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The coral $\delta^{15}\text{N}$ record of terrestrial nitrate loading varies with river catchment land use

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Abstract

We analysed the nitrogen isotopes in two coral cores ($\delta^{15}\text{N}_{\text{coral}}$) from the mouth of the Todoroki River, Ishigaki Island, Japan to examine whether the $\delta^{15}\text{N}_{\text{coral}}$ reflects the runoff of nitrate related to the land use in the river catchment. The two coral cores were used to examine the seasonal variation in $\delta^{15}\text{N}_{\text{coral}}$ for 14 years (CORE1; 1993–2007) and the annual variation of $\delta^{15}\text{N}_{\text{coral}}$ for 52 years (CORE2; 1958–2010). $\delta^{15}\text{N}_{\text{coral}}$ In CORE1, the 5-month running mean of $\delta^{15}\text{N}_{\text{coral}}$ was positively correlated with that of monthly precipitation, excluding all strong precipitation events ($>150\text{ mm day}^{-1}$). In CORE2, the $\delta^{15}\text{N}_{\text{coral}}$ mean in the earlier period (1958–1980) was 1.0‰ greater than that in the later period (1981–2010). The annual averages of $\delta^{15}\text{N}_{\text{coral}}$ are positively correlated with the total precipitation in the rainy season (May–June) for both time periods. The difference in the $\delta^{15}\text{N}_{\text{coral}}$ between the earlier and later periods would be caused by the land use changed from paddy fields with ^{15}N -rich manure to sugar cane fields in the early 1980s. Although some uncertainties still remain regarding the precision of $\delta^{15}\text{N}$ coral proxy records, this study emphasises the clear potential for their use in reconstructing terrestrial nitrate discharge records from corals.

Keywords: coral skeletons, nitrogen isotopes, nitrate, land-use, river discharge, coral reefs

42 **Introduction**

43 Coral reef degradation is rapidly increasing throughout the world due to local and
44 global stresses such as pollution and climate change (Bellwood et al. 2004;
45 Hoegh-Guldberg et al. 2007; De'ath et al. 2012). With anthropogenic
46 development of the areas surrounding coastal reefs, terrestrial runoff into the coral
47 reefs is impacting reef water quality and ecosystem functioning (Fabricius 2005).
48 The detection of nutrient sources is useful to assess reef environments. The
49 nitrogen isotope compositions of seawater, macroalgae, sediments and coral tissue
50 have been used to trace the sources of nitrogen in coral reefs (e.g., Heikoop et al.
51 2000; Miyajima et al. 2001; Umezawa et al. 2002a, 2008; Yamamuro et al. 2003).
52 Coral skeletons have been widely used as palaeo-environmental archives in coral
53 reefs and communities (e.g., reviewed by Druffel et al. 1997; Gagan et al. 2000;
54 Grottoli and Eakin 2007). Marion et al. (2005) suggested that the nitrogen isotopic
55 signature in the organic matrix of coral skeletons ($\delta^{15}\text{N}_{\text{coral}}$) records the history of
56 nutrient loading into coral reefs. High-resolution analysis of $\delta^{15}\text{N}_{\text{coral}}$ has also
57 suggested that $\delta^{15}\text{N}_{\text{coral}}$ records the origins of nitrogen in coral reefs at the seasonal
58 scale (Uchida et al. 2008; Yamazaki et al. 2011a). $\delta^{15}\text{N}_{\text{coral}}$ could be a useful proxy
59 to reconstruct nitrogen loading into coral reefs.

60

61 The Todoroki River flows into the Shiraho coral reef at the southeast end of
62 Ishigaki Island, and is one of the major nitrate sources for the sites in this study
63 (Blanco et al. 2010). Seasonal variation in the nitrogen isotopic signature of
64 nitrate ($\delta^{15}\text{N}_{\text{nitrate}}$) at the mouth of the Todoroki River suggests that the nitrate
65 inflow from the Todoroki River is triggered by the rainy season and typhoons
66 (Electronic Supplemental Material, ESM Fig. S1). Another form of dissolved
67 inorganic nitrogen, ammonium, is primarily emitted from reef sediments and sea
68 grass beds, not from the Todoroki River (Miyajima et al. 2001; Blanco et al.
69 2008).

70

71 Yamazaki et al. (2011b) observed a correspondence among the intra reef
72 distribution of $\delta^{15}\text{N}_{\text{coral}}$ in *Porites*, $\delta^{15}\text{N}_{\text{nitrate}}$, and $\delta^{15}\text{N}$ in macro algae (dissolved
73 inorganic nitrogen (DIN) consumers, reported by Umezawa et al. 2002a).

74 These results suggested that $\delta^{15}\text{N}_{\text{coral}}$ in the Shiraho coral reef records the variation
75 of $\delta^{15}\text{N}_{\text{nitrate}}$. Ammonium could also be a source of DIN for corals. However, as

76 nitrogen sources, the volume of nitrate at the mouth of the Todoroki River is
77 much larger than that of ammonium. The concentrations of ammonium are less
78 than 1% of those of nitrate in this study site (Blanco et al. 2008).

79

80 In this study, we examined $\delta^{15}\text{N}_{\text{coral}}$ as a proxy to reconstruct nitrate loading from
81 terrestrial origins into Shiraho coral reef, Ishigaki Island, Japan. Yamazaki et al.
82 (2011b) reported that a zonal distribution of $\delta^{15}\text{N}_{\text{coral}}$ was found within the Shiraho
83 coral reef, which corresponded with the $\delta^{15}\text{N}$ of seawater nitrate. The distribution
84 of $\delta^{15}\text{N}_{\text{nitrate}}$ was from two nitrate sources: the Todoroki River flowing into the
85 reef and slight nitrate ($<1\ \mu\text{M}$) in water from the outer reef ocean.

86

87 We collected coral cores at the mouth of Todoroki River to reconstruct the origins
88 of nitrate loading into coral reefs. We (1) investigated the relationship between the
89 seasonal variation of $\delta^{15}\text{N}_{\text{coral}}$ and precipitation, and (2) compared the 52-year
90 record of the annual $\delta^{15}\text{N}_{\text{coral}}$ to changes in the land-use history in the Todoroki
91 River catchment.

92

93 **Materials and Methods**

94 **Study site**

95 Coral cores were collected at the mouth of the Todoroki River on Ishigaki Island,
96 southwest of the Ryukyu Islands, Japan ($24^{\circ}21' - 31^{\circ}\text{N}$, $124^{\circ}4' - 16^{\circ}\text{E}$); this site has
97 a subtropical climate. The river catchment area is composed of sugarcane, pasture,
98 pineapple and paddy fields (Fig. 1a). The mouth of Todoroki River crosses the
99 coral reef (Fig. 2a). The average annual precipitation is approximately 2000 mm,
100 60% of which falls in the rainy season from May to June or is caused by a
101 typhoon in August or September.

102

103 To analyse the $\delta^{15}\text{N}_{\text{nitrate}}$ and the oxygen isotopic signature of nitrate ($\delta^{18}\text{O}_{\text{nitrate}}$),
104 we collected water samples in March and August 2009 from the Todoroki River
105 (RW1–3), ground water in sugar cane (GW1 and GW2), paddy fields (GW3), and
106 a cattle barn (GW4) from the drainage basin (Fig. 1a). We also collected rainwater
107 samples in August 2009.

108

109

110 Based on the data in Table 1 of Yamazaki et al. (2011b), we compared the nitrate
111 concentrations and $\delta^{15}\text{N}_{\text{nitrate}}$ of seawater samples collected at 50 m intervals along
112 a sampling line from the mouth of the Todoroki River to offshore (Fig. 2b).
113 $\delta^{15}\text{N}_{\text{nitrate}}$ was positively correlated ($R=0.85$, $P<0.004$) with the logarithm of
114 nitrate concentrations in the range from +2‰ in the outer ocean nitrate to +9‰ in
115 the nitrate from the Todoroki River. Time series analyses of $\delta^{15}\text{N}_{\text{coral}}$ at the mouth
116 of the Todoroki River demonstrated the $\delta^{15}\text{N}_{\text{nitrate}}$ changes with terrestrial nitrate
117 discharges.

118

119 **Coral core sampling**

120 Coral drilling was performed at the mouth of Todoroki River using an air drill
121 (Adachi and Abe 2003). On 2 September 2007, we vertically drilled a 60-cm
122 length core from the top of a live *Porites* coral colony at 272 m offshore from the
123 shoreline (CORE1; project ID: SPc070902, sampled from N24°23'12.40",
124 E124°15'20.56", ~2 m depth). The record distance of CORE1 was 14 years
125 (1993–2007), which was determined in monthly resolution by an age model using
126 carbonate Sr/Ca ratios and oxygen isotopes (K. Ohmori, pers. comm.). The annual
127 growth rate of CORE1 was approximately 20 mm year⁻¹ (ESM Fig.S2).
128 Microsampling was performed at 3-mm (~2 month) intervals along the major
129 growth axis to obtain 30–40 mg of coral powder (~100 μmolN). We reconstructed
130 the seasonal variation in the $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 for the past 14 years. To sample a
131 longer core, we also performed coral micro-atoll boring on 2 September 2010
132 (CORE2; project ID: IStr-p100902-2, sampled from N24°23'04.6",
133 E124°15'21.5"), 299 m offshore from the shoreline. CORE2, which was 1.2 m
134 length, was horizontally drilled from the side of a micro-atoll with a depth of less
135 than 2 m. The age model of CORE2 was also determined by fitting the density
136 bands of X-radiographs and Sr/Ca ratios and oxygen isotopes (T. Miyaji, personal
137 communication), and its record distance was the sub-annual variation in $\delta^{15}\text{N}_{\text{coral}}$.
138 The age models and X-radiographs of the two cores (CORE1 and CORE2) were
139 described in Inoue et al. (2014) and ESM Figure S2.

140

141 **$\delta^{15}\text{N}_{\text{coral}}$ analysis**

142 The sampled powder was treated with NaOH (2N, 60°C) for 3 h and rinsed using
143 Milli-Q water to remove the extra organic matter (e.g., algal and fungal
144 bioeroders) in the coral powder according to Yamazaki et al. (2013), who

145 suggested that this cleaning process provides the same values of $\delta^{15}\text{N}$ in
146 intra-crystal aragonite as determined by stepwise heating methods. The tissue
147 layer in the core top (< 4 mm depth from the top of the core) was not used for
148 nitrogen isotope analysis.

149

150 Nitrogen isotope values of organic nitrogen in coral skeletons were analysed using
151 the method developed by Tsunogai et al. (2008) and Yamazaki et al. (2011b). This
152 method involves oxidation/reduction methods such as the oxidation of organic
153 nitrogen to nitrate using persulphate (Knapp et al. 2005; Tsunogai et al. 2008),
154 reduction of nitrate to nitrite using spongy cadmium, and further reduction of
155 nitrite to nitrous oxide using sodium azide. Wet conditions were maintained
156 throughout the chemical treatments to avoid the evaporation of dissolved organic
157 nitrogen, which would affect the $\delta^{15}\text{N}$ values obtained after the re-drying process
158 after acid treatment and to recover $\delta^{15}\text{N}$ in coral skeletons without isotope
159 fractionation.

160

161 First, organic nitrogen in the coral skeletons was oxidised to NO_3^- using
162 persulphate under alkaline conditions. The coral skeletal powder (28 mg) was
163 decalcified with 0.6 ml of 1 N HCl in 30-ml Teflon bottles for 2 h. Then, 0.4 ml of
164 deionised water (DIW) and 50 μl of oxidising reagent (peroxodisulphate;
165 Tsunogai et al. 2008) were added. The Teflon bottles were capped tightly with
166 Teflon screw caps and autoclaved for 1 h at 121°C . After the samples were cooled
167 for 8 hours, needle crystals of CaSO_4 were deposited. A 1-ml volume of the
168 sample solution, excluding the CaSO_4 crystals, and 9 ml of DIW were pipetted
169 into 10-ml vials with butyl rubber caps. For two coral samples, we prepared
170 internal standards, including L-alanine ($\delta^{15}\text{N}=+1.78\pm0.06\%\text{AIR}$), L-histidine
171 ($\delta^{15}\text{N}=-7.96\pm0.05\%\text{AIR}$), and tuna flakes ($\delta^{15}\text{N}=+12.55\pm0.06\%\text{AIR}$). Organic
172 nitrogen standards diluted with DIW (400 $\mu\text{M-N}$) were oxidised to NO_3^- using the
173 same methods. The internal standard samples contained the organic material of
174 the coral skeletons (1 ml), 400 $\mu\text{M-N}$ (1 ml), and 8 ml of DIW in 10-ml vials.
175 Next, NO_3^- was reduced to NO_2^- by adding 0.5 g of spongy cadmium to each vial,
176 followed by 0.3 g of NaCl and 0.1 ml of a 1 M NaHCO_3 solution to yield a final
177 pH of approximately 8.5. The samples were then shaken for 5 h on a horizontal
178 shaker at a rate of 2 cycles sec^{-1} . Subsequently, NO_2^- was reduced to N_2O using

sodium azide. Then, 10 ml of the samples was decanted into a clean 20-ml vial and capped tightly with a butyl rubber cap. After purging with helium to evacuate the air from the headspace and the sample solution for 2 min, 0.4 ml of azide/acetic acid buffer was added to each vial via a syringe, and the mixture was shaken. After 2 h, the solution was made basic by adding 0.2 ml of 8 M NaOH with a syringe and shaking to prevent residual HN_3 from escaping into the laboratory during the subsequent isotopic analysis. These chemical treatments were performed under wet conditions to prevent the evaporation of dissolved organic nitrogen, which would affect the $\delta^{15}\text{N}$ values obtained after the re-drying process after acid treatment and to recover all of the nitrogen in the skeletons. The stable isotopic N_2O composition was determined using our Continuous-Flow Isotope Ratio Mass-Spectrometry (CF-IRMS) system (Tsunogai et al. 2008, Konno et al. 2010; Hirota et al. 2010), which consists of an initial helium purge and trap line, a gas chromatograph (Agilent 6890), and a Finnigan MAT 252 (Thermo Fisher Scientific, Waltham, MA, USA) with a modified Combustion III interface. $\delta^{15}\text{N}$ values were determined relative to $\delta^{15}\text{N}$ of air. The standard deviation of the coral sample measurements was less than 0.2‰ (σ , $n=4$) (Yamazaki et al. 2013).

197

198 **Environmental data**

Daily precipitation data for 1958–2010 on Ishigaki Island were available at the website of the Japan Meteorological Agency (<http://www.jma.go.jp>). Monthly and annual precipitation averages were calculated from the daily data. The 52-year $\delta^{15}\text{N}_{\text{coral}}$ record was compared with the land-use changes revealed by historic aerial photographs and satellite images from Hasegawa (2011) and Ishihara et al. (2014). Five land-use classes (forest, pasture, pineapple, paddy field and sugarcane) were assigned. Aerial photographs from 1962, 1972, 1977/78, 1986, 1989, 1991, and 1995 were classified by visual interpretation based on the texture of the image (Hasegawa 2011), and satellite images from 2006 to 2008 were classified using the decision tree method (e.g., Pal and Mather 2003) based on a crop calendar as each category has specific seasonal changes in vegetation cover (Ishihara et al. 2014).

211

212 **Results**

213 **Isotope composition of nitrate in the river water**

214 The groundwater (GW1, GW2, GW3, and GW4 in Fig.1a) had higher nitrate
215 concentrations ($>450\ \mu\text{M}$) than the river water. $\delta^{15}\text{N}_{\text{nitrate}}$ in the river water
216 increased from $+5.5\text{--}+6.4\text{‰}$ in the upstream area to $+8.5\text{‰}$ at the mouth. The
217 linear relationship ($R=0.91$, $P=0.01$) between $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ suggested
218 that the river water nitrate was a mixture of nitrate from spring water, field
219 drainage, and rainwater (Fig. 1b).

220

221 **Seasonal variation in $\delta^{15}\text{N}_{\text{coral}}$ for 1993–2007 (CORE1)**

222 The $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 varied between $+0.1\text{‰}$ and $+11\text{‰}$ in monthly resolution
223 for 1993–2007 (Fig. 3a). The average $\delta^{15}\text{N}_{\text{coral}}$ for these 14 years was $+6.4\text{‰}\pm 4\text{‰}$
224 (3σ). The monthly $\delta^{15}\text{N}_{\text{coral}}$ in CORE1, calculated after linear interpolation to
225 replace the partially missing monthly values, was compared with the monthly total
226 precipitation (Fig. 3a). However, no relationship was found between the $\delta^{15}\text{N}_{\text{coral}}$
227 and precipitation in a direct comparison. To define the seasonal characteristics of
228 $\delta^{15}\text{N}_{\text{coral}}$ and precipitation, the 14-year averages of each monthly value of $\delta^{15}\text{N}_{\text{coral}}$
229 and total precipitation were calculated (Fig. 3b, 3c). The rainy and typhoon
230 seasons for Ishigaki Island were in May–June and August–October, respectively
231 (Fig. 3c). The $\delta^{15}\text{N}_{\text{coral}}$ (Fig. 3b) gradually increased from May to October and
232 then gradually decreased over the following 5 months. The 5-month running mean
233 of $\delta^{15}\text{N}_{\text{coral}}$ had no correlation with that of monthly total precipitation; however,
234 with the exception of 1993–1995 and 2000–2001, the 5-month running mean of
235 $\delta^{15}\text{N}_{\text{coral}}$ was positively correlated with that of precipitation less than 150 mm/day
236 ($R=0.45$, $P<<0.0001$). Heavy rain (precipitation more than 150 mm/day),
237 indicated by white bars in Figure 3, corresponded with several positive peaks in
238 $\delta^{15}\text{N}_{\text{coral}}$ but not all. From 1993 to 1995, $\delta^{15}\text{N}_{\text{coral}}$ was continuously high ($>+6\text{‰}$)
239 regardless of precipitation, and significantly different from 1996–2007 (analysis of
240 covariance; ANCOVA test (Schwarz 2011): $P<<0.001$). During 2000–2001, the
241 5-month running mean of $\delta^{15}\text{N}_{\text{coral}}$ had a positive correlation with that of
242 precipitation of less than 150 mm/day ($R=0.70$, $P<0.0005$), and the average of
243 $\delta^{15}\text{N}_{\text{coral}}$ was $+5.3\text{‰}$, which was 0.7‰ lower than during 1996–2007 excluding
244 2000–2001. This difference was statistically significant (ANCOVA test:
245 $P<<0.001$).

246

247 **The 52-year variation in $\delta^{15}\text{N}_{\text{coral}}$ for 1958–2010 (CORE2)**

248 The $\delta^{15}\text{N}_{\text{coral}}$ values in CORE2 varied between +0.5‰ and +14.8‰. The average
249 $\delta^{15}\text{N}_{\text{coral}}$ decreased from +5.4‰ in 1958–1980 to +4.4‰ in 1981–2010. The
250 annual averages of $\delta^{15}\text{N}_{\text{coral}}$ in CORE2 were compared with that in CORE1 during
251 1994–2006 (Fig.4a). During 1994–2006, the variations of $\delta^{15}\text{N}_{\text{coral}}$ were 2.7‰,
252 (between +4.9‰ and +7.6‰) for CORE1, and 3.9‰ (between +2.9‰ and
253 +6.8‰) for CORE2. The $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 and CORE2 were not correlated. The
254 average values of $\delta^{15}\text{N}_{\text{coral}}$ were +6.2‰ and +5.0‰ for CORE1 and CORE2,
255 respectively.

256 The annual averages of $\delta^{15}\text{N}_{\text{coral}}$ in CORE2 were compared with the total
257 precipitation of the rainy season (May–June) (Fig. 4a). The cross-plot of the
258 average annual $\delta^{15}\text{N}_{\text{coral}}$ and the total precipitation of the rainy season showed a
259 weak linear relationship of $R=0.39$ ($P=0.009$) for 1958–2010. The co-relationships
260 between $\delta^{15}\text{N}_{\text{coral}}$ and total precipitation of the rainy season were shifted to ~1‰
261 lower for $\delta^{15}\text{N}_{\text{coral}}$ and 51 mm higher for total precipitation from 1958–1980 to
262 1981–2010 (ANCOVA test: $P=0.036$ (<0.05)). The linear relationships between
263 $\delta^{15}\text{N}_{\text{coral}}$ and the total precipitation of the rainy season showed $R=0.80$
264 ($p<<0.0001$) for 1958–1980 and $R=0.72$ ($p=0.0005$) for 1981–2010 (Fig. 4b),
265 which was statically significant except for 1966, 1974, 1995, 1999, 2002, and
266 2006. The slopes in the former (1958–1980) and the latter (1981–2010) periods
267 were 144 mm %⁻¹ and 166 mm %⁻¹ respectively. In 1966, 1974, 1995, 1999, 2002,
268 and 2006, the $\delta^{15}\text{N}_{\text{coral}}$ and precipitation values of the rainy season were plotted
269 outside the standard deviation (2σ) from the linear regression lines in the former
270 and latter periods (Fig. 4b). The $\delta^{15}\text{N}_{\text{coral}}$ values for 1966 and 1974 were -2.5‰
271 and -3.8‰, respectively, which were along the minima and smaller than expected
272 based on the linear trend of $\delta^{15}\text{N}_{\text{coral}}$ and precipitation in 1958–1980. By contrast,
273 the $\delta^{15}\text{N}_{\text{coral}}$ values for 1995, 1999, 2002, and 2006 were +2.5‰, +3.9‰, +3.2‰
274 and +2.4‰, respectively, which were along the maxima and larger than expected
275 based on the linear trend of $\delta^{15}\text{N}_{\text{coral}}$ and precipitation in 1981–2010.

276

277 **Discussion**

278 **Possible factors controlling $\delta^{15}\text{N}_{\text{coral}}$**

279 This study examined the assumption that $\delta^{15}\text{N}_{\text{coral}}$ at the mouth of the Todoroki
280 River records nitrate loading from terrestrial origins, as suggested by Yamazaki et

al. (2011b). The $\delta^{15}\text{N}_{\text{nitrate}}$ that flows from the Todoroki River into the coral reef is +8.5–+9‰ (Fig.3), indicating that it is affected by the land use in the catchment. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ composition of nitrate has been used for identification of denitrification in river watershed. The dual fractionation factor of $\delta^{15}\text{N}/\delta^{18}\text{O}$ is ~1.3 for denitrification (Fukuda et al. 2003). In Todoroki River water, the fractionation factor of $\delta^{15}\text{N}/\delta^{18}\text{O}$ was ~3.0 (Fig. 3), which suggests enrichment of ^{15}N in river water is not affected by denitrification and but affected by external nitrogen sources. We measured the $\delta^{15}\text{N}$ of total nitrogen in the agricultural water from the dam, the mixture of chemical fertiliser and manure in the sugarcane fields, and the excretion from cattle using same methods of $\delta^{15}\text{N}_{\text{coral}}$; the results were +2.5‰, +9.1‰, and +26.6‰, respectively. The mixture of each source comprises the nitrate in the Todoroki River water. In this section, we discuss other possible factors controlling $\delta^{15}\text{N}_{\text{coral}}$.

Terrestrial sediment. Inoue et al. (2014) reported the records of sediment loading in CORE1 (as core L1) and CORE2 (as core L2) using iron (Fe) and manganese (Mn) as proxies. The effect of sediment loading was much smaller at the CORE1 site than at the CORE2 site (Inoue et al. 2014). In CORE2, sediment loading was small until the 1980s and increased remarkably from the 1990s (Inoue et al. 2014). However, the variations in $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 and CORE2 were not similar to those of the Fe and Mn proxies, suggesting that terrestrial nitrate discharge is not simultaneous with sediment loading.

Light effect. Muscatine and Kaplan (1994) and Heikoop et al. (1998) reported that deeper coral colonies had increased $\delta^{15}\text{N}$ in coral tissues due to increasing coral heterotrophy. The light effect on $\delta^{15}\text{N}$ in coral tissues was -1~ -2‰ between corals living at the surface and those at 30 m depth (Heikoop et al. 1998). $\delta^{15}\text{N}$ differences were not observed in live corals at a depth of less than 10 m (Heikoop et al. 1998). In this study, we examined corals living on a shallow reef (less than 2 m depth). The effect of the position of the core top (~50 cm depth differences between the top and side) should be negligible. The seasonal cycle of solar radiation is at a maximum in July-August and a minimum in December-January in Ishigaki Island, as defined from 5-year solar irradiance data (1993-1997) for N25°, E125° (CAYAN solar irradiance database;

315 <http://iridl.ldeo.columbia.edu/SOURCES/.CAYAN/.Si/>). The seasonal variation of
316 $\delta^{15}\text{N}$ in CORE1 (Fig. 3b) did not correspond with the seasonal cycle of solar
317 radiation. In Reynaud et al. (2009), coral culture experiments also suggested that
318 light intensity does not affect $\delta^{15}\text{N}$ in coral tissue. In this study, the variations of
319 $\delta^{15}\text{N}_{\text{coral}}$ at the mouth of the Todoroki River cannot be explained by light intensity.

320

321 **Isotope fractionation between DIN and zooxanthellae.** Heikoop et al. (1998)
322 suggested that $\delta^{15}\text{N}$ in coral tissues may vary due to isotope fractionation between
323 DIN in seawater and zooxanthellae. Isotope fractionation between DIN and
324 dinoflagellates was reported to be less than 3‰ (Needoba et al. 2003). We cannot
325 explain the 14‰ range of variation in coral $\delta^{15}\text{N}$ by fractionation of DIN
326 assimilation of zooxanthellae alone. Yamazaki et al. (2011b) observed a
327 correspondence of $\delta^{15}\text{N}$ in nitrate and coral skeletons. This result also suggested
328 that the effect of isotope fractionation is negligible at the mouth of the Todoroki
329 River. For CORE1 and CORE2, possible factors controlling $\delta^{15}\text{N}_{\text{coral}}$ mainly
330 included $\delta^{15}\text{N}_{\text{nitrate}}$ in ambient seawater.

331

332 **Coral $\delta^{15}\text{N}$ of the nitrate outflow of the Todoroki River**

333 The $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 was continuously high ($>+6\text{‰}$) in 1993-1995. Blanco et
334 al. (2010) suggested that the controlling factor of NO_3^- -N concentration at the
335 Todoroki River was mostly the percentage of sugarcane cover and bedrock type
336 (e.g., limestone) in the watershed. The percentage of sugarcane cover in Todoroki
337 watershed decreased from 68% in 1995 to 52% in 2006-2008 (Fig.5).

338

339 Since 1996, The results of CORE1 (Fig.3a) showed that the 5 month running
340 mean of monthly $\delta^{15}\text{N}_{\text{coral}}$ corresponded with that of precipitation, except during a
341 flood event (precipitation >150 mm/day). The amount of river discharge
342 correlates with precipitation at present ($R=0.78$, ESM Fig.S3). At the mouth of the
343 Todoroki River, the $\delta^{15}\text{N}_{\text{coral}}$ could not respond to flood events because the nitrate
344 concentration of the rainwater runoff was 2–10% of the river/groundwater (Fig. 1,
345 Umezawa et al. 2002b). Blanco et al. (2010) reported that the nitrate concentration
346 at the mouth of Todoroki River tended to decrease during flood events in 2006
347 (NO_3^- -N; 1 mg/l of river discharge at ~ 8 m³/s) and to increase after the discharge
348 of the Todoroki River had decreased back to baseflow (NO_3^- -N; 3 mg/l of river

349 discharge at 0.5~1 m³/s), which suggested that 1) most of precipitation run off as
350 floods with lower nitrate concentration, and 2) a portion of the rainwater soaked
351 into the soil of the river catchments, converted to groundwater accompanied by
352 nitrate and gathered in the Todoroki River after the flood event. In ESM Figure S1,
353 the nitrate concentration and $\delta^{15}\text{N}_{\text{nitrate}}$ at the mouth of Todoroki River were
354 smaller (118 μM and +8.1‰) on 11 June 2011, two week after the flood event
355 (228 mm/day), than in November 2010 (335 μM and +9.1‰) without flood
356 events. This result suggests that floods dilute nitrate concentration and $\delta^{15}\text{N}_{\text{nitrate}}$
357 and that precipitation did not correspond with $\delta^{15}\text{N}_{\text{nitrate}}$ in flood events. The
358 seasonal variation of $\delta^{15}\text{N}_{\text{coral}}$ in Figure 3b also suggests that rainwater was
359 reserved in the catchment area as groundwater in the rainy seasons and that nitrate
360 gradually seeped into the river with the stored water over the 4-5 months from
361 November to February. The $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 recorded the loading of nitrate
362 from the land cover soil through the ground to river flow.

363

364 The seasonal variation of $\delta^{15}\text{N}_{\text{coral}}$ suggests that precipitation less than 150
365 mm/day controlled the nitrate drainage into the Todoroki River through
366 groundwater. However, during 2000-2001, the $\delta^{15}\text{N}_{\text{coral}}$ was 0.7‰ lower than the
367 previously discussed 14-year average (Fig. 3), the cause of which is unknown.
368 The total monthly precipitation (except daily precipitation over 150 mm/day) in
369 2000-2001 was consistently higher than the average of total monthly precipitation
370 over the 14 years (126 mm/month), which suggested the river water discharges
371 increased (ESM Fig.S3). The lower $\delta^{15}\text{N}_{\text{coral}}$ in 2000-2001 might suggest that
372 nitrate was diluted by the rainwater flow that was not converted to groundwater.
373 The $\delta^{15}\text{N}_{\text{coral}}$ of CORE1 suggested that the nitrate flowed into the coral reef with
374 precipitation and that the land use in the Todoroki River watershed could be the
375 cause of the quantity of discharged nitrate.

376

377 During 1994-2006, the average $\delta^{15}\text{N}_{\text{coral}}$ in CORE1 were 1.2‰ higher than that in
378 CORE2 (Fig.4a). The annual averages of CORE1 were varied around positive
379 peaks of CORE2. These results suggest that CORE1 was more influenced on the
380 nitrate discharge than CORE2 because the colony of CORE1 was located closer to
381 the shoreline than that of CORE2 (Fig.2a). In the Shiraho coral reef, the inner reef
382 distribution of $\delta^{15}\text{N}_{\text{nitrate}}$ has large gradient from inshore (~+9‰) to offshore

383 ($\sim +3\text{‰}$) (Fig. 2a, Yamazaki et al. 2011b). $\delta^{15}\text{N}_{\text{coral}}$ was sensitively changed by
384 $\delta^{15}\text{N}_{\text{nitrate}}$ changes with the locations of the coral colonies.

385

386 **The nitrate sources have shifted with the land-use history in the catchment**
387 **area**

388 The annual average of $\delta^{15}\text{N}_{\text{coral}}$ in CORE2 was correlated with the total
389 precipitation in the rainy season (May–June) (Fig. 4b). The 52-year record of the
390 $\delta^{15}\text{N}_{\text{coral}}$ in CORE2 was divided into two periods: 1958–1980 and 1981–2010 (Fig.
391 4). Before 1980, the land use of the Todoroki River catchment was primarily
392 paddy fields, which were transformed into sugarcane fields after 1980 (Fig. 5).
393 The reclamation works began in the Todoroki River catchment after the Okinawa
394 reversion was agreed upon by Japan and the U.S. in 1972. The area of the paddy
395 fields decreased after the late 1970s, and sugarcane fields were cultivated using
396 chemical fertilisers beginning in the 1980s. The linear relationships between the
397 annual average of $\delta^{15}\text{N}_{\text{coral}}$ and the total precipitation in the rainy season were
398 similar between 1958–1980 and 1981–2010; however, the $\delta^{15}\text{N}_{\text{coral}}$ values
399 decreased approximately $+1\text{‰}$ (Fig. 4b).

400

401 We analysed the nitrogen isotopes of the total nitrogen in the soil in sugarcane
402 fields and manure in the Todoroki River catchment using the same methods as in
403 the $\delta^{15}\text{N}_{\text{coral}}$ analysis. In the present day, the $\delta^{15}\text{N}$ of the mixture of chemical and
404 manure fertiliser was $+9\text{‰}$ in the sugarcane fields. The $\delta^{15}\text{N}$ of the manure was
405 $+26\text{‰}$, which was approximately three times greater than that of the fertiliser in
406 the sugarcane fields. The slopes of the linear relationships between $\delta^{15}\text{N}_{\text{coral}}$ and
407 precipitation were similar before and after 1980 (Fig. 4b). Given that the isotopic
408 composition of the nitrogen source term was approximately three times higher
409 prior to 1980, it may be reasonable to assume that the nitrogen loading was only
410 approximately one-third as high to yield similar relationships between $\delta^{15}\text{N}_{\text{coral}}$
411 and precipitation before and after 1980. Before the 1980s, the nitrate
412 concentration in the river water was one-third the nitrate concentration at present
413 (1981–2010), which assumes that 1) manure fertiliser was used in the paddy fields
414 before the 1980s, 2) the rate and magnitude of nitrate transport into the coral reef
415 due to the precipitation rate before and after 1980 were the same, and 3) current
416 values of nitrate in the sugarcane soil and manure were applied to the calculation.

417 Hasegawa (2011) reported that sea grass bed coverage of Shiraho Coral Reef was
418 increased from 1.2% in 1972 to 7.2% in 2004 from the aerial photographs, which
419 also suggested terrestrial nutrient input was increased in these 30 years.

420

421 It was unclear why there were six outliers of $\delta^{15}\text{N}_{\text{coral}}$ in CORE2. The outliers of
422 $\delta^{15}\text{N}_{\text{coral}}$ values in the pre-1980s, those for 1966 and 1974 were 2.5 and 3.8‰,
423 respectively, which was lower than expected even though the total precipitation of
424 the rainy season was higher than 700 mm. The years 1966 and 1974 had the
425 second and third most precipitation before 1980, which might indicate that
426 abundant rainwater runoff flowed into the coral reefs through the river and diluted
427 the nitrate concentrations at the river mouth, as was recorded in 2000-2001 for
428 $\delta^{15}\text{N}_{\text{coral}}$ in CORE1. By contrast, the four maxima $\delta^{15}\text{N}_{\text{coral}}$ values in 1995, 1999,
429 2002, and 2006 were 2.4–3.9‰ higher than expected. In typhoon events, it is
430 possible that the nitrogenous nutrients in the fertiliser were directly loaded with
431 sediments into the coral reefs through the Todoroki River. In Ishigaki Island, the
432 sediment loading from the paddy fields into the river is smaller than usual in flood
433 event because the paddy fields work as sediment reservoir (Ikeda et al. 2009).
434 However, instead of the paddy fields, the sugarcane fields prospered in the
435 Todoroki River catchments since 1980, especially after the late 1980s (Fig. 5).
436 The fertiliser inflow with sedimentation might have influenced the four maxima
437 of the $\delta^{15}\text{N}_{\text{coral}}$. We compared the $\delta^{15}\text{N}_{\text{coral}}$ values for 1995, 1999, 2002, and 2006
438 with the total precipitation in the typhoon season (August to October) (triangle
439 points in Fig. 4b). The modified cross-plots in 1995, 1999, and 2006 were plotted
440 within the standard deviation (2σ) from the linear regression lines. However, the
441 typhoon precipitation in 2002 resulted in much higher $\delta^{15}\text{N}_{\text{coral}}$ values, the reason
442 for which remains unknown and needs future works.

443

444 The $\delta^{15}\text{N}_{\text{coral}}$ at the mouth of the Todoroki River recorded the nitrate discharge
445 caused by the precipitation mainly in the rainy season, and the nitrate sources
446 changed with the changing land use in the Todoroki River catchment. Although
447 future work is needed to give the spatial and temporal inconsistencies of the proxy
448 relationship, the $\delta^{15}\text{N}_{\text{coral}}$ can be used as a proxy for the source and discharge
449 pattern of terrestrial nitrate in coral reefs.

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References

- Adachi H, Abe O (2003) Air drill for submerged massive coral drilling. *Mar Technol Soc Bull* 37: 31–36
- Bellwood DR, Hughes TP, Folke C, Nystrom M (2004) Confronting the coral reef crisis. *Nature*, 429: 827–833
- Blanco AC, Nadaoka K, Yamamoto T (2008) Planktonic and benthic microalgal community composition as indicators of terrestrial influence on a fringing reef in Ishigaki Island, Southwest Japan. *Mar Environ Res* 66: 520–535
- Blanco AC, Nadaoka K, Yamamoto T, Kinjo K (2010) Dynamic evolution of nutrient discharge under stormflow and baseflow conditions in a coastal agricultural watershed in Ishigaki Island, Okinawa, Japan. *Hydrol Process* 24: 2601–2616
- De’ath G, Fabricius KE, Sweatman H, Puotinen M (2012) The 27-year decline of coral cover on the Great Barrier Reef and its causes. *Proc Natl Acad Sci USA* 109: 17995–17999
- Druffel ERM (1997a) Geochemistry of corals: proxies of past ocean chemistry, ocean circulation, and climate. *Proc Natl Acad Sci USA* 94: 8354–8361
- Fabricius K (2005) Effects of terrestrial runoff on the ecology of corals and coral reefs: review and synthesis. *Mar Pollut Bull* 50: 125–146
- Fukada T, Hiscock KM, Dennis PF, Grischek T (2003) A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site. *Water Res* 37: 3070–3078
- Gagan MK, Ayliffe LK, Beck JW, Cole JE, Druffel ERM, Dunbar RB, Schrag DP (2000) New views of tropical paleoclimates from corals. *Quat Sci Rev* 19: 45–64
- Grottoli A, Eakin C (2007) A review of modern coral $\delta^{18}\text{O}$ and $\Delta 14\text{C}$ proxy records. *Earth Sci Rev* 81: 67–91
- Hasegawa H (2011) The decline of coral reef conditions caused by the extensive land modification: A case study of the Shiraho area on Ishigaki Island, Okinawa, Japan. *Journal of the Remote Sensing Society of Japan* 31: 73–86
- Heikoop JM, Dunn JJ, Risk MJ, Sandeman IM, Schwarcz HP, Waltho N (1998) Relationship between light and the $\delta^{15}\text{N}$ of coral tissue: Examples from Jamaica and Zanzibar. *Limnol Oceanogr* 43: 909–920
- Heikoop JM, Dunn JJ, Risk MJ, Tomascik T, Schwarcz HP, Sandeman IM, Sammarco PW (2000) $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of coral tissue show significant inter-reef variation. *Coral Reefs* 19: 189–193
- Hirota A, Tsunogai U, Komatsu DD, Nakagawa F (2010) Simultaneous determination of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of N_2O and $\delta^{13}\text{C}$ of CH_4 in nanomolar quantities from a single water sample. *Rapid Commun Mass Spectrom*, 24: 1085–1092
- Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A, Hatziolos ME (2007) Coral reefs under rapid climate change and ocean acidification. *Science* 318: 1737–1742
- Ikeda S, Osawa K, Akamatsu Y (2009) Sediment and nutrients transport in watershed and their impact on coastal environment. *Proc Jpn Acad Ser B* 85: 374–390
- Inoue M, Ishikawa D, Miyaji T, Yamazaki A, Suzuki A, Yamano H, Kawahata H, Watanabe T (2014) Evaluation of Mn and Fe in coral skeletons (*Porites* spp.) as proxies for sediment loading and reconstruction of 50 yrs of land use on Ishigaki Island, Japan. *Coral Reefs* 33: 363–373.
- Ishihara M, Hasegawa H, Hayashi S, Yamano H (2014) Land cover classification using multi-temporal satellite images in a subtropical area. In: Nakano S, Yahara

509 T, Nakashizuka T (eds) The biodiversity observation network in the Asia-Pacific
510 region: Integrative observations and assessments of Asian biodiversity. Springer,
511 pp231-237

512 Knapp AN, Sigman DM, Lipschultz F (2005) N isotopic composition of dissolved
513 organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site.
514 Global Biogeochem Cycles 19: GB1018

515 Konno U, Tsunogai U, Komatsu DD, Daita S, Nakagawa F, Tsuda A, Matsui T, Eum
516 YJ, Suzuki K (2010) Determination of total N₂ fixation rates in the ocean taking
517 into account both the particulate and filtrate fractions. Biogeosciences 7:
518 2369–2377

519 Marion G, Dunbar R, Mucciarone D, Kremer J, Lansing J, Arthawiguna A (2005)
520 Coral skeletal $\delta^{15}\text{N}$ reveals isotopic traces of an agricultural revolution. Mar Pollut
521 Bull 50: 931–944

522 Miyajima T, Suzumura M, Umezawa Y, Koike I (2001) Microbiological nitrogen
523 transformation in carbonate sediments of a coral–reef lagoon and associated
524 seagrass beds. Mar Ecol Prog Ser 217: 273–286

525 Muscatine L, Kaplan IR (1994) Resource partitioning by reef corals as determined
526 from stable isotope composition. II. ^{15}N of symbiotic dinoflagellates and animal
527 tissue versus depth. Pac Sci 48: 304–312

528 Needoba JA, Waser NA, Harrison PJ, Calvert SE (2003) Nitrogen isotope
529 fractionation in 12 species of marine phytoplankton during growth on nitrate. Mar
530 Ecol Prog Ser 255: 81-91

531 Pal M, Mather PM (2003) An assessment of the effectiveness of decision tree methods
532 for land cover classification. Remote Sens Environ 86: 554–565

533 Reynaud S, Martinez P, Houlbrèque F, Billy I, Allemand D, Ferrier-Pagès C (2009)
534 Effect of light and feeding on the nitrogen isotopic composition of a zooxanthellate
535 coral: role of nitrogen recycling. Mar Ecol Prog Ser 392: 103-110

536 Tsunogai U, Kido T, Hirota A, Ohkubo SB, Komatsu DD, Nakagawa F (2008)
537 Sensitive determinations of stable nitrogen isotopic composition of organic nitrogen
538 through chemical conversion into N₂O. Rapid Commun Mass Spec 22: 345–354

539 Schwarz CJ (2011) Sampling, regression, experimental design and analysis for
540 environmental scientists, biologists and resource managers. Department of
541 Statistics and Actuarial Science, Simon Fraser University, p57

542 Uchida A, Nishizawa M, Shirai K, Iijima H, Kayanne H, Takahata N, Sano Y (2008)
543 High sensitivity measurements of nitrogen isotopic ratios in coral skeletons from
544 Palau, western Pacific: Temporal resolution and seasonal variation of nitrogen
545 sources. Geochem J 42: 255–262

546 Umezawa Y, Miyajima T, Koike I (2008) Stable nitrogen isotope composition in
547 sedimentary organic matter as a potential proxy of nitrogen sources for primary
548 producers at a fringing coral reef. J Oceanogr 64: 899–909

549 Umezawa Y, Miyajima T, Kayanne H, Koike I (2002b) Significance of groundwater
550 nitrogen discharge into coral reefs at Ishigaki Island, southwest of Japan. Coral
551 Reefs 21: 346–356

552

553 Umezawa Y, Miyajima T, Yamamuro M, Kayanne H, Koike I (2002a) Fine scale
554 mapping of land-derived nitrogen in coral reefs, by $\delta^{15}\text{N}$ values in macroalgae.
555 Limnol Oceanogr 47: 1405-1416

556 Yamamuro M, Kayanne H, Yamano H (2003) $\delta^{15}\text{N}$ of seagrass leaves for monitoring
557 anthropogenic nutrient increases in coral reef ecosystems. Mar Pollut Bull 46:
558 452–458

559 Yamazaki A, Watanabe T, Tsunogai U (2011b) Nitrogen isotopes of organic nitrogen in
560 reef coral skeletons as a proxy of tropical nutrient dynamics. Geophys Res Lett 38:
561 L19605

562 Yamazaki A, Watanabe T, Takahata N, Sano Y, Tsunogai U (2013) Nitrogen isotopes
563 in intra-crystal coralline aragonites. Chem Geol 351: 276–280

564

565 Yamazaki A, Watanabe T, Ogawa NO, Ohkouchi N, Shirai K, Toratani M, Uematsu M
566 (2011a) Seasonal variations in the nitrogen isotope composition of Okinotori coral
567 in the tropical western Pacific: A new proxy for marine nitrate dynamics. J

569 Figure Legends

570 Fig. 1. Land-use and nitrate isotope compositions of the Todoroki River catchment. (a)
 571 Land use of the Todoroki river catchment in October 2010. The white (○) and black (●)
 572 circles show the nitrate concentrations with the $\delta^{15}\text{N}_{\text{nitrate}}$ in river water (RW) and
 573 ground water (GW), respectively. The RW samples were taken in March and August
 574 2009. The GW, and rainwater were also sampled in August 2009. (b) Cross-plot of the
 575 $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ in RW, GW and rainwater from August 2009. Isotope
 576 composition of RW1 was affected by rainwater. Except for RW1, the correlation
 577 coefficient was $R=0.91$ ($p=0.01$).

578
 579 Fig. 2. (a) The relationships between the distance of the sampling sites from the
 580 shoreline and $\delta^{15}\text{N}$ in *Porites* coral skeletons, seawater nitrate, and macro algae (DIN
 581 consumers), compiled from Yamazaki et al. (2011a) and Umezawa et al. (2002). $\delta^{15}\text{N}$
 582 values decreased from +9‰ inshore to +2~+3‰ offshore. (b) The relationship between
 583 the nitrate concentration and the $\delta^{15}\text{N}_{\text{nitrate}}$ in the seawater of the Shiraho coral reef.
 584 The $\delta^{15}\text{N}_{\text{nitrate}}$ from +2 to +9‰ positively correlates with the natural logarithm of the
 585 nitrate concentration ($R=0.85$, $p<0.004$).

586
 587 Fig. 3. (a) The time series of the $\delta^{15}\text{N}_{\text{coral}}$ (green line graph with dots) in CORE1 from
 588 1993 to 2007 compared with the monthly total precipitation for Ishigaki Island. The
 589 blue bar graph shows the monthly total precipitation without the heavy precipitation
 590 (>150 mm/day, white bar). The black lines indicate five-month running averages. The
 591 5-month running mean of $\delta^{15}\text{N}_{\text{coral}}$ was positively correlated with that of precipitation
 592 of less than 150 mm/day ($R=0.48$, $P<0.0001$), with the exception of 1993–1995 and
 593 2000–2001. From 1993 to 1995, $\delta^{15}\text{N}_{\text{coral}}$ was continuously high (>+6‰), regardless of
 594 precipitation. During 2000–2001, the 5-month running mean of $\delta^{15}\text{N}_{\text{coral}}$ was positively
 595 correlated with that of precipitation of less than 150 mm/day ($R=0.62$, $P<0.0005$), and
 596 the average of $\delta^{15}\text{N}_{\text{coral}}$ was +5.3‰, which was 0.7‰ lower than during 1996–2007
 597 excluding 2000–2001 (b) The bar graph of 14-year averages of 12 monthly $\delta^{15}\text{N}_{\text{coral}}$ in
 598 CORE1. (c) The bar graph of 14-year averages of 12 monthly total precipitations.

599
 600 Fig. 4. (a) The time series of the $\delta^{15}\text{N}_{\text{coral}}$ in CORE2 from 1958 to 2010 compared with
 601 the bar graphs of the total precipitation in the rainy season (May–June). The dotted
 602 line shows the analysed $\delta^{15}\text{N}_{\text{coral}}$ in sub-annual to annual intervals. The green bold line
 603 shows the annual averages with the plots of the symbols corresponding with (b). The
 604 red solid line shows annual average of $\delta^{15}\text{N}_{\text{coral}}$ from CORE1. (b) The cross plot
 605 between the annual average of $\delta^{15}\text{N}_{\text{coral}}$ and the total precipitation in the rainy season
 606 (May–June); black circles (●) indicate 1958–1981, and white circles (○) indicate
 607 1981–2010. The outliers in 1966 and 1974 are shown as grey circles (●). The
 608 outliers of $\delta^{15}\text{N}_{\text{coral}}$ in 1995, 1999, 2002, and 2006 are showed as white circles (○)
 609 compared with precipitation in rainy season (May–June), and white circles connected with dashed
 610 line to triangles are compared with precipitation in typhoon season (September–October).
 611 The correlation coefficients (R) are 0.80 ($P<<0.0001$) and 0.72 ($P=0.0005$) in the former
 612 (1958–1980) and latter (1981–2010) periods, respectively. The ranges of standard
 613 deviation (2σ) are indicated as green and yellow shades for the former and latter
 614 periods. The slopes are 166 mm ‰⁻¹ and 144 mm ‰⁻¹, respectively. The cross-plots of
 615 average $\delta^{15}\text{N}_{\text{coral}}$ and average total precipitation in May–June are described as a black
 616 square (■: +5.4‰, 430mm) and a white square (□: +5.4‰, 430mm) for the former and
 617 latter periods.

618
 619 Fig. 5. The land-use history in the Todoroki River catchment and pie charts of the area
 620 ratios.

621

622 Fig. S1. The seasonal variation of nitrogen isotopes and nitrate concentrations at the
623 mouth of the Todoroki River. The nitrogen isotopes in the samples of nitrate
624 concentrations less than 0.5 μ M are unknown due to the detection limits. The allows
625 indicate the direction of prevailing currents based on Tamura et al. (2007)

626

627 Fig.S2. X-radiographs and analytical lines for CORE1 and CORE2.

628

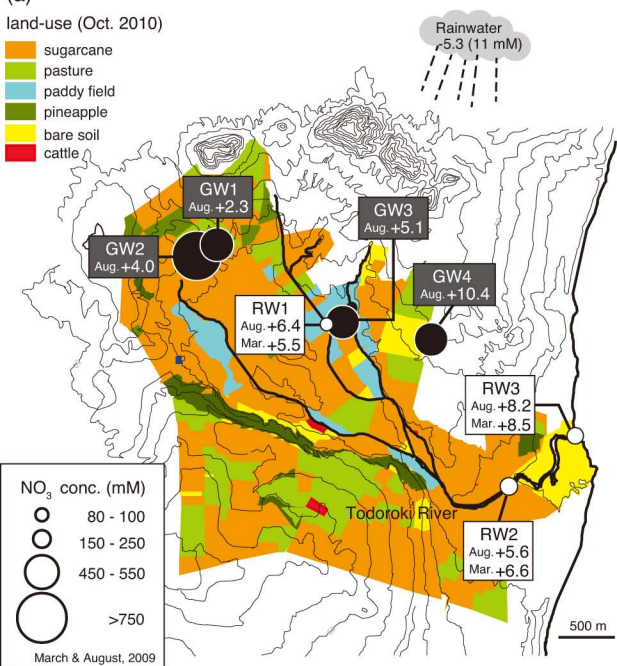
629 Fig.S3. Relationship between monthly river discharge and monthly precipitation in
630 the Todoroki River catchment. The data was collected from November 2006 to
631 November 2007 by the government of Okinawa prefecture.

632

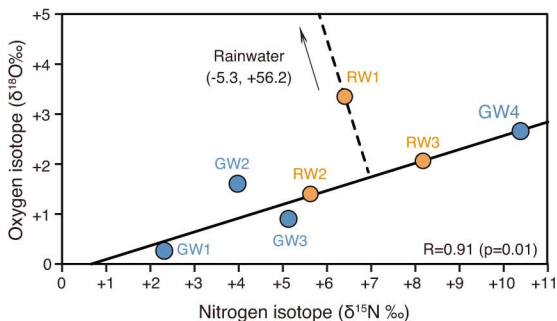
633 References. Tamura H, Nadaoka K, Paringit EC (2007) Hydrodynamic characteristics
634 of a fringing coral reef on the east coast of Ishigaki Island, southwest Japan. Coral
635 Reefs 26: 17–34

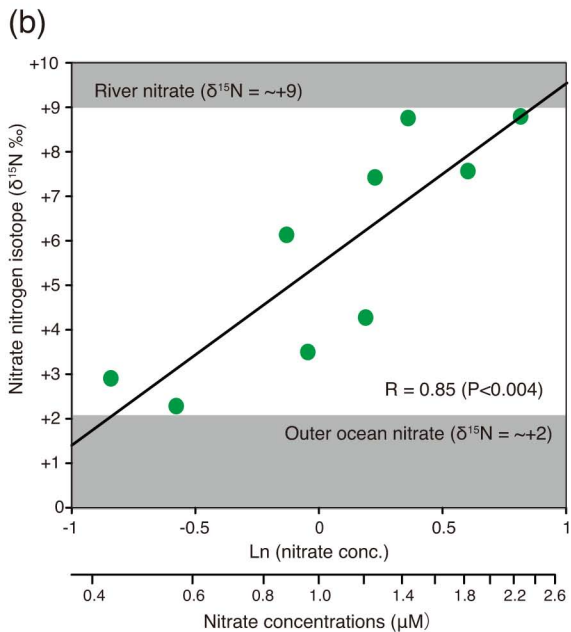
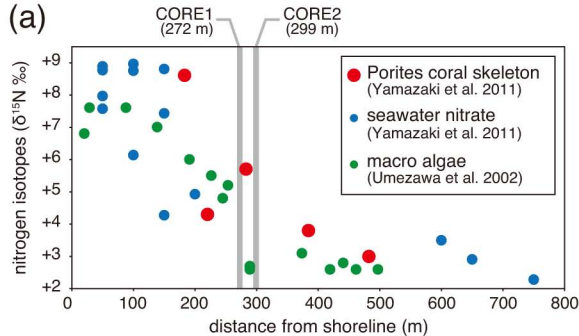
(a)

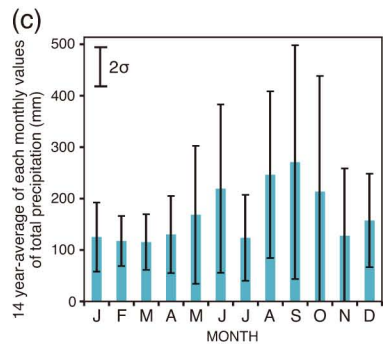
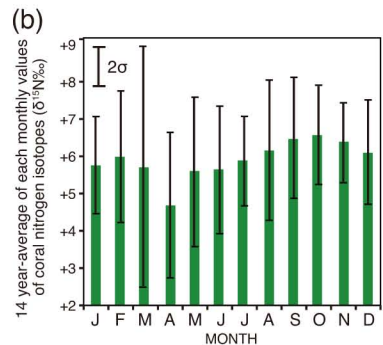
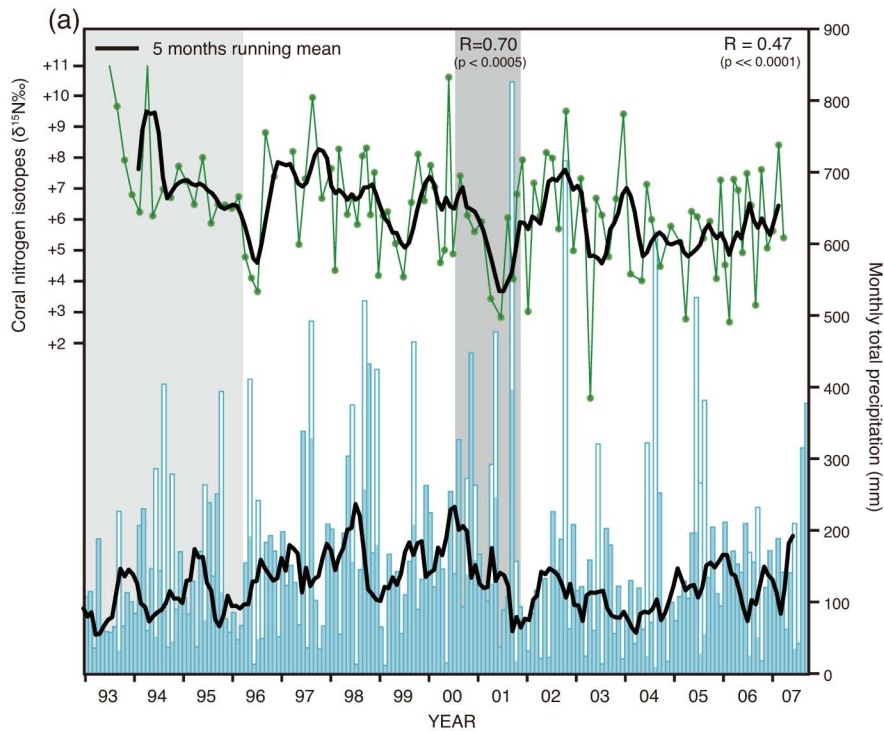
land-use (Oct. 2010)



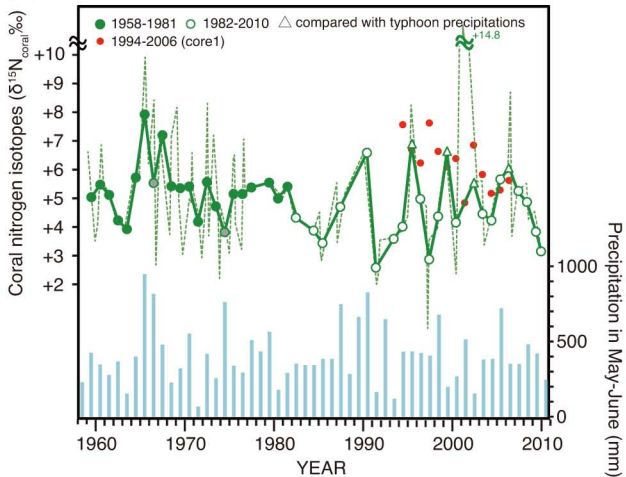
(b)



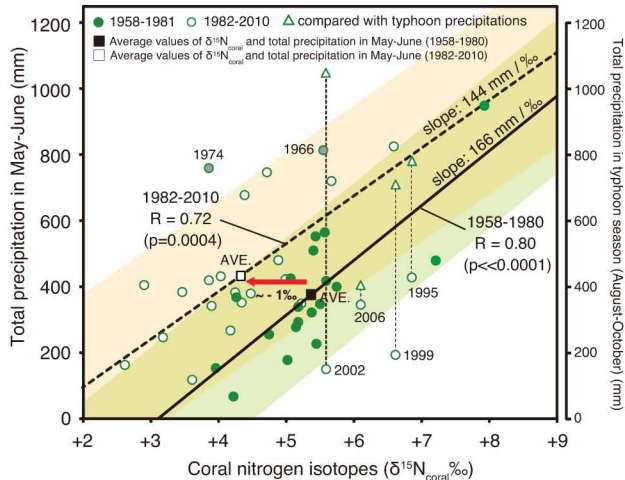


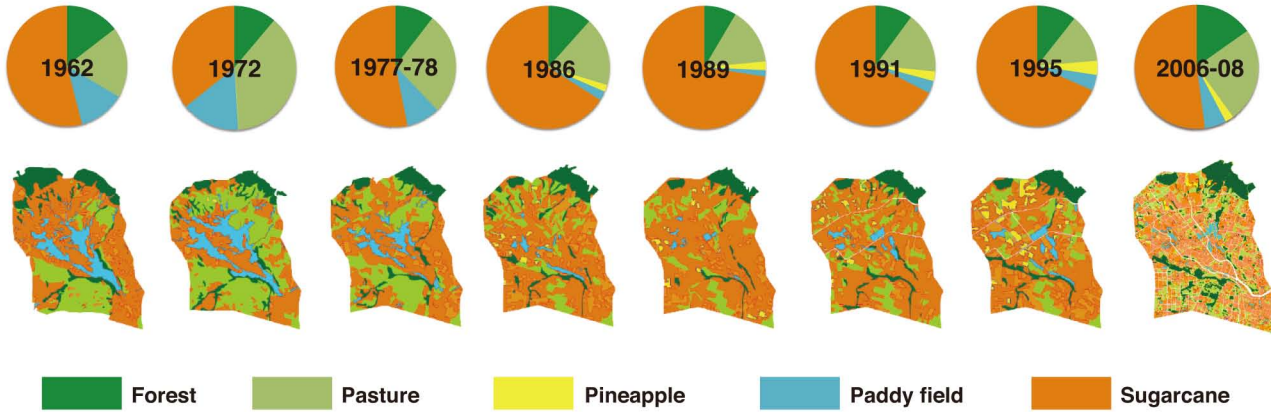


(a)

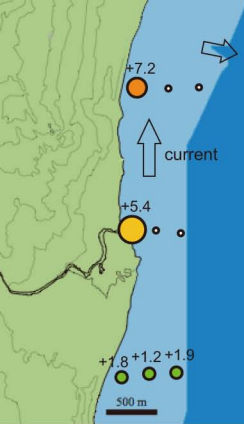


(b)



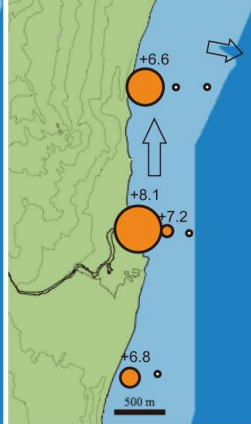


Land-use history of Todoroki watershed



Mar 2011

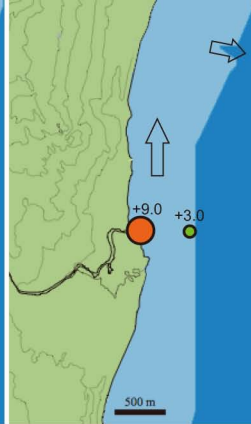
Precipitation rate: 8.7 mm/day



Rainy season (Jun 2011)

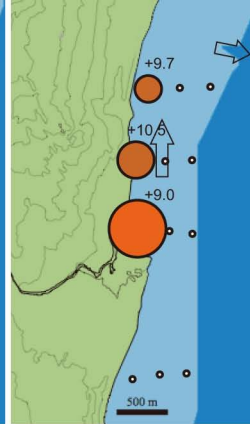
Precipitation rate: 18.5 mm/day

Flood events: 288 mm/day (5/28)



Aug 2009

Precipitation rate: 6.3 mm/day



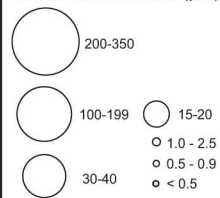
Nov 2010

Precipitation rate: 12.8 mm/day

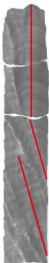
δ¹⁵N (‰)



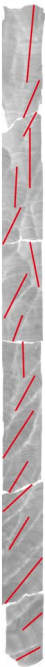
nitrate concentration (μM)



CORE1



CORE2



5 cm

