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REVIEW ARTICLE

Soil organic phosphorus transformation during ecosystem development: A review

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Abstract
Background Soil organic phosphorus transformation during ecosystem development exerts a crucial influence on soil fertility and ecosystem properties.
Scope This paper reviews the use of solution ^{31}P NMR spectroscopy for characterizing organic phosphorus speciation in soil chronosequence and long-term field experiments in order to improve our understanding of the temporal changes, fundamental processes, and associated natural and anthropogenic controls of organic phosphorus transformation during long-term ecosystem evolution. Published soil chronosequence studies show that organic phosphorus compounds under aerobic conditions are dominated by phosphate monoesters (occurred mainly as inositol phosphates) followed by phosphate diesters (occurred mainly as DNA) and phosphonates, irrespective of the different parent materials, vegetation covers and climatic conditions. This contrasted markedly with wetland soils in which phosphate monoesters and diesters maintained approximately equal proportions, which is attributed to the limited reactive clay surfaces for stabilization and/or decomposition of *myo*-inositol hexakisphosphate under frequent anaerobic conditions. Most organic phosphorus compounds in soil chronosequences increase with age to reach a maximum and then decline with time, although the apex varies significantly among different organic phosphorus compounds and chronosequences. Variations of the potential for phosphorus stabilization resulting from mineralogical transformation, changes in phosphorus sources due to shifts in plant and microbial communities, and differences in the biological utilization of various phosphorus compounds have been suggested as three main mechanisms controlling the temporal changes in organic phosphorus species, abundance and availability during natural ecosystem development. In agricultural soils, the amounts, forms, and dynamics of organic phosphorus are determined by internal soil properties, external environmental conditions and managements, including the history and intensity of land use, different tillage practices and fertilizer treatments. These mechanisms are interlinked and more research is required to isolate both internal and external factors that regulate organic phosphorus transformation in agricultural ecosystems.

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Conclusions Given the universal dependence on organic phosphorus for life and its critical roles in biogeochemical cycling, we put forward several open questions that need to be resolved in the future studies by emphasizing the multidisciplinary collaborations, the use of multiple analytical techniques and the establishment of quantitative organic phosphorus transformation models.

Keywords Organic phosphorus speciation · NMR spectroscopy · Biogeochemical cycling · Chronosequence · Pedogenic threshold · Long-term field experiment · Anthropogenic impact

Introduction

Phosphorus is an essential nutrient element for life, and its transformation during ecosystem development exerts a crucial influence on soil fertility and ecosystem properties (e.g. Walker and Syers 1976; Crews et al. 1995; Huang et al. 2013; Chen et al. 2015; Turner and Laliberté 2015). Investigations on natural soil chronosequences in tropical (e.g. Crews et al. 1995), subtropical (e.g. Zhou et al. 2013; Chen et al. 2015), temperate (e.g. Walker and Syers 1976; Richardson et al. 2004; Eger et al. 2011; Turner et al. 2013), Mediterranean (Turner and Laliberté 2015), and the (semi)arid (e.g. Lajtha and Schlesinger 1988; Selmants and Hart 2010) regions have shown that during long-term ecosystem development the phosphorus originally present in primary minerals (mainly in the form of apatites) is weathered and depleted at varying rates, and that phosphorus gradually becomes more limiting due to its accumulated losses and/or occlusion by secondary minerals or organic complexation. The decline of inorganic phosphorus amounts and availability during continued soil development (Walker and Syers 1976; Turner and Laliberté 2015) results in the widening of carbon/nitrogen-to-phosphorus ratios (i.e. C : P, N : P) and drives accelerated phosphorus limitation of terrestrial ecosystems (Vitousek et al. 2010). Thus at more advanced stage of weathering soil organic phosphorus cycling becomes increasingly important for the biological availability of phosphorus and rates of carbon and nitrogen changes (Wardle et al. 2004; Turner et al. 2013).

Despite the widely recognized importance of organic phosphorus as a fertilizer resource for soil biota and its critical role in biogeochemical cycling and ecosystem function (Dalal 1977; Stewart and Tiessen 1987; Sims and Sharpley 2005; Nash et al. 2014), the chemical nature as well as the transformation of organic phosphorus continues to be largely overlooked and remains poorly understood in comparison of inorganic phosphorus. For instance, previous phosphorus transformation models during natural pedogenesis (Walker and Syers 1976; Lajtha and Schlesinger 1988; Crews et al. 1995; Richardson et al. 2004; Selmants and Hart 2010; Eger et al. 2011; Zhou et al. 2013; Chen et al. 2015) depict the extracted organic phosphorus as a single functional pool of limited availability to plants. In sharp contrast to the simple interpretation of this operationally defined term, soil organic phosphorus actually consists of a variety of compounds that differ markedly in their behavior and bioavailability in the natural environment (Condron et al. 2005). Yet the full identification of organic phosphorus speciations is much more difficult than that of inorganic phosphorus. As a result, little is known about the dynamics of different organic phosphorus compounds during long-term ecosystem development. The limited understanding of the sources and types of organic phosphorus as well as its transformations in soils not only inhibit the development of sustainable management practices, but also constrain our ability to predict the response of ecosystem processes to the nutrient stoichiometry changes (e.g. C: N: P).

The recent development of solution phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectroscopy and the successful application of this method for characterization of organic phosphorus speciations in natural soil chronosequences and anthropogenic long-term field experiments have significantly advanced our understanding of organic phosphorus dynamics in native and agricultural ecosystems. In this article, we overview the state of organic phosphorus transformation during ecosystem development by focusing on the achievements obtained from the use of solution ^{31}P NMR spectroscopy. We first summarize various organic phosphorus forms present in soils and address the methods for the characterization of organic phosphorus with a particular focus on solution ^{31}P NMR spectroscopy. Then we describe the recent advances in organic phosphorus transformations and their influencing factors in both natural and agricultural ecosystems. Finally, we put forward some open questions that need to be resolved in the future studies by emphasizing the multidisciplinary collaborations, the use of multiple analytical techniques and the establishment of quantitative organic phosphorus transformation models.

Forms of organic phosphorus in soils

Organic phosphorus is defined as phosphorus present as a constituent of organic compounds that contain carbon-hydrogen bonds (Turner et al. 2005). It is derived mainly from biological processes involving assimilation of orthophosphate and subsequent release as microbial and animal manure or plant residual. Organic phosphorus in soils is generally classified into three groups based on the different phosphorus bonds (Fig. 1): (i) phosphate esters; (ii) phosphonates; and (iii) phosphoric acid anhydrides (i.e. organic polyphosphate) (Dalal 1977; Harrison 1987; Stewart and Tiessen 1987; Sanyal and De Datta 1991; Condron et al. 2005).

Phosphate esters are sub-classified into two groups according to the number of esters linked to each phosphate (Condron et al. 2005) (Fig. 1): (i) phosphate monoesters (i.e. one carbon moiety per phosphorus); and (ii) phosphate diesters (i.e. two carbon moieties per phosphorus). Phosphate monoesters are the predominant form of organic phosphorus in soils under aerobic conditions, which occur mainly as inositol phosphates (Condron et al. 2005). There may be one to six phosphate groups linked to the parent inositol, forming several stereoisomers (e.g. *myo*-, *scyllo*-, *D-chiro*-, and *neo*-) that have different abundance in soils. Other phosphate monoesters, such as sugar phosphates, phosphoproteins, and mononucleotides, present in the soil in trace quantities (Fig. 1). Phosphate diesters include nucleic acids (i.e. DNA and RNA), phospholipids and teichoic acids (Condron et al. 2005) (Fig. 1). The proportion of phosphate diesters in well-drained soils is generally less than that of phosphate monoesters (Condron et al. 2005). The different kinds of phosphate diesters generally follow the decreasing order of nucleic acids, phospholipids and teichoic acids in terms of their abundance in soils.

Phosphonates consisting of carbon-phosphorus bonds (C-P) are markedly different from other soil organic phosphorus compounds that contain carbon-oxygen-phosphorus bonds (C-O-P) (Condron et al. 2005). The first organic phosphorus compound with a C-P bond identified in the environment is 2-aminoethylphosphonic acid, which has been isolated from rumen protozoa by Horiguchi and Kandatsu (1959). Although phosphonates are regarded as having great chemical stability as a result of their C-P bonds, it has been found that bacteria are capable of using phosphonates as substrates (Cook et al. 1978). Thus, phosphonates tend to accumulate in wet, cold or acidic soils with few phosphonate enzymes (Cade-Menun et al. 2000).

Phosphoric acid anhydrides (i.e. organic polyphosphate), which contain phosphate monoester and anhydride bonds, are important for biochemical energy transfer (Emsley and Hall 1976; Corbridge DEC 2000). The most important phosphoric acid anhydrides are adenosine diphosphate (ADP) and adenosine triphosphate (ATP) (Fig. 1), but they are rarely detected in soil due to their thermodynamic instability in natural environment (De Nobili et al. 1996).

The structure of some common organic phosphorus compounds in soils is presented in Supplementary Fig. S1. More detailed descriptions about the characteristics, abundance, mineralization and/or transformation of organic phosphorus in soils as well as the their importance in plant nutrition are available in Dalal (1977), Harrison (1987), Stewart and Tiessen (1987),

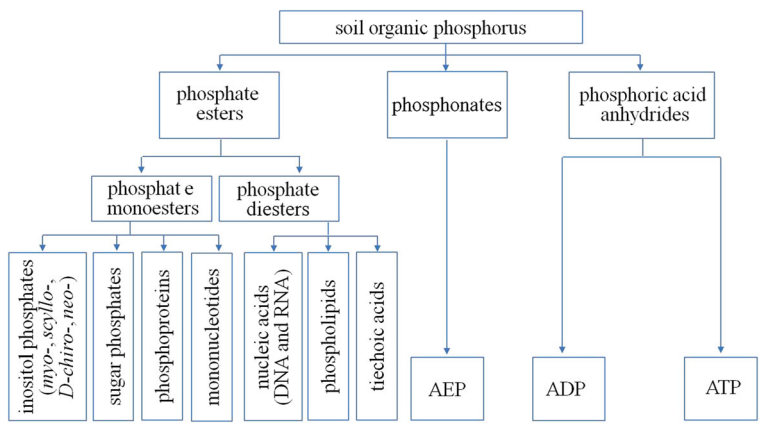

Fig. 1 Systematic diagram of soil organic phosphorus forms. *Myo*-, *scyllo*-, D-*chiro*, and *neo*- are four stereoisomeric forms of inositol phosphates; DNA: deoxyribonucleic acid; RNA: ribonucleic acid; AEP: 2-aminoethy lphosphonic acid; ADP: adenosine diphosphate; ATP: adenosine triphosphate

Sanyal and De Datta (1991), Corbridge DEC (2000), Condron et al. (2005), Richardson et al. (2005), and Nash et al. (2014).

Characterization of soil organic phosphorus

Many methods have been developed to measure soil organic phosphorus (Supplementary Table S1), including the determination of total soil organic phosphorus by ignition or alkaline extraction (e.g. Saunders and Williams 1955; Bowman and Moir 1993), measurement of a specific soil organic phosphorus compound after extraction using a particular reagent (e.g. Adams et al. 1954; McKercher and Anderson 1968; Kowalenko and Mckercher 1970; Mueller-Harvey and Wild 1987), and the identification of different soil organic phosphorus forms by sequential fractionation (e.g. Hedley et al. 1982; Tiessen and Moir 1993) or solution ^{31}P NMR spectroscopy (e.g. Turner et al. 2003a, b; Cade-Menun 2005a, b; Doolette et al. 2009; Cade-Menun and Liu 2013). Detailed information about the principles, steps, advantages and disadvantages of a particular method in Supplementary Table S1 could be found elsewhere (e.g. Condron et al. 2005; Turner et al. 2005; Doolette and Smernik 2011; Cade-Menun and Liu 2013 and references therein). Here we only focus on the solution ^{31}P NMR spectroscopy, which is the most widely used method in the recent decades for the full identification of the various organic phosphorus speciations.

There are three major steps for obtaining meaningful ^{31}P NMR data, including soil extraction, NMR experiment, and the spectral assignments of phosphorus compounds in soil extracts (Keeler 2005; Claridge 2009; Gorenstein 2012). Here we briefly summarize the key point of each step and outline current limitations of solution ^{31}P NMR spectroscopy.

Extraction of soil organic phosphorus

Various extractants have been employed for characterization of phosphorus species in solution ^{31}P NMR experiments, which have been summarized by Condron et al. (2005), Turner et al. (2005), and Cade-Menun and Liu (2013). These extractants include (i) water, (ii) water followed by 0.4 M NaOH, (iii) the cation exchange resin Chelex in water, (iv) HCl followed by NaOH and then the cation exchange resin Chelex, (v) 0.5 M NaOH, (vi) 0.5 M NaOH plus Chelex, (vii) 0.1 M or 0.5 M NaOH plus 0.4 M NaF, (viii) 0.5 M NaOH plus 0.1 M Na_2EDTA, and (ix) 0.25 M NaOH plus 0.05 M Na_2EDTA. Previous studies have demonstrated that different extractants not only influence the recovery of organic phosphorus from soils, but also affect the composition of the extracted compounds (e.g. Cade-Menun and Preston 1996; Cade-Menun et al. 2002; Briceño et al. 2006). Thus, the use of different extractants makes it difficult to compare the results of different studies among laboratories. Cade-Menun (2005b) suggests that one option to solve this problem is to select a standard method for extraction, and then compare the results from other extractants to this standard with organic phosphorus compounds in the reference soils. To date, NaOH–EDTA is the most widely used extractant for solution ^{31}P NMR spectroscopy and it has been suggested as a baseline extraction method (Cade-Menun and Liu 2013) for comparison of data obtained by different studies. Based on previous studies, the recommended conditions for NaOH–EDTA procedure are extraction in a solution containing 0.25 M NaOH and 0.05 M Na_2EDTA in a 1: 20 solid to solution ratio for 16 h at ambient laboratory temperature (Supplementary Table S1). It should be noted that the optimum conditions for NaOH–EDTA extraction may vary with different soil types. Detailed descriptions about the effect of preparing soil samples, soil/extractant ratio, extraction time, and the pre- and/or post-extraction treatments on the recovery of soil organic phosphorus are available in a recent review by Cade-Menun and Liu (2013).

The percentage of phosphorus recovery by NaOH–EDTA extraction for solution ^{31}P NMR varied from 2% to 100% and was generally highest for the manure-amended soils with high total phosphorus concentrations and lowest for soils with high pH and very low total phosphorus concentrations without manure amendments (McDowell et al. 2006, 2007a; Turner et al. 2007a; Doolette et al. 2009; Dou et al. 2009). Few studies have examined the differences of phosphorus compositions in samples before and after the NaOH–EDTA extraction. Cade-Menun et al. (2005) characterized phosphorus compounds in three marine particulate samples before and after NaOH–EDTA extraction by using ^{31}P NMR spectroscopy. They found that NaOH–EDTA removed the majority of phosphate monoesters and diesters but only a variable portion of phosphonates (39 ~ 67%). The phosphorus remaining in the residues accounted for 64 ~ 68% of total phosphorus and was mainly in the form of orthophosphate. Further

investigation of soil samples, especially those with low phosphorus recovery after NaOH–EDTA extraction, is required to determine the phosphorus forms remaining in the residues for ^{31}P NMR. Such studies will contribute to a better understanding of soil organic phosphorus dynamics.

The soil extracts after NaOH–EDTA treatments are commonly concentrated by freeze-drying (Condron et al. 2005; Turner 2008; Cade-Menun and Liu 2013) to maximize phosphorus concentration and improve the spectral resolution prior to analysis by solution ^{31}P NMR spectroscopy. It remains to be tested that whether freeze-drying soil extracts at high pH is causing organic phosphorus degradation. Because solution ^{31}P NMR spectroscopy requires liquid samples, freeze-dried soil extracts must be dissolved before analysis (Cade-Menun and Liu 2013). Samples could be re-dissolved in a range of solvents as summarized by Cade-Menun and Liu (2013), including (i) deuterium oxide, (ii) sodium deuteroxide, (iii) deuterium oxide plus water, (iv) deuterium oxide plus sodium deuteroxide, (v) deuterium oxide plus NaOH–EDTA, (vi) deuterium oxide plus 1 M or 10 M NaOH, and (vii) deuterium oxide plus NaOH–EDTA plus 10 M NaOH. Deuterium is used as a signal lock in the spectrometer, while sodium deuteroxide and NaOH are used to adjust the pH to greater than 10 for optimal spectral resolution (Cade-Menun 2005a). Re-dissolved samples may be filtered or centrifuged prior to decanting into NMR tube. To prevent hydrolysis, samples should be analyzed as soon as possible after dissolution.

NMR spectroscopy experimental parameters

The use of appropriate experimental parameters during ^{31}P NMR experiment is essential for obtaining meaningful spectral for the determination of various phosphorus forms. In a ^{31}P NMR experiment, after nuclei are activated by the radio-frequency pulse, they relax or recycle back to equilibrium by exchanging energy with their surroundings or with each other during the acquisition time and pre-acquisition delay (Cade-Menun and Liu 2013). The sum of the acquisition time and pre-acquisition delay is referred to as the relaxation or recycle delay. A properly executed ^{31}P NMR experiment requires a sufficiently long recycle delay between pulses for quantitative measurement (Cade-Menun and Liu 2013). The delay times could be established based on the analysis of T_1 (the exponential time constant) values (Cade-Menun et al. 2002). For example, a 90°, 45°, and 30° radio-frequency pulse would respectively require 5 × T_1, 4 × T_1 and 3 × T_1 for magnetization to return to ≥99% equilibrium. Shorter radio-frequency pulses thus require less delay time for magnetization to return to equilibrium, but the signal per pulse is reduced. In addition, McDowell et al. (2006) reported a strong relationship between T_1 and the ratio of phosphorus concentration relative to the concentrations of Fe and Mn [P / (Fe + Mn)] in soil extracts. They suggested that the predetermined P / (Fe + Mn) ratio in soil extracts could be used to estimate the T_1 values required for NMR experiment. The delay times reviewed by Cade-Menun and Liu (2013) ranged from 0.2 s with a 30° radio-frequency pulse to 65 s with a 90° radio-frequency pulse. A key concern of using delay times less than 2 s without justification in many previous studies (e.g. Murphy et al. 2009; Cheesman et al. 2010a) is that it may not be long enough to collect quantitative data. Cade-Menun and Liu (2013) recommend careful calibration of pulse lengths and determination of T_1 values for representative soil extract samples or comparable test samples before actual ^{31}P NMR experiments to ensure that appropriate delay times are used. Proton decoupling may or may not be applied during ^{31}P NMR experiment depending on implementation. While proton decoupling could simplify the spectral for peak identification, the radio-frequency power used to decouple protons is widely recognized to heat the samples and thus may induce degradation (Cade-Menun and Liu 2013). To reduce sample heating and improve spectral quantification, composite-pulse decoupling (vs. continuous-wave decoupling) should be used and applied only during the ^{31}P pulse and acquisition times (inverse gated, as opposed to decoupling continuously throughout the entire experiment) (Cade-Menun and Liu 2013). The number of scans collected in experiments ranges from approximately 1000 to 112,000 as reviewed by Cade-Menun and Liu (2013), which depends on a combination of factors, such as the time required for each scan and delay between scans, the concentration of phosphorus in the sample, the desired signal-to-noise ratio (S/N) of the spectral, and the size of the probe (Cade-Menun 2005a, 2005b). Due to the potential risk of hydrolysis by heating, experiments should be kept as short as possible. The hydrolysis during ^{31}P NMR experiments as well as during NaOH-EDTA extraction (as mentioned above) would result in the disappearance of peaks

for original organic phosphorus compounds and the appearance of peaks for degradation products. For instance, the degradation peaks of RNA have been identified as mononucleotides, such as adenosine monophosphate (Turner et al. 2003b; Vestergren et al. 2012). To minimize degradation, it is recommended that keep the length of experiments to 8 h or less and maintain the experiment temperature at 20 °C (Cade-Menun and Liu 2013). If more scans are required to improve the S/N ratio, consider collecting them as two or more shorter experiments on multiple samples and add the experiments together later (Cade-Menun and Liu 2013).

Spectral assignments of phosphorus compounds measured by ^{31}P NMR spectroscopy

The identification of phosphorus compounds determined by solution ^{31}P NMR spectroscopy is based on their chemical shifts relative to an external standard of 85% H_3PO_4 (Turner et al. 2003a). Chemical shift is defined as: $(V_S\text{-}V_R) / V_R \times 10^6$, where V_S and V_R are respectively the frequency of the sample and reference standard relative to that of the applied magnetic field (Wilson 1987). The chemical shift values depend primarily on the degree of molecular shielding around the phosphorus nuclei, but are modified by the surrounding chemical environment, such as pH conditions, ionic strength, probe temperature and the presence of paramagnetic ions (Cade-Menun et al. 2002). Thus, both variations in extraction matrices and experimental parameters complicate the spectral assignments (Turner et al. 2003a). Here we summarize solution ^{31}P NMR chemical shifts of model phosphorus compounds in alkaline soil extracts (0.25 M NaOH and 0.05 M EDTA) that have been lyophilized and redissolved in D_2O and 1 M NaOH based on previous literatures (Table 1). It should be noted that the chemical shift of a particular phosphorus compound may be different from the values reported below due to differences in sample preparation and the associated variations in solution pH, ionic strength and paramagnetic ion concentration. Nevertheless, these characteristic values could provide a reference for future studies of soil phosphorus forms.

Phosphate monoesters resonate between 3.0 ppm and 6.0 ppm (Table 1), and these compounds generally do not degrade in NaOH-EDTA. The differences in chemical shift for phosphate monoesters range from 0 to 0.42 ppm in the study of Turner et al. (2013a) and Cade-Menun (2015), despite they use similar matrices for analyzing phosphorus compounds. Myo-inositol hexakiphosphate (phytic acid) give four characteristic signals, which are 5.85, 4.92, 4.55 and 4.43 ppm according to Turner et al. (2003a), and 5.49, 4.52, 4.13 and 4.02 ppm according to Cade-Menun (2015) (Table 1). Scyllo-inositol hexakisphosphate resonate at 4.20 ppm according to Turner et al. (2003a) and 3.71 ppm according to Abdi et al. (2014). Other phosphate monoesters resonate in this region include α-glycerophosphate (4.96 and 4.97 ppm reported by Turner et al. (2003a); 4.88 ppm reported by Cade-Menun (2015), β-glycerophosphate (4.63 and 4.80 ppm reported by Turner et al. (2003a); 4.53 ppm reported by Cade-Menun (2015)), sugar phosphates (e.g., glucose phosphates at 3.39 ppm), and mononucleotides (4.27 to 4.78 ppm) (Table 1). Phosphate diesters resonate between −1.0 ppm and 2.0 ppm (Table 1), which are more susceptible to degrade in NaOH-EDTA than phosphate monoesters. Signals from nucleic acids (DNA, −0.37 and −0.63 ppm, RNA, 0.54 ppm) and phospholipids (phosphatidyl choline, 0.78 ppm, phosphatidyl serine, 1.57 ppm, phosphatidyl ethanolamine, 1.75 ppm) could be differentiated in the phosphate diester region according to Turner et al. (2013a) (Table 1). The differences in chemical shift for phosphate diesters measured by Turner et al. (2013a) and Cade-Menun (2015) range from 0.02 to 0.36 ppm (Table 1). Many studies have shown that RNA and some of the phospholipids degrade over time during ^{31}P NMR analysis at high pH (Makarov et al. 2002; Turner et al. 2003a; Cade-Menun 2015), resulting in the disappearance of peaks for these organic phosphorus compounds and the appearance of peaks for their degradation products. For instance, degradation peaks for phospholipids are consistent with peaks for α- and β-glycerophosphate (Cade-Menun 2015). Phosphonates give signals between 12 ppm and 23 ppm, with 2-aminoethylphosphonic acid (AEP) resonating at 20.72 ppm (Turner et al. 2003a) or 20.36 ppm (Cade-Menun 2015) (Table 1). Phosphoric acid anhydrides (i.e., organic polyphosphates) give multiple signals in the negative region of the spectra, with ADP resonating at −4.71 and −9.20 ppm, and ATP resonating at −4.28, −9.68 and −19.68 ppm according to Turner et al. (2003a) (Table 1). The differences in chemical shift for organic polyphosphates (e.g., ADP and AEP) measured by Turner et al. (2013a) and Cade-Menun (2015) range from −0.05 to −0.46 ppm (Table 1). Differences in

Table 1 Solution ^{31}P nuclear magnetic resonance (NMR) chemical shifts of some model phosphorus compounds in an alkaline soil extract (0.25 M NaOH and 0.05 M EDTA) that has been lyophilized and redissolved in D_2O and 1 M NaOH

Phosphorus compounds	Chemical formula	Chemical shift (ppm) and references
Inorganic orthophosphate	H_3PO_4	6.04 (Turner et al. 2003a); 6.00 (Cade-Menun 2015)
Inorganic polyphosphate (end groups)	$H_{2n}O_{3n+1}P_n$	−4.0 (Turner et al. 2003a)
Inorganic polyphosphate (mid chain groups)		−19.2, −20.1, −20.5 (Turner et al. 2003a)
Pyrophosphate	$H_4P_2O_7$	–4.39 (Turner et al. 2003a), −4.16 (Cade-Menun 2015)
Phosphate monoesters		3.0 ~ 6.0 (Turner et al. 2003a; Cade-Menun 2015)
myo-inositol hexakiphosphate (phytic acid)	$C_6H_{18}O_{24}P_5$	5.85, 4.92, 4.55, 4.43 (Turner et al. 2003a); 5.49, 4.52, 4.13, 4.02 (Cade-Menun 2015)
scyllo-inositol hexakisphosphate	$C_6H_{18}O_{24}P_6$	4.20 (Turner et al. 2003a); 3.71 (Abdi et al. 2014)
α-glycerophosphate	$C_3H_9O_6P$	4.96, 4.97 (Turner et al. 2003a); 4.88 (Cade-Menun 2015)
β-glycerophosphate	$C_3H_9O_6P$	4.63, 4.80 (Turner et al. 2003a); 4.53 (Cade-Menun 2015)
sugar phosphates (e.g., glucose phosphates)	$C_6H_{13}O_9P$	3.39 (Turner et al. 2003a); 3.39 (Cade-Menun 2015)
mononucleotides (e.g., guanosine 2′ and 3′ monophosphate)	$C_{10}H_{14}N_5O_8P$	4.75, 4.32 (Turner et al. 2003a); 4.50, 4.27 (Cade-Menun 2015)
Phosphate Diesters		−1.0 ~ 2.0 (Turner et al. 2003a; Cade-Menun 2015)
DNA (i.e., deoxyribonucleic acid)	(A-C-G-T)n [a]	−0.37, −0.63 (Turner et al. 2003a); −0.73, −0.92 (Cade-Menun 2015)
RNA (i.e., ribonucleic acid)	(A-C-G-U)n [b]	0.54 (Turner et al. 2003a); 0.52 (Cade-Menun 2015)
phospholipids	$C_{10}H_{19}NO_8P(2R)$ [c]	0.78, 1.57, 1.75 (Turner et al. 2003a); 0.42, 0.75, 1.35, 1.51 (Cade-Menun 2015)
Phosphonates		12 ~ 23 (Turner et al. 2003a; Cade-Menun 2015)
AEP (i.e., 2-aminothyl phosphonic acid)	$C_2H_8NO_3P$	20.72 (Turner et al. 2003a); 20.36 (Cade-Menun 2015)
Phosphoric acid anhydrides (i.e., organic polyphosphates)		−4 ~ −20 (Turner et al. 2003a; Cade-Menun 2015)
ADP (i.e., adenosine diphosphate)	$C_{10}H_{15}N_5O_{10}P_2$	–4.71, −9.20 (Turner et al. 2003a); −4.52, −9.05 (Cade-Menun 2015)
ATP (i.e., adenosine triphosphate)	$C_{10}H_{16}N_5O_{13}P_3$	–4.28, −9.68, −19.68 (Turner et al. 2003a); −4.08, −9.73, −19.22 (Cade-Menun 2015)

[a] A, C, G, and T respectively represents adenine, cytosine, guanine, and thymine; [b] A, C, G, and U respectively represents adenine, cytosine, guanine, and uracil; [c] Chemical formula of L-a phosphatidyl choline, R represents hydrophobic fatty acyl chains, which may not be identical

chemical shifts for phosphorus compounds in spite of using similar matrices and experimental parameters during the experiments highlight the need to combine phosphorus form library with spiking experiments to confirm peak identifications (Cade-Menun 2015). Cade-Menun (2015) has given some suggestions and recommendations for standardized spiking experiments to improve the peak identification.

Limitations of solution ^{31}P NMR spectroscopy and possible solutions

Although solution ^{31}P NMR spectroscopy has been successfully used to characterize organic phosphorus species in environmental and agricultural samples, the possibility of the creation of artifacts by hydrolysis during the extraction and/or NMR experiment influences the accuracy of data collected. The alkaline hydrolysis was reported for a wide range of soil organic phosphorus species and this has been discussed in detail by Turner et al. (2005). They suggested that a better understanding of the various hydrolysis processes can minimize the misinterpretation of results, given that organic phosphorus degradation during the extraction and/or NMR experiment is inevitable. On the other hand, recent studies showed that the solid-state NMR analysis of intact samples can avoid possible species alterations caused by chemical extraction

and provide a better opportunity for identifying inorganic phosphate minerals (Conte et al. 2008; Kizewski et al. 2011; Simpson et al. 2012). However, it is more difficult to distinguish organic phosphorus species by solid-state NMR than with solution NMR analysis of sample extracts. A combination of solid-state and solution ^{31}P NMR spectroscopy will provide a more promising means for a complete analysis of both inorganic and organic phosphorus species present soils. The quantitative analysis of the ^{31}P NMR spectra is also complicated by the overlapping peaks in the orthophosphate/monoester region, because the observed signals usually have line-widths of tens of hertz and the ^{31}P chemical shift dispersion is small. Overlap is often exacerbated by the presence of paramagnetic metal ions, even if they are in complexes with EDTA following NaOH–EDTA extraction. This problem can be resolved through spectral deconvolution, but the results of deconvolution are highly dependent on the way in which it is carried out, especially on the underlying assumptions regarding the number of peaks present, their lineshape, and identity. There is ongoing debate in the literature concerning the presence of a possible broad based peak irrespective of the procedure used for deconvolution, because organic phosphorus in high molecular weight (polymeric) material could also give rise to the broad feature in the NMR spectra (McLaren et al. 2016). Doolette and Smernik (2015) reviewed the multiple approaches to dealing with the overlap of broad and sharp signals. They suggested that the methods dealing with the NMR spectral overlap in the biomedical literature may be used to analyze the overlapping peaks of soil organic phosphorus after some degree of adaptation, but there was still no standard procedure for overcoming the spectral overlap (Doolette and Smernik 2015). Recently, Vestergren et al. (2012) found that the use of two dimention (2D) ^{1}H-^{31}P correlation spectra could effectively resolve the overlapping after removing the paramagnetic ions and allowed unambiguous identification of different phosphorus species based on their ^{31}P chemical shifts in one dimension and their ^{1}H chemical shifts and signal fine structure in the second dimension. For identification of unknown organic phosphorus compounds, the 2D NMR experiment may be extended to a third dimension that enable the chemical shifts of all hydrogens in the chemical moiety linked to phosphorus to be determined as suggested by Vestergren et al. (2012).

Soil organic phosphorus transformation and its influencing factors during long-term ecosystem development

We summarized the use of solution ^{31}P NMR spectroscopy for characterizing organic phosphorus speciation in soil chronosequences and long-term field experiments (Tables 2, 3, 4 and 5) in order to improve our understanding of the temporal changes, fundamental processes, and associated natural and anthropogenic controls of soil organic phosphorus transformation during long-term ecosystem evolution. Although there are minor differences in the analytical methods among different studies (Tables 2 and 4), the trend and pattern of organic phosphorus transformation during long-term ecosystem evolution could be achieved by considering that the method difference is a systematic error in a single soil chronosequence and/or long-term field experiment.

Soil organic phosphorus transformation and its controls in natural ecosystems based on chronosequence study

The biogeochemical changes during ecosystem development could be studied through the use of chronosequence approach (Walker et al. 2010). The principle of this method is a space-for-time substitution with soils that differ only with respect to time (i.e. soil age) while assuming that all of the other soil-forming factors (e.g. climate, organisms, parent material, relief) remain constant (Huggett 1998; Huang et al. 2015). Although changes in inorganic phosphorus during natural ecosystem development have been extensively studied (e.g. Walker and Syers 1976; Lajtha and Schlesinger 1988; Crews et al. 1995; Richardson et al. 2004; Selmants and Hart 2010; Eger et al. 2011; Huang et al. 2013; Huang et al. 2014; Zhou et al. 2013; Chen et al. 2015; Turner and Laliberté 2015), the use of chronosequence in studies of organic phosphorus transformation is still in its infancy. This is due at least partly to the difficulty in identifying the diverse organic phosphorus speciations in soils. Nevertheless, the recent work by a combination of solution ^{31}P NMR spectroscopy and the chronosequence approach (Tables 2 and 3) have provided evidence that the chemistry of organic phosphorus changes dramatically during long-term ecosystem evolution (e.g. McDowell et al. 2007a; Turner et al. 2007, 2014; Celi et al. 2013; Vincent et al. 2013), which along with inorganic phosphorus and possibly

Table 2 Site conditions of the natural ecosystems used for studying organic phosphorus transformation based on soil chronosequences

Chronosequence Site	Climate	MAP (mm)	MAT (°C)	Vegetation	Parent material	Soil age	Reference	Extractant, time h), soil (g): water (ml) ratio
Manawatu/Reefton, New Zealand	temperate	850	12	forest or scrub	sand-dune	50	McDowell et al. (2007a)	0.25 M NaOH–0.05 M EDTA, 4, 1:20
						500		
						3000		
						10,000		
		2030	11	forest or scrub	alluvium	1000		
						14,000		
						16,000		
						23,000		
						70,000		
						130,000		
Franz Josef, New Zealand	temperate	6520	10.8	angiosperms	post-glacial schist	5	Turner et al. (2007)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
		6576				60		
		6188				130		
		6300				280		
		6278		angiosperms, podocarp		500		
		6427				5000		
		3706				12,000		
		3623				60,000		
		3652				120,000		
Korovsky district, Russia	semi-humid	563	4.2	-	glacial sands	0	Celi et al. (2013)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
				Scots pine		3		
				pine forest		20		
				pine–birch–alder forest		40		
Northern Sweden, Swede	boreal	660	2.7	grey alder	glacial till deposits	90	Vincent et al. (2013)	0.25 M NaOH–0.05 M EDTA, 4, 1:20
				spruce, pine		150		
						1200		
						2700		

Table 2 (continued)

Chronosequence Site	Climate	MAP (mm)	MAT (°C)	Vegetation	Parent material	Soil age	Reference	Extractant, time h), soil (g): water (ml) ratio
						4200		
						5600		
						6800		
						7800		
Haast, New Zealand	temperate	3455	11.3	podocarp, tree ferns	sand dune	181	Turner et al. (2014)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
						290		
						392		
				cunoniaceae,podocarp		517		
						787		
						1826		
						3384		
				cunoniaceae,podocarp		3903		
				ectomycorrhizal tree		4422		
						6500		

Table 3 Changes in organic phosphorus compounds (mg kg^{-1}) determined by solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy during natural ecosystem development using chronosequence approach in the literature

Chronosequence Site	Soil age	Phosphate monoesters						
		Inositol phosphates						Mononucleotides
		myo-IP_6	*scyllo*-IP_6	*D-chiro*-IP_6	*neo*-IP_6	α-glycerophosphate	β-glycerophosphate	
Manawatu/Reefton	50	9	3	33[a]				-[b]
	500	31	18	65				-
	3000	18	18	103				-
	10,000	18	18	149				-
	1000	16	16	81				-
	14,000	35	35	83				-
	16,000	45	45	124				-
	23,000	41	41	98				-
	70,000	15	15	50				-
	130,000	52	5	33				-
Franz Josef	5	-	-	5	-	-	-	-
	60	15	11	56	-	-	-	-
	130	46	30	108	-	-	-	-
	280	28	29	126	-	-	-	-
	500	28	30	118	-	-	-	-
	5000	23	30	76	-	-	-	-
	12,000	22	27	71	-	-	-	-
	60,000	10	12	47	-	-	-	-
	120,000	6	3	35	-	-	-	-
Korovsky district	0	-	-	-	-	-	-	-
	3	-	-	-	-	-	-	-
	20	-	-	-	-	-	-	-
	40	-	-	-	-	-	-	-
Northern Sweden	90	10	8	-	-	35	154	-
	150	2	1	-	-	12	121	-
	1200	0	6	-	-	12	114	12
	2700	217	18	-	-	19	147	25
	4200	5	5	-	-	19	117	13
	5600	80	13	-	-	23	153	17
	6800	10	6	-	-	18	98	10
	7800	6	2	-	-	12	96	12
Haast	181	-	-	-	-			-
	290	151	66	24	-			-
	392	178	61	22	17[c]			-
	517	129	79	19	12			-

Table 3 (continued)

Chronosequence Site	Soil age	Phosphate monoesters						
		Inositol phosphates						Mononucleotides
		myo-IP_6	*scyllo*-IP_6	*D-chiro*-IP_6	*neo*-IP_6	α-glycerophosphate	β-glycerophosphate	
	787	119	76	21	24			-
	1826	63	33	15	7			-
	3384	86	56	14	15			-
	3903	52	31	5	-			-
	4422	63	37	18	-			-
	6500	48	63	17	-			-

Chronosequence Site	Sum	Phosphate diesters			Sum	Phosphonate
		Nucleic acids		Phospholipids		
		DNA	RNA			
Manawatu/Reefton	45	2	-	2	4	2
	114	1	-	2	3	2
	139	5	-	3	8	3
	185	16	-	12	28	7
	113	9	-	3	12	3
	153	27	-	5	32	9
	214	39	-	9	48	22
	180	48	-	8	56	12
	80	11	-	2	13	3
	43	8	-	1	9	2
Franz Josef	5	-	-	-	-	-
	82	14	-	-	14	< 1
	184	24	-	5	29	9
	183	38	-	10	48	23
	176	45	-	13	58	25
	129	31	-	7	31	12
	120	40	-	-	40	14
	69	24	-	-	24	3

Table 3 (continued)

Chronosequence Site	Sum	Phosphate diesters			Sum	Phosphonate
		Nucleic acids		Phospholipids		
		DNA	RNA			
	44	15	-	-	15	-
Korovsky district	-	-	-	-	-	-
	-	-	-	-	-	-
	26	-	-	-	-	-
	19 ~ 217	-	-	9 ~ 70	24 ~ 243	-
Northern Sweden	207	63	-	26	89	-
	136	70	-	53	123	-
	132	92	-	50	142	12
	401	106	-	75	181	25
	146	75	-	34	109	13
	269	85	-	38	123	17
	132	70	-	23	93	10
	116	76	-	35	111	12
Haast	37 ~ 296	-	-	-	5 ~ 52	-
	118 ~ 244	-	-	-	8 ~ 66	0 ~ 2
	120 ~ 278	-	-	-	13 ~ 89	0 ~ 5
	107 ~ 238	-	-	-	11 ~ 85	0 ~ 4
	129 ~ 237	-	-	-	9 ~ 55	0 ~ 4
	87 ~ 119	-	-	-	9 ~ 87	0 ~ 4
	83 ~ 171	-	-	-	7 ~ 98	0 ~ 1
	64 ~ 91	-	-	-	5 ~ 70	-
	69 ~ 117	-	-	-	7 ~ 74	-
	57 ~ 154	-	-	-	7 ~ 88	-

[a] sum of *D-chiro*-IP_6, *neo*-IP_6, α-glycerophosphate and β-glycerophosphate; [b] no data; [c] sum of *neo*-IP_6, α-glycerophosphate and β-glycerophosphate

Table 4 Site conditions of the agricultural ecosystems used for studying organic phosphorus transformation based on long-term field experiments

Site	Climate	MAP (mm)	MAT (°C)	Vegetation	Parent material	Soil treatments	Reference	Extractant, time (h), soil (g): water (ml) ratio
Ginninderra Experiment Station, Australia	temperate	635	12	grass	acid lava	unfertilized low-level fertilized [a] high-level fertilized [b]	McLaren et al. (2016)	0.25 M NaOH–0.05 M EDTA, 16, 1:10
Elora, Stratford, Kincardine, Canada	continental	1000	7	alfalfa, timothy and crop rotation	alluvium	conventional organic manure	Schneider et al. (2016)	0.50 M NaOH–0.10 M EDTA, 16, 1:10
Zürich Organic Fertilizer Experiment	temperate	1040	9	grass and crop rotation	fluvioglacial deposits	non-fertilizer manure compost dried sewage sludge	Annaheim et al. (2015)	0.25 M NaOH–0.05 M EDTA, 16, 1:10
Dehui County, Jilin Province, China	continental monsoon	500 ~ 600	4.4	maize-sobean	phaeozem	moldboard plow ridge tillage no-tillage	Wei et al. (2014a)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
32 sites across the UK	temperate	1000	10	wheat, barley, oats	various	arable	Stutter et al. (2015)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
				grass	various	intensive grassland		
				grass	various	extensive grazing pasture		
Fenqiu State Key Agro-Ecological Experimental Station, Henan Province, China	temperate monsoon	355 ~ 800	13.9	wheat, maize	alluvium	moldboard plow without crop residue moldboard plow with 50% crop residue moldboard plow with 100% crop residue no tillage without crop residue no tillage with 50% crop residue no tillage with 100% crop residue	Wei et al. (2014b)	0.25 M NaOH–0.05 M EDTA, 16, 1:20

Table 4 (continued)

Site	Climate	MAP (mm)	MAT (°C)	Vegetation	Parent material	Soil treatments	Reference	Extractant, time (h), soil (g): water (ml) ratio
Arenas de San Pedro, Southern Avila, Spain	cold continental	1510	14.2	pine	granites	unburned	Turrion et al. (2010)	0.50 M NaOH–0.10 M EDTA, 16, 1:10
						burned		
Dunedin, Otago, New Zealand	temperate	3200	11	flax,	loess, basalt, sandstone, limestone	native	McDowell and Stewart (2006)	0.25 M NaOH–0.05 M EDTA, 16, 1:20
				douglas fir		pasture		
				ryegrass,fog		forest		

[a] fertilized treatment to maintain a target soil phosphorus fertility of 10 ~ 15 mg extractable P kg^{-1} ; [b] fertilized treatment to maintain a target soil phosphorus fertility of 20 ~ 25 mg extractable P kg^{-1}

other nutrient (e.g., carbon and nitrogen) transformations, contributes to the concurrent changes in biological communities and ecosystem functions.

In all of the studied chronosequences under aerobic conditions, soil organic phosphorus determined by solution ^{31}P NMR was dominated by phosphate monoesters, followed by phosphate diesters and phosphonates, irrespective of the different parent materials, vegetation covers and climatic conditions (Tables 2 and 3). The phosphate monoesters in the studied chronosequences occurred mainly as inositol phosphates (e.g., *myo*-IP_6, *scyllo*-IP_6, *D-chiro*-IP_6, and *neo*- IP_6, etc.), while phosphate diesters were dominated by DNA (Tables 2 and 3). This contrasted markedly with a 4000-year-old subtropical peatland from Florida in which phosphate monoesters and diesters maintained approximately equal proportions and the myo-inositol hexakisphosphate was absent (Fisher et al. 2014). In a similar study of organic phosphorus composition in argo-gray soils with periodic water logging, Kovalev and Kovaleva (2011) also found the proportion of phosphate monoesters decreased as the degree of the soil hydromophism increased. The notable difference of organic phosphorus composition in these flooded soils (Kovalev and Kovaleva 2011; Fisher et al. 2014) and other wetland soils (Turner and Newman 2005; Turner et al. 2006) was attributed to the limited reactive clay surfaces for stabilization and/or decomposition of *myo*-inositol hexakisphosphate under frequent anaerobic conditions. It is currently difficult to assess the relative importance of chemical hydrolysis and biological mineralization on the dynamics of inositol phosphates in soils. On the one hand, the reduction of metal oxides under reducing conditions could release the associated inositol phosphates for biological attack (Kovalev and Kovaleva 2011; Fisher et al. 2014) and this would affect the availability of inositol phosphates for hydrolysis. On the other hand, there is evidence that inositol phosphates could be mineralized by various soil microorganisms (Cosgrove 1970; Chen et al. 2004; Giaveno et al. 2010). A better understanding of inositol phosphate dynamics in soils will require a comprehensive assessment of the reactivity of various stereoisomers of inositol phosphates with soil constituents as well as the efficiency of inositol phosphate mineralization by different microorganisms.

McDowell et al. (2007a) investigated the proportions and concentrations of different organic phosphorus forms within two chronosequences (Manawatu and Reefton) in order to build the organic phosphorus

Table 5 Changes in organic phosphorus compounds (mg kg^{-1}) determined by solution ^{31}P nuclear magnetic resonance (NMR) spectroscopy in agricultural ecosystems based on long-term field experiments in the literature

Site	Soil Treatments	Inositol phosphates				Total phosphomonoesters	Nucleic acids		Total phosphodiesters	Phosphonate
		myo-IP_6	scyllo-IP_6	α-glycerophosphate	β-glycerophosphate		DNA	RNA		
Ginninderra Experiment Station, Australia	unfertilized	5.1	3.9	7.2[a]		66.0	-[b]	-	3.6	-
	low-level fertilized	6.5	4.9	10.7[a]		90.1	-	-	7.5	-
	high-level fertilized	6.1	4.2	10.1 [a]		83.4	-	-	6.4	-
Ontario, Canada	conventional	17.9	14.5	4.8	8.7	184	3.2	-	17	3.1
	organic	19.5	19.0	6.0	10.1	226	4.4	-	23	3.6
Zürich Organic Fertilizer Experiment	non-fertilizer	29	12	5 [a]		54	-	-	-	-
	manure	23	11	4 [a]		49	-	-	-	-
	compost	23	12	5 [a]		51	-	-	-	-
	dried sewage sludge	34	12	8 [a]		61	-	-	-	-
Dehui County, Jilin Province, China	moldboard plow	-	-	-	-	98 (73 ~ 94)[c]	-	-	3.5 (2.1 ~ 5.7)[a]	-
	ridge tillage	-	-	-	-	80 (68 ~ 83)[c]	-	-	2.8 (1.8·6.2)[a]	-
	no-tillage	-	-	-	-	79 (67 ~ 82)[c]	-	-	3.0 (1.2 ~ 5.0)[a]	-
32 sites across the UK	arable	-	-	-	-	243 (105 ~ 446)[d]	-	-	0	0
	intensive grassland	-	-	-	-	401 (200 ~ 658)[d]	-	-	9 (0 ~ 50)[d]	0
	extensive grazing pasture	-	-	-	-	353 (37 ~ 621)[d]	-	-	50 (0 ~ 102)[d]	17 (0 ~ 80)[d]
Fenqiu State Key Agro-Ecological Experimental Station, Henan Province, China	moldboard plow without crop residue	-	-	-	-	26.2 (20.8 ~ 25.4)[c]	-	-	9.1 (3.4 ~ 5.5)[c]	-
	moldboard plow with 50% crop residue	-	-	-	-	21.1 (24.4 ~ 28.2)[c]	-	-	8.4 (4.4 ~ 6.2)[c]	-
	moldboard plow with 100% crop residue	-	-	-	-	29.4 (27.0 ~ 39.7)[c]	-	-	10.4 (6.2 ~ 11.1)[c]	-
	no tillage without crop residue	-	-	-	-	25.8 (22.5 ~ 23.4)[c]	-	-	7.3 (4.6 ~ 5.9)[c]	-
	no tillage with 50% crop residue	-	-	-	-	26.9 (24.6 ~ 33.9)[c]	-	-	9.1 (9.0 ~ 10.1)[c]	-
	no tillage with 100% crop residue	-	-	-	-	32.5 (26.9·46.5)[c]	-	-	11.5 (6.0 ~ 18.6)[c]	-
Southern Avila, Spain	unburned	-	-	-	-	117 ~ 118	13 ~ 16	-	-	-
	burned	-	-	-	-	62 ~ 86	0 ~ 12	-	-	-
Dunedin, Otago, New Zealand	native	-	-	-	-	158 ~ 369	-	-	10 ~ 60	-
	pasture	-	-	-	-	209 ~ 848	-	-	7 ~ 43	-
	forest	-	-	-	-	102 ~ 337	-	-	6 ~ 25	-

[a] sum of α-glycerophosphate and β-glycerophosphate; [b] no data [c] Values in the parentheses represent organic phosphorus concentrations in different size fractions; [d] Values in the parentheses represent organic phosphorus concentrations in different site; Note data for the Ginninderra Experiment Station are only collected for 0–10 cm at the site of 9 sheep ha^{-1}

dynamics into Walker and Syers' (1976) phosphorus transformation model during natural pedogenesis. They found that the major phosphorus compounds in the studied soils extracted by NaOH-EDTA was orthophosphate (on average 45% of total extracted phosphorus defined as $P_{NaOH\text{-}EDTA}$), followed by phosphate monoesters (on average 28% of $P_{NaOH\text{-}EDTA}$), phosphate diesters (on average 7% of $P_{NaOH\text{-}EDTA}$), pyrophosphate (on average 4% of $P_{NaOH\text{-}EDTA}$), phosphonates (0 ~ 2% of $P_{NaOH\text{-}EDTA}$) and polyphosphates (0 ~ 2% of $P_{NaOH\text{-}EDTA}$). The monoester subclasses *myo*-inositol hexakiphosphate and *scyllo*-inositol hexakisphosphate comprised, on average, 10% and 5% of $P_{NaOH\text{-}EDTA}$. The diester subclasses DNA and phospholipids constituted, on average, 5% and 1% of $P_{NaOH\text{-}EDTA}$. In the older Reefton chronosequence (1 ~ 130 ka), phosphate esters (including phosphate monoesters and diesters) and phosphonates increased with age to reach a maximum and then declined with time as the readily available phosphorus became scarcer (Tables 2 and 3). In the relatively young Manawatu chronosequence (0 ~ 10 ka), however, phosphate esters and phosphonates increased consistently with soil age (Tables 2 and 3). The Manawatu chronosequence may not be old enough to study the threshold for organic phosphorus changes, especially for those that are more resistant to chemical degradation and microbial mineralization. There was no trend in organic polyphosphates changes in the studied soils due to its extremely low concentrations. The monoester to diester ratio as well as the relative proportion of *myo*-inositol hexakisphosphate to *scyllo*-inositol hexakisphosphate tended to decrease with soil age in both chronosequences. The buildup of labile phosphorus species (diesters and pyrophosphate) and *scyllo*-inositol hexakisphosphate in the Reefton and Manawatu chronosequences was attributed to the increase of microbial biomass, while the decline of highly sorptive and recalcitrant *myo*-inositol hexakisphosphate with time was attributed to the reduction of mineral sorptive sites by continuous weathering (McDowell et al. 2007a). In addition, the mineralization of *myo*-inositol hexakisphosphate by ectomycorrhizal fungi in soils under pine seedlings (Chen et al. 2004) may also explain the decline of *myo*-inositol hexakisphosphate during natural pedogenesis. Several studies have shown that *scyllo*-inositol hexakisphosphate is more resistant to phytase activity than *myo*-inositol hexakisphosphate as reviewed by Turner (2007). Greaves et al. (1967) reported that phytase isolated from *Aerobater aerogenes*, a Gran-negative facultative anaerobic bacteria, had no activity towards *scyllo*-inositol hexakisphosphate. In contrast, Cosgrove (1970) found that the "SB2" phytase from a soil *Pseudomonas* sp. was active towards *scyllo*-inositol hexakisphosphate, but the rate of hydrolysis was slowest among the four isomers tested, being in the order of *myo*- > *neo*- > D-*chiro*- > *scyllo*-. The rates of mineralization not only vary significantly among various stereoisomers of inositol phosphates, but also differ substantially among soils (Cosgrove 1970; Chen et al. 2004; Giaveno et al. 2010). Further studies are required to elucidate the precise mechanisms involved in the stabilization and turnover of different stereoisomers of inositol phosphates as well as other soil organic phosphorus compounds in order to better understand phosphorus transformations during ecosystem evolution. Turner et al. (2007) studied organic phosphorus transformations along a 120,000-year postglacial chronosequence at Franz Josef on the west coast of the South Island in New Zealand. They found that inositol phosphates, DNA, phospholipids, phosphonates and total phosphorus extracted by NaOH-EDTA solutions accumulated rapidly during the first 500 years of soil development characterized by nitrogen limitation of biological productivity, but then declined slowly to low concentrations in older soils characterized by intensive phosphorus limitation (Tables 2 and 3). The proportion of inositol hexakisphosphate (considered to be relatively recalcitrant) to total organic phosphorus declined markedly in older soils, coinciding with the decline of amorphous metal oxides resulted from mineral crystallization during pedogenesis. In contrast, DNA (considered to be relatively bio-available) increased as a proportion of total organic P as soils age, which they attributed to the incorporation within organic structures that provide protection from biological attack. The whole-ecosystem phosphorus budget (including estimates of phosphorus in plant biomass, soil microbial biomass, and other soil pools) in the same chronosequence demonstrated the dominance of microbial phosphorus (accounting for 68 ~ 78% of total biomass phosphorus) in the mature soils (Turner et al. 2013). The large disparity between the amounts of phosphorus in plants and microorganisms in the late stages of the Franz Josef chronosequence may reflect the organisms' intense competition for available phosphorus, resulting in alterations of organic phosphorus compositions (Turner et al. 2007). This may in turn affect biological communities by favoring species with root symbiotic associations adapted to acquire phosphorus from the organic and recalcitrant inorganic phosphorus dominated in highly-weathered

soils. Therefore, changes in organic phosphorus occurred in coincidence with the marked shifts in plant and microbial communities across the Franz Josef chronosequence. In addition, the progressive depletion of soil phosphorus during ecosystem evolution may drive plants and microorganisms to evolve more effective in enhancing mineral weathering and phosphorus recycling (e.g. Quirk et al. 2012). Despite the complex coupling and feedbacks between biological communities and phosphorus speciations, Turner et al. (2007) suggested that soil organic phosphorus transformation and dynamics during the 120,000-year of pedogenesis was regulated by three main factors: variations of the potential for phosphorus stabilization resulting from mineralogical transformation, changes in phosphorus sources and inputs due to shifts in plant and microbial communities, and differences in the biological utilization of various phosphorus compounds. The two pioneer studies of chronosequential changes of soil organic phosphorus forms during long-term ecosystem evolution (McDowell et al. 2007a; Turner et al. 2007) not only complement Walker and Syers' (1976) phosphorus transformation model, but also demonstrate the increasing reliance on organic phosphorus nutrition at the later stage of weathering due to the depletion of available inorganic phosphorus.

More recently, the development of soil phosphorus pools during natural revegetation of *Pinus sylvestris* on disused sand quarries in Northwestern Russia was examined by Celi et al. (2013) in order to understand biogeochemical cycling of phosphorus and the recovery of soil functionality during initial stages of pedogenesis. Rapid transformation of soil properties occurred within 40 years, with a marked decline in soil pH and an accumulation of organic matter. Phosphorus transformations were shaped by geochemical processes, with a rapid release of inorganic phosphorus from primary minerals and accumulation of organic phosphorus to concentrations exceeding those found in the undisturbed site. The adsorbed or precipitated phosphorus increased rapidly in spite of the relatively low reactive mineral surfaces. The phosphate monoester and diesters increased with time and enriched in the surface horizon, although these species were not detected in soils less than 20 years of revegetation (Tables 2 and 3). The natural succession of Scots pine in post-mining landscapes thus promotes ecosystem restoration through the rapid re-establishment of the biogeochemical cycles of organic matter and phosphorus. Vincent et al. (2013) used 1-dimensional ^{31}P and 2-dimensional ^{1}H, ^{31}P correlation NMR spectroscopy to characterize soil organic phosphorus transformations in humus horizons across a 7800-year old chronosequence in Västerbotten, northern Sweden. The results showed that the largest changes in soil organic phosphorus composition tended to occur in young sites which also experience the largest shifts in plant community composition (Tables 2 and 3). The concentrations of DNA, 2-aminoethyl phosphonic acid, and polyphosphate increased initially (< 3000 yrs) and then declined, while the abundances of α- and β-glycerophosphate, nucleotides, and pyrophosphate were higher at the youngest site compared with other sites (Tables 2 and 3). The contents of inositol hexakisphosphate (e.g., *myo*-IP_6, *scyllo*-IP_6) fluctuated with soil age (Tables 2 and 3). Based on the 2-dimensional NMR spectra, approximately 40% of the extractable organic phosphorus in the studied soil chronosequence appeared to originate from living microbial cells, suggesting a link between microbial dynamics and soil organic phosphorus composition. In a similar young chronosequence (0 ~ 6500 years) at Haast on the west coast of the South Island in New Zealand, Turner et al. (2014) found that the concentrations of DNA, phospholipids, and long chain polyphosphate increased markedly in the organic horizon of older sites while inositol hexakisphosphate was abundant in mineral soils and its concentration peaked in the intermediate age. In contrast to previous reports of simultaneous declines in inositol hexakisphosphate and amorphous metal oxides in the late of stage of pedogenesis (McDowell et al. 2007a; Turner 2007), there were no evidence for unidirectional changes in geochemical sinks for inositol hexakisphosphate with time along the relatively young chronosequences (< 10,000 years) (Vincent et al. 2013; Turner et al. 2014). Based on previous results, Turner et al. (2014) proposed two mechanisms that may explain the decline of inositol hexakisphosphate with time in different sites (Tables 2 and 3): (i) the decline of stabilization potential as supported by the strong relationships between inositol hexakisphosphate and amorphous metal oxides during pedogenesis (McDowell et al. 2007a; Turner 2007); and (ii) the declining phosphorus availability favors organisms' utilization of inositol hexakisphosphate, which is confirmed by the absence of inositol hexakisphosphate in spite of abundant stabilization potential (Vincent et al. 2013; Turner et al. 2014).

The analysis of results from Tables 2 and 3 highlights that comparative studies between various chronosequences

are a potentially powerful way to elucidate the origins, dynamics, and controls of organic phosphorus during natural pedogenesis. This also helps us to understand and evaluate the presence and performance of plants or microorganisms during long-term ecosystem development, because organisms vary in the extent to which they are adapted to acquire phosphorus from various forms in soils. However, quantitative data on the feedbacks between organic phosphorus and biological communities are still fragmentary and insufficient to draw firm conclusions on how plants and microorganisms affect or respond to the various organic phosphorus compounds. More soil chronosequences are thus needed to be established for investigating the dynamic changes of organic phosphorus and biological communities as well as their complex interactions in order to answer this question.

Soil organic transformation and its controls in agricultural ecosystems based on long-term field experiments

In addition to the data from chrono- and environmental sequences of soils, information on the organic phosphorus cycling and its controlling factors can be obtained from the long-term field experiments. There is a growing body of literature on the characteristics of organic phosphorus species in agricultural soils with differing land uses, fertilizer inputs and edaphic properties, which significantly improves our understanding of organic phosphorus transformation in relation to changes in the type and intensity of land uses and variations of fertilizer applications and/or tillage practices.

It is well known that the anthropogenic phosphorus additions can significantly alter the rates of total and inorganic phosphorus accumulation as well as inorganic phosphorus forms in agricultural soils (e.g. Huang et al. 2013). In contrast, the type and amount of organic phosphorus are less affected by phosphorus additions than inorganic phosphorus species (Gatiboni et al. 2005; Dou et al. 2009; Requejo and Eichler-Löbermann 2014; Annaheim et al. 2015; Schneider et al. 2016; McLaren et al. 2016). For instance, the comparison of soils from long-term (>20 years) organically and conventional managed forage fields showed that organic phosphorus compounds were more abundant in organic managed systems (Tables 4 and 5), but the difference of organic phosphorus compounds between these two managed systems was not statistically significant (Schneider et al. 2016). However, McLaren et al. (2016) reported that the total phosphate monoesters and diesters in the surface pasture soils (0 ~ 10 cm) with phosphate fertilization were significantly higher than those without fertilization, but there was no significant alteration of specific forms of phosphate monoesters (e.g., *myo*-inositol hexakisphosphate and RNA mononucleotides) (Tables 4 and 5). Annaheim et al. (2015) studied the effects of 62 years of application of three organic fertilizers (diary manure, compost and dried sewage sludge) on organic phosphorus forms in a field experiment on a slightly acidic Luvisol in northern Switzerland. They found that despite the presence of different forms of organic phosphorus in the applied organic fertilizers, the corresponding soil organic phosphorus forms (e.g. myo-IP_6, scyllo-IP_6, and the sum of α-glycerophosphate and β-glycerophosphate) remained largely unaffected by 62 years of different fertilization treatments (Tables 4 and 5). The similar composition of organic phosphorus in all treatments suggests that the specific organic phosphorus compounds added with the three organic phosphorus fertilizers were completely transformed in the soil or lost from it. This may be related to the rapid turnover of organic phosphorus by soil microorganims (Oberson and Joner 2005; Achat et al. 2010a), which has been widely recognized to enhance phosphorus availability to plants and accelerate phosphorus cycling (Richardson and Simpson 2011). The long-term field experiment conducted in Northern Germany (Requejo and Eichler-Löbermann 2014) confirmed that organic phosphorus forms in soil are more reliant on the turnover processes than on the forms of phosphorus added by 14 years of different phosphorus amendments (control, cattle manure, biowaste compost, and biowaste compost in combination with triple-superphosphate). The little effects of different fertilizer treatments on organic phosphorus forms was further confirmed by the study of Dou et al. (2009), showing that soils receiving ≥8 years of dairy, poultry, swine manure or spent mushroom compost had similar concentrations of inositol hexakisphosphate (52 ~ 116 mg P kg^{-1}) compared with the untreated soils (43 ~ 137 mg P kg^{-1}). In addition, Gatiboni et al. (2005) found that the phosphate monoesters and diesters remained relatively constant after 15 successive crops in a very clayey Rhodic Hapludox that received different phosphorus application rates (0, 156, and 312 kg P ha^{-1}). Similarly, there is also no marked change in organic phosphorus speciation in plant tissues regardless of the different phosphorus application rates (5, 30, 60 kg P

ha^{-1}) as examined by Noack et al. (2014). Thus, the large pool of organic and inorganic phosphorus applied to croplands does not accumulate in soils or plants either caused by off-site transport losses or resulted from in situ biological activities (i.e. biodegradation). More research is required to fully understand the uptake, retention, migration and transformation of applied organic and inorganic phosphorus in agricultural soils. There is also a need to measure the microbial biomass phosphorus and phosphatase activity in soils with and without phosphorus fertilization to elucidate both potential and actual rates of organic phosphorus mineralization, which is important to evaluate the balance and dynamics of soil organic phosphorus.

Despite the little change of organic phosphorus forms under different fertilizer treatments, variations of organic phosphorus compositions in relation to tillage practices have been observed in many agricultural soils (Vu et al. 2009; Cade-Menun et al. 2010; Redel et al. 2011; Abdi et al. 2014; Wei et al. 2014a, b). For instance, a field experiment was conducted by Wei et al. (2014a) to study the effects of tillage practices (moldboard plow, ridge tillage, and no-tillage) on the distribution of soil phosphorus composition in different size fractions of aggregates (>2, 1 ~ 2, 0.25 ~ 1, <0.25 mm) at the 0 to 20 cm depth in northeastern China. The results showed that soils under moldboard plow had higher organic phosphorus (monoesters and diesters, Tables 4 and 5) contents in bulk soil and different size fractions compared to the ridge tillage and no-tillage treatments, suggesting that moldboard plow may be the right practice to conserve organic phosphorus under cold monsoon climate. In a similar study, Wei et al. (2014b) evaluated how tillage systems (conventional tillage and no tillage) and crop residue management (0, 50%, 100% crop residue coverage) affect phosphorus composition and phosphatase activities in soil aggregates (> 2 mm, 0.25 ~ 2 mm, 0.05 ~ 0.25 mm) in subtropical China. They found that no tillage with crop residue input could increase organic phosphorus store and sustainable supply in soil aggregates (Tables 4 and 5). In addition, the results demonstrated that 0.25 ~ 2 mm size aggregates play an important role in soil organic phosphorus maintenance and transformation. The influence of soil aggregate size on phosphorus changes was also observed in a soil cultivated intermittently in New Zealand (McDowell et al. 2007b), which showed that the smaller aggregates had higher content of orthophosphate, phosphate monoesters and diesters, and pyrophosphate. By investigating the effects of tillage systems (no tillage and conventional tillage) and crop rotation (oat-wheat and lupine-wheat) on organic phosphorus forms in a Chilean Utisol, Redel et al. (2011) found that phosphate monoesters were larger under no tillage than conventional tillage and that lupine-wheat rotation had higher organic phosphorus content than oak-wheat rotation in both tillage systems. Furthermore, Redel et al. (2011) demonstrated that the tillage effects were greater than crop rotation effects in enhancing phosphorus availability. In addition to the variations of soil organic phosphorus compositions among different tillage practices, some researchers have shown that tillage practices could change the distribution of phosphorus forms in the soil profile. Abdi et al. (2014) found that the liable inorganic phosphorus concentrated in the topsoil (0 ~ 5 cm) and organic phosphorus (e.g., scyllo-IP_6, nucleotides) accumulated in the deeper layer (10 ~ 20 cm) under no-tillage as compared with moldboard plow. The phosphorus stratification under no-tillage was reported elsewhere and was attributed to the lack of mixing of applied fertilizer (Vu et al. 2009; Cade-Menun et al. 2010).

In addition to investigating the response of organic phosphorus to different fertilizer treatments and tillage practices, the effects of land uses and soil properties on organic phosphorus compounds were also evaluated by different researchers. For instance, the investigation of organic phosphorus distribution in 32 temperate soils with differing land uses and edaphic properties (Stutter et al. 2015) demonstrated that a number of biotic and abiotic processes resulted from the complex interplay of land uses and soil properties control the organic phosphorus concentrations and species abundance in the studied soils. Stutter et al. (2015) showed that arable soil phosphorus was dominated by inorganic orthophosphate (276 ~ 2520 mg kg^{-1}) and phosphate monoester (105 ~ 446 mg kg^{-1}), while the phosphate diester and polyphosphate (< 10 mg kg^{-1}) was limited. Intensive grassland had inorganic orthophosphate concentrations (233 ~ 842 mg kg^{-1}) similar to phosphate monoesters (200 ~ 658 mg kg^{-1}), which were much higher than phosphate diester (0 ~ 50 mg kg^{-1}) and polyphosphate (1 ~ 78 mg kg^{-1}). As grazing became more extensive, soil phosphorus was dominated by diverse organic phosphorus, with phosphate monoesters (37 ~ 621 mg kg^{-1}) greater than phosphate diester (0 ~ 102 mg kg^{-1}) and polyphosphate (0 ~ 108 mg kg^{-1}). McDowell and Stewart (2006) also examined the influence of pastoral, native and forest land use on organic phosphorus forms

in soils with contrasting properties and found that phosphate diesters were greatest in native soils (10 ~ 60 mg P kg^{-1}) and declined in pasture (7 ~ 43 mg P kg^{-1}) and forest (6 ~ 25 mg P kg^{-1}) soils (Tables 4 and 5), coinciding with the decrease of the diester to monoester ratio. McDowell and Stewart (2006) suggest that both soil properties and land use influence the distribution of phosphorus in inorganic and organic forms with different availability. Studies of organic phosphorus composition across environmental gradients also demonstrated that soil properties exert a strong control on the amounts and forms of organic phosphorus in soils. Turner and Engelbrecht (2011) found a greater proportion of organic phosphorus in the form of phosphate monoesters in neutral soils with high concentrations of phosphorus and organic matter, whereas the contribution of phosphate diesters to organic phosphorus was greater in acidic soils low in phosphorus and organic matter across a tropical rainfall gradient (1730 ~ 3404 mm $yr.^{-1}$). The preferential accumulation of phosphate diesters (DNA) and phosphonates in acidic soils was confirmed by Turner and Blackwell (2013) and Cheesman et al. (2014). By investigating soil organic phosphorus species along two groundwater recharge and discharge gradients in Fennoscandian boreal forest, Vincent et al. (2012) found that phosphate diesters and their degradation products, as well as polyphosphates, were proportionally more abundant in low Al and Fe sites, whereas phosphate monoesters such as *myo-*, *scyllo-* and unknown inositol phosphates dominated in high Al and Fe soils due to the stabilizing effect of these metal oxides that protect inositol phosphate from microbial degradation. Compared with the non-basaltic soils, Murphy et al. (2009) showed that basaltic soils with larger Fe and Al content had higher concentration of phosphate monoesters. The long-term effects of fire on organic phosphorus composition in forest Cambisols were examined by Turrion et al. (2010). They found that the fire-induced changes on the structure of alkali-soluble phosphorus were an increase in orthophosphate and a decrease in phosphate monoester and diester (DNA). However, the diester to monoester ratio was not sensitive to the fire effect.

In summary, soil organic phosphorus compounds not only change with natural ecosystem development over time scales more than thousands of years due to chronic changes of soil properties and biological communities, but also change with agroecosystem development over time scales less than decades due to anthropogenic managements. The amounts, forms, and dynamics of organic phosphorus in agricultural soils are determined by both internal soil properties and external environmental conditions, which are in turn influenced by the history and intensity of land use, different tillage practices and fertilizer treatments. These mechanisms are interlinked and more long-term field experiments are required to isolate both internal (soil properties) and external (environmental conditions) factors that regulate organic phosphorus transformations in agricultural soils.

Summary and perspectives

With the use of ^{31}P NMR spectroscopy in soil science for more than twenty years, organic phosphorus compounds have been characterized both in native soils under natural vegetation and agricultural soils subjected to intensive anthropogenic managements. This has significantly advanced our understanding of the amounts, forms and dynamics of organic phosphorus and its controls in native and agricultural ecosystems. Given the universal dependence on organic phosphorus for life and its critical roles in biogeochemical cycling (Gulick 1955; Smil 2000; Vance et al. 2003), more natural chrono- and environmental sequences as well as anthropogenic field experiments need to be studied in combination with the use of state-of-the-art techniques to better understand the basic principles and mechanisms governing organic phosphorus transformation under different conditions and to develop extensive databases for quantitatively modelling these changes. We put forward three potential goals for future organic phosphorus research based on a need to develop effective management strategies that optimize the use of organic phosphorus for plant nutrition and minimize the adverse impacts on environment.

Rates, pathways and thresholds of soil organic phosphorus transformation

Despite sustained efforts to understand the intricate chemistry of organic phosphorus dynamics during long-term ecosystem development, the rates, pathways and thresholds of organic phosphorus transformation in soils remain largely unknown. This is due partly to the concurrent formation and mineralization of different organic phosphorus compounds in soils as well as the difficulty in differentiating biological, chemical and

physical properties and processes that determine these changes. Nevertheless, there has been substantial progress on mineralization rates of total organic phosphorus or microbial biomass phosphorus based on incubation experiments (Achat et al. 2010a; Achat et al. 2010b; Bünemann et al. 2007; Bünemann 2015; Oehl et al. 2001; Oehl et al. 2004). The rates measured in the laboratory should be compared to rates derived in the field. Further studies on the residence time and turnover of both living and non-living organic phosphorus in different soils are required to elucidate the relative importance of biological and biochemical processes in organic phosphorus transformation. There is also a need to investigate rates and controls of changes in different organic phosphorus compounds across various chronosequences in order to formulate numerical models that can predict future soil organic phosphorus transformations. For agricultural ecosystems, a comprehensive understanding of organic phosphorus cycling requires not only to quantify fertilizer phosphorus uptake by organisms (especially the plants and microorganisms) and retention in soils but also to determine to which extent and over which time period fertilizer phosphorus stored in soil microorganisms and organic matter is released again for cop uptake.

How does soil organic phosphorus transformation affect or respond to changes of nutrient status and biological communities

The recent study of carbon-driven mineralization of organic phosphorus during early stage of soil development (Wang et al. 2016) highlights the coupling between carbon and organic phosphorus cycling in the newly established ecosystems. Linkages between nitrogen and organic phosphorus cycling have also been demonstrated by the co-limitation of terrestrial ecosystem by nitrogen and phosphorus according to Elser et al. (2007) and Vitousek et al. (2010). More specifically, the investigation of 29 temperate pasture soils from England and Wales demonstrated negative correlations between *scyllo*-inositol hexakisphosphate concentrations and carbon/nitrogen-to-organic phosphorus ratios (Turner et al. 2005). These studies provide tentative evidence that nutrient status regulates organic phosphorus dynamics. In addition to nutrient status, the plant and microbial communities that co-vary with changes in organic phosphorus compositions (Turner et al. 2007) may also act as important drivers of organic phosphorus transformation. Given organic phosphorus consists of a variety of compounds that differ markedly in their behavior and bioavailability, it is expected that different organic phosphorus compounds would have different response time to the changes of nutrient status and biological communities during long-term ecosystem development. Future researches concerning the interactions of organic phosphorus transformation, nutrient status and biological communities are needed to elucidate the complex reality of organic phosphorus changes. This would require a multidisciplinary approach involving the development and application of appropriate molecular biology (Nannipieri et al. 2012) and isotope labeling methods (Tamburini et al. 2012). Such knowledge will provide a basis for management strategies that promote sustainable use of organic phosphorus for plant nutrition and ecosystem function.

Quantitative models for soil organic phosphorus transformation

Soil organic phosphorus transformation during ecosystem development comprises a set of interconnected physical, chemical and biological processes that function as a whole transferring mass and energy under the influences of both natural and anthropogenic forcings, which is characterized by multiple nonlinear responses and thresholds with linkages between disparate components. Future advances in soil organic phosphorus transformation will require careful application of numerical models that quantitatively describe the past and present changes of different organic phosphorus compounds and forecast their variation trends in the future. The recent development of a numerical modeling approach for data evaluation (Müller and Bünemann 2014) provides new opportunities to study microbial phosphorus transformations, but the extrapolation of this model to fields under non-steady-state conditions (e.g. in the presence of a growing plant, under drying-rewetting conditions, or with continuous phosphorus additions) requires further evaluation. It should be noted that the quantitative models for inorganic phosphorus transformation have been established in a wide variety of native and agricultural ecosystems (e.g. Walker and Syers 1976; Crews et al. 1995; Huang et al. 2013; Turner and Laliberté 2015). Similar approaches could be applied to modeling organic phosphorous transformation with the inclusion of how environmental conditions and

human activities influence individual organic phosphorus species.

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