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Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary

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Abstract

We hypothesize that nutrient cycling in a Gulf of Mexico subterranean estuary (STE) is fueled by oxygen and labile organic matter supplied by tidal pumping of seawater into the coastal aquifer. We estimate nutrient production rates using the standard estuarine model and a non-steady-state box model, separate nutrient fluxes associated with fresh and saline submarine groundwater discharge (SGD), and estimate offshore fluxes from radium isotope distributions. The results indicate a large variability in nutrient concentrations over tidal and seasonal time scales. At high tide, nutrient concentrations in shallow beach groundwater were low as a result of dilution caused by seawater recirculation. During ebb tide, the concentrations increased until they reached a maximum just before the next high tide. The dominant form of nitrogen was dissolved organic nitrogen (DON) in freshwater, nitrate in brackish waters, and ammonium in saline waters. Dissolved organic carbon (DOC) production was two-fold higher in the summer than in the winter, while nitrate and DON production were one order of magnitude higher. Oxic remineralization and denitrification most likely explain these patterns. Even though fresh SGD accounted for only ~5% of total volumetric additions, it was an important pathway of nutrients as a result of biogeochemical inputs in the mixing zone. Fresh SGD transported ~25% of DOC and ~50% of total dissolved nitrogen inputs into the coastal ocean, with the remainder associated with a one-dimensional vertical seawater exchange process. While SGD volumetric inputs are similar seasonally, changes in the biogeochemical conditions of this coastal plain STE led to higher summertime SGD nutrient fluxes (40% higher for DOC and 60% higher for nitrogen in the summer compared to the winter). We suggest that coastal primary production and nutrient dynamics in the STE are linked.

1. INTRODUCTION

Subterranean estuaries (STE) are defined as areas where groundwater derived from recharge on land mixes with seawater that has invaded the aquifer (Moore, 1999). This term was coined to emphasize the importance of mixing and chemical reactions that occur in coastal aquifers. STE are usually characterized by longer residence times, stronger particle–water interactions, and lower dissolved oxygen than surface estuaries. The biogeochemical processes regulating the input, recycling, and removal in surface estuaries have been studied in great detail over the last few decades (Kaul and Froelich, 1984; Boynton et al., 1995; Bianchi et al., 1999; Windom et al., 1999; Pinckney et al., 2001; Valiela et al., 2002; Seitzinger et al., 2005), but their subterranean counterparts are only beginning to be explored.

Recent investigations addressed nutrient distributions in STE. Silicate and dissolved organic carbon (DOC) appeared to behave conservatively, while phosphate and nitrate had non-conservative removal in a STE from New York (Beck et al., 2007). In southern Brazil, high ammonium concentrations indicated remineralization of organic detritus (Windom and Niencheski, 2003). In two Florida environments, nutrient concentrations and ratios in coastal groundwater were strongly related to redox potential

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(Kroeger et al., 2007; Santos et al., 2008a). Such a control was also indicated by field observations in Massachusetts and biogeochemical modeling in an idealized STE (Spiteri et al., 2008). Even in organic carbon poor conditions, the nearshore aquifer is a biogeochemically active zone, where attenuation of nitrogen can occur (Kroeger and Charette, 2008). Relevant biogeochemical and physical processes removing nutrients from subterranean estuaries include denitrification (An and Joye, 2001; Addy et al., 2005), calcium phosphate precipitation (Cable et al., 2002; Slomp and Van Cappellen, 2004), sorption of P to Fe-oxides (Charette and Sholkovitz, 2002; Charette and Sholkovitz, 2006), and submarine groundwater discharge (SGD).

Significant SGD inputs of nitrogen may be a key factor initiating and maintaining phytoplankton blooms in the coastal ocean (Hu et al., 2006). Globally, fresh groundwater discharge has been estimated to be only a few percent of the total freshwater flux to the oceans (Burnett et al., 2006). However, as dissolved species concentrations in groundwater often exceed those in surface waters, groundwater can play a significant role in dissolved species budgets even when the volume contribution is small (Santos et al., 2008b). A series of investigations demonstrated that nutrient inputs via SGD were either comparable or higher than local river inputs in a variety of environments, including salt marshes (Charette et al., 2003), coral reefs (Paytan et al., 2006), coastal lagoons (Deborde et al., 2008), and river-dominated shelves (Burnett et al., 2007). It has even been suggested that high N:P ratios in contaminated groundwaters may drive the coastal ocean towards P-limitation within the coming decades, perhaps shifting the present N-limited primary production (Slomp and Van Cappellen, 2004).

The common approach for calculating SGD-derived nutrient exports to coastal waters does not consider modifications as nutrients pass through subterranean estuaries. Simply multiplying the average nutrient concentration in continental groundwater by the fresh SGD rate will lead to accurate fluxes only for conservative species. The scientific community now recognizes the dynamic nature of SGD (Burnett et al., 2006). The view that discharge is controlled exclusively by seasonal oscillations of the water table on land has been revised. Geochemical tracer (^{222}Rn), modeling, and seepage meter results indicate that SGD may be highly variable over short time scales as a consequence of transient processes, such as tidal pumping and wave setup (Kim and Hwang, 2002; Taniguchi and Iwakawa, 2004; Robinson et al., 2007; Santos, 2008). To obtain dissolved species fluxes, temporally integrated SGD fluxes are still often multiplied by the average elemental concentration in the coastal aquifer neglecting temporal changes in groundwater biogeochemistry. Even though this may be a reasonable assumption in some cases, we suspect that endmember nutrient concentrations may be as variable as SGD rates.

In a recent investigation at the same site reported here, we described nutrient distributions in 2D transects sampled across the subterranean salinity gradient. We described qualitatively the role biogeochemical processes play in the alteration of endmember nutrient concentrations in the subsurface (Santos et al., 2008a). We hypothesized that marine forces control nutrient biogeochemistry in this STE, i.e., tidal pumping supplies oxygen and reactants in the form of particulate marine organic matter. We further hypothesized that the remineralization of these organic reactants represents a major nutrient source to shallow beach groundwaters. Our objective in the current investigation was to explore these hypotheses and to determine the factors driving nutrient biogeochemistry in a STE over short time scales. We use the standard estuarine model developed for surface estuaries and a non-steady-state box model to estimate nutrient production and consumption rates in the freshwater–seawater transition zone. We also discuss nitrogen speciation and separate the nutrient fluxes derived from fresh and saline SGD.

2. MATERIALS AND METHODS

We conducted a series of field experiments in a STE near the Florida State University Coastal and Marine Laboratory (FSUCML) in the north-eastern Gulf of Mexico (Turkey Point), a site where several previous SGD studies have been conducted. A detailed description of the study site can be found in these prior studies (Cable et al., 1996; Burnett and Dulaiova, 2003; Lambert and Burnett, 2003; Santos et al., 2008a).

In order to plan the location of the permanent monitoring wells sampled here, we used a push-point piezometer (Charette and Allen, 2006) to determine where the freshwater–seawater interface was located. Monitoring wells were then installed about 1 week before the experiments to allow the well casing to equilibrate with the surrounding sediments. In our first experiment, hereafter referred to as "vertical time series (VTS)", four wells were installed at the high tide mark at depths ranging from 0.5 to 2.5 m. This is the layer where permeable sediments occur (Fig. 1) and where groundwater is more dynamic. Samples were collected every 90 min during a tidal cycle (total of 16 h) on 30 May 2007 following standard procedures described elsewhere (Charette and Allen, 2006). Based on the results of the VTS, we designed a second experiment (hereafter referred to "as horizontal time series or HTS"). In this experiment, we sampled five wells that were horizontally distributed perpendicular to the beach face (0.5 m deep; 20 cm long screens) in the summer (August 2007) and in the winter (January 2008; Fig. 1).

Samples for inorganic nutrients, DOC and total dissolved nitrogen (TDN) analyses were collected with plastic, acid-cleaned syringes and immediately filtered through disposable 0.7 μm Whatman® GF/F syringe filters. Replicate samples were collected after discarding a small amount of filtered water. Immediately after filtering, nutrient samples were kept on ice in the dark until they could be frozen (within a few hours of collection). Nutrient analysis was conducted within 1 week of sampling using standard colorimetric methods (Grasshoff et al., 1999). Analytical errors, based on the standard deviations of triplicate samples, were lower than 6% for nitrate, phosphate, and silicate and 7% for ammonium. DOC and total dissolved nitrogen (TDN) samples were acidified to pH 2 with HCl, sealed into glass ampoules in the field, and analyzed with a Shimadzu