

POULTRY CRC LTD

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Sub-Project No: 2.2.1

PROJECT LEADER: Dr Matt Redding

**Sub-Project Title: Maximising spent litter
fertiliser returns through nutrient
management**

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Maximising spent litter fertiliser returns through nutrient management
Sub-Project No. 2.2.1

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Executive Summary

Background

Despite decades of agricultural research, applications of conventional fertiliser products, such as urea and superphosphate, result in only 40 to 60% plant uptake of the target nutrients. Waste organic nutrient sources may possess characteristics that do not simply match conventional fertiliser performance, but could provide a means of ongoing nutrient mineralisation and release to more closely match plant uptake requirements. This study centres on the general proposition that poultry litter and poultry litter products formulated with sorbents are nutrient sources capable of delivering agricultural and environmental benefits well beyond those provided by conventional inorganic fertiliser products.

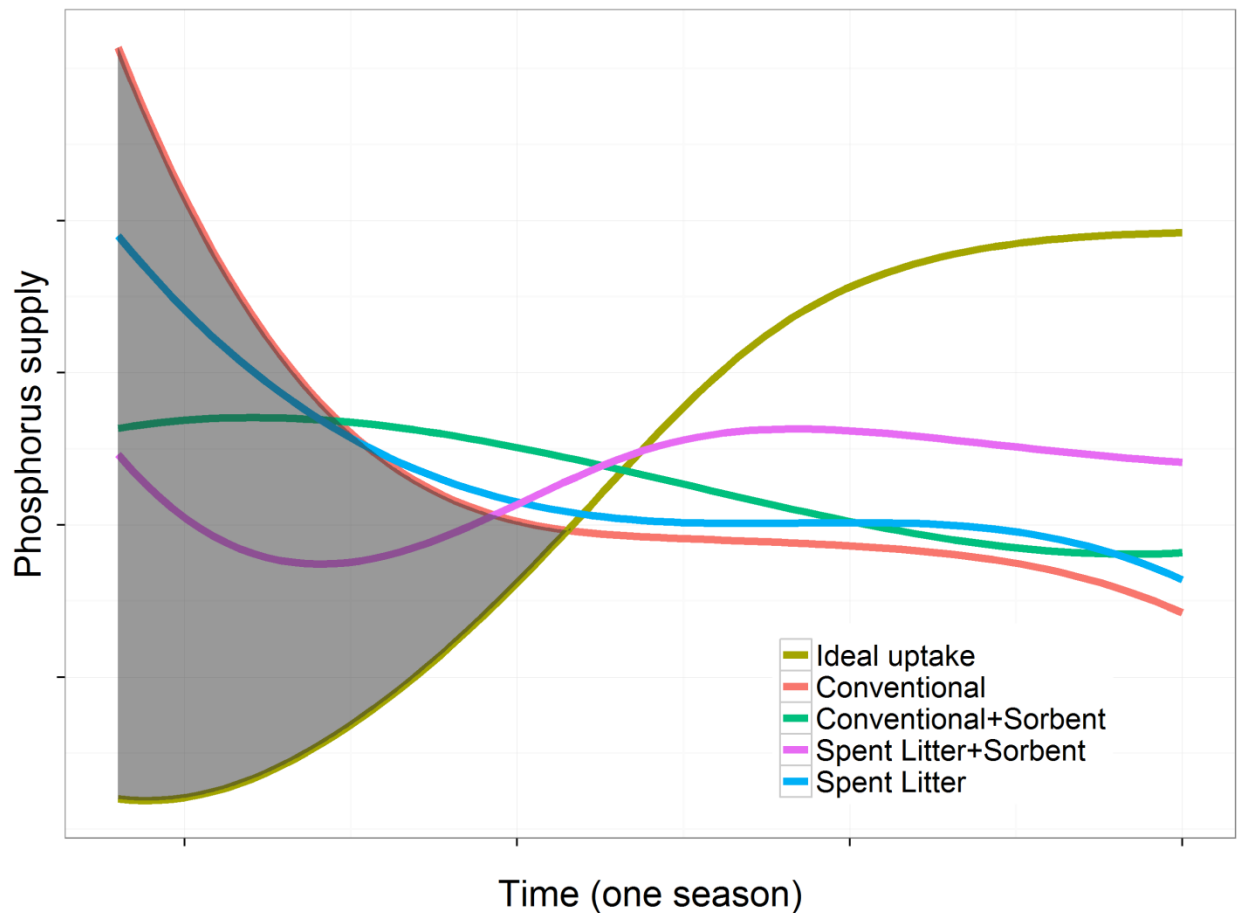
Research methods

The project included field and glasshouse agronomic trials, sorbent bedding trials, a technology adoption study, and agronomic modelling. Sorbents investigated included hydrotalcite and bentonite.

Agronomic outcomes

Common crop uptake profiles involve a greater nutrient requirement later in the season than at the beginning. This differs considerably from the nutrient supply behaviour of conventional fertilisers which over-supply nutrients during initial plant establishment, resulting in large nutrient losses.

Spent litter nutrient forms and formulations with sorbents tend to defer initial nutrient availability, decreasing the initial nutrient over-supply. Where a multi-season approach can be taken for nutrient management, we have demonstrated that these formulations are capable of better matching the ideal nutrient uptake profiles of many crops relative to conventional fertiliser treatments (Executive Summary Figure 1). While the excess initial nutrient availability associated with the conventional treatment is vulnerable to losses, this is not the case where hydrotalcite is used as an additive.



Executive Summary Figure 1. Predicted performance of the conventional phosphorus source versus a sorbent treated form, as well as spent litter with and without the sorbent for the *third consecutive cycle of fertiliser application and crop production*. The unmodified Conventional and Spent Litter treatments both show excess initial availability that may be subject to losses (shaded region). The ideal uptake curve of many plants is provided as a reference.

It was also evident that the use of cation exchangers (in this case bentonite) can allow greater carry-over of nitrogen value between crops, without a decrease in productivity, simply by decreasing nutrient losses.

Mitigating nutrient losses

Collectively, the runoff, leaching, and ammonia volatilisation trials indicate that the rates of sorbent additions employed in the field and pot trials were sufficient to significantly decrease or eliminate losses of phosphorus or nitrogen. Data collected as part of a concurrent project also suggests that the bentonite and vermiculite additions can significantly decrease emissions of nitrous oxide (a potent greenhouse gas and ozone layer degrader).

Sorbent additions are therefore confirmed as a technically viable means to decrease losses of fertiliser value, and to decrease environmental contamination. This success applies both to spent litter formulations and in some cases to formulations involving conventional fertilisers. The economics of applications of sorbers in this role is dependent on circumstances.

Sorbent additions to bedding materials in-shed

Due to the ability of bentonite to decrease ammonia volatilisation, additions of bentonite to bedding in-shed could be used to decrease atmospheric ammonia. In-shed benefits of sorbent additions to bedding will help defray the cost of purchase, transport, and incorporation of these materials, and improve the economic viability of spent litter sorbent formulations as fertilisers.

Our trials indicated that both acidifying and adsorbent litter additives have potential to significantly decrease shed atmosphere ammonia concentrations on reused litter. Further work is required to determine optimum inclusion rates and more clearly identify effects on welfare and performance. In response to our research, industry trials have since been progressing independent of this research project.

Nutrient supply and uptake modelling

Output parameters from the modelling exercise were used in the development of recommendations to improve the use of spent litter as fertilisers (Appendix K). Additionally, the models provide a quantitative basis to set specifications, and fine-tune the spent litter/sorbent formulations for nutrient supply, nutrient availability deferral, and mitigation of nutrient-loss pathways in different soil types. This will have a positive impact on our continuing research, and will be made available to other research groups via publication.

Recommendations

The combination of project field trial data, pot trial data, and the observations from our other studies indicate that it is possible to match the productivity of conventional nitrogen and phosphorus sources, and achieve decreased potential for nutrient losses via the use of spent litter additions and ion exchange sorbents. We recommend that quantitative management approaches to enable this be extended to end users along with the backing evidence.

Appendix K details the recommended approach to spent litter management to obtain agronomic benefits and decreased nutrient excess or losses to the environment.

It is recommended that a multi-season, multi-application management approach be adopted in extension documents and industry workshops. With this approach it is also likely to be

possible to achieve **nutrient supply that better matches the phosphorus uptake profile of many crops** than is possible with conventional fertiliser sources.

As a result of this project, bentonite is currently undergoing further trials led by industry, independent of this project, as a bedding additive in-shed and is currently on the market. It is recommended that the further steps and opportunities for the development spent litter fertiliser formulations, as detailed in the Deployment and Commercialisation section, be followed through to derive maximum benefit from spent litter and this research project.

Comments from those marketing conventional composts and spent litter products reveal that the perceived major barrier to uptake of spent litter as fertilisers was the lack of education of end users about the true value of spent poultry litter. These comments relate to composts and conventional spent poultry litter materials, not only to the nutrient content but benefits relating to soil quality which can be difficult to value. It is therefore recommended to continue the research program to establishing quantifiable benefits of manure materials, and then extending how to access the full value of these materials to end-users.

Research and education should also focus on extending approaches that step beyond conventional composting which results in poor nutrient use efficiency and does not address the opportunity to produce superior in-season nutrient supply products.

Since transport costs remain as a major barrier to the accessibility of spent litter materials, we recommend following through on approaches to add value to spent litter, such as this fertiliser formulation project, to enable a wider transport radius. However, sorbent additions are potentially expensive due to the purchase, transport, and incorporation of these materials. We recommend that one means to help offset these costs, is to take approaches that realise sorbent benefits in-shed, for example, their ability to decrease in-shed air concentrations of ammonia. This may help defray the cost of the use of sorbents. In turn, decreasing this ammonia volatilisation also retains more nitrogen that may then be accessed by the target crops and pastures.

The fact that most spent litter is removed by contractors at little return to most poultry producers, suggests that integrated producers (enterprises including composting and fertiliser formulation components) and third party fertiliser producers are the initial likely technology target. As such, these stakeholders are recommended additional partners for future technology development, which would ultimately increase demand for the material (and potentially its value to poultry producers). Dual benefit technologies, those that have benefits in-shed (such as bedding/fertiliser formulation additives such as those studied), are also recommended approaches to enable greater returns to poultry producers.

Regulatory controls also limit flexibility in terms of storage and composting off-farm and in the use of product in agricultural production, emphasising the need to ensure these regulations remain equitable and reasonable and do not unnecessarily limit use of manure materials. We recommend effective engagement with the agencies involved and rigorous supporting science in this area. We also recommend following through on high-value formulation technologies that could readily incorporate measures to overcome perceived risks.

Increasing interest in **biofuels and energy production** is a competitor for the use of spent litter for fertilisers – as are alternative manures (e.g. feedlots) closer to farming areas. It appears likely that this will continue while spent litter materials are under-valued as a fertiliser.

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Plain English Compendium Summary

Sub-Project Title:	Maximising spent litter fertiliser returns through nutrient and carbon management
Poultry CRC Sub-Project No.:	2.2.1
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Sub-Project Overview	We developed waste stream value-adding strategies that decrease nutrient losses to the environment, and provide better nutrient supply characteristics than conventional fertiliser. This included development of spent-litter fertiliser formulations, with field and laboratory validation.
Background	Despite decades of agricultural research, applications of conventional fertiliser products, such as urea and superphosphate, result in only 40 to 60% plant uptake of the target nutrients. Waste organic nutrient sources may possess characteristics that do more than simply match conventional fertiliser performance: they could provide a means of ongoing nutrient mineralisation and release to more closely match plant uptake requirements. This study centres on the general proposition that poultry litter and poultry litter products formulated with sorbents are nutrient sources capable of delivering agricultural and environmental benefits well beyond those provided by conventional inorganic fertiliser products.
Research	The project included field and glasshouse agronomic trials, sorbent bedding trials, and agronomic modelling.
Implications	Studies demonstrated that sorbent-modified spent litter could provide more timely supply of nutrients to crops than conventional fertilisers where multi-season management was implemented. Sorbent additions decreased leaching, runoff, and gaseous losses of nitrogen and phosphorus. Sorbent additions could also decrease ammonia volatilisation in-shed.
Publications	Islam, A.F.M.F., A. Van Den Heuvel, and S.W. Walkden-Brown. 2013. Effect of high level inclusion of adsorbent materials in litter on chicken welfare, performance and litter ammonia production. p. 183–186. <i>In</i> Proceedings of the 24th Australian Poultry Science Symposium. University of Sydney, Sydney, Australia. Redding, M.R. 2011. Bentonites and layered double hydroxides can decrease nutrient losses from spent poultry litter. <i>Appl. Clay Sci.</i> 52(1-2): 20–26. Redding, M.R. 2013. Bentonite can decrease ammonia volatilisation losses from poultry litter: laboratory studies. <i>Animal Production Science</i> 53(10): 1115–1118. Redding, M.R. 2014. Poultry litter as a value-added by-product. <i>In</i> Poultry Information Exchange. Gold Coast. Redding, M.R., Lewis, R., T. Kearton, and Smith, O. 2015. Manure and sorbent fertilisers increase ongoing nutrient availability relative to conventional fertilisers. <i>Plant and Soil In Review</i> . Walkden-Brown, S., A. Islam, A. Van Den Heuvel, M. Cressman, and M. Redding. 2013. Effects of various additives to reused broiler litter on ammonia

Introduction

A problem and opportunity

Despite decades of agricultural research, applications of conventional fertiliser products, such as urea and superphosphate, result in only 40 to 60% plant uptake of the target nutrients (Bolland and Gilkes, 1998a; Van der Molen et al., 1998; David & Gentry, 2000; Galloway & Cowling, 2002; Drinkwater & Snapp, 2007). For phosphorus and nitrogen, losses take different forms via different paths. The residual value of previously applied conventional phosphorus fertilisers declines with time after application (Bolland & Gilkes, 1998a). This is due to the rapid conversion of soluble forms to more stable, less soluble forms. In contrast, where high yields are sought, without regard to nitrogen fertiliser efficiency, the result can be the contamination of adjacent environments (e.g. Di & Cameron, 2002b; Perego et al., 2012).

Internationally, this presents a problem, given that the productivity of agricultural land will be required to rapidly increase. For example, it is foreseeable that China will require 30 to 50% more food to meet demand in the next two decades (Zhang et al., 2013). However, the problem is not restricted to China. For Australia, there is both a requirement and an economic opportunity to increase productivity.

The in-season nutrient supply concept

To date, Australian and international agriculture has achieved improved crop production at the expense of increasingly leaky fertiliser practices (Drinkwater & Snapp, 2007; Zhang et al., 2011). Decreasing the losses associated with crop fertiliser delivery is becoming a substantial community focus. For example, where intensive crop production may occur adjacent to sensitive environments (e.g. The Great Barrier Reef), community concern has followed after scientists have suggested causal links (Queensland Government, 2015). Solutions to enable efficient, yet high-yield, agriculture are being sought.

It is known that precise application of fertiliser nutrients just in time to meet a maturing crop's demand can substantially decrease system losses and inefficiency. By managing nitrogen fertiliser in a manner that ensured non-limiting nitrogen supply with minimum excess through in-season root zone nitrogen management (compare Figure 1), Chen et al. (2006, 2010b) were able to almost double maize yields with no increase in fertiliser use (Zhang et al., 2011). In this

management, total fertiliser nitrogen additions are divided into sub-applications that are applied throughout the growing season (Cui et al., 2010). This practice would only suit agricultural production systems where it is feasible to access the crop for additional fertiliser applications during the growing cycle. For production systems where this is not possible, other options that are able to efficiently supply nutrients to meet growth requirements may enable the same benefits to be achieved.

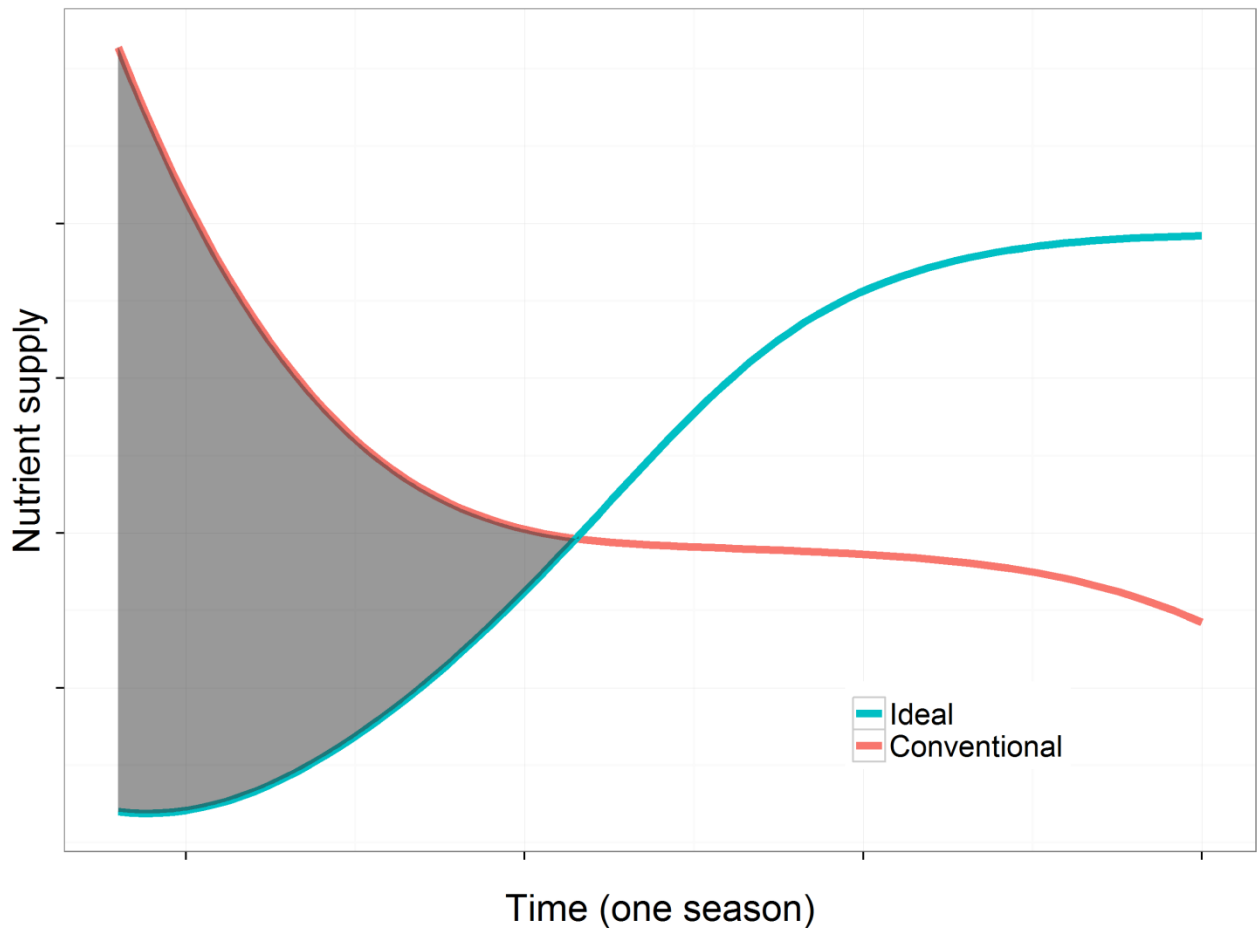


Figure 1. Nutrient supply from conventional fertilisers (such as mono-ammonium phosphate, MAP, or urea) leaves much to be desired. The initial highly soluble nutrient greatly exceeds early season crop requirements (“Ideal”) and is vulnerable to losses (shaded region between the two curves).

Innovations in fertiliser formulation

Innovation in fertiliser efficiency has a long history (e.g. Ellis, 1907; Figure 2), and a range of approaches have been taken to enhance the effectiveness of fertiliser materials, dominantly via controlled or slow nutrient release or via the application of nitrification or urease hydrolysis inhibitors (Halvorson et al., 2014; Timilsena et al., 2015). The nutrient delivering efficiency of

these products tends to be higher than that of conventional fertilisers, due to their enhanced potential for in-season nutrient supply, and decreased potential for leaching, run-off, and gaseous nutrient losses (Dave et al., 1999; Trenkel, 2010). Another important advantage is a decrease in the damage to leaves and roots due to osmotic stress (Shaviv, 2001; Trenkel, 2010). While some of these approaches have demonstrated substantial agronomic or environmental advantages, they tend to be expensive (2 to 13 times the cost of equivalent masses of conventional fertiliser nutrient; Lammel, 2005).

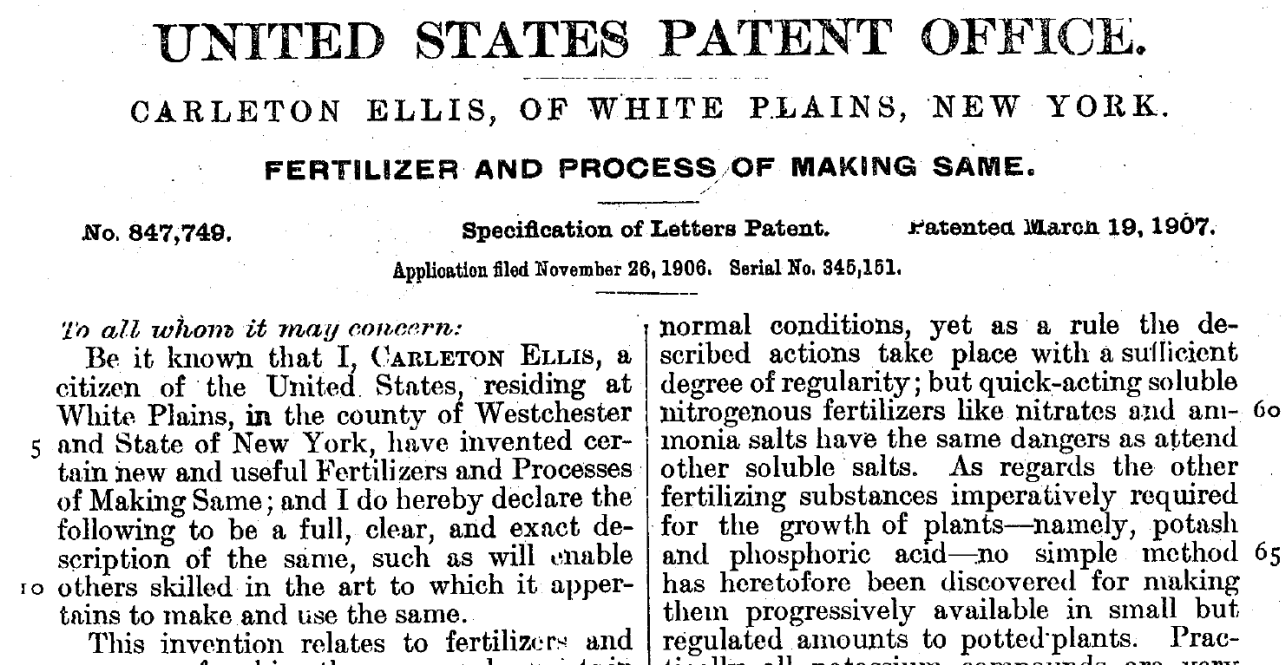


Figure 2. Improving fertiliser performance has long been a focus of research attention. This patent application originates from 1906.

Nitrogen transformation inhibitors (urease and nitrification inhibitors) may be less expensive than encapsulated fertiliser products; however, they tend to be temperature sensitive (breaking down as temperatures increase; Irigoyen et al., 2003; Ruser & Schulz, 2015), and there are health concerns regarding the application of some forms of inhibitors (e.g. hydroquinone; Trenkel, 2010). Even where there is no demonstrated health effect, observation of residues in agricultural products can be a barrier to adoption of these technologies (e.g. Danaher & Jordan, 2013).

Ion exchange materials

Ion exchange materials (Figures 3 to 5) have been proposed as a means to tailor nutrient supply to meet plant demand without excesses to allow for losses (Gillman & Noble, 2005). The advantage of the ion-exchange mechanism in nutrient supply is that these materials will

tend to buffer solution concentrations, potentially supplying further nutrient as the plant lowers solution concentrations in the rhizosphere. Materials investigated in this role include: hydrotalcite, an anion exchanger able to retain phosphorus and nitrogen (as nitrate or nitrite); and bentonite (Gillman, 2011; Redding, 2011) and zeolite (Li et al., 2013), both of which have an affinity for ammonium cations. This study seeks to further investigate this potential through the application of an anion exchanger for phosphorus delivery and a cation exchanger for nitrogen delivery.



Figure 3. Three ion exchange sorbents that have been used by the research team for agronomic purposes: Top: bentonite, which is a mixture of clays dominated by montmorillonite; right: hydrotalcite, a layered double hydroxide; bottom: vermiculite, a platy clay mineral.

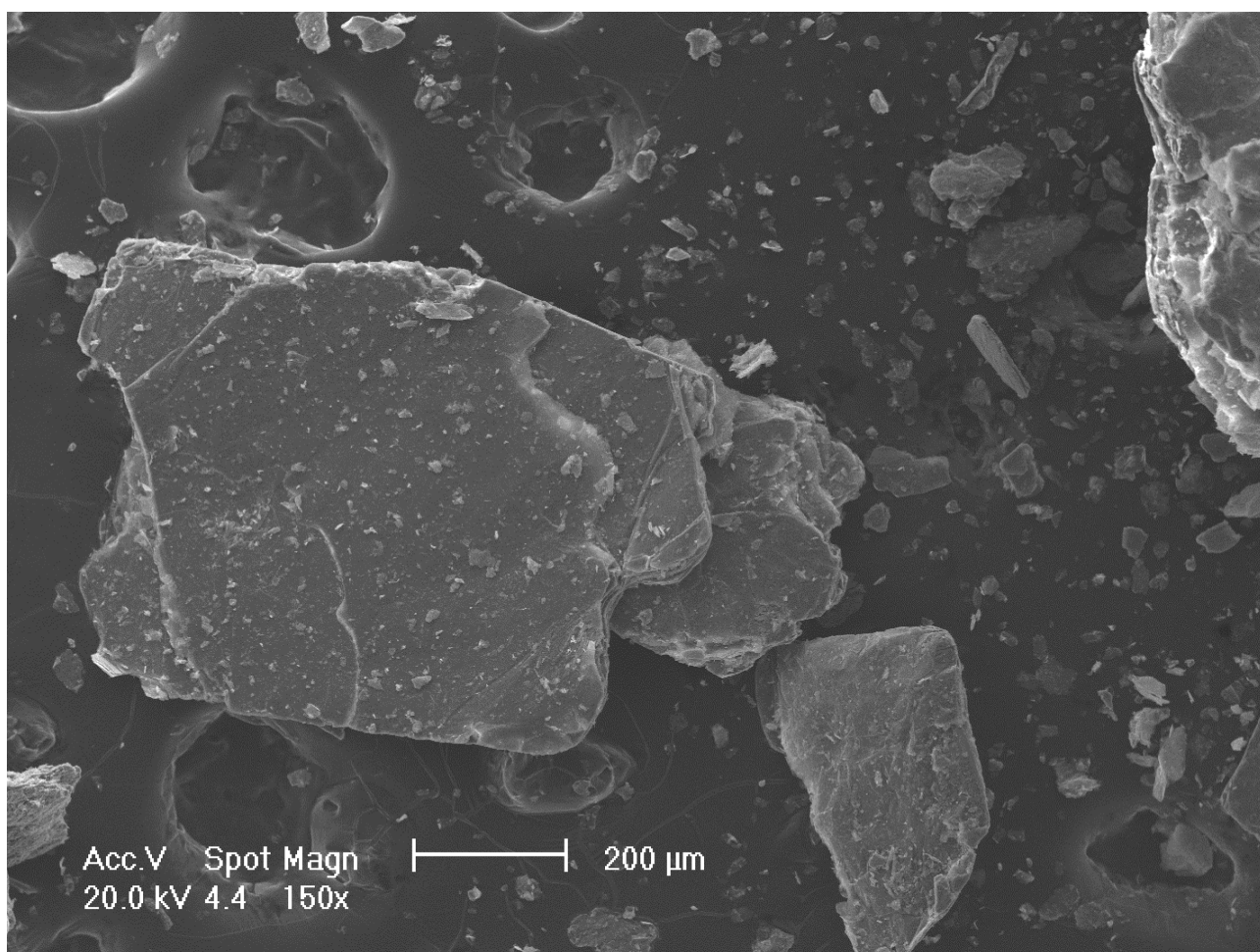


Figure 4. An electron micrograph of vermiculite, displaying the layered structure that gives the material an enormous surface area.

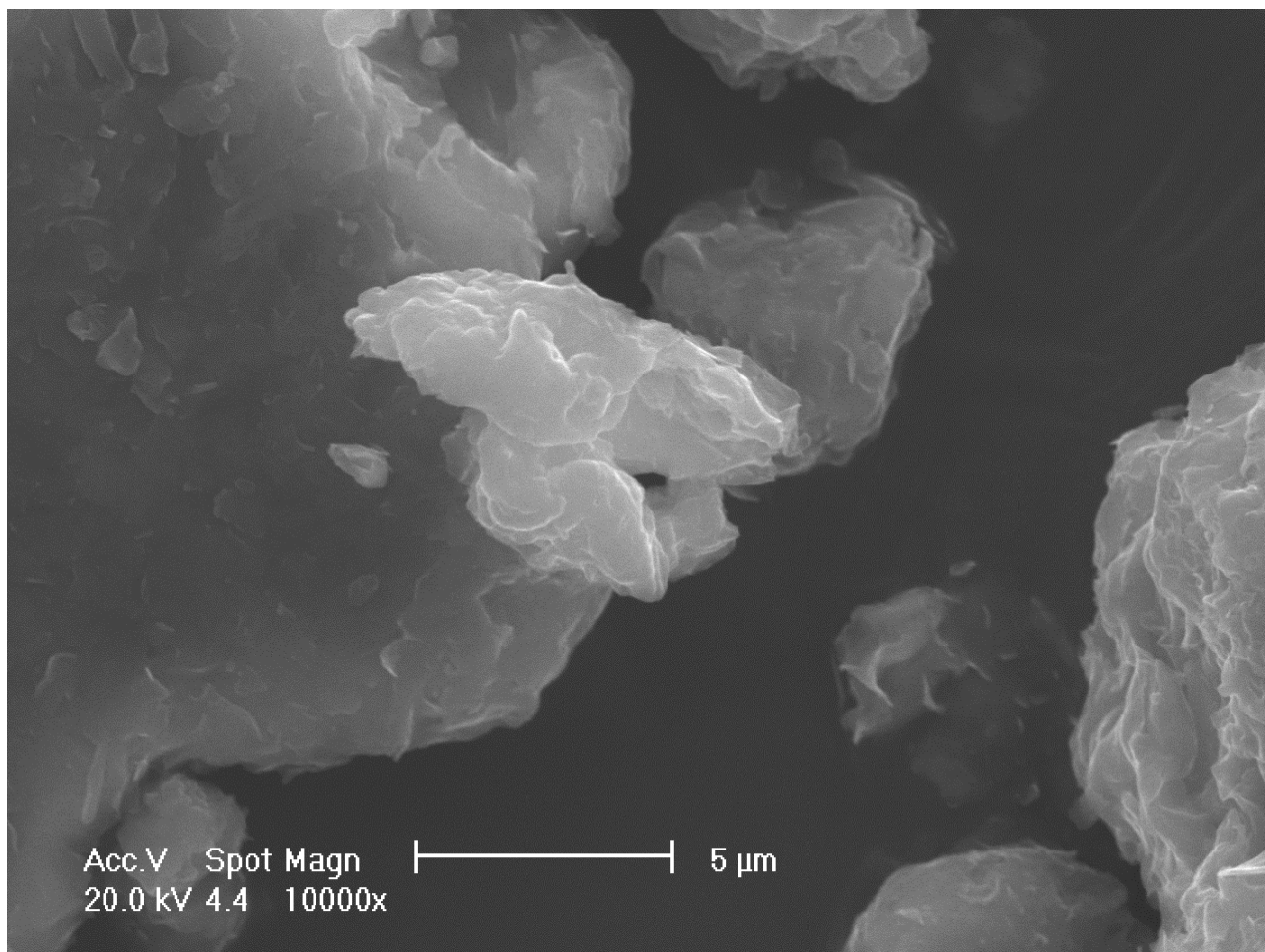


Figure 5. An electron micrograph of bentonite revealing its platy structure at an extremely fine scale (image magnified 10 000).

Manure: a superior fertiliser?

Conventional fertiliser practice emphasises the uptake of inorganic nutrient forms. However, it is known that some organic nutrients are available to plants (Paungfoo-Lonhienne et al., 2008, 2012; Schmidt et al., 2013). The relative importance of organic nutrient uptake (compared to inorganic nutrient forms) remains unknown (Nasholm et al., 2009).

Models have been used to predict nutrient availabilities from manure or organic waste applications to soils in experimental crop management (Beraud et al., 2005; e.g. composts and manures, Archontoulis et al., 2014). However, no attempt appears to have been made to tie waste material nutrient release to in-season nutrient requirements of crops or pastures.

One approach may be to utilise waste organic nutrient sources, not simply to match conventional fertiliser performance, but to provide a means of ongoing nutrient mineralisation and release (Smith et al., 1998; Kihanda et al., 2005; Adeli et al., 2011). This may prove to be a means to re-couple the nutrient and carbon cycles, potentially resulting in less nutrient losses

from excess supply (Drinkwater & Snapp, 2007). Conventional use of manures as fertilisers often do not achieve this end, as demonstrated by a range of studies into nutrient losses (e.g. Chardon et al., 1997; Smith et al., 2007; Rasouli et al., 2014). However, it is likely that continued seasonal applications of moderate quantities of manure nutrients will result in steadily increasing availability of nitrogen, phosphorus, and potassium with successive applications (Bar-Tal et al., 2004).

Initial groundwork identifying potential key advantages of manure use is already in place. A meta-analysis of available data suggests that manure applications to soil (without formulation) as fertilisers resulted in significantly greater organic carbon (OC) in soils and comparable yields to conventional nutrient sources (Edmeades, 2003). Given a history of annual manure application, it is possible to reach a point where annual nitrogen and phosphorus made available in the rhizosphere is equal to the manure nitrogen and phosphorus applied (Helgason et al., 2007). One study achieved ongoing nutrient release matching crop requirements within nine years of application of un-composted and composted cattle manure (Miller et al., 2009). Effectively, these observations suggest that manure nutrient forms defer nutrient availability relative to conventional fertiliser forms. As the agricultural paradigm shifts to a need for precise and efficient nutrient supply with low environmental losses, can these manure characteristics offer an advantage?

Maximising the fertiliser value of spent litter

This study centres on the general proposition that poultry litter and poultry litter products are nutrient sources capable of delivering agricultural and environmental benefits well beyond those provided by conventional inorganic fertiliser products. Proponents have optimistically advocated organic waste use for a range of intangible benefits, with equally intangible evidence. Alternatively, many research projects have sought to “match fertiliser performance” – ignoring the true advantages of these materials.

The development of profitable products from spent litter is a commercial opportunity for industry; however, it also addresses a developing and critically important national and international issue. Global population is set to increase by one-third before 2050 (United Nations estimates). In response, international food supply needs to increase each decade, and nutrient supply is a key factor for global food security. It is preferable that this increased nutrient demand is met by fertilisers that, unlike soluble synthetic fertilisers, produce environmentally sustainable outcomes. Spent poultry litter products can be part of this solution. Spent poultry litter is a valuable nutrient resource, but is not currently utilised to its full potential. End-use is hampered by negative perceptions and the characteristics of the spent litter itself.

Spent litter is perceived as bulky, and having inconsistent nutrient content, and there are concerns that use as a land-applied fertiliser may result in environmental damage due to nutrient leaching or run-off. The off-site consequences of this type of nutrient loss are well known and, unfortunately, widespread (Carpenter et al., 1998). These impacts include toxic algal blooms, reduction in water body oxygen, fish kills, loss of biodiversity, loss of aquatic plant beds and coral reefs, and a range of other effects that combine to impair the use of water for drinking, industry, agriculture, and recreation.

Spent litter, like any organic material, releases nutrients to the surrounding plants as it decays, at a rate that may not match plant requirements. However, spent litter is not a balanced fertiliser. Where this material is applied solely on the basis of its nitrogen content this is likely to result in phosphorus oversupply, which increases the potential for environmental contamination of waterways through run-off. Additionally, any excess phosphorus remaining in the soil will eventually become unavailable to plants (through binding to the soil or losses to the environment). Significant ammonia volatilisation also occurs from spent litter contributing to odour nuisance, nitrous oxide (greenhouse gas) emissions, and exacerbation of the nitrogen to phosphorus imbalance.

These negative perceptions prevent the true economic value of the litter from being achieved and have made the on-selling of spent litter difficult in some locations. To address these concerns, and increase the value of spent litter, technologies are required to:

- allow plants to more precisely meet their nutrient requirements from a spent litter formulation
- decrease the risk of losses to the environment.

While not in the required ratios, poultry litter contains the range of critical nutrients commonly applied as inorganic fertiliser. These nutrients occur in slow-release forms and are accompanied by a substantial input of biologically active carbon (Drinkwater & Snapp, 2007). Litter effectively provides a feedstock for microbial biomass nutrient conversion activities (Okur et al., 2006) resulting in the retention of nutrient forms with much longer persistence in soil than occurs with inorganic fertilisers.

This is the starting point for our agronomic research. We sought to identify if we could use two ion exchange materials and a manure nutrient source (spent poultry litter; the bedding material collected from a commercial production facility after the production of a batch of broiler chickens) to defer nitrogen and phosphorus availability relative to a conventional fertiliser source and decrease nutrient losses. To this end we conducted glasshouse and field trials over

multiple seasons, observing a considerable offset of availability of phosphorus relative to the conventional source.

Objectives

High-value fertiliser. Develop and facilitate adoption of waste stream value-adding strategies that decrease nutrient losses to the environment, and provide better nutrient supply characteristics than conventional fertiliser. This will include the development of a spent-litter fertiliser formulation or range of formulations. These strategies will be validated through field and laboratory experimentation.

Underlying this objective is the following hypothesis: *The ongoing process of nutrient mineralisation from spent poultry litter and sorber technologies can be used to formulate spent-litter products that result in greater plant uptake and lower nutrient losses than conventional nitrogen and phosphorus fertiliser sources.*

Methods

Detailed descriptions of all methods applied are supplied in Appendices A to J. This section provides a rapid overview of the approaches applied, and is necessarily limited to a few pages.

Literature review

A review of the literature surrounding enhanced-efficiency and manure-based fertilisers was completed, and is included as Appendix A.

Pot trials

Pot trials were conducted to determine spent litter nitrogen and phosphorus supply behaviour, to compare this behaviour to conventional fertilisers sources, and to investigate the impact of sorbent additions (bentonite at $47.7 \text{ g [g of N]}^{-1}$, approximately 100% of the dry litter mass; and hydrotalcite at $26.2 \text{ g [g P]}^{-1}$, approximately 74% by dry mass). Each replicated trial consisted of 96 pots, spanned two soils, six nutrient application rates, and multiple cuts. The phosphorus trial in particular continued for 20 months and 15 cuts. Pasture species were employed as model plants, because of their ability to be cut multiple times during the season, providing a representation of maximum potential nutrient uptake. Full details of the methods employed are given in Appendices B and C.

Field trial

A small-plot ($1.5 \times 2 \text{ m}$) field trial (64 plots) was established with pasture as the plant model, with a treatment structure designed to investigate the effect of sorbents (HT at a rate of 3.75 and 7.5 g [g P]^{-1} , 10 to 33% by dry mass of spent litter; bentonite at 25 to $85 \text{ g [g of N]}^{-1}$, or 100 to 330% by dry mass of litter) and spent litter versus conventional nitrogen and phosphorus sources. Spent litter contains both nitrogen and phosphorus, so it was necessary to differentiate observations of these two nutrients through the use of basal fertiliser applications.

The site was located on a red clay soil with solid-set irrigation to eliminate water limitations. Cuts were completed using a domestic push-style lawn mower with an attached catcher. These samples were then ground, subsampled, and analysed. Before and after the trial, soil in each plot was sampled (8 cores 40 mm in diameter, pooled) and analysed as described for the pot trial. Three pasture cuts were completed on the trial plots before treatment applications to assess site uniformity, and to help remove any evident plot effects from the trial data (as an analysis covariate). Basal applications of non-trial nutrients and lime were applied individually to each plot.

Fifteen cuts were completed throughout the period from 23 January 2013 to 15 September 2014. Maintenance nutrients were applied throughout the trial to optimise nutrient conditions. Full experimental details are available in Appendix B.

Sorbents as a means to modify gaseous and water-borne losses

Studies were completed to compare water-borne losses of nitrogen and phosphorus from spent litter compared to conventional fertiliser sources, and the impact of sorbent additions (bentonite and hydrotalcite). A range of approaches were applied, including rainfall simulation, column leaching studies, and ammonia volatilisation trials conducted in the laboratory. Refer to Appendices D, G, and H for full method descriptions.

Bentonite bedding trials

Two trials of bentonite as a bedding additive were conducted with meat chickens at a pilot scale at the University of New England. Descriptions of the methods employed are available in Appendices E and F.

Nutrient supply and uptake modelling

A detailed mathematical modelling study was completed by AgResearch New Zealand to develop calculation algorithms for the supply of nutrients from spent poultry litter and sorbent-modified spent poultry litter. Full details of this exercise are reported in Appendix I.

Technology adoption study and participatory research component

An adoption specialist (J&R Coutts Consulting) conducted interviews with stakeholders, an adoption workshop in collaboration with the DAF team, and prepared a report on adoption potential (Appendix J). Outputs from this workshop led to the development of the participatory research trial conducted in collaboration with spent litter fertiliser formulators, centred around investigating the water mobilisation of nitrogen from various products (Appendix D).

Discussion of results

Agronomic trials

The pot trials (both the nitrogen and phosphorus trials) and the field trial are discussed here collectively to build a coherent picture of the agronomic findings of the project.

The two soils chosen for these studies represented two extremes:

- The sandy soil has little positive or negative charge, and is representative of soils with extremely poor ability to retain nutrients.
- The red clay soil is representative of soils with an extreme ability to retain P. This characteristic is so strongly expressed that it greatly decreases the agronomic availability of phosphorus.

While the sandy soil provided much stronger treatment contrasts than were evident for the red clay, these results are largely relevant to two scenarios:

1. Situations of potentially high nutrient-loss soils via leaching and runoff.
2. As a representation of maximum potential nutrient release from the formulations, where there is minimal influence or chemical interaction between the soil and the fertiliser.

In terms of nutrient retention, the behaviour of other agronomic soils is likely to fall between these two extreme soil types.

While each of the trials employed pasture species, these trials were not designed as pasture trials. Rather, pasture species were grown due to their ability to sustain multiple cuts during the season. This allowed collection of detailed data sets representing the maximum nutrient supply potential of the formulations spent litter at multiple time points during the conduct of the trials (up to 15 cuts). This was particularly important, given the desire to represent in-season nutrient supply and uptake behaviour.

Phosphorus pot trial

Sorbent additions (hydrotalcite) to the conventional treatment tended to defer nutrient availability in the phosphorus pot trial (Figure 6). This was most evident for the sandy soil, but was also evident for the red clay following re-planting. The spent litter source of phosphorus also tended to defer phosphorus availability in the sandy soil, where phosphorus uptake following replanting exceeded nutrient supply from the conventional treatment. This would be expected from previously published observations of the use of other manure forms as fertilisers (Helgason et al., 2007; Miller et al., 2009).

Overall, nutrient uptake from the conventional treatment exceeded that from treatments with hydrotalcite or the spent litter source. Given the effect of sorbent addition or spent litter in deferring availability, and the limited potential for nutrient losses in this pot trial, this is an expected consequence. Over a longer time scale, a greater proportion of uptake from the hydrotalcite and spent litter sources would likely occur. Indeed, it is evident from the sandy soil data that phosphorus delivery by the conventional treatments began to be exceeded by the spent litter and hydrotalcite treatments around the seventh cut (of 15 in the trial). At the completion of the experiment, the hydrotalcite treatments contained greater available phosphorus than those without hydrotalcite.

Addition of hydrotalcite was also observed to eliminate leaching losses of soluble inorganic phosphorus from the sandy soil, while they were significantly decreased via replacement of the conventional source by spent litter. Though total phosphorus losses were not measured in addition to soluble inorganic forms, these results are comparable to total phosphorus run-off and leaching data following hydrotalcite treatment reported previously (Redding, 2011).



Figure 6. The phosphorus pot trial in action. The smaller pots were a germination trial associated with the nitrogen pot trial.

Nitrogen pot trial

Across both soils and all cuts there were significant treatment effects of bentonite addition on total nitrogen uptake ($P < 0.1$, decreased nitrogen uptake by 13%), delaying delivery of nitrogen relative to those treatments that did not receive bentonite. Using nitrogen uptake by the model pasture species as maximum potential uptake (Redding et al., 2015), it is evident that nutrient availability is greater in the first cut where bentonite additions have been made ($P < 0.1$), but no different in later cuts (second and third). This represents a four week deferral of availability, during the period in which the classic nutrient requirement curve is at its lowest point (Figure C.1).

A similar pattern was evident for nitrogen-source type. Spent litter application significantly decreased maximum potential uptake for the first two cuts relative to the conventional source ($P < 0.001$). Throughout the trial, there was a 61% decrease in total nitrogen uptake associated with the use of spent litter relative to the conventional treatments ($P < 0.001$).

These results need to be considered in the light of the extended field trial to identify the likely ongoing uptake of nitrogen from spent litter and bentonite treatments. While total nitrogen uptake here was less from the spent litter and bentonite treatments, the field trial (Redding et al., 2015) suggests that over the longer term, equivalent nitrogen will be available.

Field trial

Lower rates of hydrotalcite addition were applied in the field trial (Figure 7) than were applied in the pot trial, in an attempt to raise initial available phosphorus concentrations to allow higher productivity, while simultaneously attempting to defer excess nutrient availability. This rate allowed dry matter production and phosphorus uptake to reach the same magnitude as that from the conventional treatments. However, the rate decrease also eliminated measureable evidence of deferral of phosphorus availability, including in the final trial soil samples.

The spent litter treatments performed largely equivalently to, or slightly better than, the conventional treatments in terms of phosphorus uptake ($P < 0.05$; Figure 4), and equivalently in terms of nitrogen uptake. This contrasts with the results of the phosphorus pot trial for this soil. Containment of the plants within pots would have a number of effects on nutrient-plant interactions that would not occur in the field. First, nutrient losses would be less likely in the pot system, and so any advantage of spent litter versus conventional treatments with regard to nutrient retention may not be as fully expressed. Second, the root confinement that occurs in the pots may prevent observation of any root development contrast that could occur with spent litter versus conventional treatments in the field. Manure applications to soils are known to alter root development or increase root length density (Mosaddeghi et al., 2009).

At the end of the trial spent litter treated plots contained less residual mineral-nitrogen (19%) than the conventional treated soils. It is likely that a proportion of spent litter-derived nitrogen is retained in complex organic forms. Literature suggests that this nitrogen will later become available (Helgason et al., 2007; Miller et al., 2009).

The rates of hydrotalcite applied have already been demonstrated to greatly decrease nutrient losses via leaching, runoff (in terms of P), and gaseous nitrogen losses (Redding, 2011, 2013; Hill et al., 2015; Pratt et al., 2015), and it is likely that these benefits also accrued in the field trial. It is the effect on loss pathways that is probably responsible for the observation that **bentonite additions increased the residual extractable mineral-nitrogen in the soil by around 19%.**



Figure 7. Soon after establishment of the field trial.



Figure 8. Synthesizing hydrotalcite.

Effect of sorbent additions and pelletisation on loss pathways

Ammonia volatilisation

Nitrogen losses due to volatilisation from un-modified spent litter amounted to 62% of total nitrogen after 64 days – representing both a potential poultry production concern and loss of fertiliser value. Bentonite additions to spent litter at a rate appropriate for fertiliser formulation (treatment 127% of the dry mass; 15% loss of N in water saturated conditions, 34% in moist conditions) retained more ammonia than alum additions at a recommended rate (treatment 4% of dry mass; 54% loss of N in water saturated conditions)(Redding, 2013).

Leaching and rainfall simulation

Some of this work was completed as part of the Poultry CRC pilot trial related to this project, but was more recently published.

Sorbent additions (Figure 8) were successful in decreasing losses of N and P via leaching and runoff, as determined by laboratory leaching trials (for phosphorus) and rainfall simulation (nitrogen and phosphorus; Figures 9 and 10).

Addition of bentonite increased the proportion of mineral nitrogen retained in exchangeable form, from 19% to up to 54% (bentonite rates from 35 to 158% of dry litter mass).

Hydrotalcite additions equivalent to 20 and 30% of the mass of dried litter resulted in 60 and 90% decreases in the quantity of phosphorus leached from bentonite-treated spent litter during

extended leaching. These additions also eliminated the measureable ongoing phosphorus release from the bentonite-only treated spent litter.

However, under rainfall simulation, the 10% hydrotalcite addition rate combined with bentonite (127%) was sufficient to effectively eliminate initial run-off phosphorus losses from untreated spent litter. The combination of hydrotalcite (10%) and bentonite appeared to exceed the performance of conventional rates (2 to 11%) of alum addition.

Spent litter and a range of alternative formulations resulted in significantly lower short-term mineral-nitrogen runoff losses relative to ammonium nitrate during rainfall simulations (Figures 9 to 11). Spent litter itself decreased nitrate and ammonium losses (Figure 11).



Figure 9. Rainfall simulation flumes loaded with turf.

Increasing rates of bentonite addition also resulted in decreasing mineral nitrogen losses (significant $P < 0.1$; treatment rates up to 254% of the dry litter mass).

As discussed previously, spent litter is not a balanced fertiliser, containing far too little nitrogen to match the plant production potential of the phosphorus content. We tested a formulation that supplied the spent litter with additional nitrogen in the form of nitrate-loaded hydrotalcite. We found that adding nitrogen-loaded hydrotalcite (Figure 8) formulated with spent litter resulted in lower N losses than the ammonium nitrate treatment.

Part of the reason that so little mineral-N loss was recorded for many of the treatments was that the experiment represented losses immediately after fertiliser application. While this is a point at which there is a high risk of nitrogen mobilisation, it did not allow time for conversion of ammonium to nitrate, the most mobile nitrogen form. None of the formulations included significant nitrate except for the ammonium nitrate and nitrate-hydrotalcite treatments.



Figure 10. The "Pellet Litter" treatment ready for rainfall simulation.

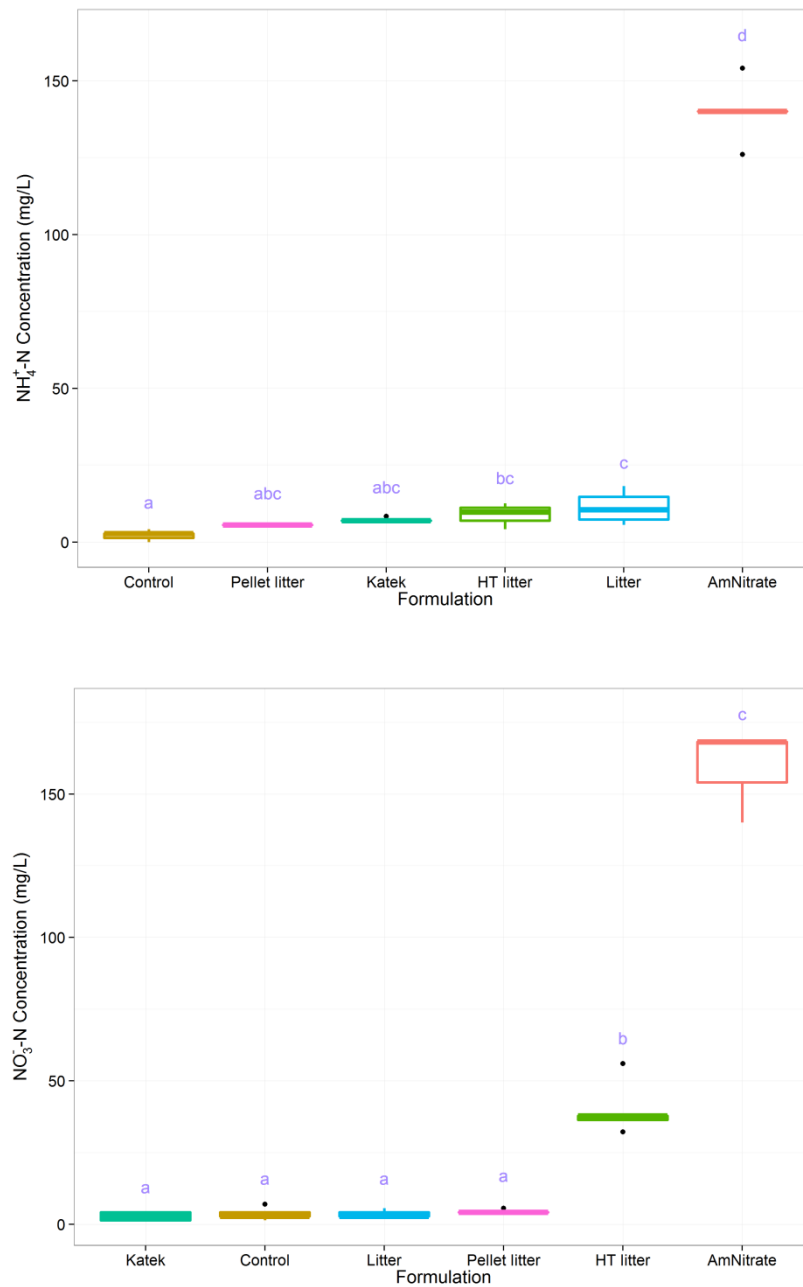


Figure 11. Formulation effects on mineral-N runoff. Several pelletised forms were included in the studies (Katek, a pelletised spent poultry litter already on the market, and a new formula simply labelled “Pellet litter”). Formulations plotted with the same letter above them are not significantly different from each other.

Sorbent additions to bedding materials

Full descriptions of experimentation and discussion of results are available in Appendices E and F (Islam et al., 2013; Walkden-Brown et al., 2013). The following summary material was derived from these publications.

Excessive nitrogen volatilization from poultry litter as ammonia (NH₃) is harmful for chickens and poultry workers' health. Litter amendments such as bentonite and zeolite can decrease NH₃ and improve air quality in the poultry shed. Inclusion of these materials in poultry litter can reduce nitrogen volatilization and the solubility of phosphorus thus increasing the fertilizer value of the spent litter.

Treatments were nil amendment and 33% and 50% by weight addition of each of bentonite and zeolite. Inclusion of bentonite but not zeolite at these levels increased mortality of chickens during brooding, but did not adversely affect chicken live weight, footpad dermatitis, hock burn, breast blister and breast feathering of chickens up to day 42. Both amendments significantly reduced ammonia volatilisation from the litter up to day 28.

In a second experiment, we investigated the effects of adding alum, sodium bisulphate, bentonite, zeolite and NaturClean CSM® at 3.2, 3.2, 13, 13 and 0.9% by weight respectively to reused litter on moisture content, pH, ammonia production, bird liveweight and conditions linked to welfare including scores for footpad dermatitis, hock burn, breast burn and breast feathering.

All litter amendments except NaturClean CSM® reduced ammonia production with the greatest reductions seen with alum and sodium bisulphite on days 7 and 14. Amendments worked similarly in litter with or without water addition.

There were no significant effects of litter amendment on bird weights or measures of welfare with welfare measures generally worsening with time and with initial addition of water. Ranking of reused litter treatments from 1 to 6 (best to worst) for each welfare measure, followed by the averaging of those rankings, provided mean rankings of 1.75, 2.25, 3, 3.75, 4.75 and 5.5 respectively for reused litter without amendment, bentonite, alum, sodium bisulphite, NaturClean CSM® and zeolite treatments.

Nutrient supply and uptake modelling

A conceptual model of nutrient release to the soil from spent litter and pasture growth was developed. Additional input variables to the model included temperature and radiation. The

nonlinear model was fit to data from pot trials that measured the effect of spent litter on plant growth and nitrogen/phosphorus uptake by the plant.

The model was validated in a field trial that measured the effect of spent litter on plant growth and nitrogen/phosphorus uptake by the plant. The model can predict total pasture dry matter (DM) production over the two year trial with a correlation coefficient of 0.92-0.95 in the field trial and > 0.9 in the pot trials.

To achieve these results, the following characteristics of the nutrient supply systems were successfully represented:

- Contrasting characteristics of the soils were represented as differences in phosphorus sorption capacity between the red clay (high) and the sandy soil (low).
- The effect of sorbent addition in decreasing P leaching. The combination of sorbents bound excessive fertiliser-derived soluble nitrogen and phosphorus and released it again as plants require it (fertiliser release was smoothed out).
- Representing differences in nutrient release and mineralisation from the different spent litter and conventional sources. Nutrient release from manure was slower than the inorganic fertiliser treatment. This is consistent with ongoing nutrient supply with the manure treatment. There was lower available P for plant uptake with both manure and sorbent treatments.

Technology adoption

A detailed discussion is available in the report attached as Appendix J (Coutts et al., 2015); the following is an extract representing key findings of the study:

There was strong support among all stakeholder groups that the technology – i.e. adding clays and other additives to improve the fertiliser value (more even release of N and P) of spent poultry litter – was a positive contribution to the value chain. The advantages were seen to have application to the range of agricultural uses of the spent litter.

Financial benefits are more likely to accrue to the fertiliser supplier/seller than the poultry producers themselves – who are under pressure to remove the spent litter and are price takers rather than price makers. Large producers who compost/treat and either use the spent fertiliser on their own enterprises and/or ‘retail’ product to other users can also use and reap the benefits of the technology.

Manure fertiliser suppliers were found to be the key stakeholder group that could benefit from and best implement the technologies being developed. Meat chicken litter was exclusively used by the informants as it was seen as more easily handled and a better product for farm fertilisers. Suppliers used a mix of composting, blending and pelletising in

preparing the product. Some were adding clays or other additives to their mix. Fertiliser products were supplied to a mix of landscaping, market gardens, broadacre and horticultural purposes.

All meat chicken producers respondents cleaned out their sheds each batch – although it was reported that some companies encouraged producers to re-use litter in the growing part of the shed because of shortages of bedding material. One-batch litter and litter with extra bedding (25% under new RSPCA recommendations) was reported to have less manure value than reused litter. Bedding materials were reported to consist of sawdust, shavings, rye or rice hulls – depending on where farms were located. Although some composted litter was used on site, most was collected by contractors – often at no direct cost to either party. Composted manure was reported as selling for \$5-6/cubic metre. Spent litter was reported as being used on grain, dairy, grazing and market garden enterprises. Meat chicken farms tend to be in clusters, and transport distance and cost are a limitation to spent litter use.

A strong theme emerging from the study was that end users (agricultural enterprises using manures to supplement or replace inorganic fertilisers) undervalued the nitrogen and phosphorus value of spent poultry litter and hence were not prepared to pay equivalent prices. Adding transport costs to the low prices being obtained for the product limited the potential to further add value through the technology.

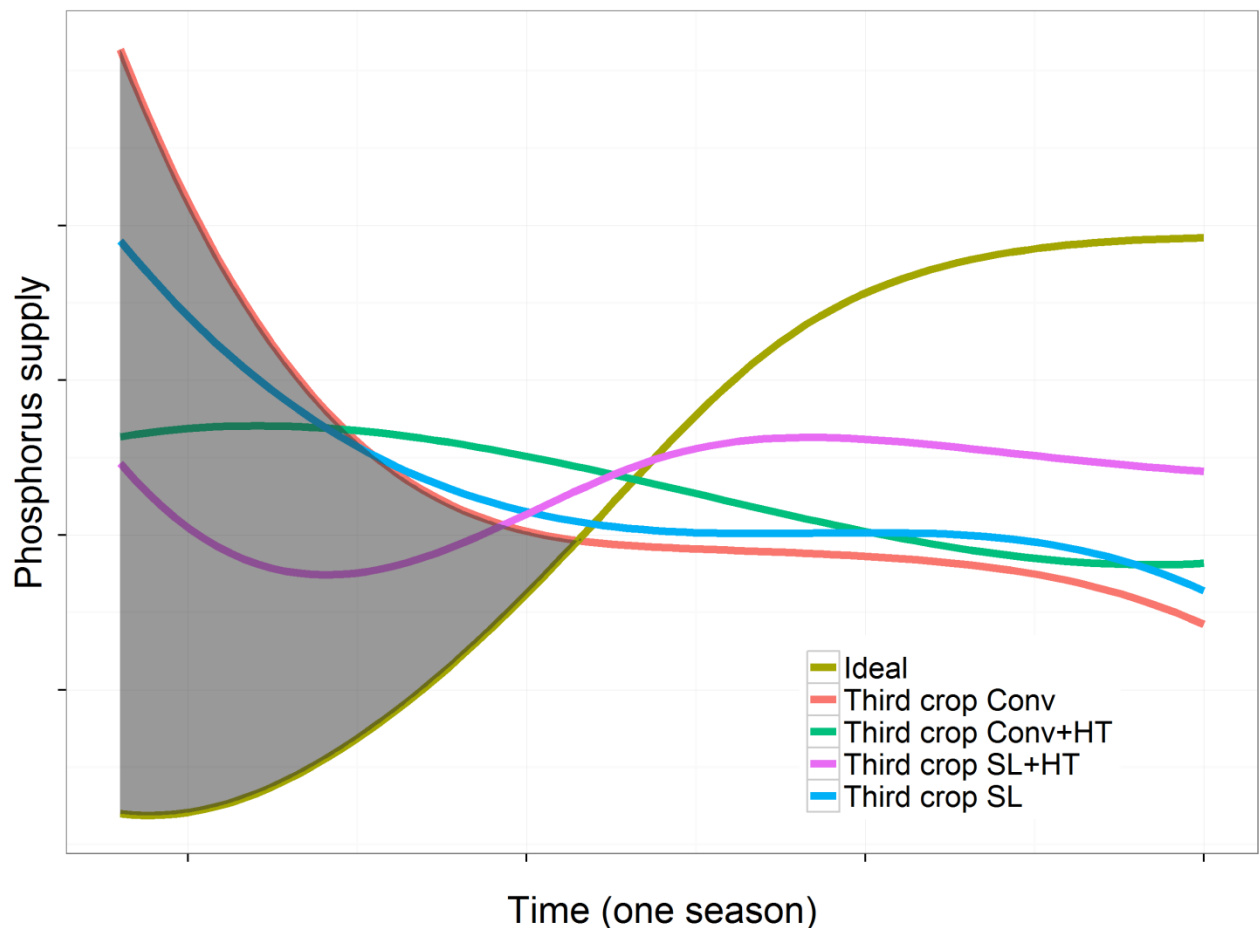


Figure 12. Based on the pot trial data, this figure predicts the performance of the conventional phosphorus source (Conv; spent litter, SL) versus a hydrotalcite-treated form (+HT), and spent litter+hydrotalcite (SL+HT) for the third consecutive cycle of fertiliser application and crop production. The unmodified conventional and spent litter treatments both show excess initial availability that may be subject to losses (shaded region). The ideal uptake curve of many plants is provided as a reference.

Implications

Agronomic implications

Common crop uptake profiles involve a greater nutrient requirement later in the season than at the beginning (Figure 1). The ability to defer phosphorus supply via hydrotalcite addition or the use of spent litter as demonstrated in the pot trial will likely be useful in achieving this goal.

The results from the sandy soil enable an examination of the likely behaviour of spent litter and hydrotalcite treatments after three consecutive fertilised crops (Figure 12). It appears likely that the hydrotalcite + spent litter and hydrotalcite + conventional forms will better match the ideal nutrient uptake profiles of many crops relative to conventional fertiliser treatments. While the excess initial nutrient availability associated with the conventional treatment is vulnerable to losses (Figure 12, shaded region), this is not the case where hydrotalcite is used as an additive.

The combination of our field trial results, our pot trial leaching data, and the observations from our other studies (Redding, 2011, 2013; Hill et al., 2015; Pratt et al., 2015) indicate that it is possible to match the productivity of conventional nitrogen and phosphorus sources, and achieve decreased potential for nutrient losses via the use of manure materials and ion exchange sorbents.

It was also evident that the use of cation exchangers (in this case bentonite) can allow greater carry-over of nitrogen value between crops, without a decrease in productivity – simply by decreasing nutrient losses.

Mitigating nutrient losses

Collectively, the runoff, leaching, and ammonia volatilisation trials indicate that the rates of sorbent additions employed in the field and pot trials were sufficient to significantly decrease or eliminate losses of phosphorus or nitrogen via these pathways. Data collected as part of a concurrent project also suggests that the bentonite and vermiculite additions can significantly decrease nitrous oxide emissions (a potent greenhouse gas) (Hill et al., 2015; Pratt et al., 2015).

Sorbent additions are therefore confirmed as a technically viable means to decrease losses of fertiliser value, and to decrease environmental contamination. This success applies both to spent litter formulations and in some cases to formulations involving conventional fertilisers and sorbents. The economics of applications of sorbents in this role is dependent on circumstances.

Laboratory ammonia volatilization

The rates of application of bentonite in this trial were large (about 127% of the dry litter mass) with a view to the subsequent manufacture of a fertiliser product from the mixture (Gillman 2007). Such heavy applications of bentonite may well be uneconomic where a significant return on the sale or use of the spent litter product is not achieved.

Application of bentonite may prevent losses of N both in-shed or after removal of spent litter from the poultry housing – possibly providing a more effective fertiliser product (Gillman 2006). If application in-shed translates into a production benefit (e.g. higher growth rates due to decreased atmospheric ammonia concentrations), this benefit may decrease the cost of production of a high-efficiency bentonite + spent litter fertiliser from the waste material. The combination of a potential in-shed production benefit (e.g. higher growth rates due to decreased atmospheric ammonia concentrations, and decreased expenditure on other bedding materials) and increased returns from the fertiliser value (production of a high efficiency bentonite + spent litter fertiliser) may out-weigh the benefits from using alum. Alum addition to spent litter is an established practice to decrease ammonia volatilisation. However, alum additions may be detrimental to the agronomic phosphorus value of the spent litter (Guo & Song 2009; Warren *et al.* 2008).

These potential benefits were further investigated in bedding trials.

Mitigating leaching and runoff nutrient losses

Spent litter application was found to generate less mineral-N in runoff than equivalent rates of ammonium nitrate, where rainfall occurs immediately after application. However, given a few days for nitrate to form, the magnitude of the difference between the sources would change. Observations suggest that bentonite additions to spent litter are a potential tool to decrease runoff nitrogen losses.

Where it is necessary to supplement the nitrogen content of spent litter, nitrate-loaded hydrotalcite may be a means to do this while decreasing nitrate losses relative to additions of a free nitrate or rapidly nitrate-forming nitrogen source.

The rainfall simulation data suggested that under realistic run-off generation conditions, a 10% rate (by mass) of hydrotalcite would be sufficient to effectively eliminate initial run-off phosphorus losses from spent litter. More aggressive conditions indicated that a 20% rate was required to halt phosphorus leaching.

Sorbent additions to bedding materials in-shed

Both acidifying and sorbent litter additives have potential to significantly decrease shed atmosphere ammonia concentrations on reused litter. Further work is required to determine optimum inclusion rates and more clearly identify effects on welfare and performance. In response to this research project, industry trials of bentonite are in progress.

Established in-shed benefits of sorbent additions to bedding may also help defray the cost of purchase, transport, and incorporation of these materials, and improve the economic viability of spent litter sorbent formulations.

Nutrient supply and uptake modelling

The decay-related nutrient release constants developed in the modelling components of the project underlie the end use recommendations for spent litter (Appendix K), providing a quantitative basis for the multi-season management recommendations; for example, the rate constants (equation 16 r value) for nitrogen supply from spent litter (Appendix I), for phosphorus supply (equation 8 r value) and the k and Q_{10} values developed for phosphorus supply (Crohn, 2006).

Additionally, the models now provide a quantitative basis to set specifications, and fine-tune the spent litter/sorbent formulations for nutrient supply, nutrient availability deferral, and mitigation of nutrient loss pathways in different soil types. This will have a positive impact on our continuing research, and will be made available to other research groups via publication.

Technology adoption

The research direction was strongly supported by all stakeholder groups. Poultry producing stakeholders indicated that financial benefits may be more likely to accrue to the fertiliser supplier/seller than the poultry producers themselves.

However, sought after end-products of spent poultry litter will undoubtedly drive demand for this material. Integrated enterprises that not only farm poultry, but produce compost products (a key group of current poultry producers in Australia) have the option to adopt these technologies to increase the value of the by-product formulations they market.

A range of potential barriers to adoption were raised (Appendix J):

- Education requirements with regard to the value of spent litter and composts
- Transport costs of bulky spent litter decreasing access to the materials
- Low returns to poultry producers for their spent litter
- Regulatory barriers to the use of the materials
- Competition for the material as a biomass energy source.

These and recommended solutions are discussed in the following section.

Recommendations

The combination of our field trial results, our pot trial leaching data, and the observations from our other studies indicate that it is possible to match the productivity of conventional nitrogen and phosphorus sources, and achieve decreased potential for nutrient losses via the use of spent litter additions and ion exchange sorbents.

Both sorbent additions and spent litter use, relative to conventional fertilisers, tended to defer nutrient availability without losses. Where a multi-season, multi-application management approach is taken, it is also likely to be possible to achieve nutrient supply that better matches crop uptake profile for phosphorus than is possible with conventional fertiliser sources. The models developed to represent these behaviours provide a quantitative basis to fine tune the formulations, provide a means of common comparison between testing, and provide a framework to decrease the experimental load to complete this work.

However, sorbent additions are potentially expensive due to the purchase, transport, and incorporation of these materials. This is particularly the case for bentonite where larger masses are required.

One means to help offset these costs is to realise the air quality benefits from using these materials in-shed. Incorporation of cation exchangers such as bentonite (or zeolite) into the bedding material in-shed can have production and worker safety benefits by decreasing the concentration of ammonia in the air. In turn, decreasing this volatilisation retains more nitrogen that may then be accessed by the target crops and pastures.

Appendix J discusses a range of important potential barriers to adoption. A lack of education into the benefits of spent litter products was a noted current barrier. This concern, based on notes from the adoption workshop, originated from those marketing conventional composts and spent litter products. These comments relate to composts and conventional spent poultry litter materials, not only to the nutrient content but benefits relating to soil quality which can be difficult to value. It is therefore **recommended to continue the research program** to establishing quantifiable benefits of manure materials, and then extending how to access the full value of these materials to end-users.

However, current managements and conventional composting will not realise the full potential of in-season nutrient supply, based on our trial data. Research and education should also focus on extending approaches that step beyond conventional composting which results in poor nutrient use efficiency and does not address the opportunity to produce superior in-season nutrient supply products.

Since transport costs remain as a major barrier to accessibility of spent litter materials, we **recommend following through on approaches** to add value to spent litter, such as this fertiliser formulation project, to enable a wider transport radius. However, sorbent additions are potentially expensive due to the purchase, transport, and incorporation of these materials. Fortunately there is potential to realise benefits in terms of decreased ammonia volatilisation in-shed through sorbent additions. We **recommend following through on industry trials** in this area to see if the benefits of in-shed use of bentonite or other sorbents can help offset fertiliser formulation costs. In turn, decreasing this ammonia volatilisation also retains more nitrogen that may then be accessed by the target crops and pastures.

The fact that most spent litter is removed by contractors at little return to most poultry producers, suggests that integrated producers (enterprises including composting and fertiliser formulation components) and third party fertiliser producers are the initial likely technology target. As such, these stakeholders are **recommended additional partners for future technology development**. This would ultimately increase demand for the material, and potentially increase returns from this material to poultry producers. Dual benefit technologies, those that have benefits in-shed (such as bedding/fertiliser formulation additives such as those studied), are also **recommended approaches** to enable greater returns to poultry producers.

Regulatory controls also limit flexibility in terms of storage and composting off-farm and in the use of product in agricultural production, emphasising the need to ensure these regulations remain equitable and reasonable and do not unnecessarily limit use of manure materials. We **recommend effective engagement with the agencies involved** and rigorous supporting science in this area. We also **recommend following through on high-value formulation technologies** that could readily incorporate measures to overcome perceived risks.

Increasing interest in biofuels and energy production is a competitor for the use of spent litter for fertilisers – as are alternative manures (e.g. feedlots) closer to farming areas. It appears likely that this will continue while spent litter materials are under-valued as a fertiliser.

Appendix K details the recommended approach to spent litter management to obtain agronomic benefits and decreased nutrient excess or losses to the environment. Bentonite is currently undergoing industry trials as a bedding additive in-shed and is currently on the market. Recommendations in Appendix K also apply to the management of this material, when spent, as an alternative fertiliser formulation.

Deployment and Commercialisation

The project has produced a range of technologies, at different levels of maturity. This includes some technologies that are ready for deployment or industry trials, and useable recommendations for spent poultry litter use, along with promising technologies that can be developed for future deployment.

Deployable technologies

The project has led to a range of recommendations and technologies that are currently deployable (Figure 13). Recommendations enabling application of these technologies are contained within this report and the Appendices. Another technology, bentonite as a bedding additive, attracted early attention at an industry conference (Redding, 2014), leading to industry trials and implementation championed by a poultry industry service company.

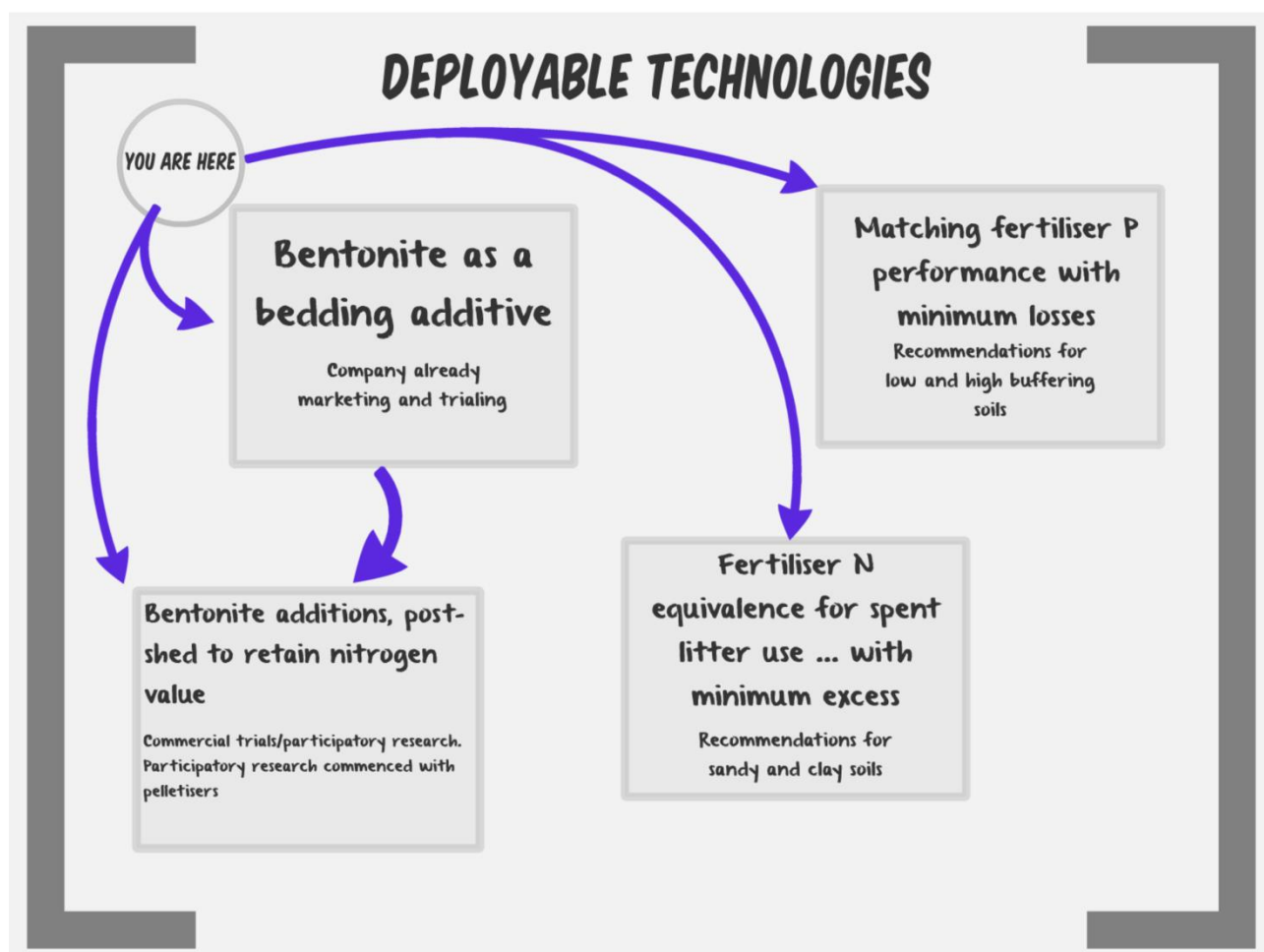


Figure 13. Technologies that are mature enough to influence enterprise practice, or have already been adopted by industry at a relatively early stage for industry trials.

Technologies on the road to commercialisation

Formulation of crop-specific nitrogen and phosphorus fertilisers based on the technologies developed from this project, and the concurrent National Agricultural Manure Management project, are the subject of active and on-going research (Figure 14). The team has had significant agronomic success with novel fertiliser formulations; however, transport radius concerns remain for bulky materials such as spent litter.

This problem is being tackled via the extraction of nutrients from manure materials in our current Australian Pork Limited project, where we have identified a pathway around the major barrier to the efficient utilisation of extracted struvite, and have been able to use this manure-derived impure extract to stimulate root development as well as supply nutrients.

While the bentonite cation exchange material employed in this project, and the vermiculite material trialled in our National Agricultural Manure Management project (Hill et al., 2015; Pratt et al., 2015) now have established benefits in agronomic and loss mitigation terms, these materials themselves are bulky and could limit the transportability of fertiliser formulations. The cation exchange capacity of these materials ($\approx 100 \text{ cmol kg}^{-1}$), is only around a quarter of the anion exchange capacity delivered by the phosphorus sorbent (hydrotalcite). However, the problem is further inflated by the fact that more nitrogen is required for plant production than P.

A range of promising pathways to solve this issue are already being pursued:

- The team has actively pursued improved cation exchange materials, through modifications of existing natural materials in a small exploratory collaboration with the Australian Institute for Bioengineering and Nanotechnology. Initial results are available, and opportunities are being followed through. The prototype material developed based on a modified vermiculite has a cation exchange capacity of 341 cmol kg^{-1} .
- Nitrate-loaded hydrotalcite has begun to be investigated, though only initial nutrient transport work has been completed (as reported in Appendix E).
- Investigation of the use of nitrogen transformation inhibitor additives for use in manure-based fertiliser formulations as part of a current project, and potentially several additional projects, led by the DAF team. Particular attention is being focussed on decreasing the rate of temperature-dependent breakdown – a critical failure of these products under Australian conditions.

The applications of technologies developed from this Poultry CRC project are not restricted to the use with spent litter materials, but are widely applicable to conventional nutrient sources (e.g. urea, mono-ammonium phosphate), and other waste materials (sewage sludges and other animal manures).

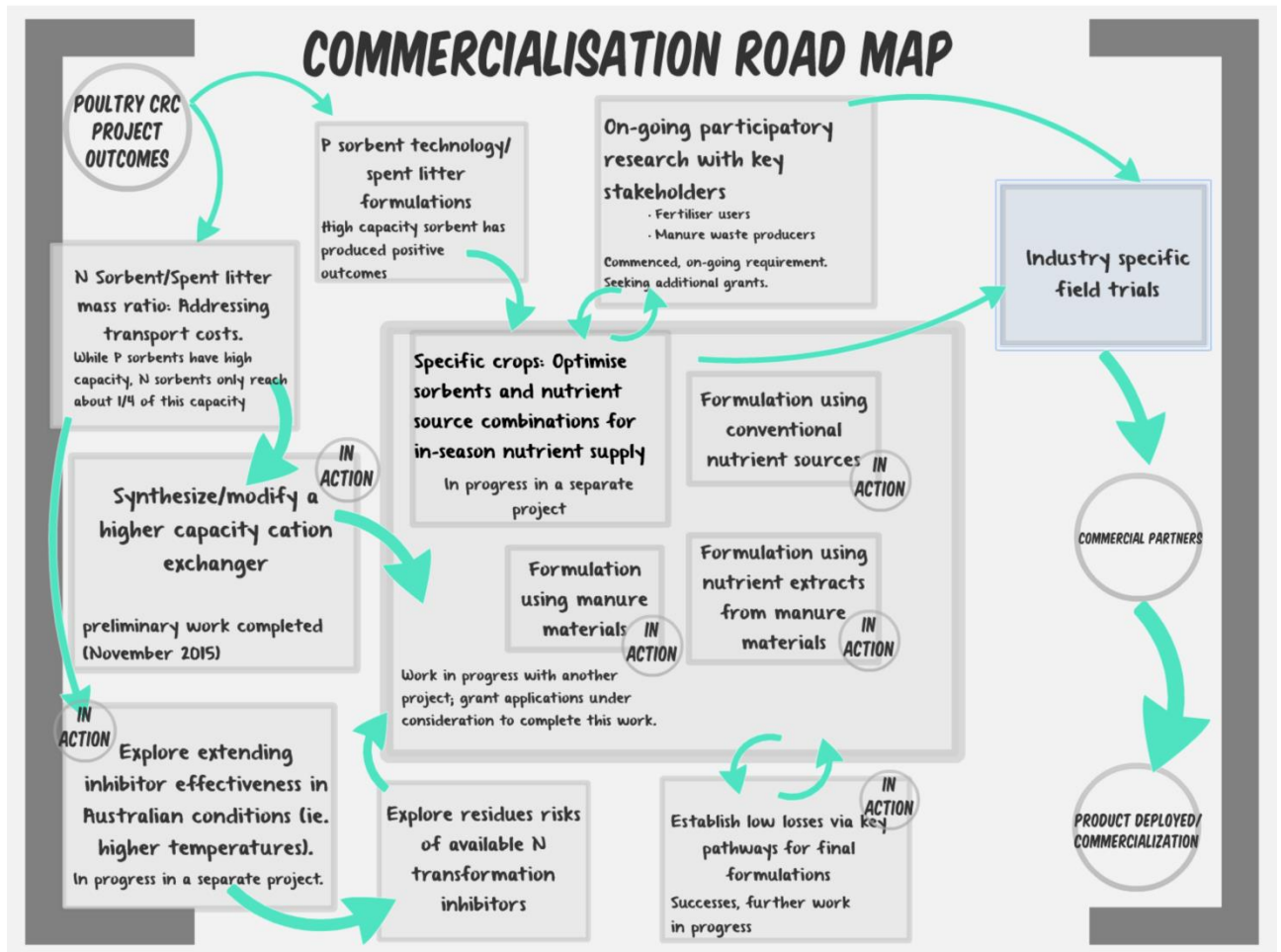


Figure 14. The opportunities and the desired outcome of other technologies investigated as part of this Poultry CRC project. The label “In Action” is used to signify studies in progress as a part of other projects led by the DAF team.

Appendix A: Project initial literature review

M.R. Redding, C. Pratt, T. Duncan, J. Hill

Summary

Key findings from this literature review are the confirmation or formulation of the following research directions:

- Pursuing the benefits of ongoing nutrient supply, termed in-season supply in literature, which is capable of delivering peak yields with minimal nutrient losses. While published approaches involve physical application of nutrients during the growing season, our approach will be to tailor fertilisers that deliver nutrients as they are required from a single pre-season application.
- Conceptually there are very substantial benefits of nitrification inhibitor use, and potentially urease inhibitors if the poultry-derived nutrient source contains urea, in conjunction with fertiliser formulations. This could be a means of achieving in-season nutrient delivery and decreased losses. Major unsolved hurdles exist, particularly in terms of the decay of the inhibitor materials in-soil at Australian agricultural temperatures. We will be pursuing at least two approaches to solve this problem, namely loading sorbents with inhibitors and polymer encapsulation of inhibitors.
- Precursor research by the project team has demonstrated substantial benefits of the use of sorbents in conjunction with manure materials in decreasing nutrient losses via each of the potential pathways. Data also suggest that with the use of sorbents, nutrient availability can be deferred to later in the growing season, indicating that these substances could be used to achieve effective in-season nutrient supply. This benefit should be further pursued.
- The cation exchangers used for our previous research projects have had relatively limited sorption capacity ($< 100 \text{ cmol } ^{-}\text{ve charge kg}^{-1}$). This leads to bulky additions of sorbents to manure-derived fertilisers to gain the desired effects on losses and availability deferral. Realistic prospects exist to obtain cation exchangers of 400 to 600 $\text{cmol } ^{-}\text{ve charge kg}^{-1}$, and this opportunity should be pursued. Additionally, there are some prospects to obtain higher capacity anion exchangers, though the current material is fairly high capacity (355 $\text{cmol } ^{+}\text{ve charge kg}^{-1}$). This opportunity will also be pursued.
- Our previous research, and that of our collaborators, has observed effects of organic compounds, including those contained in manure materials, on root development. It is appropriate to pursue this line of research to determine if root invasion into the fertiliser

placement volume can be significantly increased relative to conventional fertilisers. This would be a benefit that would differentiate poultry-derived fertiliser materials from conventional fertilisers.

- Recovered nutrients in the form of struvite have an incomplete and sometimes poor record as fertilisers. Agronomic research into their use as fertilisers is largely lacking; however, solubility and performance have been shown to be a concern in some situations. It appears that the very characteristic that allows these materials to be separated from waste streams (their insolubility) may be their disadvantage as a fertiliser. However, the recovery of struvite is probably not a convenient method of concentration of poultry waste streams.

The research opportunities are real and the potential is exciting. However, the scope of the current Australian Pork Limited project does not provide for field trials of final formulations. The research team will therefore be pursuing the development of companion projects to allow findings to be developed into final ready-for-market products.

Objectives of literature review

- a. To identify recent advances in the understanding of the controls on crop/nutrient (nitrogen, N, and phosphorus, P) use efficiency, nutrient requirements and uptake.
- b. To examine new technologies that may assist formulation of superior fertilisers (N and P).

Introduction

The nutrient use efficiency of conventional fertiliser products (e.g. urea or superphosphate) is very poor. Conventional fertiliser applications result in less than 40 to 60% plant uptake of the target nutrients, despite decades of agricultural research (Bolland & Gilkes, 1998a; b; Van der Molen et al., 1998; David & Gentry, 2000; Galloway & Cowling, 2002; as reviewed by Drinkwater & Snapp, 2007). Internationally, this presents a problem as the productivity of agricultural land will be required to rapidly increase in the next few decades. It is foreseeable that China will require 30 to 50% more food to meet demand in the next two decades (Zhang et al., 2013). This problem is not restricted to China, and it is predicted that global food production must double by 2050 to meet demand (United Nations, 2009). Approximately 80% of the related global increase in crop production is likely to be the result of intensification of plant production (Alexandratos & Bruinsma, 2012). There is both a requirement and an economic opportunity for food exporting nations (like Australia) to increase productivity.

Since the advent of industrially manufactured fertilisers, and the success of the green revolution, plant production has increasingly adopted practices capable of high yields via

approaches that are inherently “leaky” (Drinkwater & Snapp, 2007). Conventional fertiliser practices result in excess supplies of nutrients whose ultimate fate is not within the tissues of the targeted crop. Decreasing the losses associated with providing crops with nutrients is a substantial focus in Australia, where intensive crop production may occur adjacent to sensitive environments (e.g. The Great Barrier Reef).

While a substantial proportion of the increased crop production required to achieve global food security in the future will be achieved via intensification of crop production, the emphasis amongst high-level planners and scientists is to achieve this via sustainable intensification (Alexandratos & Bruinsma, 2012; Grafton et al., 2015), where more food is produced from an area of land with less impact on the environment.

Proponents have optimistically advocated application of organic wastes as fertilisers for a range of intangible benefits, with equally intangible evidence. Alternatively, many research projects have sought to “match fertiliser performance” – when performance and benefits superior to conventional fertiliser may be achievable.

The development of profitable products from poultry waste streams is a commercial opportunity for industry, however, it addresses a developing and critically important national and international issue. It is preferable that increased nutrient demand is met by fertilisers that, in contrast to increasing the application of soluble synthetic fertilisers, produce environmentally sustainable outcomes. Waste streams are a valuable nutrient resource, but are not currently utilised to their full potential. Spent litter/ poultry waste streams are perceived as bulky, having inconsistent nutrient content, and there are concerns that their use as a land-applied fertiliser may result in environmental damage due to nutrient leaching or run-off. This poor utilisation and negative perception are to some degree based on a poor understanding of the plant-soil-organic nutrient source interactions that proceed when these materials are used as fertilisers.

To enable better use of these materials as formulated, high-efficiency fertilisers the following literature review seeks to (a) identify recent advances in the science surrounding nutrient needs, formulation performance, and controls of nutrient uptake and nutrient use efficiency in plants and crops and (b) describe formulation approaches to minimise nutrient product bulk and optimise nutrient supply to meet plant requirements.

Potential advantages of manure

Some initial groundwork identifying potential key advantages of manure use is already in place. Data suggests that the cumulative effect of manure applications (without sophisticated formulation) could result in ongoing nutrient release from the soil profile that would be

equivalent to crop requirements for nitrogen and phosphorus (Helgason et al., 2007). Ongoing nutrient release equivalent to crop requirements was achieved after nine years of application of un-composted and composted cattle manure in field trials (Miller et al., 2009). Results from our team's research with phosphorus (P) fertilisers formulated from spent poultry litter indicate that manure-formulated fertilisers are capable of ongoing nutrient release that is not achieved via conventional fertiliser applications (mono-ammonium phosphate; manuscript in preparation).

A meta-analysis of available data (conventional fertilisers and manure materials) suggests that while manure applications to soil (without formulation) as fertilisers resulted in significantly greater OC in soils, the yield effects of these two nutrient sources were comparable (Edmeades, 2003).

A recent review of the long-term effects of organic amendments on soil fertility highlighted a range of positive effects of the use of these sorts of materials as fertilisers (Diacono & Montemurro, 2010):

- Ongoing annual applications of composted materials appears to build the soil's store of organic nitrogen (N), a form that can later be mineralised during cropping seasons but which is a form not usually associated with induced nitrate leaching.
- These applications can improve biological functions of soils, and can result in large increases in carbon content of soil (especially relative to conventionally fertilised soils; this may be beneficial for nutrient cycling and soil structure).
- Ultimately, substantial yield benefits are possible through the application of stabilised organic wastes.

The research team's findings during two isotopic studies of carbon sequestration suggest that the addition of a range of manure materials to soils (un-composted materials) may actually induce decomposition of old soil organic matter via priming effects (two manuscripts in preparation). This may well be a difference between composted organic materials and as-received manure materials.

This is the starting point for further research, where we seek to improve on the use of raw waste materials from the meat chicken production as fertilisers to develop fertiliser products for more stringent requirements for sustainable intensification of crop production.

The nutrient uptake efficiency concept

For the purposes of this work, the research team will be using a fairly simple interpretation of nutrient uptake efficiency, namely the amount of nitrogen uptake produced per unit of applied

N. This is fairly similar to the early concept of nitrogen use efficiency (Moll et al., 1982), which used the amount of yield produced per unit of soil N. We have adopted this approach as there is no requirement during our experimentation for comparisons between crop types or for identification of carry-over nutrients in perennial plants, however, a nutrient mean residence measure as proposed for other experimental systems (Berendse & Aerts, 1987; Weih et al., 2011), may be advantageous and could be explored further.

Factors controlling nutrient uptake efficiency

In order to maximise nutrient uptake from applied fertiliser, not only does a material have to be applied that directly favours uptake by the plant (in a manner that favours uptake), but nutrient losses from the system must be minimised to increase the potential for uptake.

In-season nutrient supply

Conventional fertiliser practice with fertiliser application restricted to the commencement of the growing season results in substantial nutrient excesses beyond the immediate plant requirement (Figure A.1).

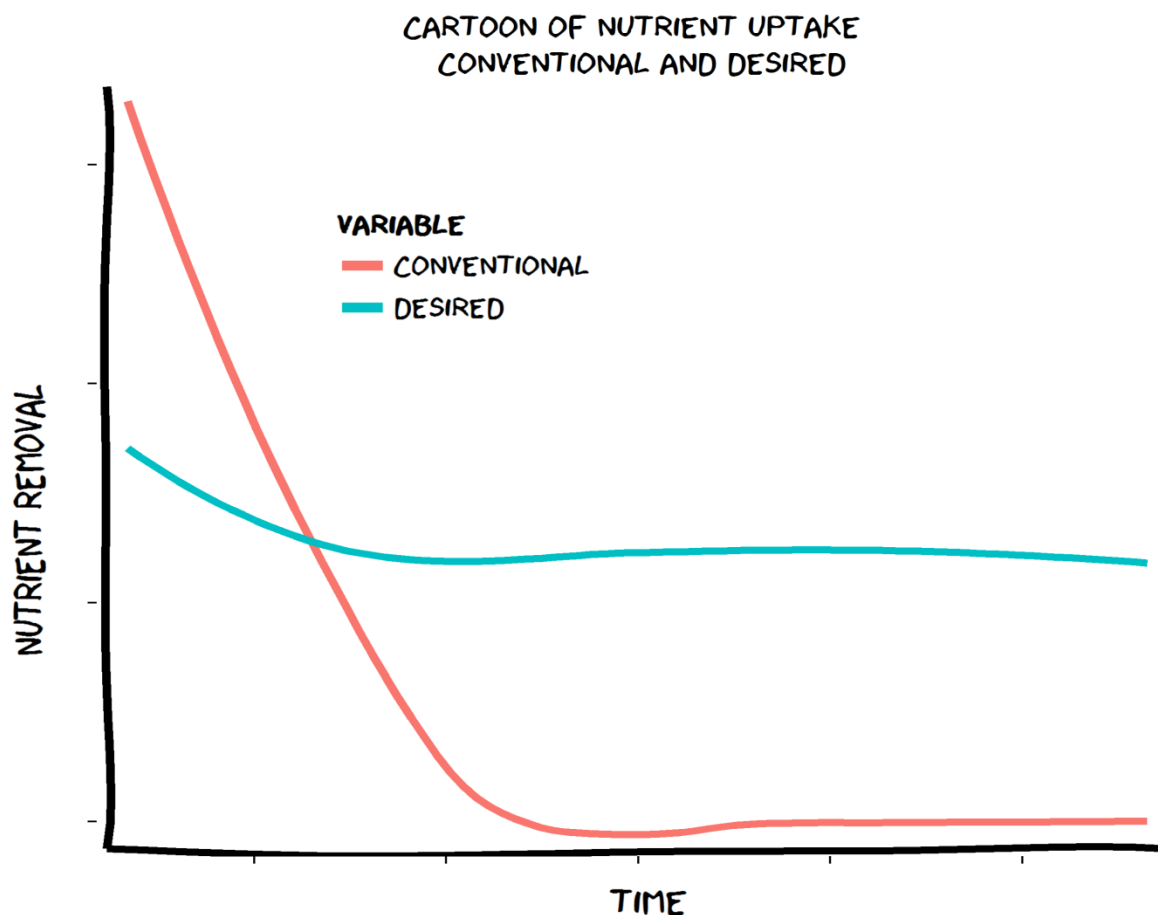


Figure A.1. A cartoon of the nutrient supply behaviour of conventional fertilisers, with a marked initial excess of nutrient availability. Depending on the production system, it would be advantageous to decrease that initial excess and prolong availability.

This is a recognised source of the inefficiency of conventional fertiliser practice (Drinkwater & Snapp, 2007; Chen et al., 2011). Overseas, this problem has been tackled via an initial decreased nutrient application (in this case N), followed by appropriate further applications during the growing season (in-season nutrient applications; Chen et al. 2011), where the growing season nutrient requirements are predicted via production system models or simplified distillations of those models (an In-Season Root Zone Nutrient Management Strategy; Chen et al., 2010b). For 63 farms across China, this approach was able to almost double maize yields (mean yields of 13 t ha⁻¹), with no increase in fertiliser use (Chen et al. 2011).

This approach is not practical in the mechanised agricultural systems employed in many developed countries. The exception may be the application of controlled traffic approaches that may be adapted to some production systems – at the cost of additional labour, fuel, and machine costs, combined with a proportion of the production area dedicated to machine

access. No publications appear to be available with regard to in-season nutrient management via controlled traffic.

The challenge and opportunity of this research project is to deliver a single nutrient application that gains the advantages of in-season nutrient management (Chen et al. 2011), through the use of poultry waste stream characteristics (e.g. ongoing nutrient mineralisation and release), and innovative formulations using these by-product streams and nutrient forms extracted from these materials.

Nutrient loss pathways

Limiting nutrient losses is an essential component of increasing nutrient use efficiency. A range of pathways of loss are evident for applied fertiliser nutrients:

- Leaching. For example inorganic and organic forms of nitrogen and phosphorus being leached downward in the soil profile, beyond the volume of soil from which the plant is actively deriving its nutrients, potentially degrading surface or ground water.
- Run-off. For example inorganic or organic forms of nitrogen and phosphorus being mobilised by overland flow, interflow, or ex-filtrating water, and transported off-site where the nutrient resource may become an environmental contaminant.
- Gaseous losses. Generally restricted to nitrogen forms, mineralised nitrogen may be lost via ammonia volatilisation, or as oxidised nitrogen forms such as N_2O , NO , or NO_2 . In general, losses of ammonia exceed the losses of other forms, however, N_2O is a potent greenhouse gas and a concern in its own right.

Controlling ammonia volatilisation

Ammonia volatilisation from the poultry waste-stream before and after land application represents a loss of fertiliser value, decreasing economic returns or increasing costs of removal for this waste stream.

A range of additives have been studied for use in-shed in animal production systems to decrease the volatilisation of ammonia (Sevi et al., 1995; Tymczynna et al., 1995; including alum and bentonite, Li et al., 2008). Bentonite as an additive to bedding material at low rates ($0.4\text{--}0.8\text{ kg m}^{-2}$) had no effect on atmospheric ammonia concentrations (Sevi et al., 1995), while at 1.5 kg/m^2 litter ammonia concentration was decreased (Tymczynna et al., 1995). Recent studies have demonstrated that ammonia in poultry litter can readily be sorbed in exchangeable forms by bentonite additions to poultry litter (Redding, 2011, 2013).

The combined effect of bentonite (a cation exchanger) and hydrotalcite (an anion exchanger) as additives in inorganic fertiliser formulations was introduced by Gillman and Noble (2005) and further explored by Gillman (2011). The addition of these materials to agricultural wastes such as piggery pond sludge and chicken litter has also been studied (Gillman, 2006). Apart from their fertiliser value, these exchanger-plus-manure formulations may be beneficial as soil amendments when added to sandy soils, because each application will result in an increase in clay content, giving the soil increasing capacity to retain nutrients and water.

Several other additives (ferric sulfate, alum, and dissolved alum) are already used to decrease ammonia volatilisation and phosphorus (P) loss via runoff or leaching when a spent poultry litter is land-applied as a fertiliser (Lefcourt & Meisinger, 2001; Li et al., 2008; Warren et al., 2008; Bautista et al., 2011). However, because these additives tend to retain phosphorus in forms that may not be plant available they may decrease the fertiliser value of the spent litter (Guo & Song, 2009).

Another approach is the addition of urease inhibitors to fertiliser materials. Researchers have assessed the efficacy of urease inhibitors to decrease ammonia (NH₃) volatilisation from agricultural soils (Zhengping et al., 1991; Varel, 1997; Sanz-Cobena et al., 2011; Rogers et al., 2015). Although itself not a GHG, NH₃ leads to indirect N₂O emissions (Intergovernmental Panel on Climate Change; IPCC, 2006). In a global review Saggar et al. (2013) was reported an average 50% decrease in NH₃ emissions from urea-fertilised soils using the urease inhibitor N-(n-butyl) thiophosphoric triamide.

Runoff and leaching losses

A range of materials have been investigated as additives to fertilisers and manure materials to decrease losses from the leaching and runoff pathways.

Early attempts to decrease these losses used waste materials as sorbents applied to the surface of soils, mixed with the soils, or in run-off interception structures. Additives studied included zeolites, gypsum, red mud (bauxite residue) (Phillips, 1998), slag and fly ash (Lee et al., 1996; McDowell, 2004, 2005), and alum water treatment residue (Peters & Basta, 1996; Zvomuya et al., 2006; Redding et al., 2008). Surprisingly, simple studies continue to be published in this area (Colombani et al., 2015).

A significant modification of this approach has also been developed, where fertilisers are formulated to contain nutrients and sorbents. This approach favours sorption of the nutrients much more strongly than separate application of the two materials to the soil, due to the higher solution concentrations achieved (coupled with basic sorption theory). Layered double hydroxides, due to their high anion exchange capacity (355 cmol ^{-ve} charge kg⁻¹), have been

used as nutrient sorbents for both phosphorus and nitrogen (as nitrate) fertiliser formulations. The use of this material originates from the time of CSIRO patent application (CSIRO Australia, 2003), but its advantages are expanded in later publications (Gillman & Noble, 2005; Gillman, 2006, 2011).

Formulations of sorbents with fertilisers has proven advantageous in decreasing leaching and runoff losses of phosphorus in manure-fertiliser formulations (Redding, 2011), and it is likely that similar advantages in terms of stabilising nitrate losses are possible where the nitrate ion forms part of the layered double hydroxide structure. Unfortunately, because of the low sorption preference of the clay form for nitrate, this requires that the hydrotalcite is manufactured with the nitrate in its structure (Gillman et al., 2008).

Cation exchangers are purported to perform the same sort of function achieved for phosphorus by the use of anion exchangers (e.g. layered double hydroxides). For example bentonite has been suggested (Gillman, 2011), and successfully tested in-lab and via rainfall simulation for this role (unpublished data, Redding). Vermiculite and bentonite are currently undergoing further study by the research team to decrease run-off losses.

Emission of N₂O

Several additives have already been pursued aimed at decreasing the N₂O emission losses from fertiliser and manure formulations. While these losses as a proportion of total nitrogen are unlikely to be as large as NH₄⁺-nitrogen losses (e.g. the inventory calculations, IPCC, 2006), they also represent a potentially very significant greenhouse gas emission.

McTaggart et al. (1997) reported up to a 70% decrease in N₂O emissions from a chemically fertilised pasture overlying a clay loam in the UK, using the nitrification inhibitor dicyandiamide (DCD). Zaman et al. (2013) reported a 40%-50% decrease in N₂O emissions from urine patches on a silty loam in New Zealand, also using DCD. However, in the same study the DCD caused a 15% to 40% increase in NH₃ emissions. Moreover, there has been recent concern over DCD detection in agricultural products such as milk (Danaher & Jordan, 2013).

Rather than using chemical-based technologies, geological materials could be used to mitigate N₂O emissions. Zaman et al. (2007) pioneered this idea in their work using zeolites to mitigate N₂O, reporting a 30% to 40% decrease in N₂O emissions from soils amended with urea and dairy cattle urine. Zeolites certainly appear to be promising for mitigating N₂O, however, the global distribution of these minerals is limited. By contrast, clay minerals of the phyllosilicate class are ubiquitously distributed with abundance far exceeding that of zeolites. Like zeolites, clays have negatively charged surface, or interlayer, sites and the cation exchange capacities

(CEC) of some clays are the highest (>150 cmol/kg) of any naturally occurring materials (Faure, 1998).

Recent successes have been achieved in directly decreasing nitrous oxide emissions from manures treated with vermiculite and bentonite (Pratt et al., In Press). Regression analysis revealed that the clay additions decreased gas emissions in 13 of the 15 modelled treatments; up to 80% for NH_3 , and 90% for N_2O . Subsequent experiments (manuscripts in preparation) demonstrated that these benefits could be realised in glasshouse and field experiments.

Nitrogen uptake

The uptake of inorganic nitrogen forms, nitrate and ammonia by plants is well described in literature, and it is conventional to approach the subject of nitrogen uptake from this standpoint. However, an increasingly large range of plants are known to be deriving nutrients via other means, including directly from the atmosphere via nitrogen-fixing bacteria; mycorrhizal symbionts (mycoheterotrophs); carnivory; parasitism; engulfing bacteria in root tissue and absorbing entire microbes (rhizophagy, Lonhienne et al., 2014a), and mounting evidence of uptake of organic nutrient forms of nitrogen and phosphorus (Schmidt et al., 2013).

The nitrogen cycle

The nitrogen cycle is composed of a range of nitrogen transformations that may occur in soil or manure substrates. It is important to understand something about these processes if nitrogen uptake is to be optimised (Figure A.2). The conventional view of these transformations can be summarised as follows (Bolan et al., 2004):

- Mineralisation, the conversion of plant-unavailable organic nitrogen to available inorganic forms via a microbial process. Nitrogen mineralisation from faeces is slower than from the plant matter from which it was derived or from urine. Manure tends to contain more fibrous carbon forms than the original plant matter, which degrades more slowly, though C:N ratios may be similar.
- Aminization, where macromolecules are hydrolysed to simple nitrogen compounds such as amines and amino acids. For example, proteins are converted to amines and CO_2 .
- Ammonification, the process of microbial conversion of amines and amino acids to ammonium ions. An example is urea hydrolysis, as carried out in the presence of the

urease enzyme. In this particular case, the reaction also produces hydroxide ions, raising the pH at the reaction site.



Equation 1

- The ammonia thus formed may be lost through volatilisation, fixed to soil, immobilised by soil microbes, nitrified by microbes, or taken up directly by plants.
- Nitrification. The two-step, microbially driven conversion of ammonium-nitrogen to nitrate-nitrogen is known as nitrification. The first step in this reaction produces nitrite (NO_2^-), but since the reaction rate of this step is much slower than the step to produce nitrate (NO_3^-), plant-toxic nitrite is unlikely to accumulate in soils. More H^+ ions are produced during nitrification than OH^- ions during ammonification (per unit of N), and overall the combination of these reactions on urine and ammonifying manures is expected to acidify the soil. Once formed, nitrate can be taken up directly by plants, lost via leaching, immobilised by microbial processes, or it may be subject to denitrification.
- Immobilisation, the microbial process where nitrate and ammonium are converted to organic nitrogen forms, unavailable to plants. Addition of carbon rich materials to cultivated soils can promote immobilisation, and the same process may operate during composting where carbon substrates are added to manures. Where the ratio of carbon:nitrogen is high, microbial access to nitrogen may become a limitation, and competition for scarce nitrogen will tend to occur between microbes and higher plants. Microbes will, if necessary, source nitrogen from the soil's mineral nitrogen — immobilising it. Microbial carbon:nitrogen ratios are about 8:1. Where materials added to soils have carbon:nitrogen ratios of > 30 , immobilisation is generally dominant. Where carbon:nitrogen is in the range 20 to 30, immobilisation tends to match mineralisation, and below 20, mineralisation dominates.
- Denitrification. Some microorganisms, under waterlogged soil conditions obtain oxygen by reducing NO_3^- . This reduction process, when allowed to continue to completion, proceeds through a range of steps, producing NO_2^- , then nitric oxide (NO), nitrous oxide (N_2O), and finally N_2 gas.

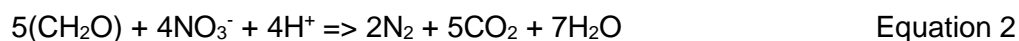
The scale of denitrification in soil systems is such that it is of concern as an economic loss of fertiliser N. Each of the steps in the denitrification process is conducted by anaerobic bacteria, where free oxygen is limiting. The microbes responsible for denitrification are very widespread in soils, and usually facultative aerobes - microbes that prefer to use oxygen as their electron acceptor, but will use nitrate where oxygen is not available (e.g. from genera

Pseudomonas, *Bacillus*, *Alcaligenes*, and *Flavobacterium*)(Tiedje, 1988; Tsuruta et al., 1998; Philippot et al., 2007).

The trophic approaches of the organisms responsible can be divided as follows:

Chemoheterotrophs, where nitrate is used as the primary electron acceptor to source energy from organic compounds, and **Autotrophs**, where energy is obtained by oxidising inorganic compounds such as elemental sulphur using nitrate.

Fungal denitrification may be particularly important to nitrous oxide emissions. The widespread ability of fungi to reduce nitrate to nitrous oxide in order to supply energy for other reactions (dissimilatory reduction) has been demonstrated. Critically, the ability to reduce N_2O to N_2 for most fungi is lacking (Shoun et al., 1992). The contribution of fungi to nitrous oxide emissions has been demonstrated (Laughlin and Stevens, 2002). In fact denitrification in some arid soil systems is dominantly the result of fungal activity (Crenshaw et al., 2008). However, information regarding the role of fungi in denitrification from manure or effluent substrates is lacking. One study found a decrease in fungal hyphae in soil treated with manure (Bittman et al., 2005), though this was not linked to denitrification measurements. A more recent study involving pig wastes found that treatment of soils did not result in any significant change in fungal populations (Pratt, 2008). When the process is allowed to reach its ultimate extent, it may be represented as follows, using glucose as the substrate, resulting in N_2 emission rather than N_2O :



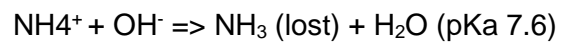
However, organisms do not have a uniform ability to produce the range of denitrification products (nitrate, NO , N_2O , or N_2). Some organisms may produce mixtures of nitrous oxide and N_2 , while others may be restricted to N_2O or N_2 (Stouthamer, 1988).

The ratios of N_2O to N_2 produced from soils vary according to the substrate, organisms, environmental conditions, and period of denitrification (Sahrawat & Keeney, 1986; Arah & Smith, 1990). It appears that the proportion of N_2O to N_2 increases as oxygen availability decreases (Firestone, 1982), and small nitrate concentrations have been observed to stimulate nitrous oxide reduction in soils more than large concentrations (Blackmer & Bremner, 1979), possibly as a result of the production of nitrous oxide reductase in response to low nitrate concentrations rather than in response to the nitrous oxide itself (Soohoo & Hollocher, 1990). The general understanding is that high concentrations of nitrate and or nitrite decrease reduction of nitrous oxide, raising the $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ ratio of the reduction products (Khalil et al., 2005). In order for denitrification to proceed, the following requirements must be met:

- Presence of nitrate, nitrite, NO, or N₂O.
- Anaerobic conditions or locally restricted oxygen availability
- Organic compounds suitable as electron donors
- The presence of appropriate microbes.

Promotion of the process therefore occurs under high soil nitrate, moisture contents sufficient to result in water-logging, and in the presence of a ready carbon source. It increases with pH and temperature. Nitrate may also be reduced to N₂ via non-enzymatic reactions under anaerobic conditions.

- NH₃ volatilization. When soil or manure pH is greater than 7.5, ammonium ions dissociate into gaseous ammonia (NH₃), which is subject to volatilisation losses:



Equation 3

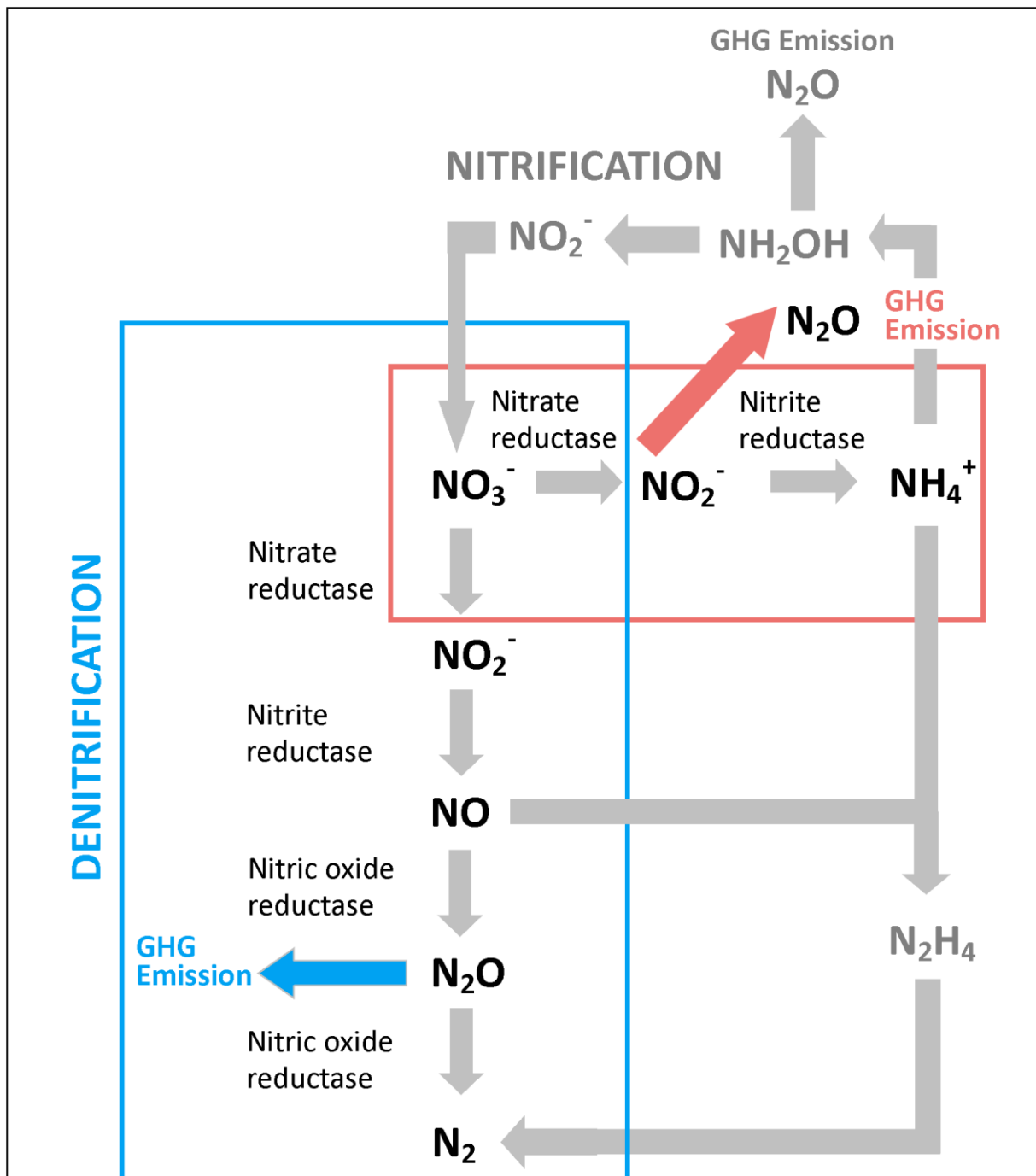


Figure A.2. A modern view of the nitrogen cycle, including recent observations of dissimilatory nitrate reduction to ammonium (modified from Giles et al., 2012).

The contribution of dissimilatory nitrate reduction to ammonium has also attracted recent research attention (Figure A.2), and can also be responsible for the production of N_2O (Giles et al., 2012). In coastal sediments, in 26 out of 55 sites, dissimilatory nitrate reduction to ammonium was found to account for more than 30% of nitrate reduction (Giblin et al., 2013).

Phosphorus forms

The phosphorus cycle is no less complex than the nitrogen cycle, though it lacks a gaseous component (Figure A.3). Phosphorus in soils exists in a range of organic and inorganic forms, in both solid precipitates, adsorbed to mineral surfaces, or in the liquid phase. Organic phosphorus accounts for between 30 and 65% of the total phosphorus in soils (Shen et al., 2011). This organic phosphorus exists in labile or transformable forms such as orthophosphate diesters, orthophosphate monoesters, and organic polyphosphates or in more recalcitrant forms such as inositol phosphates and phosphonates (Turner et al., 2002; Condon et al., 2005).

Plants take up phosphorus as phosphate ions (mainly HPO_4^{2-} and H_2PO_4^-), and while soils typically contain substantial total P, only a very small proportion of this occurs in solution phosphate forms (orthophosphate concentrations ranging from 1 to 5 μM have been reported; Bielecki, 1973; Richardson et al., 2009). Therefore, this pool must be rapidly replenished to continue supplying plant requirements.

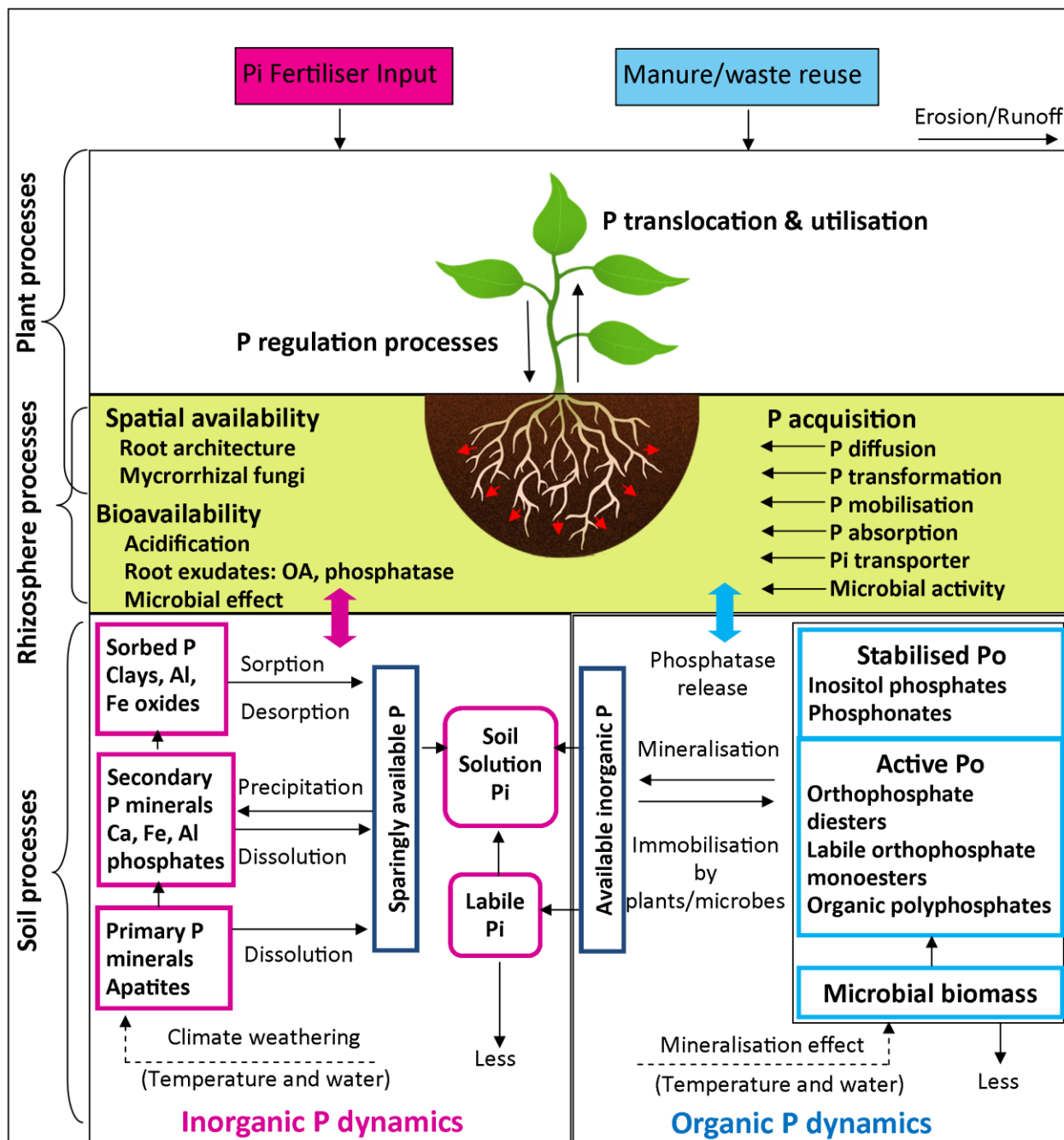


Figure A.3. Phosphorus dynamics in the rhizosphere, with CP representing carbon phosphorus, NO represents nitric oxide, and OA represents organic acid (modified from Shen et al., 2011).

Phosphorus uptake

Though strong concentration gradients develop in response to plant uptake (Gahoonia & Nielsen, 1997), diffusion of phosphorus into these rapidly developing zones of depletion is slow and therefore diffusion limits uptake rather than the actual phosphorus uptake capacity at the root surface (mechanisms described by Nye, 1966; evidence reviewed by Richardson et al., 2009). On this basis it appears that root and microbial processes and the exploitation of new regions of soils

are of greater importance for phosphorus acquisition than phosphorus uptake kinetics (Richardson et al., 2009). Rapid root elongation, high root to shoot ratio, root branching, high root length per mass, and certain root structures (such as cluster roots) can all be adaptations to facilitate exploration of soil for phosphorus resources and phosphorus uptake.

Mycorrhizal fungi also contribute to the uptake of P, and these interactions have been the subject of a wide range of publications (as reviewed by Richardson et al., 2009). Just as root hair development increases the explored volume of soil and the root surface area (root hairs can constitute from 0 up to 90% of nutrient uptake, Fohse et al., 1991), so do mycorrhizae.

Phosphorus transformations

Primary phosphorus minerals – those originating from igneous or volcanic origins – tend to be very insoluble and weather slowly. This includes such minerals as apatite and strengite. In general these are not viable sources of phosphorus for plants, although in some environments (acid soils) apatite application (phosphate rock) has proven an effective fertiliser. Secondary Ca, Fe, and Al phosphate minerals vary in solubility, with control factors including particle size, and soil acidity (Shen et al., 2011). For example, solubility of Fe and Al phosphates increases as pH increases, but Ca phosphate solubility decreases (Hinsinger, 2001). Desorption processes can also gradually release sorbed phosphorus (Shen et al., 2011) from clays and sesquioxides as solution concentrations fall.

A range of inorganic solid phases contain P. Sesquioxides and crystalline Fe and Al oxides dominate phosphorus sorption in acidic soils (Parfitt, 1989). In alkaline soils precipitation reactions dominate sorption, with some surface sorption on calcium carbonates (reviewed in Shen et al., 2011). Precipitated dicalcium phosphate can be available to plants but over time converts to hydroxyapatite (which forms a large proportion of soil phosphorus in calcareous soils) and octocalcium phosphate which are more stable and less available.

The release of organic phosphorus occurs through processes mediated by soil organisms and plant roots in association with phosphatase secretion, and are strongly influenced by temperature, pH, moisture, mineral surface characteristics, and redox potential (Shen et al., 2011). This will occur dominantly from the more labile soil organic phosphorus fractions, including orthophosphate monoesters, orthophosphate diesters, and organic polyphosphates, while inositol phosphates and phosphonates are relatively unavailable (Turner et al., 2002; Condon et al., 2005). In the case of myo-inositol hexakisphosphate, this form of inositol phosphate (one very important in soils and plant seeds) is more available where sorption is less pronounced (e.g. sandy soils, Turner et al., 2007). While these organic interactions are complex, they make a major contribution to phosphorus supply (Shen et al., 2011).

Research directions and prospective technologies

Overcoming the caveats with the use of nitrification and urease inhibitors

Conventional nitrification inhibitors and their disadvantages

Nitrification inhibitors can be used in agricultural systems to improve nitrogen fertiliser efficiency through reducing NH_3 volatilisation, N_2O emissions and NO_3 leaching (Timilsena et al., 2015).

Nitrification inhibitors delay the bacterial oxidation of NH_4 to NO_3 within the soil by deactivating the ammonia monooxygenase enzyme of ammonia-oxidising bacteria (Amberger, 1989; Chen et al., 2008; Akiyama et al., 2010; Timilsena et al., 2015). Dicyandiamide (DCD), (nitrpyrin) 2-chlor-6-(trichloromethyl) pyridine and DMPP (3,4-dimethylpyrazole phosphate) are among the most commonly used commercially available nitrification inhibitors (Chien et al., 2009). Nitrpyrin (the active ingredient in N-serve) is an effective inhibitor of nitrification, is primarily used with anhydrous ammonia, and may be used with liquids (Blaylock et al., 2005). However, nitrpyrin is a strong inhibitor of CH_4 oxidation (Bronson & Mosier, 1994), is often ineffective due to losses by volatilisation and sorption onto soil colloids (Chen et al., 2008), and cannot be used with solid fertilisers (Chen et al., 2010a).

DCD is less expensive to produce than nitrpyrin, is water soluble, and is less volatile than nitrpyrin, making it more suitable for use with solid fertilisers (Di and Cameron, 2002a). Unlike nitrpyrin, DCD has been shown to exhibit preferential inhibition for nitrification compared to CH_4 oxidation (Bronson and Mosier, 1994). Furthermore, DCD degrades in soils into CO_2 and NH_4 (Di & Cameron, 2002a; Kelliher et al., 2008), and therefore can be regarded as a slow-release nitrogen fertiliser itself since it contains about 65% N.

These compounds have proved successful within some environments; however, concerns have been raised about the persistence of these chemicals within the environment as well as their presence within the food chain. Recently a number of studies have detected DCD in dairy cattle milk produced for human consumption (Danaher & Jordan, 2013; Inoue et al., 2014; Lin et al., 2015).

Due to the high solubility of DCD, translocation of the inhibitor within the soil can occur including spatial separation from the nitrogen fertiliser (Bronson & Mosier, 1994). Solubility combined with a lack of surface charge are also likely to result in leaching of DCD under very wet soil conditions (Zaman & Nguyen, 2012). Furthermore, DCD has a low efficiency and requires high application rates, making it too expensive for large-scale application in agriculture (Zerulla et al., 2001). In contrast, DMPP, a relatively new nitrification inhibitor, is effective at very low rates (0.5-1.5 kg

DMPP ha⁻¹) and can achieve nitrification inhibition comparable to DCD at less than one-tenth of the application rate. The mode of action for DMPP is only assumed, however, no toxic or eco-toxic effects have been observed as yet. Furthermore, an overdose of DMPP did not lead to phytotoxicity whereas DCD caused pronounced phytotoxic damage at the same dose (Zerulla et al., 2001; Ruser & Schulz, 2015). While there are no international standards for DCD levels in food, high doses of DCD are considered toxic to humans (Inoue et al., 2014). While DMPP is completely degraded in soil, it has a slower degradation rate than DCD. At excessive field application rates (>90 times), DMPP inhibits non-target microbial activity more than DCD, thus DMPP and DCD are considered environmentally safe at recommended rates (Inoue et al., 2014).

The most important factor driving the degradation of nitrification inhibitors in soils is temperature, affecting both DMPP and DCD (Zerulla et al., 2001, Di et al., 2007, Chen et al., 2008, Kelliher et al., 2008, Ruser and Schulz, 2015). Kelliher et al. (2008) quantified the relationship between temperature and the half-life of DCD based on published data with application rates ranging from 5-32 kg ha⁻¹ and temperatures ranging from 0-30 °C. DCD is strongly affected by soil temperature and thus should be applied when soils are relatively cool (DCD half-life of 72 days at <10°C soil temperature). At 5 °C, a 1 °C increase in temperature reduced the half-life of DCD from 110 to 101 days while 25 °C reduced the half-life by 19-20 days. Di et al., (2007) found that DCD is most effective when average soil temperatures are below 10 °C and drainage is high. They found that at soil temperatures of 20 °C, the half-life of DCD was 18-25 days. DMPP is similarly affected by temperature, with Zerulla et al. (2001) reporting complete nitrification at 5 °C within approximately 140 days without DMPP, compared to practically no nitrification when DMPP was added. However, at 20 °C, without DMPP, nitrification was completed in 7-21 days compared to 40 days when DMPP was added.

A range of natural nitrification inhibitors also exist including natural essential oil by-products (Patra et al., 2009). Karanjin from the Karanja seed (Majumdar, 2002), and certain plant roots also have the ability to produce and release nitrification inhibitors (Subbarao et al., 2015). Majumdar (2002) observed higher nitrification inhibition for karanjin compared to DCD for incubations up to 30 days.

Conventional urease inhibitors and their disadvantages

Urease inhibitors are another option for enhancing the efficiency of nitrogen fertilisers, delaying the hydrolysis of urea into NH₄ by interfering with the urease enzyme thus allowing the urea to move into the soil before hydrolysis occurs and releases NH₃ (Chen et al., 2008, Timilsena et al., 2015). The most readily available urease inhibiting compound is (n-N-Butyl) thiophosphoric triamide (nBTPT) which is sold in Australia as Agrotain (Chen et al., 2008). One of the most efficient urease inhibitors nBTPT, can be effective at low concentrations of urea (Gioacchini et al., 2002; Chen et

al., 2008). The mechanism of inhibition of nBTPT is assumed to involve the binding of the nickel ion which is a component of the urease enzyme (Varel et al., 1999).

Two additional urease inhibitors, nBTPT and cyclohexyl phosphoric triamide (CHPT), another phosphoryl amide, have successfully been used to inhibit urease activity in cattle feedlot manure and control NH_3 emissions from manures (Varel et al., 1999). However, the effectiveness of nBTPT is also affected by temperature, requiring higher concentrations at 32 °C compared to 18 °C (Carmona et al., 1990). Increased temperature could cause the rate of urea hydrolysis to be more rapid than the rate of nBTPT conversion to the oxygen analogue form, which is a more powerful inhibitor than the nBTPT itself (Carmona et al., 1990). Leaf tip necrosis has been observed in plants grown in soils treated with urea and nBTPT due to accumulation of toxic amounts of urea through inhibition of urease activity, however, extensive necrosis was only observed in excessive concentrations. Furthermore, NH_3 produced through hydrolysis of urea fertiliser is more detrimental to plant growth than urea accumulation induced by urease inhibitors (Krogmeier et al., 1989). Ammonium thiosulfate and thiourea have been shown to inhibit both nitrification and urease but are less reported on than other inhibitors (Goos, 1985), and thiourea has been classified as very toxic to NH_4 -oxidising bacteria (Zacherl and Amberger, 1990).

Nutrient recovery and fertiliser formulation

Recovery technologies

Precipitation of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) is a well-established technique for extraction of phosphorus and nitrogen from liquid waste streams at higher solutions concentrations (certainly > 10 mg P L⁻¹, but up to much higher concentrations; reviewed by Pratt et al., 2012). Other approaches include the precipitation of amorphous calcium phosphates (Qiu and Ting, 2014), and extraction via production of bacteria (as struvite, Soares et al., 2014), plants (Shilton et al., 2012), or algae (Shi et al., 2014).

These technologies appear capable of phosphorus and nitrogen removal from waste streams, with varying scales and economics. The character of the extractant materials, however, provides many challenges for the re-cycling of these nutrients as fertilisers.

Recovery via precipitation from waste-water systems, logically, usually produces materials that are very insoluble. This low solubility has proven problematic for the use of these materials (e.g. struvite) as fertilisers.

Extraction of nutrients from waste streams via plant uptake and removal produces plant material with tissue nutrient concentrations at the high-end of those possible (e.g. up to 3% P). However, these concentrations are quite low in terms of fertiliser nutrient concentrations (Shilton et al., 2012).

A range of additional approaches are possible for ammonium extraction from waste streams including liquid effluents. A recent review highlights that nanofiltration (generally producing liquids with less than 100 mg NH_4^+ L^{-1}), membrane distillation combined with ultrafiltration, air stripping, and reverse osmosis (generally producing liquids with less than 13 g total ammoniacal nitrogen L^{-1}) appear to be the best choices (Zarebska et al., 2015). Data presented in the review also indicated that membrane distillation was demonstrated to be capable of producing a concentrate with 53 g of NH_4^+ -nitrogen L^{-1} . This approach uses gas permeable membranes to separate NH_3 , and then captures this nitrogen in sulphuric acid (Rothrock, Jr. et al., 2013). Recent advances have been made in applying this technology to piggery effluent (Garcia-Gonzalez et al., 2015).

Immersed membrane contactor tubes connected to a flow of sulphuric acid are also capable of NH_4^+ removal (Norddahl et al., 2006; Wäeger-Baumann & Fuchs, 2012), though direct contact with the effluent liquid may have disadvantages relative to a gas membrane approach in a headspace, due to surface fouling.

In contrast to the review of Zarebska et al. (2015), Mehta et al. (2015) included likely costs and disadvantages in their assessments, concluding that struvite extraction remained the most viable technology. A major hurdle for these technologies with regard to spent litter materials is the fact that they are not liquids, and solubilising spent litter nutrients would be a major cost.

Recovered nutrient fertilisers

The potential for struvite to be used as a fertiliser nutrient source is well recognised (e.g. Mehta et al., 2015). Research suggesting approaches to pelletise and formulate struvite into fertilisers has been published (Latifian et al., 2012), and yet, conclusive literature on the agronomic performance and management of struvite-based fertiliser is lacking.

Several glasshouse trials of variable rigour are available. One trial concluded that struvite can be an effective fertiliser in acid and alkaline soils (Massey et al., 2009), though questions remain as to the appropriateness of the basal nutrient regime applied. Another glasshouse trial reported phosphorus availability from urine-derived struvite that was comparable to conventional fertiliser sources (Antonini et al., 2012), however, the utility of these findings is hampered by the lack of description of the soil used in the trial. An unconventionally designed greenhouse trial claimed struvite to be an effective fertiliser (Cerrillo et al., 2015), however, the statistical analysis seems contradictory, with strongly overlapping standard deviations of means.

Personal communication with Chirag Mehta (University of Queensland) suggests that his glasshouse trials did not establish the agronomic benefits of struvite as a phosphorus source. This is likely attributable to the low solubility of the product under the experimental conditions. If this is

the case, modifications to struvite and formulations that improve nutrient supply to plants from this material, and studies establishing the agronomic performance of these formulations are likely to be an essential development for the wide acceptance of this material as a fertiliser. In any event, agronomic testing of struvite as a fertiliser appears to be largely lacking, and studies published so far seem to have deficiencies.

Root development and association with fertiliser placement

Root structure alterations in response to organic compounds in axenic culture are known both from animal protein additions (Lonhienne et al., 2014b) and from waste product additions (the findings of the DAF National Agricultural Manure Management Project, using extracts from poultry manure). These effects are concentration dependent, with optimal intermediate concentrations being observed (Lonhienne et al., 2014b). It is unknown if or how these effects can be translated into greater productivity. However, if manure-based fertiliser formulations can be developed to “attract” root development in closer proximity to the fertiliser formulations, this would have a number of advantages:

- Diffusion paths to roots would be shorter. This could significantly improve uptake efficiency of phosphorus in particular, where this is a major limitation (Richardson et al., 2009).
- Nutrient losses via leaching and gaseous transport pathways would likely be decreased.
- Competition for fertiliser phosphorus between the soil's sorption complex and plant uptake would be decreased.

This remains a very novel area, with substantial unexplored research potential. Mechanistically the benefits of directing roots to penetrate and invade the fertiliser placement volume appear sound.

Novel exchanger materials

Most key plant nutrients are present in soil as ions (e.g. NO_3^- , NH_4^+ , PO_4^{3-} , K^+). There is an opportunity to harness this soil solution chemistry and use both cation and anion exchangers to improve plant nutrient use efficiency. Where exchangers are present in the soil, concentration gradients gradually drive the nutrient bound by the exchanger into solution where it is available for further plant uptake. In this sense, the exchanger acts as a kind of ‘supply-on-demand’ fertiliser. The principle of attaching positively charged ammonium ions to the negatively charged surfaces of high cation exchange materials has been widely adopted to suppress ammonia (NH_3) volatilisation in a variety of disciplines, including agriculture (Mumpton & Fishman, 1977; Witter & Lopez-Real,

1988; Bernal & Lopez-Real, 1993; Lefcourt & Meisinger, 2001; Redding, 2011). There is the potential that this suppressed volatilisation might lead to improved nitrogen availability and use-efficiency in agronomic applications via slowing the kinetics of nitrogen mineralisation. A number of researchers have recognised this potential and, indeed, investigations into the ability of ion exchange materials to retain nutrients have extended beyond just ammonium attachment to cation exchangers (van Raij et al., 1986; Gillman & Noble, 2005; Kaya & Ören, 2005). Yet, most of these studies are perhaps best classified as ‘preliminary’ undertakings, and very few detailed campaigns have rigorously assessed the impact of high-exchange capacity materials on plant performance and nutrient uptake from a mechanism-based standpoint. Here we review the state of knowledge on applying high-exchange capacity materials to control nutrient supply in agronomic systems.

High ion exchange materials: brief background

High ion exchange materials are compositionally diverse, and include several classes of naturally occurring minerals, organic materials and synthetic compounds. Some of the more commonly investigated high ion exchange materials, and their properties, are listed in Table 1. Zeolites have been the most widely studied exchangers in relation to their potential benefits to agronomic systems. Even as far back as the 1970s zeolites were generating interest due to the growing recognition of their unique suite of chemical and physical properties: “The zeolite group of minerals stands out among the rest, and its exciting bag of physical and chemical tricks promises to contribute to many areas of agriculture and aquaculture in the next decade” (Mumpton & Fishman, 1977). Natural zeolites are three dimensional aluminosilicate minerals formed directly in aqueous solutions of lava flows or in sedimentary environments from reactions between water and volcanic glass (Faure, 1998; Oste et al., 2002). The substitution of aluminium for silicon in their structure gives rise to their negative charge and high cation exchange capacity (CEC) values (Table 1). However, access of ions into their lattice structure can also be impeded due to ion sieving and blocking which can result in much lower observed cation exchange than their theoretical or ideally measured values (Mumpton & Fishman 1977). Synthetic zeolites are widely produced using silica gels and aluminium salts at high temperature (Oste et al., 2002).

Table 1 – some common ion exchange materials and their properties

Group name	Specific type	Naturally- occurring (N) or synthetic (S)	Cation or anion exchanger	CEC/AEC cmol/kg
<i>Zeolites</i>	<i>Clinoptilolite</i>	N	Cation	200 (Gholamhoseini et al., 2013)
	<i>Analcime</i>	N	Cation	450 (Mumpton, 1999)
	<i>Mordenite</i>	N	Cation	230 (Mumpton 1999)
	<i>Phillipsite</i>	N	Cation	333 (Dwairi, 1998)
	<i>Synthetic zeolites</i>	S	Cation	600 (Oste et al., 2002)
	<i>Surface-modified zeolites</i>	S	Both	Not reported
<i>Clays</i>	<i>Vermiculite</i>	N	Cation	150 (Faure 1998)
	<i>Montmorillonite a.k.a bentonite</i>	N	Cation	100 (Faure 1998)
<i>Double layered hydroxides</i>	<i>Hydrotalcite</i>	S/N	Anion	400 (Gillman & Noble 2005)
<i>Resin polymers</i>		S	Either	>200 (Kang et al., 2004)

The clays are the other major ‘family’ of high-CEC minerals. They are among the most abundant mineral groups on the Earth’s surface but their composition and exchange properties are widely variable (Faure 1998). Vermiculite and montmorillonite have the highest reported CECs of all clays yet their physical properties are markedly different. Montmorillonite, unlike vermiculite, is a swelling-clay so its addition to soils can improve water retention but limit gas exchange. The mechanism behind the high CEC in clays is the same as for the zeolites; i.e., substitution of aluminium for silicon.

Other materials with high ion exchange properties listed in Table 1 include the vast variety of artificially produced ion exchange resins or polymers and the layered double hydroxide mineral hydrotalcite which is naturally occurring, albeit in small reserves (Gillman & Noble 2005).

Nonetheless, the mineral can be readily produced artificially using aluminium and magnesium salts in the presence of ammonium solution.

Case studies and state-of-knowledge

Zeolites

Several studies have assessed the feasibility of natural zeolite addition to soils to improve agronomic performance through NH_4 -nitrogen exchange and enhanced nitrogen retention and plant uptake. Gholamhoseini et al., (2013) and de Campos Bernardi et al., (2013) both conducted field experiments with zeolite-amended soils and a variety of model crops including lettuce, tomato, rice, grass and sunflower. Both trials reported approximately 20% improvement in dry matter yields with the zeolite addition. Moreover, Gholamhoseini et al., (2013) observed an increase in nitrogen uptake with increasing zeolite additions at a commensurate nitrogen loading rate of 130 kg/ha across all treatments.

Dwairi (1998) assessed the feasibility of using NH_4 -saturated zeolites as a controlled nitrogen release source for agronomic applications. They concluded that the material showed potential as an effective slow-release fertiliser, yet this was based on laboratory-scale results involving isotherm studies examining the kinetics of NH_4 sorption and chemically-induced NH_4 release into solution.

Natural zeolites have not been used exclusively for improved nitrogen use-efficiency. Williams and Nelson (1997) studied the uptake of potassium (K) by chrysanthemum plants grown in K-spiked clinoptilolite-amended soils at the glasshouse-scale. They observed similar growth and K uptake rates by the plants in the zeolite-amended soils to control plants that received K from conventional fertiliser addition. Moreover, these authors alluded to the potential for ongoing K supply from the zeolite which could improve the overall agronomics of the approach: "*A substantial percentage (61% to 78%) of the applied K from the precharged Cp (zeolite) remained in the pots at the end of the experiment and would presumably be released and available for plant uptake later*" (Williams & Nelson, 1997). Notario del Pino et al., (1995) also reported a positive slow release of K^+ from a phillipsite-based zeolite fertiliser. However, the real-world applicability of their finding needs to be viewed with caution as the research was conducted under laboratory conditions with no agronomic component.

Surprisingly few studies have assessed potential agronomic benefits from applying high-CEC synthetic zeolites to soils. Park et al., (2005) reported effective desorption of NH_4 from a synthetic zeolite and subsequently alluded to a potential fertiliser benefit, although no agronomic experiments were conducted. Bansawal et al., (2006) successfully modified the surfaces of natural zeolites to achieve a high anion rather than cation exchange capacity. In their laboratory-scale work, they adsorbed orthophosphate onto the surface of the modified zeolite and subsequently

slowly desorbed the anion via chemically induced percolation. The authors reported that the internal sites of the zeolite remained negatively charged indicating the potential for simultaneous cation and anion exchange. However, there was no agronomic experimental component to the research and the chemical used to modify the zeolite surface (hexadecyltrimethylammonium bromide) could raise some environmental concerns.

Clays and layered hydroxides

Clays are a natural constituent of most soil types and much work has reported the effect of clay content on plant production. However, the addition of pure clays to agricultural soils offers a reasonably novel way to supply plant nutrients through ion exchange. Certainly, there has been less focus on the clays than the zeolites regarding this approach. There is the potential that clays' effective CEC is in fact higher than for the zeolites because clays' structures are more two dimensional and so the effects of ion sieving and blocking are less pronounced than for zeolites.

Crocker et al., (2004) assessed the effect of bentonite (montmorillonite) addition to sorghum crop yields in a glasshouse-scale experiment. The study involved the incorporation of 'freshly' mined bentonite as well as recycled bentonite from the food processing industry. Interestingly, increasing addition of both bentonite types resulted in lower dry matter yields, possibly due to increased water repellence caused by the swelling clay. By contrast, Gillman and Noble (2005) observed a 100% increase in sorghum dry matter yields amended with montmorillonite at an application rate of 60 tonnes/ha. Gillman and Noble (2005) also assessed the efficacy of anion exchangers known as double layered hydroxides, also referred to as hydrotalcite (HT), to retain nitrate. These authors documented a three-fold improvement in dry matter yield using nitrate-HT compared with urea at a nitrogen application rate of 80 kg/ha.

A number of researchers have conducted studies targeted at harnessing the high CEC properties of vermiculite clays to improve nutrient use efficiency. Russell and Fraser (1977) postulated the development of a slow-release NH_4 fertiliser using vermiculite based on laboratory-scale research while Headlee et al., (2014) found vermiculite to be an effective nutrient supplier at the glasshouse-scale.

Resins/polymers

There are numerous resins/polymers that have been developed in the field of agronomy. It is important to differentiate between those polymers that have been developed for slow-release fertiliser technologies via soluble coatings on conventional nutrient sources from those that have been specifically developed to carry a high ion exchange capacity. Coating polymers like chitosan (Jamnongkan & Kaewpirom, 2010), include materials sought after for their protective properties

and their ability to slow dissolution rates and these materials are covered elsewhere in this review. Here, we focus on polymers designed specifically to carry a high ion exchange capacity. In this sense, most high ion exchange polymers have been used as an indicator of nutrient sorption in soils. They are more often used as a tool for monitoring soil health status in fertiliser trials (Agbenin & van Raij, 2001; Qian & Schoenau, 2005; Paz-Ferreiro et al., 2012; Schreeg & Porder, 2014) rather than directly as fertiliser materials themselves.

Nonetheless, some researchers have investigated the fertiliser application potential of high ion exchange polymers. Sengupta and Pandit (2011) looked at phosphorus recovery from waste water using iron oxide-impregnated anion exchange resins and postulated strong potential for application of the recovered products (struvite or apatite) as a fertiliser material. However, the fact that these types of products were formed suggested a recovery mechanism other than anion exchange (precipitation or chemisorption). The problem in that case is that while the formed compounds might be rich in key plant nutrients, practical methods for harnessing their nutrient supply are not yet fully developed.

Sendrowski and Boyer (2013) also investigated phosphorus removal from waste water using an anion exchange resin embedded with hydrated ferric oxide nanoparticles. Again, these authors proffered the prospect for nutrient reuse in agricultural settings yet the study lacked an agronomic assessment of the final products.

Future research needs

The studies reported on in this review suggest that there is strong potential to tap into the ion exchange capacity of a variety of materials to improve nutrient cycling in agronomic systems. The feasibility of such approaches will undoubtedly hinge on a range of drivers pressuring the need to find alternatives to conventional fertiliser sources. Yet the general consensus is that fertiliser prices will increase and established deposits will soon exhaust, so development of suitable alternatives is prudent (Cordell et al., 2009). With this in mind, there are a number of key research areas identified in this review relating to improving the use of ion exchangers to achieve efficient nutrient cycling in agronomic settings.

To begin with, the application of synthetic zeolites looks promising, particularly given their exceptionally high cation exchange capacities. These materials are commercially abundant and manufactured for a wide range of applications. Further studies on their agronomic behaviour from a nutrient use efficiency perspective are needed to assess expected performance at field scale and to formulate cost-benefit analyses associated with developing them as a fertiliser technology.

High cation exchange capacity non-swelling clays could also form the basis of a feasible nutrient cycling technology because they are abundant and widespread, potentially don't present ion

occlusion problems associated with zeolites, and don't drastically alter the moisture content of soils like swelling-clays.

There is also potential to modify existing ion exchange materials to achieve greater efficiency. We saw that zeolite surfaces have been modified to accommodate an anion as well as cation exchange capacity. Other researchers have similarly applied novel approaches to existing technologies. For example, Pereira et al., (2012) found that nano-bentonite crystals imbedded in urea could form the basis of an effective slow-release fertiliser product. This novel way of thinking will be critical in developing sophisticated nutrient-cycling approaches that are capable of challenging established fertilisers.

Finally, there is a massive effort underway into detecting and developing increasingly high surface area materials for a range of applications (McIntyre, 2012). It will certainly be worthwhile to test some of these materials from the perspective of improving nutrient cycling in agronomic settings. Yet it is also crucial that we understand the mechanisms of nutrient cycling involved with these new materials. Ion exchange is an excellent process for nutrient cycling in agronomy because it involves the combined likelihood of: a) the exchanger adsorbing high nutrient levels to itself; and b) subsequently delivering these nutrients to plants. Some newly developed high-tech materials may well have excellent nutrient binding efficiencies but without understanding the mechanisms of how the nutrients are bound it is very likely that cases will arise where the nutrients are not plant available. Consequently, investment into developing these emerging materials as efficient nutrient suppliers could be very costly.

Conclusions

- In-season nutrient supply is a key target for fertiliser formulation, both to decrease nutrient losses and increase uptake efficiency.
- In-season nutrient delivery could be achieved via inhibitor use, if the decay rate of these materials under (elevated-temperature) Australian conditions can be radically decreased.
- Sorbents are able to defer nutrient supply and decrease nutrient loss via each of the pathways. This benefit should be further pursued to tailor in-season nutrient supply.
- Better exchange materials are likely available (especially cation exchangers) and development of fertiliser formulations based on these materials will be pursued to decrease the bulk of the fertiliser products produced.
- By increasing root invasion into the fertiliser placement volume it may be possible to significantly increase nutrient uptake efficiency relative to conventional fertilisers and previous

use of poultry-sourced nutrients. This benefit would differentiate spent litter fertiliser materials from conventional fertilisers.

- Agronomic research into their use as fertilisers is largely lacking, however, solubility and performance have been shown to be a concern in some situations. The research team will rigorously investigate how these materials can be used in superior fertiliser products designed to achieve in-season nutrient supply.

Appendix B: Manure and sorbent fertilisers increase ongoing nutrient availability relative to conventional fertilisers

Attach the submitted manuscript here (Redding et al., 2015).

Appendix C: Nitrogen pot trial

Introduction

This experiment was completed in association with the activities described in a manuscript currently in review (Redding et al., 2015, submitted to Plant and Soil). Introductory considerations and the research question are identical to those stated in that publication. In this case we dealt with the short-term nitrogen uptake, in formulations using ion exchange materials and the spent-litter nutrient source to defer nitrogen and phosphorus availability relative to a conventional fertiliser source.

Methods

Experimental design for the nitrogen trial mirrored that for the phosphorus trial. However, there were key differences. Firstly, the active sorbent in this trial was bentonite, and the treatment rate of this material was fixed for the + bentonite treatments at $0.0477 \text{ g [mg of N]}^{-1}$. However, the intent is to use hydrotalcite formulated with bentonite. Since hydrotalcite will tend to buffer pH to a higher level, potentially influencing the effectiveness of the bentonite, hydrotalcite was included at a rate of $0.86 \text{ g [kg of soil]}^{-1}$.

Smaller pots were employed to minimise adverse effects on glasshouse staff with back injuries. In this case sandy soil pots contained 1.89 kg of soil (oven dry equivalent), while the red clay pots contained 1.33 kg of soil (oven dry equivalent). Addition rates of nitrogen were 0, 60, 120, 180, 240 and 300 mg of N.

Basal applications of phosphorus rather than nitrogen were applied, along with the other nutrients. A total of three cuts were made between 15 December 2013 (planting) and March 2014.

A total of 10 pore volumes of water were leached through each pot (both soils) between 12 December 2014 to 6 March 2014. Analysis of the leachate aliquots failed due to operator error or instrument failure, with no remaining sample available for alternative analysis.

Statistics

Statistical techniques applied to experimental design and data are identical to those described in the attached manuscript (Redding et al., 2015).

Results and discussion

The pot trial was observed to be strongly responsive to added nitrogen (nitrogen rate, $P < 0.001$), with a coefficient of variation of 14%. Across both soils and all cuts there were significant treatment effects of bentonite addition on total nitrogen uptake ($P < 0.1$, decreased nitrogen uptake by 13%).

The sorbent addition (bentonite) successfully deferred nutrient availability. Using nitrogen uptake by the model pasture species as maximum potential uptake (Redding et al., 2015), it is evident that nutrient availability is greater in the first cut where HT additions have been made ($P < 0.1$), but no different in latter cuts (second and third). This represents a four-week deferral of availability, during the period in which the classic nutrient requirement curve is at its lowest point (Figure C.1).

A similar pattern was evident for the nitrogen source, where spent litter application significantly decreased maximum potential uptake for the first two cuts relative to the conventional source ($P < 0.001$). Throughout the trial, there was a 61% decrease in total nitrogen uptake associated with the use of spent litter relative to the conventional treatments ($P < 0.001$).

These results need to be considered in the light of the extended field trial to identify the likely ongoing uptake of nitrogen from spent litter and bentonite treatments. While total nitrogen uptake here was less from the spent litter and bentonite treatments, the field trial (Redding et al., 2015) suggests that over the longer term, equivalent nitrogen will be available.

Conclusions

Both the use of a cation exchanger (bentonite) and spent litter were able to delay delivery of nitrogen relative to the conventional treatments.

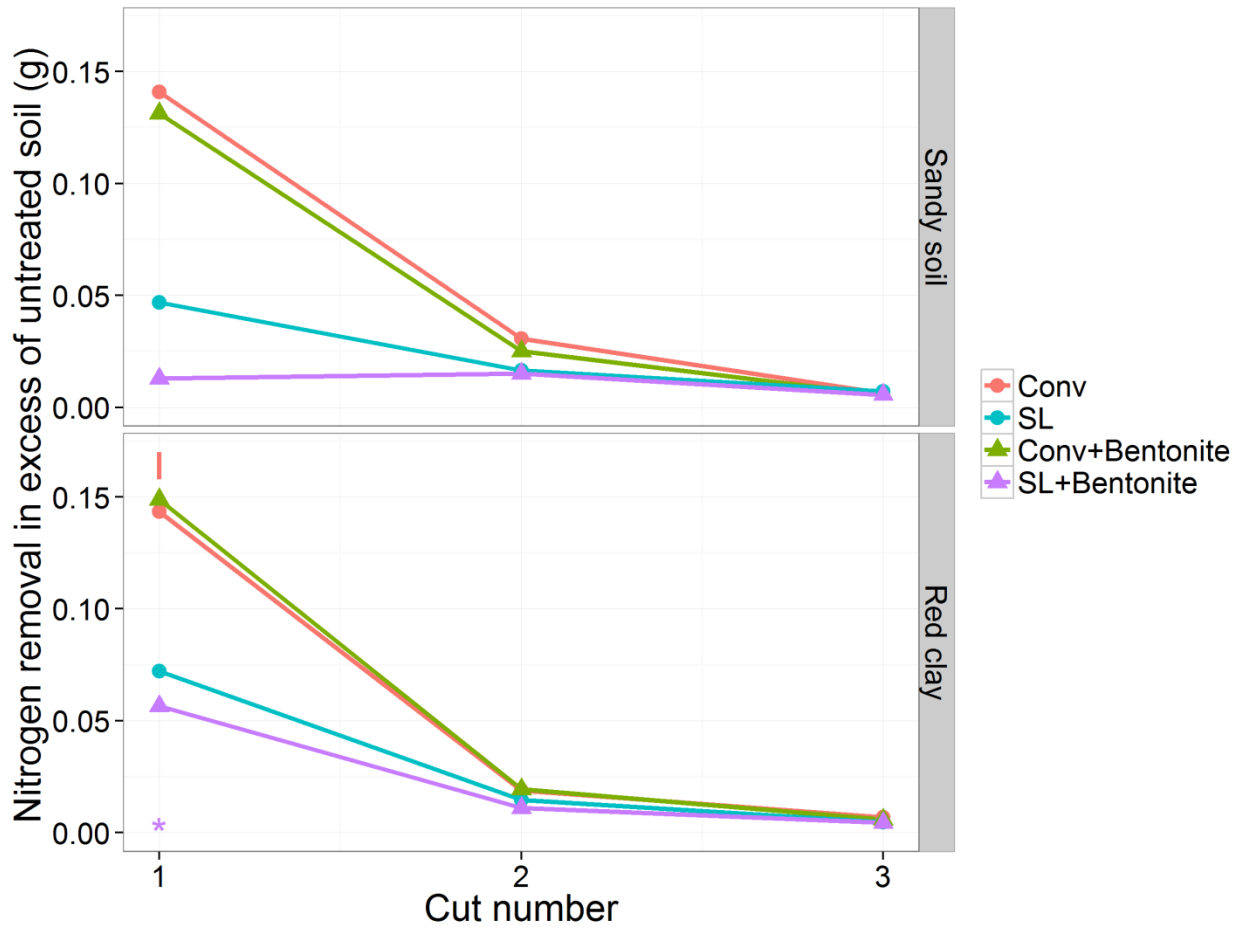


Figure C.1 Nitrogen uptake in the nitrogen pot trial, observed significantly less nitrogen uptake from the spent litter (SL; $P < 0.001$) and Bentonite ($P < 0.1$) treatments compared to conventional treatments (Conv), however the interaction of these two factors on a per cut basis was only significant for cut 1 of the red clay ($P < 0.05$, marked with “*” and an LSD bar).

Appendix D: Rainfall nitrogen runoff trial

T. Duncan, R. Lewis, M. Redding

Summary

Spent poultry litter is a considerable source of nutrients and has a history as an effective fertiliser. However, nutrient runoff from fertiliser application is an economic loss to farmers and can have devastating effects on surrounding waterways. This study sought to determine the nitrogen (N) losses from spent poultry litter following rainfall simulation and compared these losses to nitrogen runoff from conventional fertilisers. A nitrate-hydrotalcite + poultry litter formulation was included in this comparison. We also sought to determine whether adding bentonite or vermiculite to spent poultry litter could reduce nitrogen runoff as well as establish the rates of bentonite or vermiculite needed to achieve this. Rainfall simulations conducted on turf-applied spent poultry litter showed that the subsequent runoff ammonium-nitrogen ($\text{NH}_4\text{-N}$) and nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations were significantly lower than that of conventional ammonium nitrate (NH_4NO_3) fertiliser. Spent poultry litter resulted in <1% of the total nitrogen applied being lost as $\text{NH}_4\text{-nitrogen}$ and $\text{NO}_3\text{-nitrogen}$ combined, compared to 27.7% for NH_4NO_3 fertiliser. The nitrate-hydrotalcite + litter formulation lost 3.5% of total nitrogen applied as $\text{NO}_3\text{-N}$. The addition of increasing rates of vermiculite to poultry was hampered by experimental variability, however, the addition of increasing rates of bentonite resulted in a negatively correlated linear trend between bentonite addition and mineral-nitrogen losses ($P < 0.1$). Further studies are required to elucidate the specific application rates of bentonite needed to minimise $\text{NH}_4\text{-nitrogen}$ runoff from spent poultry litter.

Introduction

With the global human population rising, world food production must also increase to ensure world food security. The world population is around seven billion people, and is projected to increase to nine billion by 2050 (United Nations, 2015). With an estimated extra two billion people on Earth, soil resources and crop nutrient supply are crucial in increasing and maintaining food production on a global scale. Most soils require regular treatments of macronutrients such as nitrogen (N) and phosphorus (P) to sustain adequate plant growth, but the sources of nitrogen and phosphorus fertiliser production are finite and depleting (Dawson & Hilton, 2011). Significant energy input is required for the energy intensive Haber-Bosch process necessary for manufacturing ammonia (NH_3) (Dawson and Hilton, 2011). Phosphorus is derived from phosphate rock, a non-renewable resource with peak phosphorus production estimated to be around 2033 (Cordell et al., 2009) and total depletion estimated within decades or a century depending on the utilisation trend (Cordell &

White, 2011). Thus, utilisation of agricultural manures as a replacement for traditional fertilisers is becoming more attractive, particularly poultry litter due to its high phosphate concentrations.

In Australia, runoff of nitrogen and phosphorus from agricultural areas is an issue of particular interest, as it can result in economic losses to farmers and negatively affect surrounding water ways (Chen et al., 2008). The influx of nutrient-rich river discharge associated with runoff from agricultural land in northern Queensland has resulted in intense and extensive phytoplankton blooms occurring in the Great Barrier Reef (GBR) (Brodie et al., 2011). Since European settlement it has been estimated that the total nitrogen (TN) load discharged to the GBR has increased by 66,000 tonnes/year (5.7x) and total phosphorus (TP) has increased by 14,000 tonnes/year (8.9x) (Kroon et al., 2012). Therefore, areas of agricultural production, particularly in northern Queensland, require adequate nutrient runoff management strategies to reduce the impact of excessive nutrient loads to the GBR. The Reef Water Quality Protection Plan 2013 (the Reef Plan) aims to improve land management of reef catchments to reduce diffuse source pollution to the GBR (Queensland Government, 2013). In order to achieve nutrient load targets and goals set out in the Reef Plan, a 50% reduction in dissolved inorganic nitrogen loads and a 20% reduction in particulate nutrients is required by 2018 in priority areas (Queensland Government, 2013).

Careful management of agricultural nutrients is required to effectively control losses of nitrogen and phosphorus to water resources. Soil has a limited capacity for adsorbing soluble elements in cationic and anionic form. However, the addition of ion exchanger materials to fertilisers has been proposed as a viable tool that allows uptake of nutrients by plants whilst protecting the nutrients from rapid leaching (Gillman & Noble, 2005). These ion exchanger materials, referred to here as “sorbents”, include clays such as bentonite and vermiculite (cation exchangers) and synthetic layered double hydroxides such as hydrotalcite (HT) (anion exchanger).

Previously, Redding (2011) investigated the effect of the anion exchanger hydrotalcite on phosphorus runoff from spent poultry litter. Under rainfall simulation, hydrotalcite additions equivalent to 10% of dry spent litter mass were sufficient to effectively eliminate initial phosphorus losses from spent poultry litter runoff. Redding (2011) also concluded that the addition of bentonite to spent poultry litter decreased the soluble ammonium-nitrogen ($\text{NH}_4\text{-N}$) content from 81% to less than 50%. However, rainfall simulations were not conducted on potential reductions in $\text{NH}_4\text{-N}$ nitrogen runoff from spent poultry litter following bentonite addition. Other studies have been conducted on phosphorus runoff from poultry litter (e.g. Shreve et al., 1995; Moore et al., 1999), but fewer studies have investigated nitrogen runoff losses from poultry litter and techniques to minimise such losses.

We conducted this study to identify the NH_4 -nitrogen and nitrate-nitrogen ($\text{NO}_3\text{-N}$) runoff immediately after application of spent poultry litter formulations, and how this nutrient runoff compares with conventional fertilisers. This study also sought to determine if addition of sorbents (vermiculite, bentonite, or hydrotalcite) might achieve decreases in nitrogen runoff in the period immediately after land application.

The impetus for this study was an outcome of the project adoption workshop. Initially, the intent was to develop an agronomic participatory trial from that workshop with a range of stakeholders from the workshop participating. However, there appeared to be greater interest to investigate mineral nitrogen losses from pelletised, formulated, or unmodified spent litter. Despite plot preparation for the agronomic trial, the project team responded, working closely with several individuals and companies particularly interested in litter products.

Methods and materials

Poultry litter source

Spent poultry litter was collected from a meat chicken production shed located in the Lockyer Valley (south-east Queensland) upon completion of an eight-week batch rotation of meat chickens. The litter comprised hardwood shavings to a bedding depth of 50 mm. A bulked litter sample was collected using a randomised sampling design to be representative of the whole depth of the litter and the full area of bedding material. Litter collected was homogenised in the laboratory through mechanical mixing and stored in a cold room (4 °C) until used. Litter was analysed for pH and electrical conductivity (1:5 mass ratio of sample to water, 4A1, 3A1), total-nitrogen and carbon (Dumas high frequency induction furnace 7A5 and 6B2), NH_4 -nitrogen and NO_3 -nitrogen (2M KCl extractable steam distillation, 7C2), trace elements (aqua regia digest ICP) and moisture content (oven dried at 85 °C for 48 hours).

Super Growth (Katek)

A commercially available fertiliser product, Super Growth (Katek Fertilizers Australia), was used in experimentation. The main constituent of Super Growth is composted poultry litter. The fertiliser is balanced by mixing the poultry litter with rock phosphate, potassium sulphate, zeolite, blood and bone, gypsum, worm castings and seaweed extract. The resulting product is available in pellets (two sizes) and fines. For this experiment we have chosen the large pellets (approx. 5 mm) as it is the most practical form for conventional fertiliser spreaders. Product information on Super Growth fertiliser states 3.5% (Wt) nitrogen, 1.85% (Wt) phosphorus, 4%(Wt) potassium.

Sorbents (anion and cation exchangers)

Hydrotalcite (HT)

Hydrotalcite (HT) for this experiment was prepared using the NO₃-HT method modified from Gillman et al. (2008). Solutions were prepared, heated, and stirred for approximately five hours at 80 °C. Multiple batches of HT were produced in order to gain a sufficient dry weight of HT required from experimentation. Each batch of HT underwent the same processing. The centrifuged HT slurry was washed with ultrapure water (> 18MΩ cm, MilliQ Academic reverse osmosis unit) at a rate of approximately four times the mass of the remaining slurry, resuspended and agitated on an end-over-end shaker for an hour. This was repeated for a total of three washes. It should be noted that the HT began to disperse in the final wash. The HT was oven-dried at 50°C for 72 hours and ground to 1 mm. Multiple batches of ground HT were combined and homogenised for experimentation. This formed a HT product containing about 6% nitrogen by mass.

A HT-litter formulation was prepared to create a balanced nitrogen and phosphorus fertiliser consisting of litter and HT sources of nitrogen. The NO₃-loaded HT was added to the litter in proportions appropriate to achieve a total N:P ratio of 6.65 (for the HT litter). This N:phosphorus ratio was derived from plant analysis of the average N:phosphorus ratio observed in the digit grass plot trial previously conducted. The N-loading rate remained at the 150 kg nitrogen ha⁻¹ used for all rainfall runoff trials in this experiment.

Bentonite

Bentonite was sourced from a local coal mine as a by-product of mining. The bentonite was in a powdered form and composed primarily of montmorillonite clay. Analysis confirmed a carbon content of <0.005% (Walkley and Black, 1934) and nitrogen content of <0.005% (Dumas method, Watson & Galliher, 2001), which is below detection limits for such analyses. A cation exchange capacity of 90 cmol kg⁻¹ was determined by the University of Queensland using the unbuffered salt extraction method (Sumner et al., 1996).

Vermiculite

Vermiculite used in experimentation was sourced from Auspearl. The company website states the vermiculite is light to dark brown, accordion shaped granules with a bulk density of 640 - 1120kg m⁻³. Chemically the vermiculite is 38 – 46% silicon dioxide, 10 – 16% aluminium oxide, 16 – 35% magnesium oxide, 6 – 13% iron oxide and 8 – 16% water. Smaller concentrations of calcium oxide, potassium oxide, titanium dioxide and “other materials” are present in the vermiculite at concentrations ranging from 0.2 – 6% (<http://www.australianperlite.com/vermiculite/>). The cation

exchange capacity for the vermiculite was measured to be 105 cmol kg⁻¹ as determined by the unbuffered salt extraction method (Sumner et al., 1996).

Novel Pelletisation Option

Samples of litter and litter + vermiculite were pelletised by tumbling raw litter samples in a modified cement mixer whilst adding approximately 0.4 grams (dissolved in water) of a proprietary surfactant blend (John Webster, manmineral1@aol.com). Further water was added to the raw material until spheres began to form. At the completion of litter pelletisation, the material was air dried for approximately six days and then stored in polyethylene bottles until used in rainfall simulation experiments.

Rainfall Simulator

The flume-rainfall simulator apparatus was identical to that previously employed by the research team (Redding, 2011). For each measurement replicate, homogenous kikuyu turf (*Pennisetum clandestinum*) was cut and laid to cover one of two trays (0.4 by 2.1m, 0.04m deep) positioned under a rainfall simulator built to published USDA specifications (Humphry et al., 2002). Runoff from the two trays (angled at 2.5°) was collected by a small H flume assembly (Walkowiak, 2006), which allowed flow rates to be measured. The turf was pre-wet with 10 L of water followed by the application of litter treatment/fertiliser which was spread directly on the turf tray immediately before rainfall simulation. Runoff flow rates from the twin flume setup were determined by Equation 1 (Teledyne Isco, 2006).

$$F = 310 H^{2.31} \quad (1)$$

where F is the flowrate in litres per second (litres s⁻¹) and H is the head in meters (m) measured at a known point in the flume. The constants are supplied by Walkowiak (2006).

Rainfall simulation was conducted at a nozzle pressure of 28 kPa in order to deliver 70 mm h⁻¹ for a 20-minute period. Two turf sections and their treatments were evaluated simultaneously by applying rainfall evenly across the entirety of the turf surfaces. A composite sample of runoff water was collected automatically (WS750 water sampler, Global Water Instrumentation Inc.), bulking samples at the beginning of flow and every subsequent 5 minutes (100 ml aliquot every 5 minutes). A sample of the irrigation water used was also collected during each simulation for analysis. A subsample of each solid fertiliser treatment was frozen and analysed for total nitrogen and phosphorus (methods 4500-NH₃, 4500-N_{org}, 4500-P), (APHA, 2012). Each runoff sample collected was subsampled and filtered through glass fibre pre-filters (Whatman GF/C) and then 0.45 µm membrane filters (MF Merck Millipore 0.45 µm). Filtrate was analysed for NH₄-nitrogen and NO₃-nitrogen using a steam distillation method (7C1, 7Cb) (Rayment & Lyons, 2011). The sediment

retained on the filters was dried, weighed and analysed for total Kjeldahl nitrogen and phosphorus (7A2, 9A3a) (Rayment and Lyons, 2011).

Fertiliser treatments

For comparison, three types of commercially available agricultural fertilisers were selected for use in the rainfall simulation trial: urea, ammonium nitrate (NH_4NO_3) and Katek Super Growth (Table D.1). The mass of fertiliser was sufficient to ensure an equivalent rate of $150 \text{ kg nitrogen ha}^{-1}$ was used on each flume within the rainfall simulator (López-Bellido et al., 2005; Chen et al., 2008).

Table D.1. Mass of fertilisers used for rainfall simulation runoff testing and the relative replications. All fertiliser rates based on an application rate of $150 \text{ kg nitrogen ha}^{-1}$.

Fertiliser	Number of samples	Mass used in rainfall simulator (g)
Super Growth (Katek)	5	414
Urea	4	21
NH_4NO_3	5	41

Litter Treatments

Samples of poultry litter were mixed with increasing rates of sorbents (bentonite or vermiculite) (Table D.2) and incubated in polyethylene bottles for 10 days at 25°C under saturated conditions. The rates of sorbent (bentonite or vermiculite) were calculated based on the CEC contribution of the sorbent (90 cmol/kg for bentonite, 105 cmol/kg for vermiculite). For the level 1 treatment, sorbent was added to the litter in a 1:1 ratio with the NH_4 -nitrogen concentration of the poultry litter. This ratio increased to 1.5, 2, 4 and 8x for levels 2 to 5, respectively.

Pressure build-up during incubation was released through the lid of the bottle via an airlock constructed using quick-release bulkhead fittings with a vinyl hose (fitting and hose both $\frac{1}{4}$ " truck break line components) leading to an impinger filled with water ($> 18\text{M}\Omega \text{ cm}$, MilliQ Academic reverse osmosis unit). Water from the impinger was incorporated into the sample at the end of the incubation period to minimise nitrogen volatilisation losses. Samples were retained and stored at 4°C until rainfall simulation was conducted. A batch of vermiculite + litter samples were also pelletised using the method outlined above for litter pelletisation.

Table D.2: Litter treatments used in rainfall simulation. Mass of litter was determined based on an application rate of 150 kg nitrogen ha⁻¹. Mass of litter + NO₃⁻-loaded HT was determined based on a 150 kg nitrogen ha⁻¹ and accounting for a N:phosphorus ratio of 6.65.

Treatment	Number of samples	Litter (g oven dry equivalent)	Sorbent mass (g oven dry equivalent)
Litter	10	370	0
Pelletised litter	5	370	0
+ HT (NO ₃ loaded)	5	112	164
+ Vermiculite 1	1	370	132
+ Vermiculite 2	1	370	198
+ Vermiculite 3	1	370	264
+ Vermiculite 4	1	370	528
+ Vermiculite 5	1	370	1057
+ Bentonite 1	1	370	154
+ Bentonite 2	1	370	231
+ Bentonite 3	1	370	308
+ Bentonite 4	1	370	616
+ Bentonite 5	1	370	1233
+ Vermiculite (pellets) 1	1	370	132
+ Vermiculite (pellets) 2	1	370	198
+ Vermiculite (pellets) 3	1	370	264
+ Vermiculite (pellets) 4	1	370	528
+ Vermiculite (pellets) 5	1	370	1057

Statistical analysis

Two statistical techniques were employed throughout the trial: the different fertilisers were compared using an unbalanced one-way Analysis of Variance (ANOVA) followed by Tukey's pairwise analysis with 95% confidence levels, and the effect of sorbent rate on nitrogen runoff was analysed using linear regression. Statistical analyses were conducted using GenStat (2013) and the R statistical package (R Core Team, 2014).

Results and Discussion

The experimental design and the lack of a delay between treatment and rainfall simulation allowed losses immediately after land application to be investigated. What this approach did not allow was for significant nitrification processes to occur in the aerobic environment of the soil surface, something that would likely occur within a couple of days in an aerobic field environment (O'Sullivan et al., 2013). Under these conditions, only one of the spent litter materials contained substantial nitrogen in the highly mobile nitrate form (the NO_3^- -loaded HT; Table D.3). The observations are therefore discussed in the light of these experimental conditions.

Table D.3: Fertiliser treatment characteristics, reported on an oven dry basis.

	Litter	Vermiculite	Bentonite	HT+ litter	Super Growth (Katek)	Urea
Moisture % (wet weight)	31 \pm 1.2	-	-	19.9 \pm 7.2	-	
pH	7.99 \pm 0.03	-	-	-	7.1 \pm 0	
C _{org} %	-	<0.005	<0.005	-	-	
Dumas N (%)	2.98 \pm 0.1	<0.005	<0.005	-	2.7 \pm 0.04	46.6 \pm 0.26
Dumas C (%)	33.1 \pm 0.5	-	-	-	22.8 \pm 0.31	19.8 \pm 0.12
NH ₄ ⁺ -N g kg ⁻¹	4.007 \pm 0.09	-	-	2.60 \pm 0.78	2.66 \pm 0.08	
NO ₃ ⁻ -N g kg ⁻¹	0.132 \pm 0.01	-	-	2.91 \pm 1.44	0.04 \pm 0.001	
CEC cmol kg ⁻¹	-	105 \pm 1.5	90 \pm 2.5		-	

Comparison of spent poultry litter with conventional fertilisers

From the rainfall simulator experiment, we found that soluble (<0.45 μ m) mean NH₄-nitrogen runoff concentrations from the NH₄NO₃ fertiliser were significantly higher than all other fertilisers investigated (Figure D.1). Although the mean NH₄-nitrogen runoff concentrations from the spent poultry litter (litter) were significantly lower (12.7x) than the NH₄NO₃ fertiliser, the NH₄-nitrogen leached from the litter was still significantly higher than the control (Figure D.1). Urea, pelletised litter and Katek (Super Growth) fertilisers were not significantly different from the control, indicating that there was very little NH₄-nitrogen runoff from these formulations. Urea (CH₄N₂O) does not contain NH₄-nitrogen but is water soluble and is rapidly hydrolysed to NH₄-nitrogen by urease; however, the results from the rainfall simulation experiment suggest urea hydrolysis was negligible.

This was most likely due to the small timeframe between application and rainfall simulation since the experiment was designed to investigate initial runoff occurring immediately after application of fertilisers. It would be valuable to investigate NH_4 -nitrogen and NO_3 -nitrogen runoff from urea application after a hydrolysis period and this could be included in future studies.

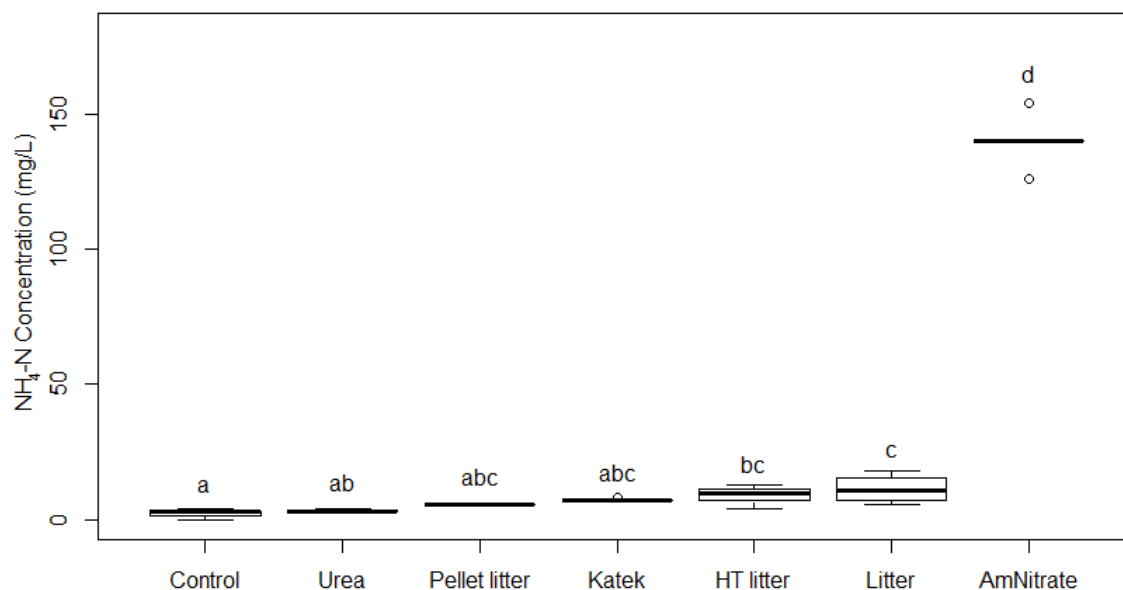


Figure D.1. Concentrations of NH_4 -nitrogen runoff from spent poultry litter compared to conventional fertilisers. Same letters indicate no significant difference between means at $P < 0.001$.

Pelletisation resulted in NH_4 -nitrogen runoff losses from at the same concentration as those from the control. However, the pelletised litter was not significantly different from the raw litter. Overall, rainfall simulation experiments demonstrated that the litter, pelletised litter, Super Growth (Katek) and litter + HT all shared statistically similar NH_4 -nitrogen runoff concentrations. Results also demonstrated that all of these fertiliser treatments performed better than conventional NH_4NO_3 fertiliser in regards to NH_4 -nitrogen runoff (Figure D.1). As pellets break down over time, these results may change.

Similar to NH_4 -nitrogen runoff, the NO_3 -nitrogen runoff from NH_4NO_3 fertiliser was significantly higher than from all other fertiliser treatments (Figure D.2). Nitrate-nitrogen runoff for Katek (Super Growth), urea, litter and pelletised litter were not significantly different from the control, indicating that NO_3 -nitrogen runoff was not evident from these treatments. This is certainly as a result of the lack of NO_3^- -nitrogen in these treatment forms (Table D.3), and the lack of an opportunity for the transformation of NH_4^+ -nitrogen to NO_3^- -N.

As expected, our results suggest that the addition of HT to poultry litter has no effect on NH_4 -nitrogen runoff (which is expected since it is an anion exchanger not a cation exchanger). Redding

(2011) found that the addition of HT significantly reduced the quantity of phosphorus leached from spent poultry litter. However, our experiment used nitrate HT rather than chloride HT, and thus the addition of nitrate from the HT resulted in increased levels of soluble $\text{NO}_3\text{-N}$. Spent poultry litter is a substantial source of phosphorus but when applied as an N-source it can result in over application of phosphorus (Shreve et al., 1995; Redding, 2011). Therefore, nitrate HT was used with the intention of increasing the nitrogen content of the spent poultry litter to an acceptable N:phosphorus ratio for plants.

The $\text{NO}_3\text{-nitrogen}$ runoff from the HT + litter treatment was lower than the NH_4NO_3 fertiliser but was significantly higher than the control with a mean $\text{NO}_3\text{-nitrogen}$ concentration of 40mg $\text{NO}_3\text{-N/L}$ (Figure D.2), largely as a result of the high concentrations of NO_3^- -nitrogen in this formulation. Over time, where nitrogen transformations are allowed to take their course, the performance of the nitrate-loaded HT relative to the other formulations studied is an open question.

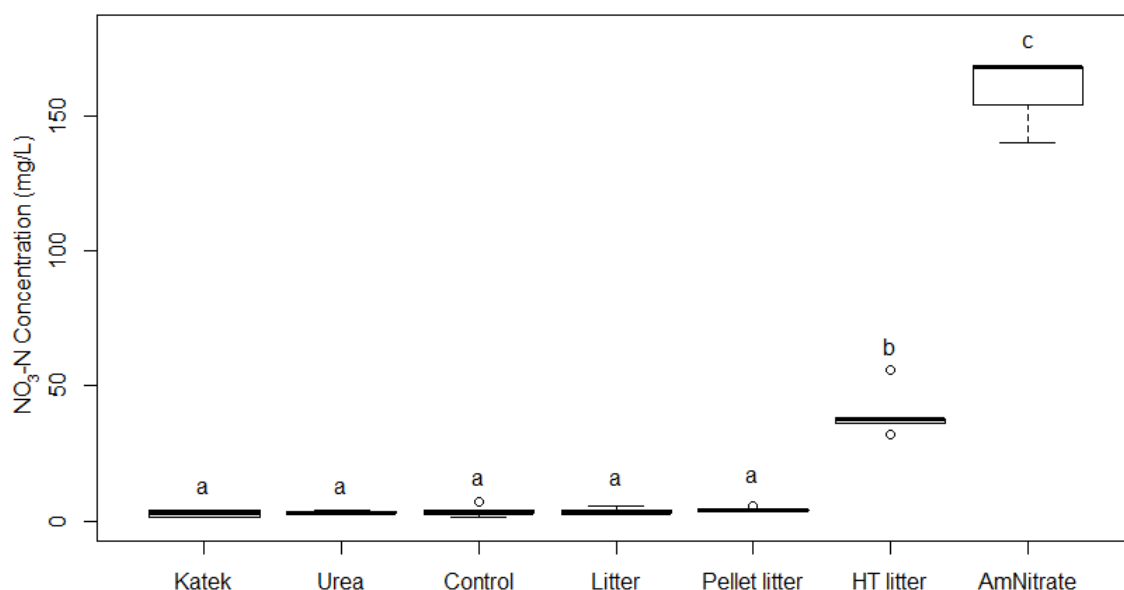


Figure D.2: Concentrations of $\text{NO}_3\text{-nitrogen}$ runoff from spent poultry litter compared to conventional fertilisers. Same letters indicate no significant difference between means at $P<0.001$.

Our results suggested that NO_3^- -nitrogen desorbed into the irrigated water, as would be expected for any exchangeable ion exposed to a low concentration volume of water. Consequently, the addition of nitrate HT to poultry litter to increase the nitrogen content resulted in $\text{NO}_3\text{-nitrogen}$ (3.48%) being lost as runoff if applied immediately before a rainfall event without incorporation (Table D.4), contrasting with much greater losses of nitrogen from the conventional fertiliser (NH_4NO_3 28% losses of added N, versus about 4% from the nitrate-loaded HT). In the short term, use of nitrate-loaded HT in formulations with spent litter may assist retention of litter P, but

increase NO_3 runoff relative to spent litter alone. In the longer term, as spent litter nitrogen becomes mineralised and more becomes transformed to $\text{NO}_3\text{-N}$, it remains an open question as to which option would better manage nitrate losses.

Table D.4: NH_4 -nitrogen and NO_3 -nitrogen runoff concentrations (mg) from fertiliser treatments as a percentage of the total nitrogen applied (background nitrogen runoff from turf has been subtracted).

Treatment	NH_4 -nitrogen lost as runoff (%tot nitrogen applied)	NO_3 -nitrogen lost as runoff (%tot nitrogen applied)
Urea	0.10	0.01
Litter	0.84	0.04
Pellet litter	0.33	0.14
HT litter	0.64	3.48
Katek	0.48	0
NH_4NO_3	12.95	14.70

After rainfall simulation, the percentage of NH_4 -nitrogen lost relative to the quantity of total nitrogen applied was relatively low (<1%) for all fertiliser treatments excluding NH_4NO_3 (Table D.4). At a similar rainfall intensity (50 mm h^{-1} for 30 min), Edwards and Daniel (1993) observed a 4% loss of total nitrogen attributed to runoff 24 hours after the application of poultry litter. They observed, that of this total nitrogen lost as runoff, 20.8% of the NH_3 -nitrogen applied was lost as runoff, which equates to 1.7% of the total nitrogen lost as $\text{NH}_3\text{-N}$. The percent loss of NO_3 -nitrogen was 0.0% of the total nitrogen applied (Edwards & Daniel, 1993), similar to the results of our study (0.04%).

Furthermore, nitrogen loss can occur via other pathways following fertiliser application, with the dominant fertiliser nitrogen losses from Australian ecosystems being gaseous losses via NH_3 volatilisation, nitrification and denitrification pathways (Chen et al., 2008). Depending on the fertiliser form and the method of application, the relative importance of nitrogen runoff can vary widely (Chen et al., 2008), and this was evident in our study. In our experiment, NH_4NO_3 fertiliser resulted in a 27.7% loss of nitrogen after 20 minutes of rainfall simulation immediately after litter application. The nitrogen runoff (as a % of total nitrogen applied) observed for NH_4NO_3 fertiliser in our study is comparable to reports of nitrogen losses via denitrification and NH_3 volatilisation

pathways observed from agricultural systems in Australia (Chen et al., 2008). This reflects the experimental conditions we applied, with a high rainfall intensity, no incorporation, and no significant opportunity for plant assimilation or gaseous loss. The greatest nitrogen and phosphorus losses typically occur in the first runoff event following fertiliser application (Robinson & Sharpley, 1995; Harmel et al., 2009). From the results of our study, NH_4^+ -nitrogen runoff from spent poultry litter did not result in considerable nitrogen losses (<1%) even with simulated rainfall applied immediately after application. Furthermore, spent poultry litter as a fertiliser results in considerably less nitrogen runoff compared to conventional fertilisers (NH_4NO_3), and if application is avoided before rainfall events, nitrogen runoff could be minimised further (Edwards & Daniel, 1993; Robinson & Sharpley, 1995).

Adding sorbents to poultry litter at increasing rates

After incubation of increasing levels of sorbents with poultry litter, rainfall simulation experiments revealed variable results between the different sorbent additives and their rates. Results revealed a negatively correlated linear trend between the rate of bentonite added and the soluble (<0.45 μm) NH_4 -nitrogen runoff concentrations after rainfall simulation (Figure D.3). The trend was significant at $P < 0.1$. It appears that the highest rate of bentonite used (254% of the dry litter mass) reduced NH_4 -nitrogen runoff from litter by 64.7%. The potential for bentonite to reduce NH_4 -nitrogen runoff from poultry litter seems promising and could offer a way to markedly decrease nitrogen losses via runoff. However, further work is still required to resolve the specific application rates need.

However, incubation of spent litter with bentonite tended to increase overall runoff losses relative to un-incubated spent litter. The 10-day incubation procedure used in the preparation of the bentonite formulations also provided conditions favourable for organic nitrogen mineralisation (the proportion of nitrogen in mineral forms increased 1.75 times with incubation; related trial data suggest a 2.5 fold increase in NH_4^+ -nitrogen). It is probably for this reason that ammonia-losses from all bentonite treatments exceeded those from the untreated litter.

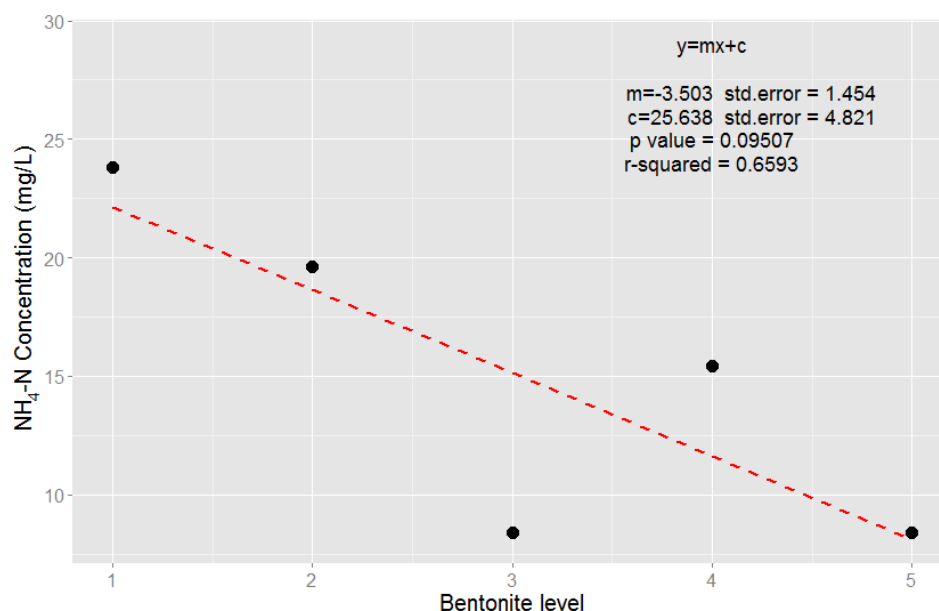


Figure D.3: Effect of increasing bentonite rates (maximum rate = 5) on NH₄-nitrogen runoff from poultry litter after rainfall simulations.

For the vermiculite sorbent, results from rainfall simulation did not reveal a significant relationship between vermiculite addition and NH₄-nitrogen runoff from poultry litter (Figure D.4). Similarly, the relationship between the pelletised litter and vermiculite blend was not significant ($P>0.1$) (Figure D.5). Therefore, from this experiment, we cannot conclude that vermiculite was effective in mitigating NH₄-runoff from poultry litter.

Increasing rates of vermiculite sorbent added to poultry litter should theoretically result in diminished soluble NH₄-nitrogen concentrations in rainfall simulation runoff since vermiculite is a high cationic exchange material. The vermiculite material used in this experiment had a higher CEC than bentonite (105 cmol/kg compared to 90 cmol/kg). The lack of a significant trend observed in this study could possibly be the result of experimental variability, or transport losses of the very light vermiculite itself, taking any sorbed nitrogen with it. However, the filtration process would have removed any vermiculite-sorbed NH₄-nitrogen from the analysis, leaving only that that desorbed into solution. The results for particulate nutrient analysis are still being processed and could provide further insight into this issue.

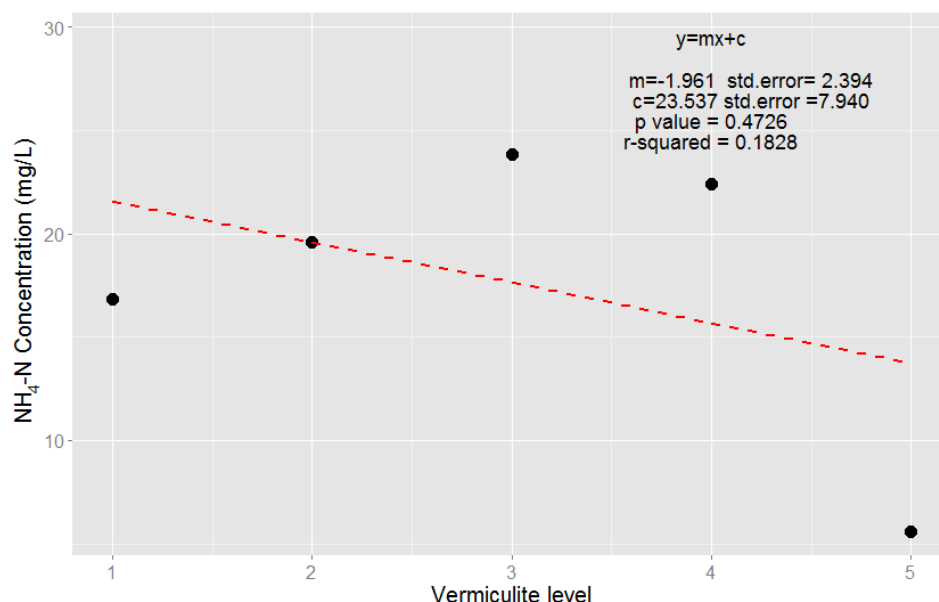


Figure D.4. Effect of increasing vermiculite rates (maximum rate = 5) on NH₄-nitrogen runoff from poultry litter after rainfall simulations.

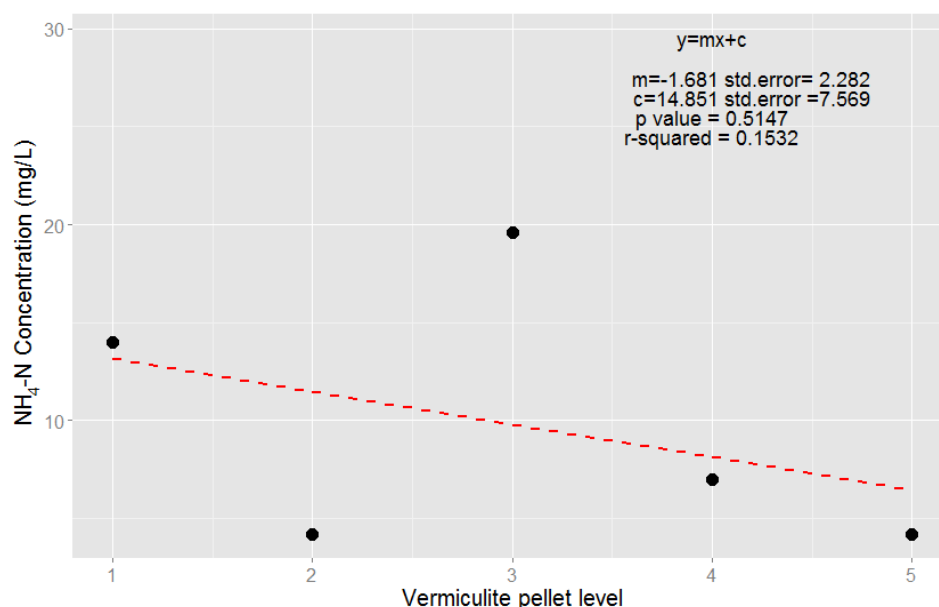


Figure D.5. Effect of increasing vermiculite rates (maximum rate = 5) on NH₄-nitrogen runoff from pelletised poultry litter after rainfall simulations.

The addition of bentonite to poultry litter did demonstrate the potential to decrease NH₄-nitrogen concentrations in runoff from rainfall simulation experiments, albeit further work is needed to elucidate its effectiveness. In the literature, there have been various studies investigating the effects of adding materials to poultry litter to reduce runoff; however, these have primarily focused on reducing phosphorus runoff (Shreve et al., 1995, Moore et al., 2000, Redding, 2011). According to Redding (2011), the addition of bentonite can increase the proportion of mineral nitrogen present

in exchangeable form, resulting in the reduction of soluble NH_4 -nitrogen content of poultry litter by 34% - when bentonite is applied at 1.58x the dry litter mass. In our rainfall simulation experiment, a 64.7% reduction in soluble NH_4 -nitrogen concentrations in runoff was observed using bentonite level 5 (3.33x dry litter mass) compared to bentonite level 1 (0.42x dry litter mass). Therefore, the addition of bentonite could be useful in decreasing NH_4 -nitrogen runoff poultry litter but would need to be applied at higher rates than tested in this experiment. An 81% reduction in NH_4 -nitrogen runoff concentrations would be required to bring the soluble NH_4 -nitrogen concentration of poultry litter to the background levels observed in this rainfall simulation experiment. Further studies could investigate the effects of higher rates of bentonite than investigated in this study, although the economical and practical viability of incorporating such amounts of bentonite would need to be considered.

The effect of increased sorbent rate (for both bentonite and vermiculite) on NH_4^+ -nitrogen runoff from poultry litter should be further investigated, including increased replication of samples within the same rate of sorbent addition. This would help to eliminate any experimental error and would improve the precision of the trend identified for bentonite.

Appendix E. Bentonite bedding trial 1

Insert attached acrobat document here (Islam et al., 2013), as prepared by the University of New England team.

Appendix F. Bentonite bedding trial 2

Insert attached acrobat document here (Walkden-Brown et al., 2013), as prepared by the University of New England team.

Appendix G. Mitigating ammonia volatilisation with bentonite

Insert published paper here (Redding, 2013).

Appendix H. Bentonites and layered double hydroxides can decrease nutrient losses from spent poultry litter

Some of the work for this paper was completed in the pilot trial before commencement of the larger Poultry CRC project. The remainder was completed subsequently. Insert published paper here (Redding, 2011).

Appendix I. Modelling the uptake of phosphorus and Nitrogen from spent poultry litter

Insert AgResearch New Zealand's report here (Shorten and Redding, 2015).

Appendix J. Factors Affecting the Use and Adoption of a New Technology for the use of Poultry Manure as a Balanced Fertiliser

Insert technology adoption report here (Coutts et al., 2015).

Appendix K. Poultry litter as a value-added Fertiliser

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This document is developed as an extension and significant update of a paper presented to the Poultry Information Exchange (Redding, 2014), capitalising on the final results from the Poultry CRC-funded project 2.2.1 “Maximising spent litter fertiliser returns through nutrient and carbon management”. It also draws on the results of Federal DAFF/MLA/APL/RIRDC/AECL research from the project 2012/2402.465 “Advancing Livestock Waste as Low Emission - High Efficiency Fertilisers”.

Introduction

Approximately 76 000 Australian agricultural businesses applied fertiliser in the period from 2011 to 2012 – to a total of about 41.8 million hectares of land (Australian Bureau of Agricultural Resource Economics, 2014). Around 64% of these businesses are applying fertiliser to supply nitrogen.

This represents a strong demand for plant nutrients, some of which is already used in slow-release forms (23%; also termed enhanced efficiency fertilisers).

Spent poultry litter contains very substantial quantities of a range of sought after nutrients, including nitrogen, phosphorus, potassium, and also the carbon required to maintain soil quality and function. Total production of spent litter was probably around 775 000 t in 2008 (Dorahy & Dorahy, 2008). While this is a lot of material, it cannot satisfy a large proportion of the plant production requirements of Australia. However, continued and increased demand for spent litter as a fertiliser is important to offset the cost of poultry production, and to enable continued industry expansion.

Given this scenario, what advantages can spent poultry litter offer, and how can we obtain them?

As a fertiliser manure use has some competition

The current prevailing agricultural view, which actually originated in the 1940s (Drinkwater & Snapp, 2007), holds that inorganic fertilisers can support high yields without additions of organic amendments or diverse rotations. Plant nutrient management has become closely focussed on some very transient quantities in soils, for example, mineral-nitrogen and inorganic phosphorus.

In this regard, agriculture now benefits from a large body of research to support the use of inorganic fertilisers which are available on-demand. In many agricultural systems there is already a body of literature available to use these products to meet the demands of crop yields, and a body of experience in their application has been developed.

The very short-lived nature of these inorganic fertiliser nutrients in soils assisted their acceptance. We know that mineral nitrogen is rapidly lost as gases, leached, or lost in runoff. Likewise, soluble inorganic phosphorus forms are very rapidly “captured” by many soils and may become unavailable. However, this delivers an advantage for researchers and manufacturers. Trials have been able to focus on single season nutrient availability (Schreiner & Anderson, 1938), while a range of soil phosphorus tests have become available that reflect the behaviour of inorganic phosphorus sources.

These benefits are more difficult to deliver for manure nutrient sources – or at least have not been delivered to date. This may well be because of the almost exclusive focus on what have become “conventional” fertilisers.

What can spent litter nutrients and sorbent formulations deliver?

Spent poultry litter is a good source of a range of nutrients, particularly phosphorus, carbon, potassium, and nitrogen (Dorahy & Dorahy, 2008; Craddock and Wallis, 2012; Wiedemann et al., 2012). Key additional spent-litter nutrients that are less commonly considered include sulphur, calcium, magnesium, manganese, zinc and copper (Wiedemann et al., 2012).

It is known that precise application of fertiliser nutrients, just in time to meet a maturing crop's demand can substantially decrease system losses and inefficiency. By managing nitrogen fertilisers in a manner that ensures non-limiting nitrogen supply with minimum excess or losses (Figure K.1) through in-season root zone nitrogen management, Chen et al. (2006, 2010b) were able to almost double maize yields with no increase in fertiliser use (Zhang et al., 2011). In this management, total fertiliser nitrogen additions were divided into sub-applications that are applied throughout the growing season (Cui et al., 2010). This practice would not be feasible in many Australian situations or production systems, due to the lack of viable mechanised approaches to access crops in-season. However, for these production systems, other options that are able to efficiently supply nutrients to meet growth requirements may enable the same benefits to be achieved.

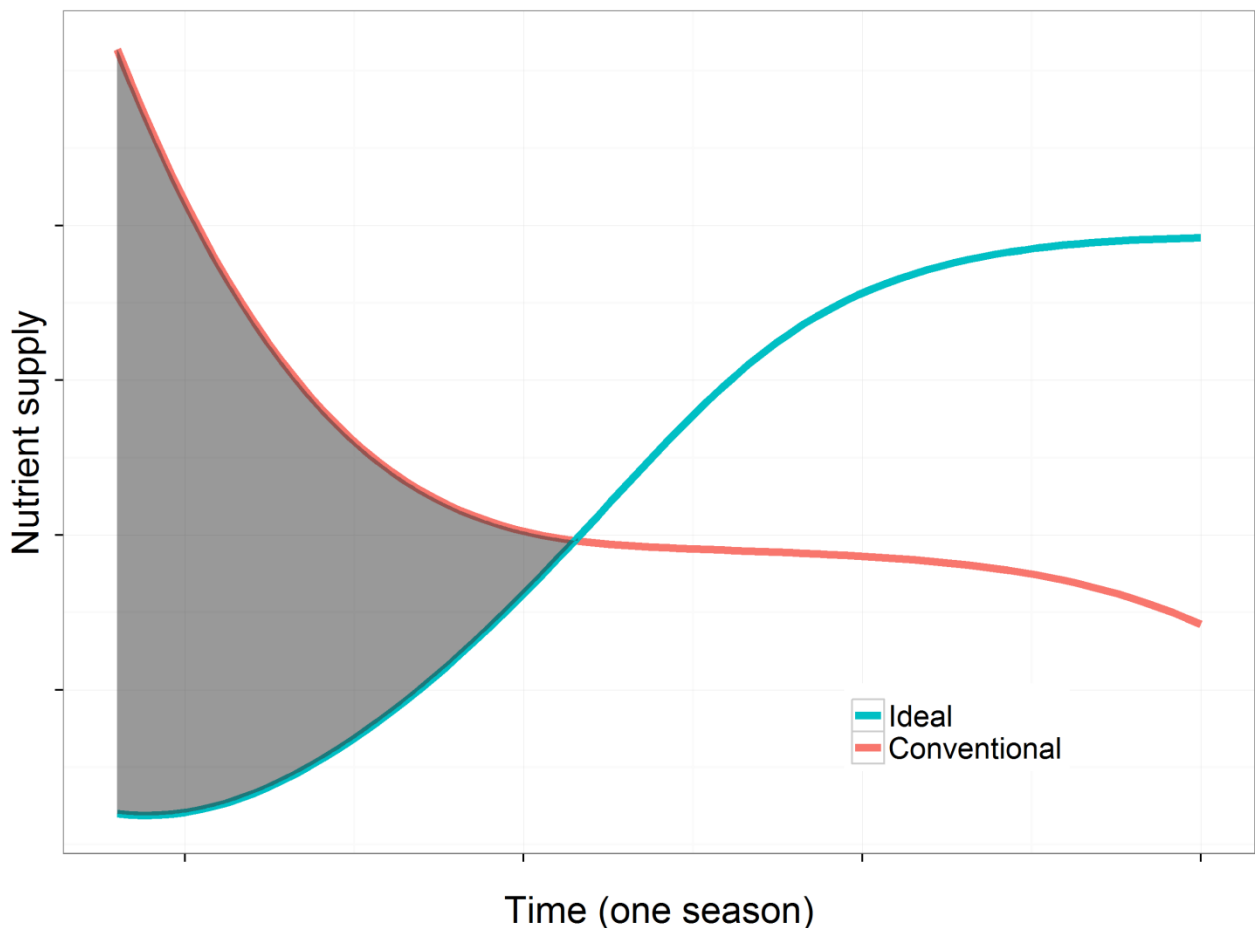


Figure K.1 Nutrient supply curve from conventional fertilisers (such as mono-ammonium phosphate [MAP] or urea) leaves something to be desired. The initial highly soluble nutrient greatly exceeds early season crop requirements (“Ideal”) and is vulnerable to losses (shaded region between the two curves).

With a different management approach many characteristics of spent litter could be advantageous. For example, like any organic material, spent litter releases nutrients to the surrounding plants as it decays. The advantage of this is that the material becomes a “slow release” fertiliser, with well-known advantages – so long as the delivery of nutrients can be made to match the requirements of the target plants.

As a source of a range of nutrients (including nitrogen, phosphorus, and potassium), all being delivered at varying rates from reservoirs of different sizes, unmodified spent poultry litter will never be a balanced fertiliser, and use of spent poultry litter to supply the total nutrient requirement of crop or intensive pasture production is likely to result in off-site consequences (Carpenter et al., 1998). These impacts include toxic algal blooms, reduction in water body oxygen, fish kills, loss of

biodiversity, loss of aquatic plant beds and coral reefs, and a range of other effects that combine to impair the use of water for drinking, industry, agriculture, and recreation.

While not in the required ratios, poultry litter contains the range of critical nutrients commonly applied as inorganic fertiliser. These slowly released nutrients are also accompanied by a substantial input of biologically active carbon (Drinkwater & Snapp, 2007). Litter effectively provides a feedstock for microbial biomass nutrient conversion activities (Okur et al., 2006), resulting in the retention of nutrients in forms with much longer persistence in soil than occurs with inorganic fertilisers. Additionally, the carbon contained may help combat carbon decline in soils.

The microbially controlled release of nutrient from these materials should be more than a footnote in our considerations (Figure K.2). This characteristic allows the end user to tackle one of the major disadvantages of conventional inorganic fertilisers: the lack of synchrony between nutrient supply and requirement (Drinkwater & Snapp, 2007). Inorganic fertilisers have been highly successful at maximising yields, but at the cost of large nutrient losses. Conventional fertiliser applications result in less than 40 to 60% plant uptake of the target nutrients, despite decades of agricultural research (Bolland & Gilkes, 1998a; Van der Molen et al., 1998; David & Gentry, 2000; Galloway & Cowling, 2002; Galloway et al., 2002; Drinkwater & Snapp, 2007). With requirements to increase the yield from productive land to meet demands, these losses and the pressure to reign in this inefficiency will likewise increase.

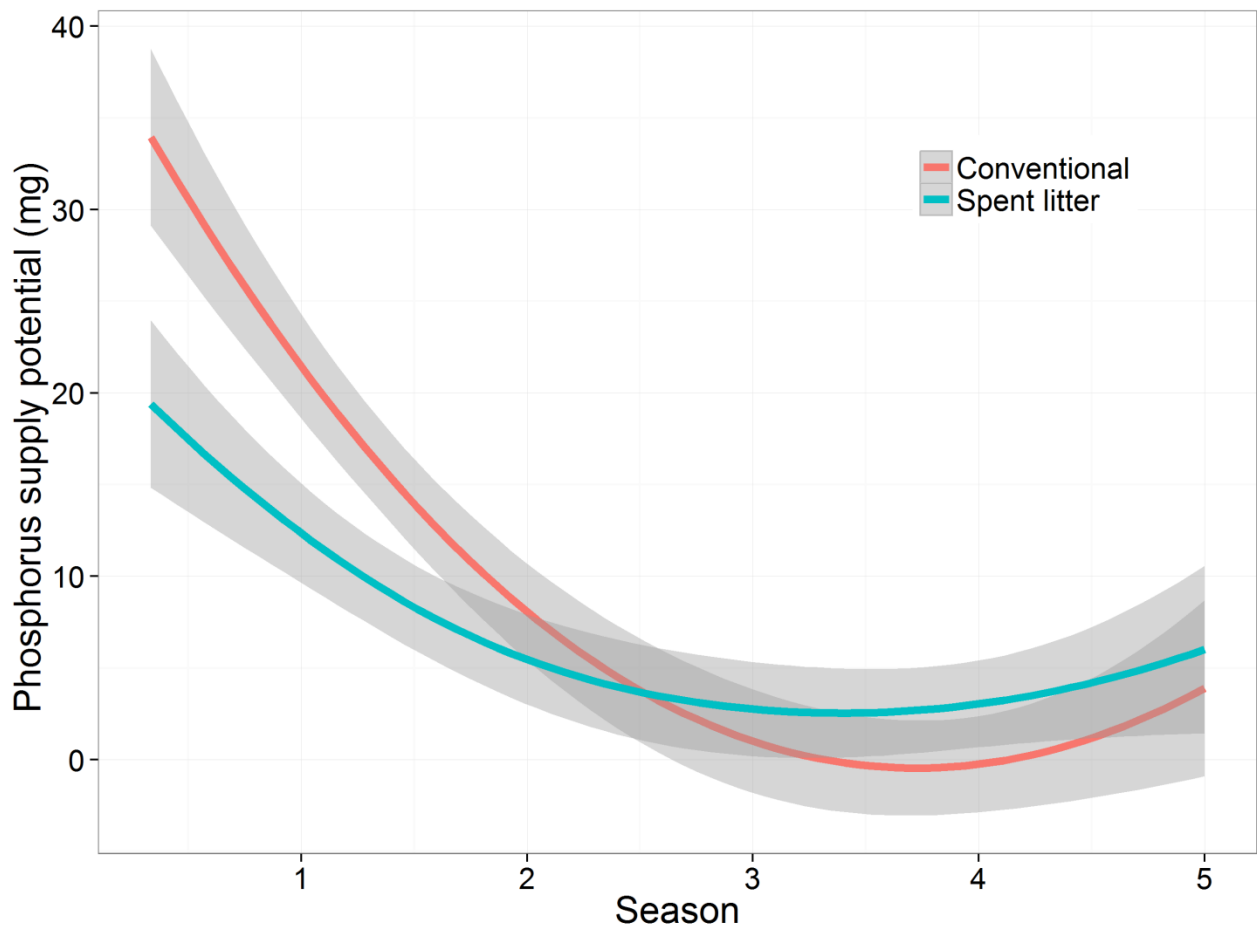


Figure K.2. Minimising the influence of the soil on nutrient release, it is evident that conventional fertilisers result in intense initial availability, followed by a rapid decline. Spent litter tends to continue to release nutrient. Splines displayed, statistics indicate significant differences in early and latter seasons.

Other controlled-release fertilisers are available – but are usually expensive, especially encapsulated or coated products (Timilsena et al., 2015). Spent litter is a by-product of poultry production – and as such entails no manufacturing costs.

A range of inter-dependent processes control nutrient availability in soil profiles. The conventional approach to inorganic fertiliser use has allowed us to manage nutrients in a way that disregards these processes, but also treats the soil profile as a very leaky system. More efficient nutrient use may be achieved by using manures as a tool to improve the soil's reservoirs of slower-cycling nutrients as suggested by some researchers (Drinkwater & Snapp, 2007).

Sorbent additions to spent litter (in this case materials that tend to retain nitrogen and phosphorus forms) can be used to take further advantage of spent litter characteristics (Figure K.2) to more closely mimic the ideal uptake curve of a plant (Figure K.1). The research team has successfully

used sorbent additions in this role, simultaneously decreasing the potential for nutrient losses (Figure K.3, note the pink line representing the sorbent-treated spent litter relative to the ideal curve). Further optimisation is possible.

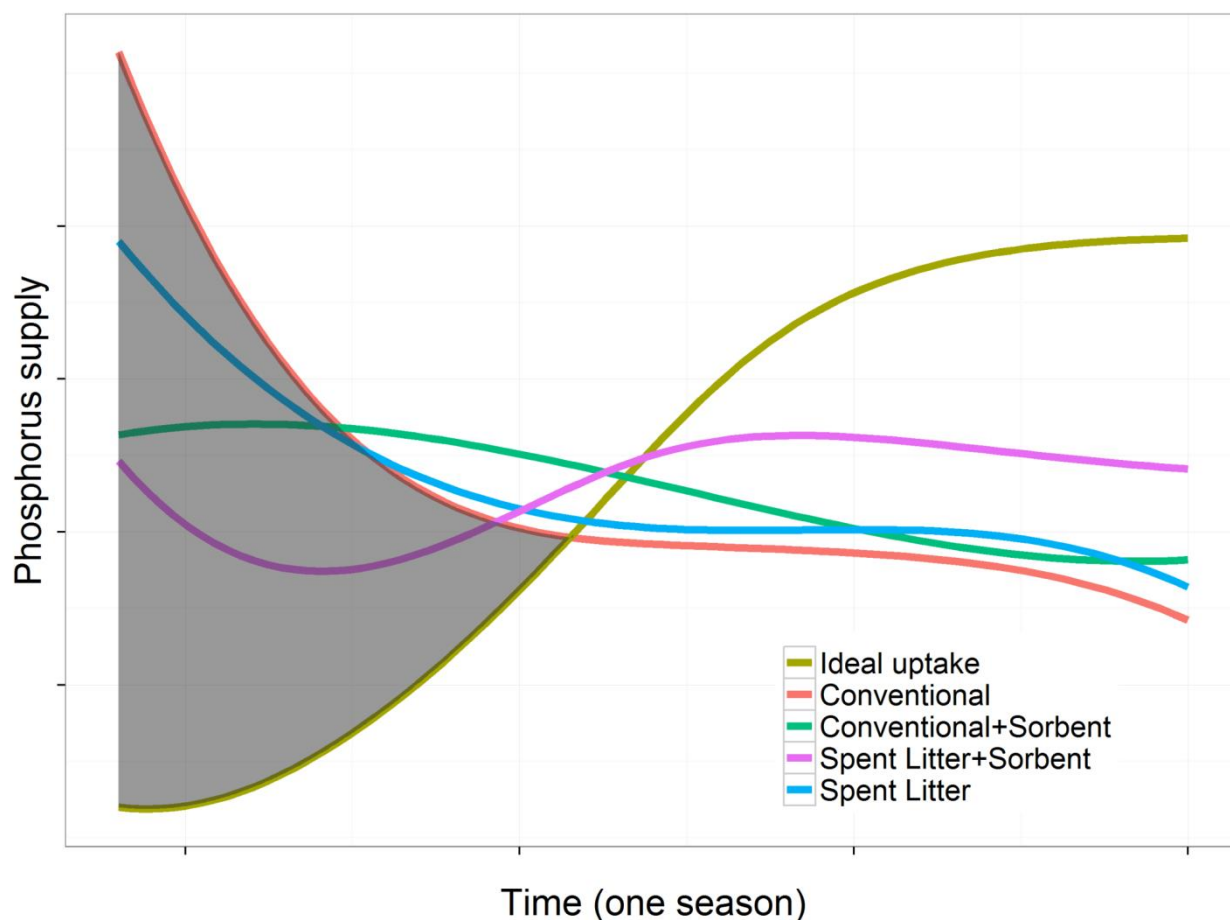


Figure K.3. Based on the pot trial data, this figure predicts the performance of the conventional phosphorus source versus a sorbent treated form, and spent litter plus the sorbent for the *third consecutive cycle of fertiliser application and crop production*. The unmodified conventional and spent litter treatments both show excess initial availability that may be subject to losses (shaded region). The ideal uptake curve of many plants is provided as a reference.

The commonly available clay material, bentonite, is able to retain the ammonium form of nitrogen, and a synthetic clay (hydrotalcite) can retain phosphorus. The use of these materials was able to decrease the potential for leaching (established for phosphorus), runoff losses (established for nitrogen and phosphorus), greenhouse gas emissions, and ammonium volatilisation.

Sorbent additions contribute to the mass and volume of the spent litter material, particularly in the case of ammonium retention materials as more nitrogen than phosphorus is required by plants. Since this is likely to decrease the economically viable transport radius around the poultry farm of

origin, higher capacity materials are being sought, and the use of nitrification inhibitors in manure materials is being investigated. However, the control of ammonium volatilisation, as a contributor to poor in-shed atmospheric quality, led to testing of bentonite as a bedding additive, highlighting some advantages and disadvantages to the use of these materials, and commercial trials are now in progress. In-shed advantages of sorbent materials, and dual benefits (in-shed and fertiliser characteristics) may make the use of bentonite more attractive where the combined benefits of better shed air quality, greater nitrogen retention in the spent litter, and fertiliser benefits are being derived.

How to get the best from spent litter as a fertiliser

Take a multiple year view

The characteristics of spent poultry litter mean that not all its nutrient content will be readily available for plant uptake within the first year. However, whether this translates into improved or degraded crop or pasture uptake of total applied nutrient relative to conventional fertilisers depends on management choices and on the same conditions that can exacerbate nutrient losses from conventional fertiliser applications.

For example, phosphorus uptake efficiency in our field trial on a phosphorus deficient red clay (over 20 months) for **conventional** treatments ranged from 13% at a low application rate (24 kg phosphorus ha⁻¹) to 8% at higher rates (80 kg phosphorus ha⁻¹). The trial was irrigated, potentially increasing water-borne losses of nutrients, and the soil at the site (possibly more significantly) has a very strong capacity to retain phosphorus. This may have decreased the ability of plants to access phosphorus during the 20-month period of the trial. Equivalent phosphorus applications derived from spent litter resulted in 8 to 17% uptake, while sorbent-modified spent litter resulted in 14 to 30% uptake. In terms of nitrogen uptake, regular irrigation accelerated nitrogen losses. Under these extreme conditions, spent litter and sorbent-treated spent litter performed equivalently in terms of their ability to supply nitrogen and phosphorus.

If nutrient use efficiency from conventional fertilisers is low due to large losses via water transport, binding to the soil, or nitrogen gas emissions, spent litter or sorbent treated materials may deliver equivalent or better agronomic performance, with more of the balance of nutrient carried over to the next season due to slow mineralisation processes (and due to sorbent retention).

However, previous literature, and our own pot studies, suggest that the ongoing nutrient mineralisation from spent litter where losses are more restricted (Figure K.2) requires a different

management approach to that employed for conventional fertilisers. This introduces the concept of steady-state nutrient supply, which should become part of the spent litter user's vocabulary:

As the period of annual or more frequent, regular, spent litter applications increases, the amount of nutrient available to crops (or pastures) increases toward a limit. This limit is effectively the total application of spent litter nutrient. At this point the applications are said to have reached steady-state mineralisation.

Some research with other manure-based materials suggests that at some sites, this point would be reached after a period of about seven years of regular application (in terms of nitrogen, Crohn, 2006). At our field site and in maximum potential release studies, this point occurred much sooner for phosphorus supply from spent poultry litter. Field trials on a soil with a strong capacity to retain phosphorus suggested spent litter was equivalent to conventional phosphorus sources (compared to the red clay, Figure K.4), while maximum potential release in a sand suggests equivalence between spent poultry litter and conventional fertiliser begins to be approached by the third six-monthly application (steady state is probably within a few additional applications).

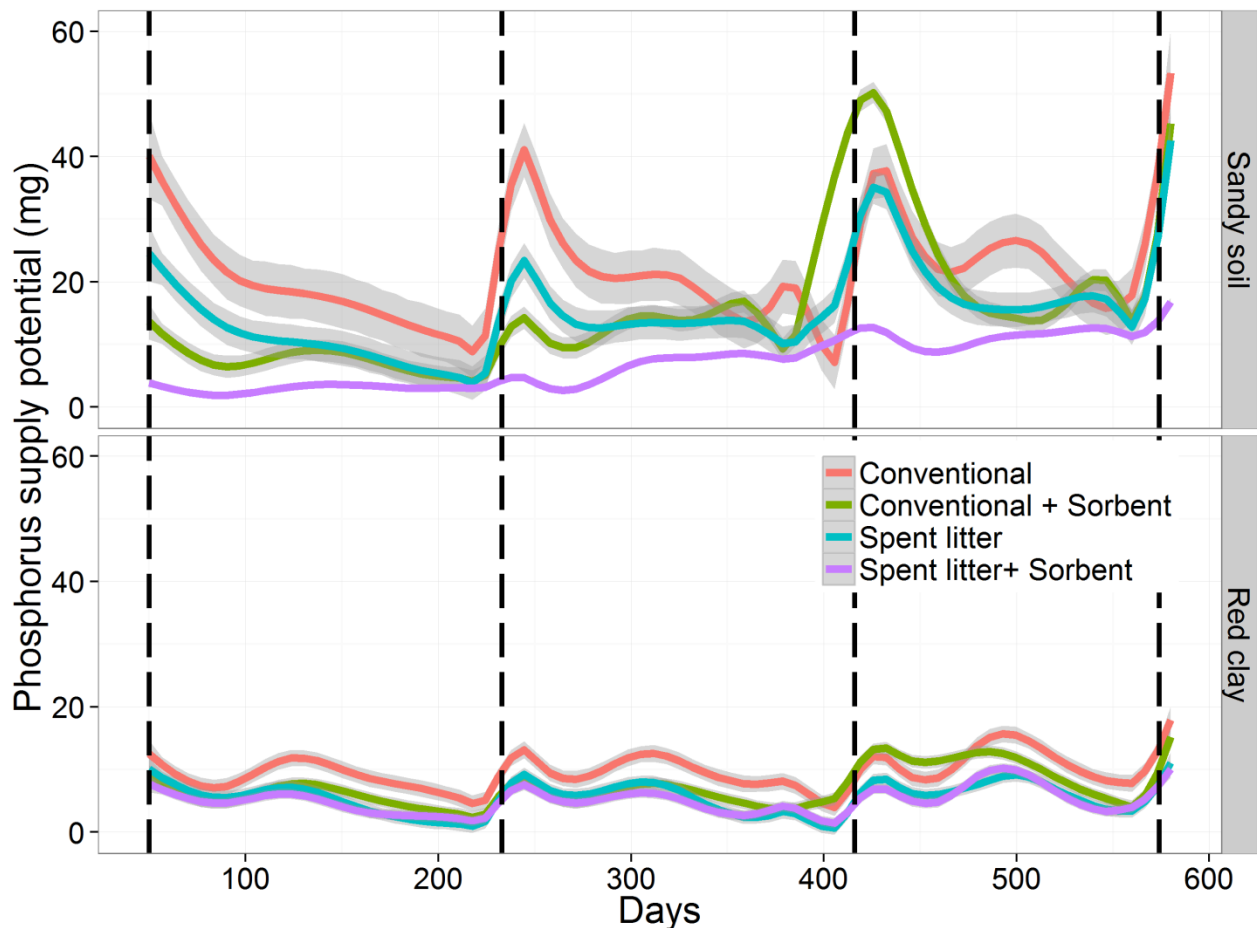


Figure K.4. Using the phosphorus pot trial data to simulate the effect of repeated applications (vertical dashed lines) of equivalent quantities of phosphorus in the different forms. For the sandy soil, spent litter phosphorus supply at the third application has reached that of the conventional source.

It is probably partly this ongoing release behaviour that leads to the need to apply spent litter in conjunction with “starter” rates of conventional fertiliser (applied with the seed; Craddock and Wallis, 2012), a practice that may not need to continue on a site with regular spent litter application. This behaviour also leads to the concept of “relative availability” of the key nutrient content of spent litter, which varies greatly between nutrients (e.g. Table K.1; Wiedemann, et al., 2012). Conventional fertiliser nutrient availability can vary from soil to soil, and it is evident that this is also the case for spent litter nutrients (Figure K.4). The simple manure-fertiliser model developed by Crohn (2006), will not account for this variability. However, Crohn’s model probably does account for differences in nutrient availability with different sources of spent litter, which is a very good step in estimating equivalent supply between conventional and spent litter nutrient sources.

Table K.1. Nutrient availability in the first year after application varies for each nutrient based on an existing report (Wiedemann, et al., 2012). Availability of nitrogen in our experimentation was greater than that represented here (over 90% in the first year).

Nutrient	Year 1 Availability
Nitrogen	20-50%
Phosphorus	30-80%
Potassium	90%

Analyse the spent litter!

Researchers consistently observe a great deal of variability in the nutrient content of spent litter (Table K.2). When using spent litter as a fertiliser, it is critical to analyse the material to prevent waste or production losses. Using analyses obtained from someone else's analysis is of little value, and is a recipe for failure.

Table K.2. The range of Australian spent litter characteristics (Dorahy and Dorahy, 2008). Note that spent litter has a bulk density of about 2.5 m³ t⁻¹.

Characteristic		Minimum	Maximum
pH		5.8	8
Salinity	dS/m	11.5	28
Organic C	%	34	83
Nitrogen	%	1.6	6.5
Phosphorus	%	1	2.8
Potassium	%	0.4	2.8
Sulphur	%	0.5	4
Calcium	%	0.5	4.4
Magnesium	%	0.4	0.9
Sodium	%	0.1	0.6

Be aware of several risk factors

Spent litter can also contain undesirable toxic trace elements, or normally beneficial trace elements at toxic concentrations. Toxic or potentially toxic trace elements that can be of interest in this regard are copper (Cu), zinc (Zn), arsenic (As) (from roxarsone), and in some cases cadmium (Cd). Limits for unrestricted use in New South Wales and Victoria for these metals are: As, 20; Cd, 1; Cu, 100; Zn, 200 mg kg⁻¹ (as reviewed by Dorahy & Dorahy, 2008). Other elements may be of concern in specific situations. Ideally, poultry producers should monitor these constituents, identify sources, and limit them accordingly to assure useability of spent litter. Where levels are exceeded, ensure applications of spent litter never raise soil concentrations above the in-soil limits. Be aware that these soil concentrations are likely to be permanent. Toxic trace metals often “chemisorb” to soils, and soils are a primary non-renewable resource.

A risk exists that food produced using spent poultry litter and sent for human consumption could be contaminated by pathogens from litter. These risks need not be significant, and a number of precautions are recommended, and described more fully in the Rural Industries Research and Development Corporation land application users guide (e.g. Wiedemann et al., 2012). Approaches can include separating litter storage and cropping areas, use of a Hazard Analysis and Critical Control Points program in handling and application, incorporation prior to planting, and instituting a minimum period between application of spent litter and the planned harvest (Wilkinson et al., 2004).

Additionally, prevent stock access to land to which spent litter has been applied to avoid stock health risks (e.g. botulism). A three-week period between application and grazing has been suggested (Wiedemann, et al., 2012).

Our pot trial work also suggests that spent litter can have a negative effect on germination of some sensitive plant species (in our case, digit grass which appears sensitive to any type of fertiliser in close proximity to the seed). This requires further investigation, and may require adaptation of practices for some species.

Application rate

Firstly, consider spent litter as a phosphorus source, not primarily a nitrogen source. While spent litter does contain nitrogen, it is insufficient to balance the phosphorus content of these materials.

Annual mineralisation of the residual nutrient in land-applied spent litter is controlled by soil and spent-litter biogeochemical characteristics. Our phosphorus trials with spent litter in pots revealed that over an 18 month period a single application of spent litter to a sandy soil resulted in 63% of the dry matter production observed for an equivalent application of inorganic phosphorus. In a red Toowoomba soil (ferrosol) pot trial, the corresponding dry matter production was 54% of that produced for the same soil treated with inorganic phosphorus. In our nitrogen pot trial, a similar pattern was evident. Spent litter application resulted in 39% of the nitrogen uptake of the conventional nitrogen fertiliser in the first 15 weeks.

While mineralisation was continuing at the finalisation of our studies, a strategy is required to ensure that spent litter and bentonite-modified spent litter can be utilised in a way that maintains the same kind of yields achieved with inorganic fertiliser – from the first application onward.

One approach is to apply spent litter (and bentonite-modified forms) to meet a yield target equivalent to that achieved via application of conventional fertiliser. Supplemental inorganic fertiliser can then be used to meet the deficit. In an example scenario a phosphorus application of 25 kg ha⁻¹ is required annually, and annual mineralisation is known to be approximately 36% (i.e. as observed for the sandy soil used for pot trials; Figure K.5). Given that about 40% of the applied phosphorus will be mineralised in the first year, it is apparent that, if applications of spent litter continue for eight years at the same rate, annual mineralisation in the soil profile will increase (Figure K.6, top panel) almost to the steady-state point. At this point supplemental inorganic phosphorus application can be eliminated (Figure K.6, bottom panel). With six monthly spent litter additions (Figure K.4), this point can probably be reached in fewer years.

To some extent a similar effect can be achieved by “pre-loading” the soil profile with a much larger initial application of spent litter ($1/\text{mineralisation} \times \text{inorganic fertiliser rate}$; e.g. $1/0.6 \times \text{inorganic fertiliser rate}$, or $1.667 \times \text{inorganic fertiliser rate}$). The disadvantage of this approach is there is a much greater risk of nutrient losses to the environment, including gaseous losses of nitrogen, and nitrogen and phosphorus losses to water resources. This is both an economic and environmental

loss. Sorbent additions to the spent litter material are a potential tool to eliminate this additional risk.

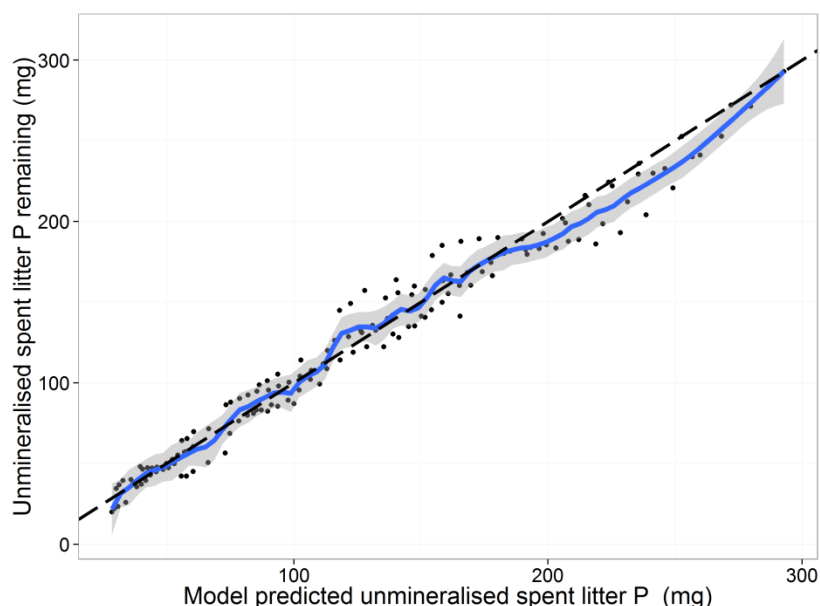


Figure K.5. Modelling of spent litter phosphorus mineralisation revealed that about 40% was mineralised in the first year, demonstrating an effective half-life of about 810 days.

The nitrogen content of the spent litter, based on our field trials, was far more quickly mineralised and available to plants than the phosphorus the material contained. Almost all of the spent litter nitrogen was available within the first year, compared to only 36% of the phosphorus content. This contrasts with the findings of other authors, where it is indicated that less than 50% of the nitrogen will be available in the first year (Table K.1).

A combination of this approach with annual soil and spent litter analysis may well produce the best results, for example:

1. Analyse the litter and soil. Get advice on an appropriate inorganic fertiliser nitrogen or phosphorus application rate.
2. Determine the quantity of spent litter required to match this rate based on the litter analysis.
3. Assume a low- to mid-range mineralisation rate. For example selecting a mineralisation fraction of 0.30 for phosphorus or nitrogen.
4. Calculate and apply appropriate supplemental conventional fertiliser additions. From Figure K.1, top panel, this corresponds to 0.7 x the target inorganic nutrient in the first year.
5. Test the soil at the beginning of the next growing season, and record productivity. Evaluate if profile stored nutrient has increased. If production targets were met, but some further nutrient is required for production, apply the same quantity of spent litter as previously but decrease the

supplemental fertiliser application (Figure K.6, bottom panel). Note that collecting soil samples at approximately the same date and soil conditions each year would be advantageous.

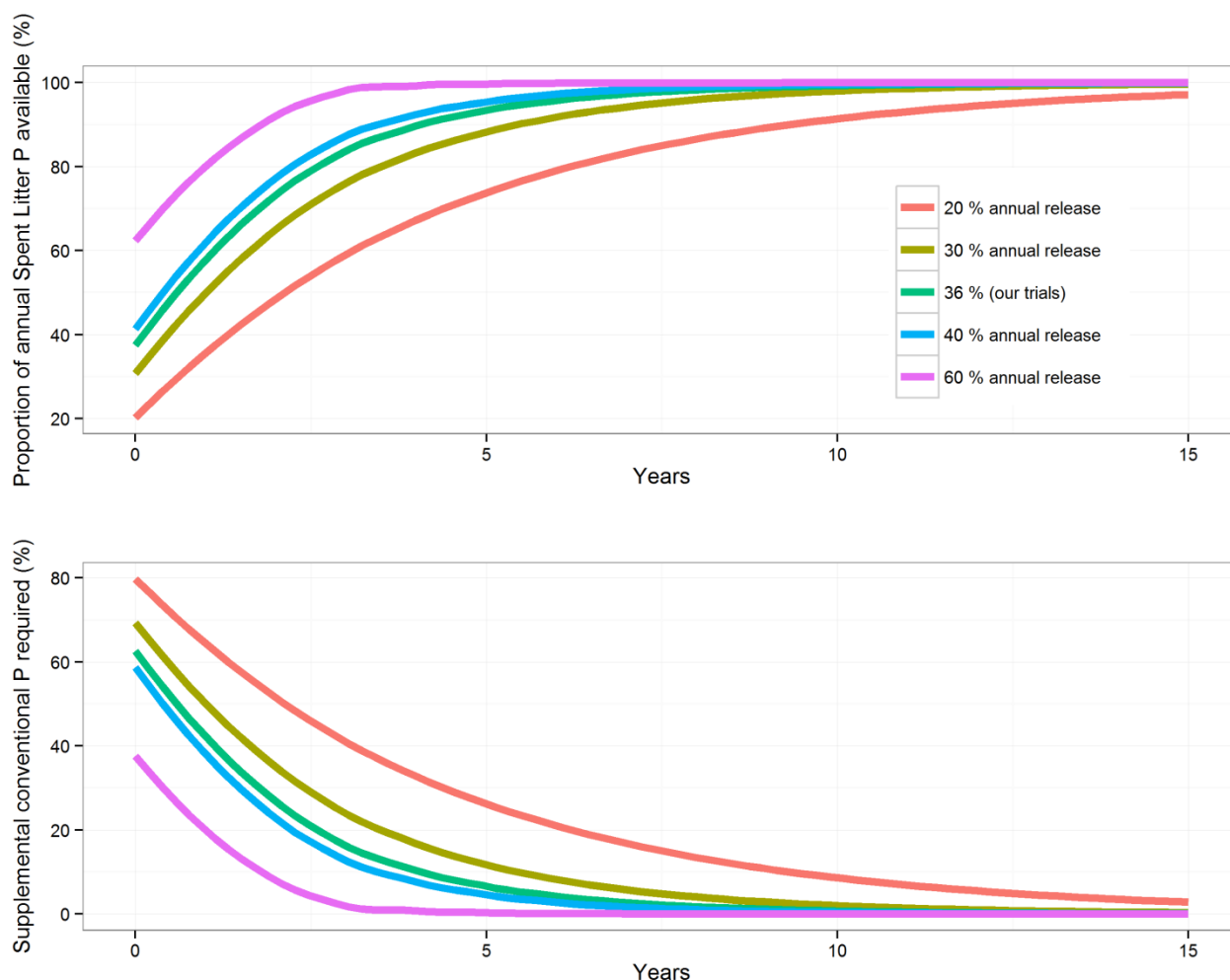


Figure K.6. Equal annual applications of spent litter would result in phosphorus release finally reaching the steady state, where annual mineralisation is equal to the spent litter input (top panel, 95% on the y-axis). One strategy is to apply gradually decreasing applications of supplemental conventional inorganic fertiliser until this steady state is approximately achieved.

How did spent litter and sorbent modified spent litter perform in our trials?

In a sandy soil, phosphorus delivery by the conventional fertiliser treatments fell behind the sorbent and spent litter treatments by about the seventh cut (28 weeks). Addition of sorbent also increased post-trial Colwell phosphorus. The nutrient availability effect of the sorbents in our sandy soil phosphorus trials may well have been too strong.

In a red clay field trial, **phosphorus uptake from spent litter treatments performed similarly to (or better than) conventional fertiliser treatments**. These sources were also **equivalent in terms of nitrogen uptake**. With sorbent treatment, dry matter production, phosphorus uptake, and

nitrogen uptake matched those of conventional fertiliser treatments and increased residual mineral-nitrogen in the soil at trial completion. The rates applied were also sufficient to decrease leaching and run-off losses of phosphorus, based on rainfall simulation and leaching trials.

Conclusions and future work

While discussions in published literature suggest that it may be possible to deliver greater productivity with spent litter nutrient sources and other manures than is possible via conventional fertilisers, specific advice on how to achieve these advantages has not been provided. However, mineralisation profile data (Figure K.3) suggests that substantial advantages could be achieved via the use of sorbent-treated spent litter, if multi-year, responsive management is applied.

It is also immediately practical to achieve productivity comparable to that achieved with conventional non-manure fertilisers with spent litter contributing a major proportion of the nutrients required. Spent litter contains not one, but a range of nutrients. The key to unlocking this value lies in determining the target nutrient contents in the spent litter source, monitoring and managing the soil profile, and selecting applications of this material and supplemental fertilisers to prevent nutrient deficits.

Given that only a proportion of the total nutrient value of spent litter will be available within the first year, a multi-year approach to increase the soil's nutrient mineralisation rate is recommended.

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