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# Variation in environmentally- and agronomically-significant soil phosphorus concentrations with time since stopping the application of phosphorus fertilisers

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ABSTRACT

Following the cessation of P fertiliser to a P enriched pasture soil, indicators of potential P loss (WEP and $CaCl_2$-P) decreased exponentially with time. Soil P fractionation revealed a similar pattern occurred in bioavailable inorganic P fractions (principally $NH_4Cl$, $HCO_3$ and NaOH extractable pools). However, the addition of 50 kg N $ha^{-1}$ $year^{-1}$ to one treatment was not great enough to speed up the rate of decline in P fractions or P loss indicators compared to the same treatment without N applied. $^{31}P$ NMR data indicates that while the frequency of detecting orthophosphate diesters was greater in the N treated soils, the concentrations of organic P species stayed relatively stable with time. Our data suggest that the depletion of high soil P concentrations to decrease P loss in a pastoral soil in New Zealand operated under cut and carry, while maintaining agronomic potential, can be monitored with the use of a soil Olsen P test.



## 1. Introduction

The enrichment of soils with phosphorus (P) can result in loss of P from land and the impairment of surface water quality (Carpenter et al., 1998). One strategy to decrease soil P concentrations is to stop applying P fertiliser (O'Connor et al., 1990). However, studies have shown the decline in soil P concentrations, and the potential for P loss, can be slow. For instance, McCollum (1991) found that it took >17 year for Mehlich-1-extractable P concentrations within a fine sandy loam cropped in a corn-soybean rotation in North Carolina to decline from 99 mg $kg^{-1}$ to the agronomic-optimum value of 20–25 mg $kg^{-1}$. Coad et al. (2014) found changes in $CaCl_2$-P, an indicator of potential P loss in subsurface flow (McDowell and Sharpley, 2001), had decreased on average by 56% 4.5 years after the cessation of fertiliser-P applications to six soils in Tasmania, Australia. In contrast, Olsen P only decreased on average 25%. Reasons for the different rates of change both among and within soil P tests include: the initial level of enrichment (Dodd et al., 2012), soil texture (Rowe et al., 2015), soil aluminium (Al)- and iron (Fe)-hydrous oxide content (Dodd et al., 2013), and crop P removal in harvest (including the grazing of forage) (McDowell and Condron, 2012). A soil that is highly enriched with P, coarse textured, has low levels of Al- and Fe-hydrous oxides, and is heavily cropped or grazed will exhibit a fast rate of decline. The rate also tends to be faster for soil tests such as $CaCl_2$-P which tend to represent readily leachable pools compared to agronomically-focused soil P tests such as Olsen or Colwell P that include some estimate of loosely stored P (Dodd et al., 2013).

Recently, a management practise trialled to quicken the rate of soil P decline while maintaining crop productivity has been to apply nitrogen (N) fertiliser, but discontinue applications of P fertiliser (Dodd et al., 2014). Koopmans et al. (2004) found that $CaCl_2$-P and water extractable P (WEP), used as an indicator of the potential for P loss in surface runoff (McDowell and Sharpley, 2001), decreased on average 93% in greenhouse pot experiments over 978 days where grass was regularly harvested and N fertiliser added. Furthermore, Dodd et al. (2014) found that the addition of 150 or 300 kg N $ha^{-1}$ $year^{-1}$ to two dairy pastures, but no P, decreased filtered reactive P (FRP) concentrations in drainage by 53–76% compared to the same soil receiving no N. The difference was attributed to an increase in pasture yield and uptake of P into inorganic and organic forms by the microbial biomass.

Changes in P forms have been well documented in soils with increasing P concentration. Generally, at low soil P concentrations, P will tend to be housed in organic P forms as P is tightly cycled within the soil-plant system (Sharpley et al., 1985). However, with the addition of fertiliser-P more P is available and accumulated in the soil as inorganic P (McDowell and Condron, 2012). The rate of inorganic P enrichment quickly increases when there is a large surplus of P in the soil (Blake et al., 2000; Sharpley, 1986). In contrast, there are few data available on what forms and at what rate soil P decreases to once an enriched soil

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is managed to decrease soil P concentrations. This knowledge is important if we are to know when soil P can be mined to a level that does not compromise productivity, but still achieve environmentally acceptable P losses.

Methods to investigate the change in soil organic P forms are plentiful. Over the past four decades, $^{31}$P nuclear magnetic resonance of NaOH-EDTA extracts of soil have revealed changes in organic P forms in response to factors such as: landuse (McDowell and Stewart, 2006), soil fertility (Lookman et al., 1996), pH (Turner and Blackwell, 2013), and soil texture (Ahlgren et al., 2013). Some of these have also been related to changes in plant production (McDowell et al., 2008). Therefore, we used $^{31}$P NMR as one method to investigate changes in specific organic P forms in a pasture soil where fertiliser-P had been stopped for 19 years. Gross changes in inorganic and organic P were also characterised using soil P fractionation. This method separates P into operationally defined pools depending on plant bioavailability (Hedley et al., 1982). The overall aim was to see if environmentally- (e.g. WEP, $CaCl_2$-P) and agronomically-significant soil P forms changed with time since fertiliser-P was stopped, and if this rate of change was associated with particular P forms and quickened with the addition of N fertiliser.

## 2. Materials and methods

### 2.1. Soil sites and sampling

Soils were taken from the long-term ecology trial at Lincoln University, New Zealand. The trial was established in 1994 to examine the impacts of grassland management on soil properties, plant diversity and insect ecology. Prior to 1994, the soil (Udic Ustochrept, USDA Classification; Mottled Immature Pallic soil, New Zealand Classification) had been used for mixed cropping for c. 15 years and had a moderate to high soil Olsen P concentration (mean over the 15 years was 36 mg $kg^{-1}$). In 1994 the site was cultivated and sown with a mixture of white clover (*Trifolium repens* L. cv. Tahora), red clover (*Trifolium pratense* L. cv. Pawera), perennial ryegrass (*Lolium perenne* L.), and cocksfoot (*Dactylis glomerata* L. cv. Kahu). Six treatments were established on plots (5 by 5-m) arranged in randomised blocks with four replicates per treatment (24 plots). The treatments were: with and without nitrogen fertiliser (50 kg N $ha^{-1}$ $year^{-1}$ applied as urea in spring); mowing when the sward reached 20-cm or not mown; and with clippings either left or removed. The trial was not grazed and did not receive any other fertiliser or irrigation.

Soil samples have been taken in April of each year since 1994 from the 0–7.5 cm depth, air-dried, ground and sieved to <2-mm. Soils samples were taken from the mown plots with clippings removed, and with and without N fertiliser. These are referred to as the 0P 50N and 0P 0N treatments, respectively. Soils samples for 1994, 1995, 1998, 2002, 2005, 2010 and 2013, representing 0, 1, 4, 8, 11, 16 and 19 years, respectively, since P had been applied were sub-sampled from archived samples for analysis.

### 2.2. Soil analyses

All soils were air-dried, crushed and sieved (<0.5 mm). Soil analyses included $CaCl_2$- and water-extractable P (1:5 and 1:300 soil to solution ratios, respectively) (McDowell and Sharpley, 2001), pH in water (1:2.5 soil to water ratio; Thomas, 1996), Olsen P (Olsen, 1954), organic C by Shimadzu total organic C/N analyzer, and exchangeable Ca, K and Mg (Sumner and Miller, 1996).

### 2.3. $^{31}$P NMR

Air-dry soil (1.5 g) was shaken with 30 ml of 0.25 M NaOH + 0.05 M EDTA (Na form) overnight, centrifuged for 15 min (4000 ×*g*), and the supernatant filtered (Whatman GF/F). This extract was deemed more appropriate for the detection of organic P compounds without interference from paramagnetic ions than either NaOH on its own or more concentrated NaOH-EDTA (Zhang et al., 2013). A sub-sample of each extract (1 ml diluted 10-fold) was analyzed via colorimetry (Watanabe and Olsen, 1965) for orthophosphate concentration (limit of detection = 2 μg $ml^{-1}$) before and after digestion by $K_2S_2O_8$ (yielding total NaOH EDTA-extractable P and organic P by difference from orthophosphate before digestion; Bowman and Moir, 1993). The remaining bulk (ca. 29 ml) of each extract was frozen and lyophilized.

Lyophilized NaOH-EDTA extracts were dissolved in 0.8 ml $D_2O$, 0.4 ml 10 M NaOH and 1.4 ml of deionized water and allowed to stand for 30 min with occasional vortexing. After dissolving, samples were centrifuged for 20 min at approximately 1500 ×*g*, after which the supernatant was transferred to a 5-mm tube for $^{31}$P NMR analysis.

Spectra were obtained using a Bruker AVANCE III 400 MHz spectrometer equipped with a BBFO 5-mm broadband probe operating at 161.98 MHz for $^{31}$P and 400.13 MHz for $^{1}$H. The NMR parameters were: 45° $^{31}$P pulse, 2 s acquisition time with inverse gated $^{1}$H decoupling, 5 s recycle delay, 25 °C and 7680 transients (ca. 15 h). The long delay between pulses ensured that the spin-lattice relaxation time ($T_1$) was reached and that spectra were quantitative (McDowell et al., 2006). Phosphorus compounds were identified by their chemical shifts (ppm) relative to an external orthophosphoric acid standard. The orthophosphate peak for each sample was standardized to 6 ppm in all spectra to simplify comparisons among samples. Peak areas were calculated by integration on spectra processed with 5 Hz exponential line-broadening (and checked with 1 Hz line-broadening), using NUTS software (Acorn NMR, Livermore CA, 2000 edition). Peaks were subsequently grouped into compounds (orthophosphate, 6.5 ppm and pyrophosphate, −3 to −6 ppm) or compound classes if specific identifications could not be made (orthophosphate monoesters from 3 to 6 ppm and orthophosphate diesters from −1 to 2 ppm) (e.g. Fig. 1; McDowell and Stewart, 2005).

### 2.4. P fractionation

To determine the chemical speciation of P within soils, as relevant to pasture production (Condron et al., 1985), the fractionation scheme of Condron et al. (1990) was used. Briefly, triplicate samples of each soil (1 g) were sequentially extracted via shaking with 30 ml of 1 M $NH_4Cl$ (shake 2 h), 0.5 M $NaHCO_3$ (shake 16 h), 0.1 M NaOH (shake 16 h), 1 M HCl (shake 16 h), and finally 0.1 M NaOH (sonicate for 5 min then shake 16 h), before the remaining P is removed by persulphate digestion (0.3 g $K_2S_2O_8$ in 2 ml 0.5 M $H_2SO_4$, 150 °C for 2 h). These fractions remove, in sequential order, water soluble or soil solution P ($H_2O$-P), loosely sorbed bioavailable P largely associated with Al and Fe ($HCO_3$-P), inorganic and organic P associated with Al, Fe and humic substances (NaOH-P), Ca associated P ($H_2SO_4$-P), recalcitrant or occluded inorganic and organic P (NaOH II-P) and residual P. Following extraction each soil-suspension was centrifuged (4000 ×*g*) for 10 min, and an aliquot taken of the supernatant for P determination before being discarded and the next extractant added. Both inorganic and organic P (by difference from total P after persulphate digestion and inorganic P by colorimetry) were determined on the water, $NaHCO_3$, and two NaOH extracts.

### 2.5. Statistical analyses

Data from sequential P fractions were subjected to an analysis of variance and regression procedures using the Genstat software package v 17.0 (Genstat Committee, 2015). Due to the expense and time for analysis by $^{31}$P NMR it was not possible to do replicates for each soil.

## 3. Results

### 3.1. Soil chemical characteristics and P fractionation

General soil chemical characteristics for the two treatments are given in Table 1. There were no differences between treatments despite a likely increase in pasture production associated with the addition of