

## Nitrogen transformations within a tropical subterranean estuary



Dirk V. Erler<sup>a,\*</sup>, Isaac R. Santos<sup>a</sup>, Ying Zhang<sup>b</sup>, Douglas R. Tait<sup>a</sup>,  
Kevin M. Befus<sup>c</sup>, Alicia Hidden<sup>a</sup>, Ling Li<sup>b</sup>, Bradley D. Eyre<sup>a</sup>

<sup>a</sup> Centre for Coastal Biogeochemistry, School of Environmental Science and Management, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia

<sup>b</sup> School of Civil Engineering, University of QLD, St Lucia, QLD 4067, Australia

<sup>c</sup> Department of Geosciences, University of Texas, Austin, TX, USA

### ARTICLE INFO

#### Article history:

Received 29 October 2012

Received in revised form 30 January 2014

Accepted 29 May 2014

Available online 17 June 2014

#### Keywords:

Nitrogen

Subterranean estuary

Groundwater

Geochemistry

Denitrification

Stable isotope

### ABSTRACT

A detailed geochemical groundwater survey was conducted within a carbonate sand subterranean estuary (STE) system on the tropical island of Rarotonga, Cook Islands, to identify N sources and transformation along the groundwater flow paths. There were two distinct sources of N to the STE: (1) local organic material which produced  $\text{NH}_4^+$  in the anoxic deeper groundwater (3.5–4 m below the aquifer surface), and (2) an  $\text{NO}_3^-$  rich upper saline plume located in the shallow groundwater near the high tide mark of the STE. Ammonium concentrations decreased away from the organic source and the  $\delta^{15}\text{N-NH}_4^+$  signature became increasingly enriched. The calculated kinetic fractionation factor for  $\text{NH}_4^+$  loss was much less than that reported for nitrification in other systems, implying that mixing was important in reducing concentration. A simple fractionation/mixing model showed that  $\text{NH}_4^+$  loss via nitrification increased towards the surface where it contributed up to 80% of the observed decrease in  $\text{NH}_4^+$  concentration. A fast moving ( $\sim 2 \text{ m d}^{-1}$ ) upper saline plume of shallow  $\text{NO}_3^-$  rich groundwater was a major feature of the studied STE. Denitrification was estimated to account for up to 88% of the decrease in  $\text{NO}_3^-$  concentration in this plume. The potential denitrification rate based on an isotope tracer addition experiment was  $270 \mu\text{mol L}^{-1} \text{d}^{-1}$ . Assuming that similar  $\text{NO}_3^-$  rich plumes occur all along the foreshore of the studied lagoon, we estimate that groundwater can contribute 4–15% of the daily lagoon N standing stock. We conclude that submarine groundwater discharge of shallow N rich porewater into the studied lagoon system is strongly regulated by denitrification within the STE.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Prior to entering coastal ecosystems, groundwater must first travel across the 'subterranean estuary' (STE) (Moore, 1999). This mixing zone between fresh and saline aquifers is geochemically active and can initiate rapid changes in nutrient concentration and speciation. In some cases, the STE can act as a barrier to the movement of fresh groundwater contaminants into coastal waters (Charette and Sholkovitz, 2002; Loveless and Oldham, 2010; Spiteri et al., 2008). Despite its capacity to regulate nutrient discharge to the coastal ocean, our understanding of the biogeochemical transformations within the STE remains incomplete (Moore, 2010; Taniguchi et al., 2002). In particular, the transformation pathways of nitrogen (N) are not well-constrained for permeable aquifers, especially those found in carbonate sand-dominated tropical islands.

Most STE studies have dealt with slow to intermediate flow in silica sand groundwater systems (i.e. flows between 1 and  $150 \text{ m y}^{-1}$ ) and we now have a reasonable understanding of nutrient transformation in these types of systems (Kroeger and Charette, 2008; Santoro et al., 2008; Slomp and Van Cappellen, 2004). Much less attention has been

paid to the permeable carbonate groundwater systems of tropical islands. Pacific Islands are characterised by minimal surface water flow due to the very high soil infiltration rates (Edworthy, 1985). Consequently SGD can be the dominant freshwater source to island lagoons (Tait et al., 2013) in contrast to most silica sand systems where recirculated seawater is often relatively more important than fresh SGD (de Sieyes et al., 2008).

Given the rapid and often unregulated coastal development over the last 50 years there are concerns that groundwater may be heavily contaminated with septic-borne nutrients in many Pacific Islands. Much research has shown that septic effluent is indeed a source of contamination to groundwater (Gill et al., 2009; Katz et al., 2010). The STE of tropical islands could thus play a pivotal role in regulating the nutrient flux into nearby coastal lagoons. The mixing zone within STE's contains a spectrum of biogeochemical conditions (i.e., oscillating dissolved oxygen, high dissolved organic carbon) that are often required to fully transform DIN into gaseous products (Kroeger and Charette, 2008). However in rapid flow systems such as carbonate sands, the reduced contact between groundwater metabolites and aquifer solids may limit the capacity for nutrient processing (Slomp and Van Cappellen, 2004). In order to better manage the tropical lagoons of the Pacific Islands we need to establish if there is significant N reaching the STE and, if so, how it is processed within the STE.

\* Corresponding author. Tel.: +61 2 6620 3256.  
E-mail address: [dirk.erler@scu.edu.au](mailto:dirk.erler@scu.edu.au) (D.V. Erler).

If the groundwater of tropical Pacific Islands is heavily contaminated with N, subterranean estuaries may be crucial in regulating the amount of N entering coastal lagoons. In order to test this concept we conducted a detailed geochemical survey of a tropical subterranean estuary system on the island of Rarotonga, Cook Islands to identify the likely sources of N to the STE and to determine how N is processed within this system. Based on studies that show permeable sediments to be efficient nutrient filters during advective flow Eyre et al. (2008), Eyre et al. (2013), Meile et al. (2010), we predict that the permeable carbonate sands of an STE on the island of Rarotonga will attenuate groundwater nutrients seeping into the lagoon. This paper builds the growing SGD literature by (1) focusing on a carbonate sand STE, (2) using multiple approaches (i.e., dinitrogen concentrations, stable isotope observations) to gain insights into denitrification, (3) and using a stable isotope addition experiment in a STE for the first time.

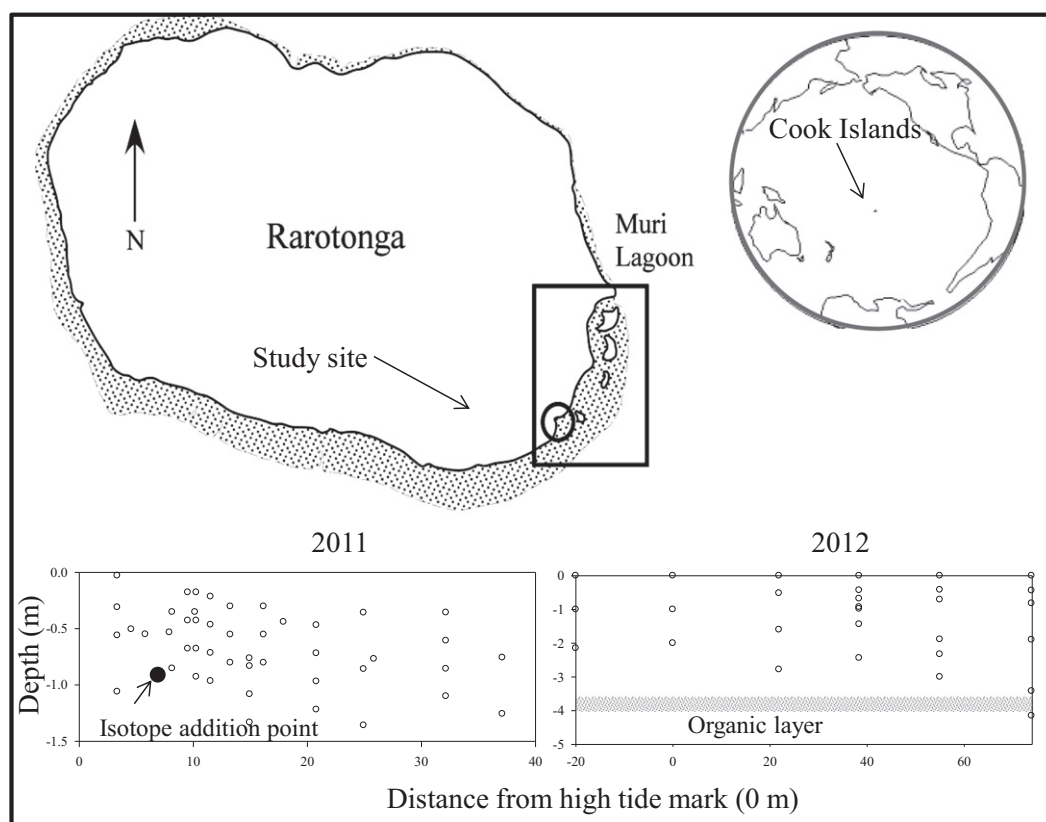
## 2. Methods

### 2.1. Experimental approach

The studied STE is located along the Muri Lagoon on the island of Rarotonga, Cook Islands ( $21^{\circ} 15.848'S$ ,  $159^{\circ} 44.089'W$ ) (Fig. 1). The STE was chosen to represent a typical groundwater/marine interface on the island. Sediments at the study site had high porosity ( $\sim 0.65$ ) and hydraulic conductivity ( $\sim 17.3 \text{ m d}^{-1}$ ), and low organic matter content (loss on ignition  $\sim 2.5\%$  dry weight). Sediments were predominantly carbonate sands (11% inorganic C content by weight) with low N content (0.036% dry weight). The lagoon itself is on the south east corner of the island and has an area of approximately  $1.75 \text{ km}^2$  and an average depth of

1.4 m. The lagoon has a semi diurnal tidal cycle with a range of approximately 1 m. Salinity in the lagoon averaged 35.6 during the study.

Two studies were performed at the site, one in February 2011 and one in March 2012. In 2011, we measured groundwater geochemical parameters along a 40 m transect stretching from the high tide mark (HTM) and the low tide mark (LTM) of the beach-face to map the distribution of nitrogen species in the STE. Multilevel porewater samplers ( $\sim 2 \text{ m}$  apart; up to 1 m deep) similar in design to those described by Martin et al. (2003) were installed along the 40 m STE transect (Fig. 1). In addition, a stable isotope addition experiment was also conducted in 2011 to gain insight into nitrogen transformations. In 2012 we investigated groundwater geochemistry across a longer transect (90 m) that stretched 20 m landward and 70 m seaward of the HTM. The longer transect was designed to capture fresh groundwater flow discharging deeper and further out along the STE. The potential for this discharge was identified in electrical resistivity profiling conducted in 2011 (Befus et al., 2013). In 2012 six multilevel samplers were installed along the 90 m STE (Fig. 1). The total depth of the samplers was 4.2 m below the aquifer surface. Each piezometer contained between 4 and 8 sampling ports. Once installed the multilevel samplers were left for two days before sampling commenced to allow sediments to settle around the sampling ports. Samples were collected using a peristaltic pump ( $100 \text{ mL min}^{-1}$ ) attached to the flexible tubing of the multi-level samplers. Firstly about 100 mL of porewater was allowed to flow to waste. Next the pump outlet was attached to the flow-through cell of a Hydrolab MiniSonde (MS5) water quality unit containing calibrated dissolved oxygen (DO), temperature and salinity probes. After readings stabilised the porewater was collected for dissolved  $\text{N}_2$  concentration analysis in triplicate glass stoppered 10 mL vials containing 0.1 mL of saturated  $\text{HgCl}_2$  preservative.



**Fig. 1.** Position of the study site within the Muri Lagoon on the main island of Rarotonga, Cook Islands. The inset plots show the positioning of the multilevel porewater samplers during both years of the study. The filled circle in the 2011 plot is the addition point for the isotope tracer experiment. The shaded bar in the 2012 plot shows the approximate location of an organic rich peat layer that ran along the length of the transect.

Download English Version:

<https://daneshyari.com/en/article/1261355>

Download Persian Version:

<https://daneshyari.com/article/1261355>

[Daneshyari.com](https://daneshyari.com)