Title

Crop residue contributions to phosphorus pools in agricultural soils: a review

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1. Summary

The phosphorus (P) content of crop residues and its availability to a subsequent crop can range from agronomically insignificant, to quantities in excess of crop P requirement. However, the contribution of crop residues to the P nutrition of subsequent crops has not been widely recognised, and simple predictive tools are lacking. By reviewing the published literature in which quantitative measurements of P transformations from plant residues applied to soil have been reported, we have evaluated the contribution of crop residue-derived P to the P nutrition of subsequent crops, assessed the key factors involved and summarised the knowledge as an empirical model. The contribution of crop residues to P availability is likely to be significant only under conditions where large amounts of crop residues of relatively high P concentration are applied to soil. Crop residues with low P concentration, such as cereal stubble (eg. due to re-translocation of a large proportion of stubble P into grain), will not make an agronomically significant contribution to soil P availability, but may reduce P availability due to assimilation in the microbial biomass. However, a productive green manure crop may release sufficient P to meet the requirements of a subsequent cash crop. The release of P from crop residues is significantly reduced in systems where the P-status of crops and soils is low, which reinforces the reliance on external P inputs for sustained crop productivity. The large variability in the potential contributions of plant residues to the P nutrition of subsequent crops suggests that there is a strong need to integrate model predictions of organically-cycled P with current fertiliser management strategies.

2. Introduction

Optimising phosphorus (P) use efficiency will deliver agronomic, economic and environmental benefits as agricultural production systems adjust to meet future global food production targets (Heffer and Prud'homme, 2013). Such optimisation will rely on adequate knowledge of the dynamics of soil P pools

to enable accurate predictions of the required external P inputs to achieve optimum growth of subsequent crops. While our understanding of soil inorganic phosphate (Pi) pools is relatively comprehensive, the value of P returned to the soil in crop residues has not been fully resolved. Agronomically significant amounts of P can be present in crop residues and the microbial biomass associated with their decomposition, and the potential contribution of this pool to the P nutrition of cropping systems is significant (*eg.* Chauhan *et al.*, 1979; Dalal, 1979; White and Ayoub, 1983; Thibaud *et al.*, 1988; Umrit and Friesen, 1994; Kwabiah *et al.*, 2003a; Nachimuthu *et al.*, 2009). The main factors influencing the amount of crop residue P, its rate of mineralisation and subsequent availability to crops have been identified (Stockdale and Brookes, 2006; Guppy and McLaughlin, 2009; Simpson *et al.*, 2011); but their interactions remain poorly elucidated and largely unquantified. By reviewing the published literature in which quantitative measurements of P transformations from plant residues applied to soil have been reported, we will evaluate the contribution of crop residue-derived P to the P nutrition of subsequent crops, assess the key factors involved and summarise the knowledge as an empirical model.

The dynamics of organically-derived nitrogen (N) and carbon (C) in agricultural soils has been extensively described, and a wide range of predictive tools have been developed. These have proved a valuable asset for landholders, agronomists and policy makers by providing good estimates of the impacts of agronomic management options on the dynamics of both C (*eg.* Parton *et al.*, 1988; Coleman and Jenkinson, 1999; Grace *et al.*, 2006) and N (see Herridge *et al.*, 2008) in agricultural soils. Considering our extensive knowledge of the N cycle in agricultural systems, and the benefits (economic, social and environmental) that have been obtained by our ability to predict and manipulate it, similar knowledge of the organic P cycle could also yield significant benefits. Yet, although the principal driving factors of organic P cycling have long been recognised and modelled (Cole *et al.*, 1977), models have not proven to be universally applicable (Gijsman *et al.*, 1996; Schnepf *et al.*, 2011). Several models have demonstrated a capacity to incorporate P release from crop residues and manures into projected crop growth and yield, notably The Agricultural Production Systems Simulation (APSIM) (Keating *et al.*, 2003),

Century (Parton *et al.*, 1988) and CERES-Wheat (Ritchie *et al.*, 1988; Godwin *et al.*, 1989; Singh *et al.*, 1991; Daroub *et al.*, 2003) modelling frameworks. However, these models require detailed climate and site information that may not be available, and are specialised tools that cannot be operated by the layperson. The contribution of crop residue P to the nutrition of subsequent crops has not been widely recognised, and there is currently no decision support system (DSS) that can predict it from a simple, readily-available set of variables.

Plant uptake of residue-derived P has predominantly been evaluated using isotope labelling and isotopic dilution methodologies. Residues labelled with ^{32}P or ^{33}P isotopes have been applied to soil, enabling the differentiation of residue-derived P, native soil P and mineral fertiliser P through the plant-soil system (eg McLaughlin and Alston, 1986). Such studies have typically been conducted over a short term (1-2 months), according to the half-life of the available P isotopes, with the amounts of residue-derived P recovered in plants generally being 5 % to 10 % of the total P content of the residues (Blair and Boland 1987; Nachimuthu *et al.*, 2009), 20 to 30% (Umrit and Friesen, 1994) and as high as 40% (Dalal, 1979). Similarly, a large proportion of crop residue P is generally recovered from soil as inorganic P (P_i) in plant-available and sorbed pools (Chauhan *et al.*, 1979; White and Ayoub, 1983; Kwabiah *et al.*, 2003a) in proportions similar to those observed when P is applied as mineral P fertiliser (Friesen and Blair, 1988; Cong and Merckx, 2005).

Where P pools and mineralisation were measured over a period of decades, rotation management has been shown to have a significant effect on the dynamics and partitioning of soil P. In the context of a pasture/cereal cropping rotation, Bünemann *et al.* (2006) measured accumulation of P in the organic fraction during a wheat/pasture rotation at $\sim 2 \text{ kg ha}^{-1} \text{ year}^{-1}$ (a trend previously reported by McLaughlin *et al.*, 1988), but no accumulation under continuous cropping. Soil organic matter has been shown to increase under legume pasture phases, with subsequent release of nutrients through mineralisation of

the organic matter during cropping phases (*cf.* Simpson *et al.*, 2011). Although the accumulation of soil N is usually the focus of pasture phases, there is also the potential for pasture or green manure phases to augment soil P availability in the subsequent cropping phase (Horst *et al.*, 2001). Interestingly, pulse crops including chickpea, white lupin, and faba bean have been shown to enhance the P nutrition of subsequent cereal crops even when legume residues have been removed from the soil (Nuruzzaman *et al.*, 2005; Rose *et al.*, 2010), and some legume genotypes improve the P nutrition of subsequent cereals more than others (Rose *et al.*, 2010b). However, the mechanism(s) responsible for this are not clear, the impact of the time lapse between legume harvest and subsequent cereal sowing on potential P benefits is unresolved, and there are currently insufficient data to incorporate such mechanisms into predictive models for P turnover.

Although the processes determining the cycling of P in soils are indisputably complex, several key factors have consistently been demonstrated to govern the mineralisation and availability of crop residue-derived P. These main factors can be broadly grouped as the quality of the crop residues, the activity of the soil microbial biomass, and the subsequent sorption reactions of mineralised P in soil (summarised in Figure 1 as a conceptual model). We characterise the process of P release from crop residues based on four key P pools; namely the inorganic and organic P components of crop residues, P assimilated in the microbial biomass and P_i associated with the soil. The key processes of P transfer between these pools are represented by five vectors: the rate of release of the inorganic and organic P fractions from residues (k_{P_i} and k_{P_o}) and the microbial biomass pool (k_{P_m}), the assimilation of P_i by the microbial biomass as it proliferates after the addition of crop residues (M_{P_m}), and the uptake of native soil P_i by the stimulated microbial biomass (M_{P_i}) when P_i released from crop residues is less than M_{P_m} .

Figure 1: A schematic representation of the conceptual pools and vectors as described and quantified. 'Residue P_i ' represents water-soluble phosphate and 'Residue P_o ' represents the organically bound

component of P in 'Crop Residues'. 'Soil Pi' represents all Pi that is associated with the mineral component of soil that is potentially exchangeable with the soil solution. ' k_{pi} ' and ' k_{po} ' represent the decay constants for the rate of release of 'Residue Pi' and 'Residue Po', respectively. ' M_{pm} ' represents the amount of Pi assimilated by the 'Microbial Biomass' as it proliferates in response to the availability of C substrate from 'Crop Residues', whereas ' M_{pi} ' represents the uptake of 'Soil Pi' by the stimulated 'Microbial Biomass' where P released from crop residues is less than ' M_{pm} '. ' k_{pm} ' represents the decay constant for the rate of release of Pi from the 'Microbial Biomass' as it decays in response to diminishing availability of C substrate from 'Crop Residues'.

We present herein a quantitative summary of the available literature resources, with respect to the rate and magnitude of P transfer from crop residues to the plant available soil pools, and the major environmental and management factors involved. We discuss how the pools and vectors represented in Figure 1 describe the major processes governing the transfer of crop residue P to plant available soil P, and quantify them. This knowledge is then integrated as a simple empirical model of the response of soil P availability to various crop residue scenarios. We draw as broadly as practicable on the published literature, to represent averaged values that can be expected across a diversity of conditions, thereby summarising key areas of scientific consensus, and processes that are as yet poorly elucidated. As the sum of existing knowledge and in the interest of robustness and simplicity, the release of P from crop residues is described according to major processes illustrated in Figure 1; they have been quantified widely. The numerous interacting factors that have yet to be completely elucidated (*eg.* tillage effects, P sorption in soil, pH of soil) are not accounted for, but their potential relevance is discussed. Likewise, the interaction of growing plants with residue P during its release from crop residues is not addressed, as this level of understanding has not been reported in the literature yet. We propose that the model be used as a template for i) targeted elucidation of the mechanisms controlling the mineralisation and fate of organic matter-associated P, and ii) the development of more refined predictive models that

147 integrate the P contributions from various crop residue handling scenarios into decision support systems
148 for P fertiliser management.

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150 3. Amount and fractions of P in crop residues

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152 The amount and forms of P in residues have a large bearing on the immediate bioavailability of P in the
153 residue material and on the subsequent reactions of P with soil constituents. The P characteristics of
154 crop residues are highly dependent on environmental and soil conditions and on the physiological age of
155 the crop from which they are derived. The P concentration of applied residues is the principal factor
156 determining whether P will be mineralised in the short term as a result of residue decomposition.
157 Generally, P will be mineralised if the P concentration in residues is greater than 3 mg g⁻¹ or immobilised
158 if it is less than 3 mg g⁻¹, although reported threshold values range from 2 to 3 mg g⁻¹ (eg Fuller *et al.*,
159 1956; White and Ayoub, 1983; Friesen and Blair, 1988; Umrit and Friesen, 1994; Iyamuremye *et al.*,
160 1996; Kwabiah *et al.*, 2003a; Iqbal, 2009). Immobilisation of soil P occurs when the total P content of the
161 residue is insufficient to meet the P requirement of the microbial biomass as it proliferates in response
162 to the new C substrate; the relevant issues will be discussed in detail in a following section.

163

164 The forms of P in crop residues as they influence the dynamics of P release can be characterised as
165 soluble Pi, which is rapidly leached within days and an insoluble organic phosphorus (Po) component,
166 which decays at a rate several orders of magnitude slower (Figure 1). Water-soluble Pi typically
167 constitutes from 40 to 60 % (average 50 %) of the total P content in mature crop residues at grain
168 harvest (Chang, 1939; Kaila, 1949; Birch, 1961; Jones and Bromfield, 1969; Kwabiah *et al.*, 2003b; Noack
169 *et al.*, 2012) and from 60 to 80 % (average 70 %) of total P content in green crop residues during the
170 vegetative stage (Jones and Bromfield, 1969; Bromfield and Jones, 1972; White and Ayoub, 1983;
171 Friesen and Blair, 1988; Ha *et al.*, 2008). The root component of crop residues can be assumed to have

comparable P release (per unit of biomass) to the shoot component (Martin and Cunningham, 1973, Thibaud *et al.*, 1988).

During plant growth the concentration of P in the cytoplasm is tightly regulated (Schachtman *et al.*, 1998), and P in excess of these requirements is stored primarily in the vacuole as Pi (Shane *et al.*, 2004). Data from studies with tobacco suggest that the proportion of Pi can range from 20 % of total P in leaves at low P availability to 50 % at high P availability (Kakie, 1969). Cytoplasmic Pi (often referred to as metabolically-active Pi) is typically around 0.1-0.8 mg P g⁻¹ dry matter (Veneklaas *et al.*, 2012); this Pi, as well as that stored in the vacuole, is water-soluble and should be readily available for plant/microbial uptake (or sorption in soil) upon return to the soil. The amount of P in vacuoles therefore has a significant impact on the short to medium-term release of P from residues. While it is generally accepted that the Pi concentration in tissues is a reflection of the P supply from the growth medium (White and Hammond, 2008), the range of variation that can be encountered in typical crop species grown and the key factors affecting speciation need elucidation.

During grain maturation, P is transferred from vegetative plant parts to developing grains where it is stored primarily as phytate (Marschner, 2012). In wheat, 80-90% of total plant P content can be translocated to grain during maturation and subsequently exported with the harvested product (Batten and Khan, 1987), so that total P concentrations in mature residues can be an order of magnitude lower than those in green residues. However, the partitioning of P between grain and straw/roots at maturity is highly dependent on crop species, genotype and environment. For example, the P harvest index (PHI, or proportion of aboveground plant P located in the grain at maturity) of wheat can range from 30-90% depending on genotype and environment (Batten, 1992). In contrast, most studies consistently report that canola has a PHI of 70-80 % (Jackson, 2000; Rose *et al.*, 2007, 2008), but this narrow range may be

more of a reflection of limited published data, as opposed to lack of variation in PHI across genotypes and environments.

Regardless of whether variation in PHI arises due to species or genotype differences, the key question is how these differences impact on the speciation of P in the residue, i.e. does a greater proportion of P retained in straw mean an increased proportion of Pi in the straw? Unfortunately, the speciation of P compounds in crop residues remains poorly documented. Noack *et al.* (2012) recently demonstrated a large variability in the amount of P residing as Pi in mature crop residues across crop species, but examining the effect of genotype, soil fertility, seasonal conditions, or crop management on P speciation was beyond the scope of that study. The effect of crop management strategies that interrupt the translocation of P into the exported product, such as swathings or chemically desiccating an indeterminate canola crop vs direct harvesting a determinate canola crop may have a large bearing on P cycling. Seasonal events such as frosting and terminal drought, which reduce grain yields, may also result in a substantial increase in the amount of P retained in residues. Given a relatively high proportion of Pi in residues of a range of crops compared with the high proportion of phytate in seeds (Noack *et al.* 2012), efforts to restrict the loading of P into grains (Rose *et al.* 2010c; Richardson *et al.* 2011; Rose and Wissuwa 2012; Veneklaas *et al.* 2012) may have substantial implications for P mineralised in crop residues. In contrast, it is difficult to predict the impact of soil P fertility on the amount and forms of P in residues. Even though high-P supply to plants increases tissue P concentrations in vegetative biomass (White and Hammond 2008), such high P supply also tends to increase yields, which, in turn, increases the amount of P located in seeds at maturity. Presumably, once yield potential is achieved there comes a point where any P taken up beyond maximum yields (luxury P) leads to higher inorganic P in straw as well as higher seed P (see Rose *et al.* 2008), but there is presently little information available on the impact of P supply on P speciation and the distribution of the P in crop residues.

Table 1 summarises the average biomass and P content of common crop residues that can be expected under low, medium and high productivity situations in the southern Australian grain cropping regions. The values presented are referenced from survey data for multiple sites and seasons where available, and values representing consensus in the literature where survey data was unavailable. The data represent the southern Australian cereal cropping regions, but may be applicable to other dryland cropping regions, particularly where highly weathered soils predominate. The data confirm that the most influential factor with respect to the quantity and speciation of P in crop residues is the developmental stage of the crop, exemplified by the differences in P between mature crop residues remaining after grain harvest (less than 1 kg P ha⁻¹ in a low-yielding wheat crop residues) and those residues utilised at the vegetative growth stage (more than 30 kg P ha⁻¹ in a productive green manure crop).

4. Microbial biomass P

The soil microbial biomass has two main roles in the dynamics of crop residue P in soil; i) the principal driver for the transformation of organically-bound phosphorus to plant-available phosphate, and ii) the accumulator of a significant pool of P. The notable effect of crop residues on soil P dynamics, when compared to mineral fertiliser, is their stimulation of the soil microbial biomass with subsequent uptake and immobilisation of P (and other minerals) in this biomass. Upon the addition of crop residues, the microbial biomass is generally the predominant soil P pool that is influenced in the short term, regardless of the characteristics of either the crop residues or the soil (eg Chauhan *et al.*, 1979, White and Ayoub 1983; McLaughlin and Alston 1986). In comparison, application of mineral P fertiliser causes little (McLaughlin and Alston 1986; Marschner *et al.* 2006), or no increase (Chauhan *et al.*, 1979) in the amount of P in the microbial biomass.

The size of the microbial biomass in soil is stimulated rapidly upon addition of crop residues. The magnitude of the increase in microbial biomass is proportional to the amount of C in residues, since C-substrate availability is the primary factor limiting microbial activity in agricultural soils (eg. Van Veen *et al.*, 1984; Bünemann *et al.*, 2004a). The magnitude of microbial biomass proliferation may respond to other characteristics of the crop residues that are related to age, species and environmental factors; however, these factors have not been thoroughly elucidated. The C concentration in crop residues is typically 450 mg g⁻¹ (45 %) (Baldock, 2009), on average, and we will assume this value represents all crop residues considered herein.

Phosphorus from the crop residue substrate and from soil P pools is taken up by the proliferating microbial biomass. Microbial biomass P responds rapidly to the addition of C substrate to soil, reaching a maximum within days of substrate addition (Chauhan *et al.*, 1979; White and Ayoub, 1983). In the short term, net mineralisation will occur if the amount of soluble P in residues is in excess of that taken up by the microbial biomass. However, residue P content is often insufficient to meet the requirements of the growing microbial biomass, under which circumstances the microbial biomass will take up Pi from the solution and exchangeable pools in soil; leading to net immobilisation of soil Pi. Hence, the importance of crop residue characteristics in determining the dynamics of P release is due to the interaction between the crop residues and the microbial biomass.

Phosphorus is taken up by the proliferating microbial biomass to meet its growth and metabolic requirements according to relatively flexible ratio of C:P within the microbial biomass. The C:P ratio and forms of P in the microbial biomass differ widely between microbial communities and ecosystem types, and Bünemann *et al.* (2011) present a thorough review and assessment on the subject. In cereal cropping soils the C:P ratio of the microbial biomass has been reported to range from 10:1 (Oehl *et al.*, 2004; Bünemann *et al.*, 2007) to 35:1 (Chauhan *et al.*, 1979; Butterly *et al.*, 2010). Chauhan *et al.* (1979)

found the C:P ratio of new microbial biomass formed after residue addition to be 20:1, compared to 35:1 for the resident soil microbial biomass. Parton *et al.* (1988) proposed that the C:P ratio of the microbial biomass varies as a function of soil P availability. As a simplistic representation of the concurrent short-term effects of microbial biomass proliferation and P uptake, we propose that the proliferation of the microbial biomass and the amount of P taken up as a consequence of this proliferation are in proportion to the amount of C substrate in crop residues. The amount of P taken up by the microbial biomass was $1 \text{ mg P g}^{-1} \text{ C}$ applied as organic residues (M_{pm} ; Figure 1) on average for a range of crop residues and soil types (Chauhan *et al.*, 1979; Kwabiah *et al.*, 2003a; Iqbal, 2009). Therefore, assuming the C content of crop residues is 450 mg kg^{-1} , if the concentration of soluble P_i in residues is greater than 0.45 mg P g^{-1} , k_{pi} will exceed the demands of the microbial biomass, and M_{pi} will be zero. Where the soluble P_i content is less than 0.45 mg P g^{-1} , k_{pi} will not meet the P requirements of the microbial biomass in the short term, and P_i from soil pools will be immobilised in the microbial biomass, quantified as M_{pi} (Figure 1).

Although the C:P ratio of the microbial biomass responds to P availability in the soil and crop residue substrate, the microbial biomass has a high capacity to acquire P from soil P fractions that are generally not considered to be plant-available, and will be more competitive than plants for solution and exchangeable P (Chauhan *et al.*, 1979; White and Ayoub, 1983; Friesen and Blair, 1988; Bünemann *et al.*, 2004b; Cleveland and Liptzin, 2007; Iqbal, 2009; Ehlers *et al.*, 2010; Oberson *et al.*, 2011). It has been demonstrated that even for highly P-limited environments, such as tropical soils with high P sorption capacity and sparse P fertiliser history, the microbial biomass dominates geochemical processes for competitive uptake of applied P (Kwabiah *et al.*, 2003a; Olander and Vitousek, 2004) and is limited by C and N rather than by P availability (Bünemann *et al.*, 2004a).

The microbial biomass in soil and its response to substrate addition is significantly influenced by soil pH, a concept reviewed in detail by Wardle (1992). Briefly, the size of the microbial biomass typically decreases with decreasing soil pH. Thompson *et al.* (1954) and Harrison (1982) both reported soil pH to be a significant factor influencing rates of organic P mineralisation. The stability of soil organic P to mineralization increased as soil pH decreased, so soil organic P may be more stable, and mineralisation rates slower, in soils with acidic pH. Indeed mineralisation rates of C and N have been widely demonstrated to be lower, and soil organic C retention to be higher, in soils at acidic pH (eg. Amato and Ladd, 1992; Motavalli *et al.*, 1995; Li *et al.*, 2007). However, empirical data to quantify the influence of soil pH on mineralisation rates is poorly developed for both C and for P.

Microbial biomass P is potentially available for plant uptake. In the short term, there is potential for competitive uptake by plant roots following predation by soil fauna. During transient periods of drying and re-wetting of soil, desiccation and lysis of microbial cells and the subsequent transfer of microbially-held P to extractable soil pools can be significant (Turner *et al.*, 2003). In the medium term, the size of the microbial biomass decays at a rate similar to the decay of organic C (Oehl *et al.*, 2001; Bünemann *et al.*; 2004a; Grace *et al.*, 2006) as the availability of C substrate decreases. The incubation studies of Oehl *et al.* (2001) and Bünemann *et al.* (2004a) demonstrated that the decrease in microbial P after exhaustion of C-substrate resulted in an increase in plant-available P. However, the work of Marschner *et al.* (2005; 2006; 2007) indicates that crop reliance on microbial biomass-derived P may be strongly influenced by soil properties and plant species, a subject that indeed warrants further investigation.

Ladd *et al.* (1995) proposed that the microbial biomass derived from residue addition could be allocated into 2 pools; unprotected (due to its presumed association with crop residues) and protected (that with opportunities for protection within the soil). The ratio of protected / unprotected biomass is dependent on clay content and the CEC of the soil, and ranges from 0.6 (high clay soil) to 0.4 (sandy loam soil).

However, for the purpose of simplicity and with consideration of the limits of the published data, we will adopt a single pool for the microbial biomass P, and assume that its size decays at the same rate as the stable residue pool.

Martin and Cunningham (1973) reported a relatively non-significant role of the microbial biomass in P transformations during the decomposition of intact wheat roots. They proposed that the use of finely-ground plant residues in many studies may have misrepresented its availability to microorganisms and resulted in an over-estimate of the microbial biomass response. It is likely that the rate, but not the magnitude of microbial biomass proliferation may be influenced by the particle size of the substrate (*eg.* Ambus and Jensen, 1997; Singh *et al.*, 2006).

The data presented are almost exclusively derived from studies where finely-ground crop residues were incorporated into soil. Given the widespread adoption of no tillage cropping practices worldwide, it is imperative to investigate how the assumptions translate into systems where the majority of crop residues are a) largely intact and b) either standing or at the soil surface. The factors that may differ between finely-ground crop residues incorporated into soil (classical tillage) and no-till systems include variable moisture content at the soil surface, greater potential for separation of soluble and insoluble components by leaching, reduced availability of soil nutrients for uptake by the microbial biomass during decomposition and lower surface area of intact residues for decomposition. The influence of tillage practices on the dynamics of mineralisation remains poorly elucidated even for C and N, which have been more extensively studied than P. The simulation models APSIM, RothC (Coleman and Jenkinson, 1999) and Ceres Wheat, have cultivation increase the rate that “litter” (residues) are incorporated and become fresh soil organic matter, but thereafter, the rates of mineralisation are not changed by cultivation. Whilst Daroub *et al.* (2000) measured no effect of tillage on the release of P from plant residues applied to soil, Chauhan *et al.* (1979) found that mixing soil increased microbial

biomass P to a greater extent than the addition of grass residue, indicating a potential tillage effect. Due to a lack of empirical data we have not quantified the effect of tillage on the release of P from crop residues.

5. Soil phosphate fractions

The plant uptake of P from soil occurs predominantly in the form of Pi (HPO_4^{-2} and H_2PO_4^- ; Bucher, 2007); hence, the soil Pi pool (Figure 1) represents soil P forms that are potentially available for uptake by plants. The soil Pi pool (Figure 1) incorporates the net release of Pi from crop residues and is a simplified representation of a complex, dynamic, and diverse system. Soluble Pi can be readily leached from crop residues (Jones and Bromfield, 1969), resulting in a direct, rapid transfer from crop residue to the soil Pi and microbial P pools (with the assumption that there is no new crop interacting with these pools). Phosphorus that is taken up by the microbial biomass as it proliferates in response to the crop residue-C substrate availability is subsequently released as the microbial biomass decays with the exhaustion of C substrate (Oehl *et al.*, 2001; Bünemann *et al.*, 2004a). The size of the soil Pi pool (Figure 1) is the sum of Pi released from crop residues and the microbial biomass at a time point in the P mineralisation process, together with Pi from fertiliser inputs and background native P in the soil. Biological and geochemical processes of mineralisation, sorption and dissolution of P contribute to background native soil Pi.

5.1. Forms and transformations

The soil Pi pool includes soil solution Pi and chemically sorbed Pi, which interact in a dynamic equilibrium. The distribution of soil phosphorus between the sorbed and solution phases is dominated by sorption reactions (Barrow, 1983; Barrow, 1999), while its availability to plants (and microbes) is also affected by diffusion processes (Probert and Keating, 2000). Sorption reactions are highly influenced by

the chemistry and mineralogy of soil, and their influence on P availability is greatest in soils with high P sorption capacity, such as tropical soils dominated by iron and aluminium sesquioxides. The availability of Pi in soil, whether derived from mineral fertiliser or from crop residues, can be short-lived in soils with high P sorption capacity. For the purpose of this exercise, we have represented soil Pi as a single pool, into which all P released from crop residues is allocated and from which the microbial biomass may acquire P.

Organic P compounds released into soil either directly from crop residues or after the lysis of microbial cells are subject to sorption and precipitation reactions in soil, after which their potential for mineralisation into Pi is greatly reduced (Celi and Barberis, 2005). Organic P compounds are readily adsorbed onto iron oxides and to a lesser extent, aluminium oxides, with the amount of iron oxides generally governing the capacity for Po adsorption (Anderson *et al.*, 1974). As such, sorption and stabilisation of Po is greatest in highly weathered, tropical soils with high P fixing capacities, hence there is often an accumulation of Po in these soils (Reed *et al.*, 2011). The sorption and subsequent stabilisation of Po in soils remain the major processes whereby the dynamics of P release from crop residues may deviate from that of C and N, for which there is a more refined understanding. However, methodological problems have hindered the elucidation of the long-term fate of crop residue Po in soil, notably the relatively short half-life of ^{32}P and ^{33}P isotopic tracers, and a limited capacity to characterise P-containing compounds that cannot be extracted from the soil matrix.

Organic P forms can constitute up to 80 % of total P in soil (Anderson, 1980) and can be associated with soil organic carbon (C), or adsorbed by soil minerals (Celi and Barberis, 2005). Stimulation of the microbial biomass to mineralise soil Po is referred to as a “priming effect” and is a potential strategy for matching soil Pi supply with crop demands (Simpson *et al.*, 2007). Where Po is associated with organic C, it can be released into soil solution by C mineralisation and subsequently hydrolysed by enzymes

released from the microbial biomass (Randhawa *et al.*, 2005; Richardson 2007). Although the absence of suitably stable P isotopes makes direct measurement of Po mineralisation difficult to measure, the “priming effect” was found to be negligible where ^{14}C was used as a tracer for C mineralisation (Dalenberg and Jager, 1989). Hydrolysis of sorbed Po compounds, such as inositol phosphates, by the microbial biomass may be stimulated after addition of crop residues to soil, particularly where a high C:P ratio of crop residues promotes the uptake of soil P by the microbial biomass. However, there is evidence that assimilation of soil P by the microbial biomass occurs predominantly from the available soil Pi fraction (White and Ayoub, 1983; Wu *et al.*, 2007; Jalali, 2009), even in low P soils (Bünemann *et al.*, 2012). Although the “priming effect” will not be addressed in our modelling, further investigation is warranted, given the potential benefits of manipulating the release of Pi from the significant pools of soil Po.

5.2. Availability to plants

Sorption of Pi by soil minerals is the principal factor influencing plant availability of P mineralised from crop residues (White and Ayoub, 1983; Friesen and Blair, 1988; Umrit and Friesen 1994; Jalali, 2009; Jalali and Ranjbar, 2009). The availability of Pi released from crop residues is influenced by sorption reactions in a similar way to Pi applied to soil as mineral fertiliser (Friesen and Blair, 1988; Cong and Merckx, 2005). Iyamuremye *et al.* (1996) used the method of Hedley *et al.* (1982) to investigate the role of both residue and soil characteristics on the fate of crop residue-derived P in soil. The majority of P released from crop residues was recovered as chemically-sorbed Pi (NaOH-extractable) for all soils, although the proportion recovered in readily available (resin and bicarbonate-extractable) pools was related to the P sorption capacity of the soil. Friesen and Blair (1988) measured almost no increase in the soil solution P during the mineralisation of crop residues, with almost all mineralised P sorbed to Fe (NaOH-extractable) and Al minerals (NH_4F -extractable). Although the Al-sorbed P fraction was readily depleted by plants (and the microbial biomass), the Fe-sorbed fraction was unavailable. The factors governing the sorption of phosphate ions in soil are well understood, and it is evident that the P release

from crop residues occurs primarily as P_i ; hence the existing models targeted toward fertiliser and native soil P should adequately describe the reactions of crop residue P in soil.

Addition of crop residues to soil can indirectly influence the availability of P within the soil P pool by altering the chemical and physical properties of the soil (Joffe, 1955). Cong and Merckx (2005) measured significant changes to a suite of chemical and physical characteristics, leading to an increase in both the chemical availability and diffusive supply of P following a high rate of organic matter addition to soil. They demonstrated the capacity of plant residues to increase pH, decrease extractable Al, and increase the net negative charge surfaces in soil, with the net effect of increased solubility and reduced sorption of P_i in soil. Greater macro-aggregation and reduced specific surface area and porosity of soil were also measured, reducing P sorption and increasing P diffusion rates. A review by Guppy *et al.* (2005) concluded that the application of organic matter to soils at agronomically feasible rates does not reduce the sorption of P by soil, and that any increase in soil P availability could be directly attributed to P released from the crop residues. However, it should be noted that the distribution of crop residues is often locally concentrated after deposition by harvesting operations at rates many-fold greater than if crop residues were evenly distributed (eg. Brennan *et al.*, 2000). It is likely that soil P availability is influenced by physical and chemical changes in soil following the addition of crop residues; however the magnitude of these changes under diverse scenarios has not been elucidated.

6. An empirical model

The mobilisation of P from crop residues added to soil typically exhibits two distinct phases, with an initial rapid release of labile P in the first weeks after addition (the soluble P_i content), followed by a prolonged phase of slower release of the more recalcitrant organic P species (eg Blair and Boland, 1987; Friesen and Blair, 1988; Umrit and Friesen, 1994). Carbon mineralisation from crop residues has been

observed to follow a similar two stage pattern, and two-component exponential decay functions have been widely adopted to describe the decay and nutrient loss from organic residues (eg Grace *et al.*, 2006, van Veen *et al.*, 1985), ascribing decay coefficients to the labile and recalcitrant fractions (eg Shammas *et al.*, 2003). This approach was found to adequately describe the mobilisation of P from a range of organic residues with contrasting characteristics when added to soil (Jalali and Ranjbar, 2009). Equation 1 describes the exponential decay function in the model presented, whereby the rate of decomposition is quantified by the decay coefficient (k).

Equation 1: Exponential decay functions and P release from individual pools

$$P_t = P_0 \exp^{(-k \cdot t)}$$

P_t = P released at time t (kg ha⁻¹)

P_0 = initial P content (kg ha⁻¹) of the labile or recalcitrant fraction

k = decay constant

t = time after residue addition (weeks)

The soluble component of residue P has a typical residence time of about 4 weeks in residues (eg Blair and Boland, 1987; Friesen and Blair, 1988 (2 weeks); Umrit and Friesen, 1994; Jalali and Ranjbar, 2009) at 25 °C and optimal moisture conditions, which is well fitted by the decay constant of the SOCRATES model (Grace *et al.*, 2006) for the labile component of crop residue C. We therefore allocate the decay constant of 0.29 week⁻¹ to vector k_{pi} (Figure 1) at 25 °C and optimal moisture conditions.

Mineralisation of C and P has been reported to be well correlated (Cole *et al.*, 1977; Baggie *et al.*, 2004; Bünemann *et al.*, 2004a); hence, the release of the stable component of crop residue P was assumed to occur in parallel with the mineralisation of the stable C component. The decay constant for C mineralisation in the Socrates model (Grace *et al.*, 2006) predicted a half-life of 35 weeks (at 25 °C and

optimal moisture) for the stable component. This figure is similar to that reported by Jalali and Ranjbar (2009) for the release of the stable component of P from a range of plant residues in a soil-less system. Hence, we assume the recalcitrant component of residue P will decay according to the decay constant of 0.02 week⁻¹ at 25 °C and optimal moisture (k_{Po} ; Figure 1).

The microbial biomass is a significant pool of P associated with the decomposition of crop residues in soil, and the dynamics of the pool size have a significant influence on the release of P from residues (Oberson and Joner, 2005; Richardson and Simpson, 2011). The accumulation of soluble residue P_i in the microbial biomass after addition of crop residues to soil (M_{pm} ; Figure 1) was assumed to occur within the first week after addition, at the rate of 1 mg P g⁻¹ C substrate applied in crop residues, as described above. The subsequent decay (or longevity) of the microbial biomass during the decomposition of crop residues is largely determined by the quantity of C substrate remaining, but is influenced by the clay content and cation exchange capacity (CEC) of the soil (Amato and Ladd, 1992). For simplicity in this exercise, soil clay properties were not accounted for and the microbial biomass-P was assigned to decay in parallel with the stable P component, since the two pools were adequately described by similar decay constants in the SOCRATES model (Grace *et al.*, 2006). Therefore, k_{pm} (Figure 1) is equal to k_{Po} , at 0.02 week⁻¹ at 25 °C and optimal moisture conditions.

The main effects of temperature and moisture on C mineralisation rates from crop residues in soil have been intensively studied and described, with substantially less advanced developments for P mineralisation. Decay constants were adjusted for the mean annual temperature (18 °C) and precipitation (364 mm) at Cunderdin, in the central wheat belt of WA (31.65° S, 117.24° E) using the multiplicative temperature and moisture factors of the SOCRATES model (Grace *et al.*, 2006). The adjusted decay constants were 0.16, 0.01 and 0.01 for k_{Pi} , k_{Po} and k_{pm} , respectively. Climate averages for Cunderdin, Western Australia, are comparable to Aleppo, Syria (36°10'N, 37°12'E), and other locations with Mediterranean-type climate (eg. South Africa, parts of Chile, California, etc.).

497 The model was applied to the amounts of crop residues and their P characteristics under various
 498 scenarios typical of the southern Australian grain cropping region (Table 1), and the amount of P
 499 released into soil or assimilated in the proliferating microbial biomass are presented in Table 2.
 500 Phosphorus transformations in the short and medium term (Table 2) range from rapid net release of Pi
 501 into soil (green manure) to microbial biomass immobilisation of Pi from the soil exchangeable fractions
 502 that is sustained up to 1 year (wheat stubble). The predictions support the large variation reported in
 503 the literature for Pi released from crop residues under different scenarios (*eg.* Fuller 1956). Model
 504 predictions estimated half-lives for the labile P component (4 weeks) and the recalcitrant residue P and
 505 microbial biomass components (70 weeks) under average climatic conditions at Cunderdin, Western
 506 Australia. Most of the P release from crop residues occurred within 1 year of their application to soil;
 507 hence, we propose the model is most relevant over this time-span.

508

509 Model predictions were compared under the contrasting climate scenarios of Los Baños, Philippines
 510 (14°10'N 121°13'E) and Harpenden, United Kingdom (51°48'N 0°21'W). Harpenden, the site of
 511 Rothamsted Research, has a temperate maritime climate, with a mean temperature of 9.5 °C and mean
 512 annual precipitation of 697 mm, which is comparable with the central corn belt of North America. Los
 513 Baños, the site of the International Rice Research Institute headquarters, has a tropical marine climate
 514 with a mean temperature of 27.1 °C and mean annual precipitation of 1942 mm. At Los Baños, the
 515 predicted half-lives of soluble (Pi) and stable (Po) components of residue P were 2 weeks and 21 weeks,
 516 respectively, compared to half-lives of 7 weeks and 100 weeks at Harpenden.

517

518 Although typical residue characteristics will differ under contrasting climates, we compared the model
 519 predictions for the release of P from the medium-productivity green manure and wheat crops (see Table
 520 1) under the contrasting climate scenarios. For the green manure crop, there was rapid release of P
 521 under the tropical climate scenario in the first 4 weeks (7.1 kg P ha⁻¹) compared to the temperate
 522 climate scenario (1.4 kg P ha⁻¹) (Table 1). However, after 1 year, P release was similar for the tropical and

temperate climate scenarios. Predicted P release from the wheat crop residue (Table 1) after 1 year was 0.7 kg P ha⁻¹ and 0.3 kg P ha⁻¹ under the tropical and temperate climate scenarios, respectively, but was similar at 4 weeks. The assimilation of P and its release by the microbial biomass was largely unaffected by climate factors.

A sensitivity analysis was conducted to assess the robustness of model predictions against variation in the model parameters (Table 3). Model predictions of P release from crop residues were highly sensitive to doubling or halving the parameters for the concentration and speciation of P in the residues, and in the uptake of P by the microbial biomass following residue addition (Table 3). By comparison, doubling or halving the coefficients for decay of the water-soluble and stable components of crop residue P and for microbial biomass P had a smaller effect on P release. The initial P concentration of the crop residues, notably cereal straw or green manure, influenced the sensitivity of the model predictions to other parameters. While predicted P release from cereal straw (0.05 % P) was dramatically influenced by P uptake by the microbial biomass, this parameter had a smaller effect on P release from green manure residue (Table 3).

The amount of P immobilised by the microbial biomass was the most important parameter in predicting the dynamics of P release from residues, and emphasised the importance of the microbial biomass as a pool of soil P as well as the driver of P mineralisation and organic matter decomposition. Doubling or halving the estimate of 1 mg P taken up by the microbial biomass per gram of C added to soil as wheat straw resulted in model predictions ranging from 30 % of initial P content immobilised to 47 % of initial P content released after 1 year, respectively (Table 3). For a green manure crop, the effect was less significant, but the timing of P release was affected, with 6 % or 27 % of P content released, respectively after 4 weeks if microbial biomass P uptake was doubled or halved. Given the range of reported values in the literature, there is cause for uncertainty over the averaged value applied in the model. For example, in a single soil type, Kwabiah *et al.* (2003) found the amount of P taken up by the microbial biomass to range from less than 1.5 to more than 3 mg P g⁻¹ C applied for different organic residues.

Microbial biomass P uptake was not correlated with any of the residue characteristics measured. Other studies reported that the microbial biomass took up 0.3 mg P/g C added as cellulose + N, 0.8 mg P/g C added for grass + N (Chauhan *et al.*, 1979), 1.0 mg P/g C added as mature wheat straw or 1.5 mg P/g C added as young wheat residues (Iqbal, 2009). The factors determining variation in the amount of P taken up by the microbial biomass after addition of C substrate is unclear (eg Kwabiah *et al.*, 2003a), but may be related to the fractions and lability of C in residues. Alternatively, Oberson and Joner (2005) make a detailed assessment of the significant methodological problems related to the determination of microbial P in soil, which may account for some of the differences among and even within studies. Notably, they highlight inaccuracies associated with predicting total microbial biomass P from the proportional amount that is extracted and measured (by application of K_p factors). The significant influence of soil type and microbial community composition on the proportion of microbial biomass P that is released by cell lysis and extracted from soil can lead to significant differences in the estimation of microbial P in soil. Given the range of reported values, and the impact on model predictions, there is certainly cause for further elucidation of P uptake by the microbial biomass following the addition of crop residues to soil.

7. Concluding remarks

The body of literature as well as our modelling confirm that the contribution of crop residues to P availability is likely to be significant only under conditions where large amounts of crop residues with relatively high P concentration are applied to soil. Crop residues with low P concentration, such as cereal stubble (eg. due to re-translocation of a large proportion of stubble P into grain), will not make an agronomically significant contribution to soil P availability either in the short or long term. However, a productive green manure crop may release sufficient P to meet the requirements of a subsequent cash crop.

Much research and discussion has been devoted towards developing productive low-input farming systems. However, the consensus of the works discussed in this review is that the organic cycling of P is intricately linked with the inherent productivity of the site, including climate. The release of P from crop residues is significantly reduced in systems where the P-status of crops and soils is low, compared to where it is high (*eg.* Blair and Boland, 1987). In fact, addition of crop residues to soil in low-P systems can stimulate the uptake and immobilisation of significant amounts of soil P by the microbial biomass (*eg.* Bünemann *et al.*, 2012), reinforcing the reliance on P inputs for sustained crop productivity. Whilst the most significant management option impacting the biological cycling of P is a green manure rotation, one must consider whether there is any net benefit to the P nutrition of a subsequent crop if P is mined from the exchangeable fractions and subsequently returned to those fractions after cycling through the microbial biomass in the following cropping rotation. Any P benefit may relate to the capacity of the manure crop to scavenge or solubilise pools of P that are otherwise unavailable to the cash crop.

The literature review and modelling have identified key areas of knowledge gaps that should be prioritised for further elucidation. Notably, P release from crop residues is strongly influenced by the concentration and speciation of P in the residues, as well as by the uptake of P by the microbial biomass following residue addition. However, a wide range in values has been reported for these key parameters, and the factors that determine them remain poorly elucidated. Soil pH and tillage practices are both known to influence organic matter mineralisation rates in soil, but empirical data relating to their impact on P release from crop residues are lacking. Although burning crop residues is a common practice in many farming systems, there is currently little information on the effect of burning on soil P availability. We envisage that future elucidation of the identified knowledge gaps will increase our capacity to estimate P release from crop residues and will consolidate the model presented here, enhancing its capacity to accurately predict the contribution of crop residue P to soil P availability.

This review has not addressed the capacity for P supply from organic sources other than crop residues. Indeed, there is a requirement for crop models to take into account the P supply to crops from a variety of sources, including composts, animal manures (*eg.* APSIM Manure; Probert *et al.*, 2004), green manures and mineral fertilisers as we move towards more sustainable sources for managing the P nutrition of cropping systems (Palm *et al.*, 1997).

Of the identified opportunities to enhance the efficient cycling of P in cropping systems, the potentially most readily manipulated is reducing P loading into grain with greater retention of P in crop residues; its feasibility, at least, warrants investigation. The long-term, cumulative effect of repeated cropping cycles where high-P residues are returned to soil may lead to a significant accumulation of organically-cycled P and reduced requirement for fertiliser P inputs.

We propose that the work described here i) presents a basis for estimating the contribution of crop residues to soil P availability to a subsequent crop, and ii) acts as a template for further research to identify priority aspects of organic P cycling for elucidation.

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Table 1: Typical biomass and P content of post harvest residue of common crops under low, medium (med) and high productivity scenarios in the southern Australian grain cropping region. The values presented are referenced from survey data for multiple sites and seasons where available, and values representing consensus in the literature where survey data was unavailable. Extreme values were omitted hence the range of possible scenarios will extend beyond the “high” and “low” productivity scenarios depicted.

	Green manure			wheat stubble			legume stubble			canola stubble		
	low	med	high	low	med	high	low	med	high	low	med	high
Residue biomass (t ha^{-1}) ^{*,a}	2.4	4.8	7.2	1.8	3.6	5.4	2.1	5.4	7.2	1.8	4.2	5.4
Residue P concentration (kg t^{-1})	1 ^b	3 ^b	4 ^b	0.2 ^c	0.5 ^c	1 ^c	0.2 ^d	0.5 ^d	1.2 ^d	0.5 ^e	0.7 ^e	1.1 ^d
Residue P amount (kg ha^{-1})	2.4	14	30	0.4	1.8	5.4	1.1	2.7	7.2	0.9	2.9	5.4
Soluble Pi (% of total P) ^{**}	70	70	80	50	50	50	50	50	50	50	50	50

^{*}Based on average yield expectation and average harvest index, includes roots at a root:shoot ratio = 0.2 after grain export (Jackson *et al.*, 1996)

^{**}Estimates of soluble Pi in crop residues are averaged values were derived from various sources and described in detail in ‘Amount and fractions of P in crop residues’, above. (Chang, 1939; Kaila, 1949; Birch, 1961; Jones and Bromfield, 1969; Bromfield and Jones, 1972; White and Ayoub, 1983; Friesen and Blair, 1988; Ha *et al.*, 2008; Noack *et al.*, 2012).

a. Jackson *et al.* (1996); b. Reuter and Robinson (1997); c. Schultz and French (1976); d. Schultz and French (1978); e. Rose *et al.* (2008) and Bill Bowden, unpublished data.

Table 2: Model predictions of the fate of crop residue P from common crops under low, medium (med) and high productivity scenarios in the southern Australian grain cropping region. Model predictions are based on the typical crop biomass and P content scenarios described in Table 1 and adjusted for mean temperature and precipitation at Cunderdin, in the central wheatbelt of Western Australia (31.65° S, 117.24° E). Transformations after 4 weeks and 1 year depict the half-life of the soluble component of crop residue P and the term of an annual crop rotation, respectively.

	Green manure			wheat stubble			legume stubble			canola stubble		
	low	med	high	low	med	high	low	med	high	low	med	high
P release after 4 weeks (kg ha^{-1})	-0.2	2.9	6.8	-0.7	-1.1	-0.9	-0.7	-1.6	-1.3	-0.5	-1.1	-0.9
Δ microbial biomass P after 4 weeks (kg ha^{-1})	1.0	2.1	3.1	0.8	1.6	2.3	0.8	2.3	3.1	0.8	1.8	2.3
P release 1 year (kg ha^{-1})	1.3	11	22	-0.2	0.3	2.3	-0.2	0.4	3.1	0.2	0.9	2.4
Δ microbial biomass P after 1 year (kg ha^{-1})	0.6	1.3	1.9	0.5	1.0	1.4	0.5	1.4	1.9	0.5	1.1	1.4

Negative values of P release = microbial biomass immobilisation of Pi from the exchangeable soil Pi pool.

917 Table 3: The effect of halving (x0.5) or doubling (x2) model parameters on the predicted
 918 release/immobilisation of P from crop residues after 4 weeks and 1 year of decomposition. Two
 919 contrasting crop residues: a mediu- productivity wheat stubble and a medium-productivity green
 920 manure crop (described in Table 1) are presented. The sensitivity to soluble Pi content was assessed at
 921 20 % or 80 % of the total P content. Values represent the percentage of the initial P content of the crop
 922 residue, with negative values representing immobilisation of soil Pi.

										decay			
		P				P uptake		decay		decay		constant	
		concentration				by microbial		constant		constant		microbial	
		(mg g dry	Soluble Pi	biomass				soluble Pi		stable Po		biomass	
		weight ⁻¹)	(% of total P)	(M _{pm})				(k _{pi})		(k _{po})		(k _{pm})	
		x0.5	x2	20	80	x0.5	x2	x0.5	x2	x0.5	x2	x0.5	x2
Green manure (3 kg P t ⁻¹)													
4 weeks		4	27	-1.0	24	27	5.6	6.1	38	19	21	20	21
1 year		43	79	46	80	79	66	74	75	69	82	72	78
Wheat straw (0.5 kg P t ⁻¹)													
4 weeks		-147	-18	-74	-48	-18	-147	-70	-48	-62	-58	-62	-57
1 year		-30	47	3	38	47	-30	20	22	12	33	3	43

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