Adyasari, D.; Waska, H.; Daehnke, K.; Oehler, T.; Pracoyo, A.; Putra, D.; Moosdorf, N.:

Terrestrial Nutrients and Dissolved Organic Matter Input to the Coral Reef Ecosystem via Submarine Springs.

In: ACS ES & T Water. Vol. 1 (2021) 8, 1887 - 1900.

First published online by ACS: 29.07.2021

https://dx.doi.org/10.1021/acsestwater.1c00134

Terrestrial nutrients and dissolved organic matter input to the coral reef ecosystem via submarine springs

Dini Adyasari[a,b*], Hannelore Waska[c], Kirstin Daehnke[d], Till Oehler[a], Atas Pracoyo[e], Doni Prakasa Eka Putra[f], Nils Moosdorf[a,g]

[a]Department of Biogeochemistry and Geology, Leibniz Centre for Tropical Marine Research (ZMT), Bremen 28359, Germany

[b]Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487, USA

[c]Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, Oldenburg 26129, Germany

[d]Department of Ecosystems and Biogeochemical Cycles, Helmholtz Centre for Materials and Coastal Research, Geesthacht 21502, Germany

[e]Faculty of Engineering, Universitas Mataram, Mataram 83115, Indonesia

[f]Department of Geological Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

[g]Institute of Geosciences, Christian-Albrechts-Universität zu Kiel, Kiel 24118, Germany

[*]Corresponding author:

Email: dadyasari@ua.edu

Abstract

Submarine groundwater discharge (SGD) transports terrestrial nutrients and dissolved organic matter (DOM) to the ocean. Elevated concentration of nutrients and DOM can act as stressors enhancing coral disease and mortality, but only a few studies address the impacts of groundwater-borne nutrients and DOM on coral reef ecosystems. This study quantifies and characterizes nutrients, nitrate (NO_3^-) stable isotopes, and DOM molecular composition of coastal groundwater discharging to the reef ecosystem via submarine springs in Lombok, Indonesia. NO_3^- isotopic values point to both natural (soil) and anthropogenic (wastewater and fertilizer) origins of nutrients in the coastal aquifer. Submarine springs are fed by different groundwater sources and deliver land-based NO_3^-, dissolved silica, phosphate, and labile DOM to the reef water column. Terrestrial nutrients and DOM undergo rapid turnover in the reef water column due to biogeochemical processes and biological uptake. Meanwhile, reef and offshore water likely act as sources of more stable, reworked DOM formulae and its mineralization product, ammonium. We observed that submarine springs consistently deliver similar nutrient loadings, creating a long-term environmental threat to coral reef sustainability. This study emphasizes the importance of understanding coastal biogeochemistry and hydrological processes in sensitive tropical ecosystems, particularly those adjacent to modified land-use watersheds.

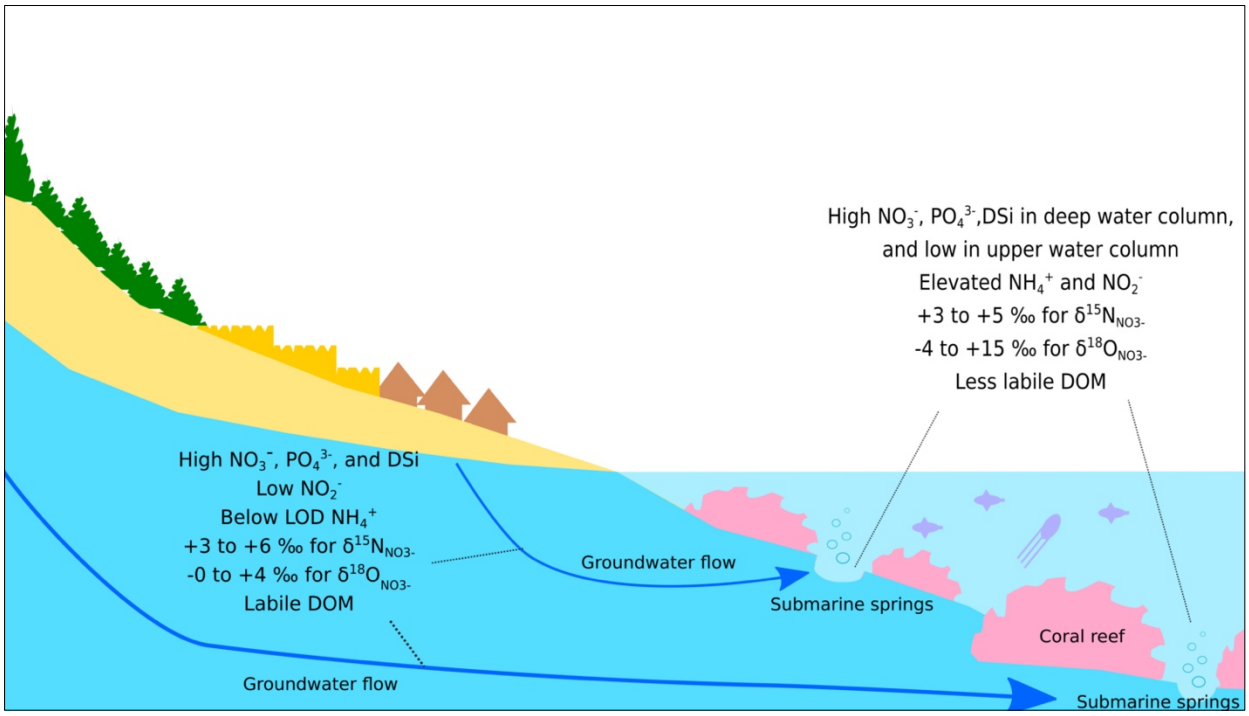
Keywords

Submarine groundwater discharge, nutrients, dissolved organic matter, coral reef ecosystem, ultrahigh-resolution mass spectrometry, tropics, Coral Triangle.

Synopsis

Understanding the source and transformation of terrestrial nutrient and organic matter transported to coral reef ecosystems via submarine groundwater discharge is important to protect coral's health.

Graphic for TOC



INTRODUCTION

Submarine groundwater discharge (SGD) is defined as direct groundwater outflow across the land-ocean interface into the coastal ocean[1,2]. More than 90% of total SGD is estimated to be in the form of recirculated seawater or "marine SGD" at a global scale, while terrestrial or "fresh SGD" does not exceed 10% of SGD volume[3,4]. However, fresh SGD can also create ecological impact in local scale. For example, as SGD is known to transport land-based nutrients[5], heavy metals[6], organic matter (OM)[7], or biological matter[8], it may cause eutrophication or harmful algal bloom[9], as well as a change in phytoplankton communities or other marine biota in the receiving coastal water[10]. In this study, we focus on fresh SGD via submarine springs. Submarine springs usually occur as terrestrial groundwater conduits in a karstic or volcanic setting and may play a major role in delivering land-based dissolved materials into the ocean, particularly in the tropical regions[11,12]. Southeast Asia, one of the most populated subregions in the tropics, is characterized

by hydrogeological and societal conditions favoring ubiquitous occurrence of, in particular, fresh SGD and its associated solute fluxes: The region is characterized by heavy precipitation year-round, high aquifer permeability, and fast weathering, nutrient-rich rocks[13]. In addition, Southeast Asia is listed among the regions with the strongest human modifications of the coastal zone worldwide[14], which usually leads to increasing amounts of anthropogenic contaminants in the natural water system. The region also hosts native coastal ecosystems such as coral reefs, seagrass, and mangrove communities, which are sensitive to even slight increases in terrestrial nutrient and OM input[15].

The impact of the enrichment of dissolved inorganic nutrients (nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and phosphate (PO_4^{3-})) on coral reef ecosystems has been widely studied, and it is generally suggested that they negatively affect coral physiology and functioning[16]. Previous organic matter-related studies on the coral reef ecosystem suggest that elevated dissolved organic carbon (DOC) concentration can be a primary stressor resulting in coral mortality[17,18]. In recent days, DOM molecular characterization is employed to distinguish its origin and distribution in this ecosystem, which may be an important step towards understanding the role of DOM subsidies in reef ecosystem function[19,20]. However, the analysis of DOM molecular composition is limited due to its high complexity[21]. The recent advance of ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) allows the characterization of thousands of molecular formulae in the complex DOM mixtures from water samples[22]. FT-ICR-MS has been implemented to study DOM characterization in different hydrological settings, e.g., groundwater[23], rivers[24,25], subterranean estuaries (STE) [26,27], and ocean waters of temperate[28,29] and boreal regions[28], but high-resolution DOM studies from tropical ecosystems are scarce. Considering that the coastal tropics of Southeast Asia are challenged with elevated terrestrial nutrient and DOM export in the next years[30] and the adverse impact these solutes may cause to the coral reef ecosystem; understanding the sources, fate, and

transformation of nutrients and DOM in this system is essential in predicting and managing how these ecosystems will respond to global change.

In this study, we present physical and geochemical observations from a submarine spring complex in the volcanic tropical island of Lombok, Indonesia, which discharges into a coral reef ecosystem. A recent review from Indonesia shows that nutrients and organic pollutants are the two major contaminants contaminating coastal water quality and ecosystems in this region, with coral reef ecosystem is found as the most sensitive to terrestrial anthropogenic disturbance[31]. Therefore, the objectives of this study are (1) to explore the source, fate, and transformation of nutrients in the coastal groundwater, submarine springs, and water column in a coral reef ecosystem, (2) to examine the previously unknown DOM molecular composition in the coastal groundwater, submarine springs, and water column in a coral reef ecosystem, and (3) to evaluate the potential long term environmental impact on coral reef ecosystems receiving terrestrial nutrient and DOM via submarine springs.

MATERIAL AND METHODS

Study site

The submarine spring complex is located on the island of Lombok, Indonesia (Figure 1A). The coral reef ecosystem in this island is a part of the Coral Triangle, a marine area across six countries (Indonesia, Malaysia, Papua New Guinea, the Philippines, the Solomon Islands, and Timor-Leste) which contains 76% of the world's coral species[32]. The land use in the island consists of natural forest in the hinterland and agriculture and plantation in the coastal area (Figure 1A). Mount Rinjani (3726 m a.s.l) is the highest active volcano in Lombok, situated approximately 15 km south of the submarine spring complex where we conducted our study. In the northern part of the island, it can be expected that about 15% of the rainwater percolates into groundwater, which is vulnerable to pollution based on the local hydrogeology[33]. The aquifers most likely discharge their freshwater in the nearshore area below the sea as submarine springs[34]. River discharge into the coastal water

in this area is located approximately 1 km towards north and south of the submarine spring complex; however, these are non-perennial rivers. Several local studies have been implemented at the springs, e.g., related to the springs and their identification via thermal satellite[35,36], the potential occurrence of coral reef diseases surrounding the springs[37], and the utilization of the springs as freshwater resources for local communities[38]. The morphology of the springs, SGD rates, and their associated nutrient fluxes were studied by Oehler, et al. [12]. In general, the springs investigated in the previous works and this study are divided into three sub-complexes: Spring A, Springs B-C, and Springs D-E due to their distance from each other and spring type. In the largest and deepest spring in the area (Spring A), submarine groundwater discharges from an eight-meter-deep structure in the form of a crater in the reef, whereas in other sites, groundwater discharges from fissures and cracks in the reef (Springs B, C, D, and E) (Figure 1B).

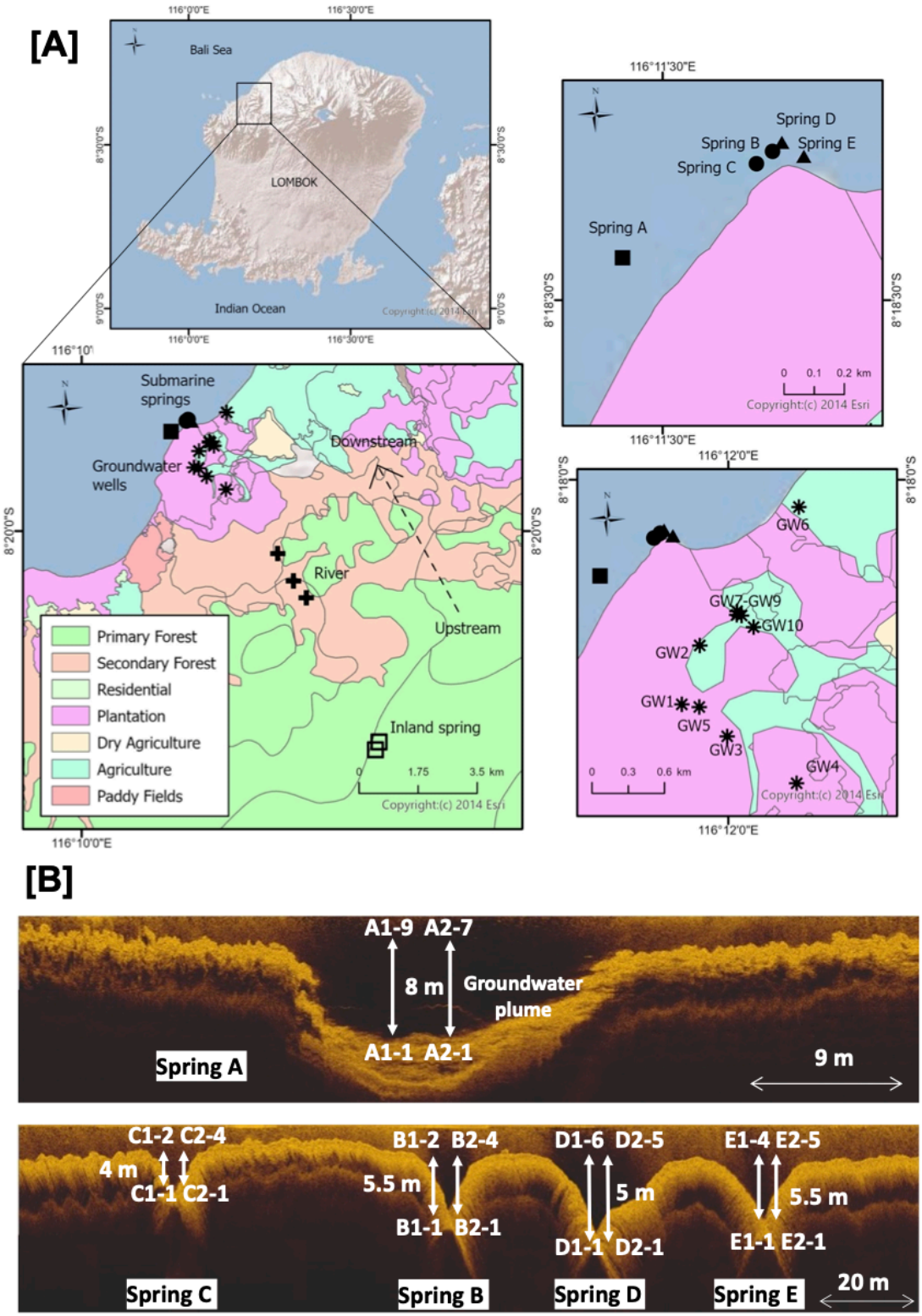


Figure 1. (A) Map of land use and sampling points in Lombok, Indonesia, and (B) vertical sampling points in the submarine springs, projected onto echosounder profiles from Oehler, et al. [12]. The samples collected from December 2019 were named A1, B1, C1, D1, and E1 for submarine springs A, B, C, D, and E, respectively; while A2, B2, C2, D2, and E2 were samples from January 2020. The numbering after hyphenation indicates depth where samples were taken, where low number signify deeper depth and high number signify upper depth.

Field sampling

The field expedition was conducted in December 2019 and January 2020. Water samples were collected from inland springs, rivers, groundwater wells, submarine springs, and reef water (Figure 1A). Two inland spring samples were collected from the northern slope of Mount Rinjani. Inland spring water samples were collected by submerging the sample bottle in discharge points. River samples were taken approximately 6 km to the hinterland from the coastline because they were non-perennial rivers and did not discharge to the coastal area at the time of our study. River water samples were collected from a depth of about 20 cm below the surface water level. Coastal groundwater was sampled from ten wells owned by the local residents and consisted of three shallow dug wells (depth < 3 m, i.e., GW1, GW2, GW5), and the rest of the groundwater samples were taken from drilled wells (depth 12-25 m). Coastal groundwater samples were taken through plastic tubing by submersible pump and the samples were collected after letting the water from the well flow for a few minutes, until standing water in the surface/upper part of the well were removed. Figure 1A shows the collection points from upstream to downstream, and Figure 1B displays the naming of samples taken from submarine springs and their plumes. The samples collected from December 2019 were named A1, B1, C1, D1, and E1 for submarine springs A, B, C, D, and E, respectively; while A2, B2, C2, D2, and E2 were samples from January 2020. Samples were also collected from the submarine spring plume, i.e., from discharge point to surface water. Samples from discharge points were obtained from each submarine spring by inserting a 2-inch diameter PVC pipe into the center of each respective spring and the water which flowed through the pipe was captured in a low-density polyethylene plastic bag. The samples collected from these pipes were further named A1-1, A2-1, B1-1, B2-1, C1-1, C2-1, D1-1, D2-1, E1-1, and E2-1. More spring samples were collected along a vertical gradient of the submarine spring plume from bottom to the surface, as seen in Figure 1B. Samples were processed on the boat based one each parameter's requirement as soon as the divers reached the surface. Samples from submarine springs were taken between 10.00-12.00, in the period following the low

tide. Water samples for seawater/ocean end member were collected approximately 1 km in the offshore direction from the submarine spring complex.

Water sample analysis

Physical parameters were measured using a Hach Lange Multi 410d portable multimeter. Salinity and temperature were measured with a Hach CDC401 probe, while pH and dissolved oxygen (DO) were measured using Hach PHC101 and LDO101 probes, respectively. DO was measured immediately after collection to prevent contamination of atmospheric oxygen. Submarine springs and offshore water samples were measured immediately in the boat inside a sample bottle before filtration. Water samples for nutrient analyses were filtered in the field using Whatman cellulose acetate filters with a pore size of 0.45 µm and transferred into clean high-density polyethylene (HDPE) vials. For nutrient measurement (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, dissolved silica (DSi)), the samples were frozen until analysis. Nutrient analyses were conducted at the Leibniz Centre for Tropical Marine Research (Germany), using a segmented flow Skalar SANplus System Instrument for marine samples and a Tecan microtiter plate reader for freshwater samples. These samples were measured spectrophotometrically as described by Grasshoff, et al. [39]. Tecan microtiter plate reader has a limit of detection (LOD) of 12 µM (NO_3^-), 0.2 µM (NO_2^-), 4 µM (NH_4^+), 0.2 µM (PO_4^{3-}), and 1.4 µM (DSi). In this paper, dissolved inorganic nitrogen (DIN) refers to total NO_3^-, NO_2^-, and NH_4^+.

Samples for nitrogen and oxygen isotopic composition of dissolved NO_3^- ($\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$) were frozen until analysis at the Helmholtz Centre for Materials and Coastal Research, Germany. The water samples were analyzed using the denitrifier method[40,41]. NO_2^- was removed using sulfamic acid prior to N and O isotope analysis if the samples contained NO_2^- concentrations of more than 2% of the respective NO_3^- concentrations[42]. The isotopic composition was determined on a GasBench II coupled to a Delta V Advantage mass spectrometer (ThermoFinnigan). Replicate measurements were performed using two international standards (IAEA-N3, $\delta^{15}N$ =

+4.7‰, $\delta^{18}O$ = +25.6‰ and USGS 34 $\delta^{15}N$=−1.8‰, $\delta^{18}O$=−27.9‰ [43]) with each batch of samples. The standard deviation of samples and standards was < 10% for $\delta^{15}N$ and 28% for $\delta^{18}O$. To correct for exchange with oxygen atoms from water, a bracketing correction was applied based on Sigman, et al. [44]. $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ values are reported per mill (‰) relative to AIR and VSMOW, respectively. We applied a conservative mixing calculation by Fry [45] to assess the mixing pattern of groundwater and coastal NO_3^- isotopes and to detect internal sources and sinks over the course of the mixing gradient.

Samples for DOC, DOM, and total dissolved nitrogen (TDN) were filtered with 0.22 µm polyethersulfone filter, acidified with HCl to pH=2, and kept at 4°C temperature until analyzed in the laboratory of the Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Germany. DOC and TDN concentrations were measured by high-temperature catalytic oxidation (HTCO) on a Shimadzu TOC-VCPH instrument equipped with a TDN unit against a deep Atlantic seawater reference material (D.A. Hansell, University of Miami, FL, USA). Accuracy and precision were better than 5% and 15%, respectively. DON was calculated as the difference between TDN and DIN concentration. Note that this might lead to uncertainties due to the use of two different analytical methods, especially when DIN concentrations highly exceed DON concentrations[46]. Therefore, DON results have to be interpreted with caution.

Before DOM molecular composition analyses, the HCl-acidified samples were desalinated and pre-concentrated using Agilent BOND ELUT PPL cartridges following the protocol of Dittmar, et al. [47]. 50 mL subsamples were extracted into a methanol matrix of ~1.2 mL volume. DOC recovery was quantified in extract subsamples, dried in an oven to remove the methanol solvent and re-dissolved in ultrapure water acidified to pH=2 with HCl for DOC measurement. From the remainder of the DOM extracts, subsamples were diluted to a DOC concentration of 2.5 ppm in a 1:1 mixture of methanol and ultrapure water. The subsamples were then measured via flow injection on a 15T solariX XR FT-ICR-MS with electrospray ionization (ESI) in negative ionization mode, using a

HyStar Autoanalyzer. Sample mass spectra were uploaded into the online freeware ICBM-OCEAN[48] to remove instrument blanks and align samples based on their masses. Based on the elemental stoichiometry of assigned molecular formulae, ICBM-OCEAN groups them into the categories "aromatic," "highly unsaturated," "unsaturated," and "saturated." We normalized the relative abundance of each category by multiplying them with SPE-DOC concentration to determine their distribution and quantities in the DOM pool. For each assigned formula, ICBM-OCEAN also calculates an aromaticity index ($AI._{mod}$), which is indicative of the presence of aromatic ring structures in the compound. H/C and O/C molar ratios were calculated to indicate degrees of saturation and oxygenation[49]. For all of the abovementioned characteristics, intensity-weighted averages were calculated for each sample after normalizing the relative intensities of each formula to the sum of intensities of the whole respective sample.

Furthermore, for this study, we calculated molecular indices of provenance or processing which have been reported in the literature: A microbial productivity index $I_{bioprod}$[50], a DOM degradation index I_{deg}[51], a terrestrial index I_{Terr}[52], and a lability index MLB.I[53]. $I_{bioprod}$ comprises of ten ubiquitous molecular formulae associated with fresh DOM release from aquatic primary production in a controlled marine mesocosm[50]. I_{deg} consists of ten ubiquitous molecular formulae that were developed in an open ocean setting and calibrated against the Δ14C radiocarbon age of DOM[51]. I_{Terr} consists of 80 ubiquitous molecular formulae, which were significantly correlated with the salinity gradient of the Amazon estuary[52]. MLB_I index considers the H/C ratio of all molecular formulae in a sample, dividing them along a “molecular lability boundary” of H/C = 1.5[53].

Data analysis

Figure visualization and multivariate statistical analysis for DOM composition were performed in R (R version 4.0.3[54]) using 'vegan' R package version 2.5-6[55]. Correlation between environmental parameters was analyzed using Spearman correlation, and only correlations with p-value < 0.001 were considered for analysis and discussion. Non-metric multidimensional scaling (NMDS) was

performed as an ordination method for DOM molecular composition. DOM molecular indices and intensity-weighted averages of characteristics such as oxygen content, saturation, and aromaticity were mapped to the NMDS plot using *envfit*. Distance based linear model (DistLM) using the function *adonis2* was applied to relative abundances of assigned formulae in DOM to determine which environmental variables best explained the variation in DOM molecular composition.

RESULTS AND DISCUSSION

Biogeochemistry of coastal groundwater

The range of physicochemical water parameters is displayed in Figure 2, while measurement results of all samples are included in the Supplementary Material. Groundwater was characterized by medium temperature (range 26 - 30 ^{o}C), low salinity (range 0.09 - 0.19), medium to oxygenated condition (DO range 48 to 98%), and mildly acidic (range 6.3 - 7.2) water (Figure 2).

Nutrients

NO_3^- composed the major species of the dissolved nitrogen pool in the groundwater with a concentration between 29-125 µM, followed by DON (range 0-60 µM), NO_2^- (range 0-0.05 µM), and NH_4^+ (< 4 µM, below LOD) (Figure 2). NO_3^- concentration in the inland spring located on the mountain slope was slightly higher (range 78 – 142 µM, n = 2) than in the coastal groundwater (range 29 – 125 µM, n = 10). The stable isotope values for groundwater were in the range of +3.24 to +6.56 ‰ for $\delta^{15}N_{NO3-}$ and -0.49 to + 4.50 ‰ for $\delta^{18}O_{NO3}$, while the inland springs spanned a narrower range ($\delta^{15}N_{NO3-}$ range +4.06 to +4.19 ‰, $\delta^{18}O_{NO3}$ range -0.85 to + 0.46 ‰) (Figure 2, Figure 3A).

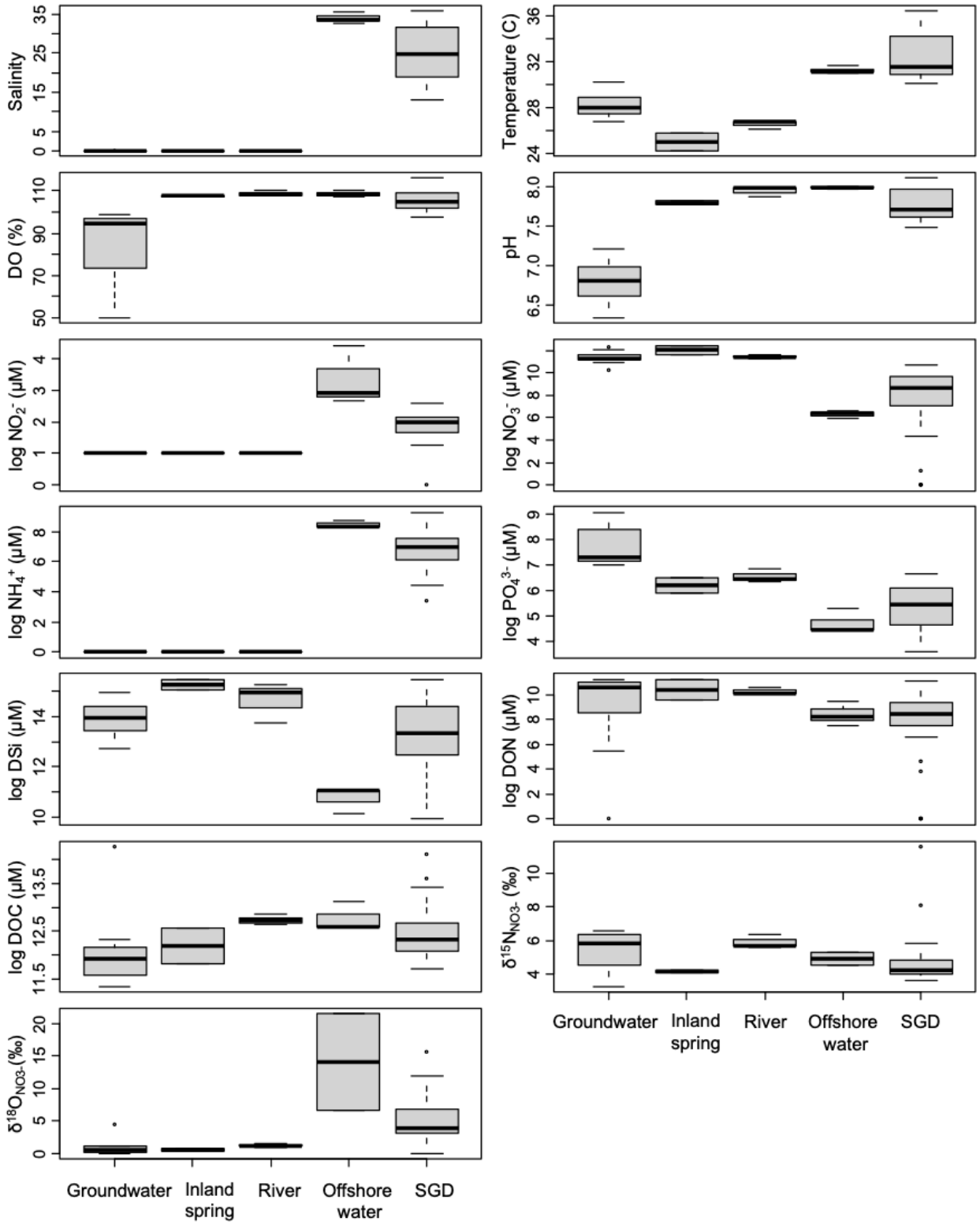


Figure 2. Concentrations of different physicochemical properties in groundwater, inland spring, river, seawater, and SGD samples. Nutrient (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, DSi, DON) and DOC concentrations are given in (log x) + 1 µM.

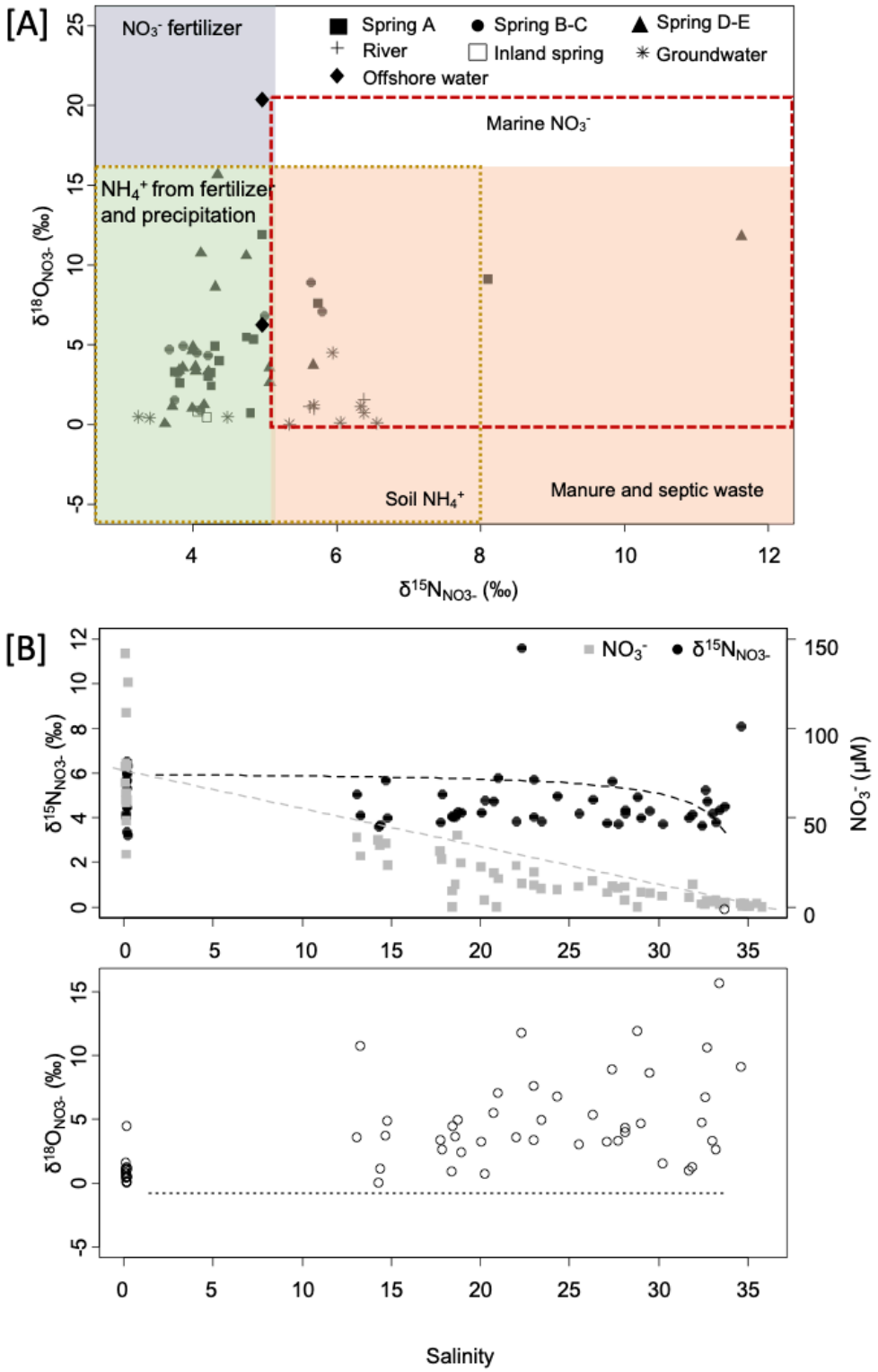


Figure 3. (A) $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ plotted in a diagram of the isotopic composition of potential NO_3^- sources, modified from Kendall, et al. [56]. (B) NO_3^- concentration and $\delta^{15}N_{NO3-}$ plotted versus salinity (top), and $\delta^{18}O_{NO3-}$ plotted versus salinity (bottom). In both figures B, dashed lines indicate theoretical conservative mixing.

The NO_3^- isotope value signatures have long been employed to determine N sources in the groundwater system. NO_3^- isotope values from coastal groundwater samples in this study are plotted in the overlapping signatures characteristic for natural and anthropogenic activities: soil NH_4^+, manure and septic waste, or NH_4^+ in fertilizer and precipitation (Figure 3A). We ruled out precipitation as the area had not received rainfall three months before the sampling activity. Soil NH_4^+ was a potential source of NO_3^- even though its concentration in groundwater was below LOD, considering NH_4^+ is usually immobile in soils due to adsorption and ion exchange to clay particles[57].

The $\delta^{15}N_{NO3-}$ signature also pointed to possible anthropogenic sources such as septic waste, manure, and fertilization. Northern Lombok only had a household sanitation coverage of roughly 80%[58]. Approximately 20% of the household do not have access to discharge their wastewater properly and might contribute to the groundwater $\delta^{15}N_{NO3}$. Manure or wastewater from livestock was also not regulated and could be a potential contribution. As for fertilization, the Ministry of Agriculture reported that farmers in Lombok used a mixture of inorganic fertilizers, i.e., urea, ZA (ammonium sulfate, 21% N and 24% S), SP-36 (superphosphate, 36% P_2O_5), and KCl (potassium chloride, 60% K_2O) to fertilize their agricultural fields two times per year[59]. Theoretically, urea and ZA could contribute to the low isotope signature, as NO_3^- that is initially formed from these fertilizers should be isotopically depleted because nitrification strongly discriminates against the heavy isotope species. Overall, we could not delineate specific sources of groundwater NO_3^- based on $\delta^{15}N_{NO3-}$ signature alone. However, the highly elevated PO_4^{3-} concentration (3.20-13.20 µM), which exceeded the environmental regulation limit for groundwater[60], points towards anthropogenic contamination.

If anthropogenic sources indeed contaminate the coastal area, we expect higher groundwater NO_3^- concentration in the cultivated downstream area than in the pristine upstream area. On the other hand, we presume that there are other sources other than the inland springs we sampled feed into the coastal aquifer. These other sources may contain low NO_3^- concentration and dilute

295 NO_3^- concentration in the downstream area relative to inland spring NO_3^- concentration. A locally
296 important contribution of additional water sources was also supported by considerable scatter on
297 the NO_3^- isotope data in Figure 3A. Considering the coastal land use map where the downstream
298 area consists of agriculture and plantation (Figure 1A), we propose that anthropogenic sources
299 contribute to groundwater NO_3^- concentration in the downstream area; however, their contributions
300 were weakened by different water input to the coastal aquifer.
301 The relatively low $\delta^{18}O_{NO3-}$ values (< 5‰) in coastal groundwater samples suggests the occurrence
302 of nitrification, which was also supported by high NO_3^- concentration and low NH_4^+ concentrations.
303 $\delta^{18}O_{NO3-}$ of newly generated NO_3^- is tied to ambient water, making $\delta^{18}O_{NO3}$ a sensitive marker of
304 nitrification. We did not find evidence for parallel evolution of $\delta^{18}O_{NO3-}$ and $\delta^{15}N_{NO3-}$ along a 1:1 line
305 in groundwater samples, which was usually a strong signal of denitrification process. All the
306 sampled groundwater samples were oxic; however, their DO saturation ranged between 49% to
307 98%, indicating oxygenated groundwater condition was not homogenous across the downstream
308 area. Therefore, denitrification of groundwater NO_3^- in the coastal aquifer was plausible, as
309 theorized by Oehler, et al. [12].
310 Groundwater PO_4^{3-} concentration in this study was similar compared to two years prior[12], which
311 was in a higher range than other sites in Indonesia[61]. High PO_4^{3-} concentration can be attributable
312 to fertilizer or wastewater input, both were presumably contributed to the elevated groundwater
313 NO_3^- concentration as well. In addition, natural sources also affect soluble PO_4^{3-} concentration in
314 groundwater. A recent study conducted in western Lombok found that in the absence of NH_4^+
315 concentration in some parts of the island, the elevated groundwater PO_4^{3-} concentration was
316 derived from the dissolution of hydroxyapatite and/or vivianite minerals, which originated from
317 volcanic lava deposits of Mount Rinjani [62].
318 DSi concentrations in the coastal groundwater were in a range of 170-780 μM; however, two inland
319 spring samples from the mountain slope had DSi concentrations up to 1140 μM (Table 1, Figure
320 2). These inland springs receive their water from recharge at the slopes of Mt. Rinjani, and the

DSi enrichment in these samples is most likely due to water-rock interactions in the volcanic aquifer[63]. The different lithology between the mountain slope and coastal area can explain the one magnitude DSi concentration difference between inland spring and coastal groundwater. For instance, while the mountain slope aquifer is composed of quaternary volcanic rocks resulting in elevated DSi concentration, the coastal aquifer is presumably characterized by a mix of volcanic rocks and alluvial sand, which usually has a lower DSi range, e.g., 200 - 300 μM[64]. The varying DSi concentration supports the previous notion that coastal groundwater was fed by several water sources besides the inland springs we sampled.

DOC and DOM

Coastal groundwater was characterized by DOC concentrations in the range of 65-200 μM, while DON concentrations were between 0-60 μM. Figure 4A shows that the DOM pool in groundwater was divided evenly between labile formulae (i.e., unsaturated aliphatic and saturated formulae) and the less labile formulae (i.e., highly unsaturated and aromatic formulae[53]). The unsaturated aliphatics had the highest average relative composition of 48%, followed by highly unsaturated (average relative contribution 41%), saturated (average relative contribution 6%), and aromatic formulae (average relative contribution 4%). The prevalence of unsaturated aliphatics in groundwater was consistent with previous studies conducted in fissured aquifers, where DOM tends to be enriched with labile, unsaturated aliphatic compounds in this geological setting[19,65]. The low abundances of aromatic formulae in the volcanic aquifer can be caused by the soil column's retention as aromatic-rich surface water percolates into the aquifer[66]. DOM sorption to soils, especially to iron hydroxides abundantly found in volcanic soil, can efficiently remove aromatics and carboxyl moieties[67,68]. In these cases, preferential sorption of the hydrophobic fraction of aromatic DOM, which consists of high molecular weight, humic substances, and vascular plant-derived matters, causes the aquifer to contain more aliphatic organic matter relative to surface water[69].

Freshwater samples were characterized by high indices of $I_{bioprod}$, MLB.I, H/C ratios, and I_{Terr} (Figure 4B, Supplementary Material). The occurrence of simultaneously high lability indices (MLB.I, and H/C ratios) with high microbial production ($I_{bioprod}$) in groundwater samples indicates that labile DOM was autochthonously produced in the aquifer[19,65] or in the soils before entering the aquifer by microbial activities[70]. For example, soil fungi and bacteria are found to be capable in altering and remineralizing DOM components during their percolation through the soil[71]. Biologically reworked DOM in soils tend to be hydrogenated (high H/C ratios) and less likely to be retained by soil minerals, resulting in elevated H/C ratio in groundwater DOM[70].

A surprisingly high I_{Terr} index was observed in the groundwater samples (range 0.54 - 0.76), even comparable to river samples (ranged 0.63 - 0.69). A high groundwater I_{Terr} index is usually associated with peat-influenced groundwater[72], which was not the case in Lombok. As I_{Terr} calculation was originated from Amazonian surface water samples[52], it is usually correlated to high aromaticity and may not be suitable to characterize groundwater attributes, as also observed in another STE study[73]. In contrast to groundwater samples, river samples contained elevated aromatic compound abundances, up to twofold higher than any other type of sample (Figure 4A). This finding is attributable to the fact that most aromatic pool is composed of vegetal or plant-derived organic matter directly deposited in the rivers through leaf litter.

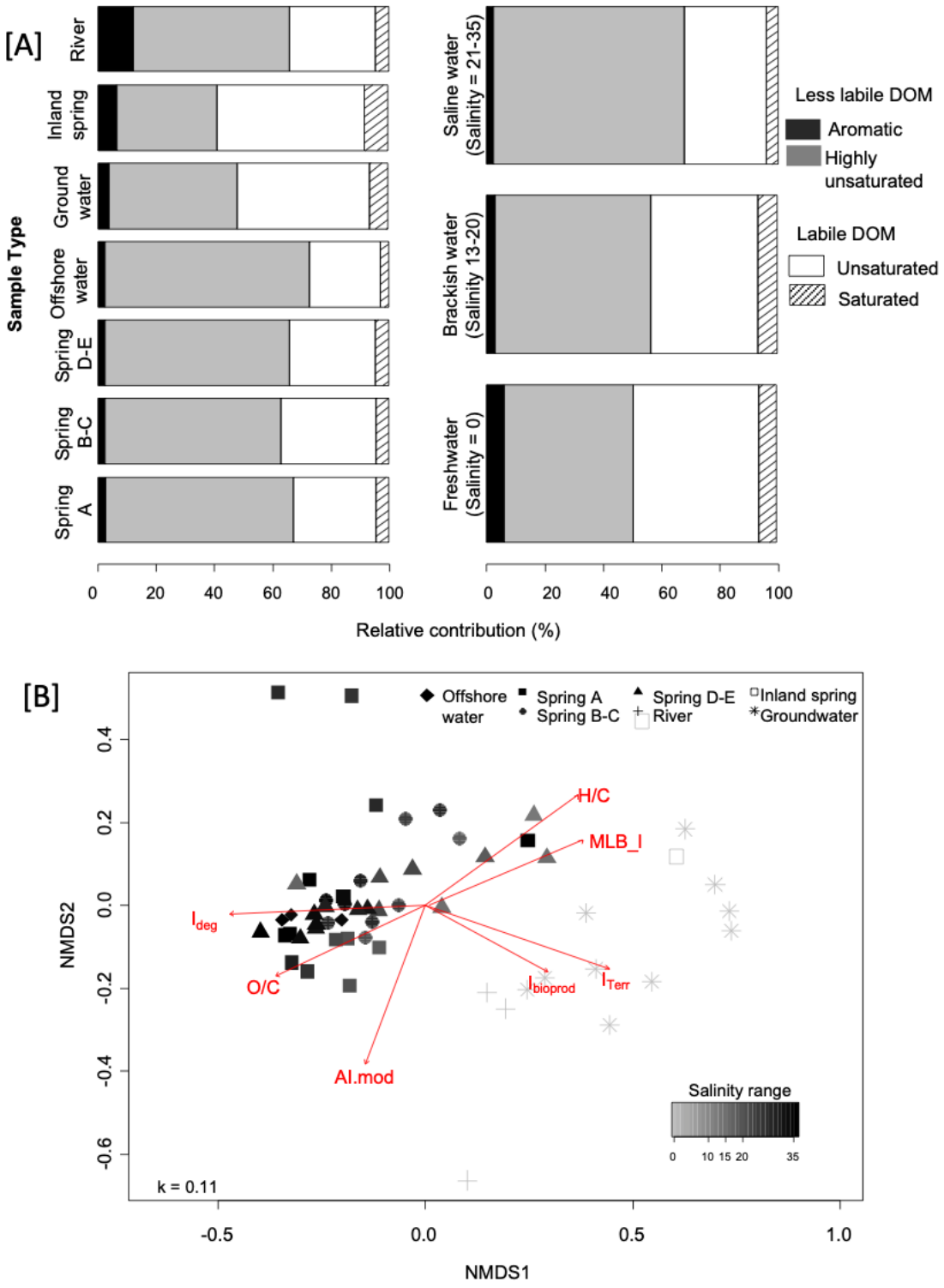


Figure 4. (A) Relative, intensity-weighed contributions of DOM molecular groups across end members and samples. (B) NMDS plot based on Bray-Curtis dissimilarity of the relative abundance of all DOM molecular formulae in each sample, color coded by respective sample salinities (bottom). Red arrows indicate the association of specific DOM molecular characteristics (indices, elemental ratios, aromaticity) with different sample groups.

An NMDS plot based on DOM molecular composition shows that the samples were grouped by their salinity (Figure 4B). All the freshwater samples such as groundwater, river, and inland spring samples were plotted on the right side of NMDS. Samples collected from discharge points were plotted in the middle of the plot, while the high salinity samples were clustered on the opposite side of freshwater samples. DistLM results applied to all samples indicated that differences in salinity and temperature shaped the DOM molecular composition shift. In total, 25.59% of DOM composition variability was explained by the observed parameters (Table 1). Salinity was the most significant contributor shaping DOM molecular composition distribution between these parameters with up to 13.49% contribution. Interestingly, a similar approach applied to only SGD samples resulted in almost identical outcomes, where salinity and temperature were the determinant contributors. DistLM applied to freshwater samples shows that pH was the primary variable explaining DOM molecular composition with 23.49% total explainable variances. This finding is consistent with other studies investigating pH as the main driver of the molecular differences between DOM, particularly in terrestrial surface and pore water[74,75]. We did not find significant results when conducting this approach for groundwater samples only.

Overall, all of DistLM calculations resulted in a total explainable variance of below 30%, suggesting that additional factors may control the DOM molecular distribution that we did not measure or analyze (i.e., source heterogeneity). Such factors include soil type, microbial transformations, or other abiotic processes such as flocculation, adsorption, desorption and photochemistry[76,77]; the latter particularly could be significant in seawater.

Table 1. Contribution and significance of observed environmental factors shaping DOM composition based on DistLM

Source of variation	Adjusted R^2 (%)	Df	F	p-value
All samples				
Final model	25.59	2	8.47	0.001 ***
Salinity	13.49	1	8.89	0.001 ***
Temperature	5.38	1	3.55	0.001 ***
SGD samples				
Final model	22.37	2	4.61	0.001 ***
Salinity	14.07	1	5.80	0.001 ***
Temperature	12.69	1	5.23	0.001 ***
Fresh water samples (groundwater, inland spring, river)				

Source of variation	Adjusted R^2 (%)	Df	F	p-value
Final model	23.49	1	1.84	0.001 ***
pH	14.62	1	1.29	0.001 ***

393

394 **Biogeochemistry of submarine springs and reef water column**

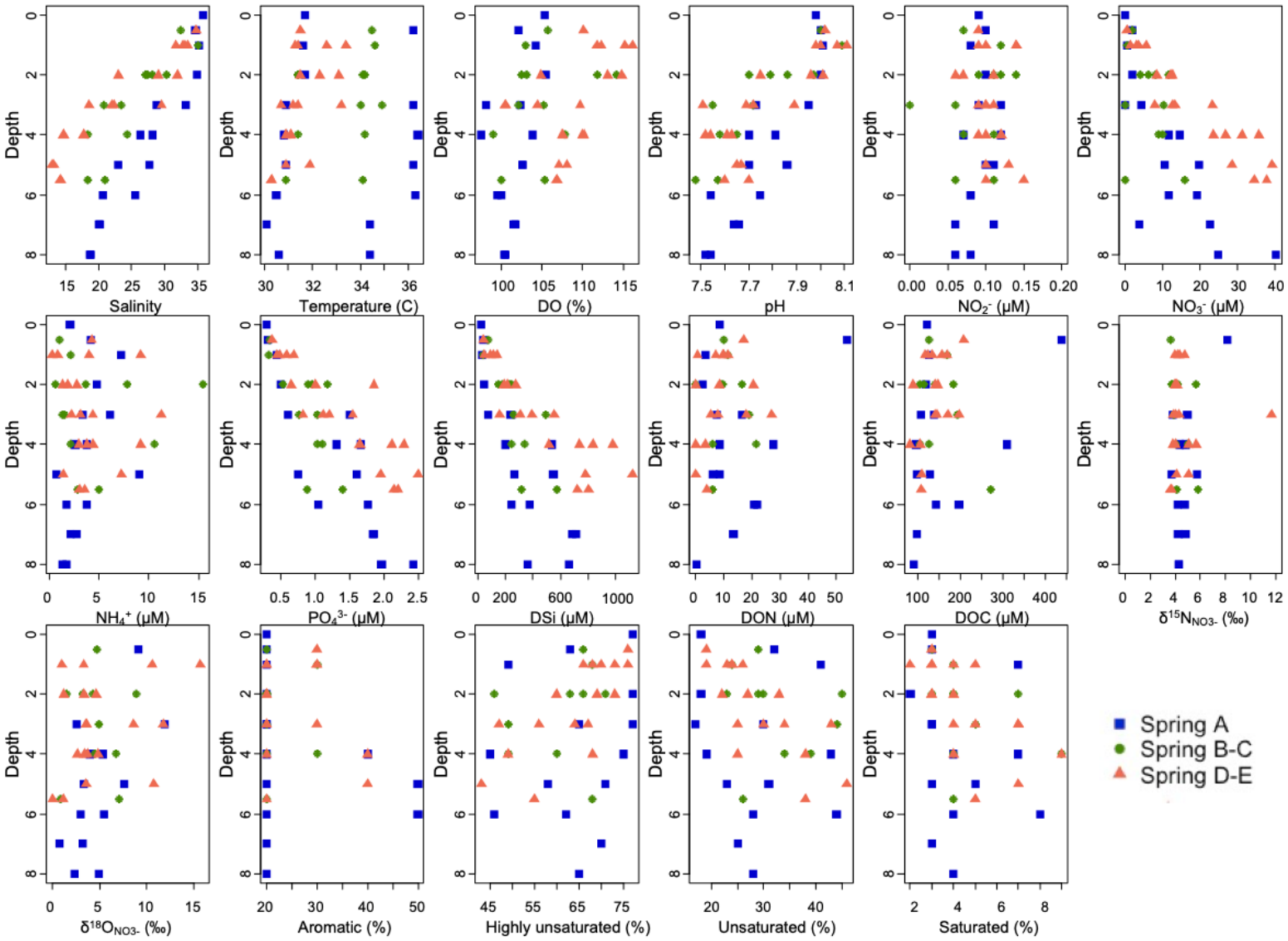
395 *Submarine spring groundwater source*

396 A previous study in northern Lombok found that nutrient concentrations behaved non-
397 conservatively between fresh groundwater on land and discharging groundwater in the reef, i.e.,
398 e.g., NO_3^- removal by denitrification or biological uptake [12]. It was observed that the underlying
399 mechanisms for these dynamics are either reactions in the coastal aquifer and the STE or different
400 sources of water for the submarine springs. This study provides detailed insights into the
401 previously hypothesized processes.

402 In general, submarine springs and reef water columns were characterized with warmer
403 temperature than coastal groundwater (range 30 – 36 °C), medium pH (range 7.4 – 8.1), and
404 oxygenated conditions (range 90-115%) (Figure 2). Salinity increased from brackish in the SGD
405 discharge points (salinity = 13 - 20) to marine salinity at the surface water (salinity = 35) (Figure
406 5). Salinity was more enriched in the submarine spring discharge points (salinity = 13 - 20) than
407 in groundwater (salinity = 0) due to recirculated seawater in the STE. In every spring, salinity and
408 pH increased from the discharge point towards the surface water (Figure 5). This pattern was
409 followed by temperature and DO, albeit with a slighter increase. Our data revealed that
410 groundwater discharging via submarine springs generally had a lower pH than the surrounding
411 reef water. A pH as low as 7.7 is considered a threat to the coral reef system, as it is detrimental
412 to calcifier recruitment and reef builders[78]. Therefore, the relatively low pH delivered by SGD may
413 promote coral acidification in the long term in this ecosystem.

414 The geochemistry of groundwater discharging via submarine springs differed between locations,
415 particularly in salinity, DSi concentration, and DOM composition. Figure 5 shows that Springs D-
416 E had slightly lower salinity at the discharge point (i.e., D1 and E1, salinity = 13-14) compared to
417 Springs A, B, and C (salinity = 18-20) in both of sampling periods. The different pattern between

Springs A, B, C and Springs D-E discharge points was also displayed by DSi concentrations, where its concentration ranged between 246 - 712 µM in Springs A, B, and C, while DSi concentrations in Springs D-E amounted to 720 - 1121 µM or almost thrice the concentration in Spring A. This concentration was higher than expected based on conservative mixing and even comparable with the range of springs sampled in the hinterland at the lower slope of Mt. Rinjani. Characteristics revealed by the DOM molecular properties also showed that the discharge points of Springs D-E had a higher relative proportion of labile molecular formulae compared to Springs A, B, and C (Figure 5). The possible explanations for this finding were (1) specific processes occurred in the STE of Springs D-E adding significant amount of DSi, such as dissolution of lithogenic particles or biogenic silica[79], and/or (2) Springs D-E were fed by different sources than Springs A, B, C. This would support previous reports of different groundwater sources feeding the spring complex by Oehler, et al. [12]. For instance, this study found that Spring A had a similar $\delta^{18}O$-H_2O and radon signature with coastal groundwater; thus, it potentially received groundwater from the coastal catchment area. In contrast, Springs D-E may have received water from confined or semi-confined aquifers in the hinterland as they consisted of heavier $\delta^{18}O$-H_2O isotopic composition and had higher radon activities. The different aquifers feeding coastal water are reportedly typical for tropical volcanic islands[80].



436

437 Figure 5. Vertical depth profile of physicochemical parameters in submarine springs.

Nutrients

Nutrient samples were collected from the submarine spring plumes, i.e., from discharge point to surface water, from two sampling periods. Statistical analyses showed no significant difference in dissolved inorganic nutrient concentrations between two sampling periods (Wilcox test, n = 66, p > 0.05). DON composed the major species of the dissolved nitrogen pool in the submarine springs and reef water with a concentration between 0 - 54 μM, followed by NO_3^- (range 0-40 μM), NH_4^+ (range 0-15 μM), and NO_2^- (0-0.15 μM) (Figure 2).

In submarine springs and reef water columns, NO_3^- concentration was one magnitude lower than in coastal groundwater. In general, NO_3^- concentration had a significant correlation with salinity (Spearman ρ = - 0.87, n = 66, p-value < 0.001), which indicates that NO_3^- in the submarine springs originated from the groundwater. NO_3^- concentrations were elevated at the discharge point of submarine springs; however, its relative composition in the bulk N decreased towards higher salinity and reached 0 μM in the sampling points closest to the surface (Figure 5).

$\delta^{15}N_{NO3-}$ values were almost uniform on either end of the salinity scale (Figure 3B). The majority of $\delta^{15}N_{NO3-}$ values in submarine springs and reef water column (+3‰ to + 5‰) was similar with $\delta^{15}N_{NO3-}$ in coastal groundwater, indicating similar, terrestrial NO_3^- origin. The $\delta^{18}O_{NO3-}$ values in submarine springs and reef water (range -4‰ to +15‰) were generally distributed over a wider range and were enriched in comparison to coastal groundwater (range -0‰ to +4‰).

Despite uncertainties regarding the inland source end-member assessment, we find that within the submarine springs and reef water column, NO_3^- concentration plotted against theoretical mixing line suggested non-conservative behavior. We rule out two NO_3^- sink pathways, i.e., denitrification or dissimilatory nitrate reduction to ammonia (DNRA), in the reef water column due to the well-mixed, oxygenated condition in the water column. However, no data were available for the intermediate salinity range from 1 to 15, which would occur in the STE. Therefore, we could not exclude possible denitrification or DNRA in this salinity interval. For example, denitrification could occur in the anoxic pockets of the STE sediments, and it would not result in any apparent

isotopic fractionation in the water samples because the diffusion of NO_3^- into reactive sediment zones is the rate-limiting step[81].

Figure 3B also shows that both $\delta^{15}N_{NO3-}$ and $\delta^{18}O_{NO3-}$ values deviated from the theoretical conservative mixing line. $\delta^{15}N_{NO3-}$values were slightly below the mixing line, while $\delta^{18}O_{NO3-}$ values were generally enriched compared to conservative mixing. We did not observe any specific pattern of depth or discharge from specific springs in the scatter plots. The low $\delta^{15}N_{NO3-}$ values in the submarine springs and reef water, i.e., below the average marine $\delta^{15}N_{NO3-}$ of +5 ‰ in the region[82], could be explained by: (1) a balance between consumption (assimilation, denitrification) that may isotopically enrich NO_3^- and NO_3^- production (nitrification) that may reduce the isotopic value, or (2) the prevalence of N_2 fixation.

The (albeit low) increase in NO_2^- concentration in Figure 5 suggests active NO_3^- turnover in the reef water column. However, we did not find a clear trend in the enrichment of $\delta^{15}N_{NO3-}$ versus $\delta^{18}O_{NO3-}$, which would be inarguable proof of active consumption. We found a slight relative enrichment of $\delta^{18}O_{NO3-}$ versus $\delta^{15}N_{NO3-}$ along a slope of ~ 0.8: 1. Enrichment is close to the slope of 1: 1 that is proposed for NO_3^- assimilation. We assume that assimilation occurs in the water column but that the isotope signatures of N and O are partly decoupled due to the co-occurrence of nitrification and assimilation in the water column[83]. Additional isotopically light N might derive from N_2 fixation, consistent with the elevated NH_4^+ concentration and the low DIN: PO_4^{3-} ratio in reef surface water.

In contrast with NO_3^-, NO_2^- and NH_4^+ were generally enriched in the submarine springs and reef water compared to groundwater (Figure 2). NO_2^- concentrations were below 0.05 μM in all groundwater samples, while its concentration was between 0.05 - 0.5 μM in submarine springs and reef water columns and appeared stable throughout the SGD vertical depth profile (Figure 5). The relatively higher concentration of NO_2^- was presumably related to the active turnover of NO_3^- in the water columns. Meanwhile, NH_4^+ concentrations ranged between 0-15 μM in the submarine springs and reef water columns, compared to its concentration below LOD in all groundwater

samples. However, we observe slight enrichment of NH_4^+ vertical depth profile (Figure 5), which can be attributable to the production of NH_4^+ from the mineralization of marine organic matter [84]. NH_4^+ is also commonly found as a DOM photoproduct[85,86], which may define their slight enrichment in the upper level of the seawater column and offshore water (Figure 2). The enrichment of NH_4^+ in the reef water column is rather surprising, considering NH_4^+ is usually preferred by phytoplankton or other heterotrophic microorganisms over NO_3^-. We assume that the uptake and recycling of NH_4^+ in the upper water column are partially inhibited by light limitation of nitrifiers or varying DIN preferences depending on the biota species [87].

Like NO_3^-, PO_4^{3-} concentrations in submarine springs and reef water were one magnitude lower than in coastal groundwater (Figure 2). Overall, PO_4^{3-} concentration was negatively correlated with salinity (Spearman ρ = - 0.88, n = 66, $p < 0.001$) and PO_4^{3-} concentration plotted against salinity suggested non-conservative behavior. During its transport from land to ocean, PO_4^{3-} could be attenuated in the STE as it has high affinity with iron oxide[88], which was potentially abundant in a volcanic island. In the reef water, SGD vertical depth profile shows higher PO_4^{3-} concentration in deeper depth/SGD discharge points compared to surface water (Figure 5). Coupled with non-conservative mixing behavior, this finding indicates possible PO_4^{3-} biological uptake in the water column. At the time of our sampling expedition, DIN: PO_4^{3-} ratios of brackish and saline samples were in the range of 1 – 28, with P-limitation occurring in samples taken close to submarine springs and N-limitation dominating in the surface seawater column.

Overall, findings from nutrient data suggest that in a well-mixed, sunlit coastal water, groundwater-derived nutrients may experience rapid turnover from the discharge point to the surface water column.

DOC and DOM

In submarine springs and reef water column, DOC and DON were measured in the range of 82 – 437 µM and 0 - 54 µM, respectively. Overall, the molecular composition of DOM in submarine

springs and reef water was distinctly different from that in the groundwater samples (Figure 4A). For example, the relative contribution of all formulae shifted from groundwater samples to SGD discharge points: aromatics (4% to 2%), highly unsaturated (44% to 58%), unsaturated (45% to 34%), and saturated (6% to 4%). In general, the biggest relative contribution shifts were experienced by highly unsaturated (14% increase) and unsaturated compounds (11% decrease) during their transport in the STE. In the same interval, we also observed a decrease of DON (130 to 110 μM) and an increase of I_{deg} from lower to higher degradation state (0.2 to 0.4). This finding suggests that the DOC supplied by the groundwater, mostly the labile ones, was actively utilized or degraded in the STE. Furthermore. the slight removal of aromatic compounds could be attributable to adsorption to iron oxide in the STE[89].

In the submarine springs and reef water, DOC concentration was also mostly homogenous along the SGD vertical depth profile, except for mid- and upper- depth samples from Spring A (Figure 5). Therefore, tight coupling is assumed between DOC consumption and production in the reef water. The less labile fraction dominated DOM composition in the reef water column: the highly unsaturated formulae were prevalent in all submarine springs and reef water column with an average relative contribution of 63% (Figure 4A), and their proportion increased from deeper towards the upper layer of reef water, particularly in Springs D-E (Figure 5). Unsaturated aliphatics composed the second-highest composition of these samples (average relative contribution of 30%), followed by saturated (average relative contribution 4%) and aromatic (average relative contribution of 3%) formulae (Figure 4A). The unsaturated aliphatic relative composed 30% relative contribution of reef water samples indicates that labile DOC was produced in the reef water, e.g., from phytoplankton or reef organisms[90]. As aromatic compounds in this study were highly enriched in river water, their low abundance in reef water indicates no surface runoff contribution to the coral reef ecosystem at the time of our study.

Submarine springs and reef water DOM samples were distinguished by relatively high O/C ratios and an elevated degradation index (I_{deg}) (Figure 4B). A simultaneous increase of I_{deg} and highly

unsaturated formulae in the vertical depth profile indicates increasing amounts of reworked DOM from the bottom to the top layer of the water column. The enrichment of less labile formulae could originate from rapid microbial degradation of labile compounds[91], reef production[90] or physical processes such as remineralization or photochemical activity. We also cannot rule out the influence of horizontal water exchange with the open sea, as the oceanic endmember had the highest relative contribution of highly unsaturated formulae (Figure 4A). The highly unsaturated formulae could consist of carboxyl-rich alicyclic molecules (CRAM), a type of degraded DOM often found in the open sea that derives from non-aromatic OM decomposition[92,93] or photochemical products in seawater[94,95]. CRAM in the coral reef ecosystem can be resistant to degradation on the scale of weeks[96] to months[90].

Implications for the coral reef ecosystem

Considering the socio-anthropogenic development in northern Lombok, it is surprising how consistent some of the nutrient concentrations behave with time. While nutrient concentrations in karstic coastal aquifers usually vary over time scales of days to weeks[97], the result from Spring A showed similar salinity, DSi, and NO_3^- concentrations when compared with the study by Oehler, et al. [12], where samples were taken four years ago during a different season. Therefore, we assume that the submarine springs provide a constant delivery of DSi, NO_3^-, and PO_4^{3-} into the coral reef regardless of the season.

In this study, we observe anthropogenic influence on the groundwater system in Lombok. An annual population growth of 1.1% per year and an urbanization rate of 5.5% per year is predicted for Lombok, which is even faster than the Indonesian megacity of Jakarta[98]. Therefore, it is likely that inputs of anthropogenic pollutants to groundwater, and hence via SGD to coastal water, will increase. At the study site, the early symptoms of coral health disturbance have already been discovered: a local study found an elevated algal cover on the coral reef in Spring A[37]. In this location, algae cover 30.85% of the total coral ecosystem, compared to 19.21% coverage in

Springs B-C. In many cases, the algal cover was attributable to excess nutrients and DOC, particularly labile DOC, as they stimulate the growth of non-calcifying turf algae and fleshy macroalgae[99]. In the long term, an increase of algal cover instead of calcifying organisms may cause the prevalence of copiotrophic organisms and often potentially virulent microbial populations[100]. Therefore, future environmental management should include measuring nutrient and organic matter concentration to prevent coral mortality cases.

CONCLUSIONS

Overall, our study points to the role of SGD in delivering nutrients and labile DOM into the coral reef ecosystem. We observed that the composition of nutrient and DOM pool transported by SGD changed in the submarine springs and reef water due to biology (fixation, production, and uptake), hydrology (dilution, mixing), and diagenetic processing (degradation). This study may lay a foundation for more in-depth research on groundwater sources and pathways, SGD-derived nutrients and DOM bioavailability and uptake potential in the coral reef, and subsequently the association between SGD and coral health. In particular, other countries in the Coral Triangle marine area are categorized as either low or middle economy countries, usually associated with densely populated coastal areas with limited environmental measures for land-based pollution. However, as far as we know, only two studies associating SGD-derived anthropogenic nutrients with the coral reef ecosystem in this region, i.e., in Indonesia[12] and the Philippines[101]. Going forward, considering coral reef ecosystems is highly sensitive to terrestrial anthropogenic activities and global climate change, strong attention has to be paid to addressing these knowledge gaps not only in the Coral Triangle region but also in similar tropical ecosystems worldwide.

Acknowledgment

We are grateful for the assistance in the field by Dr. Eko Pradjoko and Dr. I Wayan Yasa from University of Mataram, as well as student assistants Anisa Nindyasari, Fawqa Anugerah, Alan

Maulana, and Jarrid Tschaikowski for their help in sample collection. We thank Matthias Birkicht (ZMT), Markus Ankele (HZG), Ina Ulber (ICBM), Matthias Friebe (ICBM), and Katrin Klaproth (ICBM) for their assistance with nutrient, NO_3^- isotope, DOC, and DOM analyses. DA is funded by the German Research Foundation through Walter Benjamin Fellowship (#446330207). HW is funded by the Niedersächsisches Ministerium für Wissenschaft und Kultur (MWK) in the scope of project "BIME" (ZN3184). This project was funded by German Federal Ministry for Education and Science (BMBF Grant No #01LN1307A to Nils Moosdorf).

Supporting Information

The supporting information (Supplementary Table on Data Measurement and DOM Molecular Composition for each of the samples) is available free of charge via the internet at https://pubs.acs.org/.

References

1 Church, T. M. An underground route for the water cycle. *Nature* **380**, 579-580 (1996).
2 Moore, W. S. The effect of submarine groundwater discharge on the ocean. *Annual review of marine science* **2**, 59-88 (2010).
3 Kwon, E. Y. *et al.* Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model. *Geophysical Research Letters* **41**, 8438-8444 (2014).
4 Luijendijk, E., Gleeson, T. & Moosdorf, N. Fresh groundwater discharge insignificant for the world's oceans but important for coastal ecosystems. *Nature communications* **11**, 1-12 (2020).
5 Slomp, C. P. & Van Cappellen, P. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* **295**, 64-86 (2004).
6 Windom, H. L., Moore, W. S., Niencheski, L. F. H. & Jahnke, R. A. Submarine groundwater discharge: A large, previously unrecognized source of dissolved iron to the South Atlantic Ocean. *Marine Chemistry* **102**, 252-266 (2006).
7 Kim, J. & Kim, G. Inputs of humic fluorescent dissolved organic matter via submarine groundwater discharge to coastal waters off a volcanic island (Jeju, Korea). *Scientific reports* **7**, 1-9 (2017).
8 Boehm, A. B., Shellenbarger, G. G. & Paytan, A. Groundwater discharge: potential association with fecal indicator bacteria in the surf zone. *Environmental science & technology* **38**, 3558-3566 (2004).
9 Paerl, H. W. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. *Limnology and oceanography* **42**, 1154-1165 (1997).

10 Lecher, A. L. & Mackey, K. R. Synthesizing the effects of submarine groundwater discharge on marine biota. *Hydrology* **5**, 60 (2018).
11 Carruthers, T. J. B., van Tussenbroek, B. I. & Dennison, W. C. Influence of submarine springs and wastewater on nutrient dynamics of Caribbean seagrass meadows. *Estuarine, Coastal and Shelf Science* **64**, 191-199, doi:https://doi.org/10.1016/j.ecss.2005.01.015 (2005).
12 Oehler, T. *et al.* Nutrient dynamics in submarine groundwater discharge through a coral reef (western Lombok, Indonesia). *Limnology and Oceanography* **64**, 2646-2661 (2019).
13 Moosdorf, N., Stieglitz, T., Waska, H., Dürr, H. H. & Hartmann, J. Submarine groundwater discharge from tropical islands: a review. *Grundwasser* **20**, 53-67 (2015).
14 Elvidge, C. D. *et al.* Radiance calibration of DMSP-OLS low-light imaging data of human settlements. *Remote Sensing of Environment* **68**, 77-88 (1999).
15 Fabricius, K. E. Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. *Marine Pollution Bulletin* **50**, 125-146, doi:https://doi.org/10.1016/j.marpolbul.2004.11.028 (2005).
16 D'Angelo, C. & Wiedenmann, J. Impacts of nutrient enrichment on coral reefs: new perspectives and implications for coastal management and reef survival. *Current Opinion in Environmental Sustainability* **7**, 82-93, doi:https://doi.org/10.1016/j.cosust.2013.11.029 (2014).
17 Kline, D. I., Kuntz, N. M., Breitbart, M., Knowlton, N. & Rohwer, F. Role of elevated organic carbon levels and microbial activity in coral mortality. *Marine Ecology Progress Series* **314**, 119-125 (2006).
18 Kuntz, N. M., Kline, D. I., Sandin, S. A. & Rohwer, F. Pathologies and mortality rates caused by organic carbon and nutrient stressors in three Caribbean coral species. *Marine Ecology Progress Series* **294**, 173-180 (2005).
19 Tedetti, M., Cuet, P., Guigue, C. & Goutx, M. Characterization of dissolved organic matter in a coral reef ecosystem subjected to anthropogenic pressures (La Réunion Island, Indian Ocean) using multi-dimensional fluorescence spectroscopy. *Science of the total environment* **409**, 2198-2210 (2011).
20 Nelson, C. E. *et al.* Fluorescent dissolved organic matter as a multivariate biogeochemical tracer of submarine groundwater discharge in coral reef ecosystems. *Marine Chemistry* **177**, 232-243 (2015).
21 Hedges, J. I. *et al.* The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic geochemistry* **31**, 945-958 (2000).
22 Koch, B. P., Witt, M., Engbrodt, R., Dittmar, T. & Kattner, G. Molecular formulae of marine and terrigenous dissolved organic matter detected by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Geochimica et Cosmochimica Acta* **69**, 3299-3308 (2005).
23 Longnecker, K. & Kujawinski, E. B. Composition of dissolved organic matter in groundwater. *Geochimica et Cosmochimica Acta* **75**, 2752-2761 (2011).
24 Osterholz, H., Kirchman, D. L., Niggemann, J. & Dittmar, T. Environmental drivers of dissolved organic matter molecular composition in the Delaware Estuary. *Frontiers in Earth Science* **4**, 95 (2016).
25 Lusk, M. G. & Toor, G. S. Dissolved organic nitrogen in urban streams: biodegradability and molecular composition studies. *Water research* **96**, 225-235 (2016).
26 Seidel, M. *et al.* Benthic-pelagic coupling of nutrients and dissolved organic matter composition in an intertidal sandy beach. *Marine Chemistry* **176**, 150-163 (2015).
27 Schmidt, F., Elvert, M., Koch, B. P., Witt, M. & Hinrichs, K.-U. Molecular characterization of dissolved organic matter in pore water of continental shelf sediments. *Geochimica et Cosmochimica Acta* **73**, 3337-3358 (2009).

28 Lechtenfeld, O. J. *et al.* Molecular transformation and degradation of refractory dissolved organic matter in the Atlantic and Southern Ocean. *Geochimica et Cosmochimica Acta* **126**, 321-337 (2014).
29 Rossel, P. E., Bienhold, C., Boetius, A. & Dittmar, T. Dissolved organic matter in pore water of Arctic Ocean sediments: Environmental influence on molecular composition. *Organic Geochemistry* **97**, 41-52 (2016).
30 Seitzinger, S. P. *et al.* Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections. *Estuaries* **25**, 640-655, doi:10.1007/BF02804897 (2002).
31 Adyasari, D. *et al.* Anthropogenic impact on Indonesian coastal water and ecosystems: Current status and future opportunities. *Marine Pollution Bulletin* **171**, 112689, doi:https://doi.org/10.1016/j.marpolbul.2021.112689 (2021).
32 Asian Development Bank. State of the Coral Triangle: Indonesia 84 (Asian Development Bank Manila, Philippines, 2014).
33 Nugraha, G. U., Bakti, H., Lubis, R. F., Sudrajat, Y. & Arisbaya, I. Aquifer vulnerability in the Coastal Northern Part of Lombok Island Indonesia. *Environment, Development and Sustainability*, doi:10.1007/s10668-021-01459-0 (2021).
34 Matrais, I. B., Pfeiffer, D., Soekardi, R. & Stach, L. *Hydrogeology of the island of Lombok (Indonesia)*. (Schweizerbart, 1972).
35 Lestiana, H., Sukristiyanti, S., Bakti, H. & Lubis, R. F. PEMANFAATAN BAND TERMAL CITRA LANDSAT UNTUK IDENTIFIKASI KELUARAN AIRTANAH LEPAS PANTAI (KALP) DI PANTAI UTARA LOMBOK. *2017* **27**, 11, doi:10.14203/risetgeotam2017.v27.422 (2017).
36 Lubis, R. F., Bakti, H. & Suriadarma, A. Submarine groundwater discharge in Indonesia. *Jurnal RISET Geologi dan Pertambangan* **21**, 57-62 (2011).
37 Johan, O., Kusumah, G. & Wisha, U. J. Kondisi Terumbu Karang di kawasan KALP Pantai Krakas, Lombok Utara. *Jurnal Segara* **13**, doi:http://dx.doi.org/10.15578/segara.v13i3.6548 (2017).
38 Moosdorf, N. & Oehler, T. Societal use of fresh submarine groundwater discharge: An overlooked water resource. *Earth-Science Reviews* **171**, 338-348 (2017).
39 Grasshoff, K., Kremling, K. & Ehrhardt, M. *Methods of seawater analysis*. (John Wiley & Sons, 2009).
40 Sigman, D. M. *et al.* A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical chemistry* **73**, 4145-4153 (2001).
41 Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. & Hilkert, A. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Analytical Chemistry* **74**, 4905-4912 (2002).
42 Granger, J. & Sigman, D. M. Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry* **23**, 3753-3762 (2009).
43 Böhlke, J., Mroczkowski, S. & Coplen, T. Oxygen isotopes in nitrate: New reference materials for 18O: 17O: 16O measurements and observations on nitrate-water equilibration. *Rapid Communications in Mass Spectrometry* **17**, 1835-1846 (2003).
44 Sigman, D. M. *et al.* The dual isotopes of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen. *Deep Sea Research Part I: Oceanographic Research Papers* **56**, 1419-1439 (2009).
45 Fry, B. Conservative mixing of stable isotopes across estuarine salinity gradients: a conceptual framework for monitoring watershed influences on downstream fisheries production. *Estuaries* **25**, 264-271 (2002).

46 Vandenbruwane, J., De Neve, S., Qualls, R. G., Salomez, J. & Hofman, G. Optimization of dissolved organic nitrogen (DON) measurements in aqueous samples with high inorganic nitrogen concentrations. *Science of the Total Environment* **386**, 103-113 (2007).

47 Dittmar, T., Koch, B., Hertkorn, N. & Kattner, G. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnology and Oceanography: Methods* **6**, 230-235 (2008).

48 Merder, J. *et al.* ICBM-OCEAN: Processing Ultrahigh-Resolution Mass Spectrometry Data of Complex Molecular Mixtures. *Analytical Chemistry* **92**, 6832-6838, doi:10.1021/acs.analchem.9b05659 (2020).

49 Koch, B. & Dittmar, T. From mass to structure: An aromaticity index for high-resolution mass data of natural organic matter. *Rapid communications in mass spectrometry* **20**, 926-932 (2006).

50 Rossel, P. E., Bienhold, C., Hehemann, L., Dittmar, T. & Boetius, A. Molecular Composition of Dissolved Organic Matter in Sediment Porewater of the Arctic Deep-Sea Observatory HAUSGARTEN (Fram Strait). *Frontiers in Marine Science* **7**, doi:10.3389/fmars.2020.00428 (2020).

51 Flerus, R. *et al.* A molecular perspective on the ageing of marine dissolved organic matter. *Biogeosciences* **9**, 1935-1955 (2012).

52 Medeiros, P. M. *et al.* A novel molecular approach for tracing terrigenous dissolved organic matter into the deep ocean. *Global Biogeochemical Cycles* **30**, 689-699, doi:10.1002/2015GB005320 (2016).

53 D'Andrilli, J., Cooper, W. T., Foreman, C. M. & Marshall, A. G. An ultrahigh-resolution mass spectrometry index to estimate natural organic matter lability. *Rapid Communications in Mass Spectrometry* **29**, 2385-2401 (2015).

54 R Core Team. (R Foundation for Statistical Computing, Vienna, Austria, 2018).

55 Oksanen, J. *et al.* vegan: Community Ecology Package. R package version 2.5–6. (2019).

56 Kendall, C., Elliott, E. M. & Wankel, S. D. in *Stable Isotopes in Ecology and Environmental Science* 375-449 (2007).

57 Alshameri, A. *et al.* Adsorption of ammonium by different natural clay minerals: Characterization, kinetics and adsorption isotherms. *Applied Clay Science* **159**, 83-93, doi:https://doi.org/10.1016/j.clay.2017.11.007 (2018).

58 NTB Bureau of Statistics. NTB dalam Angka ("NTB Province in Figures"). 434 (NTB Bureau of Statistics, Mataram, 2020).

59 Katam. *Agricultural Cultivation Calendar*, <http://katam.litbang.pertanian.go.id/> (2020).

60 Ministry of Environment and Forestry. in *82/2001* (ed Ministry of Environment and Forestry) (Jakarta, 2001).

61 Adyasari, D., Oehler, T., Afiati, N. & Moosdorf, N. Environmental impact of nutrient fluxes associated with submarine groundwater discharge at an urbanized tropical coast. *Estuarine, Coastal and Shelf Science* **221**, 30-38 (2019).

62 Ioka, S. *et al.* Species and potential sources of phosphorus in groundwater in and around Mataram City, Lombok Island, Indonesia. *SN Applied Sciences* **3**, 27, doi:10.1007/s42452-020-03975-6 (2021).

63 Schopka, H. H. & Derry, L. A. Chemical weathering fluxes from volcanic islands and the importance of groundwater: The Hawaiian example. *Earth and Planetary Science Letters* **339**, 67-78 (2012).

64 Rahman, S., Tamborski, J. J., Charette, M. A. & Cochran, J. K. Dissolved silica in the subterranean estuary and the impact of submarine groundwater discharge on the global marine silica budget. *Marine Chemistry* **208**, 29-42, doi:https://doi.org/10.1016/j.marchem.2018.11.006 (2019).

65 Birdwell, J. E. & Engel, A. S. Characterization of dissolved organic matter in cave and spring waters using UV–Vis absorbance and fluorescence spectroscopy. *Organic Geochemistry* **41**, 270-280 (2010).

66 Osburn, C. L. *et al.* Regional groundwater and storms are hydrologic controls on the quality and export of dissolved organic matter in two tropical rainforest streams, Costa Rica. *Journal of Geophysical Research: Biogeosciences* **123**, 850-866 (2018).
67 Kaiser, K., Guggenberger, G., Haumaier, L. & Zech, W. Dissolved organic matter sorption on sub soils and minerals studied by 13C-NMR and DRIFT spectroscopy. *European Journal of Soil Science* **48**, 301-310 (1997).
68 Kaiser, K., Guggenberger, G. & Zech, W. Sorption of DOM and DOM fractions to forest soils. *Geoderma* **74**, 281-303 (1996).
69 Cory, R., Green, S. & Pregitzer, K. Dissolved organic matter concentration and composition in the forests and streams of Olympic National Park, WA. *Biogeochemistry* **67**, 269-288 (2004).
70 Shen, Y., Chapelle, F. H., Strom, E. W. & Benner, R. Origins and bioavailability of dissolved organic matter in groundwater. *Biogeochemistry* **122**, 61-78, doi:10.1007/s10533-014-0029-4 (2015).
71 Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. & Matzner, E. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil science* **165**, 277-304 (2000).
72 Riedel, T., Biester, H. & Dittmar, T. Molecular fractionation of dissolved organic matter with metal salts. *Environmental Science & Technology* **46**, 4419-4426 (2012).
73 Waska, H. *et al.* Molecular Traits of Dissolved Organic Matter in the Subterranean Estuary of a High-Energy Beach: Indications of Sources and Sinks. *Frontiers in Marine Science* **8**, doi:10.3389/fmars.2021.607083 (2021).
74 Roth, V.-N., Dittmar, T., Gaupp, R. & Gleixner, G. Latitude and pH driven trends in the molecular composition of DOM across a north south transect along the Yenisei River. *Geochimica et Cosmochimica Acta* **123**, 93-105 (2013).
75 Roth, V.-N., Dittmar, T., Gaupp, R. & Gleixner, G. The molecular composition of dissolved organic matter in forest soils as a function of pH and temperature. *PLoS One* **10**, e0119188 (2015).
76 Hernes, P. J. & Benner, R. Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research: Oceans* **108**, doi:10.1029/2002JC001421 (2003).
77 Keil, R. G., Montluçon, D. B., Prahl, F. G. & Hedges, J. I. Sorptive preservation of labile organic matter in marine sediments. *Nature* **370**, 549-552 (1994).
78 Kleypas, J. A. & Langdon, C. Coral reefs and changing seawater carbonate chemistry. *Coastal and Estuarine Studies: Coral Reefs and Climate Change Science and Management* **61**, 73-110 (2006).
79 Ehlert, C. *et al.* Transformation of silicon in a sandy beach ecosystem: Insights from stable silicon isotopes from fresh and saline groundwaters. *Chemical Geology* **440**, 207-218 (2016).
80 Hagedorn, B., Becker, M. W. & Silbiger, N. J. Evidence of freshened groundwater below a tropical fringing reef. *Hydrogeology Journal*, 1-17 (2020).
81 Brandes, J. A. & Devol, A. H. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. *Geochimica et Cosmochimica Acta* **61**, 1793-1801 (1997).
82 Sigman, D. M., Altabet, M., McCorkle, D., Francois, R. & Fischer, G. The δ15N of nitrate in the Southern Ocean: Nitrogen cycling and circulation in the ocean interior. *Journal of Geophysical Research: Oceans* **105**, 19599-19614 (2000).
83 Wankel, S. D., Kendall, C., Pennington, J. T., Chavez, F. P. & Paytan, A. Nitrification in the euphotic zone as evidenced by nitrate dual isotopic composition: Observations from Monterey Bay, California. *Global Biogeochemical Cycles* **21**, doi:https://doi.org/10.1029/2006GB002723 (2007).
84 Froelich, P. N. *et al.* Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et cosmochimica acta* **43**, 1075-1090 (1979).
85 Bushaw, K. L. *et al.* Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. *Nature* **381**, 404-407 (1996).

86 Moran, M. A. & Zepp, R. G. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography* **42**, 1307-1316 (1997).
87 Dortch, Q. The interaction between ammonium and nitrate uptake in phytoplankton. *Marine Ecology Progress Series* **61**, 183-201 (1990).
88 Domagalski, J. L. & Johnson, H. M. Subsurface transport of orthophosphate in five agricultural watersheds, USA. *Journal of Hydrology* **409**, 157-171 (2011).
89 Linkhorst, A., Dittmar, T. & Waska, H. Molecular fractionation of dissolved organic matter in a shallow subterranean estuary: the role of the iron curtain. *Environmental Science & Technology* **51**, 1312-1320 (2017).
90 Tanaka, Y., Ogawa, H. & Miyajima, T. Production and bacterial decomposition of dissolved organic matter in a fringing coral reef. *Journal of oceanography* **67**, 427-437 (2011).
91 Hansell, D. A., Kadko, D. & Bates, N. R. Degradation of Terrigenous Dissolved Organic Carbon in the Western Arctic Ocean. *Science* **304**, 858, doi:10.1126/science.1096175 (2004).
92 Kang, P.-G. & Mitchell, M. J. Bioavailability and size-fraction of dissolved organic carbon, nitrogen, and sulfur at the Arbutus Lake watershed, Adirondack Mountains, NY. *Biogeochemistry* **115**, 213-234 (2013).
93 Fellman, J. B., D'Amore, D. V., Hood, E. & Boone, R. D. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. *Biogeochemistry* **88**, 169-184 (2008).
94 Hertkorn, N. *et al.* Characterization of a major refractory component of marine dissolved organic matter. *Geochimica et Cosmochimica Acta* **70**, 2990-3010 (2006).
95 Kieber, R. J., Hydro, L. H. & Seaton, P. J. Photooxidation of triglycerides and fatty acids in seawater: Implication toward the formation of marine humic substances. *Limnology and Oceanography* **42**, 1454-1462 (1997).
96 Vacelet, E. & Thomassin, B. A. Microbial utilization of coral mucus in long term in situ incubation over a coral reef. *Hydrobiologia* **211**, 19-32 (1991).
97 Oehler, T. *et al.* Seasonal variability of land-ocean groundwater nutrient fluxes from a tropical karstic region (southern Java, Indonesia). *Journal of Hydrology* **565**, 662-671 (2018).
98 World Bank. INDONESIA COUNTRY REPORT. THE RISE OF METROPOLITAN REGIONS: TOWARDS INCLUSIVE AND SUSTAINABLE REGIONAL DEVELOPMENT 141 (The World Bank, Jakarta, 2010).
99 Haas, A. F. *et al.* Global microbialization of coral reefs. *Nature Microbiology* **1**, 1-7 (2016).
100 Cárdenas, A. *et al.* Excess labile carbon promotes the expression of virulence factors in coral reef bacterioplankton. *The ISME journal* **12**, 59-76 (2018).
101 Senal, M. I. S. *et al.* Nutrient inputs from submarine groundwater discharge on the Santiago reef flat, Bolinao, Northwestern Philippines. *Marine Pollution Bulletin* **63**, 195-200, doi:https://doi.org/10.1016/j.marpolbul.2011.05.037 (2011).