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Dependence of coastal water pH increases on submarine groundwater discharge off a volcanic island

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ABSTRACT

During the past few decades, excessive input of nutrients and organic matter, in addition to global ocean acidification, has resulted in significant changes in the water pH of coastal ocean. In this study, we investigated the effect of submarine groundwater discharge (SGD) on pH variations in the coastal waters of Hwasun Bay off the volcanic island of Jeju, Korea, which is situated in the oligotrophic open ocean. In this region, salinities of all coastal waters depend primarily on SGD because of the lack of any contributions from the river or stream waters. We observed a significant increase in pH along the lower-salinity plume zone, extending 0.5 km horizontally from the bottom to the surface (< 15 m water depth). The observed data for the entire bay-water column showed a significant negative correlation ($r^2 = 0.82$) between salinity and pH. A simple two-endmember (submarine groundwater and offshore seawater) mixing model showed that this pH increase was caused by an enhanced biological production, which resulted from the SGD-driven nutrient inputs, rather than from groundwater dilution itself. Since a number of local and regional studies showed that SGD-driven fluxes of nutrients are comparable to or higher than their riverine fluxes, our results from an SGD-dominated environment suggest that SGD may have a significant influence on the coastal biogeochemical changes such as acidification, deoxygenation, and eutrophication.

1. Introduction

Because of significant emissions of anthropogenic CO_2 into the atmosphere, surface-ocean pH has decreased globally (>0.1 units on average) since the industrial revolution (Caldeira and Wickett, 2003, 2005; Orr et al., 2005; Feely et al., 2009). The change in ocean pH has had critical consequences for marine ecosystems and biogeochemical cycles (Feely et al., 2004; Orr et al., 2005; Wootton et al., 2008; Doney et al., 2009; Feely et al., 2009; Connell et al., 2013). In some river-dominated coastal regions, high biological production supported by riverine nutrient input leads to an increased surface-water pH (Borges and Gypens, 2010; Guo et al., 2012). The subsequent re-mineralization in subsurface waters in the coastal ocean often causes a more rapid decline in pH than that in the pelagic ocean (Cai et al., 2003; Borges and Gypens, 2010; Cai, 2011; Cai et al., 2011). Although a number of studies have dealt with pH change caused by nutrient input from rivers (Cai et al., 2011; Guo et al., 2012), studies on the effect of submarine groundwater discharge (SGD), which has recently been recognized as an important pathway for nutrients (Paytan et al., 2006; Burnett et al., 2007; Deborde et al., 2008; Johnson et al., 2008), are limited.

SGD is commonly defined as any water (meteoric groundwater, marine groundwater, or a composite of both) flowing through marginal seabed into the ocean (Church, 1996; Burnett et al., 2003). A recent study revealed that global SGD is 3–4 times greater than global river-water discharge (Kwon et al., 2014). Because nutrients are often highly enriched in submarine groundwater (Slomp and Van Cappellen, 2004; Moore et al., 2006; Kim et al., 2008; Santos et al., 2008; Kim et al., 2011), SGD-driven nutrients enhance phytoplankton production (Slomp and Van Cappellen, 2004; Hwang et al., 2005; Basterretxea et al., 2010; Kim et al., 2011) and benthic production (Waska and Kim, 2011). SGD is often enriched with dissolved inorganic carbon (DIC) as a result of the degradation of organic carbon within coastal aquifers (Gagan et al., 2002; Cai et al., 2003; Dorsett et al., 2011; Liu et al., 2012; Atkins et al., 2013; Cyronak et al., 2013; Szymczycha et al., 2013). The pH values of these waters are low. DIC fluxes derived from SGD have been reported to be comparable to the DIC loads carried by rivers in highly productive regions (e.g., salt marshes, mangroves, and lake lands) (Cai et al., 2003; Moore et al., 2006; Maher et al., 2013). Even

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in river-dominated ocean margins, the DIC flux derived from SGD represents more than 30% of the riverine flux (Liu et al., 2012). In oligotrophic coastal waters, SGD and the associated nutrient loading may have different consequences for water pH and DIC. In organic-poor sandy aquifers, pH in fresh groundwater can increase up to 10 by protonation of sandy sediments (Lee and Kim, 2015). In addition, primary production in oligotrophic coastal waters depends greatly on the SGD-driven nutrients from volcanic islands (Kim et al., 2011).

In this study, we measured the pH, DIC, and nutrients in seawater and coastal groundwater of Hwasun Bay off Jeju Island, Korea, to determine the role of SGD in an oligotrophic environment. This site is ideal for observing the effects of SGD on coastal water pH, because the SGD is distinctive, the high nutrient loading in oligotrophic waters is significant, and the site has no sustained rivers or streams (Kim et al., 2003, 2011).

2. Methods

2.1. Study area

Jeju Island is an oceanic island with an area of 1830 km^2 and is located in the South Sea of Korea (Fig. 1). The island lies within the Tsushima Current (salinity >35 and nitrate <1 μM), which originates from the oligotrophic Kuroshio Current (Gong et al., 1996; Ning et al., 1998; Chang et al., 2000). The island has a shield volcano, Halla Mountain, with an elevation of 1950 m, from which gentle slopes lead down to the coast. Because of the porous nature of the basaltic rocks that make up the island, it has few sustained streams, despite high precipitation (1140–1960 mm yr^{-1}) (Hahn et al., 1997; Koh et al., 2007). Torrents occur only occasionally, after large summer rain events. On the basis of hydrologic budget analyses, approximately 50% of the total precipitation (1.5 × 10^9 m^3 yr^{-1}) is known to be recharged as groundwater (Hahn et al., 1997; Won et al., 2006). The recharged groundwater percolates down through the permeable basaltic rocks and is discharged into the ocean as springs and seepage (Hahn et al., 1997). The total discharge rate of groundwater from coastal springs is estimated to be approximately 3.9 × 10^8 m^3 yr^{-1} (Hahn et al., 1997). In addition, rapid recirculation of seawater occurs along the coast within the sandy sediments that overlie the thick and highly permeable basaltic layer. Thus, the island's total SGD, including meteoric and marine groundwater, is much larger (~1.5 × 10^{10} m^3 yr^{-1}; ~300 m yr^{-1}) than that observed for typical continental coasts (Kim et al., 2003; Lee and Kim, 2007).

Hwasun Bay (33.14°N, 126.33°W), located in the southwestern part of the island, has a large amount of SGD (~2.3 × 10^6 m^3 d^{-1}), including substantial submarine fresh groundwater discharge (SFGD) totaling ~5.8 × 10^5 m^3 d^{-1} (Kim et al., 2011). Fresh groundwater springs, from the deep (0–80 m) aquifer (the conductivity 230–340 μS cm^{-1}) through rocks, are ubiquitous and they have uniform geochemical compositions (Won et al., 2005, 2006; Koh et al., 2007). In addition, the shallow sandy aquifer (~0.6 m) overlying the basaltic rocks is a very simple system, in which fresh groundwater and seawater become mixed (Kim et al., 2011, 2013). No sustained stream or river discharges into the bay. The coastal seawater originates from the Tsushima Warm Current and it is often diluted by Yangtze River diluted water in summer and fall (Lee et al., 2009). The area of the bay is approximately 1.38 km^2. The water is shallow (average 7.6 m, maximum ~15 m depth). The residence time of seawater in this bay, estimated by the tidal prism method (Kim et al., 2011), were approximately 1.3 days.

2.2. Sampling and analyses

Seawater samples were taken from 11 stations (8 stations inside the bay and 3 stations outside the bay at every 2–3 m of depth; n = 25) in Hwasun Bay over a 4-h period (from 8:00 a.m. to noon) on April 8, 2013 (Fig. 1). The eight stations were selected as the potential points affected by SGD within Hwasun Bay, and the three stations were selected as offshore seawater endmembers. Sampling was conducted onboard a ship by use of a submersible pump with a high-performance conductivity-temperature-depth sensor (Ocean Seven 304, IDRONAUT). At each station, samples were collected for DIC, total alkalinity (TAlk), and nutrients, such as dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved inorganic silicate (DSi). Samples for DIC and TAlk analyses were collected in 500-mL glass bottles with 1% of headspace and poisoned with 200 μL of saturated $HgCl_2$ solution following the procedures of Dickson et al. (2007). Nutrient samples were

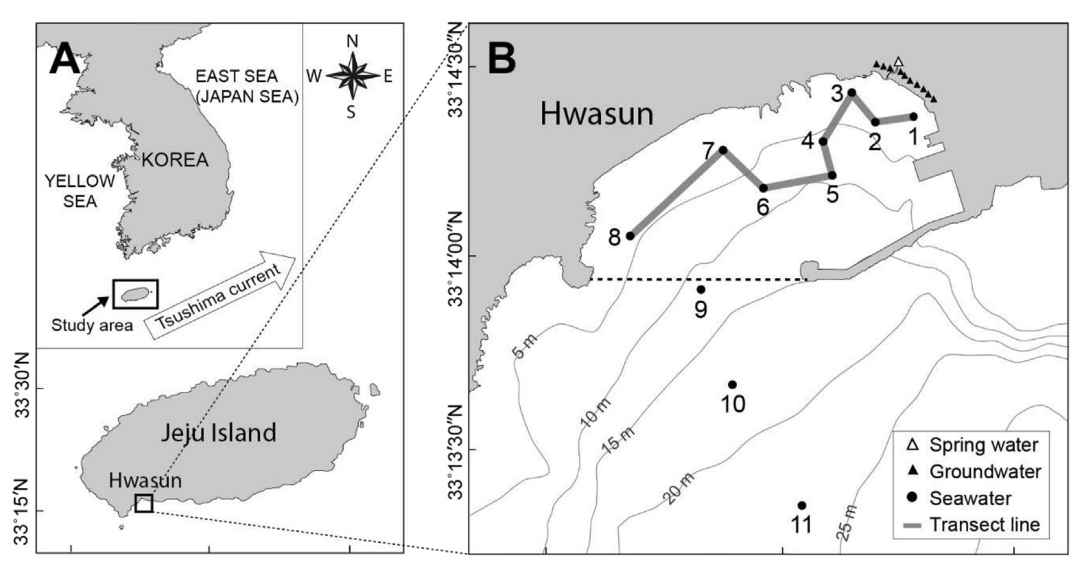

Fig. 1. Maps showing the sampling stations on Jeju Island: (A) location of Hwasun Bay; (B) sampling stations of coastal spring water (open triangle), groundwater (filled triangles) and seawater (circles), and a transect line (gray solid line).