

# Changes in soil C, N and $\delta^{15}\text{N}$ along three forest–pasture chronosequences in New Zealand

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**Abstract.** Changes in total soil carbon (C), nitrogen (N) and natural-abundance N isotopes ( $\delta^{15}\text{N}$ ) were measured along three forest-to-pasture chronosequences on pumice soils in the Central North Island of New Zealand. On each of the three chronosequences, exotic pine forests had been converted to intensive dairy pastures 2–11 years before sampling and samples were also taken from remaining pine forests and long-term pastures (40–80 years old). The primary objective of the study was to test the hypothesis that surface-soil  $\delta^{15}\text{N}$  would increase over time following conversion of forest to pasture, due to greater N inputs and isotope-fractionating N losses (e.g. ammonia volatilisation) in pasture systems. Results supported our hypothesis, with linear regression revealing a significant ( $P < 0.001$ ) positive correlation between log-transformed pasture age ( $\log_{10}[\text{pasture age} + 1]$ ) and surface-soil  $\delta^{15}\text{N}$ . There was also a positive correlation ( $P < 0.001$ ) between pasture age and total soil C and N, and a negative correlation of pasture age with C:N ratio. Surface-soil  $\delta^{15}\text{N}$  was also positively correlated ( $P < 0.001$ ) with total soil N, and negatively correlated with C:N ratio when C:N was  $< 13.6$ . These results suggested that as soils became more N-‘saturated’, isotope-fractionating N loss processes increased. Surface-soil  $\delta^{15}\text{N}$  in the pine forests was significantly less than subsoil  $\delta^{15}\text{N}$ , but there was no significant difference between the surface and subsoil in the long-term pastures, due to  $^{15}\text{N}$  enrichment of the surface soil. The difference in  $\delta^{15}\text{N}$  between the surface soil and subsoil may be a useful indicator of past land management, in addition to absolute  $\delta^{15}\text{N}$  values of surface soils.

**Additional keywords:** deforestation, land-use change, natural abundance, nitrogen isotope, pine forest.

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## Introduction

The understanding of soil properties and ecosystem development has been advanced by studying chronosequences, which are defined as ‘a set of sites formed from the same parent material or substrate that differ in the time since they were formed’ (Walker *et al.* 2010). Chronosequence studies are also referred to as space-for-time substitutions, and allow insight into how ecosystem properties change over time periods that are longer than would be possible via direct measurement (i.e. millennia, Vitousek *et al.* 1989) or studies over shorter time periods (i.e. decades) where samples have not been taken through time (Lemenih *et al.* 2005). Many decadal-scale chronosequence studies have investigated the effect that changes in land use, such as conversion of forest to agricultural land (Piccolo *et al.* 1996; Awiti *et al.* 2008) or reversion of agricultural land to natural ecosystems (Compton *et al.* 2007; Wang *et al.* 2007), have on soil properties. Soil carbon (C) and nitrogen (N) are commonly measured in chronosequence studies, due to the fundamental importance of soil organic matter

in ecosystem processes such as nutrient cycling. The natural abundance of C and N isotopes in soil and vegetation has also been shown to be a useful tool in chronosequence studies, with nitrogen isotopes ( $\delta^{15}\text{N}$ ), in particular, providing useful information on N cycling and loss processes (Piccolo *et al.* 1996; Martinelli *et al.* 1999; Brenner *et al.* 2001; Lemenih *et al.* 2005; Compton *et al.* 2007).

Before European settlement, New Zealand was predominantly covered by native forest or scrub, with forest clearance for pastoral agriculture commencing in earnest around 1850 and continuing until around 1980, although much of the currently productive land was cleared by 1920 (MacLeod and Moller 2006). Currently, 39% of New Zealand’s land area is in pastoral agriculture, 9% in exotic forest–scrub and 50% under native land cover, primarily forest in upland areas (MFE 2009). Despite the large scale and rapid conversion of forest to pasture in New Zealand, relatively few studies have measured how soil properties changed during the conversion process. Jackman (1964a, 1964b) and Walker *et al.* (1959) conducted

chronosequence studies spanning 19–66 years and found that soil C and N generally increased when native scrub or poor-producing pasture was converted to high-producing pasture. Increases in C and N were rapid during the first few years following conversion, and then slowed as a new equilibrium was approached. The C:N ratio tended to decrease with time under pasture, indicating that the soils were becoming saturated with N, therefore increasing the likelihood of N losses via leaching and gaseous pathways (Walker *et al.* 1959; Schipper *et al.* 2004; Schipper and Sparling 2011).

New Zealand's history of land-use change has been associated with various transitions between native and exotic forest and pasture. The clearing of native vegetation for pasture slowed or stopped by ~1980, but economic reforms and spikes in log prices led to conversions of large areas of pasture to exotic forest (mainly *Pinus radiata*) during the 1990s. A recent downturn in returns from plantation forestry, and good returns from dairy farming, led to conversion of large areas of exotic forest (mainly *Pinus radiata*) to dairy pastures, during the decade leading up to 2008 when article 3.3 of the Kyoto Protocol took effect. This provided an opportunity to further improve our understanding of how soil C and N changed during the first few years following forest clearance. There was particular interest in soil C dynamics because of the implications of forest conversion on New Zealand's greenhouse gas obligations under the Kyoto Protocol, and replacement of forests with pasture was expected to significantly increase N leaching losses, with implications for water quality (Hamilton 2005). With a focus mainly on estimating soil C changes associated with afforestation of pasture, several studies have compared soil properties under pasture and plantation forest sites in New Zealand (Giddens *et al.* 1997; Davis and Condron 2002; Sparling and Schipper 2004; Tate *et al.* 2005; Baisden *et al.* 2006), but we are aware of only one published chronosequence study where plantation forest had been converted to pasture (Hedley *et al.* 2009).

Globally, few studies have looked at N isotopes along forest–pasture chronosequences, and no such studies have

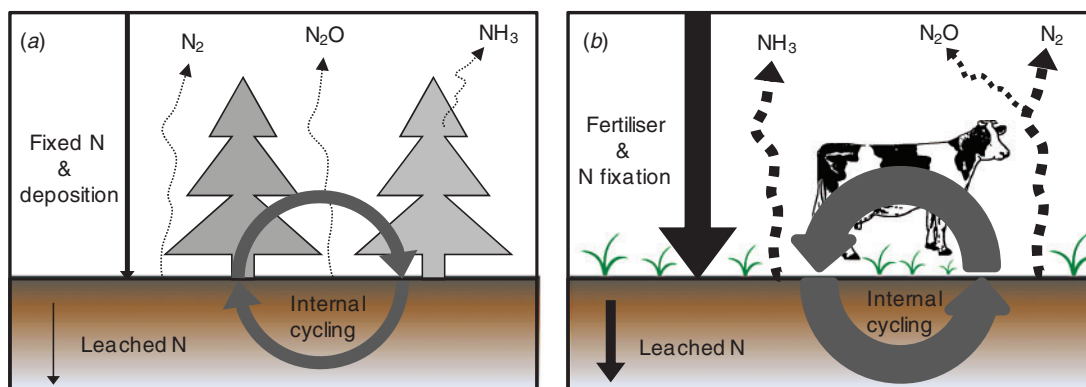
been carried out in New Zealand. Stevenson *et al.* (2010) measured natural-abundance N isotopes in surface soils from throughout New Zealand, and found a clear separation between land uses, with lower  $\delta^{15}\text{N}$  under forests (native and exotic) than under pastoral agriculture or cropping land. Lower  $\delta^{15}\text{N}$  in soils under forests than under pasture was largely attributed to differences in land-use intensity, with higher N inputs, cycling and isotope fractionating N losses (e.g. ammonia volatilisation) from the pasture sites. However, Stevenson *et al.* (2010) also pointed out that land use can be biased towards soil type or landscape position, and these factors may have also influenced soil  $\delta^{15}\text{N}$  values.

In the current study, we sampled soils from three chronosequences where plantation pine forests had been converted to intensive dairy pastures. At each chronosequence, pine and pasture sites were on the same soils, on the same topography and under the same climatic regime, and therefore we could be more certain that any differences in  $\delta^{15}\text{N}$  were due to land use. Based on the work of Stevenson *et al.* (2010), we hypothesised that surface-soil  $\delta^{15}\text{N}$  values would increase over time following conversion of plantation pine forest to pasture, due to greater N inputs and isotope fractionating N losses in the new pasture systems (Fig. 1). We tested the hypothesis that surface-soil  $\delta^{15}\text{N}$  values would increase in two ways: (i) an increase in absolute  $\delta^{15}\text{N}$  values of surface soils, and (ii) a relative increase in surface-soil  $\delta^{15}\text{N}$  values compared with a baseline estimated using subsoil  $\delta^{15}\text{N}$  values.

## Methods

### Site descriptions and soil sampling

The three chronosequences were located in the Central North Island, near the settlements of Tokoroa, Atiamuri and Wairakei. All three chronosequences were on the Taupo Pumice soil (Immature Orthic Pumice Soil; Hewitt 1998), formed on the non-welded Taupo ignimbrite (of rhyolitic composition) deposited as a pyroclastic flow around AD 232 (Hogg *et al.*



**Fig. 1.** Conceptual diagram showing the approximate magnitude of different N fluxes (depicted by the thickness of arrows), for (a) a plantation pine forest, and (b) an intensive dairy pasture. Nitrogen inputs from atmospheric deposition, N fixation and fertiliser generally have  $\delta^{15}\text{N}$  values of ~0‰, whereas N losses are usually depleted in  $^{15}\text{N}$ , with gaseous losses in particular often having very low  $\delta^{15}\text{N}$  values (e.g. –20‰; Frank *et al.* 2004; Houlton and Bai 2009). Preferential loss of  $^{14}\text{N}$  means that remaining substrate (e.g.  $\text{NH}_4^+$  and organic N) becomes enriched with  $^{15}\text{N}$ , and therefore high N inputs and greater N cycling and losses from pasture systems following conversion from forest are expected to lead to a gradual increase in soil  $\delta^{15}\text{N}$  values.

2012). This soil is classified as a Typic Udivitrand according to USDA Soil Taxonomy (Soil Survey Staff 2010). The Atiamuri and Wairakei study areas were flat or very gently sloping, whereas at Tokoroa the topography was more varied, but all samples were taken from a remnant terrace landform that was virtually flat. The Tokoroa and Wairakei chronosequences were 60 km apart, with the Atiamuri chronosequence in-between. At Atiamuri all sampling sites were within 2 km of each other, at Tokoroa sites were within 3.5 km of each other, and at Wairakei sites were within ~10 km of each other (although most sites were within 5 km). Annual rainfall and temperature was similar at the three sites (Table 1).

At all three chronosequences, second- or third-rotation pine forest (*Pinus radiata*) had been converted to intensive pastoral dairy farms 2–11 years before sampling, which occurred in March–July 2010. Before land preparation for pasture, mature forests were harvested, while immature trees were simply pulled or pushed out with diggers or bulldozers. Pine-tree debris was deposited in windrows or slash heaps, most of which were still present at the time of sampling, although at Atiamuri and Wairakei, some had been removed (for fuel), burned or buried. Where windrows and slash

heaps were no longer present, their location was determined from old aerial photographs and from talking to the respective farmers. These disturbed locations were also identifiable on the ground due to the abundance of woody debris and/or charcoal, and were avoided during sampling. Following removal of the pine trees at Tokoroa and Atiamuri, the soil was disc-cultivated, harrowed, rolled and then seeded. At Wairakei, heavy-duty mulchers were first used to break up remaining wood on or in the surface soil (excluding that deposited in windrows and slash heaps), and the land was then harrowed, rolled and seeded. At each of the three chronosequences, samples were also taken from remaining mature pine forests and long-term dairy pastures (40–80 years under pasture). A long-term sheep and beef pasture was also sampled at Tokoroa, and at Wairakei a dairy runoff (used to make silage, and to graze dairy cows during winter) was sampled (Table 1).

Management on all dairy farms was similar, with stocking rates of 2.5–2.9 cows  $\text{ha}^{-1}$  and milk-solids (milk fat + milk protein) production of 800–1100  $\text{kg ha}^{-1} \text{ year}^{-1}$ . On the recently converted farms, N fertiliser inputs were ~200–300  $\text{kg ha}^{-1} \text{ year}^{-1}$  for the first 2 years, after which rates were 150–200  $\text{kg ha}^{-1} \text{ year}^{-1}$ , which was similar to rates on the long-term dairy pastures. The long-term sheep and beef pasture at Tokoroa received ~40  $\text{kg N ha}^{-1} \text{ year}^{-1}$  and the dairy runoff at Wairakei 120  $\text{kg N ha}^{-1} \text{ year}^{-1}$ . The recently converted sites received large inputs of lime (2–3.5  $\text{t ha}^{-1}$ ), and superphosphate (~2  $\text{t ha}^{-1}$ ) or diammonium phosphate (800  $\text{kg ha}^{-1}$ ) during the first 2 years following pasture establishment, to raise soil pH and Olsen-P. Subsequently, all pastures received ~500  $\text{kg superphosphate}$  (or other fertiliser with equivalent P and S) to maintain soil P and S, and other nutrients and trace elements (e.g. K, Co, Se) were applied as required. Pastures at all sampling sites were predominantly ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*). Clover content in the recently converted pastures appeared to be higher than in the long-term pastures (although this was not specifically quantified).

At each of the sites identified in Table 1, three 50-m transects were laid out. For the Wairakei and Atiamuri pasture sites, the three transects were generally in separate paddocks, whereas at Tokoroa there was a limited number of suitable paddocks and therefore all three transects were usually within the same paddock. The three transects in the pine forest were distributed over a similar area to transects at the pasture sites (i.e. at all sites the three transects were within 200–300 m of each other). For each transect, 20 surface-soil cores (0–75 mm depth by 22 mm diameter) were taken at predetermined, random intervals and bulked into one sample. In addition, at seven of the points along each transect 25-mm-diameter cores were taken to a depth of 600 mm with the aid of a wooden maul. Each individual 600-mm core was split by horizon (with horizon depth recorded) and the seven cores were bulked by horizon to give one sample per horizon per transect. Random sampling intervals along the transects were used to avoid any potential for set sample spacing to coincide with pine tree rows. Pits were dug at 25 m along each transect, and three bulk-density samples were taken from each horizon (in each pit). Bulk-density cores were 60 mm in diameter and 50 mm deep.

**Table 1. Land use and years since conversion from forest to pasture for three chronosequences on pumice soils in the Central North Island of New Zealand**

Also shown is mean annual precipitation (MAP) and mean annual air temperature (MAT) for each chronosequence; MAP and MAT data (1980–2009) obtained from the NIWA Virtual Climate Station database (Tait *et al.* 2006). Soils were sampled from three 50-m transects for each pasture age, with transects generally located in three separate paddocks

MAP (mm)	MAT (°C)	Land use	Pasture age (years)
<i>Atiamuri</i>			
1450	12.3	Pine forest	0
		Dairy pasture	2
		Dairy pasture	5
		Dairy pasture	11
		Long-term dairy pasture	80
<i>Wairakei</i>			
1200	12	Pine forest	0
		Dairy pasture	2.5
		Dairy pasture	3
		Dairy pasture	3.5
		Dairy pasture	4
		Dairy Pasture	4.5
		Long-term dairy runoff	43
		Long-term dairy pasture	43
		Long-term dairy pasture	60
<i>Tokoroa</i>			
1520	12.4	Pine forest	0
		Dairy pasture	1.5 <sup>A</sup>
		Dairy pasture	2
		Dairy pasture	3
		Dairy pasture	5
		Long-term dairy pasture	40
		Long-term sheep and beef pasture	50

<sup>A</sup>This site was in a crop of swedes for 6 months before establishment of pasture.

### Sample preparation and analysis

Soil samples were air-dried and sieved through a 2-mm sieve, and any wood or pumice that would not pass through the sieve was discarded. Subsamples were obtained by passing each sample through a riffle, which split the sample in half until ~10 g was obtained. Each subsample was then fine-ground with an agate mortar and pestle and analysed for total C and N using a FP 2000 TruSpec Micro analyser (LECO Corporation, St. Joseph, MI, USA). All 0–75-mm samples were analysed for  $\delta^{15}\text{N}$  using a 20–20 Stable Isotope Analyser (Europa Scientific, Cambridge, UK) at the University of Waikato Stable Isotope Unit, Hamilton, New Zealand. Profile samples from one forest and one long-term pasture site at each of the three chronosequences were analysed for  $\delta^{15}\text{N}$  using an Isoprime mass spectrometer (Elementar Analysensysteme GmbH, Hanau, Germany) coupled to an EA3000 Elemental Analyser (EuroVector, Milan, Italy) modified with large-capacity carousel and combustion furnace at GNS Science, Lower Hutt, New Zealand. Profile samples were run on the Isoprime at GNS Science because this instrument provided enhanced sensitivity on samples with lower N contents in the subsoil horizons. The estimated repeatability of  $\delta^{15}\text{N}$  measurement was 0.1‰ for surface soil samples, and was inversely related to %N for subsoil samples, reaching ~0.2‰ at 0.1% N and ~0.3‰ for samples measured with the lowest N content. Ten samples were run in both laboratories, and this confirmed that results were comparable within 0.1 ‰.

Removal of pumice and wood fragments from soils (during sieving) meant that only the fine earth fraction (FEF) of soil was analysed for C, N and  $\delta^{15}\text{N}$ . Therefore, the bulk density of the FEF was required to express C and N on an area basis. Bulk density of the FEF was determined by sieving the whole bulk-density cores (after drying and weighing) through a 2-mm sieve, then re-drying the FEF and dividing the weight of soil in the FEF by the total volume of the bulk-density core. Measurements of bulk density were not specifically made for the 0–75 mm depth, and therefore, soil %C and %N data for this depth increment were converted to an area basis using measurements of bulk density from the A horizon.

### Statistical analyses

Before statistical analysis, data from the three replicate transects at each site (pasture age) were averaged. This conservative approach was taken because samples from the three transects at the same site were essentially pseudo-replicates (particularly where transects were located in the same paddock). Transects in separate paddocks could have been treated as separate replicate samples because management would have differed between paddocks. However, it was decided not to take this approach, and instead standard errors are presented for each point in Fig. 2 to show the variability between transects at each site. Data were plotted against the number of years the sites had been in pasture, but due to the large spread and uneven distribution of pasture ages, the time data was log-transformed. The transformation  $\log_{10} + 1$  was used to account for the pine forest sites where the pasture age was zero. Data were also analysed with the long-term pasture sites excluded to better understand changes soon after the conversion process. In this case, data were not

log-transformed. For full profile samples, the significance of differences between depths within the forests or pastures, and between the forests and pastures for each depth, were determined using analysis of variance in GENSTAT 13 (VSN International, Hemel Hempstead, UK).

## Results

### Surface soil samples (0–75 mm depth)

The clearest trend in the data was higher total N and  $\delta^{15}\text{N}$ , and lower C:N ratio in the surface soils at long-term pasture sites compared with pine forest or recently converted sites (Fig. 2). For example, average  $\delta^{15}\text{N}$ , %N and C:N ratio in the forest sites were 2‰, 0.47% and 17 respectively, compared with 4.3‰, 0.86% and 10.7 in the long-term pasture sites. For the three individual chronosequences, there was a significant positive correlation between log-transformed pasture age ( $\log_{10}[\text{pasture age} + 1]$ ) and soil  $\delta^{15}\text{N}$ , total N and total C and a negative correlation with C:N ratio (Table 2). One exception was the Wairakei chronosequence, where there was no significant correlation between pasture age and soil C (Table 2). Values for soil C, N and  $\delta^{15}\text{N}$  were similar between the three chronosequences (Fig. 2), and regression analysis of all data combined showed a highly significant ( $P < 0.001$ ) positive relationship between pasture age (log-transformed) and C, N and  $\delta^{15}\text{N}$ , and a negative relationship between pasture age and C:N (Table 2). The combined data were also analysed with the long-term pasture sites excluded, which revealed that there was still a significant positive correlation ( $P < 0.05$ ) between pasture age (not log-transformed in this case) and C, N and  $\delta^{15}\text{N}$  (data not shown).

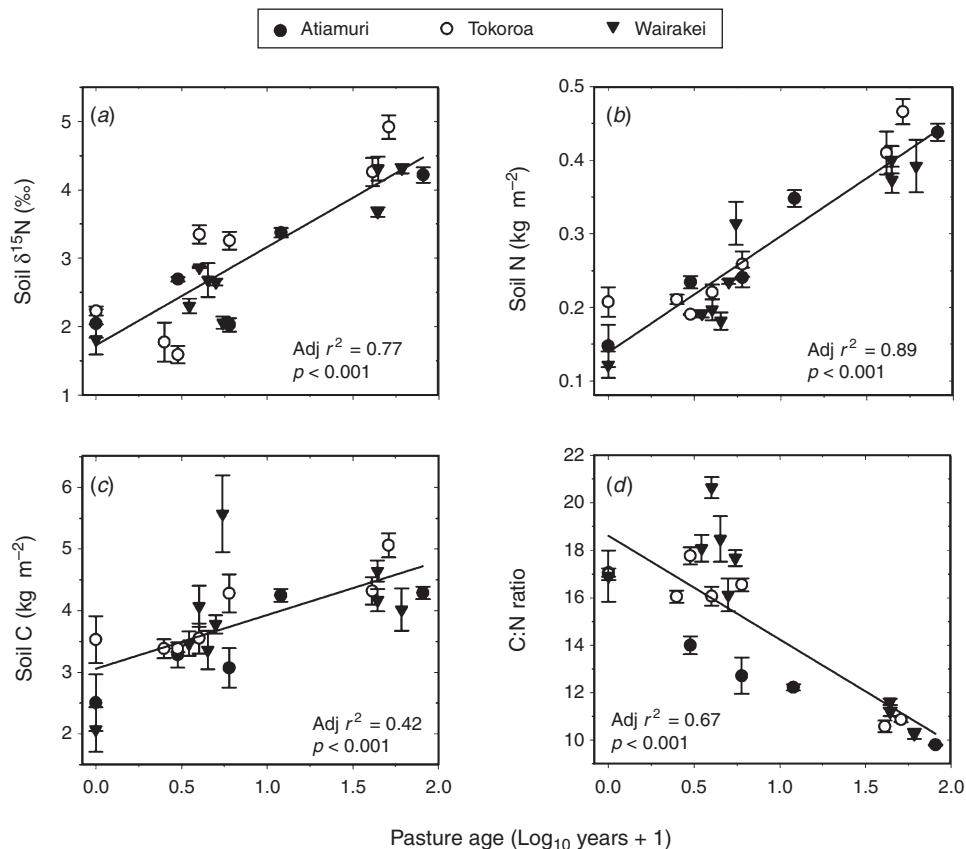
Based on the model fitted to data from the three chronosequences combined (Table 2), total N in the 0–75 mm depth increased by  $165 \text{ kg ha}^{-1} \text{ year}^{-1}$  during the first 10 years following pasture establishment, with the rate slowing to  $26 \text{ kg ha}^{-1} \text{ year}^{-1}$  between 10 and 50 years. Soil C showed a similar trend, increasing by  $908 \text{ kg ha}^{-1} \text{ year}^{-1}$  during the first 10 years, with the rate slowing to  $145 \text{ kg ha}^{-1} \text{ year}^{-1}$  between 10 and 50 years.

Plotting data from all individual transects revealed a significant ( $P < 0.001$ ) positive correlation between soil  $\delta^{15}\text{N}$  values and soil %N (Fig. 3a). Soil  $\delta^{15}\text{N}$  and C:N ratio data could be fitted with the ‘broken stick’ model, with a significant negative correlation between  $\delta^{15}\text{N}$  and C:N when C:N was  $< 13.6$ , but no significant relationship when C:N was  $> 13.6$  (Fig. 3b).

### Full soil profile samples

For the full profiles in the pine forests, %N decreased and  $\delta^{15}\text{N}$  increased significantly from the A to the B horizon, but there were no significant changes between the B and C horizons (Fig. 4a, b). At the long-term pasture sites, both %N and  $\delta^{15}\text{N}$  were significantly higher in the A horizon than they were at the forest sites, and %N decreased with depth as at the forest sites. However, there was no significant change in  $\delta^{15}\text{N}$  with depth in the long-term pastures (Fig. 4a). At all three chronosequences, total mass of N to 600 mm depth was significantly higher in the long-term pastures, and average  $\delta^{15}\text{N}$  (weighted by mass of N in each horizon) was significantly higher in the pasture profiles





**Fig. 2.** Semi-log plot showing the relationship between time under pasture and surface soil (0–75 mm) (a)  $\delta^{15}\text{N}$ , (b) total N, (c) total C, and (d) C:N ratio for three forest–pasture chronosequences on pumice soils in the Central North Island of New Zealand. Each point is the average of three replicate transects (20 bulked cores per transect) at each pasture age. Error bars are  $\pm 1$  s.e. Table 2 shows further details for the regression lines and regression lines fitted for each of the three chronosequences individually.

than the forest profiles at two of three chronosequences. This suggests the higher total N and  $\delta^{15}\text{N}$  in the surface soils of the long-term pastures were not simply due to a difference in N or  $^{15}\text{N}$  distribution within the profile (i.e. Billings and Richter 2006; Högberg *et al.* 2011).

## Discussion

Based on Stevenson *et al.* (2010), we hypothesised that surface soil  $\delta^{15}\text{N}$  would increase with time following conversion of forest to pasture. Data from the three chronosequences supported this hypothesis, with a clear increase in soil  $\delta^{15}\text{N}$  between the pine forests and the long-term pastures (Fig. 2a). These results help to confirm that the differences observed by Stevenson *et al.* (2010) were indeed driven by differences in land use, since soil and climatic conditions were the same (or very similar) between forest and pasture sites in the current study.

Varied results have been reported for soil  $\delta^{15}\text{N}$  in other land use change, chronosequence studies. In two (of the few) forest–pasture chronosequence studies where N isotopes were measured, Piccolo *et al.* (1994a, 1996) found either no difference, or lower surface soil  $\delta^{15}\text{N}$  in pasture sites compared with forest sites, in the Brazilian Amazon. At the sites where

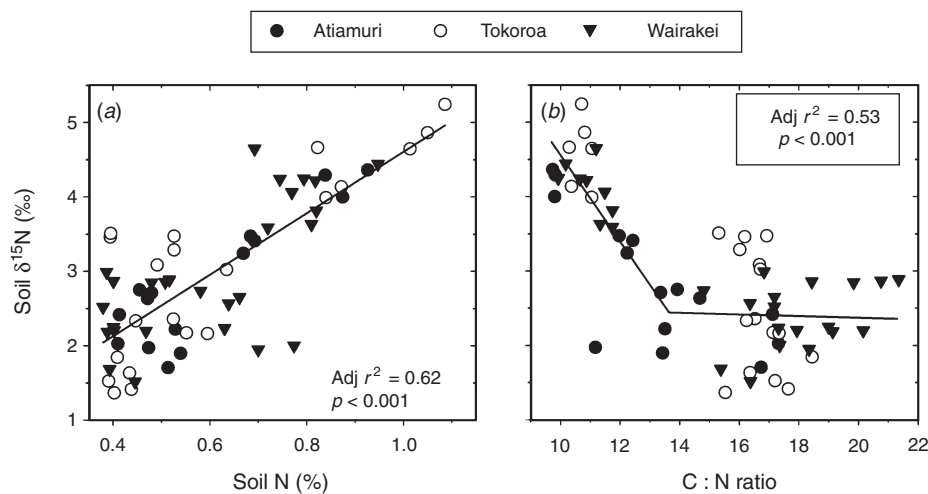
pasture soils had lower  $\delta^{15}\text{N}$  than forest soils,  $\delta^{15}\text{N}$  tended to be lowest in older pastures, which was opposite to what was observed in the current study (Fig. 2a). The lower  $\delta^{15}\text{N}$  in some pasture sites reported by Piccolo *et al.* (1994a, 1996) was suggested to be due to increased N inputs from  $\text{N}_2$  fixation (by free-living bacteria, since legumes were not sown), and N derived via fixation typically has  $\delta^{15}\text{N}$  values of  $\sim 0\text{‰}$ , which was much lower than the surface soils ( $\sim 7\text{--}12\text{‰}$ ). In addition, no fertiliser was applied to the pastures, and both N mineralisation and nitrification rates were higher in the forest soils (Piccolo *et al.* 1994a, 1994b, 1996), which suggests N cycling was tighter in the pastures, and isotope-fractionating N losses (e.g. denitrification) may have also been lower. We did not measure N mineralisation in the current study, but Stevenson *et al.* (2010) found that N mineralisation rates were twice as high in long-term pastures compared with native or exotic forests in New Zealand.

The increases in soil  $\delta^{15}\text{N}$  along the chronosequences in this study were similar to those reported when forests have been converted to cropland (Lemenih *et al.* 2005; Lemma and Olsson 2006; Awiti *et al.* 2008; Llorente *et al.* 2010). In those studies the increase in  $\delta^{15}\text{N}$  was mirrored by a decrease in total N (and C), which suggests that conversion led to increased N losses, and the

**Table 2.** Regression statistics for the relationship between time under pasture ( $\log_{10}[\text{pasture age} + 1]$ ) and surface soil (0–75 mm)  $\delta^{15}\text{N}$ , total C, total N and C : N ratio for the Atiamuri, Tokoroa and Wairakei chronosequences, and all three chronosequences combined

Values in parentheses are standard errors

Chronosequence	Slope	Slope <i>P</i>	Intercept	Intercept <i>P</i>	Adjusted <i>r</i> <sup>2</sup>
$\delta^{15}\text{N}$					
Atiamuri	1.16 (0.35)	0.044	1.89 (0.37)	0.014	0.72
Tokoroa	1.75 (0.41)	0.008	1.66 (0.41)	0.01	0.74
Wairakei	1.42 (0.20)	<0.001	1.66 (0.21)	<0.001	0.87
Combined	1.44 (0.17)	<0.001	1.73 (0.18)	<0.001	0.77
<i>N</i> ( $\text{kg m}^{-2}$ )					
Atiamuri	0.15 (0.02)	0.003	0.15 (0.02)	0.004	0.95
Tokoroa	0.17 (0.02)	0.001	0.15 (0.02)	0.002	0.88
Wairakei	0.16 (0.02)	<0.001	0.12 (0.02)	0.001	0.88
Combined	0.16 (0.01)	<0.001	0.14 (0.01)	<0.001	0.89
<i>C</i> ( $\text{kg m}^{-2}$ )					
Atiamuri	0.96 (0.29)	0.045	2.67 (0.31)	0.003	0.72
Tokoroa	0.88 (0.22)	0.011	3.23 (0.22)	<0.001	0.71
Wairakei	0.82 (0.50)	0.143	3.15 (0.54)	<0.001	0.18
Combined	0.87 (0.22)	<0.001	3.06 (0.23)	<0.001	0.42
<i>C</i> : <i>N</i>					
Atiamuri	−3.61 (0.53)	0.006	16.22 (0.56)	<0.001	0.92
Tokoroa	−4.33 (0.79)	0.003	18.43 (0.78)	<0.001	0.83
Wairakei	−5.18 (1.17)	0.003	20.44 (1.27)	<0.001	0.70
Combined	−4.37 (0.68)	<0.001	18.61 (0.72)	<0.001	0.67

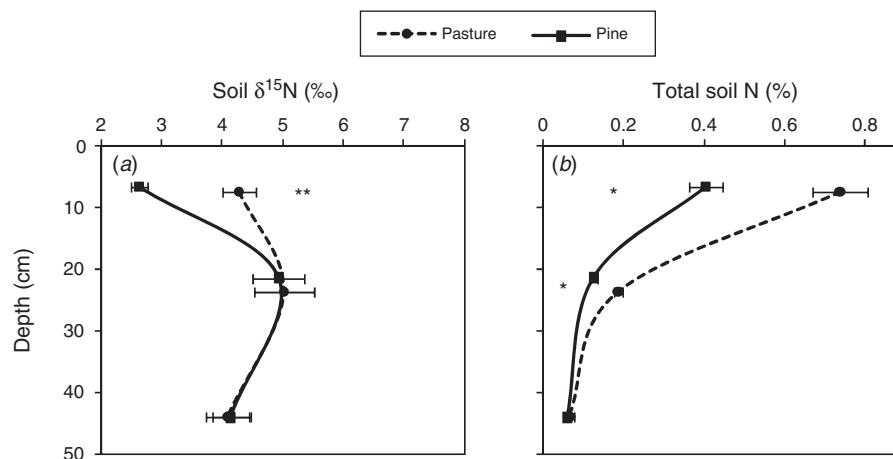


**Fig. 3.** Relationship between (a) surface soil (0–75 mm)  $\delta^{15}\text{N}$  and total N, and (b)  $\delta^{15}\text{N}$  and C : N ratio, using data from three forest–pasture chronosequences on pumice soils in the Central North Island of New Zealand. The line in (a) is a simple linear regression line, whereas data in (b) are fitted with the ‘broken stick’ model in GENSTAT 13. Each point is a value from an individual transect (20 bulked cores per transect).

N lost was depleted in  $^{15}\text{N}$ . During the conversion of agricultural land to forest, Compton *et al.* (2007) and Billings and Richter (2006) also found that soil  $\delta^{15}\text{N}$  increased with time, although this was largely attributed to re-distribution of N (depleted in  $^{15}\text{N}$ ) from the mineral soil to above-ground plant biomass, facilitated by mycorrhizal fungi, which can cause strong isotopic fractionation (Hobbie and Ouimette 2009). By contrast, Boutton and Liao (2010) and Wang *et al.* (2007) found that soil  $\delta^{15}\text{N}$  decreased in chronosequences where

agricultural land had been allowed to revert to forest or scrub. Boutton and Liao (2010) attributed the decrease in soil  $\delta^{15}\text{N}$  to an increase in soil N that was largely derived via  $\text{N}_2$  fixation, and hence had a delta value of  $\sim 0\text{‰}$ .

The increase in both  $\delta^{15}\text{N}$  and total N with pasture age in the three chronosequences in the current study differed compared with most other land-use-change chronosequence studies, where soil N and  $\delta^{15}\text{N}$  often had opposite trends (see above). The main difference between the chronosequences in the current study,



**Fig. 4.** Average (a)  $\delta^{15}\text{N}$  and (b) total N in soil profiles under pine forests and long-term (>40-year) pastures at three forest–pasture chronosequences on pumice soils in the Central North Island. Symbols are located at the midpoint of each sampling depth. Error bars are  $\pm 1$  s.e., and significant differences within the same horizon are denoted: \* $P < 0.05$ , \*\* $P < 0.01$ .

and those in the previously mentioned studies, was the high N-loading rate to the pastures. Total N input to the forest sites would have been  $<10 \text{ kg ha}^{-1} \text{ year}^{-1}$ , mainly from atmospheric deposition (Parfitt *et al.* 2006; Stevenson *et al.* 2010), while inputs to the pasture soils would have probably been  $>200 \text{ kg ha}^{-1} \text{ year}^{-1}$ , via inputs from N fertiliser and  $\text{N}_2$  fixation associated with clover. Total N in the 0–75 mm depth increased significantly with time under pasture ( $55 \text{ kg N ha}^{-1} \text{ year}^{-1}$  during the first 50 years), indicating that a portion of the added–fixed N was immobilised in the soil. Fixed N and fertiliser N generally have  $\delta^{15}\text{N}$  values of  $\sim 0\text{‰}$  (Högberg 1997; Bateman and Kelly 2007), and therefore N immobilisation should have led to a decrease in soil  $\delta^{15}\text{N}$  (Piccolo *et al.* 1996; Boutton and Liao 2010; Gubsch *et al.* 2011). The increase in soil  $\delta^{15}\text{N}$  despite N immobilisation in the soil therefore indicates that isotope-fractionating N-loss processes (e.g. volatilisation and nitrification followed by nitrate leaching or denitrification) must have occurred, leading to a loss of  $^{15}\text{N}$ -depleted N. It is well established in New Zealand pastoral systems that isotope-fractionating N-loss processes such as volatilisation and nitrification followed by nitrate leaching or denitrification increase as N inputs increase (Ledgard *et al.* 1999; Monaghan *et al.* 2005), and that N losses are much higher under pasture than forest (Di and Cameron 2002; Menneer *et al.* 2004; Stevenson *et al.* 2010).

A simple mass-balance calculation, based on a total N input of  $200 \text{ kg ha}^{-1} \text{ year}^{-1}$  (with a  $\delta^{15}\text{N}$  value of  $0\text{‰}$ ) and a net N immobilisation rate of  $55 \text{ kg ha}^{-1} \text{ year}^{-1}$  during 50 years of pasture development (calculated from the regression equation from Fig. 2b, Table 2), revealed that the net  $\delta^{15}\text{N}$  of N immobilised in the surface soil must have been  $\sim 5.7\text{‰}$ , and net  $\delta^{15}\text{N}$  of N lost  $-2.1\text{‰}$ . These values were similar to those calculated for immobilised and lost N in two long-term ( $\sim 50$ -year) superphosphate and irrigation trials at Winchmore in Canterbury, where archived soils taken through time were analysed for  $\delta^{15}\text{N}$  (Mudge *et al.* 2013). The average rate of change in surface-soil  $\delta^{15}\text{N}$  between the pine forests and 50-year-old pastures was  $0.05\text{‰}$  (calculated from the

regression equation in Table 2), which was also of a similar magnitude to the average rate of change ( $\sim 0.03\text{‰}$ ) reported in the more intensive treatments of the two Winchmore trials (Mudge *et al.* 2013).

Average soil  $\delta^{15}\text{N}$  (0–75 mm depth) under the pine forests and long-term dairy pastures was  $2\text{‰}$  and  $4.1\text{‰}$ , respectively. These values were lower than the average reported by Stevenson *et al.* (2010) for 30 plantation-forest sites ( $2.8\text{‰}$ ) and 50 dairy-farm sites ( $5.4\text{‰}$ ) throughout New Zealand. Lower  $\delta^{15}\text{N}$  values in the current study under both pine forest and long-term dairy pasture may have been due to the pumice soil being young ( $\sim 1800$  years) relative to many other soils in New Zealand. Soil  $\delta^{15}\text{N}$  tends to increase with soil age (Vitousek *et al.* 1989; Martinelli *et al.* 1999; Brenner *et al.* 2001), and therefore, there would have been less time for  $^{15}\text{N}$  enrichment to occur in the pumice soils. In addition, the long-term pasture sites in the current study had probably been in pasture for a shorter time than many of the sites reported by Stevenson *et al.* (2010), because land clearance in the Central North Island would have occurred, on average, later than in many other parts of New Zealand. Some of the pine forests reported by Stevenson *et al.* (2010) were also planted on sites that had previously been under pasture, and therefore  $\delta^{15}\text{N}$  may have become elevated before establishment of the trees. As far as we can determine, none of the pine forest sites in the current study were previously under pasture. The similarity of  $\delta^{15}\text{N}$  from the long-term dairy pastures and the long-term sheep and beef pasture at Tokoroa and the dairy runoff at Wairakei was not consistent with Stevenson *et al.* (2010), where average  $\delta^{15}\text{N}$  was higher in dairy soils. However, this was probably because both of the dry-stock pastures were intensively managed, similar to the dairy pastures.

#### Changes in soil C and N, and correlations with $\delta^{15}\text{N}$

The increase in total C and N from the pine forests to the long-term pastures for the 0–75 mm samples (Fig. 2b, c) was consistent with results from the full profiles (Lewis *et al.* 2014). Average accumulation rates for C and N during the

first 10 years following conversion were 908 kg C and 165 kg N ha<sup>-1</sup> year<sup>-1</sup>, which were within the range of values reported from other similar studies in New Zealand (Walker *et al.* 1959; Jackman 1964a, 1964b; Hedley *et al.* 2009; Schipper and Sparling 2011). The decline in C:N ratio from forests or recently converted sites to long-term pastures was also consistent with previous studies (Sparling and Schipper 2004; Hedley *et al.* 2009). Relatively high rates of N accumulation were probably due to high N inputs to the pasture systems from N fixation and N fertiliser, which, coupled with the initially high C:N ratios of the forest soils, would have provided the ideal environment for net N immobilisation. However, caution is required when drawing conclusions about changes in total C and N stocks when only surface soils are sampled, because changes often occur throughout the profile (Schipper and Sparling 2011).

The positive correlation between  $\delta^{15}\text{N}$  and total N and the negative correlation with C:N (Fig. 3a, b) suggested that, as soils became more 'saturated' with N, isotope-fractionating N-loss processes increased. The lack of any clear relationship between  $\delta^{15}\text{N}$  and the C:N ratio when C:N was >13.6 (Fig. 3b) was probably because, at higher C:N ratios, isotope-fractionating N-loss processes would have been lower, due to high rates of N immobilisation into soil organic matter, and since fertiliser and fixed N generally have  $\delta^{15}\text{N}$  values of ~0‰, immobilisation would tend to balance out  $^{15}\text{N}$  enrichment due to isotope-fractionating N losses. In a broader survey of New Zealand soils, Stevenson *et al.* (2010) also found a significant negative correlation between  $\delta^{15}\text{N}$  and C:N, which suggests that the combination of total N, C:N ratio and  $\delta^{15}\text{N}$  could provide more information on the 'N status' or history of a system than if only one of these variables were measured. For example, if a soil had high total N, high  $\delta^{15}\text{N}$  and low C:N ratio, it would probably have been subject to high N inputs and losses for several years (i.e. long-term pastures in the current study). A soil with low total N and low C:N ratio, but with high  $\delta^{15}\text{N}$ , has likely lost organic N (i.e. soil from a long-term cultivated site;

Stevenson *et al.* 2010). By contrast, if a soil had low N, low  $\delta^{15}\text{N}$  and high C:N ratio, it is likely from a natural ecosystem or an extensively managed pasture, with low N inputs and losses. These hypotheses need to be further explored.

#### Full soil profile samples

The significant difference in A-horizon  $\delta^{15}\text{N}$  between the forest and pasture sites, but no difference for the two subsoil horizons (Fig. 4a), was consistent with other studies (Piccolo *et al.* 1994a; Lemma and Olsson 2006; Llorente *et al.* 2010), and was presumably because processes affecting  $\delta^{15}\text{N}$  (e.g. volatilisation and nitrification) were higher in the surface horizon (Piccolo *et al.* 1994a).

Previous studies have shown that, in general, %N decreases and  $\delta^{15}\text{N}$  increases with soil depth in both forest and pasture ecosystems (Steele and Wilson 1981; Ledgard *et al.* 1984; Piccolo *et al.* 1996; Hobbie and Ouimette 2009). The increase in  $\delta^{15}\text{N}$  with depth is thought to occur because organic N at depth is older and more processed and, therefore, has had more opportunities for isotope-fractionating N losses, and also because plants (particularly those associated with ectomycorrhizal fungi) tend to take up N that is depleted in  $^{15}\text{N}$  relative to bulk soil N, and thus litter incorporated into the surface soil has low  $\delta^{15}\text{N}$  (Hobbie and Ouimette 2009). The trend of decreasing %N and increasing  $\delta^{15}\text{N}$  with depth in the soil profiles under the pine forests (Fig. 4a, b) was consistent with most other studies, but the lack of change in  $\delta^{15}\text{N}$  with depth in the long-term pastures was not. However, a few other studies have also found little difference between topsoil and subsoil  $\delta^{15}\text{N}$  in modified ecosystems, compared with more 'natural' systems where there was the typical increase in  $\delta^{15}\text{N}$  with depth. For example, Eshetu and Högborg (2000), and Lemma and Olsson (2006) found a greater increase in soil  $\delta^{15}\text{N}$  with depth under forests than under pastures or cropped land; in a forest ecosystem, Högborg *et al.* (1996) found that  $\delta^{15}\text{N}$  in plots fertilised with high rates of N decreased with depth

**Table 3. Summary of surface soil and subsoil  $\delta^{15}\text{N}$ , and the difference in  $\delta^{15}\text{N}$  between the two depths, at sites under different land uses or treatments**

For the first four studies, surface soil was ~0–200 mm depth and subsoil ~300–600 mm depth. In the last study (Högborg *et al.* 1996), the 'surface soil' was the top layer of litter and the 'subsurface soil' the top 50 mm of the mineral soil. Note:  $\delta^{15}\text{N}$  values other than in the current study are approximate because they were read off graphs

Land use or treatment	Surface soil $\delta^{15}\text{N}$ (‰)	Subsoil $\delta^{15}\text{N}$ (‰)	Surface soil – subsoil $\delta^{15}\text{N}$ (‰)	Reference
Plantation pine forest	2.6	4.1	–1.5	Current study
Pasture	4.3	4.1	0.2	
Native forest	7	9	–2	Eshetu and Högborg (2000)
Pasture	7.2	6.6	0.6	
Cultivated land	7.3	7.7	–0.4	Lemma and Olsson (2006)
Native forest	7	9.2	–2.2	
Cultivated land	8.3	9.0	–0.7	
Native forest	11.8 <sup>A</sup>	12.6	–0.9	Piccolo <i>et al.</i> (1994a)
Pasture	10.2	12.5	–2.3	
Unfertilised forest plots	0.3	5.1	–4.8	Högborg <i>et al.</i> (1996)
Fertilised forest plots (urea)	3.1	3.5	–0.4	

<sup>A</sup>Oe and Oa layers were included in the surface mineral soil samples from the forests in this study.



(from the top of the litter layer to 50 mm depth in the mineral soil), whereas in control plots that did not receive N there was a typical increase in  $\delta^{15}\text{N}$  with depth (Table 3). By contrast, Piccolo *et al.* (1994a) found the opposite trend, with the surface soil of pastures being more depleted in  $^{15}\text{N}$  relative to subsoils than in forests (Table 3). This was probably because of immobilisation of fixed N (with low  $\delta^{15}\text{N}$ ) in the surface soils of pastures.

These results suggest that differences between topsoil and subsoil  $\delta^{15}\text{N}$  may be a useful indicator of past land management. Undisturbed or extensively managed sites with low N inputs and losses will likely show the typical increase in  $\delta^{15}\text{N}$  with depth, whereas at more intensively managed sites, there may be no change with depth, or even decreases in  $\delta^{15}\text{N}$ . One advantage of using the difference between topsoil and subsoil  $\delta^{15}\text{N}$  is that it may be more applicable for comparing across soils that have different 'baseline'  $\delta^{15}\text{N}$  values. Subsoil  $\delta^{15}\text{N}$  in general appears less affected by land use than does surface-soil  $\delta^{15}\text{N}$  (except see Billings and Richter 2006), and therefore the difference between the topsoil and subsoil could reflect the impact of management irrespective of the soils initial  $\delta^{15}\text{N}$  value. An example of this can be seen in Table 3, where differences in mineral soil  $\delta^{15}\text{N}$  between studies varied by up to 9‰, but differences between surface soil and subsoil were relatively consistent, ranging from 0 to 2.5‰, depending on land use. Further research on multiple soil types under similar management will be required to test this hypothesis.

The much higher  $\delta^{15}\text{N}$  values (~7–13‰) reported by Eshetu and Högberg (2000), Lemma and Olsson (2006) and Piccolo *et al.* (1994a) than in the current study (~2–5‰) (Table 3) were presumably because the soils were older (thus had more time to become enriched) and were also from the tropics where N cycling tends to be more open, thus providing more opportunity for isotope-fractionating N losses (Martinelli *et al.* 1999).

## Conclusion

The key hypothesis tested in this study was that soil  $\delta^{15}\text{N}$  would increase with time following clearance of forest or scrub and conversion to pasture. Results provided strong support for this hypothesis, with a clear increase in  $\delta^{15}\text{N}$  in surface (0–75 mm) soils between pine forests (2‰) and long-term pastures (4.1‰). There was also a significant increase in total C and N, and a decrease in the C:N ratio, in the surface soils. Analysis of full soil profiles under long-term pasture and remaining forest revealed a significant increase in  $\delta^{15}\text{N}$  between the A horizon and subsoils of the pine forests, but no significant differences between depth increments in the long-term pastures (presumably due to  $^{15}\text{N}$  enrichment of the A horizon). These profile results suggest that differences in  $\delta^{15}\text{N}$  between the surface soil and subsoil may be a useful indicator of past land management, with the added advantage of potentially being more applicable for comparing across soil types with different 'baseline'  $\delta^{15}\text{N}$  values. This hypothesis needs to be tested further.

Results from this study show that soil  $\delta^{15}\text{N}$  can provide useful information about soil N dynamics in addition to that derived from total N or the C:N ratio. For example, the increase in  $\delta^{15}\text{N}$  along the three chronosequences indicated that a large

amount of N must have been lost via isotope-fractionating pathways (e.g. ammonia volatilisation), otherwise the net immobilisation of fixed or fertiliser N (with  $\delta^{15}\text{N}$  values of ~0‰) in the soil would have resulted in a decrease in soil  $\delta^{15}\text{N}$ .

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