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Phosphorus dynamics in a tropical forest soil restored after strip mining

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Abstract
Background and aims We hypothesized that successful early ecosystem and soil development in these P-deficient soil materials will initially depend on effective re-establishment of P storage and cycling through organic matter. This hypothesis was tested in a 26-year chronosequence of seven lightly fertilized, oxidic soil materials restored to eucalypt forest communities after bauxite mining.
Methods Total P (Pt) status, Hedley P fractions and partial chemical speciation (NaOH-EDTA extraction and analysed using solution ^{31}P NMR spectroscopy) were determined in the restored soils.
Results Concentrations of Pt and most Hedley fractions changed with restoration period, declined with depth and were strongly positively correlated with C and N concentrations. *Biological P* dominated the *Labile* and *Intermediate P* fractions while *Long-term P* was dominantly inorganic. Organic P concentrations in NaOH-EDTA extracts and their chemical natures were similar in restored and unburned native forest sites. Phosphomonoesters were the dominant class of organic P.
Conclusions Surprisingly rapid P accretion and fractional changes occurred over 26 years, largely in the surface soils and closely associated with organic matter status. Alkaline hydrolysis products of phosphodiesters and pyrophosphate indicated the importance of microbial P cycling. The important consequences for long-term ecosystem development and biological diversity require further study.

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Introduction

Phosphorus (P) is an essential element that widely conditions biological processes in all earth surface environments (Elser et al. 2007), including net primary production (Cleveland et al. 2011). In terrestrial environments, P availability frequently limits plant

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productivity, influences plant community composition (see, for example, Elser et al. 2007; Güsewell 2004; Knecht and Göransson 2004; Peltzer et al. 2010) and interacts with soil development processes (Crews et al. 1995; Viscarra Rossel and Bui 2016; Walker and Syers 1975).

In the highly-weathered, P-depleted, Fe and Al-enriched (Cornell and Schwertmann 2003) soils common in older tropical landscapes, the primary P-containing minerals, such as hydroxyapatite, are likely to have been long exhausted due to acidification (Vitousek et al. 2010; Yang et al. 2013). Much of the P present is likely to be associated with clays and the oxide and related minerals of Fe and Al, or to occur in refractory organic forms (Cross and Schlesinger 1995; Yang and Post 2011). Retention of P in these soils is high (IUSS Working Group WRM 2015; Short et al. 2000, 2007) and in natural environments P supply for the support of biological activity is characteristically constrained (Lang et al. 2016). In such environments, maintenance of P supply occurs largely through biological recycling, desorption and diffusion from poorly-available forms, possibly limited aerial accession (Reed et al. 2011; Tipping et al. 2014) and, in managed environments, from fertilizer inputs.

Restoration practice at many Australian tropical mine sites aims to develop resistant and resilient ecosystems, similar to those of the surrounding unmined areas. This is only likely to be achieved where nutrient cycles are effectively re-established during early pedogenesis; as potentially the most limiting element, the initiation of P cycling is critical (Vitousek 1984). The profound disturbance associated with mining and restoration processes may lead to dilution and loss of soil P, particularly of the relatively mobile organic P component (Bol et al. 2016; Frossard et al. 1989). Current knowledge of P dynamics in ecosystems restored on highly weathered soil materials is limited, and it is therefore of considerable theoretical and management interest to understand the changing status and fractional distribution of P during the early phases of pedogenesis and ecosystem development that follow restoration.

We hypothesised that early ecosystem and soil development in these P-limited oxidic materials must initially depend largely on the reestablishment of functional P pools associated with soil organic matter and on its biogeochemical cycling. Both processes are likely to be mediated through the activities of microorganisms

and other soil organisms but additionally through complex interactions with inorganic soil materials.

Our study therefore investigated how P status, fractions and species composition changed over a 26-year chronosequence period (space-for-time substitution) of forest development in surficial and deeper soil development down to, and including, the mine floor. Specifically, we wanted to understand (i) How does total P (Pt) status change with restoration period and depth? (ii) How do the different P fractions, notably the organically associated P, develop in response to restoration period and depth, and how are these related to other properties of the developing soils? (iii) How the chemical nature of organic P changes in relation to restoration period in the surface soils? In addressing these questions, contrasts are presented with local unmined soils and with the results of previous studies conducted at this mine (Cook 2012; Spain et al. 2006; 2009a; b; 2015).

Materials and methods

Study location

The studies reported here were carried out on restored tropical forest sites at the Gove bauxite mine; the mine is located at 12° 16′S, 136° 49′E on the Gove Peninsula in the Northern Territory of Australia and surrounds the airport. Climatic conditions at the site are monsoonal with *c.* 90% of average annual rainfall (1457 mm) falling within the months November to April. Total annual pan evaporation at this site averages 2153 mm. Mean monthly maximum temperatures during the hottest (December) and coldest (July) months are 33 °C and 28 °C, respectively (Bureau of Meteorology 2015).

Vegetation and soil properties

The unmined soils of the mine lease area (> 500 km^2) largely support tall open forests, mostly dominated by *Eucalyptus tetrodonta* F.Muell. and *Eucalyptus miniata* A.Cunn. ex Schauer with two highly biodiverse underlying strata dominated, respectively, by shrubs and perennial grasses (Spain et al. 2015). Extensive fires typically initiated by lightning and through traditional burning practices are a regular feature of this region

(Department of Sustainability, Environment, Water, Population and Communities 2008).

Unmined soils

These highly-weathered soils are classified as bauxitic dystrophic Red Kandosols (Isbell 1996), Oxisols (Soil Survey Staff 1999) or Ferralsols (IUSS Working Group WRB 2015) and are known for their low P status: combined values for unfertilized oxisols worldwide indicate mean Pt concentrations of 220 mg kg^{-1}, se 29, $n = 20$ (Negassa and Leinweber 2009; Yang and Post 2011). Total P stocks in the surface 0–30 cm of the soils local to the mine area are predicted to be c. 0.3–0.4 t ha^{-1}, substantially less than the average Australian topsoil stock of c. 1.0 t ha^{-1} (Viscarra Rossel and Bui 2016). Landscape relief is low throughout the study area and average solum depth over the indurated layer is *c.* 0.70 m (O'Keefe 1992).

The unmined soils are extremely permeable, mildly acid (approximate pH range: 5.6 to 6.2, 1:5 soil solution ratio, 0.01 M CaCl$_2$) and non-saline. Near-surface (0–5 cm) total (dry combustion chromatography) C and N concentrations typically range from *c.* 20 to 30 g kg^{-1} C and from *c.* 0.01 to 0.09 g kg^{-1} N, respectively; C/N ratios range from 17 at depth to more than 35 at the surface. The clay-sized fraction is dominated by kaolinite with gibbsite and the oxides and hydroxides of Fe and Al. Cation exchange capacity (CEC, silver thiourea method) is closely dependent on pH and on soil organic matter concentrations.

Restored soils

The rapidly developing soils of the restored areas are gravel-rich and highly permeable, with permeability increasing with restoration period. Over all depths, the pH (CaCl$_2$) of the restored soils ranged from 4.89 to 6.15, and was highly correlated ($r = -0.743$, $P < 0 001$, $n = 31$) with the natural logarithm of the C concentration. Over the 0–10 cm depth range and from one to 26 years following restoration, concentrations of estimated total C and total N increased, respectively, from c. 7.0 to 42.0 g kg^{-1} and from 0.04 g kg^{-1} to 2.23 g kg^{-1}. The C/N ratio of the restored soils ranged from 17 at depth to 29 at the surface, with greater values in most mine floor samples (Spain et al. 2015). Much of the C present in the replaced topsoil is likely to occur as pyrogenic C (Reisser et al. 2016) and other decomposition-resistant compounds.

Further and supporting details can be found in Spain et al. (2015).

Mining and restoration processes

Bauxite is mined using a simple strip-mining process integrated with a consistent restoration program that aims to restore a eucalypt-dominated open forest of similar composition and structure to that present prior to mining (Spain et al. 2015). Vegetation is felled and burned, remaining material is removed, and the site 'fallowed' for 2–3 years. The A and upper B horizons (up to c. 30 cm) are then transported to form the topsoil layer of another previously mined site and the subsoil is removed to permit mining. Following mining, the subsoil and topsoil are replaced, and the site is deep ripped. Tree, shrub and grass seeds are broadcast together with a surface application of single superphosphate equivalent to *c.* 25 kg P ha^{-1}. No subsequent cultivation is undertaken.

The mean concentrations of Pt, total C and total N in the 0–10 cm interval in the soil of a cleared, fallowed site prior to transport to a new site were, respectively, 206 mg kg^{-1} (se 11), 14.25 g kg^{-1} (se 1.95) and 0.52 g kg^{-1} (se 0.10) ($n = 4$ for all). In the first year following site restoration processes, the estimated C and N concentrations (0–10 cm) were 13 g kg^{-1} and 0.46 g kg^{-1}, respectively, and increased to 42 g kg^{-1} and 2.3 g kg^{-1} at 26 years, again respectively. A detailed description of the restoration process and the properties of the undisturbed and restored soils are presented in Spain et al. (2015).

Soil sampling and preparation

At the end of the monsoon season, in late April 2002, the developing soils and the upper 0–5 cm intervals of the underlying bauxitic indurated layer were sampled from pits randomly located along 100 m transects set out in a 26-year chronosequence of seven similarly restored study sites (1, 2, 4, 8, 13, 20, 26 years) and in an unmined native forest site (AB) of medium profile depth (0.66 m to the top of the bauxitic layer). Samples were taken from the pit walls at the depth intervals listed in Appendix Table 5, based on observed morphological and textural features of the materials present (Spain et al. 2015).

Within each pit, compound samples were taken of materials at several locations from a c. 0.75 m length of a single pit face over the described depth intervals. These sampling intervals were based on the homogeneity of the included materials using such measures as colour, texture, structure and, close to the surface, the presence of organic matter, organic matter staining and such biological constructs as termite and ant galleries, storage chambers and earthworm casts. At the longest restored sites, a near-surface layer of the mineral soils developed that contained substantial incorporated and decomposed organic materials; this was sampled separately where it was practical to do so.

In preparation for P fractionation analyses, sample materials were air dried, sieved (<2 mm ECD) and macroscopically observable root and other plant and animal materials were removed (Condron and Newman 2011). In addition, soils sampled from the 0–4 cm layer of selected time domains in October 2002 were used to identify the chemical nature of soil organic P using solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy. These included sites restored for 2, 4, 8, 13, 17, 20 and 26 years and two unmined native forest sites, one unburned (UB); the other (AB) had been burned approximately two years prior to sampling. These soils were prepared for chemical analysis as above.

Post-restoration plant community and litter development

The restored sites develop from bare soil at sowing and progress through transitional stages of dominance by grasses (1–5 years) with shrubs gradually assuming dominance (>5–8 years), followed by a phase of declining shrubs with emerging small eucalypt trees (>8–13 years) and finally emerging dominance by eucalypts at sites restored for more than 13 years. Canopy and litter closure typically occur between 8 and 13 years. The plant community progression implies nutritional shifts associated with initial dominance by the arbuscular mycorrhizal grasses and nitrogen-fixing acacia shrubs transitioning to the mixed arbuscular and ectomycorrhizal associations associated with the more mature forests (Reddell and Milnes 1992). Substantial litter layers (to c. 36 t ha^{-1} dry weight at 26–28 years) form at the restored sites (Cook 2012; Spain et al. 2006, 2015), particularly after canopy closure. Based on

estimates of mean litter P concentration (302 mg kg^{-1}) and biomass (2.52 kg m^{-2}) at a 26-year restored site, the litter standing crop of P was estimated c. 8 kg ha^{-1}.

The restored sites are typically protected from burning although the surrounding native forest areas are frequently burned.

Analytical methods

Total elemental analyses

Total P concentrations of the sample fine earth (< 2 mm) fraction were determined at the Advanced Analytical Centre, James Cook University, Townville using XRF spectrographic analysis of fine-ground, pressed sample materials. To establish more robust correlations with restoration period, these were supplemented with Pt records (0–10 cm) from 18 further sites obtained from previous unpublished studies and analysed using similar methods (see also Spain et al. 2015). Total C and total N values were determined using a Europa 20–20 isotope mass spectrometer with an ANCA preparation system.

Phosphorus fractionation

The P fractionation studies were carried out at James Cook University using the modified Hedley fractionation method of Tiessen and Moir (1993) to fractionate sample P (see Appendix Fig. 1 for extraction sequence and fraction titles). Briefly, following the addition of solution and overnight shaking, tubes were centrifuged (3000 rpm for c. 7 min) and the supernatant decanted prior to the addition of the subsequent extractant. Except where otherwise indicated, P concentrations in the sample solutions were determined spectrophotometrically as the phospho-molybdate complex using standard methods (Department of the Environment 1993). Detection limits for each extraction were determined by measuring digestion blanks in triplicate and expressing the limit of detection as three times the standard deviation of the blanks (Taylor 1987). The inorganic fractions *Resin P*, *Bicarbonate P_i*, *Hydroxide P_i*, *Dilute HCl P_i* and *Conc. HCl P_i* were measured directly on the extracts. Concentrations of the organic P components (*Bicarbonate P_o*, *Hydroxide P_o* and *Conc. HCl P_o*) for each fractionation stage were obtained as the difference between the total concentration of the component following digestion and that of the inorganic component.

These fractions are considered as 'chemically defined', but have been broadly associated with various classes of P.

The putative availabilities of the extracted fractions to plants and microorganisms are presented in Cross and Schlesinger (1995) and Condron and Newman (2011). *Labile P* is the sum of the concentrations of *Resin P*, *Bicarbonate P_i* and *Bicarbonate P_o* and is considered to be the P biologically available over short periods, ranging up to some months. *Intermediate P* is the sum of *Hydroxide P_i*, *Hydroxide P_o* and *Dilute HCl P_i*: this fraction is viewed as available in the medium term, perhaps at the scale of a growing season. The sum of *Conc. HCl P_i* and *Conc. HCl P_o* is *Long-term P*, which is considered as only slowly available, perhaps at a scale of many years. *Residual P* is perceived as occluded and unavailable, except possibly over extremely long periods. Nonetheless, at least some part of this fraction may become available over relatively short time periods (Condron and Newman 2011). *Biological P* is defined as the sum of *Bicarbonate P_o*, *Hydroxide P_o* and *Conc. HCl P_o*. *Labile P*, *Intermediate P*, *Long-term P* and *Biological P* fractions are here described as 'derived' fractions and are defined as follows:

$$Labile\ P = Resin\ P + Bicarbonate\ P_i + Bicarbonate\ P_o$$
$$Intermediate\ P = Hydroxide\ P_i + Hydroxide\ P_o + Dilute\ HCl\ P_i$$
$$Long-term\ P = Conc.\ HCl\ P_i + Conc.\ HCl\ P_o$$
$$Biological\ P = Bicarbonate\ P_o + Hydroxide\ P_o + Conc.\ HCl\ P_o$$

Soil Pt concentrations determined using concentrated H_2SO_4/H_2O_2 (Tiessen and Moir 1993) gave an average value of 70.2% (se 1.8, $n = 36$) of those determined using XRF analysis. *Residual P* was therefore calculated here as the difference between Pt determined by XRF spectrographic analysis and the sum of the fractions up to and including *Conc. HCl P*.

NaOH-EDTA extraction

The NaOH-EDTA extraction technique was used to extract soil organic P prior to its characterisation using solution ^{31}P NMR spectroscopy. The NaOH-EDTA extraction technique used in this study was based on the method of Cade-Menun and Preston (1996), but at a 1:4 soil to solution ratio as recommend by McLaren et al. (2015a) for soils with low concentrations of organic P. Briefly, 3 g soil samples were extracted with 12 mL of

0.25 M NaOH +0.05 M Na_2-EDTA solution for 16 h. The extracts were then centrifuged at 5000 rpm for 20 min, and the supernatant passed through a Whatman no. 42 filter paper. A 3.5 mL aliquot of the filtrate was frozen at −80 °C, and then lyophilised and weighed (on average 112 mg of lyophilised material) prior to NMR analysis. Concentrations of total P in the remaining filtrate were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES), whereas concentrations of molybdate-reactive P (MRP – analogous with inorganic P) was determined using the malachite green method of Ohno and Zibilske (1991). The difference between concentrations of total P via ICP-OES and MRP was taken as molybdate-unreactive P (MUP – analogous with organic P).

Sample preparation for NMR analysis

Preparation of lyophilised material for solution ^{31}P NMR analysis was based on a modification of the method of Vincent et al. (2013). Briefly, 600 μL of 0.25 M NaOH +0.05 M Na_2-EDTA solution was added to each centrifuge tube, placed on a vortex mixer for 2 min, and then centrifuged at 5000 rpm for 20 min. A 500 μL aliquot of the supernatant was transferred to a 1.5 mL microcentrifuge tube, and then spiked with a 50 μL aliquot of 32.3 mM methylenediphosphonic acid (MDP: Sigma-Aldrich, M9508) and 75 μL of sodium deuteroxide solution 40 wt.% in D_2O (NaOD: Sigma-Aldrich, 372,072). The microcentrifuge tube was then vortexed for 10 s and transferred to a 5 mm NMR tube prior to NMR analysis.

In addition, the NMR spectra in the Year 26 soil and both native forest soils (UB and AB) exhibited considerable line broadening for all peaks: probably due to high sample viscosity. The extraction and preparation of these soils was repeated as previously described, except additional NaOH-EDTA solution was added to the lyophilised material until spectral quality was improved (Cade-Menun and Liu 2014). Samples from site year 26, UB and AB required 1.5, 1.2 and 0.9 mL of NaOH-EDTA solution, respectively.

Solution ^{31}P NMR analysis

Solution ^{31}P NMR spectroscopy was carried out using a Bruker Avance III HD 500 NMR spectrometer (Bruker Corporation; Billerica, MA) at the combined NMR facility of the Laboratory of Inorganic Chemistry

(Hönngerberg, ETH Zürich). The NMR spectrometer was set at a ^{31}P frequency of 202.5 MHz with gated broadband proton decoupling, a 90° pulse of 14 μs, and the acquisition of 4096 scans with an average time of 14 h 16 min per sample. An inversion-recovery experiment was initially carried out to determine the spin-lattice relaxation times (T_1) of ^{31}P in order to calculate the minimum recycle delay for each soil. In general, the T_1 relaxation times ranged in descending order: orthophosphate > phosphonate (added MDP standard) > phosphomonoesters. Concentrations of phosphodiesters and pyrophosphate were too low for a reliable measure of their T_1 relaxation time. However, McDowell et al. (2006) reported their relaxation times were similar or lower than those of phosphomonoesters. Therefore, recycle delays were set at least five times the T_1 relaxation time of the added MDP standard so that more scans could be collected (from 1024 to 4096) in order to double the signal-to-noise ratio, but still quantitatively determine the P species of importance to the current study (i.e., organic P).

All spectra were processed within TopSpin® software (Bruker Corporation; Billerica, MA).

Quantification of P species in soil extracts via solution ^{31}P NMR spectroscopy was carried out as previously described by Doolette et al. (2011a) as the integral of the added MDP of known concentration is directly proportional to all other integrals in the NMR spectrum. Briefly, the integrals of all ^{31}P signals in the NMR spectrum were determined (except that of orthophosphate – δ 5.6 to 5.3 ppm). In general, this included the following regions: the added MDP (δ 17.3 to 16.2 ppm), phosphomonoesters (δ 5.2 to 2.8 ppm), phosphodiesters (δ −0.7 to −1.5 ppm), and pyrophosphate (δ −4.6 to −4.9 ppm). Concentrations of organic P were calculated by summing the pools of phosphomonoesters and phosphodiesters. Peak assignments were based on spiking experiments and comparisons with previous studies (Doolette et al. 2009; McLaren et al. 2015b; Turner et al. 2003a). Quantification of P species within the phosphomonoester region using spectral deconvolution was not carried out due to a low signal-to-noise ratio.

Data presentation and analysis

Total P results include data from the current study, Spain et al., 2009a, b) and unpublished reports (AV Spain). The P fractions are considered in terms of derived and chemically defined fractions and in terms of the interrelationships among the fractions and with other properties of the materials sampled. In the analysis of the data derived from the Hedley fractionation, values lower than the detection limit were arbitrarily assigned a value of 0.005 mg kg^{-1}. For purposes of statistical analysis and discussion, sample values from the restored sites were grouped into four depth ranges: 0–5 cm, >5–10 cm, from >10 cm to the top of the mine floor and the upper 0–5 cm interval of the mine floor. The near-surface soils of the unmined native forest site (AB) were sampled over the interval 0–12 cm and the deepest sample was taken from the upper 5 cm interval of the bauxitic layer.

Analysis of deviance log-linear models were used to estimate the change of each property over time and how that varied with depth. The variance of the responses increased with their mean values, and thus the error variance was modelled as proportional to the mean response. For analyses where there was no significant interaction between time and depth, the simpler additive model in time and depth was used. These analyses were conducted using R software (R Core Team 2016).

The probabilities arising from statistical testing are considered significant at $P < 0.05$, unless explicitly indicated otherwise.

Results

This section presents the analytical results for Pt (Appendix Table 5) and the Hedley fractionation (Appendix Table 6), together with the interrelations between the fractions and other physical and chemical properties. It also presents the properties of the organic P present within the developing surface soils. Contrasts are drawn with similar results obtained from local native forest sites, unburned and burned.

Total phosphorus

Figure 1a presents the Pt concentrations of 31 soils and mine floor materials combined over four depth intervals from the seven restored sites. An analysis of deviance of all sample Pt data was carried out to test the significances of the effects of restoration period and depth (Table 1). While Pt increased in the 0–5 and > 5–10 cm intervals, it did not vary significantly with
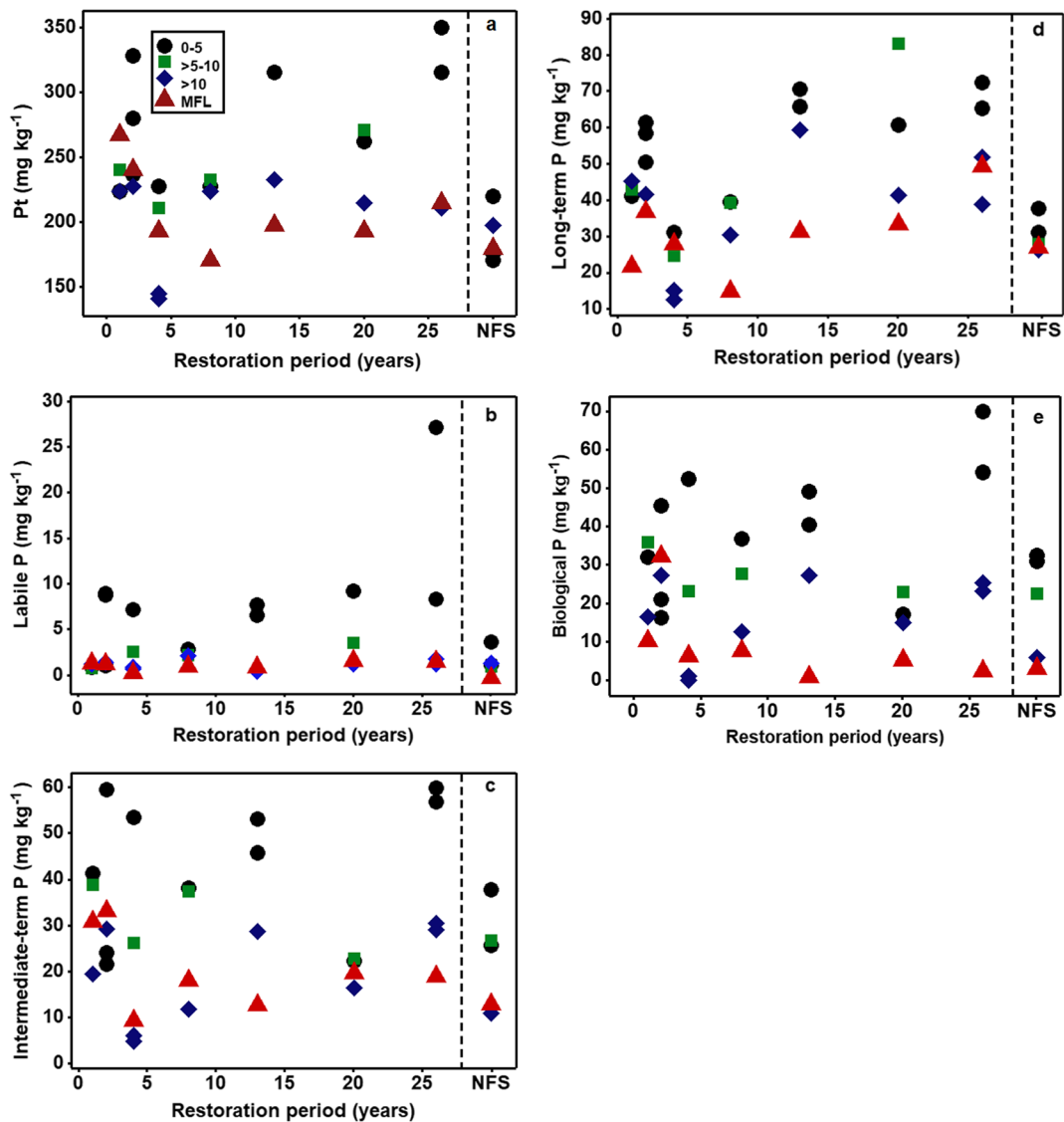
Fig. 1 Concentrations of total P and the derived fractions in relation to restoration period and depth in the restored soils and in an undisturbed native forest soil (NFS site AB, MFL mine floor) (sampled May 2002)

restoration period, although the effect of depth was highly significant; there was no significant interaction between restoration period and depth. A clear depth trend was confirmed: Pt in the surface 0–5 cm interval was not significantly different from that in the >5–10 cm layer ($t = 0.86$, $n = 15$, $P = 0.400$), but was greater than that of the soils >10 cm in depth ($t = 3.96$, $n = 19$, $P < 0.001$) and the mine floor materials ($t = 3.50$, $n = 17$, $P < 0.001$).

Mean Pt concentrations in the 0–10 cm interval of the seven restored profiles ranged from 219 to 332 mg kg^{-1}, with an overall mean of 269 mg kg^{-1} (se 12, n = 15).

The mean Pt concentration of these soils at depths greater than 10 cm was 203 mg kg^{-1} (se 12, $n = 9$) and in the mine floor samples was 210 mg kg^{-1} (se 12, $n = 7$). In the single native forest profile (AB) examined, Pt concentration in the 0–2.5 cm interval was 219 mg kg^{-1} and ranged from 170 to 197 mg kg^{-1} below this depth.

Combining the above data with unpublished Pt estimates from 18 other sites restored from one to 30 years (Spain et al. 2009a, b and unpublished reports) and sampled over a depth range of 0–10 cm gave a mean value of 316 mg kg^{-1} (se = 5, n = 91). A similar estimate from four local native forest sites was 278 mg kg^{-1} (se =

11, $n = 16$). Concentrations of Pt in the 18 restored sites were weakly positively correlated with restoration period ($r = 0.298$, $P < 0.005$).

Sequential phosphorus fractionation

Figures 1b–d present, respectively, the concentrations of *Labile P*, *Intermediate P* and *Long-term P* in relation to rehabilitation period and depth. Similarly, Fig. 1e presents the concentrations of *Biological P*. Figures 2a, b present the concentrations of *Resin P and Bicarbonate* P_o in the upper 0–5 cm interval and Fig. 2c–e present the concentrations of *Conc. HCl* P_i in, respectively, the 0–5 cm, >10 cm and mine floor layers, also with respect to restoration period and sample depth. The fitted functions are presented to these relationships.

Analysis of deviance was conducted of the derived fractions, *Residual P* and selected chemically defined fractions in relation to effects of restoration period, depth and their interactions (Table 1). Only *Labile P* and *Long-term P* showed significant variation with restoration period; increasing concentrations of *Labile P* with restoration period were due to those of *Resin P* and *Bicarbonate* P_o, largely in the upper 0–5 cm interval; *Bicarbonate* P_i concentrations were particularly low and did not differ significantly with restoration period or with depth. *Intermediate P* concentrations (Fig. 1c) showed a significant effect of depth due to significant depth variation in both *Hydroxide* P_i and *Hydroxide* P_o, both $P < 0.01$. An estimated mean value for the 0–10 cm interval is 40 mg kg^{-1}, se 4, $n = 15$, approximately twice the mean concentrations of the underlying materials. *Long-term P* concentrations (Fig. 1d) increased significantly with restoration period, both in the 0–10 cm interval and at greater depths, notably in the mine floor; this was due to increasing *Conc. HCl* P_i values in all depth intervals, including the mine floor (Fig. 2a–e). As considered below, *Conc. HCl* P_i values were virtually identical to those of *Long-term P*. *Residual P* concentrations did not vary significantly with either restoration period or depth and a mean value over all restored sites was 160 mg kg^{-1}, se 4. No significant interactions were found between restoration period and depth in the analyses of the derived fractions although significant interactions occurred between restoration period and depth in the analysis of *Resin P* and *Conc. HCl* P_i.

Table 1 Analysis of deviance of the effects of restoration period and depth for total P, the derived fractions and selected chemically defined fractions ($n = 31$ for restored soils) (sampled May 2002)

Fraction	Factor	F	df	P
Total P				
Pt	Years	2.32	1, 29	0.141
	Depth	8.28	3, 26	<0.001
	Interaction	1.77	3, 23	0.181
Derived fractions				
Labile P	Years	22.60	1, 29	<0.001
	Depth	25.78	3, 26	<0.001
	Interaction	0.47	3, 23	0.708
Intermediate P	Years	0.68	1, 29	0.417
	Depth	8.68	3, 26	<0.001
	Interaction	1.25	3, 23	0.314
Long-term P	Years	9.40	1, 29	0.005
	Depth	5.27	3, 26	0.006
	Interaction	0.14	3, 23	0.936
Residual P	Years	0.16	1, 29	0.690
	Depth	2.13	3, 26	0.124
	Interaction	2.42	3, 23	0.092
Biological P	Years	0.83	1, 29	0.373
	Depth	7.33	3, 26	0.001
	Interaction	1.08	3, 23	0.378
Chemically defined fractions				
Resin P	Years	7.77	1, 26	0.010
	Depth	4.36	3, 27	0.014
	Interaction	3.24	3, 23	0.041
Bicarbonate P_o	Years	5.54	1, 26	0.0275
	Depth	9.97	3, 27	<0.001
	Interaction	0.46	3, 23	0.709
Conc. HCl P_i	Years	11.00	1, 26	0.003
	Depth	3.04	3, 27	0.049
	Interaction	3.56	3, 23	0.030

Biological P values (Fig. 1e) did not differ significantly with restoration period although there was a very highly significant depth effect. A mean concentration for the 0–10 cm interval is 36 mg kg^{-1} (se 4, $n = 15$), markedly greater than the concentrations present in the underlying materials. Low values in the surface soils of the 20-year restored site were due to low *Hydroxide* P_o concentrations.

The *Labile* and *Intermediate P* fractions of the soil layers were dominantly organic while *Long-term P* was
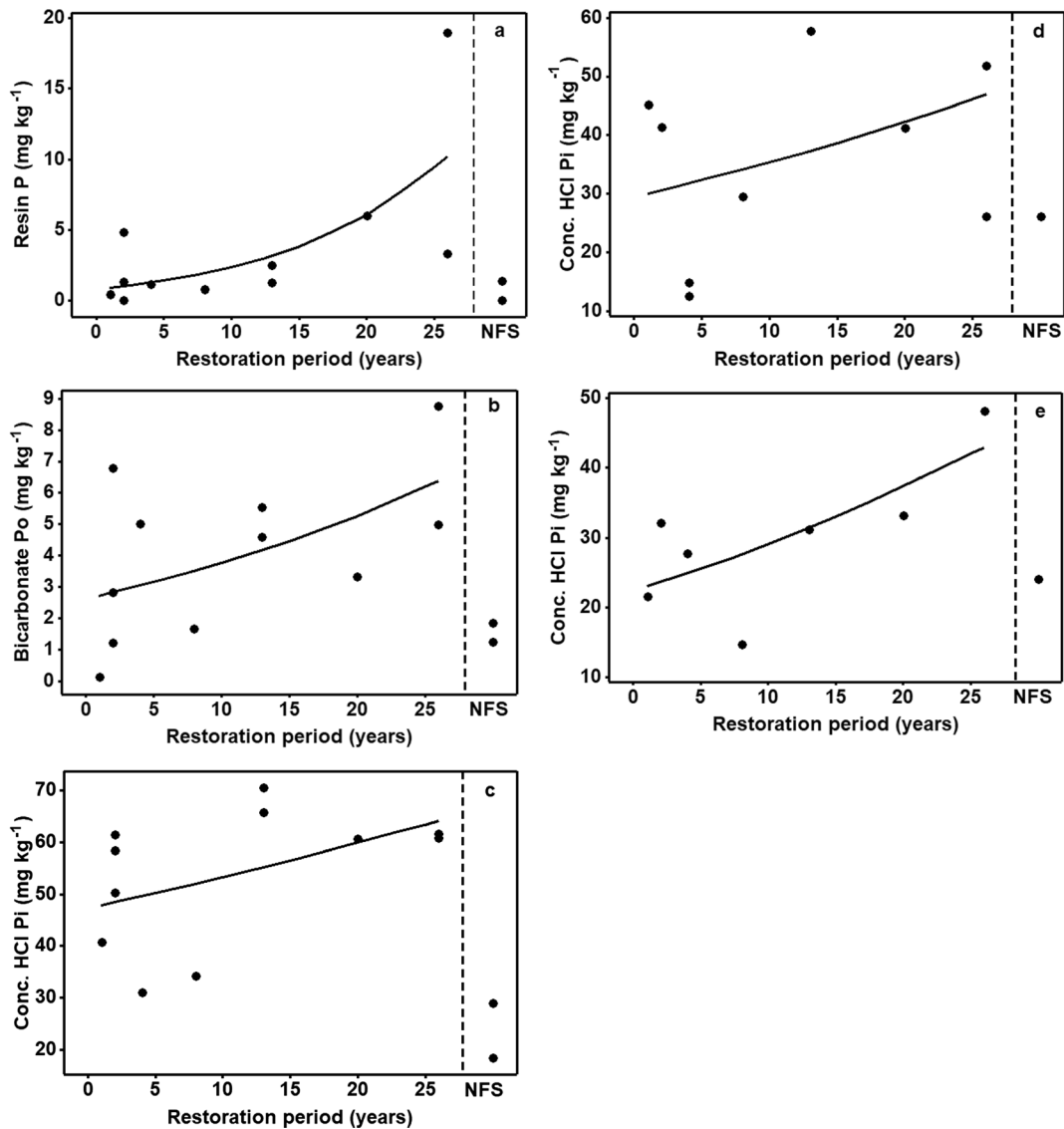
Fig. 2 Concentrations of *Resin P* (a) and *Bicarbonate P_o* (b) in the 0–5 cm interval and of *Conc. HCl P_i* in the 0–5 cm (c), >10 cm (d) and upper mine floor (e) materials in relation to restoration period and depth in the restored soils and in an undisturbed native forest soil (NFS site AB) (sampled May 2002)

dominantly inorganic. Excluding the mine floor layer and based on mean concentrations, *Bicarbonate P_o* comprised 56% of *Labile P* and *Hydroxide P_o* formed 79% of *Intermediate P*. In contrast, *Conc. HCl P_o* comprised only 2% of *Long-term P*, with highest values associated with a few near-surface samples from longer-restored sites and from the native forest site (AB). Organic P percentages in two components were lower in the mine floor layer: *Bicarbonate P_o* formed *c.* 40% of *Labile P*, *Hydroxide P_o* comprised a similar

percentage of *Intermediate P* while *Conc. HCl P_o* formed 3% of *Long-term P*.

Particularly in the 20 and 26-year sites, near-surface *Labile P* and *Long-term P* concentrations mostly exceeded values at equivalent depths in the native forest site (AB). Concentrations of *Intermediate P* at all depths and of *Labile P* and *Long-term P* at depths greater than 10 cm were generally equivalent to those of the native forest site. *Residual P* values in the restored surface 0–5 cm interval were higher than in the native forest soil

(AB). *Biological P* values from the 0–10 cm interval of the 26-year-restored site were substantially greater than those of the 0–12 cm interval of the native forest site; concentrations in the native forest profile AB were minimal below this depth interval.

Relationships between total phosphorus and the derived fractions with other soil properties

In the restored soil materials, concentrations of Pt, *Labile*, *Intermediate*, *Long-term*, *Biological* and *Residual P* over all depths were positively correlated with those of C and N and were negatively correlated with the clay concentration (Table 2, Appendix Table 5). None of first four derived fractions were significantly ($P > 0.05$ for all) correlated with the C/N ratio. Total P was not significantly correlated with the concentration of silt and only *Biological P* was positively related to silt concentration.

The ratios of C/Biological P in the upper 10 cm intervals of the restored soils varied little with restoration period and a mean value for these soils was 749 (se 159, $n = 15$); some high values were found in the surface soils of the longer restored sites. Values in the native forest site AB were 1054 in the surface 0–2.5 cm interval and c. 373 in the interval 2.5–12 cm. None of the four derived fractions were significantly ($P > 0.05$ for all) correlated with C/Biological P ratio.

In the mine floor materials, *Biological P* was strongly positively and significantly correlated with the concentrations of C ($r = 0.931$, $P = 0.002$), N ($r = 0.897$, $P = 0.006$) and silt ($r = 0.820$, $P = 0.024$).

Table 3 Concentrations (mg kg^{-1}) of P in NaOH-EDTA extracts (1:4 soil to solution ratio) of the soils (0–4 cm) of the chronosequence of restored sites, a long unburned native forest site (UB), and a previously burned native forest site (AB) (sampled October 2002)

Restoration period (years)	NaOH-EDTA extractable P (mg kg^{-1})		
	Total	MRP	MUP
2	43.3	30.2	13.1
4	37.6	16.7	20.9
8	40.9	15.2	25.7
13	49.3	32.7	16.6
17	36.6	19.7	16.9
20	39.6	27.1	12.5
26	38.3	27.9	10.4
Native forest sites			
UB	44.9	40.1	4.9
AB	27.5	25.7	1.8

MRP refers to molybdate-reactive P, and MUP refers to molybdate-unreactive P

Chemical nature of soil organic phosphorus

Concentrations of total P in NaOH-EDTA extracts across all restoration periods were on average 40 mg kg^{-1}, which was similar to that of the unburned native forest site UB, but slightly higher than that of the burned native forest site AB (Table 3). Concentrations of inorganic P and organic P across all restoration periods were variable and extremely low: on average 25 and 16 mg kg^{-1}, respectively. In general, when concentrations of inorganic P were slightly lower compared to the average, concentrations of organic P were slightly higher and vice versa. Concentrations of organic P

Table 2 Pearson product moment correlations (with associated P values) between total P, the derived fractions and four selected properties of the restored soils, excluding mine floor records ($n = 24$; $n = 23$ for *Biological P*) (sampled May 2002)

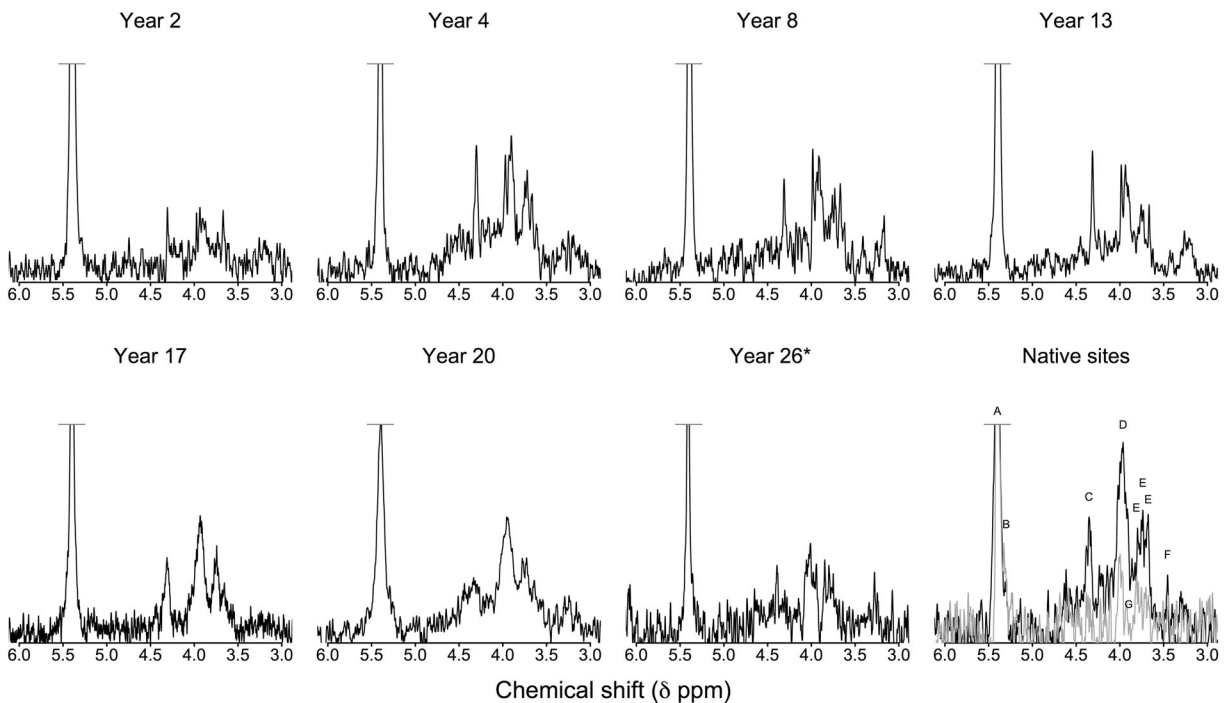| Property	Total P	*Labile P*	*Intermediate P*	*Long-term P*	*Biological P*
C	0.688	0.956	0.564	0.508	0.659
	<0.001	<0.001	0.004	0.011	<0.001
N	0.682	0.959	0.577	0.498	0.684
	<0.001	<0.001	0.003	0.013	<0.001
Clay (%)	−0.672	−0.571	−0.548	−0.635	−0.586
	<0.001	0.004	0.006	0.001	0.003
Silt (%)	0.221	0.388	0.390	0.175	0.430
	0.300	0.061	0.060	0.414	0.036

Fig. 3 The orthophosphate and phosphomonoester region (δ 6 to 3 ppm) of solution ^{31}P NMR spectra on NaOH-EDTA extracts of soils (0–4 cm) in relation to restoration period (years), and the native unburned (UB – black) and burned (AB – grey) at the Gove bauxite mine (sampled October 2002). The vertical scale of each spectrum has been independently magnified to highlight spectral features. Peaks were tentatively assigned to: orthophosphate (A = δ 5.4 ppm), an unknown phosphomonoester (B = δ 5.3 ppm), α-glycerophosphate (C = δ 4.4 ppm), an unknown phosphomonoester with a somewhat broad signal at Site UB but a sharp signal at site AB (at site UB this could be a mixture of some RNA mononucleotides and β-glycerophosphate (D = within δ 4.1 to 3.9), RNA mononucleotides (E = δ 3.81, 3.74 and 3.68 ppm), an unknown phosphomonoester (F = δ 3.5 ppm), and broad phosphomonoesters present underneath some of the sharp signals (G = within δ 4.8 to 3.4 ppm). Sample materials for Site 26 years, Site UB and Site AB were diluted with 2.5, 2.0 and 1.5 times more NaOH-EDTA than all other sites (years 2 to 20), respectively, due to high sample viscosity

across all restoration periods were much higher than at both native forest sites.

Classes of P detected in solution ^{31}P NMR spectra of all NaOH-EDTA extracts were those of orthophosphate, phosphomonoesters, phosphodiesters, and pyrophosphate. The majority of the NMR signal occurred in the orthophosphate and phosphomonoester region (δ 5.6 to 2.8 ppm), which has been magnified in Fig. 3. In general, all spectra exhibited a low signal-to-noise ratio. However, several sharp and broad signals could be observed in the phosphomonoester region. Peaks were assigned to an unknown phosphomonoester with a sharp signal (B = δ 5.3 ppm) adjacent to the orthophosphate peak, α-glycerophosphate (C = δ 4.4 ppm), an unknown phosphomonoester(s) with a somewhat broad signal (D = spanning δ 4.1 to 3.9), some RNA mononucleotides (δ 3.81, 3.74 and 3.68 ppm), an unknown phosphomonoester with a sharp signal (δ 3.5 ppm), and broad phosphomonoesters (F = spanning δ 4.8 to 3.4 ppm).

The chemical nature of phosphomonoesters at site UB was different to that at site AB, but similar to the soils along the 26-year chronosequence (Fig. 3). The chemical nature of phosphomonoesters within the 26-year chronosequence was generally the same, except that at the beginning (site year 2), which had less signal.

The concentration of organic P (phosphomonoesters and phosphodiesters) in NaOH-EDTA extracts as determined by NMR spectroscopy was 7.2 mg kg^{-1} at year 2 (Table 4). The concentration of organic P increased along the 26-year chronosequence but remained relatively constant with an average of 15 mg kg^{-1}, which was similar to site UB (Table 3). Phosphomonoesters were the dominant class of organic P across all soils, which were on average 82% of the organic P. In general, concentrations

Table 4 Concentrations (mg kg^{-1}) of P classes in NaOH-EDTA extracts (1:4 soil to solution ratio) of soils (0–4 cm) along the chronosequence of restored sites, a long unburned native forest site (UB), and an unmined, previously burned native forest site (AB) (sampled October 2002)

Restoration period (years)	Mono-P	Di-P	Pyro-P	Organic P
2	5.7	1.5	2.7	7.2
4	12.5	2.4	4.4	14.9
8	10.4	1.5	5.2	11.8
13	12.9	0.9	5.4	13.8
17	13.5	1.4	1.5	14.9
20	14.4	3.2	1.3	17.6
26	12.0	2.7	0.0	14.7
Native forest sites				
UB	12.9	3.5	1.0	16.4
AB	4.1	2.3	2.2	6.4

Orthophosphate was not included because it was not determined quantitatively using NMR spectroscopy. Organic P refers to the total concentration of phosphomonoesters and phosphodiesters

of pyrophosphate were low (< 5.4 mg kg^{-1}) but noticeably higher than those of phosphodiesters up to 13 years of restoration.

Discussion

We hypothesised that the initial phase of successful soil and ecosystem development requires the formation of a developing pool of organically associated P. Several lines of evidence indicate that this is likely to have been achieved, perhaps initiated through the initial fertilizer P subsidy. These include increases in the concentrations of Pt and in the shorter-term-available P fractions together with their strong associations with the increasing organic matter concentrations. Additionally, the reestablishment of biogeochemical P cycling is evidenced in the properties of the organic P pools, while above-ground evidence is related to the satisfactory growth and development of the plant community at these sites.

Total phosphorus

Total P concentrations in the <2 mm fraction of the unmined local surface forest soils studied here are

commensurate with the low values reported for oxisols elsewhere (Negassa and Leinweber 2009; Yang and Post 2011; Kooyman et al. 2017; Viscarra Rossel and Bui 2016). Mean Pt in the 0–10 cm interval of the restored soils was estimated to be 316 mg kg^{-1}, some 14%. higher than in local native forest soils; below 10 cm depth and in the mine floor concentrations were of similar magnitude to those of the native forest site AB. In contrast to the findings of a similar study conducted elsewhere in tropical Australia (Short et al. 2000), Pt was positively correlated with restoration period indicating the potential to accumulate P in the upper profile (Deng et al. 2017; Shi et al. 2016).

Phosphorus fractionation

The present P fractionation studies have indicated that significant increases with restoration period occurred in Labile P and Long-term P concentrations in the near-surface soils over the 26-year chronosequence of restored sites; it also seems likely that Intermediate-term P and Biological P will increase in concentration over longer restoration periods. Clear declines in these four fractions occurred with increasing depth and values in the lower soils were little different to those of a local native forest soil. Soil Labile P and Intermediate P fractions were dominantly organic while Long-term P was dominantly inorganic.

In the mine floor layer, the increases in Hydroxide P_i and Conc. HCl P_i that occur with restoration period suggest possible accumulation following eluviation and perhaps leaching from the overlying soil materials or in preferential flow (see, for example, Lang et al. 2016; McGroddy et al. 2008). Such increases further suggest the possibility of continuing losses of inorganic and perhaps organic P to underlying strata in these highly permeable materials (see also Negassa and Leinweber 2009). Alternatively, some of these effects may also result from redistribution from other fractions, possibly Residual P.

Relationships between total phosphorus, the derived fractions and other soil properties

Concentrations of Pt, Labile P, Intermediate P, Long-term P, Biological P and Residual P were all strongly positively correlated with those of total C

and total N in the restored soils, illustrating their clear associations with soil organic matter status (see also Johnson et al. 2003; Dieter et al. 2010). These associations, together with the highly significant negative correlations between the clay content and the derived fractions, with Pt and with C and N concentrations may indicate a dilution effect. This could act through the occlusion of exchange sites by soil organic matter due to the strong associations among soil organic matter, phyllosilicate clays and the oxide minerals common in these soils (see, for example, Ye et al. 2017). The ratios of C/*Biological P* varied little in relation to either depth or restoration period.

Chemical nature of soil organic phosphorus

In this study, concentrations of NaOH-EDTA extractable organic P were extremely low (between 1.8 and 26 mg kg^{-1}), and generally much lower than that typically reported in the literature for organic P characterisation using NMR spectroscopy (e.g., Doolette et al. 2011b; Stutter et al. 2012). McLaren et al. (2014) reported a NMR spectrum of a Vertisol soil taken from the 10–30 cm layer of a soil profile under cropping, which had a concentration of 18 mg kg^{-1} of NaOH-EDTA extractable organic P. The NMR spectrum was dominated by a broad signal but the identification of sharp peaks within the phosphomonoester region was difficult. Similarly, Turner et al. (2003b) reported a NMR spectrum of a sandy soil taken from the 0–30 cm layer of a soil profile under cropping, which had a concentration of 21 mg kg^{-1} of NaOH-EDTA extractable organic P. The NMR spectrum did not exhibit any identifiable peaks within the phosphomonoester region. In the current study, a narrow (1:4) soil to solution ratio was used to increase the concentration of organic P in NaOH-EDTA extracts (McLaren et al. 2015a) in order to provide some insight into the chemical nature of organic P along the 26-year chronosequence of these oxidic soils.

Solution ^{31}P NMR spectra of the NaOH-EDTA extracts revealed that phosphomonoesters were the dominant form of organic P in these soils, which is consistent with previous studies in tropical regions (Solomon and Lehmann 2000). Whilst the spectra did exhibit a low signal-to-noise ratio, several peaks could be observed within the phosphomonoester region. In particular, the alkaline hydrolysis products of phospholipids (α- and β-

glycerophosphate: δ 4.4 and ~4.0 ppm) and RNA (RNA mononucleotides: δ 3.81, 3.74 and 3.68 ppm) (Doolette et al. 2009; Turner et al. 2003a), some unknown phosphomonoesters that exhibited a sharp signal (δ 5.3 and 3.5 ppm), and some broad phosphomonoesters underneath the sharp signals (spanning δ 4.8 to 3.4 ppm), which have been attributed to complex phosphomonoesters in high molecular weight material (McLaren et al. 2015b).

In general, the chemical nature of phosphomonoesters in these soils is somewhat different to that typically found in other soils. In particular, the overall dominance of a broad signal within the phosphomonoester region is not as evident in these soils compared to those in other Ferralsol soils under grassland and cropping (Doolette et al. 2011b; Jarosch et al. 2015) and there also appears to be a lack of inositol phosphates which have also been detected in Ferralsol soils (Doolette et al. 2011b; Jarosch et al. 2015). This might indicate a rapid turnover of added organic P by microorganisms and a low input of organic P from living organisms, particularly of plant seeds (Bünemann et al. 2008; Doolette et al. 2010).

The presence of alkaline hydrolysis products of phospholipids and RNA, phosphodiesters and pyrophosphate in these soils indicates the importance of microbial cycling of P (Condron et al. 2005). Concentrations of organic P in the 'labile' fraction were on average 30% of the combined pools of phosphomonoesters and phosphodiesters in NaOH-EDTA extracts at similar soil depths across all sites (Table 4), which indicates their importance for biological cycling of P. Minimal changes in the concentration and chemical nature of soil organic P after Year 4 of the chronosequence, and a similar chemical composition of organic P in these soils to that of the unburned native forest site (UB), suggest that the accumulation of organic P is relatively fast although it is then rapidly cycled by living organisms. If further accumulation of organic P is to occur, the addition of organic inputs and soluble forms of P is likely needed.

The previously burned native forest site (AB) had the lowest concentration of organic P, and its chemical nature was markedly different to that of all other sites. It is likely that high temperatures in the soil surface during burning have an adverse effect on soil organic matter (González-Pérez et al. 2004). Therefore, strategies aimed at sequestrating P in soil organic matter would need to account for losses via burning.

Environmental significance

The overall temporal development of P status and of the various P fractions seems likely to be broadly defined by the successful and consistently applied restoration processes, extending also to the plant species sown and the initial fertilizer P subsidy (c. 25 kg P ha^{-1}) (Spain et al. 2015). This has led to the relatively rapid and even development of the plant community giving rise, in turn, to the ongoing net increases in near-surface concentrations of Pt, particularly the organic *Labile* P and long-term inorganic soil components, soil organic matter status and the other pedogenetic changes that have occurred with increasing restoration period.

Initially, P uptake is likely dominated by the sown grasses whose roots penetrate to depths below the soil profile within the first year after site restoration. The succession from grass to shrub and then to eucalypt dominance implies a change in the dominant P nutritional strategies during community development from arbuscular to mixed arbuscular and ectomycorrhizal fungal dominance. Following canopy closure, substantial litter layers develop, comprising a standing crop of P estimated at c. 8 kg ha^{-1}.

Microbial decomposition of litter and the turnover of fine roots have, together with bioturbation by termites, ants and earthworms (Spain et al. 2010; 2015), led to the formation of a pedoderm (Fey et al. 2006), a narrow organic-matter-enriched surface layer occurring at the interface with the substantial litter layers at sites restored for more than c. eight years; however, the effects of soil organic matter extend well below this layer. The higher near-surface values are also likely influenced by plant uptake and the reestablishment of biological recycling processes (Jobbágy and Jackson 2004; Nziguheba and Bünemann 2005; Dieter et al. 2010).

Phosphorus status also depends on the balance of acquisitions through fertilization and other inputs and the losses, redistributions and transformations that are associated with site vegetation clearing, soil mixing, organic matter decomposition and mineralisation, eluviation and leaching during soil handling and storage, mining and site restoration processes. Ongoing losses through eluviation and perhaps leaching will likely also continue post restoration, perhaps associated with the development of preferential flow pathways (Bol et al. 2016; Negassa and Leinweber 2009).

Such losses are to be expected during early ecosystem development (Odum 1985) and to decline with increasing maturity in these highly permeable and rapidly re-organising soils (Spain et al. 2015). As illustrated by the differences in organic P between burned and long-unburned native forest sites, the introduction of firing to the restored sites is likely to lead to profound changes in the amounts, lateral and vertical distributions and properties of organic materials and their associated organic P compounds.

At least one of the major dominant species (*E. tetrodonta*) is known to be P responsive in the presence of mycorrhizas (Jasper and Davy 1993). From a management perspective, the higher concentrations of particularly the *Labile P* and *Intermediate P* fractions in the longer-restored soils in comparison to those of the native forest reference site AB are likely to be considered satisfactory in terms of the growth of the two dominant overstorey *Eucalyptus* species. Nonetheless, it is also possible that even the moderate rate of fertilizer P applied here may directly influence the level of understorey biodiversity through its effects on the recruitment and growth of P-sensitive plant species, or by promoting weed competition (see, for example, Daws et al. 2015; Prober and Wiehl 2012).

Compliance with ethical standards

Conflicts of interest Samples were collected during field work conducted by AVS and MT and are part of a wider contract of research with CSIRO under ISBN 978–1–74,052-170-3. AVS and MT designed the project and conducted the field work. MR supervised the P fractionation analyses and the X-ray fluorescence analysis of the selected total elements. TM carried out the ^{31}P NMR analyses. The manuscript was written by AVS, MT, MR and TM. Some of the P fractionation data reported here have been previously published in summary form (Spain et al. 2006; 2009a, b; 2015).

Appendix

Table 5 Selected properties of the soils of the chronosequence of restored sites and an unmined native forest site, AB (sampled May 2002)

Years	Depth range (cm)	Pt (mg kg^{-1})	C (g kg^{-1})	N (g kg^{-1})	Clay (% of <2 mm fraction)	Silt (% of <2 mm fraction)
1	0–4	223	11.60	0.42	26.3	17.6
1	>4–8	240	11.60	0.42	27.5	16.2
1	50–60	223	13.50	0.47	25.9	16.1
1	70–80	267	2.26	0.06	17.2	6.5
[a]2	0-1.5	280	16.00	0.58	28.3	12.2
[b]2	0-1.5	328	44.00	1.67	25.8	12.1
2	>1.5–4.0	236	9.50	0.36	29.4	13.1
2	60–70	227	9.80	0.40	29.6	14.2
2	100–110	240	11.00	0.42	28.4	14.5
4	0–4	227	16.40	0.77	33.9	18.7
4	5–10	210	15.20	0.67	31.8	19.5
4	20–25	144	2.52	0.14	48.2	13.3
4	50–60	140	3.40	0.19	46.1	12.9
4	90–100	192	4.76	0.20	33.9	11.3
8	0–4	227	16.20	0.67	36.9	9.9
8	>4–8	232	10.20	0.44	39.4	10.6
8	50–60	223	7.38	0.32	39.0	9.7
8	95–105	170	2.00	0.05	24.6	5.7
13	1.5–3.0	315	26.40	1.03	26.8	15.8
13	>3–7	315	15.70	0.70	31.6	14.0
13	40–50	232	9.27	0.34	29.4	12.9
13	75–85	197	1.86	0.05	16.1	5.7
20	0–4	262	44.30	1.64	26.0	18.0
20	>4–9	271	14.50	0.70	35.0	14.2
20	40–50	214	7.63	0.32	27.1	10.6
20	60–70	192	2.22	0.07	20.4	6.8
26	0–1.5	350	114.00	5.01	14.1	20.2
26	>1.5–5.5	315	31.70	1.72	28.1	19.0
26	12–17	210	12.50	0.50	26.2	18.2
26	60–70	210	9.23	0.39	28.6	17.1
26	105–115	214	2.13	0.07	17.0	6.2
[c]N	0-2.5	219	32.50	0.93	13.2	20.4
N	>2.5–7.5	170	12.20	0.53	21.9	17.8
N	7.5–12	175	8.30	0.41	21.2	19.9
N	60–70	197	5.31	0.31	31.6	17.6
N	75–85	179	2.86	0.11	31.2	5.9

[a] Ridge top sample

[b] Furrow sample

[c] Native forest site AB, with medium profile depth

Table 6 Concentrations of the chemically defined P fractions (mg kg^{-1}) in the soils of the chronosequence of restored sites and in an unmined native forest, AB (<dl, less than detection limit) (sampled May 2002)

Age (y)	Depth range (cm)	Resin P	Bicarbonate P_i	Bicarbonate P_o	Na0H P_i	Na0H P_o	Dilute HCl-extr. P_i	Conc. HCl-extr P_i	Conc. HCl-extr P_o
1	0–4	0.4	<dl	0.1	1.7	31.6	8.0	40.7	0.2
1	>4–8	0.1	<dl	<dl	1.2	35.8	1.7	42.7	<dl
1	50–60	0.3	<dl	0.7	1.7	15.7	2.0	45.1	<dl
1	70–80	0.2	0.4	<dl	20.2	10.0	0.5	21.5	<dl
[a]2	0-1.5	1.3	<dl	6.8	7.8	14.1	2.1	58.4	<dl
[b]2	0-1.5	4.8	1.5	2.8	14.6	42.6	2.2	61.3	<dl
2	1.5–4.0	<dl	<dl	1.2	4.7	15.0	1.7	50.2	<dl
2	60–70	<dl	<dl	1.4	2.1	25.9	1.0	41.3	<dl
2	100–110	<dl	<dl	1.0	4.6	26.3	2.2	32.0	4.7
4	0–4	1.1	0.7	5.0	4.2	47.2	1.9	31.0	<dl
4	5–10	1.0	<dl	1.2	3.2	21.8	1.1	24.4	<dl
4	20–25	0.1	<dl	<dl	3.2	<dl	1.7	12.5	<dl
4	50–60	<dl	<dl	<dl	3.5	1.0	1.6	14.8	<dl
4	90–100	0.2	<dl	<dl	1.7	6.2	1.3	27.6	<dl
8	0–4	0.8	0.2	1.6	6.8	29.9	1.3	34.2	5.2
8	>4–8	0.3	0.1	1.7	6.0	25.8	5.5	39.0	<dl
8	50–60	0.5	<dl	2.1	0.9	9.7	1.1	29.4	0.7
8	95–105	0.3	<dl	<dl	9.1	7.5	1.4	14.6	<dl
13	1.5–3.0	2.4	<dl	5.5	9.6	34.9	1.1	70.5	<dl
13	>3–7	1.2	0.7	4.6	7.5	44.5	0.9	65.6	<dl
13	40–50	0.3	<dl	<dl	1.5	25.8	1.3	57.7	1.4
13	75–85	0.2	1.0	<dl	10.6	0.8	1.2	31.1	<dl
20	0–4	6.0	<dl	3.3	7.2	13.7	1.3	60.6	<dl
20	>4–9	0.9	<dl	2.8	2.2	20.0	0.6	82.9	<dl
20	40–50	0.1	<dl	1.3	1.8	13.5	1.1	41.2	<dl
20	60–70	0.3	0.7	<dl	13.0	5.2	1.34	33.1	<dl
26	0–1.5	18.9	<dl	8.7	5.9	50.1	3.8	61.5	10.8
26	>1.5–5.5	3.2	<dl	5.0	9.5	44.7	2.4	60.7	4.3
26	12–17	<dl	<dl	1.5	6.0	21.6	2.7	38.7	<dl
26	60–70	<dl	<dl	1.5	3.7	23.8	1.5	51.7	<dl
26	105–115	<dl	0.2	1.3	17.5	<dl	1.3	48.1	0.9
[c]N	0-2.5	1.3	<dl	1.8	14.6	20.3	2.7	28.8	8.7
N	>2.5–7.5	<dl	<dl	1.2	3.5	18.7	3.4	18.3	12.5
N	7.5–12	<dl	<dl	0.6	2.5	21.8	2.3	27.7	<dl
N	60–70	<dl	<dl	0.7	3.1	5.1	2.5	26.0	<dl
N	75–85	<dl	<dl	<dl	9.5	<dl	3.2	23.9	3.0

[a] Ridge top sample

[b] Furrow sample

[c] Native forest site AB, with medium profile depth

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