

NOTE

Nitrogen isotope composition of inorganic soil nitrogen and associated vegetation under a sea bird colony on the Hatana islands, Rotuma Group, Fiji

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Concentration together with the stable isotope composition ($\delta^{15}\text{N}$) of both ammonium- and nitrate-nitrogen were conducted for sedentary soils under the piscivorous seabird colony developed on Quaternary basaltic ejecta from the Hatana islands, Fiji, south Pacific. Higher inorganic nitrogen content (up to 2,420 mg-N/kg dry soil) was observed for soils under dense forest vegetation, relative to a lower nitrogen content for soils under sparse grass vegetation (270 mg-N/kg dry soil), reflecting the difference in the mulching effects of vegetative cover for leaching of nitrogen by meteoric water. Active mineralization of uric acid in the bird excreta followed by partial loss due to volatilization of ammonia, nitrification and denitrification were indicated by unique $\delta^{15}\text{N}$ values of the inorganic nitrogen as high as +50‰. This unique process was facilitated by high soil surface temperature (24 to 32°C) in combination with the humid tropical climate (annual rainfall: 3560 mm). Distinct isotopic composition of the foliar nitrogen ($\delta^{15}\text{N} = +13.6$ to +36.7‰) indicated acquisition of the inorganic nitrogen derived from bird excreta in soils.

Keywords: nitrogen isotope fractionation, mineralization, nitrification, denitrification, bird colony

INTRODUCTION

Oceanic islands located far from major landmasses often provide a base for sea bird colonies. During roosting and nesting, there is a huge input of organic nitrogen onto the soil surface in the form of excreted uric acid from the piscivorous sea birds. Under hot and humid climates, as commonly observed in tropical monsoon areas where microbial activity in soils is quite high, the uric acid once deposited is rapidly mineralized into ammonia and further nitrate. Very few isotopic studies have been conducted on the inorganic nitrogen in soils and associated vegetation in the tropics and sub-tropics, except for one case study from the Great Barrier Reef, Australia (Schmidt *et al.*, 2004). Schmidt *et al.* (2004) studied ammonium- and nitrate-nitrogen in soils on coral limestone from Heron Island. In their study, 50 to 250 mg of nitrate-nitrogen per Kg of dry soil was extracted by water (soil to water ratio = 1:2 weight/volume). Content of water-soluble ammonium-nitrogen associated with the nitrate-nitrogen was very low, ranging from 1 to 20 mg of nitrogen per Kg of dry soil. Such a low concentration

of the observed ammonium-nitrogen, relative to abundant nitrate-nitrogen may be an underestimate due to possible retention of ammonium-nitrogen by soil colloids during the extraction experiment. Nevertheless, mixed-ion exchange resin buried in the field soils for a given period extracted significant amounts of ammonium-nitrogen. Nitrogen isotope composition of ammonium-associated with nitrate-nitrogen in the soils is a prerequisite for evaluating the nitrogen dynamics on sea bird colony.

MATERIALS AND METHODS

In the present study, we studied the nitrogen isotope composition of inorganic soil nitrogen and associated vegetation from the Hatana islands, Rotuma Group, Fiji, a representative of the tropical south Pacific. The islands have a hot and humid tropical climate. The soils, well developed on Quaternary basaltic volcanic ash, tuff and lavas, are unlike those from other known colony soils below the tropics. Possible uptake of fecal nitrogen by vegetation was evaluated by comparison of the nitrogen isotopic signatures of the inorganic nitrogen in soils together with foliar parts of the predominating vegetation.

Description of study sites

Sample materials analyzed in the present study were

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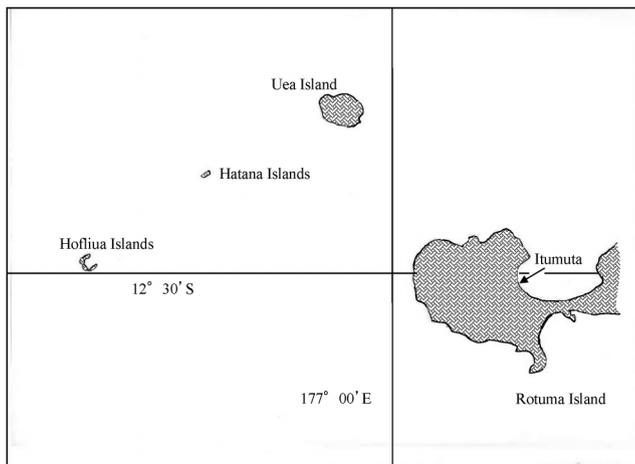


Fig. 1. Approximate location of the sample site.

collected on September 3~10, 2005. The time corresponds to the mid breeding period of predominating birds (Robinet *et al.*, 1997). Figure 1 shows the location of the Hatana islands (Lat. 12.483°S, Long. 176.967°E, maximum elevation; 7 m above sea level) on which dense bird colonies prevail. There is no human inhabitation. The area has not yet been specifically designated as a natural environment by the Fijian government. The islands are subject to a hot and very humid south Pacific climate, with total recorded annual rainfall and average daily air temperature 3,556 mm and 24 to 32°C, respectively (Wright and Twyford, 1958). The rainfall is almost uniform throughout the year and therefore there is no clear dry season. Seasonal fluctuation of air temperature throughout the year is very small.

Basement rock on the islands is basaltic volcanic ejecta consisting of ash, tuff and lava of late Quaternary age and forms almost flat geomorphic surfaces on which sedentary soils have developed. No current volcanic activity is evident. Any volcanic activity would have been completed before human colonization of the Rotuma islands. The Hatana islands consist of two discrete landmasses associated with a shallow lagoon (Fig. 2) on which sampling of soils together with vegetation was made. Very dense colonies of sea birds are developed on these islands and on neighboring Hofliua and Uea islands (Fig. 1), and visual inspection indicated nesting activity of several thousand pairs. The Hatana island site A is located on the windward side. Short grass vegetation develops on the northeastern parts of the island due to the strong influence of the prevailing northeasterly wind. Much nesting activity of the sooty tern (*Sterna fuscata*) and brown booby (*Sula leucogaster*) is observed on the ground. Four major growths of halophilic *Portulaca quadrifida*, *Capparis* sp. *Paspalum distichum* (graminaeaeous) and

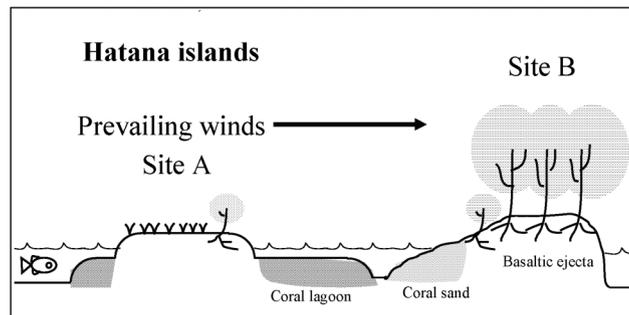


Fig. 2. Schematic illustration for the cross section of the Hatana islands as seen from the northeast-southwest side. Reflecting the effects of prevailing strong northeasterly winds, short grass and coral beach develop on the windward and wood vegetation on the leeward sides, respectively.

Ficus sp. (shrub) were observed on the site. On Hatana island site B, dense nesting of the brown nobby (*Anous stolidus*) and red-footed booby (*Sula sula*) is observed in the branches of the prevailing tree vegetation, with approximate height up to 6 to 8 m. Tall and dense cover of *Pisonia grandis* forms the climax of Hatana island site B. The plant species are not ornithocophilous, but common in areas near rocky beaches.

No reconnaissance soil survey has been made for Rotuma and the associated volcanic islands. Friable consistency and morphological characteristics including dark color of the surface horizon in the field indicate that the soils are classified into Andisols. Sedentary soil samples were collected from six sites from each island to represent the spatial distribution of different plant communities on the Hatana islands. Excluding thin decaying organic layer (leaf and twigs), soil samples (field moist, up to 500 g) from the top of the A1 mineral horizon, 0 to 10 cm deep where the input of bird excreta is marked, were collected from five points (about 1m distance) and comprised a composite sample in a plastic bag.

Each duplicated soil samples (sites 1 and 2, and 4 and 5) were collected under the major vegetation of *Portulaca quadrifida* and *Capparis* sp. from Hatana site A (Table 1). Six replicated soil samples (sites 7 to 12) (Table 1) were also collected under *Pisonia grandis* from Hatana site B. Spatial distance between sites ranged from around 20 to 30 m.

Excreta of the predominating birds deposited on the ground under nearby nests, together with the foliar part of the major vegetation, were also collected for chemical and isotopic analyses. Fresh white uric acid concentrates were handpicked from the bird excreta deposited on the leaf surface.

For control sites which are unaffected by the bird colony, two surface soils 0 to 10 cm deep under a plantation of the Sago palm (*Metroxylum warburgii*) were col-

Table 1. Concentration and nitrogen isotope composition of ammonium- and nitrate-nitrogen in soils, decaying bird excreta and uric acid from Hatana colonies, Fiji

Location ¹⁾	Site Nos.	Species of predominating vegetation cover	Inorganic nitrogen in soils			
			NH ₄ ⁺		NO ₃ ⁻	
			Content ²⁾	δ ¹⁵ N ³⁾	Content ²⁾	δ ¹⁵ N ³⁾
Hatana site A	1	<i>Portulaca quadrifida</i>	64	+16.2	215	+13.5
	2	<i>Portulaca quadrifida</i>	223	+21.2	452	+17.0
	3	<i>Paspalum distichum</i>	686	+22.6	856	+16.8
	4	<i>Capparis</i> sp.	116	+20.3	315	+15.9
	5	<i>Capparis</i> sp.	46	+15.1	216	+14.9
	6	<i>Ficus</i> sp. (Decaying bird excreta) (Handpicked uric acid)	801 7,245	+31.6 +50.1 (+17.7) ⁴⁾	916 735	+24.6 +14.9
Hatana site B	7	<i>Pisonia grandis</i>	734	+23.3	790	+26.6
	8	<i>ditto</i>	858	+25.5	1,083	+33.0
	9	<i>ditto</i>	888	+22.5	912	+27.3
	10	<i>ditto</i>	922	+24.3	1,057	+25.2
	11	<i>ditto</i>	1,038	+24.2	775	+28.1
	12	<i>ditto</i> (Decaying bird excreta) (Handpicked uric acid)	1,086 3,063	+24.0 +39.1 (+9.6) ⁴⁾	1,326 1,794	+26.5 +23.3
Itumuta, Rotuma	13	<i>Metroxylum warburgii</i>	20	ND	35	-1.3
	14	<i>Metroxylum warburgii</i>	14	ND	33	-4.1

¹⁾See Fig. 1.

²⁾mg-N/kg oven-dry soil.

³⁾Per mil deviation relative to atmospheric dinitrogen (δ¹⁵N = 0‰).

⁴⁾Determined for whole nitrogen.

ND = not determined due to insufficient recovery of nitrogen for isotopic measurement.

lected from Itumuta, Rotuma island (Fig. 1). These soils derive from similar volcanic ejecta to those on the Hatana islands (Fig. 1).

Analytical methods

After collection, all the sample materials were quickly air-dried under strong sunlight. Soil samples were pulverized to pass through a 2-mm sieve. The dried vegetation samples were finely crushed using an electric mill.

Inorganic nitrogen was extracted from the fine-earth samples by shaking with 2M KCl solution for one hour (soil to solution ratio, 10.0 g: 50 ml). Clear supernatant solution was recovered by high-speed centrifugation. Ammonium- and nitrate-nitrogen in the extract were volumetrically determined by steam distillation using a gas-tight container, 2% boric acid, and 2.5 mM H₂SO₄ solutions. For other aliquots of the soil extracts, the inorganic nitrogen was transformed into water insoluble, ammonium-tetraphenylborate derivatives on which nitrogen isotope composition was determined using an isotope ratio mass spectrometer, Delta plus (Finnigan MAT) in continuous flow mode. All the nitrogen isotopic com-

positions were expressed by common δ¹⁵N notation, ‰ variation of ¹⁵N/¹⁴N, relative to atmospheric dinitrogen (δ¹⁵N = 0‰). Probable errors associated with the overall processes of the isotopic analysis are less than ±0.2‰. Quantitative recovery of the concentration and nitrogen isotope composition of ammonium- and nitrate-nitrogen were monitored by repeated measurement, using high grade chemicals (NH₄Cl and KNO₃) with an established nitrogen isotopic composition during each batch of the analysis. Details are given elsewhere (Mizota *et al.*, 2006).

Bulk soil sample collected from the field was saturated with distilled water and allowed to drain for one night. Maximum water holding capacity of the undisturbed soil sample was estimated by weight loss of water in an electric oven maintained at 105°C.

RESULTS AND DISCUSSION

Concentration of inorganic nitrogen in soils and bird excreta

Table 1 shows the concentration together with nitrogen isotopic composition of the ammonium- and nitrate-

Table 2. Nitrogen isotope composition of foliar samples from Fiji

Location	Site characteristics	Nitrogen isotope composition (‰)* (species)
Hatana site A	Bird colony	+13.6 (<i>Capparis</i> sp.) +16.8 (<i>Ficus</i> sp.) +18.0 (<i>Paspalum distichum</i>) +36.7 (<i>Portulaca quadrifida</i>)
Hatana site B	Bird colony	+20.6 (<i>Pisonia grandis</i>)
Itumuta, Rotuma	Home garden	-1.3 (<i>Gardinia</i> sp.) +0.0 (<i>Morinda citrifolia</i>) +0.8 (<i>Scaevola faccada</i>)

*Per mil deviation relative to atmospheric dinitrogen ($\delta^{15}\text{N} = 0\text{‰}$).

nitrogen from soils under an active bird colony on Hatana islands. Included are two control soils under a Sago palm plantation on Rotuma island which are virtually free of bird excreta.

Concentration of ammonium-nitrogen in six soil samples representing the Hatana site A varied in range from 46 to 801 mg/kg dry soil (average; 323, Standard deviation; 334). The nitrate-nitrogen content in soils from the site B (215 to 916 mg/kg dry soil) (average; 551, standard deviation; 314) is always higher than those of the associated ammonium-nitrogen which indicates advanced nitrification. Soils under sparse vegetation cover of *Portulaca quadrifida* (halophilic species) and *Capparis* sp. tend to have a lower concentration of the inorganic nitrogen, whereas soils under dense vegetation cover of *Paspalum distichum* (Graminaceous grass) and *Ficus* sp. (shrub) tend to have higher values. Vegetative cover probably controls leaching of the inorganic nitrogen by meteoric precipitation.

Currently decaying bird excreta from the Hatana site A had a strong ammonia smell. High ammonium content (7,245 mg/kg dry material) together with nitrate-nitrogen (735 mg/kg dry material) in the excreta indicates quick decomposition of the uric acid under humid and high soil temperature conditions which prevail in the Hatana islands.

Concentration of ammonium-nitrogen (734 to 1,086 mg/kg dry soil, average; 921, standard deviation; 127) and nitrate-nitrogen (775 to 1,326 mg/kg dry soil, average; 991, standard deviation; 209) in soils from Hatana site B, which is under dense cover of the monotonic tree vegetation (*Pisonia grandis*), were clearly higher than at the neighboring site A. The spatial variation in the contents of six soil samples collected from site B was less pronounced, reflecting the effect of dense canopy cover. Lateral and vertical leaching of the inorganic nitrogen by meteoric water would be limited by shadowing with vegetative cover.

A bird excreta sample from Hatana site B also contained significant amounts of ammonium-nitrogen (3,063 mg/kg dry material). It had a higher content of nitrate-nitrogen (1,794 mg/kg dry soil), relative to that of the corresponding sample from Hatana site A (735 mg/kg dry material). The sample from site B indicates advanced stage of nitrification, probably reflecting a longer time after deposition on the ground.

Relative to the bird colony soils, the inorganic nitrogen content of the surface soils under the Sago palm plantation from Rotuma island was low, ranging from 14 to 35 mg/kg dry soil. These concentrations indicate a natural level of the inorganic nitrogen in common surface soils derived from volcanic ejecta.

Nitrogen isotope composition of the inorganic nitrogen in soils and bird excreta

$\delta^{15}\text{N}$ values of both ammonium- and nitrate-nitrogen in soils from the Hatana islands are characterized by distinctly high (positive) signatures (Table 1), reflecting the input of bird excreta. Two $\delta^{15}\text{N}$ values of the nitrate-nitrogen from the surface soils under the Sago palm plantation, where there is no input of bird excreta, are low, ranging between -4.1 and -1.3‰. Such low values indicate a prompt source of the meteoric (Heaton, 1986) or biologically fixed nitrogen (-2 to 0‰, Handley *et al.*, 1999).

$\delta^{15}\text{N}$ values of ammonium-nitrogen in six soil samples collected from Hatana site A ranged from +15.1 to +31.6‰, whereas those of the associated nitrate-nitrogen ranged from +13.5 to +24.6‰ (Table 1). There is a positive relationship between inorganic nitrogen content and $\delta^{15}\text{N}$ values, as observed for soil Nos. 3 and 6. A composite sample of the decaying bird excreta which was emitting ammonia showed the highest $\delta^{15}\text{N}$ value of +50.1‰.

$\delta^{15}\text{N}$ values of ammonium- and nitrate-nitrogen in six soil samples from Hatana site B showed relatively nar-

row ranges of +22.5 to +25.5‰ and +25.2 to +33.0‰, respectively.

Uric acid is known to be the major organic form of nitrogen in piscivorous bird excreta. The transformation of the organic nitrogen compounds into urea does not accompany detectable nitrogen isotope fractionation, whereas subsequent processes involving volatilization of ammonia, nitrification and denitrification accompany very large kinetic fractionation, as reviewed by Robinson (2001). Normally, the reaction products are depleted in ^{15}N , whereas residual substrate enriches in ^{15}N . This principle is well illustrated by a simple comparison of the $\delta^{15}\text{N}$ values of fresh uric acid separates with those of ammonium-nitrogen in decaying bird excreta. $\delta^{15}\text{N}$ values of two fresh uric acid separates (+17.7‰, +9.6‰) greatly increased up to +39 and +50‰, respectively, during the *in situ* decaying of the bird excreta on the soil surfaces.

As already stated above, nitrate production by a microbial nitrification process is accompanied by a large kinetic nitrogen isotope fractionation, amounting to up to 15 to 35‰ (Robinson, 2001). It means that nitrate is highly depleted in ^{15}N . Nevertheless, the apparent nitrogen isotope fractionation between ammonium- and nitrate-nitrogen in six soils from Hatana site A amounts to only 0.2 to 7.0‰ (Table 1), which are very low values relative to the expected values. The expected $\delta^{15}\text{N}$ values of the nitrate-nitrogen in soils from Hatana site A should be negative, if the nitrification proceeds as expected.

Nitrate-nitrogen is known to be further subjected to denitrification under suitable soil environments. Denitrification is also accompanied by large kinetic nitrogen isotope fractionation, documented as 28 to 33‰ (Robinson, 2001). The only plausible interpretation for the observed apparently low isotopic fractionation between ammonium- and associated nitrate-nitrogen in soil samples from Hatana site A would be simultaneous operation of both nitrification and denitrification processes, as observed when cattle slurry was applied on an Andisol grassland (Mizota *et al.*, 2006).

Along the same lines, the same interpretation could be made for $\delta^{15}\text{N}$ values of the inorganic nitrogen in soils from Hatana site B. All the nitrate-nitrogen had clearly higher $\delta^{15}\text{N}$ values than those of the associated ammonium-nitrogen. This indicates actively operating nitrification following denitrification.

Moisture content of soil samples at the time of collection from the colony field ranged from 55 to 69% and 50 to 65% for Hatana sites A and B, respectively. Since the maximum water holding capacity of the soil samples is around 70%, this indicates that pores of the surface soils are often saturated with meteoric precipitation. Under such circumstances, active nitrification and denitrification could occur (Mizota *et al.*, 2006).

Nitrogen isotope composition of major vegetative samples

Five foliar samples, representing major vegetation of the two Hatana colony sites are characterized by very high $\delta^{15}\text{N}$ values in a range from +13.6 to +36.7‰ (Table 2). The values are distinctive from four local samples ($\delta^{15}\text{N}$ = -1.3 to +0.8‰) collected from control areas which are not influenced by the addition of bird excreta on soils. Except for one value of *Portulaca quadrifida* ($\delta^{15}\text{N}$ = +36.7‰), which is one of the halophilic species, all the foliar $\delta^{15}\text{N}$ values were somewhat lower than those of the inorganic nitrogen in the corresponding soils. There would be negative fractionation associated with acquisition and allocation during the nitrogen nutrition. Determining whether such a unique $\delta^{15}\text{N}$ value of *Portulaca quadrifida* is common in other halophilic plants requires further collection and analysis of similar species from comparable habitats.

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REFERENCES

- Handley, L. L., Austin, A. T., Robinson, D., Scrimgeour, C. M., Raven, J. A., Heaton, T. H. E., Schmidt, S. and Stewart, G. R. (1999) The ^{15}N natural abundance ($\delta^{15}\text{N}$) of ecosystem samples reflects measures of water availability. *Aust. J. Plant Physiol.* **26**, 185–199.
- Heaton, T. H. E. (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem. Geol.* **59**, 87–102.
- Mizota, C., Yamaguchi, Y. and Noborio, K. (2006) Microbial transformation of nitrogen in cattle slurry as applied to an Andisol grassland. *J. Jpn. Soc. Soil Physic.* **104**, 13–26.
- Robinet, O., Sirgouant, S. and Bretagnolle, V. (1997) Marine birds of d'Entrecasteaux reef (New Caledonia, southwestern Pacific): Diversity, abundance, trends and threats. *Colonial Waterbirds* **20**, 282–290.
- Robinson, D. (2001) $\delta^{15}\text{N}$ as an integrator of the nitrogen cycle. *Trends Ecol. Evol.* **16**, 153–162.
- Schmidt, S., Dennison, W. C., Moss, G. J. and Stewart, G. R. (2004) Nitrogen ecophysiology of Heron Island, a subtropical coral cay of the Great Barrier Reef, Australia. *Funct. Plant Biol.* **31**, 517–528.
- Wright, A. C. S. and Twyford, I. T. (1958) Rainfall and Climatic Environment of Fiji. Compiled and drawn by the Soil Bureau, Department of Scientific and Industrial Research, New Zealand, 1960. Published by the Government of Fiji. 1961. One sheet; 1:760,320 scale.