Nitrogen isotopes ($\delta^{15}N$) in coral skeleton: Assessing provenance in the Great Barrier Reef Lagoon.

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The aragonitic skeleton of the massive reef-building coral species *Porites* contains trace concentrations (0.001%-0.015% wt) of organic matter (OM). Traditionally considered a "contaminant," recent studies reveal that the nitrogen isotopic composition of skeletal OM reflects past ambient N sources and the status of the coral-algal endosymbiosis, providing tantilizing new opportunities for provenance studies. Crystalline-bound endoskeletal proteins preserved over decadal to million-year timescales potentially provide a continuous record of variability in oceanic $\delta^{15}N$, and thus a context for identifying significant change in $\delta^{15}N$ end-members. These include chemical fertilizers, septic waste, and urban storm water. We present results from the Mackay Whitsunday region of the central Great Barrier Reef (GBR), where dramatic coastal land clearing for agriculture, urban and port development has resulted in topsoil erosion and an estimated 2-5 fold increase in total river-borne nutrient export since European arrival (1860). To quantify change in the coastal marine environment, cores were drilled by SCUBA from 13 *Porites* coral colonies across a representative transect of inshore (5km) to mid-shelf (25-40km) reefs. Skeletal luminescence, measured in 0.25mm increments (λ=490nm), reveals that Pioneer River flood plumes extend to reefs up to 30km offshore annually, with major floods reaching corals 70km offshore every 3 to 5 years. During $\delta^{15}N$ technique development, we compared 30 organic extraction protocols using 6 homogenous coral standards, revealing systematic, approach-dependent variability ranging from 0.2 to 2.0‰. Applying an optimal analytical approach, 5 annually-resolved chronological $\delta^{15}N$ time series, ranging from 37 to 59 years, were developed from 3 inshore to midshelf GBR reefs. Inshore $\delta^{15}N$ values range from 5.43‰ to 12.80‰ (av. 7.42 ± 0.15, n = 66) and are positively correlated with Pioneer River discharge. Maximum values coincide with the cyclonic floods of 1989 and 1991. Tributary and riverine particulate nitrogen $\delta^{15}N$ fractionates along a steep enrichment gradient within the catchment, from isotopically light values 75km upstream (1-3‰), to enriched values (6-9‰) at the estuarine-ocean interface. The coral record reveals that flood-derived coastal water $\delta^{15}N$ enrichment has intensified dramatically over the past half century, providing the first empirical evidence that pollutants in runoff, including fertilizers and urban waste, have substantially altered inshore GBR water quality.