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Nitrous Oxide and Methane Dynamics in a Coral Reef Lagoon Driven by Pore Water Exchange: Insights from Automated High-Frequency Observations

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RESEARCH LETTER

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Key Points:

- The coral reef was a net source of CH₄ and N₂O to the atmosphere
- Pore water-derived fluxes were higher than atmospheric fluxes
- Pore water exchange was the major driver of methane and nitrous oxide

Supporting Information:

- Readme
- Table S1

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Nitrous oxide and methane dynamics in a coral reef lagoon driven by pore water exchange: Insights from automated high-frequency observations

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Abstract Automated cavity ring down spectroscopy was used to make continuous measurements of dissolved methane, nitrous oxide, and carbon dioxide in a coral reef lagoon for 2 weeks (Heron Island, Great Barrier Reef). Radon (²²²Rn) was used to trace the influence of tidally driven pore water exchange on greenhouse gas dynamics. Clear tidal variation was observed for CH₄, which correlated to ²²²Rn in lagoon waters. N₂O correlated to ²²²Rn during the day only, which appears to be a response to coupled nitrification-denitrification in oxic sediments, fueled by nitrate derived from bird guano. The lagoon was a net source of CH₄ and N₂O to the atmosphere and a sink for atmospheric CO₂. The estimated pore water-derived CH₄ and N₂O fluxes were 3.2-fold and 24.0-fold greater than the fluxes to the atmosphere. Overall, pore water and/or groundwater exchange were the only important sources of CH₄ and major controls of N₂O in the coral reef lagoon.

1. Introduction

While coral reef carbon dioxide dynamics have been relatively well studied [Cyronak *et al.*, 2014b], less attention has been given to the dynamics and drivers of other major greenhouse gases such as methane and nitrous oxide. Most previous studies of greenhouse gases other than carbon dioxide focused on methane diagenesis in coral reef pore waters [Falter and Sansone, 2000]. Coral reef groundwater and shallow pore water conditions (i.e., low oxygen, high carbon, abundant microbial life, and effective flushing) [Cyronak *et al.*, 2014a; Tribble *et al.*, 1990; Wild *et al.*, 2006] may be ideal for the production and release of greenhouse gases to surface waters and the atmosphere.

Submarine groundwater discharge (SGD) and pore water exchange have been suggested to be a major source of nutrients to some coral reef ecosystems [Paytan *et al.*, 2006; Tait *et al.*, 2014]. SGD refers to “any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force” [Moore, 2010]. Groundwater is synonymous with pore water in saturated sediments. Therefore, pore water exchange falls under this modern definition of SGD. SGD can be tidally driven and related to seawater recirculation into beach sediments (i.e., tidal pumping), which may be particularly important in coral reef lagoons surrounding islands with permeable sediments [Santos *et al.*, 2010]. A number of other physical processes including wave pumping, current-topography interactions, and biorrigation may drive pore water exchange, but these small-scale processes are unlikely to be captured by geochemical tracers such as radon. Pore water exchange may drive marine particulate organic matter (i.e., phytoplankton and coral mucus) into sediments while leaching out microbial by-products including greenhouse gases [Sansone, 1993].

Denitrification in sediments and nitrification in the water column are the primary contributors of widespread N₂O supersaturation in coastal waters [Naqvi *et al.*, 2010]. Both nitrification and denitrification have been observed in coral reefs [O'Neil and Capone, 2008] with some of the highest worldwide sediment denitrification rates measured in permeable coral reef sands subject to pore water advection [Santos *et al.*, 2012]. These high rates of denitrification may be coupled to N₂O production in sediments. Biotic CH₄ is usually produced under anoxic conditions as a product of acetate fermentation or carbon dioxide reduction. In marine sediments, CH₄ is usually produced after alternative electron acceptors have been exhausted. Therefore, CH₄ generally occurs where sulfate is depleted even though methane has been observed in coral reef pore waters in the presence of sulfate [Falter and Sansone, 2000].

Recent studies have shown that groundwater and pore water can influence CO₂ dynamics in coral reef lagoons [Cyronak *et al.*, 2014a] and coastal groundwater often has high concentrations of CO₂, N₂O, and CH₄ [Porubsky *et al.*, 2014]. Here we take advantage of automated, high-precision instrumentation (i.e., cavity ring down spectroscopy) to perform time series observations of dissolved greenhouse gases in a coral reef lagoon. While focus is given to CH₄ and N₂O, carbon dioxide observations are also reported. We hypothesize that the lagoon waters will have variable CH₄ and N₂O concentrations influenced by SGD or pore water exchange. We use a well-established radon (²²²Rn; $t_{1/2}$ = 3.84 days) approach to quantify pore water exchange and compare porewater-derived fluxes to greenhouse gas fluxes at the water-air interface. The noble gas radon is a natural tracer for any water that remains in contact with sediments for at least several hours or a few days.

2. Material and Methods

We have performed lagoon water and groundwater observations to assess whether tidal pumping drives greenhouse gas dynamics in coral reef waters surrounding Heron Island (23°27'S, 151°55'E). Heron Island is a coral cay located in the Capricorn Group of islands in the southern end of the Great Barrier Reef ~80 km from the Australian mainland. The island is 800 m long, ~300 m wide, and 3 m above sea level. Heron Island is surrounded by a lagoonal coral reef, which covers an area of ~27 km² with an average depth of 1.7 m [McMahon *et al.*, 2013]. The sediments consist primarily of calcareous skeletal matter from reef organisms. The sediments exhibit high permeability, allowing seawater to recirculate through the island with the tides [Santos *et al.*, 2010]. As with many coral cays, Heron Island is subjected to high densities of seabirds that drive high concentrations of nitrates in groundwater in an otherwise nutrient-poor environment [Schmidt *et al.*, 2004].

A 2 week continuous time series in the Heron Reef lagoon was conducted in May 2014 to cover a spring-neap tidal cycle. Seawater was pumped from the lagoon at a site located about 10 m seaward of the low tide mark in front of the Heron Island Research Station into a shower head gas equilibration device (GED) at a rate of about 3 L/min [Maher *et al.*, 2013]. A closed air loop was established between the GED and gas analyzers. Two automated, high-precision cavity ring down spectroscopy (CRDS) systems were used for CO₂, CH₄, and N₂O analysis (Picarro G2308 and Picarro G2201-I). These systems were connected in line and calibrated before and after field experiments by running standard gases (CO₂ 306 ppm and 2017 ppm, CH₄ 3 ppm and 200 ppm, and N₂O 0.35 ppm). No drift was detected after the field experiments. ²²²Rn was analyzed using a commercial RAD-7 (DurrIDGE Co., Inc.) [Burnett *et al.*, 2001]. The general approach and protocols required for converting measurements in the GED to dissolved gas concentrations or saturations are described elsewhere [Maher *et al.*, 2013, and references therein]. All the dissolved greenhouse gas values are reported as a percent saturation at in situ temperature and salinities. A calibrated Hydrolab D55X was also deployed at the site to measure photosynthetically active radiation (PAR), salinity (open cell graphite electrode; 0.5% accuracy), temperature and dissolved oxygen (DO; Hach Luminescent dissolved oxygen; <0.2 mg L⁻¹ accuracy). Wind speeds and rainfall information were obtained from the Integrated Marine Observing System (<http://weather.aims.gov.au/>).

Groundwater samples were collected from six sites previously sampled for radon and dissolved nutrients [Santos *et al.*, 2010; Schmidt *et al.*, 2004]. A 24 h groundwater time series (one sample every 2 h) was conducted from a 6.5 m well located by the Heron Island Research Station (23°26'31"S, 151°54'46"E). Groundwater samples were collected using a peristaltic pump after purging at least three well volumes. Discrete samples of dissolved gas concentrations in the groundwater were measured using a headspace method within 1 h of sampling [Gatland *et al.*, 2014, and references therein].

Greenhouse gas exchange rates were calculated at the sediment-water (i.e., pore water derived) and water-air (i.e., atmospheric exchange) interfaces. The pore water exchange rates were estimated from a nonsteady state radon mass balance that was previously applied to the same location [Cyronak *et al.*, 2014a; Santos *et al.*, 2010]. The radon-derived pore water exchange rates (in units of cm d⁻¹) were then multiplied by the average greenhouse gas concentration in all groundwater and pore water samples. Our radon observations in lagoon surface waters reflect a combination of lagoon pore water and island groundwater inputs. It is not possible to quantitatively separate these two sources of radon with the data available. For simplicity, we use the term

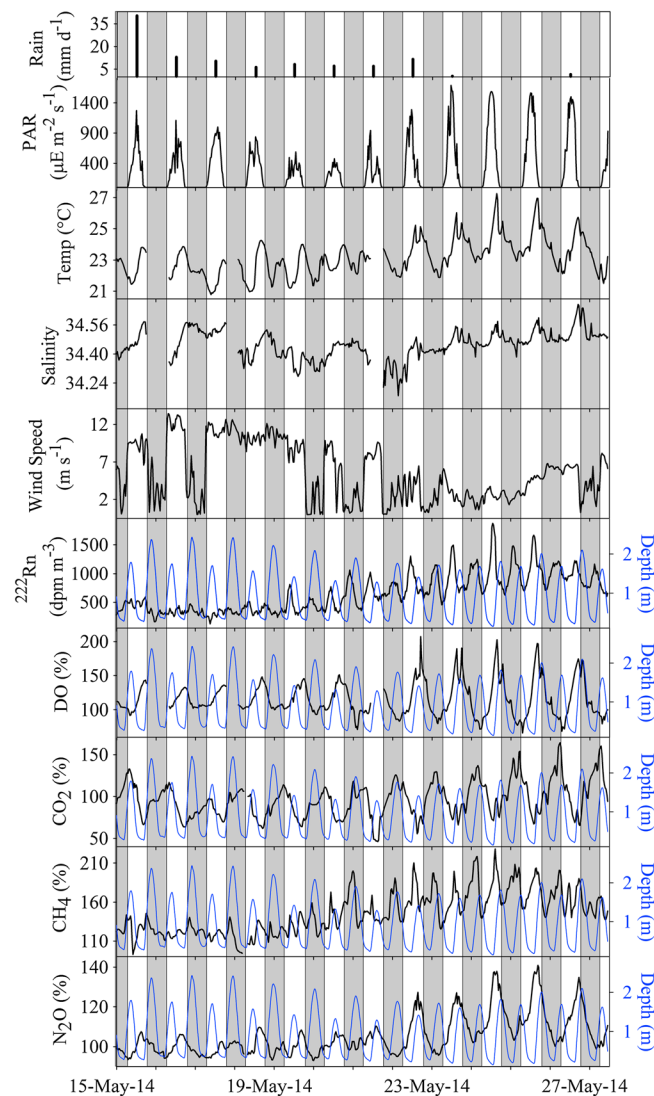


Figure 1. Results of the 12 day continuous time series conducted in the Heron Island lagoon. Vertical grey bars highlight nighttime observations. PAR stands for photosynthetically active radiation. Tidal heights are shown in blue on the right axis.

ranging between 56 and 218% and following the opposite trends of carbon dioxide which ranged from 41 to 180% saturation.

The concentrations of ²²²Rn ranged between 124 and 1873 disintegrations per minute (dpm) m⁻³ and followed a clear tidal pattern. Methane varied between 106 and 218% saturation and followed tidal patterns similar to radon with higher concentrations during low tide. Nitrous oxide was generally oversaturated with an overall range of 94–130%. The strong winds during the first half of the time series resulted in a reduction in maximum concentrations and relatively narrower diel ranges for all the gases (Figure 1). CO₂ and N₂O usually followed diurnal patterns.

The groundwater observations revealed high and variable radon and greenhouse gas values (Table 1). The average CO₂, CH₄, and N₂O saturation values in groundwaters were 7, 27, and 11 times higher than the averages observed in the lagoon surface water, implying that groundwater can be a source of greenhouse gases to the coral reef lagoon.

A nonsteady state radon mass balance resulted in average pore water exchange rates of 19.4 ± 1.8 cm d⁻¹ (or 194 ± 18 L/m⁻²/d⁻¹ as used by some authors; uncertainties refer to the 99% confidence interval of the natural

“pore water exchange” and recognize that some authors would refer to it as “submarine groundwater discharge.”

For water-air flux calculations, we relied on the concentration gradient between the water and air, and gas transfer velocities calculated as a function of wind speeds using four different empirical models described elsewhere [Borges et al., 2004; Ho et al., 2006; Raymond and Cole, 2001; Wanninkhof, 1992]. Solubility coefficients for N₂O [Weiss and Price, 1980], CO₂ [Weiss, 1974], and CH₄ [Yamamoto et al., 1976] were calculated from temperature and salinity. The atmospheric concentrations were assumed to be constant (CO₂ 400 ppm, CH₄ 1.8 ppm, and N₂O 0.326 ppm). Positive fluxes indicate gas emissions from the lagoon to the atmosphere (outgassing), while negative values indicate fluxes from the atmosphere to the lagoon (uptake).

3. Results

The lagoon observations were characterized by stormy and rainy conditions during the first half of the time series (Figure 1). However, the second half was characterized by calmer weather, with winds ranging from 0.2 to 8.4 m s⁻¹ and a maximum of 11.6 mm d⁻¹ of precipitation. Salinity remained within a narrow range of 33.3 to 34.7 and temperature ranged between 20.8 and 27.5°C. Dissolved oxygen exhibited normal diurnal variation for coral reefs,

Table 1. Results of Groundwater and Pore Water Observations^a

Sample	Site	Depth (m)	²²² Rn (dpm/m ³)	pH	Salinity	Temperature (°C)	DO (%)	CH ₄ (%)	N ₂ O (%)	CO ₂ (%)	CH ₄ (nM)	N ₂ O (nM)	[CO ₂ *] (μM)
GWTS	Research station	3.0	14,046	7.17	34.5	24.1	117	1227	1483	1979	25	101	236
GW1	Forest trail	7.6	89,166	7.29	29.2	25.6	84	1844	935	1022	38	63	120
GW 2	Forest trail	5.8	52,161	6.86	30.3	25.3	44	6667	933	1104	137	63	130
GW 3	Forest trail	13.9	89,559	7.27	30.1	25.4	85	2580	935	867	53	63	102
GW 4	Inland	7.6	5,904	7.28	19.3	24.8	23	1925	1740	1229	43	127	154
PW	Lagoon	0.2	8,763	7.66	36.5	24.2	47	1844	ND	178	37	ND	21
Mean		6.3	56,600	7.26	30.0	24.9	67	2681	1205	1063	56	83	127
Standard deviation		4.7	37,748	0.26	6.0	0.6	35	1999	382	582	41	29	70
99% Confidence interval		3.7	39,695	0.27	6.3	0.7	37	2102	402	612	43	31	74

^aThe greenhouse gas values are shown in % saturation units to allow easy comparison to surface waters and in molar units that were used to estimate pore water-derived fluxes. Additional data about the wells can be found elsewhere [Santos *et al.*, 2010; Schmidt *et al.*, 2004]. ND, no data.

variability of the radon mass balance model; $n = 305$ h) using assumptions and an approach described elsewhere [Santos *et al.*, 2010, and references therein]. When multiplied by the average greenhouse gas concentrations in Heron Island groundwaters and pore waters (Table 1), we obtain average pore water-derived fluxes of 10.8 ± 8.4 and $16.2 \pm 6.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ for CH₄ and N₂O, respectively. The pore water-derived CO₂ fluxes were $24.6 \pm 2.3 \text{ mmol m}^{-2} \text{d}^{-1}$.

The lagoon was usually a source of both CH₄ and N₂O to the atmosphere (Figure 2). The water-air fluxes ranged up to fourfold depending on the choice of the gas transfer velocity model employed (Table 2). Using an average from the four gas transfer velocity models (Table 2), the estimated CH₄ and N₂O fluxes at the sediment-water interface are 3.2 and 24.1 times higher than the water-air fluxes. The highest lagoon outgassing rates were recorded during days with strongest winds and lowest water temperatures in spite of lower CH₄ and N₂O values. Overall, the lagoon primarily acted as a sink for atmospheric CO₂ due to uptake during the initial stormy conditions.

4. Discussion

High-frequency observations for 12 days revealed that both methane and nitrous oxide were consistently supersaturated in the coral reef waters surrounding Heron Island. As expected, groundwater concentrations were much higher than concentrations observed in lagoon waters, resulting in net greenhouse gas fluxes from groundwater to the coral reef lagoon. The estimated fluxes of CH₄ and N₂O at the sediment-water interface (i.e., pore water exchange) were 1 order of magnitude greater than the fluxes at the water-air interface (Table 1). This implies that some pore water-derived dissolved CH₄ and N₂O can be exported to outside the lagoon, from where outgassing would eventually occur. In addition, some CH₄ oxidation may have occurred within the water column.

A correlation analysis provided contrasting results for the three greenhouse gases (Figure 3). Methane was significantly correlated with radon both during the day and night. Nitrous oxide was correlated with radon during

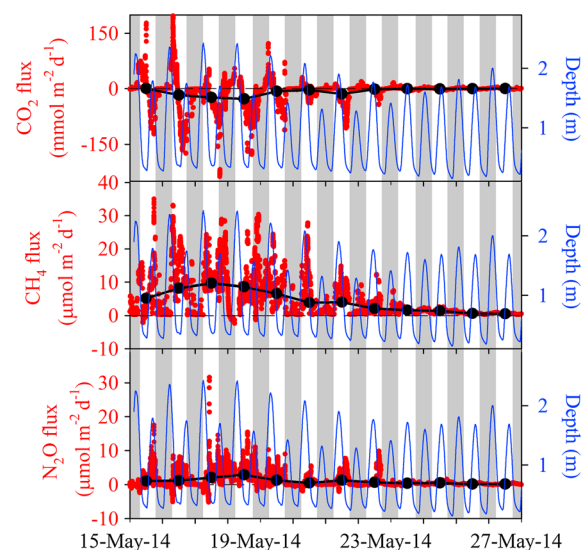


Figure 2. Instantaneous (red circles) and daily average (black circles) air-water flux rates for CH₄, CO₂, and N₂O during the lagoon time series calculated using the model from Raymond and Cole [2001]. Positive numbers indicate the lagoon as a source, whereas negative numbers indicate a sink. The vertical grey bars represent nighttime observations. The continuous blue line (right axis) shows tidal heights.

Table 2. Piston Velocities and Water-Air Fluxes of Greenhouse Gases Using Four Different Models^a

	CO ₂	CH ₄	N ₂ O
Saturation (%)	93.0 ± 0.5	141.0 ± 0.5	103.0 ± 0.1
	<i>Gas Specific Piston Velocities (m d⁻¹)</i>		
<i>Raymond and Cole</i> [2001]	8.3 ± 0.2	8.2 ± 0.2	8.0 ± 0.2
<i>Borges et al.</i> [2004]	4.7 ± 0.0	4.6 ± 0.0	4.5 ± 0.0
<i>Ho et al.</i> [2006]	3.2 ± 0.1	3.1 ± 0.1	3.1 ± 0.1
<i>Wanninkhof</i> [1992]	3.9 ± 0.1	3.8 ± 0.1	3.8 ± 0.1
	<i>Water-Air Fluxes^b</i>		
<i>Raymond and Cole</i> [2001]	-9.3 ± 0.7	5.2 ± 0.1	1.2 ± 0.0
<i>Borges et al.</i> [2004]	-4.5 ± 0.3	3.7 ± 0.0	0.3 ± 0.1
<i>Ho et al.</i> [2006]	-3.6 ± 0.2	2.2 ± 0.0	0.5 ± 0.0
<i>Wanninkhof</i> [1992]	-4.4 ± 0.3	2.6 ± 0.1	0.6 ± 0.0
<i>Average</i>	-5.4 ± 0.8	3.4 ± 0.1	0.7 ± 0.1

^aUncertainties in the overall average water-air flux were estimated by propagating the uncertainties of the individual models. Individual uncertainties refer to the 99% confidence interval of the natural variability.

^bUnits of mmol m⁻² d⁻¹ for CO₂ and μmol m⁻² d⁻¹ for CH₄ and N₂O.

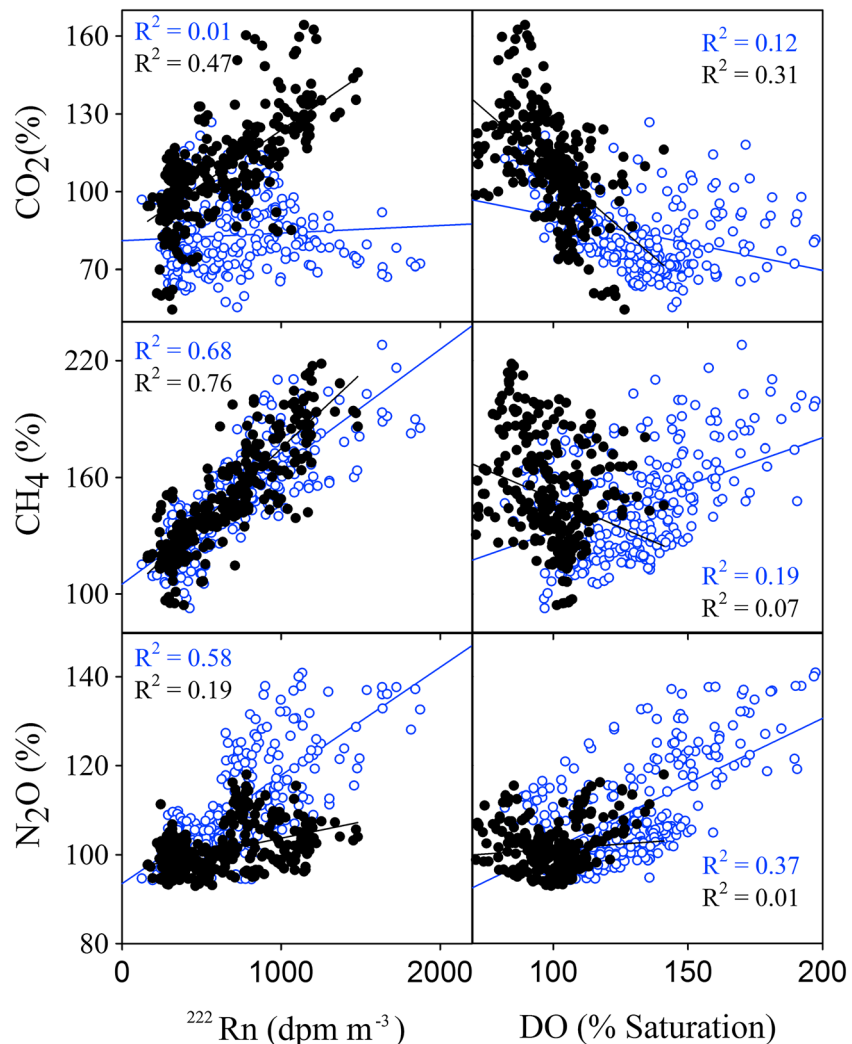


Figure 3. Correlations between greenhouse gases and ²²²Rn (left) and DO (right). Open blue symbols and text represent daytime, and closed black symbols and text represent nighttime.

the day but not during the night. Carbon dioxide was correlated with radon at night but not during the day, similar to previous CO₂ and ²²²Rn observations in Heron Island [Cyronak *et al.*, 2014a]. Interestingly, both methane and nitrous oxide had stronger correlations with radon than with dissolved oxygen. Considering that DO can be seen as a tracer of photosynthesis and respiration and that radon is an unambiguous pore water tracer in Heron Island (i.e., other radon sources such as dissolved ²²⁶Ra decay and diffusion are minor; see Santos *et al.* [2010]), these observations support our original hypothesis that pore water exchange was the major source of both methane and nitrous oxide to the lagoon.

The y axis intercept of the equation describing the CH₄ versus ²²²Rn correlation (CH₄ = 0.068²²²Rn + 102; combining day and night data from Figure 3) approaches 100% CH₄ saturation. This implies that in the absence of radon (i.e., no groundwater), methane would approach equilibrium with the atmosphere (i.e., 100% saturation) and that methane sources other than groundwater were negligible. The groundwaters of Heron Island were supersaturated with CH₄ even though some oxygen was still present (average DO saturation 66 ± 35%; Table 1) which presumably prevents methanogenesis [Naqvi *et al.*, 2010]. Carbonate sands are highly porous and have anoxic microenvironments that dramatically enhance the area available for microbial growth [Kessler *et al.*, 2014]. As a result, microbial activity within porous carbonate sand grains can be orders of magnitude higher than in pore water surrounding the grains [Wild *et al.*, 2006]. Anoxic microniches within sand grains may create intermittent conditions that are favorable for methane production that can be effectively flushed out of sediments through pore water exchange [Falter and Sansone, 2000].

Nitrous oxide had more complex dynamics than methane, showing significant correlations with radon during the day only (Figure 3). The y axis intercept in the regression of N₂O versus ²²²Rn (N₂O = 0.018²²²Rn + 94; using daytime data only) was less than 100% saturation. Hence, conditions of no or low groundwater discharge (i.e., ²²²Rn approaching zero) may coincide with negative N₂O fluxes (i.e., fluxes from the atmosphere to the lagoon). Using the average groundwater radon concentration (56,600 dpm m⁻³) in the equation describing the lagoon N₂O versus ²²²Rn relationship above, the N₂O saturation in groundwater should be 1113% if pore water exchange was the only source of N₂O to the lagoon during the day. The observed average groundwater N₂O was similar at 1205 ± 382% (Table 1). This analysis demonstrates an internally consistent data set that implies groundwater and/or pore water exchange is an important source of N₂O supersaturation within the Heron Island lagoon.

Why would pore water be a source of nitrous oxide to the lagoon during the day but not during the night? We speculate that this is related to oxygen, nitrate, and ammonium availability in pore water and higher coupled nitrification-denitrification during the day. Nitrification requires oxic conditions, and during nitrification N₂O is formed as a by-product as ammonium is oxidized to nitrate. Low nighttime DO (Figure 1) may prevent the infiltration of oxygen into shallow sediments and slow nitrification and the related production of N₂O. During the day, deeper oxygen penetration into sediments [Werner *et al.*, 2006] can create sharp oxygen gradients in pore water and expand the area where coupled nitrification-denitrification can occur and enhance the related production of N₂O. As pore waters are effectively flushed out, sediment N₂O would be released to surface waters along with radon. The relatively high groundwater N₂O is likely related to microniches within carbonate sands as well as extremely high NO₃⁻ in Heron Island groundwater due to accumulating nitrogen leached from bird guano [Santos *et al.*, 2010; Schmidt *et al.*, 2004]. Therefore, we hypothesize that the supply of N₂O from island groundwater is enhanced by daytime nitrification in shallow lagoon pore waters. The production of N₂O can be further enhanced by denitrification producing larger amounts of N₂O in suboxic conditions (daytime) than under strictly anaerobic conditions (nighttime) [Larsen and Seitzinger, 2004]. Additional specific experiments are needed to test these hypotheses.

Could coral reefs waters be major players in the oceanic CH₄ and N₂O budgets? By multiplying Heron Island average water-air fluxes (Table 2) by the global coral reef area (about 600,000 km²), coral reefs could contribute 0.0120 Tg yr⁻¹ of CH₄ and 0.0065 Tg yr⁻¹ of N₂O to the atmosphere. While we are unaware of similar estimates in coral reefs, it is likely that our outgassing estimates are at the high end of the spectrum because our lagoon observations were performed near the groundwater/pore water source (i.e., about 10 m off the low tide mark) and include stormy conditions when outgassing rates were higher (see first week of observations in Figure 2). Even if our results represent an overestimation of coral reef sources, coral reefs would still be a minor component of marine CH₄ and N₂O budgets. The global ocean is thought

to release between 11 and 18 Tg yr⁻¹ of CH₄ to the atmosphere [Bange *et al.*, 1994] and about 6 Tg yr⁻¹ of N-N₂O [Codispoti, 2010]. Our estimates also imply that coral reefs would release much lower amounts of greenhouse gases than coastal waters. For example, European coastal waters (>0.3 Tg yr⁻¹ of both N-N₂O and C-CH₄) [Bange, 2006] alone may release at least 1 order of magnitude more than the estimated global coral reef outgassing rates extrapolated from our study.

5. Conclusions

Automated time series observations revealed that the Heron Island coral reef lagoon was supersaturated in both methane and nitrous oxide during 12 days of continuous observations. The lagoon was a net source of CH₄ and N₂O to the atmosphere (average of 3.4 and 0.7 μmol m⁻² d⁻¹, Table 2). If upscaled to the global coral reef area, these outgassing rates would represent a minor global source of CH₄ and N₂O to the atmosphere. Pore water exchange was a source of all three major greenhouse gases to Heron Island lagoon. Estimated local fluxes at the sediment-water interface exceeded outgassing rates at the water-air interface. Overall, pore water and/or groundwater exchange were the only important source of methane, a major control of nitrous oxide during the day, and a minor driver of carbon dioxide dynamics in the Heron Island lagoon.

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