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Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems

Journal
Limnology and Oceanography, 51(1)

ISSN
0024-3590

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Publication Date
2006

DOI
10.4319/lo.2006.51.1.0343

Limnol. Oceanogr., 51(1), 2006, 343–348

Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems

Abstract—Using radium (Ra) isotopes and nutrient analyses, we found that submarine groundwater discharge (SGD) is an important source of ''new'' nutrients, particularly nitrogen, to coral reefs around the world. Nitrogen input estimates associated with SGD range from 3 to 800 mmol h^{-1} per meter of shoreline. The use of Ra isotopes allows us to quantify the inorganic nitrogen input from this source of nutrients. Increasing coastal population and land use practices may enhance anthropogenic nutrient loading from submarine groundwater contributing to reef degradation.

The relationship between nutrient dynamics and productivity in coral reef systems has received considerable attention. The impetus for this is the contrast between the high productivity and biomass of these systems and the typically clear, nutrient-poor surface waters bathing them (Marsh 1977; D'Eliaet al. 1981). In addition to efficient recycling of nutrients (Dubinsky 1990), coral reefs derive new nutrients by effective acquisition of both particulate and dissolved sources from seawater impinging on the reefs; vigorous water circulation and flow (Larend and Atkinson 1997); nitrogen (N) fixation (Weibeet al. 1975); and dust deposition (Hingaet al. 1991).

Terrestrially derived input from submarine groundwater discharge (SGD) has been indicated as an important source of nutrients to coastal systems in general (Corbett et al. 1999; Umezawa et al. 2002; Garrison et al. 2003) and to coral reefs in particular (Valiela et al. 1990; Paerl 1997). However, it has been notoriously difficult to track non–point source groundwater as it moves into coastal seas and to describe the interactions between fresh groundwater and seawater at the land–sea interface (Burnett et al. 2002). Accordingly, direct measurements of SGD to coastal reef systems have not been extensive, and the role of SGD as a source of nutrients to coral reef ecosystems has not been extensively and quantitatively determined.

Discharge of groundwater into the sea is widespread; it occurs anywhere that an aquifer is connected hydraulically with the sea through permeable sediments or rocks and where the aquifer head is above sea level. Submarine groundwater flows into the coast at the interface between freshwater and seawater (the mixing zone) where the unconfined aquifer outcrops at the beach (Reay et al. 1992). Toward the seaward edge of the mixing zone, water is brackish as a result of intrusion of salt water through permeable aquifer mixing as well as wave and tidal pumping (Li et al. 1999). The chemistry of the water in the mixing zone is altered such that it is chemically different than either the terrestrial freshwater or seawater components (Church 1996). This area has been referred to as the subterranean estuary (Moore 2003). Accordingly, the term SGD, as used in this article, does not refer to freshwater (meteoric) input but rather includes the freshwater-recirculated seawater mixture that is discharging at the coastline (Buddemeier 1996).

Over the last few decades, Moore and collaborators have pioneered the use of the quartet of naturally occurring radium (Ra) isotopes as tracers for ocean mixing and saline submarine groundwater input to coastal systems (Krest and Harvey 2003).

The divalent cation Ra isotopes are bound to soil particles and rocks in freshwater. They readily desorb via ion exchange in the presence of solutions of higher ionic strength (Webster et al. 1994; Yang et al. 2002). Accordingly, in coastal aquifers, where seawater with high ionic strength mixes and interacts with freshwater and aquifer rocks, waters enriched in Ra are observed (Moore 2003). Open seawater, on the other hand, has very low or constant Ra activities. Therefore, excess Ra (over the open seawater activities) indicates a coastal source that, in many cases, is due to SGD. Ra isotopes are excellent tracers for the study of SGD and mixing in coastal systems because of the distinct difference in activities between the end-member sources (e.g., open ocean and terrestrial saline waters) and because they behave conservatively after leaving the aquifer (accounting for radioactive decay). In addition, the use of Ra isotopes has advantages over other techniques used for quantifying SGD related fluxes, since it allows for temporal and spatial integration over the mean-life of the radionuclides (Moore 2003), and the different timescales of decay are useful as mixing tracers. Indeed, Ra isotopes have been extensively used to determine the discharge of freshwater, nutrients (Cable et al. 1996; Krest et al. 2000; Kelly and Moran 2002), and other dissolved constituents to the coastal ocean (Shaw et al. 1998). However, SGD-associated nutrient supply to coral reef systems has not been fully evaluated using Ra isotopes.

Recently, concern that fringing reefs are degrading through human effects, particularly as a result of increases in terrestrial-derived inputs of nutrients and sediments, has been raised (Wilkinson 1999). Therefore, evaluating and, particularly, quantifying the contribution of SGD-associated nutrient input to fringing reef systems assume critical importance.

Methods—To determine if submarine groundwater is discharging at the beach and reaching the reefs, water samples were taken along several transects from the water line to some distance offshore (typically within 100 m from the shoreline) at representative fringing reef sites around the world (Fig. 1). Other sites (Mexico, Heron Island in Australia) were also examined, and preliminary results are consistent with the data presented here; however, these data are not included because only a limited number of samples were collected. Only one representative transect is shown in the

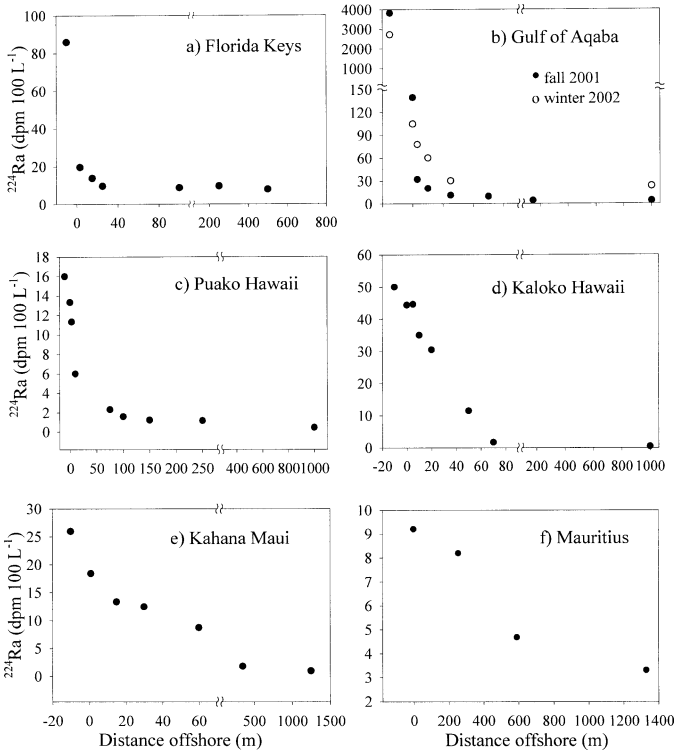

Fig. 1. ^{224}Ra activity (disintigrations per minute [dpm] 100 L^{-1}) plotted against distance from shore (m) at various sites. (a) Florida Keys, off Key Largo; note that at this site the reef track is several kilometers further offshore from the sampling area, and it is not clear if the groundwater is arriving at the reef; (b) Gulf of Aqaba, Eilat; (c) Puako, Hawaii; (d) Kaloko, Hawaii; (e) Kahana, Maui; and (f) Flic en Flac, West Coast, Mauritius. These are just a few representative transects; data in the table and excess Ra in the box used for calculations are based on averages of multiple transects sampled during various times in the tidal cycle and seasons in the year; thus, the values in the figure and table do not directly correspond to each other.

figure for each site; however, typically, at each of the sites, several transects conducted during different phases in the tidal cycle and during different seasons of the year were obtained. The average Ra activity and nutrient concentration in the groundwater and coastal zone calculated from the data collected during the different sampling events are given in Table 1. These averages at most sites are based on many discrete data points representing multiple transects at various locations at each beach that were collected during different times in the tidal cycle and that represent multiple seasons or years (>50 samples per site) (raw data may be obtained upon request from the first author). The sampling protocol (transects location, season and time of sampling, and sampling frequency) was designed to capture the spatial and temporal variability within each site. However, we note that this sampling scheme may not capture interannual variability and may not be representative of other locations along the coast. Regardless, the data illustrate the widespread occurrence and the magnitude of the SGD flux. The sites selected (Gulf of Aqaba, Hawaii, Maui, Florida, and Mauritius) represent settings with different bedrock and coastal topography, rainfall and aquifer recharge rates, and land use practices. Some of these sites (e.g., Hawaii, Florida) are known to have submarine groundwater discharge based on geologic and hydrological considerations and some direct measurements; however, the nutrient load associated with this groundwater has not been thoroughly evaluated. The sampling in Florida was conducted close to shore, as with all sites presented here; however, the reef track in Florida is several kilometers offshore, and it is not clear whether any of the SGD actually reaches the reef. At all sites, no surficial water input is evident within a close proximity to the sampling sites (no river discharge in the watershed).

Water from wells, springs, and the ocean was collected (~100 liters per sample) into containers and filtered through a column packed with manganese (Mn)–coated acrylic fiber at a flow rate not exceeding 1.5 L min^{-1}. Plugs of untreated acrylic fiber were placed at the head of each column to prevent sediment from contacting the Mn fibers. Prior to analysis, samples were rinsed well with Milli-Q Millipore water. The short-lived Ra isotope activities were measured as soon as possible using a delayed coincidence counter (Moore and Arnold 1996). The measurement error is about 10%. Subsamples for nutrient analyses were immediately filtered through 0.45-μm filters into triple-rinsed, acid-cleaned, 30-mL polyethylene bottles and were kept frozen until analysis. Nitrite, nitrate, ammonium, silica, and soluble reactive phosphate were analyzed using colorimetric methods using a Flow Injection Autoanalyzer (Model QuickChem 800, Lachat Instruments). Salinity for each sample was determined in the field using an YSI probe (Model 30).

Samples were analyzed for Ra isotope activities, salinity, and nutrient concentrations. Saline groundwater from the unconfined surficial aquifers was sampled by digging holes in the beach to the water table from above the water line and/or from coastal wells and springs (these are also shallow wells representing water in the unconfined aquifer). Samples representing open seawater were taken ~1 km offshore. Simple mass balance box model calculations (following Moore [1996]) were performed for a box that was spatially defined by the sampling transects to determine the contribution of terrestrially derived water to the nearshore (Table 1). The Ra activity in each box was determined by averaging the Ra activities for all the samples within the box (from all transects, collected at various states of the tidal cycle at each site). Groundwater from the unconfined surficial aquifer and open-ocean samples served as end-members to allow for mixing calculations; these end-member values are also averages based on repeated analyses of the end-members during different times in the tidal cycle and different seasons of the year. Accordingly, we expect that the relation obtained between Ra and total inorganic nitrogen (TIN) to be representative for each site, although by no means is this relationship constant in time and space (*see Discussion*). The amount of SGD needed to balance the excess Ra measured in the coastal box is calculated using Eq. 1:

$$\frac{(A_{\text{Box}} - A_{\text{Offshore}})V_{\text{Box}}}{RT} = A_{\text{Excess}} \quad (1)$$

where A_{Box} is the average Ra activity in the box (disintegra-

Table 1. Water residence time estimates for the box, based on cross-shore currents measured by the ADCP, heat and salt fluxes, or wave activity at these sites, range from 1–6 h. We use the conservative 6 h for flux calculations. This time scale is consistent with the tidal cycle period over which much of the water in the box is replaced, as observed in the field (e.g., at all sites the reef track is breached in many places, resulting in good communication with open seawater and no trapping of water between the reef and the shoreline). Indeed, the residence time of the water in the boxes is much shorter than the decay time for ^{224}Ra (the shortest-lived isotope), based on the relatively constant ^{224}Ra : ^{223}Ra ratio on each site (see Web Appendix 1, http://www.aslo.org/lo/toc/vol_51/issue_1/0343a1.pdf) and the general agreement between model results based on ^{223}Ra and ^{224}Ra.

Coral reef site	^{224}Ra groundwater (dpm 100 L^{-1})	^{223}Ra groundwater (dpm 100 L^{-1})	Excess ^{224}Ra (dpm 100 L^{-1})	Excess ^{223}Ra (dpm 100 L^{-1})	TIN* groundwater (μmol L^{-1})	SGD flux† ^{224}Ra (L m^{-1} h^{-1})	SGD flux† ^{223}Ra (L m^{-1} h^{-1})	TIN flux‡ (mmol m^{-1} h^{-1})	TIN flux‡ (g N m^{-2} day^{-1})
Gulf of Aqaba	Well	Well							
Winter 2002	2070	60	34	1.5	32	102	156	3.3	0.03
Fall 2002	2720	120	39	1.0	42	90	52	3.8	0.034
Hawaii–Kona	Beach Pit	Beach Pit							
Kaloko	50	3.7	33	2.7	44	4,120	4,561	182	1.63
Puako	16	1.5	7	0.5	126	2,730	2,083	344	3.08
West Maui	Beach Pit	Beach Pit							
Kahana	26	0.7	6	0.53	57	1,440	4,732	82	0.74
Florida	Beach Pit	Beach Pit							
Key Largo	86	16	8	1.5	82	625	586	51	0.46
Mauritius§	Spring	Spring							
West Coast	12	0.18	7	0.1	225	3,640	3,472	820	7.35

* TIN is total dissolved inorganic nitrogen including nitrate, nitrite, and ammonia. In the Gulf of Aqaba ammonium concentrations were not measured and the TIN reported here may underestimate the actual nitrogen discharge.

† For comparison, all fluxes were calculated for a box corresponding to 1 m length along the shore face, 25 m offshore, and 1.5 meters average water depth (37.5 m^3). At most sites, the influence of SGD is often observed further offshore than the extent of the box as seen in Fig. 1.

‡TIN flux is calculated by multiplying the SGD flux (based on ^{224}Ra calculations) by the groundwater TIN concentrations. For comparison with previously reported TIN fluxes we also converted the flux to grams of N m^{-2} day^{-1} by dividing the flux per meter of coastline by the volume of the box (37.5 m^{-3}) after appropriate unit conversions.

§ A groundwater end member was not obtained for Mauritus; calculations are based on a sample obtained from a submarine spring (salinity 32). The springwater had already been diluted with seawater (salinity 36). Flux calculations, therefore, represent a maximum value.

tions min^{-1} [dpm] 100 L^{-1} water; dpm 100 L^{-1}), *RT* is the cross-shore water residence time (days), *V* is the volume of the box (liters), and A_{Excess} (dpm day^{-1}) is the Ra flux to the box not supported by the offshore water, which must be supplied by SGD. A_{Excess} divided by the Ra activity of the groundwater end-member (dpm L^{-1}) gives an estimate of the groundwater flow required to balance the excess Ra activity (L d^{-1}). In this model, we assume that the system is in steady state and that all excess Ra is from SGD (i.e., no significant regeneration from sediments compared to the SGD source). Indeed, coastal sediments at all sites are largely coarse-grain coral fragments with relict quartz sands and granitic or basaltic gravel and are not expected to be large Ra sources. Simple desorption experiments using beach sediments, following Bollinger and Moore (1993), confirm this assumption. Using the calculated discharge and nutrient concentrations of the groundwater (based on average concentrations measured multiple times in the coastal aquifer), a nutrient flux can be determined (Table 1).

Results and discussion—At all sites, Ra activities and nutrient concentrations in groundwater (where sampled) are one to two orders of magnitude higher than in coastal waters surrounding the reefs, and the concentrations in coastal waters are typically higher than offshore in the open ocean (Fig. 1). This results in strong offshore gradients of Ra, nutrients, and, at some sites, salinity. These results indicate a terrestrial source of Ra and associated nutrients delivered to the coastal ecosystems, including the fringing reefs that are close to shore, most likely from SGD. Indeed, at some sites, discharge is sufficient to create small rivulets and intertidal rills in the sand within a meter of the water's edge as well as clear upwelling springs within the lagoon at some sites. A significant ($p < 0.05$) positive correlation between total inorganic nitrogen (TIN) concentrations and Ra activities (Fig. 2) indicates mixing between high-Ra and TIN groundwater and low-Ra and TIN seawater. Deviations from linearity (mixing) at some sites are a result of the nonconservative nature of nutrients (e.g., local sources or sinks), a mixing of multiple groundwater sources with different Ra to nutrient ratios, or some decay of ^{224}Ra.

The contribution of SGD to the nutrient budget of adjacent marine waters calculated using the box model approach (Table 1) is highly variable among sites and within each site at different times (different tidal state). This is not surprising, because the influence of SGD depends on many factors, including surficial aquifer recharge rates; the type and degree of nutrient enrichment of groundwater; the composition, porosity, and permeability of the geological substrata; tidal and wave pumping; and other hydrological factors that affect

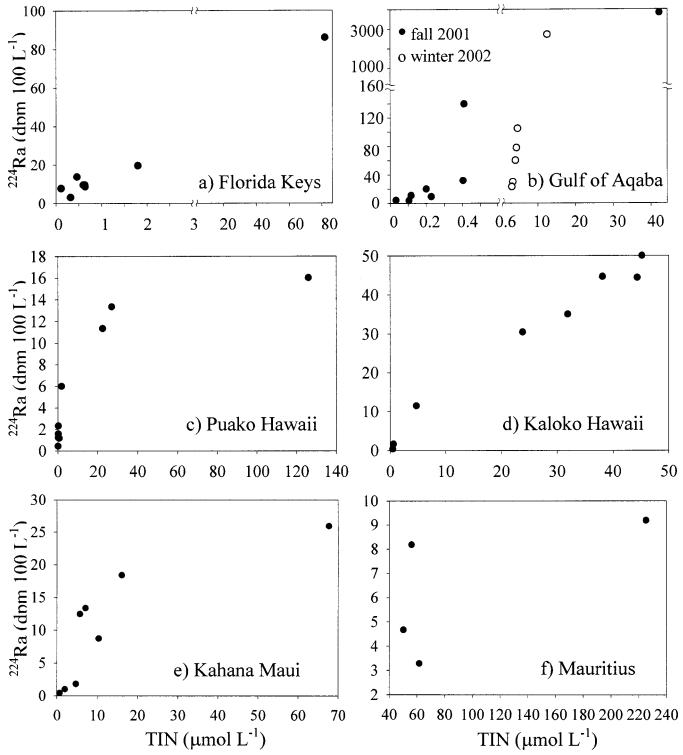

Fig. 2. ^{224}Ra plotted against total inorganic nitrogen (nitrate, nitrite, ammonia; TIN). (a) Florida Keys, off Key Largo; note that at this site the reef track is several kilometers further offshore from the sampling area, and it is not clear if the groundwater is arriving at the reef; (b) Gulf of Aqaba, Eilat; (c) Puako, Hawaii; (d) Kaloko, Hawaii; (e) Kahana, Maui; and (f) Flic en Flac, West Coast, Mauritius. As above, these are data for selected representative sampling transects, but the average values of TIN in groundwater are based on multiple sampling events at various times (tidal and seasonal) at each site.

groundwater table height, hydraulic head, and resultant groundwater flow. At most sites reported here, we addressed this variability by measuring Ra and nutrients along several coastal transects at each site several times a day during different tidal stages, during different seasons, and over a couple of years, and using the average values for each geographic location. The results of these studies indicate that groundwater input to coral reefs is a globally important phenomenon and that SGD, even at sites in which freshwater flow is minimal (e.g., Gulf of Aqaba), represents a significant input of new nutrients (particularly nitrogen) to coastal reef ecosystems. It is important to emphasize here that we use the term ''new nutrients'' to describe any terrestrially driven nutrient load, regardless of whether it is from a freshwater end-member or from the salty groundwater. These nutrients are still ''new'' in the sense of being uncoupled from the low-nutrient seawater flowing over the reef (e.g., exogenous to seawater).

Published studies on similar Ra-based nutrient flux calculations range widely in terms of their results. Krest et al. (2000) report fluxes of TIN for the North Inlet in South Carolina of between 0.0038 and 0.013 g N m^{-2} d^{-1}. Kelly and Moran (2002) report fluxes of 0.85–2.5 g N m^{-2} d^{-1} in New England. Nutrient fluxes calculated here (0.03–3 g N m^{-2} d^{-1}, excluding Mauritius) are in the same range as SGD-derived nutrient fluxes seen in other regions of the world. This is a significant contribution of N to the reef, given that the offshore concentrations are very low. For comparison, N fixation in coral reefs has been estimated to be about 0.1 g N m^{-2} yr^{-1} (Dubinsky 1990); thus, fluxes calculated here could be several orders of magnitude higher. Although reefs are efficient recyclers of nutrients, SGD-contributed N supply constitutes a ''new'' N source to the nearshore region and, thus, may support new production in coastal ecosystems. Using TIN fluxes and the carbon (C) : N ratio typical for coral reefs (~20) (Atkinson and Smith 1983), we calculate that 0.6–60 g C m^{-2} d^{-1} of new production can be supported by SGD-derived TIN at the various sites. Coral reef productivity is very high, with primary production in the back reef area as high as 40 g C m^{-2} d^{-1} (Hatcher 1990). If utilized effectively, the TIN flux from SGD, as calculated above, could support a considerable fraction (1–150%) of the primary productivity in these systems and could potentially be exported to ocean waters beyond the reef flats.

Nutrient loads associated with SGD may be heavily influenced by land cover and land use in the watershed. Accordingly, onshore activities may affect the water quality of coastal surface waters. Therefore, the impact of SGD must be considered in the selection of best management practices and water quality strategies. Additional new TIN inputs could have either a positive or negative impact on reef ecosystem production, depending on the amount and setting (water circulation on the coast). Specifically, we caution that the effect of nutrient enrichment of coastal groundwater aquifers from domestic sewage or fertilizer may initiate eutrophication problems and cause alteration of community function and structure with significant biological, economic, and social implications. In addition to high levels of nutrients, groundwater is often contaminated by a spectrum of other biogenic (bacteria and viruses) and chemical (organic compounds and metals) pollutants (Boehm et al. 2004). Hence, the delivery of these substances to the reef through SGD and the effect of these substances on marine coastal ecosystems must be considered. Our data indicate that SGD and associated nutrient and other pollutant loads to the coast are wide spread. We recommend that the sources of specific pollutant to groundwater, the mechanisms that enhance SGD and the impact of SGD pollutant loads on the coral reefs and other coastal ecosystems should be further evaluated. Specifically, there is a need for (1) more representative (spatially and temporally) quantification of the transport of groundwater and associated nutrients, pathogens, and other chemicals across the land–ocean interface at a wide range of coastal sites; (2) evaluation of the onshore sources and conditions that promote/enhance polluted groundwater discharge; (3) determination of the process/conditions by which this discharge is causing/enhancing coastal contamination and affecting coral reefs; and (4) conducting risk assessments to evaluate the impacts and to indicate the best management plans to reduce severe consequences. This could be done by monitoring of SGD and determining the relationships between

SGD-associated pollutant inputs and onshore land-cover (forest, grassland, desert), land-use (agriculture, urban, rural), and watershed characteristics (size, rock and soil types, recharge rate, permeability, etc.) along with isotopic and other natural or introduced tracers to identify specific pollution sources and their delivery pathways. In addition, the computed fluxes should be directly related to measures of coral reef and other coastal ecosystem health and the settings conducive to negative impact determined. If, indeed, it is concluded that SGD has a negative impact on certain coastal systems, management efforts of watersheds directed at reducing nutrient addition (sewage, runoff, and fertilizers) to coastal groundwater, along with other measures (e.g., limiting sediment input, protecting herbivores), should be enforced to promote the sustainability of coral reefs and other coastal ecosystems.

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Acknowledgments

We thank Stephen Monismith, Tanya Rivlin, Amatzia Genin, Stephen Dollar, Kristen Averyt, Karen McLaughlin, Gaurav Misra, Katy Elsbury, Alexandria Boehm, Scott Wankel, Roshan T. Ramessur, and Eric Grossman for assistance with sample collection and analyses. This research was funded in part by a grant from the National Oceanic and Atmospheric Administration's Undersea Research Center at the University of North Carolina at Wilmington pursuant to NOAA award number NA03OAR4300088 (Florida results), by the BIO-X Initiative at Stanford University for work in Eilat, and by the Stanford UPS Urbanization Research Fund to A.P.

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Received: 6 February 2005
Accepted: 14 August 2005
Amended: 1 September 2005