

Tracing the Impact of Submarine Groundwater Discharge on the Diel Cycle of Dissolved Inorganic Carbon Parameters in a Coral Reef

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Submarine groundwater discharge (SGD) is widely acknowledged as a key driver of environmental change in coral reefs. Previous research has shown that SGD can deliver critical compounds, in the form of increased total alkalinity (TA), dissolved inorganic carbon (DIC), or anthropogenic pollutants to reef ecosystems. Furthermore, source apportionment of SGD solutes can be conducted using its carbon-13 ($\delta^{13}\text{C}$) isotope composition. Herein, we constrain the relative effect that SGD exerts on a diel cycle of reef DIC chemistry at a coral reef setting in Moorea, French Polynesia. Concurrent time series data (TA, DIC, $\delta^{13}\text{C}$, tidal stage, salinity, dissolved silica, and water temperature), collected over a period of 24 hours at four distinct time points (high tide day, low tide day, high tide night, and low tide night) from 15 locations, indicate two principal components (PCs). PC 1 effectively illustrates the ambient organic carbon cycle, with strong positive loadings of temperature and $\delta^{13}\text{C}$ and a strong negative loading of DIC. The non-conservative dynamics of silica precipitation during the day and dissolution at night is also detailed by PC 1. PC 2 represents the fresh SGD (FSGD) impact on the reef as indicated by strong positive loadings of tidal stage, salinity and TA. Collectively these data indicate a TA (and to a lesser degree DIC) dilution effect by FSGD that we attribute to (1) short groundwater residence times in the basaltic aquifers, and (2) limited soil CO_2 -derived H_2CO_3 neutralization by silicate weathering in these aquifers. The importance of silicate weathering over carbonate weathering in generating low TA yields in FSGD is further supported by DIC and $\delta^{13}\text{C}$ end-member mixing analysis of groundwater, seawater and coastal seep samples. These findings have important implications as our data indicate FSGD impacted reef water to exhibit a dominance of the organic over the inorganic carbon cycle because of TA dilution, which may translate into an exacerbated diel spread in water pH and aragonite saturation states. Thus, the carbonate structure of the reef will become less resilient to ocean acidification and transition to a state of net dissolution as the pH paradigm of the water becomes more variable.

