 ± 0.5 μM) and May 2015 (0.1 ± 0.02 μM; Fig. 2b). The concentrations of DSi (8.8 ± 1.4 μM) in the outer-bay seawater in May 2015 were twice as high as those in August 2009 (3.1 ± 1.6 μM) and October 2014 (4.3 ± 0.4 μM; Fig. 2c). In August 2009, the outer-bay seawater was N-limited (N:P ratios < 8), which seems to be due to the influence of the N-depleted Tsushima Current passing along the island. In October 2014, the outer-bay seawater was extremely P-limited (N:P ratios > 100) owing to the input of P-depleted Changjiang River water to the Tsushima Current. During this period (October 2014), salinities for all seawater samples ranged from 29.2 to 29.7 (Fig. 3), which indicates the influence of CDW. In May 2015, higher N:P ratios (> 28) were observed in the outer-bay seawater, although the influence of CDW was not observed during this season. This seems to be due to excessive SFGD (high N:P ratios) inputs

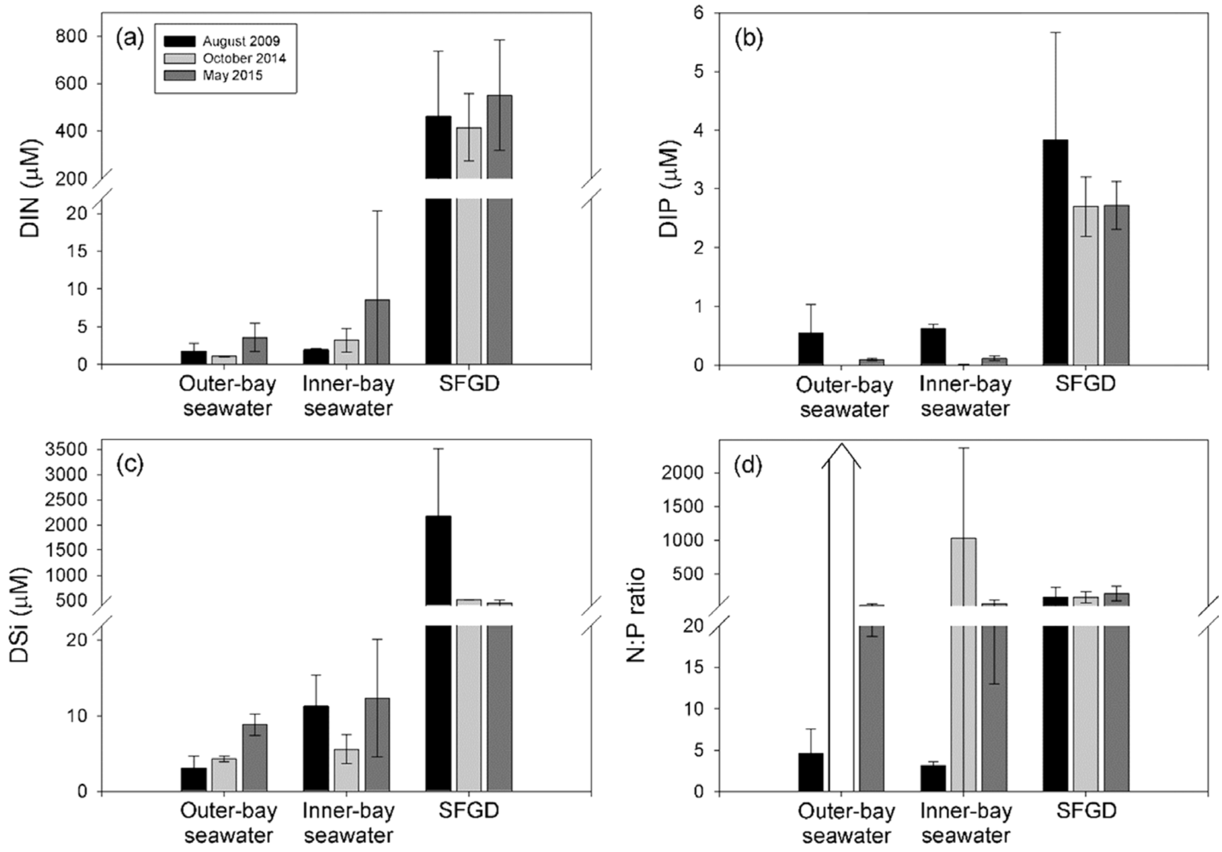

Fig. 2. Bar graphs and error bars showing mean values and standard deviations of (a) dissolved inorganic nitrogen (DIN), (b) dissolved inorganic phosphorus (DIP), and (c) dissolved silicate (DSi), and (d) N:P ratios of outer- and inner-bay seawater and coastal fresh groundwater. Black, grey, and dark grey bars represent samples in August 2009, October 2014, and May 2015, respectively

to the bay, as shown by the large salinity gradient in the bay and the conservative behavior of both nutrients with respect to salinity (Fig. 3a and b).

In the bay seawater, the mean concentrations of DIN were similarly low in August 2009 (2.0 ± 0.2 μM) and October 2014 (3.2 ± 1.6 μM) compared to those in May 2015 (8.6 ± 11.8 μM) (Fig. 2a). The mean concentrations of DIP in the bay seawater were 0.6 ± 0.1 and 0.1 ± 0.04 μM in August 2009 and May 2015, respectively (Fig. 2b), similar to those in the outer-bay seawater. Similar to the outer-bay seawater, DIP concentrations in the bay seawater in October 2014 were below the detection limit (< 0.05 μM). The concentrations of DSi in the bay seawater were 11 ± 4, 6 ± 2, and 12 ± 8 μM in August 2009, October 2014, and May 2015, respectively (Fig. 2c). The N:P ratios in the bay seawater were lower than the Redfield ratio (N:P = 16) in August 2009 (3.2 ± 0.4), while they were higher than the Redfield ratio in October 2014 (1031 ± 1332) and May 2015 (63 ± 50) (Fig. 2d).

Contributions of SGD on nutrient budgets

The concentrations of nutrients in coastal seawater decreased as salinity increased during all sampling periods. The seawater samples showed different salinity ranges of 31.2–32.5, 29.2–29.7, and 31.0–33.9 in August 2009, October 2014, and May 2015, respectively (Fig. 3). The largest anomalies of salinity in the bay seawater were observed in May 2015 (Fig. 3). Considering that there is no surface runoff in Hwasun Bay, the salinity anomalies reflect the input of SFGD into the bay. Thus, SFGD flux can be calculated based on salinity anomalies in the inner-bay seawater relative to the outer-bay seawater together with water residence times of the bay. The water residence time in this bay was calculated using a tidal prism model (Sanford et al. 1992; Moore et al. 2006). This model uses a function of the tidal range and the volume of bay seawater. In this calculation, we assumed that the return flow is negligible since the velocity of the offshore current near the coast of Jeju Island is high (10–15 cm s^{-1}; Chang et al. 2000). The residence times of seawater were 2.5 day, 2.8

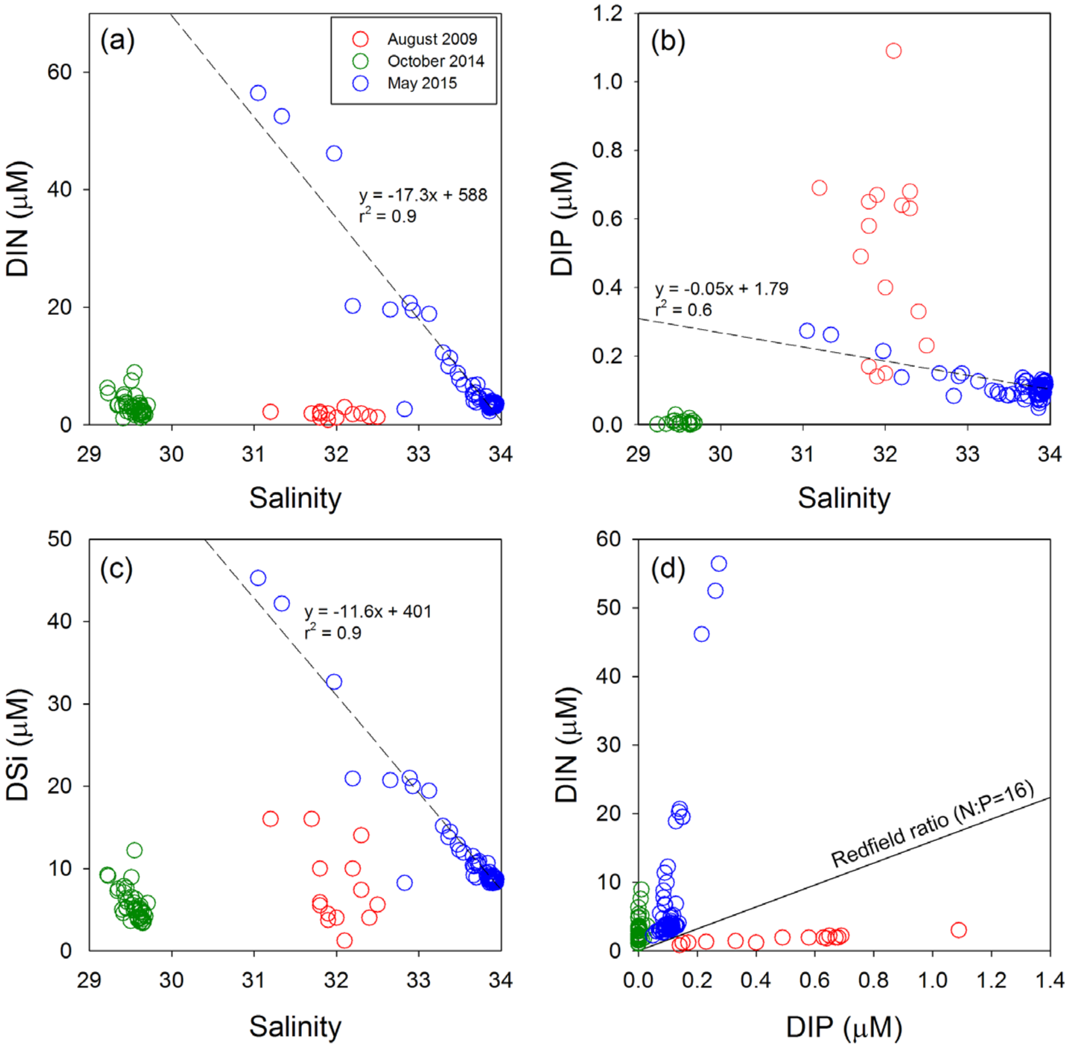

Fig. 3. Plots of (a) dissolved inorganic nitrogen (DIN), (b) dissolved inorganic phosphorus (DIP) and (c) dissolved silicate (DSi) versus salinity and (d) N:P ratios of bay seawater in Hwasun Bay. Red, green, and blue dots represent seawater samples collected in August 2009, October 2014, and May 2015, respectively. The data in August 2009 were obtained from Kim et al. (2011)

day, and 2.6 day in August 2009, October 2014, and May 2015, respectively. Based on these information, fresh groundwater fluxes were estimated to be 1.2×10^4, 0.2×10^4, and 4.2×10^4 m^3 day^{-1} in August 2009, October 2014, and May 2015, respectively.

The contribution of fresh groundwater inputs to Hwasun Bay seawater was estimated by multiplying SFGD-derived nutrient fluxes by the water residence time of bay water. The nutrient fluxes through SFGD were calculated by multiplying the groundwater discharge by the end-member concentrations of fresh groundwater. The intercepts of salinity (salinity = 0) versus nutrient curves for groundwater and seawater were used as the endmember values of each nutrient (Fig. 4). These correlations suggest that nutrient inputs through diffusion from bottom sediments and saline groundwater discharge are insignificant in this system. Thus, we simply compared the nutrient contributions to the bay seawater from SFGD to the background concentrations of the outer-bay seawater.

We used the entire range of extrapolated values as the fresh groundwater endmember values of each nutrient (194−630 μM for DIN, 1.8−3.3 μM for DIP, and 160−401 μM for DSi). In this estimation, two spring water samples (SPL2, SPL3) in August 2009 were regarded as outliers to avoid overestimation. The contribution of outer-bay seawater to the nutrient inventories of Hwasun Bay seawater was estimated by multiplying the mean concentration of nutrients in the outer-bay by the volume of bay seawater.

In August 2009, on the basis of this estimation, approximately

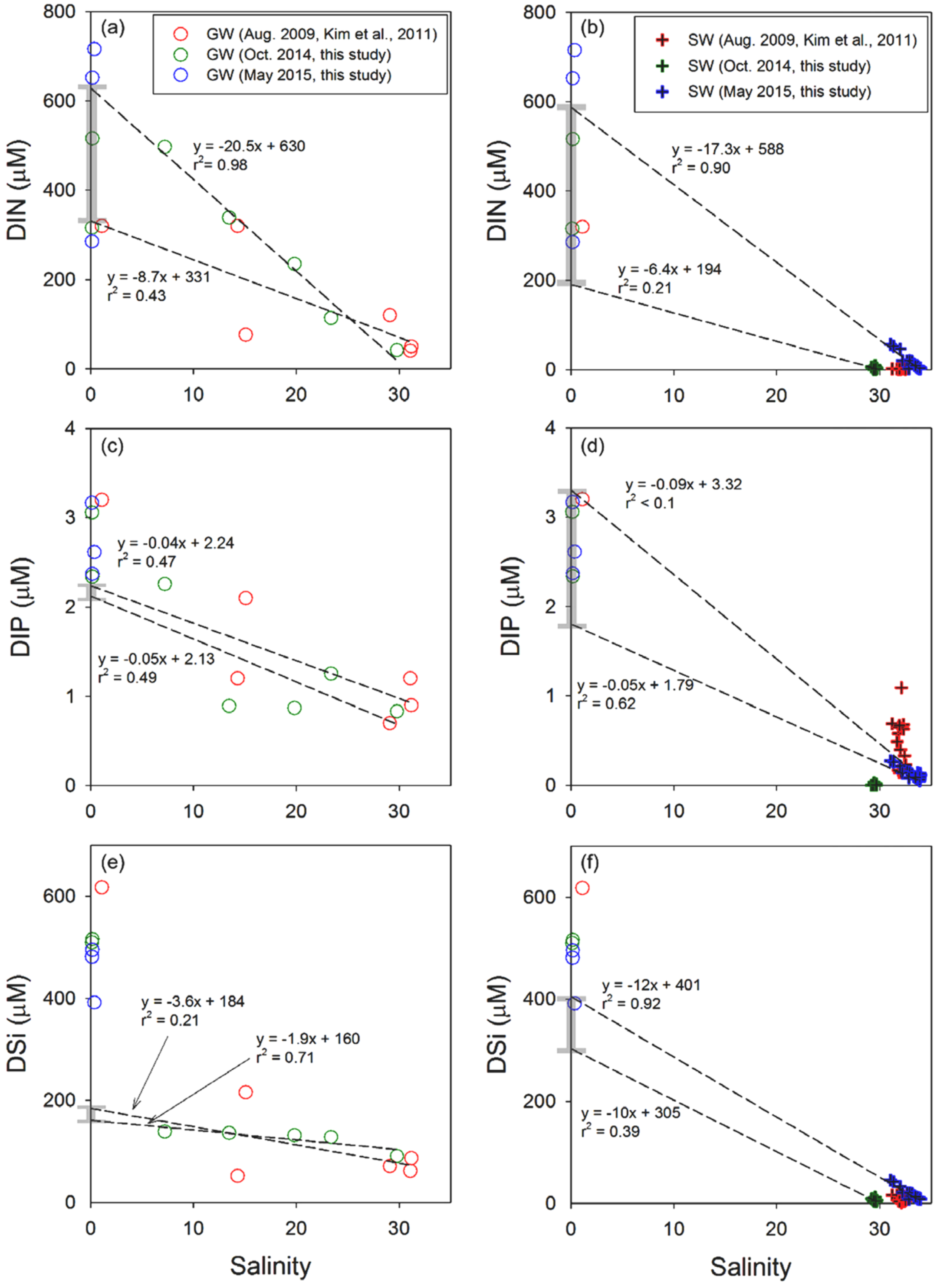

Fig. 4. Plots of salinity versus dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved silicate (DSi) concentrations in coastal groundwater (left 3 panels) and seawater (right 3 panels). The dashed lines in the left 3 panels and right 3 panels show linear regressions for salinity=0 endmembers fitted through groundwater and seawater concentrations, respectively

40% of the DIN inventory of the inner-bay was found to be from SFGD, whereas the contribution of outer-bay seawater to the DIP inventory of the inner-bay seawater was 99% (Fig. 5a). Dissolved silicate inputs via fresh groundwater contributed

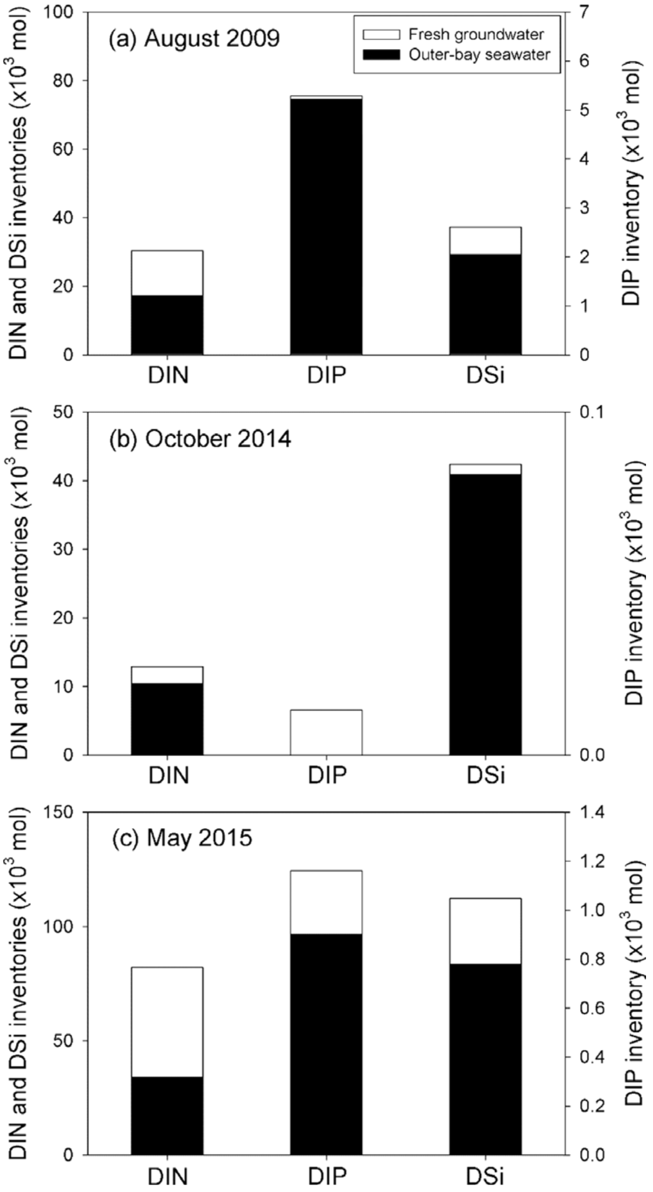

Fig. 5. Nutrient inventories (×10^3 mol) in Hwasun Bay in (a) August 2009, (b) October 2014, and (c) May 2015. The white and black bars represent the nutrient inventories originating from fresh groundwater inputs and outer-bay seawater, respectively

approximately 20% of the DSi inventory of the bay in August 2009 (Fig. 5a). These results show that inputs of DIN from SGD contributed significantly to biological production of this bay during this period as the outer-bay seawater was N-limited.

In October 2014, SFGD fluxes were lowest among the three sampling periods. During this period, DIP inputs through SFGD contributed about 100% of the DIP inventory of the bay. However, the outer-bay seawater contributed 80% and 95% of the DIN and DSi inventories in the bay, respectively (Fig. 5b). This result suggests that even the small magnitude of DIP inputs (0.5 × 10^4 mmol day^{-1}) through SFGD regulated biological production of this bay during this time because DIP concentrations in the outer-bay seawater were not detectable.

In May 2015, approximately 60, 25, and 25% of the DIN, DIP, and DSi inventories of the inner-bay were respectively attributed to SFGD (Fig. 5c). Because the concentrations of DIN, DIP, and DSi were conservative in this bay during this period due to the excessive inputs of nutrients through SGD, most of the nutrients from SGD seem to be conservatively transferred to the open ocean.

4. Conclusions

In Hwasun Bay, the concentrations of nutrients in the coastal groundwater samples were similar for different seasons. However, the influence of SGD-derived nutrients on biological production was very different for the three sampling periods. In August 2009, SGD was the major source of DIN in N-limited bay waters influenced by the N-limited Tsushima Current. In October 2014, SGD was the absolute source of DIP in P-depleted bay waters that were influenced by P-limited CDW. In May 2015, excessive inputs of nutrients from SGD resulted in almost complete transfer of SGD-derived nutrients to the open ocean. Further extensive studies are necessary for understanding large seasonal and spatial variations of SGD-derived nutrient inputs to the coastal ocean and their different roles in coastal production.

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