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Land-use change affects soil phosphorus dynamics: the assessment using ^{31}P NMR spectroscopy and chemical fractionation

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Abstract Conversion from native forest to plantation forest can have significant impacts on the transformation of soil carbon and associated nutrients, including soil phosphorus (P). Results from a paired-site study in southeast Queensland, using both chemical fractionation and ^{31}P NMR spectroscopy, demonstrated that conversion from natural forest to hoop pine plantation did not substantially affect soil total P (1290, 1289 and 1190 mg P kg^{-1} for soils under NF, 1R and 2R, respectively), but conversion significantly reduced the availability of soil P.

Introduction
Land-use change from the native forest to the plantation forest can have significant impacts on soil phosphorus (P) transformation. Adjacent natural forest (NF), and first (1R) and second rotation (2R) hoop pine plantations in south-east Queensland, Australia, were selected to investigate the effects of conversion of natural forest to hoop pine plantations and forest management (harvesting and site preparation of plantation) on the size and the nature of P pools in surface (0-10 cm) soils using solution ^{31}P NMR analysis and chemical fractionation.

Materials and Methods
Research site: The site is located within the Yarraman State Forest, SEQ, Australia (26o52' S, 151o51' E), lying in the upper catchment of the Mary River. The soil is a Snuffy Mesotrophic Red Ferrosol (Soil Survey Staff, 1999). Altitude at the site is 428 m above sea level. Annual rainfall varies from 433 to 1110 mm, with an average of 791 mm. Winter temperatures range from 4 to 20 C, and summer temperatures from 17 to 29 C. The NF site is classified as a rainforest/bastard scrub and dominated by bunya pine (*Aravcaria bidwilli*), yellowwood (*Terminalia oblongata*), crows ash (*Pentaceras australis*) and lignum-vitae (*Premna lignum-vitae*), with emergent hoop pine (*Araucaria cunninghamii*). The 1R hoop pine plantation was established in 1949 at approximately 1540 stems ha-1, and then thinned to a final stocking of 430 stems ha-1. The 2R hoop pine site was planted in November 2000 after the clearcut harvest of part of the 1R hoop pine plantation in September 1999. The stocking density at the 2R hoop pine site was approximately 620 stems ha-1 when the soil was sampled.
Soil Sampling: Each (ca 30 m x 100 m) of the research areas under adjacent NF, 1R and 2R hoop pine plantations was divided into five subplots for soil sampling. A total of 25 soil cores (0-10 cm) were randomly collected with an auger of ca 7.5 cm in diameter from each subplot and bulked in October 2001.
Chemical Fractionation: Soil P fractionation scheme described by Chen et al. (2000) was used. This involved sequential extraction of soil with 1 M NaOH NH4Cl (APi), 0.5 M $NaHCO_3$ (pH 8.5), 0.1 NaOH (N(I)P), 1 M HCl and 0.1 M NaOH (N(II)P).
^{31}P solution NMR analysis: Freeze-dried NaOH-EDTA extracts of soils were prepared according to the method described by Cade-Menun and Preston (1996). For NMR analysis, 70 mL filtrate was lyophilized. The freeze-dried extract (ca 250 mg) was re-dissolved in 0.9 mL 1 *M* NaOH and 0.1 mL D_2O and allowed to stand for 10 min with occasional vortexing. Samples were then centrifuged at 1500 x *g* for 5 min and the supernatant transferred to 5-mm diameter NMR tubes. Solution ^{31}P NMR spectra were acquired at 162 MHz on a Varian Inova 400 spectrometer using an acquisition time of 1.6 seconds, a recycle delay of 2.4 seconds and a pulse angle of 65°. A 1Hz line broadening function was applied to the data prior to Fourier Transformation. The general functional classes of P compounds were: phosphonates around 19 ppm, inorganic orthophosphate approximately 6.1 ppm, orthophosphate monoesters at 3-6 ppm, orthophosphate diesters between -0.5 and 2.0 ppm, pyrophosphate around -4 ppm, and inorganic polyphosphate about -20 ppm. Within the orthophosphate monoesters, *myo*-inositol hexakisphosphate (phytic acid) was identified by the signature signals at 5.85, 4.92, 4.55, and 4.43 ppm in the ratio of 1:2:2:1. Integral areas for all major species were determined using the deconvolution routines implicit in the Varian 6.1C software package. The identified P functional groups were expressed as percentages of total signal area, relative concentrations (mg kg^{-1}) were calculated by multiplying the percentage peak area with total P in the extracts.

Table 1 Basic chemical properties in soils under adjacent native forest and hope pine plantations (Native forest, NF; 1st rotation hoop pine, 1R; 2nd rotation hoop pine, 2R).

Vegetation type	pH	Total C (%)	Total N (%)	Bulk density ($g\ cm^{-3}$)	Soil moisture %	Sand (%)	Silt (%)	Clay (%)
NF	4.7b	7.96a	0.670a	0.688a	25.0b	32.7a	18.9c	48.5a
1R	6.0a	6.38b	0.486c	0.726a	26.2b	33.4a	30.6a	36.0a
2R	5.6a	6.40b	0.536b	0.736a	36.1a	28.0a	27.1b	44.9a

Results and Discussion
Conversion from natural forest to hoop pine plantations did not substantially affect soil total P (1290, 1289 and 1190 mg P kg^{-1} for soils under NF, 1R and 2R, respectively) (see Table 2), but significantly reduced the availability of soil P. Soil labile P (sum of solution P (APi) and $NaHCO_3$ extractable P) decreased from 125 mg P kg^{-1} under NF to 79 mg P kg^{-1} under 1R and 59 mg P kg^{-1} under 2R. But recalcitrant P pools (sum of the second NaOH extractable and residual P) increased from 504 mg P kg^{-1} under NF to 537 mg P kg^{-1} under 1R and 623 mg P kg^{-1} under 2R.

EDTA-NaOH extracted more P from soil under NF (one average, 678 mg P kg^{-1}, 52.6% of total P) than 1R (531 mg P kg^{-1}, 41.1% of total P) and 2R (494 mg P kg^{-1}, 41.5% of total P) hoop pine plantation. Results from ^{31}P solution NMR analysis showed that inorganic P (6.1 ppm) comprised

45-63% of total EDTA-NaOH extractable P, while inositol phosphate (3-6 ppm) was predominant among organic fractions in all soils under adjacent NF, 1R and 2R hoop pine plantations (Table 3, Figure 1) The concentration of orthophosphate was higher in soil under NF compared with those under 1R and 2R hoop pine plantations (Table 3) The concentration of orthophosphate diesters was also greater in soil under NF than those under 1R and 2R plantations These further indicate that land-use change from NF to plantation forests may reduce soil P availability, which is consistent with results from chemical fractionation. There was a slight increase in the concentration of pyrophosphophate after conversion from NF to 1R and 2R plantations. A distinct peak at 3.88 ppm was observed from the spectra obtained cross all soils under various vegetations. This may belong to *scyllo*-inositol hexakisphosphate (Turner et al 2003) and has yet to be confirmed. Polyphosphate was not detestable across different soils (Figure 1). The *myo*-inositol hexakisphosphate (chemical shift, 5 85, 4.92, 4.55, and 4.43 ppm in the ratio of 1:2:2:1) was not identified either across all spectra obtained

Table 2 Soil P fractions in adjacent native forest and hoop pine plantations of southeast Queensland (Native forest, NF; 1st rotation hoop pine, 1R; 2nd rotation hoop pine, 2R).

Forest type	APi	BPi	BPo	HPi	N(I)Pi	N(I)Po	N(II)Pi	N(II)Po	Res-P	TP
NF	2.5a (1.6)	42 1a (9.1)	80 1a (9.5)	51.1b (4.4)	185.9a (11.0)	422.2a (38.3)	131.2a (13.0)	79.2b (22.5	294.1b (55.8)	1289a (56 0
1R	0.8b (0.4)	24.3b (11.2)	54.1b (5.6)	68.0a (17.3)	187.7a (14.2)	416.6a (46.5)	154.6a (29.6)	90 9b (34.8	292.5b (22.6)	1289.3a (92.8)
2R	1.5ab (0.4)	19 5b (3.4)	38.7c (12.4)	38.1b (10.8)	139.7b (26.3)	328.9b (15.8)	136.1a (22.7)	151 1a (15.9)	336.1a (18.8)	1189.8b (40.5)

Table 3 Distribution of P functional groups in NaOH-EDTA extracts of soils as percentage of total peak area of the ^{31}P nuclear magnetic resonance (NMR) spectra and concentration (mg P kg^{-1}soil) (Native forest, NF; 1st rotation hoop pine, 1R; 2nd rotation hoop pine, 2R).

Forest type		Inorganic P			Organic P		
					Orthophosphate monoesters		Orthophosphate diesters
		Orthophosphate	Pyrophosphate	Polyphosphate	Unknown (x) ‡	Total monoesters	
NF	mg kg^{-1}	376 (12)	3.7 (0.5)	n/d	10.1 (2 6)	291 (11)	6.5 (0 8)
	%	55.6 (1.1)	0 55 (0.06)	n/d	1.5 (0.3)	42.9 (1.1)	0.95 (0 08)
1R	mg kg^{-1}	341 (38)	4 2 (0 3)	n/d	5 6 (0.3)	182 (8)	3.9 (0.5)
	%	63.4 (3 6)	0.80 (0 08)	n/d	1.06 (0 06)	35.0 (3 4)	0 77 (0 13)
2R	mg kg^{-1}	223 (14)	6.3 (0.6)	n/d	6.9 (0 4)	261 (11)	3 4 (0 6)
	%	45 0 (21 0)	1.26 (0.09)	n/d	1 40 (0.10)	53 0 (2.0)	0 69 (0.12)

† Data in the columns are mean (n = 5); data in parenthesis are standard errors.
‡ A peak (X) at 3.88 ppm with the identity unknown. It may be *scyllo*- inositol hexakisphosphate (Turner et al. 2005); however this has yet to be confirmed

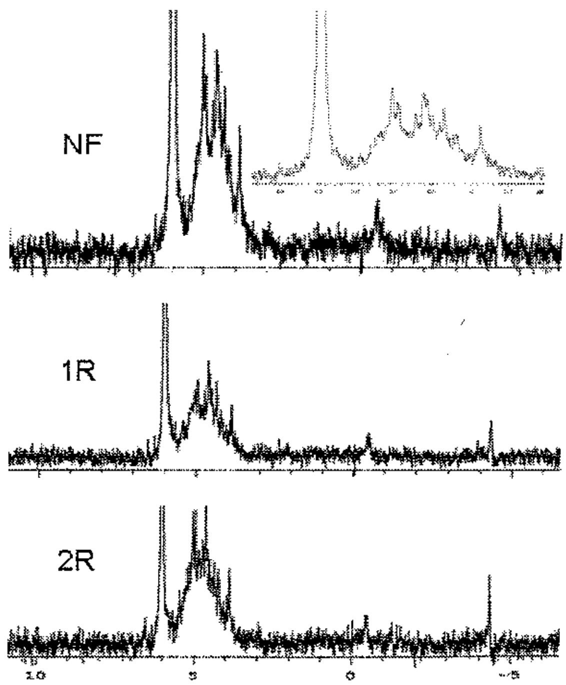

Figure 3 Solution ^{31}P {1H} nuclear magnetic resonance (NMR) spectra of NaOH-EDTA extracts of the soils.

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