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Nitrogen isotopic composition of organic matter from a 168 year-old coral skeleton: Implications for coastal nutrient cycling in the Great Barrier Reef Lagoon

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ABSTRACT

Ongoing human activities are known to affect nitrogen cycling on coral reefs, but the full history of anthropogenic impact is unclear due to a lack of continuous records. We have used the nitrogen isotopic composition of skeleton-bound organic matter (CS-δ^{15}N) in a coastal *Porites* coral from Magnetic Island in the Great Barrier Reef as a proxy for N cycle changes over a 168 yr period (1820–1987 AD). The Magnetic Island inshore reef environment is considered to be relatively degraded by terrestrial runoff; given prior CS-δ^{15}N studies from other regions, there was an expectation of both secular change and oscillations in CS-δ^{15}N since European settlement of the mainland in the mid 1800s. Surprisingly, CS-δ^{15}N varied by less than 1.5‰ despite significant land use change on the adjacent mainland over the 168-yr measurement period. After 1930, CS-δ^{15}N may have responded to changes in local river runoff, but the effect was weak. We propose that natural buffering against riverine nitrogen load in this region between 1820 and 1987 is responsible for the observed stability in CS-δ^{15}N. In addition to coral derived skeletal δ^{15}N, we also report, for the first time, δ^{15}N measurements of non-coral derived organic N occluded within the coral skeleton, which appear to record significant changes in the nature of terrestrial N inputs. In the context of previous CS-δ^{15}N records, most of which yield CS-δ^{15}N changes of at least 5‰, the Magnetic Island coral suggests that the inherent down-core variability of the CS-δ^{15}N proxy is less than 2‰ for *Porites*.

1. Introduction

Every year, 70–100 Tg of anthropogenic fixed N is transported into the coastal ocean through either riverine transport or atmospheric deposition (Fowler et al., 2013). The release of inorganic reactive N is thought to be a major driver of coastal ecosystem decline worldwide (Elser et al., 2007), and coral reefs of naturally oligotrophic tropical waters would seem particularly vulnerable (Carpenter et al., 1998).

It is generally accepted that coastal reef systems, including those of the Great Barrier Reef (GBR), are highly susceptible to eutrophication associated with terrestrial runoff (Brodie et al., 2011). Evidence to date suggests that agricultural activity since European settlement in the mid 1800s has increased the flux of sediments and nutrients to the near-shore GBR (Furnas, 2003; Kroon et al., 2012; McCulloch et al., 2003). Furthermore, spatial changes in coral reef composition have been associated with declining water quality gradients (Fabricius et al., 2005), with many inshore reef systems already considered eutrophic (Bell, 1992; Bell and Elmetri, 1995; Brodie et al., 2011). However, in the GBR, there is still no clarity as to the historical changes that have occurred as a result of anthropogenic nutrient inputs, mostly due to a lack of long term records of coastal water quality (Fabricius et al., 2005; Koop et al., 2001; Wooldridge et al., 2006).

Changes in N availability are typically accompanied by shifts in the isotopic composition of the N (δ^{15}N (in permil, ‰) $= 1000 * ((^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{reference} - 1)$, where the $^{15}N/^{14}N$ reference is N_2 in air). This is particularly true if the isotope signature of the N source changes; for example, an increase in fertiliser runoff is generally associated with a drop in the δ^{15}N of fixed N dissolved in the coastal water column and particulate N suspended in it (Kendall et al., 2007). Numerous studies have suggested that

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Table 1
The expected influences of anthropogenic changes to coastal reef N supply and N cycling on the CS-δ^{15}N of resident *Porites* corals (DIN is dissolved inorganic N and PON is particulate organic N).

Anthropogenic change	Effect on CS-δ^{15}N
Shift in the δ^{15}N of source DIN and PON to reefs	Uptake of DIN by zooxanthellae, uptake of DIN by plankton which are then consumed by the coral, or direct consumption of PON all change CS-δ^{15}N in the direction of the δ^{15}N shift (Erler et al., 2015; Hoegh-Guldberg et al., 2004; Wang et al., 2015)
Shift in food web structure	Increase in phytoplankton abundance and corresponding trophic level changes in δ^{15}N are recorded in CS-δ^{15}N (Sherwood et al., 2011)
Increase in PON (coral food source) supply	Changes in N recycling efficiency and increased ammonium leakage increases CS-δ^{15}N (Wang et al., 2015)
Sedimentation	Reduced zooxanthellae numbers, possible bleaching and increased CS-δ^{15}N (Bessell-Browne et al., 2014)

these anthropogenically induced shifts in δ^{15}N are recorded by benthic marine organisms such as corals (Baker et al., 2010b; Hoegh-Guldberg et al., 2004; Sammarco et al., 1999; Sherwood et al., 2010) and macroalgae (Costanzo et al., 2001). The δ^{15}N signal of boulder forming hard coral tissue is well preserved within the skeleton (Muscatine et al., 2005; Yamazaki et al., 2013), and several studies have now used the δ^{15}N of hard coral skeleton-bound organic N (CS-δ^{15}N) to try and detect temporal and spatial changes in the δ^{15}N of anthropogenic N discharges (Jupiter et al., 2008; Lewis et al., 2012; Marion et al., 2005; Yamazaki et al., 2011).

However the CS-δ^{15}N of hard corals will also respond to ecosystem shifts driven by changes in N availability. For instance, increased N loads to coral reefs lead to changes in microbial community structure (Furnas et al., 2005) and prey availability for higher trophic levels, which can cause changes to the δ^{15}N of zooplankton (McClelland and Montoya, 2002). Food-web structure in a marine ecosystem therefore affects the δ^{15}N of the different components of that ecosystem (Michener and Kaufman, 2007), some of which are accessed during feeding by corals. Moreover, and separate from any δ^{15}N change in a given prey item, both physiological and trophic changes in zooxanthellate corals can alter their tissue δ^{15}N (Erler et al., 2015; Reynaud et al., 2009; Wang et al., 2015). Anthropogenic N enrichment therefore works to alter CS-δ^{15}N in multiple ways, including: (1) changes in the δ^{15}N of the source of inorganic and particulate N to a system; (2) changes in the δ^{15}N of N available to the coral through shifting food-web structure; and (3) changes in the internal cycling of N between coral and symbiont as a result of coral feeding rate and/or zooxanthellae growth rate (Table 1). Given all of these factors, barring a remarkable coincidence of offsetting effects, an ecologically consequential anthropogenic nutrient enrichment on a coral reef will cause a measurable change in the CS-δ^{15}N of resident corals.

Most of the previous tropical hard coral CS-δ^{15}N records appear to support the view that anthropogenic activity has significantly altered coastal ocean N cycling (Jupiter et al., 2008; Marion et al., 2005; Yamazaki et al., 2011, 2015). However, many of the analytical protocols previously used did not sufficiently clean the coral skeletal samples to remove potential contaminants from non-coral derived organic N, or foreign organic N (FON), that become occluded within the coral skeleton during calcification. Furthermore, many of the previous studies isolated only the acid insoluble organic fraction of the skeletal organic material, causing potential bias in their CS-δ^{15}N records. Both these factors could have limited their capacity to support detailed historical studies of coral skeletal δ^{15}N as a proxy of environmental change.

Recently a new method was developed in which the organic N from small quantities (e.g. 5 mg) of cleaned coral powders is oxidised and bacterially converted to N_2O for analysis of δ^{15}N via isotope ratio mass spectrometry (Wang et al., 2015). The new method for CS-δ^{15}N analysis is adequately precise ($1\sigma = 0.2‰$) to capture even modest changes in CS-δ^{15}N (Wang et al., 2015). Further, it has already been shown that CS-δ^{15}N measured in this way can be used to trace small ($\sim$1‰) spatial fluctuations in external water column δ^{15}N (Erler et al., 2015). The natural progression in the development of this new proxy is the reconstruction of long-term (>100 yr) temporal CS-δ^{15}N records at semi-annual/annual resolution.

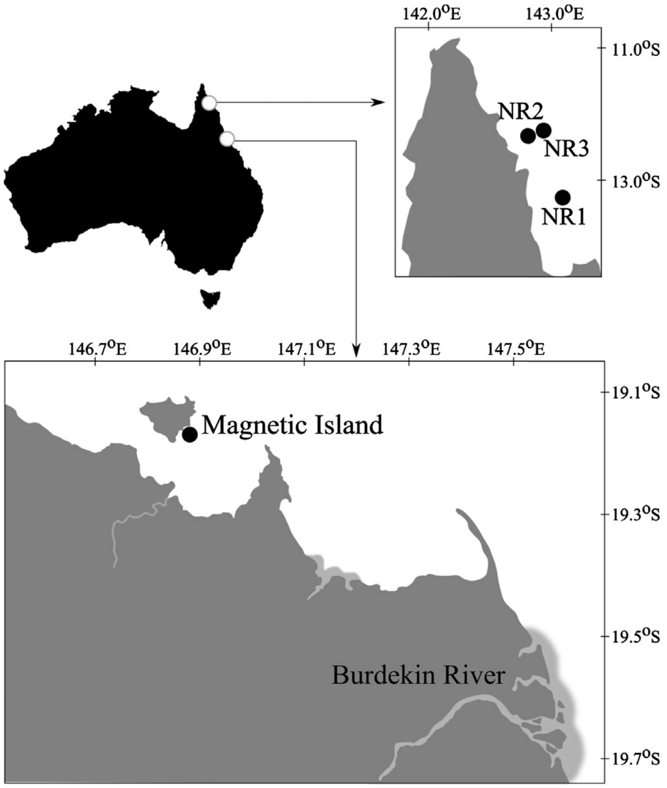

Fig. 1. Map of the coral core collection sites in relation to the Australian mainland and the Burdekin River. One core was collected from Geoffrey Bay, Magnetic Island (19.15°S, 146.87°E) in 1987, while three other cores were collected in the far northern section of the GBR in 1990.

In this study, we have applied the new CS-δ^{15}N technique to investigate possible changes in the N cycling dynamics of a coastal reef in the GBR (Fig. 1) from 1820 to 1987 AD, testing the hypothesis that CS-δ^{15}N from a coastal GBR coral has been altered substantially by previously reported increases in the input of anthropogenic fixed N over that period.

2. Methods

2.1. Coral cores

This work is based on the analysis of coral skeleton-bound organic material from four coral colonies. The main coral core used in this study was drilled from a large *Porites* colony situated in Geoffrey Bay, Magnetic Island (19.15°S, 146.87°E) (Fig. 1) in 1987.