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Terrestrial nutrient inputs restructure coral reef dissolved carbon fluxes via direct and indirect effects

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Abstract

The addition of terrestrial inputs to the ocean can have cascading impacts on coastal biogeochemistry by directly altering the water chemistry and indirectly by changing ecosystem metabolism, which also influences water chemistry. Here, we use submarine groundwater discharge (SGD) as a model system to examine the direct geochemical and indirect biologically mediated effects of terrestrial nutrient subsidies on a fringing coral reef. We hypothesize that the addition of new solutes from SGD alters ecosystem metabolic processes including net ecosystem production and calcification thereby changing the patterns of uptake and release of carbon by benthic organisms. SGD is a common land-sea connection that delivers terrestrially sourced nutrients, carbon dioxide, and organic matter to coastal ecosystems. Our research was conducted at two distinct coral reefs in Mo‘orea, French Polynesia, characterized by contrasting flow regimes and SGD biogeochemistry. Using a Bayesian structural equation model, our research elucidates the direct geochemical and indirect biologically mediated effects of SGD on both dissolved organic and inorganic carbon pools. We reveal that SGD-derived nutrients enhance both net ecosystem production and respiration. Furthermore, the study demonstrates that SGD-induced alterations in net ecosystem production significantly influence pH dynamics, ultimately impacting net ecosystem calcification. Notably, the study underscores the context-dependent

nature of these cascading direct and indirect effects resulting from SGD with flow conditions and composition of the terrestrial inputs playing pivotal roles. Our research provides valuable insights into the interplay between terrestrial inputs and coral reef ecosystems, advancing our understanding of coastal carbon cycling and the broader implications of allochthonous inputs on ecosystem functioning.

Main Text

Introduction

External sources of nutrients and energy, or allochthonous inputs, to marine ecosystems can have cascading impacts on ecosystem functioning (Polis et al. 1997, Jefferies 2000). Shallow, nearshore ecosystems, like many coral reefs, are particularly affected by terrestrial inputs of nutrients and other solutes, which are commonly transported by freshwater connections from land to sea (Deleaux et al. 2018, Sandin et al. 2022). Natural terrestrial inputs can be beneficial to coral reefs: nutrients from seabird guano can elevate critical ecosystem functions, like herbivory, by 3.2 times relative to sites where seabird populations are diminished (Graham et al. 2018). In contrast, anthropogenic terrestrial inputs (e.g., urban and agricultural run-off and sewage effluent) can negatively alter competitive dynamics on reefs leading to macroalgal blooms, coral disease, and shifts in community structure (Pastorok and Bilyard 1985, Dubinsky and Stambler 1996, Adam et al. 2021, Nalley et al. 2023). Despite the known effects of allochthonous inputs on food-web dynamics and community stability in marine ecosystems, the mechanisms of action and interaction of biotic and abiotic processes leading to ecosystem

consequences remain unclear. As climate change, coastal development, and other anthropogenic stressors continue to alter both natural and anthropogenic inputs to the ocean, it is critical to understand both the direct geochemical and indirect biologically mediated effects of these inputs on coastal ecosystem functioning.

Biological and geochemical processes continuously interact, altering the concentration of dissolved solutes that ultimately regulate ecosystem metabolism (i.e., processes that mineralize or fix organic carbon). For example, recent studies have highlighted the importance of primary producers in the dynamics of dissolved CO₂ concentrations and subsequent pH variability in coastal ecosystems (Silbiger and Sorte 2018, Lowe et al. 2019, Ricart et al. 2021, Fields and Silbiger 2022); in turn, pH variability affects other biological processes like net ecosystem calcification (NEC) (Andersson and Gledhill 2013). Added nutrients can magnify this biogeochemical interaction: a coral reef study showed that a chronic low-level increase in inorganic N and P elevated pH variability nearly thirty-fold by enhancing net ecosystem production (NEP) (Silbiger et al. 2018). There has been a growing acknowledgement that organisms not only respond to their geochemical environment but simultaneously modify it. For example, in coral reefs and other highly productive coastal ecosystems, there has been a particular focus on biologically mediated indirect effects of inorganic carbon (NEP → pH → NEC) (Cyronak et al. 2014b, Kwiatkowski et al. 2016, Silbiger et al. 2018, Silbiger and Sorte 2018, Bracken et al. 2018, Fields and Silbiger 2022). However, changes to ecosystem metabolism can alter the composition and quantity of the organic carbon pool as well (Haas et al. 2011, Quinlan et al. 2018, Wegley Kelly et al. 2022). Field and lab studies both show that benthic community composition directly alters the composition of dissolved organic matter (DOM) (Quinlan et al. 2018, Wegley Kelly et al. 2022). Added nutrients can also indirectly alter

the relationship between metabolism and DOM composition, likely through augmented productivity (Goldberg et al. 2017, Quinlan et al. 2018): In one study, corals responded to a 3-fold increase in N with a ~40% and ~150% increase in humic and proteinaceous DOM, respectively (Quinlan et al. 2018).

While these studies highlight that the biological response to nutrient inputs can affect the inorganic or organic carbon pools, few studies explicitly link the organic and inorganic carbon pools within the same study. Here, we advance the field by demonstrating that allochthonous inputs drive both direct and indirect effects on local biogeochemistry and ecosystem metabolism, whereby the addition of new nutrients to a system creates a chain reaction, indirectly affecting both dissolved organic and inorganic carbon pools by changing the patterns of uptake and release of carbon by benthic organisms (Fig. 1). Understanding the mechanism of these cascading biogeochemical processes is especially important in the context of coral reefs, where external nutrient sources alter local biogeochemistry, drive phase shifts, and, ultimately, affect ecosystem metabolism (Lesser 2021).

Submarine groundwater discharge (SGD) is a globally prevalent land-sea connection (Moosdorf et al. 2015, Santos et al. 2021) offering a natural system for investigating the influence of allochthonous inputs on the interactions between geochemical and biological processes. SGD has a complex mixture of components and is a major source of new solutes that can influence coastal salinity, carbonate dynamics, nutrient fluxes, and the composition and concentration of dissolved organic matter (Paytan et al. 2006, Cyronak et al. 2013, Nelson et al. 2015). SGD-driven solutes have been linked to changes in algal species richness (La Valle et al. 2019, 2021), coral and macroalgal growth (Lubarsky et al. 2018, Amato et al. 2018), bioerosion (Crook et al. 2013, Lubarsky et al. 2018), and important ecosystem metabolism rates including

net ecosystem production and calcification (Richardson et al. 2017, Silbiger et al. 2020) on coral reefs. Net ecosystem production (NEP) is the net amount of carbon produced in an ecosystem as a result of photosynthesis and respiration, while net ecosystem calcification (NEC) is the net calcium carbonate produced from calcification and dissolution. These biological processes also alter carbonate and nutrient chemistry, highlighting that SGD may also indirectly alter local biogeochemistry by modifying coral reef biology.

The flux of SGD and its unique biogeochemical composition vary tidally, seasonally, and spatially, and are affected by both natural and anthropogenic processes such as precipitation, coastal development, freshwater harvesting, wastewater handling, and population density (Moore 2010, Santos et al. 2012, Kealoha et al. 2024). Differences in the chemical composition of SGD can have differential impacts on coral reefs. For example, in locations where total alkalinity (TA) in SGD is higher than the receiving waters (Cyronak et al. 2013), SGD may buffer corals from low pH (Kleypas and Langdon 2006, Cyronak et al. 2013, Middelburg et al. 2020). However, in locations where TA in SGD is lower than the receiving waters, the SGD may compound the effects of low pH on calcifiers (Correa et al. 2021). Climate change and increasing coastal population densities will alter the flux and composition of SGD (Wu et al. 2013, Moosdorf and Oehler 2017, Kealoha et al. 2024) and our ability to protect coastal ecosystem services is directly impacted by our understanding of how SGD affects biological and geochemical processes.

We consider the hypothesis that SGD inputs lead to both direct geochemical and indirect biological modifications of coastal biogeochemistry and ecosystem functioning, i.e., that elevated nutrients from groundwater affect ecosystem production, calcification, and the feedbacks between organic and inorganic carbon (Fig. 1). We test our hypothesis by resolving spatial gradients of reef metabolism and biogeochemistry across diel, tidal, and seasonal

timescales at two shallow coral reef sites with differing coastal environmental conditions in Mo‘orea, French Polynesia. Using structural equation models in a Bayesian framework, we characterized the direct geochemical and indirect biologically mediated effects of SGD on the concentration and composition of dissolved organic and inorganic carbon pools.

Materials and Methods

Site descriptions

Our study was conducted at two sites on the western side of Mo‘orea, French Polynesia (Fig. 2a-c), a high volcanic tropical island with microtidal conditions, with maximum tidal amplitude at approximately 0.2 m during spring tides (Hench et al. 2008). The two experimental sites were chosen based on discussions with local residents who had historical knowledge of SGD seepage points around Mo‘orea, followed by radon and salinity surveys (shown in Hagedorn et al. (2024)). Prior analyses show that SGD delivers significant quantities of freshwater to the nearby reef, with a maximum of 9.34 ± 4.03 and 7.20 ± 3.18 cm d⁻¹ at Varari and Cabral, respectively (Hagedorn et al. 2024). This normalized SGD flux was derived from dividing the calculated radon flux (dpm cm⁻² d⁻¹) from the groundwater endmember concentration (dmp cm⁻³). To ensure that SGD was the dominant source of freshwater and land-based solutes to the coastline at the experimental sites, we selected locations that were at least 0.7 km away from any rivers or streams.

The northernmost site, Cabral (Fig. 2b; -17.52° S and -149.91° W), is much less populated (~ 2 buildings per ha), with a single family living along most of the coastline. The reef at Cabral has 20% coral cover, dominated by *Porites* spp. and *Pavona* sp., with 58% macroalgal

cover. The flow direction at Cabral is tidally driven and the flow speed is highly dampened relative to Varari (0.018 ± 0.00023 m/s [mean $\pm$ SE]; Fig. 2f). Cabral has several seepage points spread out along the coastline, with likely additional ones further on the reef (pers comm T. Cabral). There are at least two known inland springs near Cabral where we were able to sample the source water with permission, although we are unable to share the locations of the springs to protect the water rights of the local community.

The southernmost site, Varari (Fig. 2c; -17.54° S and -149.90° W), is a relatively populated area (~ 10 buildings per ha) with several vacation rentals and residents living along the coastline. Varari has approximately 13% coral cover, dominated by *Porites rus*, *Pocillopora acuta*, and *Montipora* spp., and 58% macroalgal cover. The site has a consistent northwesterly unidirectional flow, with the fastest flow speeds when water levels are high (0.15 ± 0.00092 m/s [mean $\pm$ SE]; Fig. 2f). The SGD seepage points are clustered in one area and always subtidal and conspicuous, with freshwater bubbling up through the sand near the shoreline. The location of the inland spring(s) that feeds these SGD seeps are currently unknown and there are no local accessible wells.

Experimental set-up

We characterized the biogeochemistry and benthic community composition at 20 experimental locations plus one seepage point at each site (Figs. 2b-c). We used a regression approach in our experimental design to better understand the mechanistic relationships between our measured variables (Cottingham et al. 2005). For the 20 reef locations, we collected discrete water samples within 20 cm of the benthos across tidal (high/low), diel (day/night), and seasonal (dry/wet season) timepoints for a total of eight measurements per location ($n = 320$ water

samples total) to characterize a gradient of SGD-influence over space and time. The depths of the reef sampling locations were all less than 1.3 m from the surface. At the selected seepage points for each site, we collected additional samples to better characterize the composition of the incoming groundwater (n = 25 at Varari and n = 24 at Cabral). We also collected water samples at the reef crest ~ 1km from each site (n = 13 for Varari and n = 7 for Cabral) to characterize the incoming ambient seawater conditions. To determine groundwater endmembers, we sampled an inland spring and a beach pit at Cabral and two beach pits at Varari (Table 1). Sampling occurred in August 2021 and March 2022 in the dry and wet seasons, respectively.

Water samples for nutrients (nitrate plus nitrite [NO_x], ammonium [NH₄⁺], silicate [SiO₃²⁻], and phosphate [PO₄³⁻]), fluorescent dissolved organic matter (fDOM), total alkalinity (TA), pH, and salinity were collected either by hand with an acid washed HDPE bottle or using a subsurface automated sampler (SAS) (Enochs et al. 2020). Lastly, we used an acoustic doppler current profiler (ADCP) to characterize the current velocity and direction during the sampling period. All sample collection and processing procedures are detailed in Appendix S1.

Ecosystem metabolism calculation

Ecosystem metabolism was calculated similarly to Silbiger et al. (2020) using changes in TA and dissolved inorganic carbon (DIC). DIC was calculated from TA and pH (total) using the seacarb package (Gattuso et al. 2019). The mean ± SE error propagation for the DIC calculation from TA (error of 5 μmol kg⁻¹) and pH (error of 0.01) is 7.62 ± 0.021 μmol kg⁻¹. To account for groundwater mixing, TA and DIC were first normalized to SiO₃²⁻, a common tracer for SGD (Oehler et al. 2019, Silbiger et al. 2020), using the following equation:

$$\square_I = \square_{\square\square\square} + (\square_{\square\square\square} - \square_{\square\square\square}) * \left(\frac{\square_{\square\square\square} - 0.965}{\square_{\square\square\square} - \square_{\square\square\square}} \right),$$

Where C_I is the SiO_3^{2-} - normalized TA or DIC concentration at the open-ocean reference value ($0.965 \mu\text{mol L}^{-1}$), C_{mix} is the measured TA or DIC value (SGD-marine mixture), C_{SGD} is the SGD endmember TA or DIC value, Si_{mix} is the measured SiO_3^{2-} value (SGD-marine mixture) and Si_{SGD} is the average groundwater endmember (Table 1). The reference SiO_3^{2-} value was taken from a nearby offshore location from the Global Ocean Data Project (Olsen et al. 2016).

NEC and NEP potential (sensu Cyronak et al. 2018) were calculated for each sampling location $\times$ time point: NEC potential was calculated as $\Delta\text{TA}/2$ and NEP potential was calculated as $\Delta\text{DIC} - \Delta\text{TA}/2$. ΔTA or ΔDIC is the difference between the SiO_3^{2-} - normalized TA or DIC concentration and the average offshore SiO_3^{2-} - normalized TA or DIC concentration collected at the reef crest. ΔTA was divided by two because 1 mol of CaCO_3 is produced per 2 mol of TA uptake (Chisholm and Gattuso 1991). NEC potential is subtracted from NEP potential to remove any carbon taken up or released from inorganic processes. Differences in TA or DIC are commonly used as a proxy for net calcification/production (TA or DIC depletion) or net dissolution/respiration (TA or DIC repletion) on coral reefs (Yeakel et al. 2015, Cyronak et al. 2018, Silbiger et al. 2020). NEP and NEC potential are good proxies for true NEP and NEC because changes in TA and DIC are predominantly driven by metabolism on coral reefs (Cyronak et al. 2018). We avoided calculating true NEC and NEP rates because both field sites are very shallow ($< 2\text{m}$) with a complex hydrodynamic environment, and small uncertainties in residence time calculations can lead to highly inaccurate ecosystem metabolism rates (Courtney and Andersson 2019).

Statistical analyses

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To characterize the composition of the SGD from the seepage point by each site and season, we calculated the Pearson's correlation coefficient of log-transformed values for each measured variable (TA, pH, temperature, humic fDOM, proteinaceous fDOM, NO_x , NH_4^+ , SiO_3^{2-} , PO_4^{3-}) as a function of salinity. To visualize how SGD affected reef biogeochemistry over diel, tidal, and season time frames, we used a principal components analysis on log-transformed values. The data were centered and standardized by season and individual PCAs were created for each site. Additionally, we used a multivariate analysis of variance (MANOVA) to test the hypothesis that reef biogeochemistry changes across diel and tidal cycles. To characterize the biogeochemical cascade created by SGD we parameterized individual Bayesian structural equation models (SEM) for each site and season. All data used in the SEMs were centered and standardized and NO_x and SiO_3^{2-} were log-transformed in all models to meet assumptions of normality. Bayesian models were run using the R package *brms* (Bürkner 2017, 2018), which is based on the Hamiltonian Monte Carlo algorithm from STAN. To achieve model convergence, we ran three parallel chains of length 2000, with a warm-up of 1000, and a thinning parameter of 1. We used a multivariate normal distribution, and all parameters had relatively uniform priors (student t distribution (d.f. = 3, $\mu = 0$, $\sigma = 10$)). We visually checked all trace plots and calculated Gelman-Rubin statistics (Gelman and Rubin 1992) for all parameters to assess model convergence. Posterior predictive checks using the *pp_check* function in the *tidybayes* R package (Kay 2018) were used to assess model fit. All results are reported as medians with two-tailed 95% Bayesian credible intervals. Effect sizes with credible intervals that do not overlap zero are considered to be statistically significant. All analyses were performed in the R statistical program (R Core Team 2021). All data and code are available on Zenodo (Silbiger 2025).

Model justification

Each SEM was based on a system of six equations, where each equation represents a set of hypotheses based on our current understanding of SGD and coral reef ecology (Fig. 3). Below we justify each equation used in the SEM models.

$$\text{Eq 1: } y_{NO_x} \sim \beta_{SiO_3^{2-}} + \beta_0$$

Based on many studies that show SGD as a significant source of inorganic nutrients to coastal ecosystems (Paytan et al. 2006, Nelson et al. 2015, Silbiger et al. 2020, Santos et al. 2021), we hypothesized that nitrate + nitrite is positively correlated with SGD. Similar to previous studies (Oehler et al. 2019, Silbiger et al. 2020, Cho et al. 2021), we used SiO_3^{2-} as a proxy for SGD in our model. Notably, we did not attempt to calculate a SGD flux from SiO_3^{2-} , but rather used it as a correlate for SGD which is highlighted as an acceptable method in the literature due to its relatively conservative nature in SGD (Oehler et al. 2019, Moosdorf et al. 2021)

$$\text{Eq 2: } y_{NEP\ Potential} \sim \beta_{Temperature} + \beta_{NO_x} + \beta_{DayNight} + \beta_{NO_x*DayNight} + \beta_0$$

Temperature is an important driver of metabolism and can affect NEP on coral reefs (Hatcher 1990). Further, NO_x is also an important driver of NEP as has been shown in both field and lab experiments (Hatcher 1990, Silverman et al. 2007a, Atkinson 2011, McMahon and Santos 2017, Silbiger et al. 2018). As NEP switches from light-enhanced net photosynthesis to dark community respiration from day to night, we hypothesized that the effect of NO_x on NEP potential would be mediated by the diel cycle.

$$\text{Eq 3: } y_{pH} \sim \beta_{NEP\ Potential} + \beta_{SiO_3^{2-}} + \beta_{NEP\ Potential*SiO_3^{2-}} + \beta_0$$

There are often strong positive correlations between NEP and pH on coral reefs based on both field (DeCarlo et al. 2017, Silbiger et al. 2020) and lab (Page et al. 2016, Silbiger et al. 2018) studies. Further, field studies have shown that SGD typically has a lower pH than ambient seawater and could lead to coastal acidification (Cyronak et al. 2014a, Wang et al. 2014).

Therefore, we hypothesized that there would be a positive relationship between NEP potential and pH, and a negative relationship between SiO_3^{2-} and pH. We also hypothesized that the effect of SiO_3^{2-} on pH could be mediated by NEP potential and thus included an interaction term in the model.

$$\text{Eq 4: } y_{\text{NEP Potential}} \sim \beta_{\text{pH}} + \beta_{\text{Temperature}} + \beta_0$$

Similar to NEP, NEC is also strongly correlated with temperature on coral reefs (Silverman et al. 2007b, Courtney et al. 2017). In addition, low pH can reduce calcification rates, as has been demonstrated in many observational studies (Silverman et al. 2007b, Andersson and Gledhill 2013) and manipulative studies (Albright et al. 2018, Doo et al. 2019) on coral reefs. We, therefore, hypothesized that increases both pH and temperature would increase reef calcification.

$$\text{Eq 5: } y_{\text{Humics}} \sim \beta_{\text{SiO}_3^{2-}} + \beta_{\text{NEP Potential}} + \beta_{\text{DayNight}} + \beta_{\text{NEP Potential*DayNight}} + \beta_0$$

Field measurements show strong positive correlations between SGD and humic fDOM (Nelson et al. 2015, Cho et al. 2021). Humic fDOM is composed of microbial derived fulvic acids and terrestrial detrital DOM. Thus, we hypothesized that there would be a positive relationship between SiO_3^{2-} and humic fDOM. Additionally, manipulative lab and *in situ* tent experiments show that production and microbial respiration can either augment or reduce humic fDOM

(Quinlan et al. 2018, Kelly et al. 2019). Therefore, we hypothesized that NEP would enhance humic fDOM, but that the relationship would be mediated by the diel cycle as net production occurs during the day and microbial respiration is a dominant process at night.

$$\text{Eq 6: } y_{\text{Proteinaceous}} \sim \beta_{\text{SiO}_3^{2-}} + \beta_{\text{NEC Potential}} + \beta_0$$

Similar to humic fDOM, SGD also has been shown to elevate proteinaceous fDOM on coral reefs (Nelson et al. 2015). Proteinaceous fDOM are DOM components associated with aromatic amino acids, like tyrosine and tryptophan. Lab studies have demonstrated that corals, but not algae, release significant amounts of proteinaceous fDOM into the water column (Quinlan et al. 2018). Therefore, we hypothesized that there would be a positive relationship between NEC potential and proteinaceous fDOM.

Results

Fundamental differences in SGD chemistry in adjacent aquifers

At both sites, SGD had elevated nutrient concentrations (NO_x , NH_4^{4+} , PO_4^{3-} , SiO_3^{2-}) relative to ambient seawater (Fig. 2e; Table 1). Notably, the NO_x concentrations in the SGD were up to 56- and 680-fold higher than the reef at Cabral and Varari, respectively. The SGD was also a significant source of humic-derived fDOM at both sites, and a significant source of proteinaceous fDOM at Cabral during the dry season, as indicated by the positive correlation between freshwater and fDOM (Fig. 2e). The inorganic carbon pool, however, was particularly different between the sites (Fig. 2e; Table 1). At Cabral, total alkalinity (TA) of the groundwater endmember was highly depleted relative to ambient seawater, with concentrations up to ~980

$\mu\text{mol kg}^{-1}$ lower in the SGD than the average reef TA. The TA of the Varari groundwater was highly elevated, with concentrations up to $\sim 3024 \mu\text{mol kg}^{-1}$ above ambient seawater. Although, both sites had acidified SGD relative to the ambient seawater (Fig. 2e; Table 1).

SGD interacts with biological processes to drive reef biogeochemistry

While the composition of the groundwater itself was generally stable at each site during the study, the degree to which the low tide (when SGD is pumped onto the reef) chemical composition of the reef reflected the SGD composition was strikingly different between the two sites (Appendix S2: Fig. S1; Appendix S2: Table S1). At Varari, a site with faster, unidirectional (alongshore) water flow (Fig. 2f), there was a clear separation between tidal cycles, indicating a strong direct influence of SGD on reef biogeochemistry, with low tide having higher nutrients, humic fDOM, and SiO_3^{2-} as well as lower salinity relative to high tide (Fig. 4a,b). At Cabral, a site with slower, tidally-dependent, cross-shore flow, there were also differences in the biogeochemistry across tidal cycles, but with less distinction between tides (Fig. 4d,e). While Cabral exhibited lower salinity, higher SiO_3^{2-} , and lower TA during low tides, as expected from the composition of SGD at Cabral (Table 1), the NO_x and PO_4^{3-} concentrations did not vary tidally across the reef, even though both solutes were highly elevated in the SGD.

There were clear diel patterns in biogeochemistry, with important differences between the two sites (Fig. 4; Appendix S2: Table S1). At Varari, where SGD delivers relatively high TA, daylight hours (afternoon and dusk) had a higher pH, lower TA, and lower proteinaceous fDOM relative to dark hours (midnight and dawn). The diel pH patterns align with expected decreasing water column CO_2 from daytime net photosynthesis and increasing CO_2 from nighttime respiration. The diel patterns in TA also indicate that the biological control of TA from

calcification either outweighed or magnified the geochemical controls of high alkalinity SGD flowing onto the reef during low tide. Notably, the high TA values during the dawn low tide is likely the result of both biological and geochemical processes due to high TA from nighttime dissolution as well as the high TA from the SGD (Appendix S2: Fig. S1). This contrasts with results from Cabral, where pH and TA were orthogonal to each other on the reef (Fig. 4): pH was correlated with diel patterns (i.e., biologically controlled) while TA was correlated with tide (i.e., SGD-controlled). The opposite TA patterns at Cabral are likely due to the opposite TA concentrations in the SGD endmember: the low average TA value in the groundwater at Cabral may be so strong that it masks the expected high TA on the reef as a result of nighttime dissolution.

Nutrient inputs drive a cascade of direct and indirect effects on biogeochemistry: A Bayesian SEM approach

To illustrate how nutrient inputs drive both direct and indirect effects on biogeochemistry in these reef ecosystems, we used Bayesian Structural Equation Models (SEM) to explore how diel, tidal, and spatial patterns in SGD related to biological responses and geochemical feedbacks (Fig. 3). The SEM captured the expected relationships between SGD and nutrient concentrations as described above. Specifically, there was a strong positive relationship between SiO_3^{2-} (a proxy for SGD) and NO_x (Fig. 5a,g,o; Appendix S2: Fig. S2-S3) at the higher flow site (Varari), while NO_x concentrations were unrelated or slightly negatively related to SiO_3^{2-} at the lower flow site (Cabral) (Fig. 5a,g,o; Appendix S2: Fig. S4-S5). The higher NO_x on the reef was generally related to higher net ecosystem production potential during the day, but this relationship was dependent on temperature and seasonality. Specifically, elevated NO_x from SGD at the high flow

site (Varari) increased NEP potential during the dry season but not the wet season (Fig. 5b,h,r; Appendix S2: Fig. S2-S3). At the low flow site (Cabral), there was a slight positive relationship between NEP potential and NO_x during the wet season, although neither times were statistically significant (Fig. 5b,h,r; Appendix S2: Fig. S4-S5). At night, NO_x generally increased community respiration (Fig. 5b,h,r; Appendix S2: Fig. S2-S3). Temperature, however, was the strongest predictor of NEP potential at both sites in this study (Fig. 5b,h,u; Appendix S2: Fig. S2-S5), with significant positive relationships between temperature and NEP potential during both seasons at Varari and during the dry season at Cabral.

The SGD-enhanced NEP potential drove substantial changes in pH, with significant positive relationships between NEP potential and pH at both sites and during both seasons (Fig. 5c,i,p; Appendix S2: Fig. S2 - S4). Additionally, the biological effect of NEP on pH either completely masked or modified the expected negative relationship between SGD and pH (Fig. 5c,i,p,m; Appendix S2: Fig. S2 - S5). During the dry season, augmented nutrients that generally altered NEP potential led to increased pH during the day and decreased pH at night, regardless of the addition of low pH waters from SGD. During the wet season, there was a significant interaction between NEP potential and SGD on pH at both sites indicating the negative effect of SGD on pH was present, but was altered by changing NEP (Fig. 5c,i,p; Appendix S2: Fig. S3, S5). At night when the reef was net respiring, SGD amplified the already low pH waters and decreased pH even more than expected from biology alone.

The altered pH environment, resulting from both the direct (from freshwater) and indirect effect (from altered NEP potential) of SGD, further impacted ecosystem function by changing net ecosystem calcification potential (Fig. 5d,j,s; Appendix S2: Fig. S2-S4). However, the relationship between pH and NEC potential differed between the high and low alkalinity sites. At

Varari, the high alkalinity site, there was a positive relationship between pH and NEC potential, although the relationship was not statistically significant during the wet season (Fig. 5d,j,s; Appendix S2: Fig. S2-S3). Conversely, at the low alkalinity site (Cabral), there was no relationship between pH and NEC potential (Fig. 5d,j,s; Appendix S2: Fig. S4-S5). Temperature, again, was the dominant driver of NEC potential, with a significant positive relationship between temperature and NEC potential at both sites (Fig. 5d,j,v EM; Appendix S2: Fig. S2-S5).

Finally, our data showed both direct and biologically mediated effects of SGD on the composition of dissolved organic matter fluxes. SGD was associated with the direct enrichment of both humic and proteinaceous fDOM at both sites, although the effect size between SGD and both fDOM components were nearly twice as high at Cabral (Fig. 5e,f,k,i; Appendix S2: Fig. S2-S5). Beyond the direct delivery of fDOM, NEP potential increased humics during the day and decreased humics at night (Fig. 5e,k,q; Appendix S2: Fig. S2 - S5). Contrary to our original hypothesis, NEC potential decreased proteinaceous fDOM in the water column (Fig. 5f,i,t; Appendix S2: Fig. S2-S5).

Discussion

Overall, our modeling approach demonstrates that terrestrial inputs can trigger a “biogeochemical cascade” of direct geochemical and indirect biologically mediated effects—a framework that could be incorporated more into ecosystem ecology. Using submarine groundwater discharge as a test of this framework, our data show that SGD can substantially affect local biogeochemistry of coral reefs via the direct delivery of new solutes and indirectly by interacting with ecosystem metabolism. Further, linking the organic and inorganic carbon pools in biogeochemical cycles has been identified as one of the grand challenges in ocean

biogeochemistry by the Intergovernmental Oceanographic Commission of UNESCO (Aricò et al. 2021), and by demonstrating feedbacks between these two systems our study can serve as an example of how to further integrate dissolved organic matter into coastal carbon cycling.

SGD as a direct driver of coastal biogeochemistry

Our data clearly highlight that SGD directly alters coastal biogeochemistry of coral reefs. While we show that SGD is a significant source of many organic and inorganic solutes, the inorganic nutrient concentrations were exceptionally high in the SGD relative to ambient seawater. Nutrients are expected to be higher in SGD relative to oligotrophic seawater, such as coral reefs, due to higher concentrations of nitrogen in rainwater ($\sim 1 \mu\text{mol L}^{-1} \text{NO}_x$ in Mo‘orea (Haßler et al. 2019)), downward leaching of N and P from terrestrial matter and/or dissolution of seabird guano (Slomp and Van Cappellen 2004, Robertson and Vitousek 2009, McMahon and Santos 2017), and high SiO_3^{2-} and PO_4^{3-} values from mineral weathering (Dillon and Kirchner 1975, Tamborski et al. 2018). Natural SGD is an important source of new nutrients to coral reefs (Paytan et al. 2006, Santos et al. 2021) and can benefit native algae and corals (Lubarsky et al. 2018, Dulai et al. 2023, Richards Donà et al. 2023). However, the highly elevated values at our sites (e.g., up to $\sim 280 \mu\text{mol L}^{-1}$ of NO_x at Varari; Table 1) may be a result of septic drainage, fertilizer from nearby agriculture, and other anthropogenic activities contaminating the groundwater (Haßler et al. 2019).

The SGD was also a significant source of fDOM, although the composition differed between sites. Prior studies have found elevated concentrations of fDOM in groundwater and have suggested that quantity and composition of fDOM is a good geochemical tracer for SGD (Nelson et al. 2015, Webb et al. 2019). The age of the aquifers or the microbial activity in the

SGD could be responsible for differences in the fDOM between the two sites (Nelson et al. 2015, McDonough et al. 2020). Importantly, the addition of new fDOM to the reef from SGD, if labile, could fuel the microbial loop (Azam et al. 1983) and augment ecosystem metabolism (Johnson and Wiegner 2014).

While the directionality of the relationships between SGD and nutrients and SGD and fDOM were generally consistent between the sites, the carbonate dynamics differed, chiefly with respect to total alkalinity. This pattern of contrasting TA values in the SGD of nearby sites has also been shown in other high volcanic islands of similar geologic age, like O‘ahu, Hawai‘i (Nelson et al. 2015, Silbiger et al. 2020) and is likely a result of the fresh groundwater passing through different aquifers, with different proportions of more soluble carbonate vs. less soluble silicate minerals. These different TA values between the two sites could either compound (Cabral) or buffer (Varari) the negative effects of the low pH groundwater on coral calcification (Kleypas and Langdon 2006).

SGD indirectly alters reef biogeochemistry

The clear difference in biogeochemistry across diel cycles indicated strong biological control of seawater chemistry. While there were important distinctions in the diel patterns between the sites, dawn low tides always had the most distinct biogeochemistry, with the highest concentrations of dissolved organic matter and the lowest pH. As expected, these sunrise samples had the lowest pH after a night of respiration by reef organisms compounded by the low tide flux of acidified water from SGD onto the reef. The elevated fDOM may correspond to a rapid increase in coral and algal exudates with the onset of photosynthesis at sunrise, combined with elevated fDOM from the low tide flux of SGD onto the reef. An alternative hypothesis is

that the diel differences in fDOM concentrations could have been affected by UV (Archibald et al. 2019). However, if UV were the dominant driver of fDOM diel variability, we would expect to see compositional similarities between the sunrise and sunset low tides as photobleaching would reduce both fDOM components, but we also see differences in the composition, with more proteinaceous fDOM at dawn.

SGD drives direct and indirect effects on biogeochemistry, but the magnitude of the effect is context dependent

In general, our SEM model revealed that SGD-derived nutrients augmented both net production and microbial respiration, that the indirect effect of SGD on NEP changed both the local pH conditions and humic-like fDOM concentrations in the water column, that the altered pH of the seawater then modified NEC rates, and that the altered NEC rates then led to changes in the concentration of proteinaceous fDOM. Further, the relationships between each of the measured variables in the model were generally consistent between seasons, but there were distinct differences between sites due to unique reef conditions. Differences in flow conditions and the geochemical makeup of the SGD mediated the indirect relationships between SGD and ecosystem metabolism by modifying biological uptake/production rates of dissolved solutes and by changing the pH buffering capacity of seawater which can affect calcification rates. The context dependency of the impact of terrestrial subsidies on aquatic ecosystem functioning has been well-researched in freshwater ecosystems (Marcelli et al. 2011, Richardson and Sato 2015, Subalusky and Post 2019, Allen et al. 2023). For example, climate, habitat structure, and rate of primary productivity of the receiving ecosystem can alter the efficacy of the terrestrial subsidy on myriad ecosystem processes (Subalusky and Post 2019, Allen et al. 2023). Here, we advance

the field by examining these context dependent effects along terrestrial-marine boundaries.

Nutrient inputs drive increased ecosystem productivity and respiration

While nutrients were always higher in the SGD relative to ambient seawater, the expected positive relationship between SiO_3^{2-} and NO_x was not apparent at Cabral. Given the longer water residence time at Cabral, it is likely that there was more time for the reef organisms to utilize the nutrients, decoupling the nutrient concentrations from other SGD solutes, like silicate, and masking the expected tidal effect of nutrients. Importantly, nutrients measured from seawater over the reef are “leftovers” after biological modification and do not necessarily indicate the total amount of nutrient delivery (Wegley Kelly et al. 2022). At Varari, the site with strong and predictable unidirectional flow, there was a clear delivery of new nutrients onto the reef. Further, the strong positive relationship between SiO_3^{2-} and NO_x at the Varari reef also indicates that the SGD delivery outweighed any biological drawdown.

The elevated nutrients from the SGD generally translated to elevated NEP potential, although with a weaker relationship at Cabral. The weaker relationship between NEP potential and NO_x at Cabral may reflect that nutrient drawdown from reef organisms decouples SGD from nutrient concentration more strongly where flow rates are slower. The differences in the total standing stock of producers may lead to distinct equilibriums for nutrient uptake, which would also drive differences between NEP potential and NO_x between the sites. Further, the elevated fDOM from SGD could have interacted with the relationship between NO_x and NEP, as colored and fluorescent DOM can have significant impacts on light attenuation in some ecosystems, and light is an important driver of NEP. But, the ecosystems where DOM affects light absorbance have orders of magnitude higher absolute quantity of DOM, including large river plumes, boreal

lakes, and coastal mangroves (Dittmar et al. 2005, Foden et al. 2008, Thrane et al. 2014). The concentrations and absorbance values of DOM in Mo‘orea are consistent with the surface waters of subtropical gyres with minimal photosynthetically active radiation (PAR) attenuation and, consequently, minimal indirect influence over NEP. Temperature was the strongest driver of NEP, which is unsurprising as temperature is a known driver of NEP on coral reefs (Gattuso et al. 1998). SGD can cool coastal waters (Johnson et al. 2008), therefore SGD could also be contributing to the temperature effect on ecosystem metabolism. However, the cooling effect of SGD was undetectable on the reefs in our study, even though the SGD was indeed cooler than ambient seawater, likely because the cool SGD water was masked by solar radiation on the shallow reef flats.

Indirect effects of SGD on pH mediated by ecosystem metabolic responses

Our data demonstrated that SGD could amplify diel pH dynamics on coral reefs by increasing productivity during the day and respiration at night. During the dry season, the biological control of pH completely masked the addition of low pH SGD water onto the reef. Interestingly, we saw higher pH values during the day at sites that had the highest SGD impact, likely due to augmented NEP from the SGD-driven nutrients. This pattern has also been shown in Hawai‘i (Silbiger et al. 2020) and the Great Barrier Reef (Santos et al. 2011), where reefs experience greater biological than geochemical controls of pH at sites with SGD (Santos et al. 2011). During the wet season, however, there was a significant interaction between SGD delivery and NEP on pH, with the lowest pH values occurring during dawn low tides. The compounding impact of nighttime respiration and acidified water from SGD could decrease net calcification and potentially drive reefs into net dissolution.

Cascading impacts of SGD on community calcification via metabolic controls on inorganic carbon flux

The altered pH as a result of SGD translated to differences in NEC potential at Varari, as is typically expected on coral reefs (Andersson and Gledhill 2013). Varari had higher TA in the SGD water and it has been hypothesized that this elevated TA may help buffer coral reefs from low pH waters in the SGD and possibly even from ocean acidification (Kleypas and Langdon 2006, Cyronak et al. 2013, Middelburg et al. 2020). However, we did not observe this phenomenon at our site, as our data showed evidence of net dissolution during the early morning low tides. The lack of a relationship between pH and NEC potential at Cabral could be due to depleted TA in the SGD source disrupting the expected positive relationship between pH and NEC. Differences in benthic coral composition and total cover may have also affected the relationships between pH and NEC potential between the sites. Cabral has a slightly higher coral cover (~20%) and more faster growing, “weedy” coral species compared to Varari (~13% coral cover). These differences in coral cover and community composition match the average differences in NEC potential between the two sites: NEC potential was higher on average at Cabral than Varari. Notably, prior studies show that SGD alters community composition in both corals and macroalgae (La Valle et al. 2021, Barnas et al. 2025a,b), indicating that the differences in benthic cover between our two sites could be a direct result of differences in SGD. Importantly, a mismatch in the time-scales of the processes that control pH and NEC could also have affected the relationships. A field study at Heron Island highlights that there can be a mismatch between NEC and aragonite saturation state on coral reefs (McMahon et al. 2013) (aragonite saturation state is highly correlated with pH) and this hysteresis may also explain the

weak or null effect of pH on NEC potential in some of our models. Indeed, the strong relationship between temperature and NEC in our models was expected, as temperature is considered one of the most important drivers of NEC on coral reefs (Silverman et al. 2007b, Courtney et al. 2017, Davis et al. 2021).

Whole ecosystem cascades of direct and indirect effects translate groundwater inputs into DOM production

We showed that SGD-driven changes in NEP and NEC alter the fDOM composition and concentration beyond the direct delivery from the groundwater. The strong relationships in our data between NEP potential and humics are likely because producers release exudates during the day and microbial respiration utilizes DOM at night (Nelson et al. 2023). Our results showing the negative relationship between NEC potential and proteinaceous fDOM differed from what we expected based on studies showing corals releasing significant amounts of proteinaceous fDOM (Quinlan et al. 2018, Wegley Kelly et al. 2022). However, prior studies showing these relationships were in closed systems (either aquarium or reef tent) that were dominated by corals. The sites in the current study had < 20% coral cover and it is likely that consumption of fDOM by microbial respiration outpaced the production by corals. Nevertheless, the interactions between the biological and geochemical controls of the organic carbon pool clearly indicate that SGD could fuel the microbial loop both through the direct addition of DOM and indirectly through biological changes as a result of the SGD. Additionally, as climate and land-use continues to change it will alter the concentration and composition of DOM in groundwater (McDonough et al. 2020), which could further impact ecosystem functioning on coral reefs.

Concluding remarks

Overall, we show that SGD has a substantial effect on coastal biogeochemistry and ecosystem functioning. Our research will facilitate future work to better understand the role of allochthonous inputs on driving a cascade of direct and indirect effects on ecosystem functioning. While understanding the effects of SGD on coastal processes is important because of its worldwide distribution (Moosdorf et al. 2015, Luijendijk et al. 2020, Santos et al. 2021), SGD is not the only factor that can spark these “biogeochemical cascades”. For example, loss of dominant species, or phase shifts, can indirectly affect multiple ecosystem processes as mediated by changes in biogeochemistry (Anthony et al. 2011, Fields and Silbiger 2022), and phase shifts are becoming increasingly common on coral reefs as a result of anthropogenic disturbances (Hughes et al. 2010). Changes to rivers and streams from deforestation, pollution, or changing precipitation can also add new solutes and increase sedimentation (McLaughlin et al. 2003) that could create a cascade of direct and indirect effects, leading to downstream impacts on ecosystem functioning and ecosystem services. The approach outlined in our paper allows us to uncover both the direct and indirect drivers of ecosystem processes, reinvigorating classical frameworks in ecology that connect ecosystem ecology to humans and society (Odum 1969).

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Conflict of interest statement

We declare no conflicts of interest.

References

- Adam, T. C., D. E. Burkepile, S. J. Holbrook, R. C. Carpenter, J. Claudet, C. Loiseau, L. Thiault, A. J. Brooks, L. Washburn, and R. J. Schmitt. 2021. Landscape-scale patterns of nutrient enrichment in a coral reef ecosystem: implications for coral to algae phase shifts. *Ecological applications: a publication of the Ecological Society of America* 31:e2227.
- Albright, R., Y. Takeshita, D. A. Koweeck, A. Ninokawa, K. Wolfe, T. Rivlin, Y. Nebuchina, J. Young, and K. Caldeira. 2018. Carbon dioxide addition to coral reef waters suppresses net community calcification. *Nature* 555:516–519.
- Allen, D.C., J. Larson, C.A. Murphy, E.A. Garcia, K.E. Anderson, M.H. Busch, A. Argerich, A.M. Belkis, K.T. Higgins, B.E. Penaluna, V. Saenz, J. Jones, and M. R. Whiles. 2024. Global patterns of allochthony in stream-riparian meta-ecosystems. *Ecology Letters* 27:e14401
- Amato, D. W., C. M. Smith, and T. K. Duarte. 2018. Submarine Groundwater Discharge Differentially Modifies Photosynthesis, Growth, and Morphology for Two Contrasting Species of *Gracilaria* (Rhodophyta). *Hydrology* 5:65.
- Andersson, A. J., and D. Gledhill. 2013. Ocean acidification and coral reefs: effects on

breakdown, dissolution, and net ecosystem calcification. *Annual review of marine science* 5:321–348.

Anthony, K. R. N., J. A. Kleypas, and J.-P. Gattuso. 2011. Coral reefs modify their seawater carbon chemistry - implications for impacts of ocean acidification. *Global change biology* 17:3655–3666.

Archibald, J. P., I. R. Santos, and K. L. Davis. 2019. Diel versus tidal cycles of chromophoric dissolved organic matter (CDOM) and radon in a coral reef in the Great Barrier Reef. *Regional Studies in Marine Science* 29:100659.

Aricò, S., R. Wanninkhof, and C. Sabine. 2021. Integrated Ocean Carbon Research: A Summary of Ocean Carbon Research, and Vision of Coordinated Ocean Carbon Research and Observations for the Next Decade. *in* Intergovernmental Oceanographic Commission, editor. IOC Working Group on Integrated Ocean Carbon Research next Decade. UNESCO.

Atkinson, M. J. 2011. Biogeochemistry of Nutrients. Pages 199–206 *in* Z. Dubinsky and N. Stambler, editors. *Coral Reefs: An Ecosystem in Transition*. Springer Netherlands, Dordrecht.

Azam, F., T. Fenchel, J. G. Field, J. S. Gray, L. A. Meyer-Reil, and F. Thingstad. 1983. The Ecological Role of Water-Column Microbes in the Sea. *Marine Ecology Progress Series* 10:257–263.

Barnas, D.M., M Zeff, and N.J. Silbiger. 2025a. Submarine groundwater discharge alters benthic community composition and functional diversity on coral reefs. *Diversity* 17:161

Barnas, D.M., M Zeff, and N.J. Silbiger. 2025b. Submarine groundwater discharge drives both direct and indirect effects on organismal and community metabolism on coral reefs. *Proceedings of the Royal Society: B* 292:20241554

- Bracken, M. E. S., N. J. Silbiger, G. Bernatchez, and C. J. B. Sorte. 2018. Primary producers may ameliorate impacts of daytime CO₂ addition in a coastal marine ecosystem. *PeerJ* 6:e4739.
- Bürkner, P. C. 2017. An R package for Bayesian multilevel models using Stan. *Journal of statistical software* 80:1–28.
- Bürkner, P.-C. 2018. Advanced Bayesian multilevel modeling with the R package brms. *The R Journal*, 10 (1), 395–411. DOI 10.32614/RJ-2018-017.
- Chisholm, J. R. M., and J.-P. Gattuso. 1991. Validation of the alkalinity anomaly technique for investigating calcification of photosynthesis in coral reef communities. *Limnology and oceanography* 36:1232–1239.
- Cho, H.-M., T.-H. Kim, J.-H. Moon, B.-C. Song, D.-W. Hwang, T. Kim, and D.-H. Im. 2021. Estimating submarine groundwater discharge in Jeju volcanic island (Korea) during a typhoon (Kong-rey) using humic-fluorescent dissolved organic matter-Si mass balance. *Scientific reports* 11:941.
- Correa, R. E., M. B. Cardenas, R. S. Rodolfo, M. R. Lapus, K. L. Davis, A. B. Giles, J. C. Fullon, M.-C. Hajati, N. Moosdorf, C. J. Sanders, and I. R. Santos. 2021. Submarine Groundwater Discharge Releases CO₂ to a Coral Reef. *ACS ES&T Water* 1:1756–1764.
- Cottingham, K. L., J. T. Lennon, and B. L. Brown. 2005. Knowing when to draw the line: designing more informative ecological experiments. *Frontiers in ecology and the environment* 3:145–152.
- Courtney, T. A., and A. J. Andersson. 2019. Evaluating measurements of coral reef net ecosystem calcification rates. *Coral reefs* 38:997–1006.
- Courtney, T. A., M. Lebrato, N. R. Bates, A. Collins, S. J. de Putron, R. Garley, R. Johnson, J.-

- C. Molinero, T. J. Noyes, C. L. Sabine, and A. J. Andersson. 2017. Environmental controls on modern scleractinian coral and reef-scale calcification. *Science advances* 3:e1701356.
- Crook, E. D., A. L. Cohen, M. Rebolledo-Vieyra, L. Hernandez, and A. Paytan. 2013. Reduced calcification and lack of acclimatization by coral colonies growing in areas of persistent natural acidification. *Proceedings of the National Academy of Sciences* 110:11044–11049.
- Cyronak, T., A. J. Andersson, C. Langdon, R. Albright, N. R. Bates, K. Caldeira, R. Carlton, J. E. Corredor, R. B. Dunbar, I. Enochs, J. Erez, B. D. Eyre, J.-P. Gattuso, D. Gledhill, H. Kayanne, D. I. Kline, D. A. Koweeck, C. Lantz, B. Lazar, D. Manzello, A. McMahon, M. Meléndez, H. N. Page, I. R. Santos, K. G. Schulz, E. Shaw, J. Silverman, A. Suzuki, L. Teneva, A. Watanabe, and S. Yamamoto. 2018. Taking the metabolic pulse of the world's coral reefs. *PloS one* 13:e0190872.
- Cyronak, T., I. R. Santos, D. V. Erler, and B. D. Eyre. 2013. Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). *Biogeosciences* 10:2467–2480.
- Cyronak, T., I. R. Santos, D. V. Erler, D. T. Maher, and B. D. Eyre. 2014a. Drivers of pCO₂ variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge. *Global biogeochemical cycles* 28:2013GB004598.
- Cyronak, T., K. G. Schulz, I. R. Santos, and B. D. Eyre. 2014b. Enhanced acidification of global coral reefs driven by regional biogeochemical feedbacks. *Geophysical research letters* 41:5538–5546.
- Davis, K. L., A. P. Colefax, J. P. Tucker, B. P. Kelaher, and I. R. Santos. 2021. Global coral reef ecosystems exhibit declining calcification and increasing primary productivity. *Communications Earth & Environment* 2:1–10.

- DeCarlo, T. M., A. L. Cohen, G. T. F. Wong, F.-K. Shiah, S. J. Lentz, K. A. Davis, K. E. F. Shamberger, and P. Lohmann. 2017. Community production modulates coral reef pH and the sensitivity of ecosystem calcification to ocean acidification. *Journal of Geophysical Research, C: Oceans* 122:745–761.
- Delevaux, J. M. S., R. Whittier, K. A. Stamoulis, L. L. Bremer, S. Jupiter, A. M. Friedlander, M. Poti, G. Guannel, N. Kurashima, K. B. Winter, R. Toonen, E. Conklin, C. Wiggins, A. Knudby, W. Goodell, K. Burnett, S. Yee, H. Htun, K. L. L. Oleson, T. Wiegner, and T. Ticktin. 2018. A linked land-sea modeling framework to inform ridge-to-reef management in high oceanic islands. *PloS one* 13:e0193230.
- Dillon, P. J., and W. B. Kirchner. 1975. The effects of geology and land use on the export of phosphorus from watersheds. *Water research* 9:135–148.
- Dittmar, T., Norbert Hertkorn, G. Kattner, and R. J. Lara. 2005. Mangroves, a major source of dissolved organic carbon to the oceans. *Global Biogeochemical Cycles* 20:2005GB002570.
- Doo, S. S., P. J. Edmunds, and R. C. Carpenter. 2019. Ocean acidification effects on in situ coral reef metabolism. *Scientific reports* 9:12067.
- Dubinsky, Z., and N. Stambler. 1996. Marine pollution and coral reefs. *Global change biology* 2:511–526.
- Dulai, H., C. M. Smith, D. W. Amato, V. Gibson, and L. L. Bremer. 2023. Risk to native marine macroalgae from land-use and climate change-related modifications to groundwater discharge in Hawai‘i. *Limnology and oceanography letters* 8:141–153.
- Enochs, I. C., N. Formel, L. Shea, L. Chomiak, A. Piggot, A. Kirkland, and D. Manzello. 2020. Subsurface Automated Samplers (SAS) for ocean acidification research. *Bulletin of Marine Science* 96:735–752.

- Fields, J. B., and N. J. Silbiger. 2022. Foundation species loss alters multiple ecosystem functions within temperate tidepool communities. *Marine ecology progress series* 683:1–19.
- Foden, J., D. B. Sivy, D. K. Mills, and M. J. Devlin. 2008. Spatial and temporal distribution of chromophoric dissolved organic matter (CDOM) fluorescence and its contribution to light attenuation in UK waterbodies. *Estuarine, coastal and shelf science* 79:707–717.
- Gattuso, J.-P., J.-M. Epitalon, H. Lavigne, and J. Orr. 2019. seacarb: Seawater Carbonate Chemistry. R package version 3.2. 12.
- Gattuso, J.-P., M. Frankignoulle, and R. Wollast. 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annual review of ecology and systematics* 29:405–434.
- Gelman, A., and D. B. Rubin. 1992. Inference from Iterative Simulation Using Multiple Sequences. *Statistical science: a review journal of the Institute of Mathematical Statistics* 7:457–472.
- Goldberg, S. J., C. E. Nelson, D. A. Viviani, C. N. Shulse, and M. J. Church. 2017. Cascading influence of inorganic nitrogen sources on DOM production, composition, lability and microbial community structure in the open ocean. *Environmental microbiology* 19:3450–3464.
- Graham, N. A. J., S. K. Wilson, P. Carr, A. S. Hoey, S. Jennings, and M. A. MacNeil. 2018. Seabirds enhance coral reef productivity and functioning in the absence of invasive rats. *Nature* 559:250–253.
- Haas, A. F., C. E. Nelson, L. Wegley Kelly, C. A. Carlson, F. Rohwer, J. J. Leichter, A. Wyatt, and J. E. Smith. 2011. Effects of coral reef benthic primary producers on dissolved organic carbon and microbial activity. *PloS one* 6:e27973.
- Hagedorn, B., M. Becker, B. Maine, E. Justis, N. Silbiger, D. Barnas, and M. Zeff. 2024, April 3.

Refining Submarine Groundwater Discharge Analysis Through Nonlinear Quantile
Regression of Geochemical Time Series.

- Haßler, K., K. Dähnke, M. Kölling, L. Sichoix, A.-L. Nickl, and N. Moosdorf. 2019. Provenance of nutrients in submarine fresh groundwater discharge on Tahiti and Moorea, French Polynesia. *Applied geochemistry: journal of the International Association of Geochemistry and Cosmochemistry* 100:181–189.
- Hatcher, B. G. 1990. Coral reef primary productivity. A hierarchy of pattern and process. *Trends in ecology & evolution* 5:149–155.
- Hench, J. L., J. J. Leichter, and S. G. Monismith. 2008. Episodic circulation and exchange in a wave-driven coral reef and lagoon system. *Limnology and oceanography* 53:2681–2694.
- Hughes, T. P., N. A. J. Graham, J. B. C. Jackson, P. J. Mumby, and R. S. Steneck. 2010. Rising to the challenge of sustaining coral reef resilience. *Trends in ecology & evolution* 25:633–642.
- Jefferies, R. L. 2000. Allochthonous inputs: integrating population changes and food-web dynamics. *Trends in ecology & evolution* 15:19–22.
- Johnson, A. G., C. R. Glenn, and W. C. Burnett. 2008. Aerial infrared imaging reveals large nutrient-rich groundwater inputs to the ocean. *Geophysical Research Letters* 35:15.
- Johnson, E. E., and T. N. Wiegner. 2014. Surface water metabolism potential in groundwater-fed coastal waters of Hawaii island, USA. *Estuaries and coasts: journal of the Estuarine Research Federation* 37:712–723.
- Kay, M. 2018. tidybayes: Tidy Data and Geoms for Bayesian Models.
- Kealoha, A.K., C.B Wall, and T.A. Leggett. 2024. Coastal water quality improves during the COVID-19 pandemic: Maui, Hawai‘i. *Marine Pollution Bulletin*. 209: 117088

- Kelly, L. W., C. E. Nelson, A. F. Haas, D. S. Naliboff, S. Calhoun, C. A. Carlson, R. A. Edwards, M. D. Fox, M. Hatay, M. D. Johnson, E. L. A. Kelly, Y. W. Lim, S. Macherla, Z. A. Quinlan, G. G. Z. Silva, M. J. A. Vermeij, B. Zgliczynski, S. A. Sandin, J. E. Smith, and F. Rohwer. 2019. Diel population and functional synchrony of microbial communities on coral reefs. *Nature Communications* 10:1691.
- Kleypas, J. A., and C. Langdon. 2006. Coral Reefs and Changing Seawater Carbonate Chemistry. Pages 73–110 *Coral Reefs and Climate Change: Science and Management*. American Geophysical Union.
- Kwiatkowski, L., B. Gaylord, T. Hill, J. Hosfelt, K. J. Kroeker, Y. Nebuchina, A. Ninokawa, A. D. Russell, E. B. Rivest, M. Sesboüé, and K. Caldeira. 2016. Nighttime dissolution in a temperate coastal ocean ecosystem increases under acidification. *Scientific reports* 6:22984.
- La Valle, F. F., M. B. Kantar, and C. E. Nelson. 2021. Coral reef benthic community structure is associated with the spatiotemporal dynamics of submarine groundwater discharge chemistry. *Limnology and oceanography* 66:188–200.
- La Valle, F., F. I. M. Thomas, and C. E. Nelson. 2019. Macroalgal biomass, growth rates, and diversity are influenced by submarine groundwater discharge and local hydrodynamics in tropical reefs. *Marine ecology progress series*:51–67.
- Lesser, M. P. 2021. Eutrophication on Coral Reefs: What Is the Evidence for Phase Shifts, Nutrient Limitation and Coral Bleaching. *Bioscience* 71:1216–1233.
- Lowe, A. T., J. Bos, and J. Ruesink. 2019. Ecosystem metabolism drives pH variability and modulates long-term ocean acidification in the Northeast Pacific coastal ocean. *Scientific reports* 9:963.
- Lubarsky, K. A., N. J. Silbiger, and M. J. Donahue. 2018. Effects of submarine groundwater

discharge on coral accretion and bioerosion on two shallow reef flats. *Limnology and oceanography* 63:1660–1676.

Luijendijk, E., T. Gleeson, and N. Moosdorf. 2020. Fresh groundwater discharge insignificant for the world's oceans but important for coastal ecosystems. *Nature communications* 11:1260.

Marcarelli, A.M., C.V. Baxter, M.M. Mineau, and R.O. Hall, Jr. 2011. Quantity and quality: unifying food web and ecosystem perspective on the role of resource subsidies in freshwaters. *Ecology* 92:1215-1225

McDonough, L. K., I. R. Santos, M. S. Andersen, D. M. O'Carroll, H. Rutledge, K. Meredith, P. Oudone, J. Bridgeman, D. C. Gooddy, J. P. R. Sorensen, D. J. Lapworth, A. M. MacDonald, J. Ward, and A. Baker. 2020. Changes in global groundwater organic carbon driven by climate change and urbanization. *Nature communications* 11:1279.

McLaughlin, C. J., C. A. Smith, R. W. Buddemeier, J. D. Bartley, and B. A. Maxwell. 2003. Rivers, runoff, and reefs. *Global and planetary change* 39:191–199.

McMahon, A., and I. R. Santos. 2017. Nitrogen enrichment and speciation in a coral reef lagoon driven by groundwater inputs of bird guano. *Journal of Geophysical Research, C: Oceans* 122:7218–7236.

McMahon, A., I. R. Santos, T. Cyronak, and B. D. Eyre. 2013. Hysteresis between coral reef calcification and the seawater aragonite saturation state. *Geophysical research letters* 40:4675–4679.

Middelburg, J. J., K. Soetaert, and M. Hagens. 2020. Ocean Alkalinity, Buffering and Biogeochemical Processes. *Reviews of geophysics* 58:e2019RG000681.

Moore, W. S. 2010. The effect of submarine groundwater discharge on the ocean. *Annual review*

of marine science 2:59–88.

Moosdorf, N., M. E. Böttcher, D. Adyasari, E. Erkul, B. S. Gilfedder, J. Greskowiak, A.-K.

Jenner, L. Kotwicki, G. Massmann, M. Müller-Petke, T. Oehler, V. Post, R. Prien, J.

Scholten, B. Siemon, C. M. Ehlert von Ahn, M. Walther, H. Waska, T. Wunderlich, and U.

Mallast. 2021. A State-Of-The-Art Perspective on the Characterization of Subterranean

Estuaries at the Regional Scale. *Frontiers of Earth Science in China* 9.

Moosdorf, N., and T. Oehler. 2017. Societal use of fresh submarine groundwater discharge: An overlooked water resource. *Earth-Science Reviews* 171:338–348.

Moosdorf, N., T. Stieglitz, H. Waska, H. H. Dürr, and J. Hartmann. 2015. Submarine groundwater discharge from tropical islands: a review. *Grundwasser* 20:53–67.

Nalley, E. M., L. J. Tuttle, E. E. Conklin, A. L. Barkman, D. M. Wulstein, M. C. Schmidbauer, and M. J. Donahue. 2023. A systematic review and meta-analysis of the direct effects of nutrients on corals. *The Science of the total environment* 856:159093.

Nelson, C. E., M. J. Donahue, H. Dulaiova, S. J. Goldberg, F. F. La Valle, K. Lubarsky, J.

Miyano, C. Richardson, N. J. Silbiger, and F. I. M. Thomas. 2015. Fluorescent dissolved organic matter as a multivariate biogeochemical tracer of submarine groundwater discharge in coral reef ecosystems. *Marine chemistry* 177:232–243.

Nelson, C. E., L. Wegley Kelly, and A. F. Haas. 2023. Microbial Interactions with Dissolved Organic Matter Are Central to Coral Reef Ecosystem Function and Resilience. *Annual review of marine science* 15:431–460.

Odum, E. P. 1969. The strategy of ecosystem development. *Science* 164:262–270.

Oehler, T., J. Tamborski, S. Rahman, N. Moosdorf, J. Ahrens, C. Mori, R. Neuholz, B.

Schnetger, and M. Beck. 2019. DSi as a Tracer for Submarine Groundwater Discharge.

- Olsen, A., R. M. Key, S. van Heuven, S. K. Lauvset, A. Velo, X. Lin, C. Schirnick, A. Kozyr, T. Tanhua, M. Hoppema, S. Jutterström, R. Steinfeldt, E. Jeansson, M. Ishii, F. F. Pérez, and T. Suzuki. 2016. The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean. *Earth system science data* 8:297–323.
- Page, H. N., A. J. Andersson, P. L. Jokiel, K. S. Rodgers, M. Lebrato, K. Yeakel, C. Davidson, S. D’Angelo, and K. D. Bahr. 2016. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral reefs* 35:1311–1325.
- Pastorok, R. A., and G. R. Bilyard. 1985. Effects of sewage pollution on coral-reef communities. *Marine ecology progress series*. Oldendorf 21:175–189.
- Paytan, A., G. G. Shellenbarger, J. H. Street, M. E. Gonneea, K. Davis, M. B. Young, and W. S. Moore. 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. *Limnology and oceanography* 51:343–348.
- Polis, G. A., W. B. Anderson, and R. D. Holt. 1997. Toward an integration of landscape and food web ecology: The dynamics of spatially subsidized food webs. *Annual review of ecology and systematics* 28:289–316.
- Quinlan, Z. A., K. Remple, M. D. Fox, N. J. Silbiger, T. A. Oliver, H. M. Putnam, L. Wegley Kelly, C. A. Carlson, M. J. Donahue, and C. E. Nelson. 2018. Fluorescent organic exudates of corals and algae in tropical reefs are compositionally distinct and increase with nutrient enrichment. *Limnology and Oceanography Letters* 3:331–340.
- R Core Team. 2021. R: A language and environment for statistical computing. R. <https://www.R-project.org/>.
- Ricart, A. M., M. Ward, T. M. Hill, E. Sanford, K. J. Kroeker, Y. Takeshita, S. Merolla, P.

- Shukla, A. T. Ninokawa, K. Elsmore, and B. Gaylord. 2021. Coast-wide evidence of low pH amelioration by seagrass ecosystems. *Global change biology* 27:2580–2591.
- Richards Donà, A., C. M. Smith, and L. L. Bremer (2023) Divergent responses of native and invasive macroalgae to submarine groundwater discharge. *Scientific Reports* 13:13984
- Richardson, J.S., and T. Sato. 2015. Resource subsidy flows across freshwater-terrestrial boundaries and influence on process linking adjacent ecosystems. *Ecohydrology* 8:406–415
- Richardson, C. M., H. Dulai, B. N. Popp, K. Ruttenberg, and J. K. Fackrell. 2017. Submarine groundwater discharge drives biogeochemistry in two Hawaiian reefs. *Limnology and oceanography* 62:S348–S363.
- Robertson, G. P., and P. M. Vitousek. 2009. Nitrogen in Agriculture: Balancing the Cost of an Essential Resource. *Annual review of environment and resources* 34:97–125.
- Sandin, S. A., P. A. Becker, C. Becker, K. Brown, N. G. Erazo, C. Figuerola, R. N. Fisher, A. M. Friedlander, T. Fukami, N. A. J. Graham, D. S. Gruner, N. D. Holmes, W. A. Holthuijzen, H. P. Jones, M. Rios, A. Samaniego, W. Sechrest, B. X. Semmens, H. E. Thornton, R. V. Thurber, C. N. Wails, C. A. Wolf, and B. J. Zgliczynski. 2022. Harnessing island–ocean connections to maximize marine benefits of island conservation. *Proceedings of the National Academy of Sciences* 119:e2122354119.
- Santos, I. R., X. Chen, A. L. Lecher, A. H. Sawyer, N. Moosdorf, V. Rodellas, J. Tamborski, H.-M. Cho, N. Dimova, R. Sugimoto, S. Bonaglia, H. Li, M.-C. Hajati, and L. Li. 2021. Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. *Nature reviews. Earth & environment* 2:307–323.
- Santos, I. R., B. D. Eyre, and M. Huettel. 2012. The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. *Estuarine, coastal and shelf science* 98:1–

15.

Santos, I. R., R. N. Glud, D. Maher, D. Erler, and B. D. Eyre. 2011. Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef. *Geophysical research letters* 38.

Silbiger, N.J. (2025) njsilbiger/BiogeochemicalCascades_SGD: V1.1. Zenodo. doi: 10.5281/zenodo.15104032.

Silbiger, N. J., M. J. Donahue, and K. Lubarsky. 2020. Submarine groundwater discharge alters coral reef ecosystem metabolism. *Proceedings. Biological sciences / The Royal Society* 287:20202743.

Silbiger, N. J., C. E. Nelson, K. Remple, J. K. Sevilla, Z. A. Quinlan, H. M. Putnam, M. D. Fox, and M. J. Donahue. 2018. Nutrient pollution disrupts key ecosystem functions on coral reefs. *Proceedings. Biological sciences / The Royal Society* 285:10.1098/rspb.2017.2718.

Silbiger, N. J., and C. J. B. Sorte. 2018. Biophysical feedbacks mediate carbonate chemistry in coastal ecosystems across spatiotemporal gradients. *Scientific reports* 8:796.

Silverman, J., B. Lazar, and J. Erez. 2007a. Community metabolism of a coral reef exposed to naturally varying dissolved inorganic nutrient loads. *Biogeochemistry* 84:67–82.

Silverman, J., B. Lazar, and J. Erez. 2007b. Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. *Journal of geophysical research* 112:1.

Slomp, C. P., and P. Van Cappellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* 295:64–86.

Subalusky, A.L., and D. M. Post. 2019. Context dependency of animal resource subsidies.

Biological Reviews. 95: 517-538

Tamborski, J., S. Bejannin, J. Garcia-Orellana, M. Souhaut, C. Charbonnier, P. Anschutz, M.

Pujo-Pay, P. Conan, O. Crispi, C. Monnin, T. Stieglitz, V. Rodellas, A. Andrisoa, C.

Claude, and P. van Beek. 2018. A comparison between water circulation and terrestrially-driven dissolved silica fluxes to the Mediterranean Sea traced using radium isotopes.

Geochimica et cosmochimica acta 238:496–515.

Thrane, J.-E., D. O. Hessen, and T. Andersen. 2014. The Absorption of Light in Lakes: Negative Impact of Dissolved Organic Carbon on Primary Productivity. *Ecosystems* 17:1040–1052.

Wang, G., W. Jing, S. Wang, Y. Xu, Z. Wang, Z. Zhang, Q. Li, and M. Dai. 2014. Coastal acidification induced by tidal-driven submarine groundwater discharge in a coastal coral reef system. *Environmental science & technology* 48:13069–13075.

Webb, J. R., I. R. Santos, D. T. Maher, D. R. Tait, T. Cyronak, M. Sadat-Noori, P. Macklin, and L. C. Jeffrey. 2019. Groundwater as a source of dissolved organic matter to coastal waters: Insights from radon and CDOM observations in 12 shallow coastal systems. *Limnology and oceanography* 64:182–196.

Wegley Kelly, L., C. E. Nelson, D. Petras, I. Koester, Z. A. Quinlan, M. G. I. Arts, L.-F. Nothias, J. Comstock, B. M. White, E. C. Hopmans, F. C. van Duyl, C. A. Carlson, L. I. Aluwihare, P. C. Dorrestein, and A. F. Haas. 2022. Distinguishing the molecular diversity, nutrient content, and energetic potential of exometabolomes produced by macroalgae and reef-building corals. *Proceedings of the National Academy of Sciences of the United States of America* 119:e2110283119.

Wu, P., N. Christidis, and P. Stott. 2013. Anthropogenic impact on Earth's hydrological cycle. *Nature climate change* 3:807–810.

Yeakel, K. L., A. J. Andersson, N. R. Bates, T. J. Noyes, A. Collins, and R. Garley. 2015. Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. *Proceedings of the National Academy of Sciences of the United States of America* 112:14512–14517.

Figures and Tables

Table 1. SGD endmembers from dug beach pits and inland springs as well as the mean $\pm$ SE for all collected reef samples for each measured parameter in the study. Missing data are indicated with a dash.

Parameter	Unit	Cabral Beach Pit	Cabral Spring	Cabral Reef (mean $\pm$ SE)	Varari Beach Pit 1	Varari Beach Pit 2	Varari Reef (mean $\pm$ SE)
Salinity	psu	3.11	0.44	36.6 $\pm$ 0.02	2.89	9.67	36.7 $\pm$ 0.02
Total Alkalinity	$\mu\text{mol kg}^{-1}$	1959.29	1335.7	2319 $\pm$ 3.1	3813.31	5389.84	2363 $\pm$ 1.54
pH _T	$\mu\text{mol L}^{-1}$	7.65	7.24	7.98 $\pm$ 0.01	7.18	7.73	8.01 $\pm$ 0.01
Ammonium (NH ₄ ⁺)	$\mu\text{mol L}^{-1}$	5.41	0.89	0.35 $\pm$ 0.02	1.6	0.79	0.37 $\pm$ 0.3
Nitrate + Nitrite (NO _x)	$\mu\text{mol L}^{-1}$	32.5	19.77	0.58 $\pm$ 0.02	32.63	279.15	0.41 $\pm$ 0.02
Phosphate (PO ₄ ³⁻)	$\mu\text{mol L}^{-1}$	1.85	4.06	0.2 $\pm$ 0.001	2.6	1.57	0.19 $\pm$ 0.001
Silicate (SiO ₃ ²⁻)	$\mu\text{mol L}^{-1}$	650.73	737.49	3.46 $\pm$ 0.17	713.06	229.28	1.97 $\pm$ 0.11
Humic fDOM	Raman Units	0.08	0.08	0.04 $\pm$ 0.001	0.12	-	0.02 $\pm$ 0.001
Proteinaceous fDOM	Raman Units	0.06	0.12	0.14 $\pm$ 0.01	0.06	-	0.1 $\pm$ 0.01

Figures and figure legends

Figure 1: Conceptual diagram of a cascade of direct and indirect effects, or “biogeochemical cascade”, on coral reefs. Added solutes to an ecosystem can create biogeochemical cascades where geochemical parameters indirectly influence each other by altering biological processes, and biological parameters indirectly influence each other by altering geochemical processes. Solid arrows indicate direct relationships, and dashed arrows indicate indirect relationships. The image was made by Nyssa. J. Silbiger, and all icons (coral reef and bottle) are from Canva.

Figure 2: (a) A map of Mo‘orea, French Polynesia with stars indicating the two field sites (Cabral in green and Varari in red). Insets on the left show maps of Cabral (b) and Varari (c) provided by Google maps, with the experimental locations in yellow and the selected SGD seepage point in red. A picture of each seepage point is located in the top right corner of the maps. Inset (d) shows the general sampling design for water collection for the 21 coincident samples. As Mo‘orea is an amphidromic point, high tide and low tide are at the same general time all year round. The yellow vertical lines are at sunrise and the gray vertical lines are at sunset. Inset (e) illustrates the correlation of each measured parameter with freshwater where positive relationships with freshwater are indicated in purple and negative relationships with freshwater are indicated in yellow. The size of the circle is related to the strength of the correlation, with bigger circles having stronger correlations. (f) A windrose plot of current speed (visualized with color) and direction for each site and season. The dry and wet season collections were in August and March, respectively. Photos were taken by Nyssa J. Silbiger and Shireen Rahimi.

Figure 3: Visualization of the structural equation model (SEM). Black arrows indicate direct relationships included in the SEM. Model formulas for each model within the SEM are detailed in the methods. Figure was created by Jamie R. Kerlin using icons (leaf, sun, thermometer) from Adobe illustrator and Adobe photoshop. Corals were hand-drawn in Adobe illustrator.

Figure 4: Principal component analysis of reef biogeochemistry at **(a,b,c)** Varari and **(d,e,f)** Cabral for the **(a,d)** dry season and **(b, e)** wet season. Each point represents a single water sample at a single experimental location, with open circles representing daylight (afternoon and dusk) and closed circles representing dark hours (midnight and dawn). The dark shaded polygons represent high tide and the light shaded polygons represent low tide. Points closer together have more similar biogeochemistry than points further apart. Insets **(c)** and **(f)** show the biplots for each site, where the length of the arrow represents the relative strength of the loading. The results of the MANOVA detailing significant interactions between tide and time of day in all four models are in Appendix S2: Table S1.

Figure 5: Results from the structural equation model. The central plots **(a - l)** show the effect size and 95% BCI for all parameters included in each equation. Labels on the top of each effect size plot are the dependent variables: boxes **a - f** are results from the dry season and boxes **g - l** are from the wet season. Lines that do not overlap zero are considered statistically significant effects. The closed symbols show statistically significant effects, while the open symbols show insignificant effects. The call outs **(m-v)** visualize the best fit lines for each model, with raw data shown in Appendix S2: Figures S2 - S5. Solid lines are from the dry season and dashed lines are

from the wet season. Cabral is shown in green and Varari is shown in red. Notably, NEP and NEC in the figures represent NEP and NEC potential as outlined in the methods.

Table S1: Results of multivariate analysis of variance models for each site by season.

Appendix S2: Significance of methods

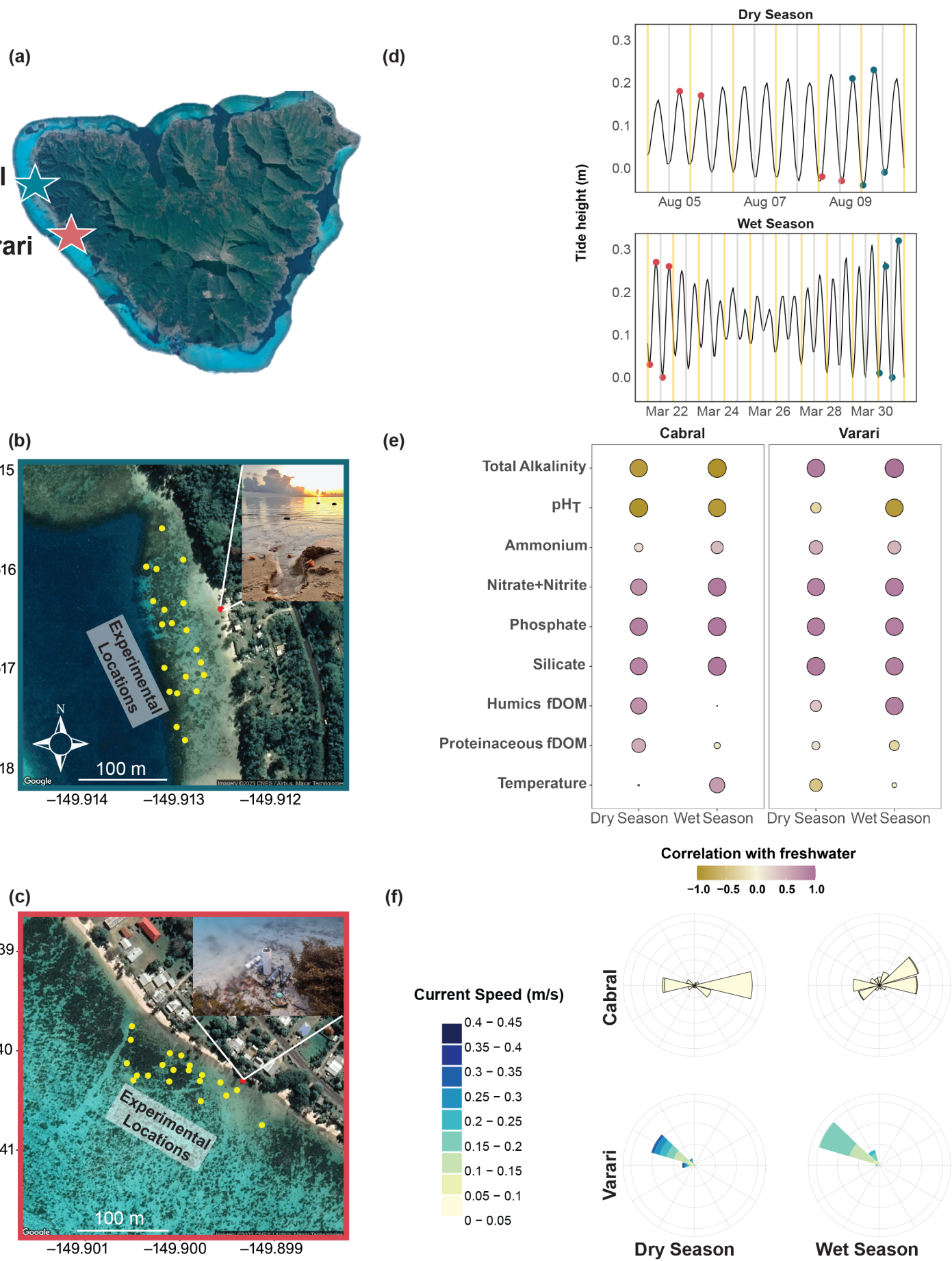
Supporting

Information

Figure S6: Linear regression of ^{222}Rn versus salinity in a subtidal stationary radon and salinity survey at

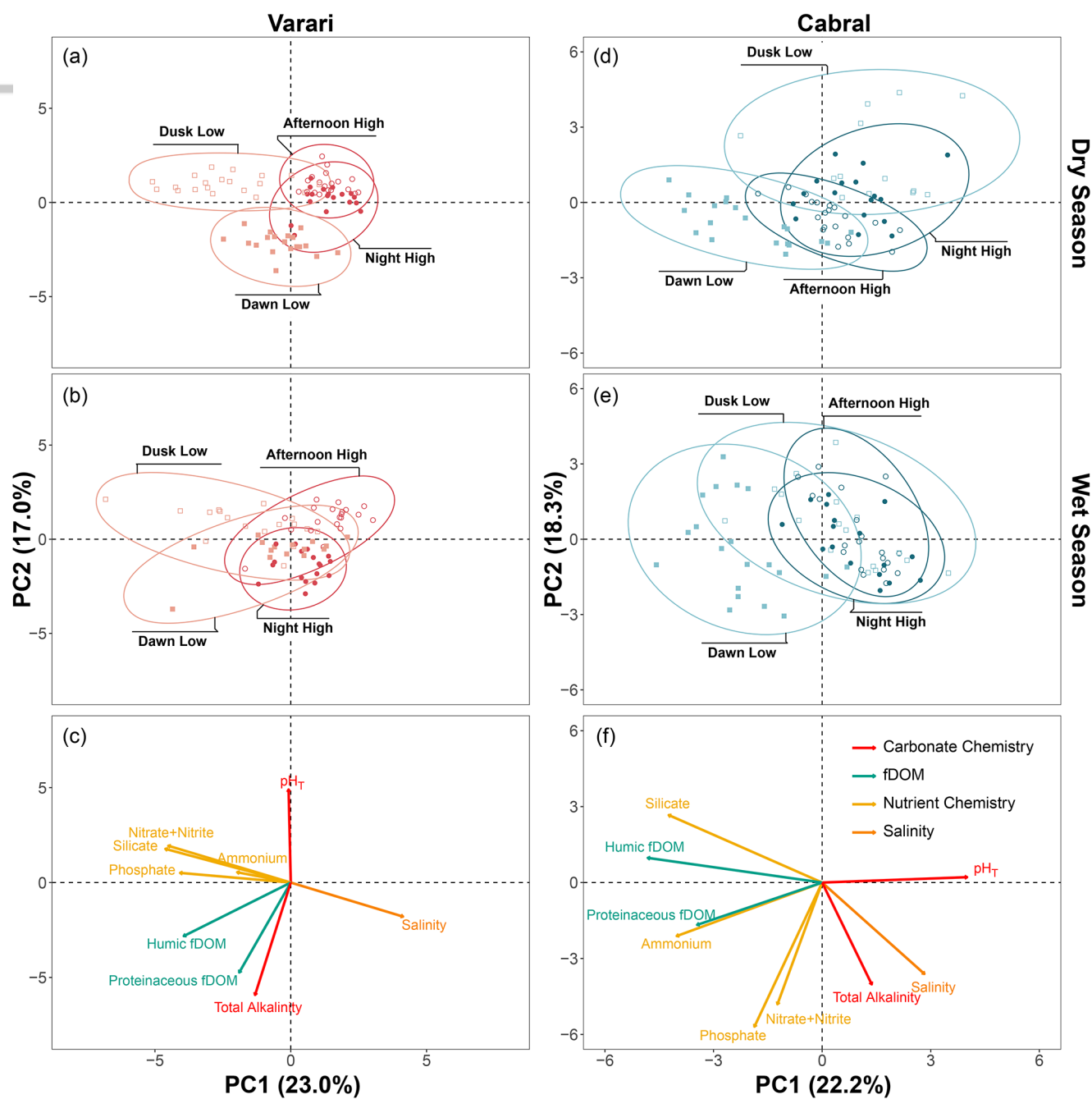
Figure S5: Marginal effects plots for all equations in the SEM model with data collected at Cabral during
Figure S4: Marginal effects plots for all equations in the SEM model with data collected at Varari during

Figure 2



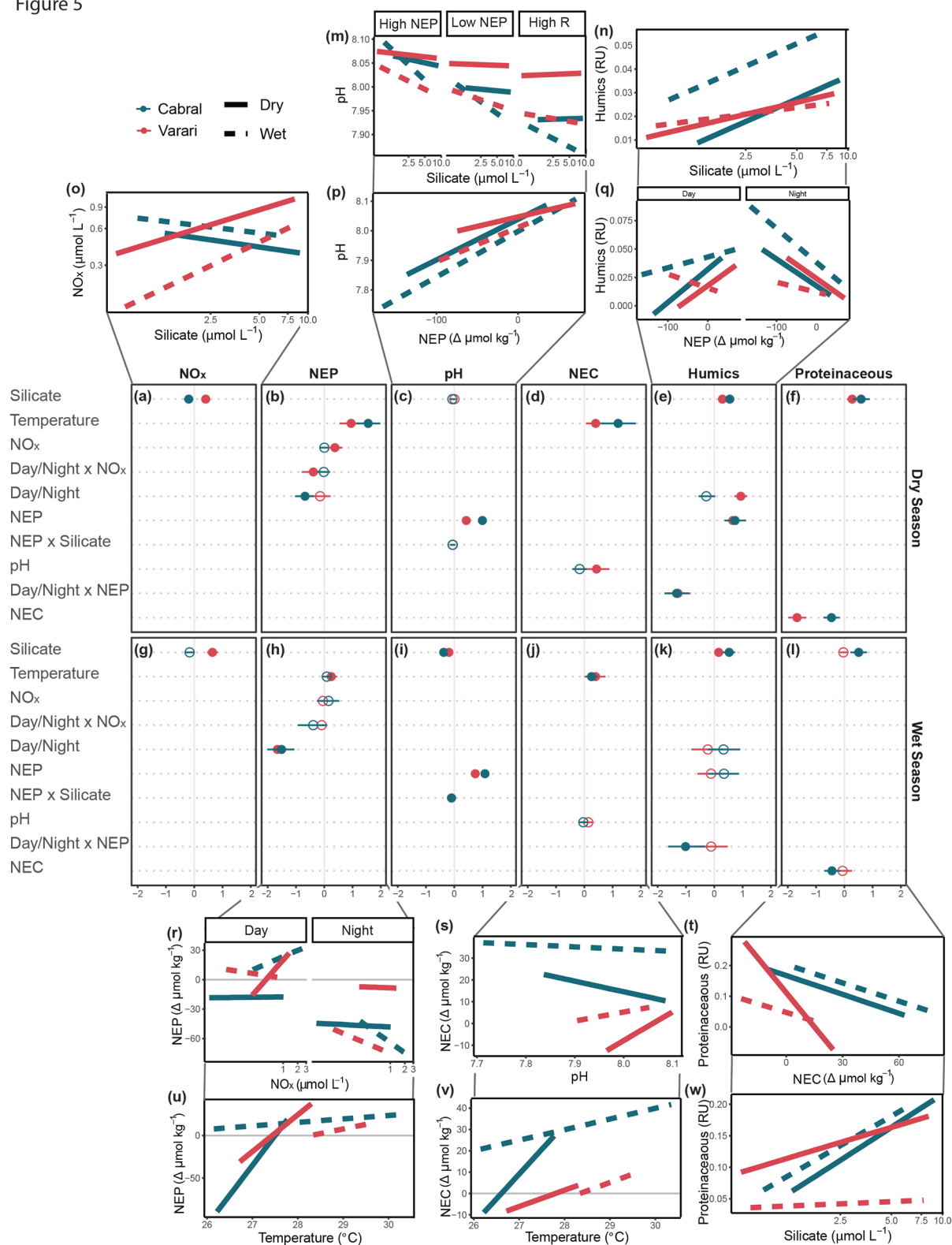
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Figure 4



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Figure 5



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Terrestrial nutrient inputs restructure coral reef dissolved carbon fluxes via direct and indirect effects

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Abstract

The addition of terrestrial inputs to the ocean can have cascading impacts on coastal biogeochemistry by directly altering the water chemistry and indirectly by changing ecosystem metabolism, which also influences water chemistry. Here, we use submarine groundwater discharge (SGD) as a model system to examine the direct geochemical and indirect biologically mediated effects of terrestrial nutrient subsidies on a fringing coral reef. We hypothesize that the addition of new solutes from SGD alters ecosystem metabolic processes including net ecosystem production and calcification thereby changing the patterns of uptake and release of carbon by benthic organisms. SGD is a common land-sea connection that delivers terrestrially sourced nutrients, carbon dioxide, and organic matter to coastal ecosystems. Our research was conducted at two distinct coral reefs in Mo‘orea, French Polynesia, characterized by contrasting flow regimes and SGD biogeochemistry. Using a Bayesian structural equation model, our research elucidates the direct geochemical and indirect biologically mediated effects of SGD on both dissolved organic and inorganic carbon pools. We reveal that SGD-derived nutrients enhance both net ecosystem production and respiration. Furthermore, the study demonstrates that SGD-induced alterations in net ecosystem production significantly influence pH dynamics, ultimately impacting net ecosystem calcification. Notably, the study underscores the context-dependent

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nature of these cascading direct and indirect effects resulting from SGD with flow conditions and composition of the terrestrial inputs playing pivotal roles. Our research provides valuable insights into the interplay between terrestrial inputs and coral reef ecosystems, advancing our understanding of coastal carbon cycling and the broader implications of allochthonous inputs on ecosystem functioning.

Main Text

Introduction

External sources of nutrients and energy, or allochthonous inputs, to marine ecosystems can have cascading impacts on ecosystem functioning (Polis et al. 1997, Jefferies 2000). Shallow, nearshore ecosystems, like many coral reefs, are particularly affected by terrestrial inputs of nutrients and other solutes, which are commonly transported by freshwater connections from land to sea (Deleaux et al. 2018, Sandin et al. 2022). Natural terrestrial inputs can be beneficial to coral reefs: nutrients from seabird guano can elevate critical ecosystem functions, like herbivory, by 3.2 times relative to sites where seabird populations are diminished (Graham et al. 2018). In contrast, anthropogenic terrestrial inputs (e.g., urban and agricultural run-off and sewage effluent) can negatively alter competitive dynamics on reefs leading to macroalgal blooms, coral disease, and shifts in community structure (Pastorok and Bilyard 1985, Dubinsky and Stambler 1996, Adam et al. 2021, Nalley et al. 2023). Despite the known effects of allochthonous inputs on food-web dynamics and community stability in marine ecosystems, the mechanisms of action and interaction of biotic and abiotic processes leading to ecosystem

consequences remain unclear. As climate change, coastal development, and other anthropogenic stressors continue to alter both natural and anthropogenic inputs to the ocean, it is critical to understand both the direct geochemical and indirect biologically mediated effects of these inputs on coastal ecosystem functioning.

Biological and geochemical processes continuously interact, altering the concentration of dissolved solutes that ultimately regulate ecosystem metabolism (i.e., processes that mineralize or fix organic carbon). For example, recent studies have highlighted the importance of primary producers in the dynamics of dissolved CO₂ concentrations and subsequent pH variability in coastal ecosystems (Silbiger and Sorte 2018, Lowe et al. 2019, Ricart et al. 2021, Fields and Silbiger 2022); in turn, pH variability affects other biological processes like net ecosystem calcification (NEC) (Andersson and Gledhill 2013). Added nutrients can magnify this biogeochemical interaction: a coral reef study showed that a chronic low-level increase in inorganic N and P elevated pH variability nearly thirty-fold by enhancing net ecosystem production (NEP) (Silbiger et al. 2018). There has been a growing acknowledgement that organisms not only respond to their geochemical environment but simultaneously modify it. For example, in coral reefs and other highly productive coastal ecosystems, there has been a particular focus on biologically mediated indirect effects of inorganic carbon (NEP → pH → NEC) (Cyronak et al. 2014b, Kwiatkowski et al. 2016, Silbiger et al. 2018, Silbiger and Sorte 2018, Bracken et al. 2018, Fields and Silbiger 2022). However, changes to ecosystem metabolism can alter the composition and quantity of the organic carbon pool as well (Haas et al. 2011, Quinlan et al. 2018, Wegley Kelly et al. 2022). Field and lab studies both show that benthic community composition directly alters the composition of dissolved organic matter (DOM) (Quinlan et al. 2018, Wegley Kelly et al. 2022). Added nutrients can also indirectly alter

the relationship between metabolism and DOM composition, likely through augmented productivity (Goldberg et al. 2017, Quinlan et al. 2018): In one study, corals responded to a 3-fold increase in N with a ~40% and ~150% increase in humic and proteinaceous DOM, respectively (Quinlan et al. 2018).

While these studies highlight that the biological response to nutrient inputs can affect the inorganic or organic carbon pools, few studies explicitly link the organic and inorganic carbon pools within the same study. Here, we advance the field by demonstrating that allochthonous inputs drive both direct and indirect effects on local biogeochemistry and ecosystem metabolism, whereby the addition of new nutrients to a system creates a chain reaction, indirectly affecting both dissolved organic and inorganic carbon pools by changing the patterns of uptake and release of carbon by benthic organisms (Fig. 1). Understanding the mechanism of these cascading biogeochemical processes is especially important in the context of coral reefs, where external nutrient sources alter local biogeochemistry, drive phase shifts, and, ultimately, affect ecosystem metabolism (Lesser 2021).

Submarine groundwater discharge (SGD) is a globally prevalent land-sea connection (Moosdorf et al. 2015, Santos et al. 2021) offering a natural system for investigating the influence of allochthonous inputs on the interactions between geochemical and biological processes. SGD has a complex mixture of components and is a major source of new solutes that can influence coastal salinity, carbonate dynamics, nutrient fluxes, and the composition and concentration of dissolved organic matter (Paytan et al. 2006, Cyronak et al. 2013, Nelson et al. 2015). SGD-driven solutes have been linked to changes in algal species richness (La Valle et al. 2019, 2021), coral and macroalgal growth (Lubarsky et al. 2018, Amato et al. 2018), bioerosion (Crook et al. 2013, Lubarsky et al. 2018), and important ecosystem metabolism rates including

net ecosystem production and calcification (Richardson et al. 2017, Silbiger et al. 2020) on coral reefs. Net ecosystem production (NEP) is the net amount of carbon produced in an ecosystem as a result of photosynthesis and respiration, while net ecosystem calcification (NEC) is the net calcium carbonate produced from calcification and dissolution. These biological processes also alter carbonate and nutrient chemistry, highlighting that SGD may also indirectly alter local biogeochemistry by modifying coral reef biology.

The flux of SGD and its unique biogeochemical composition vary tidally, seasonally, and spatially, and are affected by both natural and anthropogenic processes such as precipitation, coastal development, freshwater harvesting, wastewater handling, and population density (Moore 2010, Santos et al. 2012, Kealoha et al. 2024). Differences in the chemical composition of SGD can have differential impacts on coral reefs. For example, in locations where total alkalinity (TA) in SGD is higher than the receiving waters (Cyronak et al. 2013), SGD may buffer corals from low pH (Kleypas and Langdon 2006, Cyronak et al. 2013, Middelburg et al. 2020). However, in locations where TA in SGD is lower than the receiving waters, the SGD may compound the effects of low pH on calcifiers (Correa et al. 2021). Climate change and increasing coastal population densities will alter the flux and composition of SGD (Wu et al. 2013, Moosdorf and Oehler 2017, Kealoha et al. 2024) and our ability to protect coastal ecosystem services is directly impacted by our understanding of how SGD affects biological and geochemical processes.

We consider the hypothesis that SGD inputs lead to both direct geochemical and indirect biological modifications of coastal biogeochemistry and ecosystem functioning, i.e., that elevated nutrients from groundwater affect ecosystem production, calcification, and the feedbacks between organic and inorganic carbon (Fig. 1). We test our hypothesis by resolving spatial gradients of reef metabolism and biogeochemistry across diel, tidal, and seasonal

timescales at two shallow coral reef sites with differing coastal environmental conditions in Mo‘orea, French Polynesia. Using structural equation models in a Bayesian framework, we characterized the direct geochemical and indirect biologically mediated effects of SGD on the concentration and composition of dissolved organic and inorganic carbon pools.

Materials and Methods

Site descriptions

Our study was conducted at two sites on the western side of Mo‘orea, French Polynesia (Fig. 2a-c), a high volcanic tropical island with microtidal conditions, with maximum tidal amplitude at approximately 0.2 m during spring tides (Hench et al. 2008). The two experimental sites were chosen based on discussions with local residents who had historical knowledge of SGD seepage points around Mo‘orea, followed by radon and salinity surveys (shown in Hagedorn et al. (2024)). Prior analyses show that SGD delivers significant quantities of freshwater to the nearby reef, with a maximum of 9.34 ± 4.03 and 7.20 ± 3.18 cm d⁻¹ at Varari and Cabral, respectively (Hagedorn et al. 2024). This normalized SGD flux was derived from dividing the calculated radon flux (dpm cm⁻² d⁻¹) from the groundwater endmember concentration (dmp cm⁻³). To ensure that SGD was the dominant source of freshwater and land-based solutes to the coastline at the experimental sites, we selected locations that were at least 0.7 km away from any rivers or streams.

The northernmost site, Cabral (Fig. 2b; -17.52° S and -149.91° W), is much less populated (~ 2 buildings per ha), with a single family living along most of the coastline. The reef at Cabral has 20% coral cover, dominated by *Porites* spp. and *Pavona* sp., with 58% macroalgal

cover. The flow direction at Cabral is tidally driven and the flow speed is highly dampened relative to Varari (0.018 ± 0.00023 m/s [mean $\pm$ SE]; Fig. 2f). Cabral has several seepage points spread out along the coastline, with likely additional ones further on the reef (pers comm T. Cabral). There are at least two known inland springs near Cabral where we were able to sample the source water with permission, although we are unable to share the locations of the springs to protect the water rights of the local community.

The southernmost site, Varari (Fig. 2c; -17.54° S and -149.90° W), is a relatively populated area (~ 10 buildings per ha) with several vacation rentals and residents living along the coastline. Varari has approximately 13% coral cover, dominated by *Porites rus*, *Pocillopora acuta*, and *Montipora* spp., and 58% macroalgal cover. The site has a consistent northwesterly unidirectional flow, with the fastest flow speeds when water levels are high (0.15 ± 0.00092 m/s [mean $\pm$ SE]; Fig. 2f). The SGD seepage points are clustered in one area and always subtidal and conspicuous, with freshwater bubbling up through the sand near the shoreline. The location of the inland spring(s) that feeds these SGD seeps are currently unknown and there are no local accessible wells.

Experimental set-up

We characterized the biogeochemistry and benthic community composition at 20 experimental locations plus one seepage point at each site (Figs. 2b-c). We used a regression approach in our experimental design to better understand the mechanistic relationships between our measured variables (Cottingham et al. 2005). For the 20 reef locations, we collected discrete water samples within 20 cm of the benthos across tidal (high/low), diel (day/night), and seasonal (dry/wet season) timepoints for a total of eight measurements per location ($n = 320$ water

samples total) to characterize a gradient of SGD-influence over space and time. The depths of the reef sampling locations were all less than 1.3 m from the surface. At the selected seepage points for each site, we collected additional samples to better characterize the composition of the incoming groundwater (n = 25 at Varari and n = 24 at Cabral). We also collected water samples at the reef crest ~ 1km from each site (n = 13 for Varari and n = 7 for Cabral) to characterize the incoming ambient seawater conditions. To determine groundwater endmembers, we sampled an inland spring and a beach pit at Cabral and two beach pits at Varari (Table 1). Sampling occurred in August 2021 and March 2022 in the dry and wet seasons, respectively.

Water samples for nutrients (nitrate plus nitrite [NO_x], ammonium [NH₄⁺], silicate [SiO₃²⁻], and phosphate [PO₄³⁻]), fluorescent dissolved organic matter (fDOM), total alkalinity (TA), pH, and salinity were collected either by hand with an acid washed HDPE bottle or using a subsurface automated sampler (SAS) (Enochs et al. 2020). Lastly, we used an acoustic doppler current profiler (ADCP) to characterize the current velocity and direction during the sampling period. All sample collection and processing procedures are detailed in Appendix S1.

Ecosystem metabolism calculation

Ecosystem metabolism was calculated similarly to Silbiger et al. (2020) using changes in TA and dissolved inorganic carbon (DIC). DIC was calculated from TA and pH (total) using the seacarb package (Gattuso et al. 2019). The mean ± SE error propagation for the DIC calculation from TA (error of 5 μmol kg⁻¹) and pH (error of 0.01) is 7.62 ± 0.021 μmol kg⁻¹. To account for groundwater mixing, TA and DIC were first normalized to SiO₃²⁻, a common tracer for SGD (Oehler et al. 2019, Silbiger et al. 2020), using the following equation:

$$\square_I = \square_{\square\square\square} + (\square_{\square\square\square} - \square_{\square\square\square}) * \left(\frac{\square_{\square\square\square} - 0.965}{\square_{\square\square\square} - \square_{\square\square\square}} \right),$$

Where C_I is the SiO_3^{2-} - normalized TA or DIC concentration at the open-ocean reference value ($0.965 \mu\text{mol L}^{-1}$), C_{mix} is the measured TA or DIC value (SGD-marine mixture), C_{SGD} is the SGD endmember TA or DIC value, Si_{mix} is the measured SiO_3^{2-} value (SGD-marine mixture) and Si_{SGD} is the average groundwater endmember (Table 1). The reference SiO_3^{2-} value was taken from a nearby offshore location from the Global Ocean Data Project (Olsen et al. 2016).

NEC and NEP potential (sensu Cyronak et al. 2018) were calculated for each sampling location $\times$ time point: NEC potential was calculated as $\Delta\text{TA}/2$ and NEP potential was calculated as $\Delta\text{DIC} - \Delta\text{TA}/2$. ΔTA or ΔDIC is the difference between the SiO_3^{2-} - normalized TA or DIC concentration and the average offshore SiO_3^{2-} - normalized TA or DIC concentration collected at the reef crest. ΔTA was divided by two because 1 mol of CaCO_3 is produced per 2 mol of TA uptake (Chisholm and Gattuso 1991). NEC potential is subtracted from NEP potential to remove any carbon taken up or released from inorganic processes. Differences in TA or DIC are commonly used as a proxy for net calcification/production (TA or DIC depletion) or net dissolution/respiration (TA or DIC repletion) on coral reefs (Yeakel et al. 2015, Cyronak et al. 2018, Silbiger et al. 2020). NEP and NEC potential are good proxies for true NEP and NEC because changes in TA and DIC are predominantly driven by metabolism on coral reefs (Cyronak et al. 2018). We avoided calculating true NEC and NEP rates because both field sites are very shallow ($< 2\text{m}$) with a complex hydrodynamic environment, and small uncertainties in residence time calculations can lead to highly inaccurate ecosystem metabolism rates (Courtney and Andersson 2019).

Statistical analyses

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To characterize the composition of the SGD from the seepage point by each site and season, we calculated the Pearson's correlation coefficient of log-transformed values for each measured variable (TA, pH, temperature, humic fDOM, proteinaceous fDOM, NO_x , NH_4^+ , SiO_3^{2-} , PO_4^{3-}) as a function of salinity. To visualize how SGD affected reef biogeochemistry over diel, tidal, and season time frames, we used a principal components analysis on log-transformed values. The data were centered and standardized by season and individual PCAs were created for each site. Additionally, we used a multivariate analysis of variance (MANOVA) to test the hypothesis that reef biogeochemistry changes across diel and tidal cycles. To characterize the biogeochemical cascade created by SGD we parameterized individual Bayesian structural equation models (SEM) for each site and season. All data used in the SEMs were centered and standardized and NO_x and SiO_3^{2-} were log-transformed in all models to meet assumptions of normality. Bayesian models were run using the R package *brms* (Bürkner 2017, 2018), which is based on the Hamiltonian Monte Carlo algorithm from STAN. To achieve model convergence, we ran three parallel chains of length 2000, with a warm-up of 1000, and a thinning parameter of 1. We used a multivariate normal distribution, and all parameters had relatively uniform priors (student t distribution (d.f. = 3, $\mu = 0$, $\sigma = 10$)). We visually checked all trace plots and calculated Gelman-Rubin statistics (Gelman and Rubin 1992) for all parameters to assess model convergence. Posterior predictive checks using the *pp_check* function in the *tidybayes* R package (Kay 2018) were used to assess model fit. All results are reported as medians with two-tailed 95% Bayesian credible intervals. Effect sizes with credible intervals that do not overlap zero are considered to be statistically significant. All analyses were performed in the R statistical program (R Core Team 2021). All data and code are available on Zenodo (Silbiger 2025).

Model justification

Each SEM was based on a system of six equations, where each equation represents a set of hypotheses based on our current understanding of SGD and coral reef ecology (Fig. 3). Below we justify each equation used in the SEM models.

$$\text{Eq 1: } y_{NO_x} \sim \beta_{SiO_3^{2-}} + \beta_0$$

Based on many studies that show SGD as a significant source of inorganic nutrients to coastal ecosystems (Paytan et al. 2006, Nelson et al. 2015, Silbiger et al. 2020, Santos et al. 2021), we hypothesized that nitrate + nitrite is positively correlated with SGD. Similar to previous studies (Oehler et al. 2019, Silbiger et al. 2020, Cho et al. 2021), we used SiO_3^{2-} as a proxy for SGD in our model. Notably, we did not attempt to calculate a SGD flux from SiO_3^{2-} , but rather used it as a correlate for SGD which is highlighted as an acceptable method in the literature due to its relatively conservative nature in SGD (Oehler et al. 2019, Moosdorf et al. 2021)

$$\text{Eq 2: } y_{NEP\ Potential} \sim \beta_{Temperature} + \beta_{NO_x} + \beta_{DayNight} + \beta_{NO_x*DayNight} + \beta_0$$

Temperature is an important driver of metabolism and can affect NEP on coral reefs (Hatcher 1990). Further, NO_x is also an important driver of NEP as has been shown in both field and lab experiments (Hatcher 1990, Silverman et al. 2007a, Atkinson 2011, McMahon and Santos 2017, Silbiger et al. 2018). As NEP switches from light-enhanced net photosynthesis to dark community respiration from day to night, we hypothesized that the effect of NO_x on NEP potential would be mediated by the diel cycle.

$$\text{Eq 3: } y_{pH} \sim \beta_{NEP\ Potential} + \beta_{SiO_3^{2-}} + \beta_{NEP\ Potential*SiO_3^{2-}} + \beta_0$$

There are often strong positive correlations between NEP and pH on coral reefs based on both field (DeCarlo et al. 2017, Silbiger et al. 2020) and lab (Page et al. 2016, Silbiger et al. 2018) studies. Further, field studies have shown that SGD typically has a lower pH than ambient seawater and could lead to coastal acidification (Cyronak et al. 2014a, Wang et al. 2014).

Therefore, we hypothesized that there would be a positive relationship between NEP potential and pH, and a negative relationship between SiO_3^{2-} and pH. We also hypothesized that the effect of SiO_3^{2-} on pH could be mediated by NEP potential and thus included an interaction term in the model.

$$\text{Eq 4: } y_{\text{NEP Potential}} \sim \beta_{\text{pH}} + \beta_{\text{Temperature}} + \beta_0$$

Similar to NEP, NEC is also strongly correlated with temperature on coral reefs (Silverman et al. 2007b, Courtney et al. 2017). In addition, low pH can reduce calcification rates, as has been demonstrated in many observational studies (Silverman et al. 2007b, Andersson and Gledhill 2013) and manipulative studies (Albright et al. 2018, Doo et al. 2019) on coral reefs. We, therefore, hypothesized that increases both pH and temperature would increase reef calcification.

$$\text{Eq 5: } y_{\text{Humics}} \sim \beta_{\text{SiO}_3^{2-}} + \beta_{\text{NEP Potential}} + \beta_{\text{DayNight}} + \beta_{\text{NEP Potential*DayNight}} + \beta_0$$

Field measurements show strong positive correlations between SGD and humic fDOM (Nelson et al. 2015, Cho et al. 2021). Humic fDOM is composed of microbial derived fulvic acids and terrestrial detrital DOM. Thus, we hypothesized that there would be a positive relationship between SiO_3^{2-} and humic fDOM. Additionally, manipulative lab and *in situ* tent experiments show that production and microbial respiration can either augment or reduce humic fDOM

(Quinlan et al. 2018, Kelly et al. 2019). Therefore, we hypothesized that NEP would enhance humic fDOM, but that the relationship would be mediated by the diel cycle as net production occurs during the day and microbial respiration is a dominant process at night.

Eq 6: $y_{\text{Proteinaceous}} \sim \beta_{\text{SiO}_3^{2-}} + \beta_{\text{NEC Potential}} + \beta_0$

Similar to humic fDOM, SGD also has been shown to elevate proteinaceous fDOM on coral reefs (Nelson et al. 2015). Proteinaceous fDOM are DOM components associated with aromatic amino acids, like tyrosine and tryptophan. Lab studies have demonstrated that corals, but not algae, release significant amounts of proteinaceous fDOM into the water column (Quinlan et al. 2018). Therefore, we hypothesized that there would be a positive relationship between NEC potential and proteinaceous fDOM.

Results

Fundamental differences in SGD chemistry in adjacent aquifers

At both sites, SGD had elevated nutrient concentrations (NO_x , NH_4^{4+} , PO_4^{3-} , SiO_3^{2-}) relative to ambient seawater (Fig. 2e; Table 1). Notably, the NO_x concentrations in the SGD were up to 56- and 680-fold higher than the reef at Cabral and Varari, respectively. The SGD was also a significant source of humic-derived fDOM at both sites, and a significant source of proteinaceous fDOM at Cabral during the dry season, as indicated by the positive correlation between freshwater and fDOM (Fig. 2e). The inorganic carbon pool, however, was particularly different between the sites (Fig. 2e; Table 1). At Cabral, total alkalinity (TA) of the groundwater endmember was highly depleted relative to ambient seawater, with concentrations up to ~980

$\mu\text{mol kg}^{-1}$ lower in the SGD than the average reef TA. The TA of the Varari groundwater was highly elevated, with concentrations up to $\sim 3024 \mu\text{mol kg}^{-1}$ above ambient seawater. Although, both sites had acidified SGD relative to the ambient seawater (Fig. 2e; Table 1).

SGD interacts with biological processes to drive reef biogeochemistry

While the composition of the groundwater itself was generally stable at each site during the study, the degree to which the low tide (when SGD is pumped onto the reef) chemical composition of the reef reflected the SGD composition was strikingly different between the two sites (Appendix S2: Fig. S1; Appendix S2: Table S1). At Varari, a site with faster, unidirectional (alongshore) water flow (Fig. 2f), there was a clear separation between tidal cycles, indicating a strong direct influence of SGD on reef biogeochemistry, with low tide having higher nutrients, humic fDOM, and SiO_3^{2-} as well as lower salinity relative to high tide (Fig. 4a,b). At Cabral, a site with slower, tidally-dependent, cross-shore flow, there were also differences in the biogeochemistry across tidal cycles, but with less distinction between tides (Fig. 4d,e). While Cabral exhibited lower salinity, higher SiO_3^{2-} , and lower TA during low tides, as expected from the composition of SGD at Cabral (Table 1), the NO_x and PO_4^{3-} concentrations did not vary tidally across the reef, even though both solutes were highly elevated in the SGD.

There were clear diel patterns in biogeochemistry, with important differences between the two sites (Fig. 4; Appendix S2: Table S1). At Varari, where SGD delivers relatively high TA, daylight hours (afternoon and dusk) had a higher pH, lower TA, and lower proteinaceous fDOM relative to dark hours (midnight and dawn). The diel pH patterns align with expected decreasing water column CO_2 from daytime net photosynthesis and increasing CO_2 from nighttime respiration. The diel patterns in TA also indicate that the biological control of TA from

calcification either outweighed or magnified the geochemical controls of high alkalinity SGD flowing onto the reef during low tide. Notably, the high TA values during the dawn low tide is likely the result of both biological and geochemical processes due to high TA from nighttime dissolution as well as the high TA from the SGD (Appendix S2: Fig. S1). This contrasts with results from Cabral, where pH and TA were orthogonal to each other on the reef (Fig. 4): pH was correlated with diel patterns (i.e., biologically controlled) while TA was correlated with tide (i.e., SGD-controlled). The opposite TA patterns at Cabral are likely due to the opposite TA concentrations in the SGD endmember: the low average TA value in the groundwater at Cabral may be so strong that it masks the expected high TA on the reef as a result of nighttime dissolution.

Nutrient inputs drive a cascade of direct and indirect effects on biogeochemistry: A Bayesian SEM approach

To illustrate how nutrient inputs drive both direct and indirect effects on biogeochemistry in these reef ecosystems, we used Bayesian Structural Equation Models (SEM) to explore how diel, tidal, and spatial patterns in SGD related to biological responses and geochemical feedbacks (Fig. 3). The SEM captured the expected relationships between SGD and nutrient concentrations as described above. Specifically, there was a strong positive relationship between SiO_3^{2-} (a proxy for SGD) and NO_x (Fig. 5a,g,o; Appendix S2: Fig. S2-S3) at the higher flow site (Varari), while NO_x concentrations were unrelated or slightly negatively related to SiO_3^{2-} at the lower flow site (Cabral) (Fig. 5a,g,o; Appendix S2: Fig. S4-S5). The higher NO_x on the reef was generally related to higher net ecosystem production potential during the day, but this relationship was dependent on temperature and seasonality. Specifically, elevated NO_x from SGD at the high flow

site (Varari) increased NEP potential during the dry season but not the wet season (Fig. 5b,h,r; Appendix S2: Fig. S2-S3). At the low flow site (Cabral), there was a slight positive relationship between NEP potential and NO_x during the wet season, although neither times were statistically significant (Fig. 5b,h,r; Appendix S2: Fig. S4-S5). At night, NO_x generally increased community respiration (Fig. 5b,h,r; Appendix S2: Fig. S2-S3). Temperature, however, was the strongest predictor of NEP potential at both sites in this study (Fig. 5b,h,u; Appendix S2: Fig. S2-S5), with significant positive relationships between temperature and NEP potential during both seasons at Varari and during the dry season at Cabral.

The SGD-enhanced NEP potential drove substantial changes in pH, with significant positive relationships between NEP potential and pH at both sites and during both seasons (Fig. 5c,i,p; Appendix S2: Fig. S2 - S4). Additionally, the biological effect of NEP on pH either completely masked or modified the expected negative relationship between SGD and pH (Fig. 5c,i,p,m; Appendix S2: Fig. S2 - S5). During the dry season, augmented nutrients that generally altered NEP potential led to increased pH during the day and decreased pH at night, regardless of the addition of low pH waters from SGD. During the wet season, there was a significant interaction between NEP potential and SGD on pH at both sites indicating the negative effect of SGD on pH was present, but was altered by changing NEP (Fig. 5c,i,p; Appendix S2: Fig. S3, S5). At night when the reef was net respiring, SGD amplified the already low pH waters and decreased pH even more than expected from biology alone.

The altered pH environment, resulting from both the direct (from freshwater) and indirect effect (from altered NEP potential) of SGD, further impacted ecosystem function by changing net ecosystem calcification potential (Fig. 5d,j,s; Appendix S2: Fig. S2-S4). However, the relationship between pH and NEC potential differed between the high and low alkalinity sites. At

Varari, the high alkalinity site, there was a positive relationship between pH and NEC potential, although the relationship was not statistically significant during the wet season (Fig. 5d,j,s; Appendix S2: Fig. S2-S3). Conversely, at the low alkalinity site (Cabral), there was no relationship between pH and NEC potential (Fig. 5d,j,s; Appendix S2: Fig. S4-S5). Temperature, again, was the dominant driver of NEC potential, with a significant positive relationship between temperature and NEC potential at both sites (Fig. 5d,j,v EM; Appendix S2: Fig. S2-S5).

Finally, our data showed both direct and biologically mediated effects of SGD on the composition of dissolved organic matter fluxes. SGD was associated with the direct enrichment of both humic and proteinaceous fDOM at both sites, although the effect size between SGD and both fDOM components were nearly twice as high at Cabral (Fig. 5e,f,k,i; Appendix S2: Fig. S2-S5). Beyond the direct delivery of fDOM, NEP potential increased humics during the day and decreased humics at night (Fig. 5e,k,q; Appendix S2: Fig. S2 - S5). Contrary to our original hypothesis, NEC potential decreased proteinaceous fDOM in the water column (Fig. 5f,i,t; Appendix S2: Fig. S2-S5).

Discussion

Overall, our modeling approach demonstrates that terrestrial inputs can trigger a “biogeochemical cascade” of direct geochemical and indirect biologically mediated effects—a framework that could be incorporated more into ecosystem ecology. Using submarine groundwater discharge as a test of this framework, our data show that SGD can substantially affect local biogeochemistry of coral reefs via the direct delivery of new solutes and indirectly by interacting with ecosystem metabolism. Further, linking the organic and inorganic carbon pools in biogeochemical cycles has been identified as one of the grand challenges in ocean

biogeochemistry by the Intergovernmental Oceanographic Commission of UNESCO (Aricò et al. 2021), and by demonstrating feedbacks between these two systems our study can serve as an example of how to further integrate dissolved organic matter into coastal carbon cycling.

SGD as a direct driver of coastal biogeochemistry

Our data clearly highlight that SGD directly alters coastal biogeochemistry of coral reefs. While we show that SGD is a significant source of many organic and inorganic solutes, the inorganic nutrient concentrations were exceptionally high in the SGD relative to ambient seawater. Nutrients are expected to be higher in SGD relative to oligotrophic seawater, such as coral reefs, due to higher concentrations of nitrogen in rainwater ($\sim 1 \mu\text{mol L}^{-1} \text{NO}_x$ in Mo‘orea (Haßler et al. 2019)), downward leaching of N and P from terrestrial matter and/or dissolution of seabird guano (Slomp and Van Cappellen 2004, Robertson and Vitousek 2009, McMahon and Santos 2017), and high SiO_3^{2-} and PO_4^{3-} values from mineral weathering (Dillon and Kirchner 1975, Tamborski et al. 2018). Natural SGD is an important source of new nutrients to coral reefs (Paytan et al. 2006, Santos et al. 2021) and can benefit native algae and corals (Lubarsky et al. 2018, Dulai et al. 2023, Richards Donà et al. 2023). However, the highly elevated values at our sites (e.g., up to $\sim 280 \mu\text{mol L}^{-1}$ of NO_x at Varari; Table 1) may be a result of septic drainage, fertilizer from nearby agriculture, and other anthropogenic activities contaminating the groundwater (Haßler et al. 2019).

The SGD was also a significant source of fDOM, although the composition differed between sites. Prior studies have found elevated concentrations of fDOM in groundwater and have suggested that quantity and composition of fDOM is a good geochemical tracer for SGD (Nelson et al. 2015, Webb et al. 2019). The age of the aquifers or the microbial activity in the

SGD could be responsible for differences in the fDOM between the two sites (Nelson et al. 2015, McDonough et al. 2020). Importantly, the addition of new fDOM to the reef from SGD, if labile, could fuel the microbial loop (Azam et al. 1983) and augment ecosystem metabolism (Johnson and Wiegner 2014).

While the directionality of the relationships between SGD and nutrients and SGD and fDOM were generally consistent between the sites, the carbonate dynamics differed, chiefly with respect to total alkalinity. This pattern of contrasting TA values in the SGD of nearby sites has also been shown in other high volcanic islands of similar geologic age, like O‘ahu, Hawai‘i (Nelson et al. 2015, Silbiger et al. 2020) and is likely a result of the fresh groundwater passing through different aquifers, with different proportions of more soluble carbonate vs. less soluble silicate minerals. These different TA values between the two sites could either compound (Cabral) or buffer (Varari) the negative effects of the low pH groundwater on coral calcification (Kleypas and Langdon 2006).

SGD indirectly alters reef biogeochemistry

The clear difference in biogeochemistry across diel cycles indicated strong biological control of seawater chemistry. While there were important distinctions in the diel patterns between the sites, dawn low tides always had the most distinct biogeochemistry, with the highest concentrations of dissolved organic matter and the lowest pH. As expected, these sunrise samples had the lowest pH after a night of respiration by reef organisms compounded by the low tide flux of acidified water from SGD onto the reef. The elevated fDOM may correspond to a rapid increase in coral and algal exudates with the onset of photosynthesis at sunrise, combined with elevated fDOM from the low tide flux of SGD onto the reef. An alternative hypothesis is

that the diel differences in fDOM concentrations could have been affected by UV (Archibald et al. 2019). However, if UV were the dominant driver of fDOM diel variability, we would expect to see compositional similarities between the sunrise and sunset low tides as photobleaching would reduce both fDOM components, but we also see differences in the composition, with more proteinaceous fDOM at dawn.

SGD drives direct and indirect effects on biogeochemistry, but the magnitude of the effect is context dependent

In general, our SEM model revealed that SGD-derived nutrients augmented both net production and microbial respiration, that the indirect effect of SGD on NEP changed both the local pH conditions and humic-like fDOM concentrations in the water column, that the altered pH of the seawater then modified NEC rates, and that the altered NEC rates then led to changes in the concentration of proteinaceous fDOM. Further, the relationships between each of the measured variables in the model were generally consistent between seasons, but there were distinct differences between sites due to unique reef conditions. Differences in flow conditions and the geochemical makeup of the SGD mediated the indirect relationships between SGD and ecosystem metabolism by modifying biological uptake/production rates of dissolved solutes and by changing the pH buffering capacity of seawater which can affect calcification rates. The context dependency of the impact of terrestrial subsidies on aquatic ecosystem functioning has been well-researched in freshwater ecosystems (Marcelli et al. 2011, Richardson and Sato 2015, Subalusky and Post 2019, Allen et al. 2023). For example, climate, habitat structure, and rate of primary productivity of the receiving ecosystem can alter the efficacy of the terrestrial subsidy on myriad ecosystem processes (Subalusky and Post 2019, Allen et al. 2023). Here, we advance

the field by examining these context dependent effects along terrestrial-marine boundaries.

Nutrient inputs drive increased ecosystem productivity and respiration

While nutrients were always higher in the SGD relative to ambient seawater, the expected positive relationship between SiO_3^{2-} and NO_x was not apparent at Cabral. Given the longer water residence time at Cabral, it is likely that there was more time for the reef organisms to utilize the nutrients, decoupling the nutrient concentrations from other SGD solutes, like silicate, and masking the expected tidal effect of nutrients. Importantly, nutrients measured from seawater over the reef are “leftovers” after biological modification and do not necessarily indicate the total amount of nutrient delivery (Wegley Kelly et al. 2022). At Varari, the site with strong and predictable unidirectional flow, there was a clear delivery of new nutrients onto the reef. Further, the strong positive relationship between SiO_3^{2-} and NO_x at the Varari reef also indicates that the SGD delivery outweighed any biological drawdown.

The elevated nutrients from the SGD generally translated to elevated NEP potential, although with a weaker relationship at Cabral. The weaker relationship between NEP potential and NO_x at Cabral may reflect that nutrient drawdown from reef organisms decouples SGD from nutrient concentration more strongly where flow rates are slower. The differences in the total standing stock of producers may lead to distinct equilibriums for nutrient uptake, which would also drive differences between NEP potential and NO_x between the sites. Further, the elevated fDOM from SGD could have interacted with the relationship between NO_x and NEP, as colored and fluorescent DOM can have significant impacts on light attenuation in some ecosystems, and light is an important driver of NEP. But, the ecosystems where DOM affects light absorbance have orders of magnitude higher absolute quantity of DOM, including large river plumes, boreal

lakes, and coastal mangroves (Dittmar et al. 2005, Foden et al. 2008, Thrane et al. 2014). The concentrations and absorbance values of DOM in Mo‘orea are consistent with the surface waters of subtropical gyres with minimal photosynthetically active radiation (PAR) attenuation and, consequently, minimal indirect influence over NEP. Temperature was the strongest driver of NEP, which is unsurprising as temperature is a known driver of NEP on coral reefs (Gattuso et al. 1998). SGD can cool coastal waters (Johnson et al. 2008), therefore SGD could also be contributing to the temperature effect on ecosystem metabolism. However, the cooling effect of SGD was undetectable on the reefs in our study, even though the SGD was indeed cooler than ambient seawater, likely because the cool SGD water was masked by solar radiation on the shallow reef flats.

Indirect effects of SGD on pH mediated by ecosystem metabolic responses

Our data demonstrated that SGD could amplify diel pH dynamics on coral reefs by increasing productivity during the day and respiration at night. During the dry season, the biological control of pH completely masked the addition of low pH SGD water onto the reef. Interestingly, we saw higher pH values during the day at sites that had the highest SGD impact, likely due to augmented NEP from the SGD-driven nutrients. This pattern has also been shown in Hawai‘i (Silbiger et al. 2020) and the Great Barrier Reef (Santos et al. 2011), where reefs experience greater biological than geochemical controls of pH at sites with SGD (Santos et al. 2011). During the wet season, however, there was a significant interaction between SGD delivery and NEP on pH, with the lowest pH values occurring during dawn low tides. The compounding impact of nighttime respiration and acidified water from SGD could decrease net calcification and potentially drive reefs into net dissolution.

Cascading impacts of SGD on community calcification via metabolic controls on inorganic carbon flux

The altered pH as a result of SGD translated to differences in NEC potential at Varari, as is typically expected on coral reefs (Andersson and Gledhill 2013). Varari had higher TA in the SGD water and it has been hypothesized that this elevated TA may help buffer coral reefs from low pH waters in the SGD and possibly even from ocean acidification (Kleypas and Langdon 2006, Cyronak et al. 2013, Middelburg et al. 2020). However, we did not observe this phenomenon at our site, as our data showed evidence of net dissolution during the early morning low tides. The lack of a relationship between pH and NEC potential at Cabral could be due to depleted TA in the SGD source disrupting the expected positive relationship between pH and NEC. Differences in benthic coral composition and total cover may have also affected the relationships between pH and NEC potential between the sites. Cabral has a slightly higher coral cover (~20%) and more faster growing, “weedy” coral species compared to Varari (~13% coral cover). These differences in coral cover and community composition match the average differences in NEC potential between the two sites: NEC potential was higher on average at Cabral than Varari. Notably, prior studies show that SGD alters community composition in both corals and macroalgae (La Valle et al. 2021, Barnas et al. 2025a,b), indicating that the differences in benthic cover between our two sites could be a direct result of differences in SGD. Importantly, a mismatch in the time-scales of the processes that control pH and NEC could also have affected the relationships. A field study at Heron Island highlights that there can be a mismatch between NEC and aragonite saturation state on coral reefs (McMahon et al. 2013) (aragonite saturation state is highly correlated with pH) and this hysteresis may also explain the

weak or null effect of pH on NEC potential in some of our models. Indeed, the strong relationship between temperature and NEC in our models was expected, as temperature is considered one of the most important drivers of NEC on coral reefs (Silverman et al. 2007b, Courtney et al. 2017, Davis et al. 2021).

Whole ecosystem cascades of direct and indirect effects translate groundwater inputs into DOM production

We showed that SGD-driven changes in NEP and NEC alter the fDOM composition and concentration beyond the direct delivery from the groundwater. The strong relationships in our data between NEP potential and humics are likely because producers release exudates during the day and microbial respiration utilizes DOM at night (Nelson et al. 2023). Our results showing the negative relationship between NEC potential and proteinaceous fDOM differed from what we expected based on studies showing corals releasing significant amounts of proteinaceous fDOM (Quinlan et al. 2018, Wegley Kelly et al. 2022). However, prior studies showing these relationships were in closed systems (either aquarium or reef tent) that were dominated by corals. The sites in the current study had < 20% coral cover and it is likely that consumption of fDOM by microbial respiration outpaced the production by corals. Nevertheless, the interactions between the biological and geochemical controls of the organic carbon pool clearly indicate that SGD could fuel the microbial loop both through the direct addition of DOM and indirectly through biological changes as a result of the SGD. Additionally, as climate and land-use continues to change it will alter the concentration and composition of DOM in groundwater (McDonough et al. 2020), which could further impact ecosystem functioning on coral reefs.

Concluding remarks

Overall, we show that SGD has a substantial effect on coastal biogeochemistry and ecosystem functioning. Our research will facilitate future work to better understand the role of allochthonous inputs on driving a cascade of direct and indirect effects on ecosystem functioning. While understanding the effects of SGD on coastal processes is important because of its worldwide distribution (Moosdorf et al. 2015, Luijendijk et al. 2020, Santos et al. 2021), SGD is not the only factor that can spark these “biogeochemical cascades”. For example, loss of dominant species, or phase shifts, can indirectly affect multiple ecosystem processes as mediated by changes in biogeochemistry (Anthony et al. 2011, Fields and Silbiger 2022), and phase shifts are becoming increasingly common on coral reefs as a result of anthropogenic disturbances (Hughes et al. 2010). Changes to rivers and streams from deforestation, pollution, or changing precipitation can also add new solutes and increase sedimentation (McLaughlin et al. 2003) that could create a cascade of direct and indirect effects, leading to downstream impacts on ecosystem functioning and ecosystem services. The approach outlined in our paper allows us to uncover both the direct and indirect drivers of ecosystem processes, reinvigorating classical frameworks in ecology that connect ecosystem ecology to humans and society (Odum 1969).

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Conflict of interest statement

We declare no conflicts of interest.

References

- Adam, T. C., D. E. Burkepile, S. J. Holbrook, R. C. Carpenter, J. Claudet, C. Loiseau, L. Thiault, A. J. Brooks, L. Washburn, and R. J. Schmitt. 2021. Landscape-scale patterns of nutrient enrichment in a coral reef ecosystem: implications for coral to algae phase shifts. *Ecological applications: a publication of the Ecological Society of America* 31:e2227.
- Albright, R., Y. Takeshita, D. A. Koweeck, A. Ninokawa, K. Wolfe, T. Rivlin, Y. Nebuchina, J. Young, and K. Caldeira. 2018. Carbon dioxide addition to coral reef waters suppresses net community calcification. *Nature* 555:516–519.
- Allen, D.C., J. Larson, C.A. Murphy, E.A. Garcia, K.E. Anderson, M.H. Busch, A. Argerich, A.M. Belkis, K.T. Higgins, B.E. Penaluna, V. Saenz, J. Jones, and M. R. Whiles. 2024. Global patterns of allochthony in stream-riparian meta-ecosystems. *Ecology Letters* 27:e14401
- Amato, D. W., C. M. Smith, and T. K. Duarte. 2018. Submarine Groundwater Discharge Differentially Modifies Photosynthesis, Growth, and Morphology for Two Contrasting Species of *Gracilaria* (Rhodophyta). *Hydrology* 5:65.
- Andersson, A. J., and D. Gledhill. 2013. Ocean acidification and coral reefs: effects on

breakdown, dissolution, and net ecosystem calcification. *Annual review of marine science* 5:321–348.

Anthony, K. R. N., J. A. Kleypas, and J.-P. Gattuso. 2011. Coral reefs modify their seawater carbon chemistry - implications for impacts of ocean acidification. *Global change biology* 17:3655–3666.

Archibald, J. P., I. R. Santos, and K. L. Davis. 2019. Diel versus tidal cycles of chromophoric dissolved organic matter (CDOM) and radon in a coral reef in the Great Barrier Reef. *Regional Studies in Marine Science* 29:100659.

Aricò, S., R. Wanninkhof, and C. Sabine. 2021. Integrated Ocean Carbon Research: A Summary of Ocean Carbon Research, and Vision of Coordinated Ocean Carbon Research and Observations for the Next Decade. *in* Intergovernmental Oceanographic Commission, editor. IOC Working Group on Integrated Ocean Carbon Research next Decade. UNESCO.

Atkinson, M. J. 2011. Biogeochemistry of Nutrients. Pages 199–206 *in* Z. Dubinsky and N. Stambler, editors. *Coral Reefs: An Ecosystem in Transition*. Springer Netherlands, Dordrecht.

Azam, F., T. Fenchel, J. G. Field, J. S. Gray, L. A. Meyer-Reil, and F. Thingstad. 1983. The Ecological Role of Water-Column Microbes in the Sea. *Marine Ecology Progress Series* 10:257–263.

Barnas, D.M., M Zeff, and N.J. Silbiger. 2025a. Submarine groundwater discharge alters benthic community composition and functional diversity on coral reefs. *Diversity* 17:161

Barnas, D.M., M Zeff, and N.J. Silbiger. 2025b. Submarine groundwater discharge drives both direct and indirect effects on organismal and community metabolism on coral reefs. *Proceedings of the Royal Society: B* 292:20241554

- Bracken, M. E. S., N. J. Silbiger, G. Bernatchez, and C. J. B. Sorte. 2018. Primary producers may ameliorate impacts of daytime CO₂ addition in a coastal marine ecosystem. *PeerJ* 6:e4739.
- Bürkner, P. C. 2017. An R package for Bayesian multilevel models using Stan. *Journal of statistical software* 80:1–28.
- Bürkner, P.-C. 2018. Advanced Bayesian multilevel modeling with the R package brms. *The R Journal*, 10 (1), 395–411. DOI 10.32614/RJ-2018-017.
- Chisholm, J. R. M., and J.-P. Gattuso. 1991. Validation of the alkalinity anomaly technique for investigating calcification of photosynthesis in coral reef communities. *Limnology and oceanography* 36:1232–1239.
- Cho, H.-M., T.-H. Kim, J.-H. Moon, B.-C. Song, D.-W. Hwang, T. Kim, and D.-H. Im. 2021. Estimating submarine groundwater discharge in Jeju volcanic island (Korea) during a typhoon (Kong-rey) using humic-fluorescent dissolved organic matter-Si mass balance. *Scientific reports* 11:941.
- Correa, R. E., M. B. Cardenas, R. S. Rodolfo, M. R. Lapus, K. L. Davis, A. B. Giles, J. C. Fullon, M.-C. Hajati, N. Moosdorf, C. J. Sanders, and I. R. Santos. 2021. Submarine Groundwater Discharge Releases CO₂ to a Coral Reef. *ACS ES&T Water* 1:1756–1764.
- Cottingham, K. L., J. T. Lennon, and B. L. Brown. 2005. Knowing when to draw the line: designing more informative ecological experiments. *Frontiers in ecology and the environment* 3:145–152.
- Courtney, T. A., and A. J. Andersson. 2019. Evaluating measurements of coral reef net ecosystem calcification rates. *Coral reefs* 38:997–1006.
- Courtney, T. A., M. Lebrato, N. R. Bates, A. Collins, S. J. de Putron, R. Garley, R. Johnson, J.-

- C. Molinero, T. J. Noyes, C. L. Sabine, and A. J. Andersson. 2017. Environmental controls on modern scleractinian coral and reef-scale calcification. *Science advances* 3:e1701356.
- Crook, E. D., A. L. Cohen, M. Rebolledo-Vieyra, L. Hernandez, and A. Paytan. 2013. Reduced calcification and lack of acclimatization by coral colonies growing in areas of persistent natural acidification. *Proceedings of the National Academy of Sciences* 110:11044–11049.
- Cyronak, T., A. J. Andersson, C. Langdon, R. Albright, N. R. Bates, K. Caldeira, R. Carlton, J. E. Corredor, R. B. Dunbar, I. Enochs, J. Erez, B. D. Eyre, J.-P. Gattuso, D. Gledhill, H. Kayanne, D. I. Kline, D. A. Koweeck, C. Lantz, B. Lazar, D. Manzello, A. McMahon, M. Meléndez, H. N. Page, I. R. Santos, K. G. Schulz, E. Shaw, J. Silverman, A. Suzuki, L. Teneva, A. Watanabe, and S. Yamamoto. 2018. Taking the metabolic pulse of the world's coral reefs. *PloS one* 13:e0190872.
- Cyronak, T., I. R. Santos, D. V. Erler, and B. D. Eyre. 2013. Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). *Biogeosciences* 10:2467–2480.
- Cyronak, T., I. R. Santos, D. V. Erler, D. T. Maher, and B. D. Eyre. 2014a. Drivers of pCO₂ variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge. *Global biogeochemical cycles* 28:2013GB004598.
- Cyronak, T., K. G. Schulz, I. R. Santos, and B. D. Eyre. 2014b. Enhanced acidification of global coral reefs driven by regional biogeochemical feedbacks. *Geophysical research letters* 41:5538–5546.
- Davis, K. L., A. P. Colefax, J. P. Tucker, B. P. Kelaher, and I. R. Santos. 2021. Global coral reef ecosystems exhibit declining calcification and increasing primary productivity. *Communications Earth & Environment* 2:1–10.

- DeCarlo, T. M., A. L. Cohen, G. T. F. Wong, F.-K. Shiah, S. J. Lentz, K. A. Davis, K. E. F. Shamberger, and P. Lohmann. 2017. Community production modulates coral reef pH and the sensitivity of ecosystem calcification to ocean acidification. *Journal of Geophysical Research, C: Oceans* 122:745–761.
- Delevaux, J. M. S., R. Whittier, K. A. Stamoulis, L. L. Bremer, S. Jupiter, A. M. Friedlander, M. Poti, G. Guannel, N. Kurashima, K. B. Winter, R. Toonen, E. Conklin, C. Wiggins, A. Knudby, W. Goodell, K. Burnett, S. Yee, H. Htun, K. L. L. Oleson, T. Wiegner, and T. Ticktin. 2018. A linked land-sea modeling framework to inform ridge-to-reef management in high oceanic islands. *PloS one* 13:e0193230.
- Dillon, P. J., and W. B. Kirchner. 1975. The effects of geology and land use on the export of phosphorus from watersheds. *Water research* 9:135–148.
- Dittmar, T., Norbert Hertkorn, G. Kattner, and R. J. Lara. 2005. Mangroves, a major source of dissolved organic carbon to the oceans. *Global Biogeochemical Cycles* 20:2005GB002570.
- Doo, S. S., P. J. Edmunds, and R. C. Carpenter. 2019. Ocean acidification effects on in situ coral reef metabolism. *Scientific reports* 9:12067.
- Dubinsky, Z., and N. Stambler. 1996. Marine pollution and coral reefs. *Global change biology* 2:511–526.
- Dulai, H., C. M. Smith, D. W. Amato, V. Gibson, and L. L. Bremer. 2023. Risk to native marine macroalgae from land-use and climate change-related modifications to groundwater discharge in Hawai‘i. *Limnology and oceanography letters* 8:141–153.
- Enochs, I. C., N. Formel, L. Shea, L. Chomiak, A. Piggot, A. Kirkland, and D. Manzello. 2020. Subsurface Automated Samplers (SAS) for ocean acidification research. *Bulletin of Marine Science* 96:735–752.

- Fields, J. B., and N. J. Silbiger. 2022. Foundation species loss alters multiple ecosystem functions within temperate tidepool communities. *Marine ecology progress series* 683:1–19.
- Foden, J., D. B. Sivy, D. K. Mills, and M. J. Devlin. 2008. Spatial and temporal distribution of chromophoric dissolved organic matter (CDOM) fluorescence and its contribution to light attenuation in UK waterbodies. *Estuarine, coastal and shelf science* 79:707–717.
- Gattuso, J.-P., J.-M. Epitalon, H. Lavigne, and J. Orr. 2019. seacarb: Seawater Carbonate Chemistry. R package version 3.2. 12.
- Gattuso, J.-P., M. Frankignoulle, and R. Wollast. 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annual review of ecology and systematics* 29:405–434.
- Gelman, A., and D. B. Rubin. 1992. Inference from Iterative Simulation Using Multiple Sequences. *Statistical science: a review journal of the Institute of Mathematical Statistics* 7:457–472.
- Goldberg, S. J., C. E. Nelson, D. A. Viviani, C. N. Shulse, and M. J. Church. 2017. Cascading influence of inorganic nitrogen sources on DOM production, composition, lability and microbial community structure in the open ocean. *Environmental microbiology* 19:3450–3464.
- Graham, N. A. J., S. K. Wilson, P. Carr, A. S. Hoey, S. Jennings, and M. A. MacNeil. 2018. Seabirds enhance coral reef productivity and functioning in the absence of invasive rats. *Nature* 559:250–253.
- Haas, A. F., C. E. Nelson, L. Wegley Kelly, C. A. Carlson, F. Rohwer, J. J. Leichter, A. Wyatt, and J. E. Smith. 2011. Effects of coral reef benthic primary producers on dissolved organic carbon and microbial activity. *PloS one* 6:e27973.
- Hagedorn, B., M. Becker, B. Maine, E. Justis, N. Silbiger, D. Barnas, and M. Zeff. 2024, April 3.

Refining Submarine Groundwater Discharge Analysis Through Nonlinear Quantile
Regression of Geochemical Time Series.

- Haßler, K., K. Dähnke, M. Kölling, L. Sichoix, A.-L. Nickl, and N. Moosdorf. 2019. Provenance of nutrients in submarine fresh groundwater discharge on Tahiti and Moorea, French Polynesia. *Applied geochemistry: journal of the International Association of Geochemistry and Cosmochemistry* 100:181–189.
- Hatcher, B. G. 1990. Coral reef primary productivity. A hierarchy of pattern and process. *Trends in ecology & evolution* 5:149–155.
- Hench, J. L., J. J. Leichter, and S. G. Monismith. 2008. Episodic circulation and exchange in a wave-driven coral reef and lagoon system. *Limnology and oceanography* 53:2681–2694.
- Hughes, T. P., N. A. J. Graham, J. B. C. Jackson, P. J. Mumby, and R. S. Steneck. 2010. Rising to the challenge of sustaining coral reef resilience. *Trends in ecology & evolution* 25:633–642.
- Jefferies, R. L. 2000. Allochthonous inputs: integrating population changes and food-web dynamics. *Trends in ecology & evolution* 15:19–22.
- Johnson, A. G., C. R. Glenn, and W. C. Burnett. 2008. Aerial infrared imaging reveals large nutrient-rich groundwater inputs to the ocean. *Geophysical Research Letters* 35:15.
- Johnson, E. E., and T. N. Wiegner. 2014. Surface water metabolism potential in groundwater-fed coastal waters of Hawaii island, USA. *Estuaries and coasts: journal of the Estuarine Research Federation* 37:712–723.
- Kay, M. 2018. tidybayes: Tidy Data and Geoms for Bayesian Models.
- Kealoha, A.K., C.B Wall, and T.A. Leggett. 2024. Coastal water quality improves during the COVID-19 pandemic: Maui, Hawai‘i. *Marine Pollution Bulletin*. 209: 117088

- Kelly, L. W., C. E. Nelson, A. F. Haas, D. S. Naliboff, S. Calhoun, C. A. Carlson, R. A. Edwards, M. D. Fox, M. Hatay, M. D. Johnson, E. L. A. Kelly, Y. W. Lim, S. Macherla, Z. A. Quinlan, G. G. Z. Silva, M. J. A. Vermeij, B. Zgliczynski, S. A. Sandin, J. E. Smith, and F. Rohwer. 2019. Diel population and functional synchrony of microbial communities on coral reefs. *Nature Communications* 10:1691.
- Kleypas, J. A., and C. Langdon. 2006. Coral Reefs and Changing Seawater Carbonate Chemistry. Pages 73–110 *Coral Reefs and Climate Change: Science and Management*. American Geophysical Union.
- Kwiatkowski, L., B. Gaylord, T. Hill, J. Hosfelt, K. J. Krocker, Y. Nebuchina, A. Ninokawa, A. D. Russell, E. B. Rivest, M. Sesboüé, and K. Caldeira. 2016. Nighttime dissolution in a temperate coastal ocean ecosystem increases under acidification. *Scientific reports* 6:22984.
- La Valle, F. F., M. B. Kantar, and C. E. Nelson. 2021. Coral reef benthic community structure is associated with the spatiotemporal dynamics of submarine groundwater discharge chemistry. *Limnology and oceanography* 66:188–200.
- La Valle, F., F. I. M. Thomas, and C. E. Nelson. 2019. Macroalgal biomass, growth rates, and diversity are influenced by submarine groundwater discharge and local hydrodynamics in tropical reefs. *Marine ecology progress series*:51–67.
- Lesser, M. P. 2021. Eutrophication on Coral Reefs: What Is the Evidence for Phase Shifts, Nutrient Limitation and Coral Bleaching. *Bioscience* 71:1216–1233.
- Lowe, A. T., J. Bos, and J. Ruesink. 2019. Ecosystem metabolism drives pH variability and modulates long-term ocean acidification in the Northeast Pacific coastal ocean. *Scientific reports* 9:963.
- Lubarsky, K. A., N. J. Silbiger, and M. J. Donahue. 2018. Effects of submarine groundwater

discharge on coral accretion and bioerosion on two shallow reef flats. *Limnology and oceanography* 63:1660–1676.

Luijendijk, E., T. Gleeson, and N. Moosdorf. 2020. Fresh groundwater discharge insignificant for the world's oceans but important for coastal ecosystems. *Nature communications* 11:1260.

Marcarelli, A.M., C.V. Baxter, M.M. Mineau, and R.O. Hall, Jr. 2011. Quantity and quality: unifying food web and ecosystem perspective on the role of resource subsidies in freshwaters. *Ecology* 92:1215-1225

McDonough, L. K., I. R. Santos, M. S. Andersen, D. M. O'Carroll, H. Rutledge, K. Meredith, P. Oudone, J. Bridgeman, D. C. Gooddy, J. P. R. Sorensen, D. J. Lapworth, A. M. MacDonald, J. Ward, and A. Baker. 2020. Changes in global groundwater organic carbon driven by climate change and urbanization. *Nature communications* 11:1279.

McLaughlin, C. J., C. A. Smith, R. W. Buddemeier, J. D. Bartley, and B. A. Maxwell. 2003. Rivers, runoff, and reefs. *Global and planetary change* 39:191–199.

McMahon, A., and I. R. Santos. 2017. Nitrogen enrichment and speciation in a coral reef lagoon driven by groundwater inputs of bird guano. *Journal of Geophysical Research, C: Oceans* 122:7218–7236.

McMahon, A., I. R. Santos, T. Cyronak, and B. D. Eyre. 2013. Hysteresis between coral reef calcification and the seawater aragonite saturation state. *Geophysical research letters* 40:4675–4679.

Middelburg, J. J., K. Soetaert, and M. Hagens. 2020. Ocean Alkalinity, Buffering and Biogeochemical Processes. *Reviews of geophysics* 58:e2019RG000681.

Moore, W. S. 2010. The effect of submarine groundwater discharge on the ocean. *Annual review*

of marine science 2:59–88.

Moosdorf, N., M. E. Böttcher, D. Adyasari, E. Erkul, B. S. Gilfedder, J. Greskowiak, A.-K.

Jenner, L. Kotwicki, G. Massmann, M. Müller-Petke, T. Oehler, V. Post, R. Prien, J.

Scholten, B. Siemon, C. M. Ehlert von Ahn, M. Walther, H. Waska, T. Wunderlich, and U.

Mallast. 2021. A State-Of-The-Art Perspective on the Characterization of Subterranean

Estuaries at the Regional Scale. *Frontiers of Earth Science in China* 9.

Moosdorf, N., and T. Oehler. 2017. Societal use of fresh submarine groundwater discharge: An overlooked water resource. *Earth-Science Reviews* 171:338–348.

Moosdorf, N., T. Stieglitz, H. Waska, H. H. Dürr, and J. Hartmann. 2015. Submarine groundwater discharge from tropical islands: a review. *Grundwasser* 20:53–67.

Nalley, E. M., L. J. Tuttle, E. E. Conklin, A. L. Barkman, D. M. Wulstein, M. C. Schmidbauer, and M. J. Donahue. 2023. A systematic review and meta-analysis of the direct effects of nutrients on corals. *The Science of the total environment* 856:159093.

Nelson, C. E., M. J. Donahue, H. Dulaiova, S. J. Goldberg, F. F. La Valle, K. Lubarsky, J.

Miyano, C. Richardson, N. J. Silbiger, and F. I. M. Thomas. 2015. Fluorescent dissolved organic matter as a multivariate biogeochemical tracer of submarine groundwater discharge in coral reef ecosystems. *Marine chemistry* 177:232–243.

Nelson, C. E., L. Wegley Kelly, and A. F. Haas. 2023. Microbial Interactions with Dissolved Organic Matter Are Central to Coral Reef Ecosystem Function and Resilience. *Annual review of marine science* 15:431–460.

Odum, E. P. 1969. The strategy of ecosystem development. *Science* 164:262–270.

Oehler, T., J. Tamborski, S. Rahman, N. Moosdorf, J. Ahrens, C. Mori, R. Neuholz, B.

Schnetger, and M. Beck. 2019. DSi as a Tracer for Submarine Groundwater Discharge.

- Olsen, A., R. M. Key, S. van Heuven, S. K. Lauvset, A. Velo, X. Lin, C. Schirnick, A. Kozyr, T. Tanhua, M. Hoppema, S. Jutterström, R. Steinfeldt, E. Jeansson, M. Ishii, F. F. Pérez, and T. Suzuki. 2016. The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean. *Earth system science data* 8:297–323.
- Page, H. N., A. J. Andersson, P. L. Jokiel, K. S. Rodgers, M. Lebrato, K. Yeakel, C. Davidson, S. D’Angelo, and K. D. Bahr. 2016. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. *Coral reefs* 35:1311–1325.
- Pastorok, R. A., and G. R. Bilyard. 1985. Effects of sewage pollution on coral-reef communities. *Marine ecology progress series*. Oldendorf 21:175–189.
- Paytan, A., G. G. Shellenbarger, J. H. Street, M. E. Gonneea, K. Davis, M. B. Young, and W. S. Moore. 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. *Limnology and oceanography* 51:343–348.
- Polis, G. A., W. B. Anderson, and R. D. Holt. 1997. Toward an integration of landscape and food web ecology: The dynamics of spatially subsidized food webs. *Annual review of ecology and systematics* 28:289–316.
- Quinlan, Z. A., K. Remple, M. D. Fox, N. J. Silbiger, T. A. Oliver, H. M. Putnam, L. Wegley Kelly, C. A. Carlson, M. J. Donahue, and C. E. Nelson. 2018. Fluorescent organic exudates of corals and algae in tropical reefs are compositionally distinct and increase with nutrient enrichment. *Limnology and Oceanography Letters* 3:331–340.
- R Core Team. 2021. R: A language and environment for statistical computing. R. <https://www.R-project.org/>.
- Ricart, A. M., M. Ward, T. M. Hill, E. Sanford, K. J. Kroeker, Y. Takeshita, S. Merolla, P.

- Shukla, A. T. Ninokawa, K. Elsmore, and B. Gaylord. 2021. Coast-wide evidence of low pH amelioration by seagrass ecosystems. *Global change biology* 27:2580–2591.
- Richards Donà, A., C. M. Smith, and L. L. Bremer (2023) Divergent responses of native and invasive macroalgae to submarine groundwater discharge. *Scientific Reports* 13:13984
- Richardson, J.S., and T. Sato. 2015. Resource subsidy flows across freshwater-terrestrial boundaries and influence on process linking adjacent ecosystems. *Ecohydrology* 8:406–415
- Richardson, C. M., H. Dulai, B. N. Popp, K. Ruttenberg, and J. K. Fackrell. 2017. Submarine groundwater discharge drives biogeochemistry in two Hawaiian reefs. *Limnology and oceanography* 62:S348–S363.
- Robertson, G. P., and P. M. Vitousek. 2009. Nitrogen in Agriculture: Balancing the Cost of an Essential Resource. *Annual review of environment and resources* 34:97–125.
- Sandin, S. A., P. A. Becker, C. Becker, K. Brown, N. G. Erazo, C. Figuerola, R. N. Fisher, A. M. Friedlander, T. Fukami, N. A. J. Graham, D. S. Gruner, N. D. Holmes, W. A. Holthuijzen, H. P. Jones, M. Rios, A. Samaniego, W. Sechrest, B. X. Semmens, H. E. Thornton, R. V. Thurber, C. N. Wails, C. A. Wolf, and B. J. Zgliczynski. 2022. Harnessing island–ocean connections to maximize marine benefits of island conservation. *Proceedings of the National Academy of Sciences* 119:e2122354119.
- Santos, I. R., X. Chen, A. L. Lecher, A. H. Sawyer, N. Moosdorf, V. Rodellas, J. Tamborski, H.-M. Cho, N. Dimova, R. Sugimoto, S. Bonaglia, H. Li, M.-C. Hajati, and L. Li. 2021. Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. *Nature reviews. Earth & environment* 2:307–323.
- Santos, I. R., B. D. Eyre, and M. Huettel. 2012. The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. *Estuarine, coastal and shelf science* 98:1–

15.

Santos, I. R., R. N. Glud, D. Maher, D. Erler, and B. D. Eyre. 2011. Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef. *Geophysical research letters* 38.

Silbiger, N.J. (2025) njsilbiger/BiogeochemicalCascades_SGD: V1.1. Zenodo. doi: 10.5281/zenodo.15104032.

Silbiger, N. J., M. J. Donahue, and K. Lubarsky. 2020. Submarine groundwater discharge alters coral reef ecosystem metabolism. *Proceedings. Biological sciences / The Royal Society* 287:20202743.

Silbiger, N. J., C. E. Nelson, K. Remple, J. K. Sevilla, Z. A. Quinlan, H. M. Putnam, M. D. Fox, and M. J. Donahue. 2018. Nutrient pollution disrupts key ecosystem functions on coral reefs. *Proceedings. Biological sciences / The Royal Society* 285:10.1098/rspb.2017.2718.

Silbiger, N. J., and C. J. B. Sorte. 2018. Biophysical feedbacks mediate carbonate chemistry in coastal ecosystems across spatiotemporal gradients. *Scientific reports* 8:796.

Silverman, J., B. Lazar, and J. Erez. 2007a. Community metabolism of a coral reef exposed to naturally varying dissolved inorganic nutrient loads. *Biogeochemistry* 84:67–82.

Silverman, J., B. Lazar, and J. Erez. 2007b. Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. *Journal of geophysical research* 112:1.

Slomp, C. P., and P. Van Cappellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* 295:64–86.

Subalusky, A.L., and D. M. Post. 2019. Context dependency of animal resource subsidies.

Biological Reviews. 95: 517-538

Tamborski, J., S. Bejannin, J. Garcia-Orellana, M. Souhaut, C. Charbonnier, P. Anschutz, M.

Pujo-Pay, P. Conan, O. Crispi, C. Monnin, T. Stieglitz, V. Rodellas, A. Andrisoa, C.

Claude, and P. van Beek. 2018. A comparison between water circulation and terrestrially-driven dissolved silica fluxes to the Mediterranean Sea traced using radium isotopes.

Geochimica et cosmochimica acta 238:496–515.

Thrane, J.-E., D. O. Hessen, and T. Andersen. 2014. The Absorption of Light in Lakes: Negative Impact of Dissolved Organic Carbon on Primary Productivity. *Ecosystems* 17:1040–1052.

Wang, G., W. Jing, S. Wang, Y. Xu, Z. Wang, Z. Zhang, Q. Li, and M. Dai. 2014. Coastal acidification induced by tidal-driven submarine groundwater discharge in a coastal coral reef system. *Environmental science & technology* 48:13069–13075.

Webb, J. R., I. R. Santos, D. T. Maher, D. R. Tait, T. Cyronak, M. Sadat-Noori, P. Macklin, and L. C. Jeffrey. 2019. Groundwater as a source of dissolved organic matter to coastal waters: Insights from radon and CDOM observations in 12 shallow coastal systems. *Limnology and oceanography* 64:182–196.

Wegley Kelly, L., C. E. Nelson, D. Petras, I. Koester, Z. A. Quinlan, M. G. I. Arts, L.-F. Nothias, J. Comstock, B. M. White, E. C. Hopmans, F. C. van Duyl, C. A. Carlson, L. I. Aluwihare, P. C. Dorrestein, and A. F. Haas. 2022. Distinguishing the molecular diversity, nutrient content, and energetic potential of exometabolomes produced by macroalgae and reef-building corals. *Proceedings of the National Academy of Sciences of the United States of America* 119:e2110283119.

Wu, P., N. Christidis, and P. Stott. 2013. Anthropogenic impact on Earth's hydrological cycle. *Nature climate change* 3:807–810.

Yeakel, K. L., A. J. Andersson, N. R. Bates, T. J. Noyes, A. Collins, and R. Garley. 2015. Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. *Proceedings of the National Academy of Sciences of the United States of America* 112:14512–14517.

Figures and Tables

Table 1. SGD endmembers from dug beach pits and inland springs as well as the mean $\pm$ SE for all collected reef samples for each measured parameter in the study. Missing data are indicated with a dash.

Parameter	Unit	Cabral Beach Pit	Cabral Spring	Cabral Reef (mean $\pm$ SE)	Varari Beach Pit 1	Varari Beach Pit 2	Varari Reef (mean $\pm$ SE)
Salinity	psu	3.11	0.44	36.6 $\pm$ 0.02	2.89	9.67	36.7 $\pm$ 0.02
Total Alkalinity	$\mu\text{mol kg}^{-1}$	1959.29	1335.7	2319 $\pm$ 3.1	3813.31	5389.84	2363 $\pm$ 1.54
pH _T	$\mu\text{mol L}^{-1}$	7.65	7.24	7.98 $\pm$ 0.01	7.18	7.73	8.01 $\pm$ 0.01
Ammonium (NH ₄ ⁺)	$\mu\text{mol L}^{-1}$	5.41	0.89	0.35 $\pm$ 0.02	1.6	0.79	0.37 $\pm$ 0.3
Nitrate + Nitrite (NO _x)	$\mu\text{mol L}^{-1}$	32.5	19.77	0.58 $\pm$ 0.02	32.63	279.15	0.41 $\pm$ 0.02
Phosphate (PO ₄ ³⁻)	$\mu\text{mol L}^{-1}$	1.85	4.06	0.2 $\pm$ 0.001	2.6	1.57	0.19 $\pm$ 0.001
Silicate (SiO ₃ ²⁻)	$\mu\text{mol L}^{-1}$	650.73	737.49	3.46 $\pm$ 0.17	713.06	229.28	1.97 $\pm$ 0.11
Humic fDOM	Raman Units	0.08	0.08	0.04 $\pm$ 0.001	0.12	-	0.02 $\pm$ 0.001
Proteinaceous fDOM	Raman Units	0.06	0.12	0.14 $\pm$ 0.01	0.06	-	0.1 $\pm$ 0.01

Figures and figure legends

Figure 1: Conceptual diagram of a cascade of direct and indirect effects, or “biogeochemical cascade”, on coral reefs. Added solutes to an ecosystem can create biogeochemical cascades where geochemical parameters indirectly influence each other by altering biological processes, and biological parameters indirectly influence each other by altering geochemical processes. Solid arrows indicate direct relationships, and dashed arrows indicate indirect relationships. The image was made by Nyssa. J. Silbiger, and all icons (coral reef and bottle) are from Canva.

Figure 2: (a) A map of Mo‘orea, French Polynesia with stars indicating the two field sites (Cabral in green and Varari in red). Insets on the left show maps of Cabral (b) and Varari (c) provided by Google maps, with the experimental locations in yellow and the selected SGD seepage point in red. A picture of each seepage point is located in the top right corner of the maps. Inset (d) shows the general sampling design for water collection for the 21 coincident samples. As Mo‘orea is an amphidromic point, high tide and low tide are at the same general time all year round. The yellow vertical lines are at sunrise and the gray vertical lines are at sunset. Inset (e) illustrates the correlation of each measured parameter with freshwater where positive relationships with freshwater are indicated in purple and negative relationships with freshwater are indicated in yellow. The size of the circle is related to the strength of the correlation, with bigger circles having stronger correlations. (f) A windrose plot of current speed (visualized with color) and direction for each site and season. The dry and wet season collections were in August and March, respectively. Photos were taken by Nyssa J. Silbiger and Shireen Rahimi.

Figure 3: Visualization of the structural equation model (SEM). Black arrows indicate direct relationships included in the SEM. Model formulas for each model within the SEM are detailed in the methods. Figure was created by Jamie R. Kerlin using icons (leaf, sun, thermometer) from Adobe illustrator and Adobe photoshop. Corals were hand-drawn in Adobe illustrator.

Figure 4: Principal component analysis of reef biogeochemistry at **(a,b,c)** Varari and **(d,e,f)** Cabral for the **(a,d)** dry season and **(b, e)** wet season. Each point represents a single water sample at a single experimental location, with open circles representing daylight (afternoon and dusk) and closed circles representing dark hours (midnight and dawn). The dark shaded polygons represent high tide and the light shaded polygons represent low tide. Points closer together have more similar biogeochemistry than points further apart. Insets **(c)** and **(f)** show the biplots for each site, where the length of the arrow represents the relative strength of the loading. The results of the MANOVA detailing significant interactions between tide and time of day in all four models are in Appendix S2: Table S1.

Figure 5: Results from the structural equation model. The central plots **(a - l)** show the effect size and 95% BCI for all parameters included in each equation. Labels on the top of each effect size plot are the dependent variables: boxes **a - f** are results from the dry season and boxes **g - l** are from the wet season. Lines that do not overlap zero are considered statistically significant effects. The closed symbols show statistically significant effects, while the open symbols show insignificant effects. The call outs **(m-v)** visualize the best fit lines for each model, with raw data shown in Appendix S2: Figures S2 - S5. Solid lines are from the dry season and dashed lines are

from the wet season. Cabral is shown in green and Varari is shown in red. Notably, NEP and NEC in the figures represent NEP and NEC potential as outlined in the methods.