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# Isotopic and elemental indicators of nutrient sources and status of coastal habitats in the Caribbean Sea, Yucatan Peninsula, Mexico

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#### **Abstract**

Nutrient inputs associated with coastal population growth threaten the integrity of coastal ecosystems around the globe. In order to assess the threat posed by rapid growth in tourism, we analyzed the nutrient concentrations as well as the  $\delta^{15}$ N of NO<sub>3</sub> and macrophytes to detect wastewater nitrogen (N) at 6 locations along a groundwater-dominated coastal seagrass bed on the Caribbean coast of Mexico. We predicted that locations with greater coastal development would have higher concentrations of dissolved inorganic nitrogen (DIN) and phosphorus (P), as well as δ<sup>15</sup>N of NO<sub>3</sub>, reflecting wastewater sources of N. However, concentrations of NO<sub>3</sub> were not significantly different between developed  $(3.3 \pm 5.3 \,\mu\text{M NO}_3^-)$  and undeveloped  $(1.1 \pm 0.7 \,\mu\text{M})$  marine embayments. The most important control on DIN concentration appeared to be mixing of fresh and salt water, with DIN concentrations negatively correlated with salinity. The  $\delta^{15}$ N of NO<sub>3</sub> was elevated at an inland pond  $(7.0 \pm 0.42\%)$  and a hydrologically-connected tide pool  $(7.6 \pm 0.57\%)$  approximately 1 km downstream of the pond. The elevated  $\delta^{15}$ N of NO<sub>3</sub> at the pond was paralleled by high  $\delta^{15}$ N values of Cladophora sp., a ubiquitous green alga ( $10 \pm 1\%$ ). We hypothesize that inputs of nitrogen rich ( $NO_3^- > 30 \,\mu\text{M}$ ) groundwater, characterized by <sup>15</sup>N enriched signatures, flow through localized submarine groundwater discharges (SGD) and contribute to the elevated  $\delta^{15}$ N signatures observed in many benthic macrophytes. However, changes in nitrogen concentrations and isotope values over the salinity gradient suggest that other processes (e.g. denitrification) could also be contributing to the <sup>15</sup>N enrichments observed in primary producers. More measurements are needed to determine the relative importance of nitrogen transformation processes as a source of <sup>15</sup>N to groundwaters; however, it is clear that continued inputs of anthropogenic N via SGD have the potential to severely impact ecologically and economically valuable seagrass meadows and coral reefs along the Caribbean coast of Mexico. © 2007 Elsevier Ltd. All rights reserved.

Keywords:  $\delta^{15}$ N; nutrients; seagrass; coral reefs; eutrophication; wastewater; Mexico; Yucatan

#### 1. Introduction

Estimates indicate that approximately 50% of the world's population currently lives within 200 km of the coast and

that percentage is expected to rise (Stegeman and Solow, 2002). As a result, human impacts increasingly threaten productive and diverse coastal ecosystems such as seagrass meadows and coral reefs. One of the greatest threats to these systems is cultural eutrophication. As well, construction of buildings, roads, and aquaculture ponds can affect the biogeochemistry of coastal ecosystems by eliminating an important sink for anthropogenic nutrients as well as eliminating a source of refractory organic matter to nearshore environments (Alongi et al., 1992; Duarte and Cebrian, 1996; Alongi, 2002).

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Anthropogenic nutrients can contribute to declines in seagrass meadows and coral reefs (Short and Wyllie-Echeverria, 1996; Lapointe, 1997) because nutrient enrichment stimulates the growth of algae, which can overgrow coral reefs and limit light availability to seagrasses (Silberstein et al., 1986; Lapointe et al., 2005). Anthropogenic nutrients are the primary factor in the loss of at least 90,000 ha of seagrass meadow in a decade (Short and Wyllie-Echeverria, 1996), and as many as 58% of coral reefs worldwide are at "high" or "medium" risk of degradation due to anthropogenic stress (Bryant et al., 1998). Seagrass meadows and coral reefs are ecologically and economically valuable systems because they enhance biodiversity (Dorenbosch et al., 2005), elevate coastal productivity (Cebrian, 2002), support fisheries (Nagelkerken et al., 2000; Nagelkerken et al., 2002), and generate tourism. Early detection of changes in anthropogenic inputs to tropical coastal ecosystems is imperative to maintain these ecosystem services.

The Caribbean coast of Mexico is experiencing swift population growth and expansion in tourism. In the Riviera Maya alone, tourism and hotel density quadrupled from 1998 to 2004 (595,000 to 2.4 million tourists; Secretaría de Turismo, Quintana Roo, Mexico) (Secretaría de Turismo, 2005), and the trend is likely to continue into the near future. A byproduct of this increase in tourism may be greater wastewater production along the coast. Proper wastewater treatment and disposal in the area are critical because the bedrock of the Yucatan Peninsula consists of karstic limestone. Groundwater easily moves through karst, carrying nutrients from untreated or partially treated wastewater and faulty septic systems (Whitney et al., 2003). These nutrients enter coastal waters by submarine groundwater discharge (SGD) and may contribute to eutrophication of nearby seagrass meadows and coral reefs (Lapointe et al., 1990; Simmons and Lyons, 1994). Discharge of groundwater is often difficult to detect, however, because of its extremely localized distribution (Charette et al., 2001).

The objective of this study was to investigate the presence of anthropogenic N in coastal waters in the vicinity of Akumal, Quintana Roo, Mexico (Fig. 1) by analyzing the  $\delta^{15}$ N of NO<sub>3</sub> and primary producers. Because wastewater N typically has elevated  $\delta^{15}N$  values (5–9% in untreated wastewater and 10-22\% in treated wastewater) relative to NO<sub>3</sub> from natural soils, anthropogenic N inputs to coastal waters and producers can be identified (McClelland et al., 1997; McClelland and Valiela, 1998). Specifically, we predicted that Akumal Bay, which is surrounded by hotels and other tourism-related development, would have greater dissolved inorganic nitrogen (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and phosphorus (P) levels than at Xaak, an adjacent but comparably much more isolated lagoon. We also predicted that  $\delta^{15}N$  of  $NO_3^$ at Akumal Bay would be greater than at Xaak due to the presence of wastewater, and the  $\delta^{15}N$  values of primary producers would be elevated, reflecting uptake of anthropogenic (wastewater-derived) N. In addition to samples collected at Akumal Bay and Xaak, we also measured the  $\delta^{15}N$  of NO<sub>3</sub> at several other local water bodies to provide baseline data for future research.

#### 2. Methods

#### 2.1. Study sites

The study was conducted along the Caribbean coast of Quintana Roo, Mexico (Fig. 1). Akumal Bay is a small embayment located adjacent to the resort area of Akumal, Mexico. The Mesoamerican Barrier Reef guards the outer edge of Akumal Bay (up to 4 m deep), protecting seagrass meadows containing Halodule wrightii Ascherson, Syringodium filiforme Kützing, and Thalassia testudinum Banks ex König. The bottom slopes gradually from the shoreline to the barrier reef and there are no surface water inputs into the bay. Numerous resorts, vacation homes, and the village of Akumal surround the bay (Fig. 1). Xaak is a similar marine embayment although it is smaller in size and is surrounded by undeveloped land. Development of the surrounding area is scheduled for the near future. The three seagrass species mentioned above are found within Xaak, and the coral reefs at the site appear relatively healthy with respect to the reefs in Akumal Bay. The water clarity was high in both embayments, and the water column was relatively uniform in salinity and temperature (data not shown).

In addition to samples collected at Akumal Bay and Xaak, water samples were also collected at 4 other local water bodies. Casa Cenote is a sinkhole that formed as the ceiling of an underground cave collapsed and exposed the water under the limestone bedrock. Water enters Casa Cenote via subsurface flow of groundwater underneath mangrove forest and exits through an underground cave that upwells into the Caribbean a few meters offshore. Yal Kú Lagoon is a narrow inlet with a strong marine influence at its seaward end. The southern boundary of the lagoon is lined with vacation homes; however, its northern edge is less developed. Laguna Lagartos is a small, inland body of nearly fresh water in a forested area northeast of Akumal Pueblo and west of the developed coastline. Thick mats of the green alga Cladophora sp. cover the surface of Laguna Lagartos. Laguna Lagartos is connected to the inland edge of Yal Kú Lagoon via subsurface flow (K. Riley, Centro Ecológico Akumal, pers. commun.). Along the edge, persistent pools form in deep fissures of the bedrock and are believed to be fed by the subsurface flow between Laguna Lagartos and Yal Kú Lagoon. Yal Kú Chico is a small inlet that receives groundwater discharge from the surrounding undeveloped, forested area. The relatively fresh groundwater forms a distinct layer above the intruding saline waters of the Caribbean Sea in classic salt-wedge stratification. With the exception of the overgrown surface waters of Laguna Lagartos, water clarity at all sites is high. Light easily penetrated to the bottom of all sampling sites, even to depths >7 m in Casa Cenote.

#### 2.2. Sample collection and processing

Water and plant samples were collected in May and June 2005. Four water samples were collected from different locations in Akumal Bay and three were collected from Xaak.

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