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Smart sorbers – value adding spent litter fertiliser. A pilot trial

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Executive Summary

What the report is about

This report summarises a short-term project to provide proof-of-concept that two litter amendments, hydrotalcite and bentonite, prevent nutrient losses from spent litter to the environment but retain these nutrients in plant available forms. The report describes the methods used, findings, and provides specific recommendation for future research.

Who is the report targeted at?

Since this is a proof-of-concept project detailing the early stage development of a fertiliser product, this report is currently directed at CRC staff and industry representatives.

Background

Spent poultry litter is a valuable nutrient resource, but is not currently utilized to its full potential. Enduse 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 fertilizer may result in environmental damage due to nutrient leaching or run-off. Spent litter, like any organic material, releases nutrients to the surrounding plants as it decays, at a rate that may not match plant requirements. In addition, the material is not a balanced fertiliser.

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, and
- to decrease the risk of losses to the environment.

Hydrotalcite and bentonite are two new technologies that have emerged as candidates for improving the properties of spent poultry litter. Hydrotalcite is a 'smart sorber', a synthetic clay able to reversibly bind phosphate. Bentonite is naturally occurring clay, a common waste product of the coal industry, reversibly binds ammonium.

Previous research has loaded hydrotalcite and bentonite with nutrients and investigated plant access to nutrients from these materials. The combination of hydrotalcite and bentonite "mop up" excessive soluble nitrogen and phosphorus, yet release it again as plants require it. It is believed that previous findings about these two technologies can be applied to spent poultry litter. In comparison, the nutrient use efficiency of conventional fertiliser products (e.g. urea or superphosphate) is very poor (40 to 60% of applied nutrient is taken up by plants). According to published research the bentonite/hydrotalcite formulation is likely to greatly improve nutrient use efficiency.

Objectives

This project addresses three needs associated with poultry bedding materials:

- 1. maximising returns on spent litter as a fertiliser product;
- 2. decreasing atmospheric ammonia concentrations in-shed; and
- 3. enabling efficient nutrient use from spent poultry litter, with minimal environmental losses.

Trials undertaken in this project were designed to investigate the potential benefits of hydrotalcite and bentonite.

• Hydrotalcite was investigated as a spent litter additive to increase the fertiliser value of the litter by decreasing the potential for phosphorus losses to the environment; and ensuring continued phosphorus availability to pastures and crops.

• Bentonite was investigated as a spent litter additive to increase the fertiliser effectiveness of the nitrogen contained in spent poultry litter; and a bedding material to decrease in-housing atmospheric ammonia concentrations.

Methods

Spent litter, bentonite, and hydrotalcite were characterised in the laboratory then investigated in two laboratory trials:

- 1. An incubation trial of the bentonite mixed at six rates with spent litter to investigate the form of retention of mineral-nitrogen.
- 2. A column leaching trial of spent litter treated with bentonite (fixed rate) and hydrotalcite (at seven rates) to determine the effect of these materials on phosphorus retention.
- 3. A rainfall simulation trial of spent litter treated with variable rates of bentonite, hydrotalcite, and alum (6 rates of each) to compare the effects of these materials on phosphorus retention under realistic run-off generating conditions.
- 4. A head-space volatilisation trial to directly measure the effect of bentonite and alum treatment on ammonia volatilisation.

Results and conclusions

The combination of hydrotalcite and bentonite additions to spent poultry litter increased the fertilizer value of the spent litter material, and prevented losses of valuable nutrients.

It was found that bentonite used in-shed as a bedding material may help maintain air quality by decreasing ammonia volatilisation.

Hydrotalcite additions retained phosphorus in spent litter even under extreme leaching conditions, yet the phosphorus remained in a plant available form. The fertiliser produced through a combination of bentonite and hydrotalcite additions to spent litter was comparable to some of the market's highest value precision fertilisers. In contrast, alum treatment has previously been shown to decrease the fertiliser value of litter by making valuable phosphorus unavailable to plants.

Hydrotalcite additions equivalent to 10% of the mass of dried litter resulted in phosphorus losses being almost eliminated under rainfall simulation (rainfall intensity 56 mm hour⁻¹) and out-performed alum applications of 2.2 to 11% of the dry litter mass. The retention by hydrotalcite has proven to be in the exchangeable form, and other researchers have shown that this exchangeable phosphorus is plant available. Phosphorus retained by alum, however, is not in forms readily accessed by plants.

Bentonite additions to conventional spent litter also led to a substantial increase in the fertiliser value of the litter through an increase in bound ammonium-N forms (increases of 75–189% compared to untreated litter) that are likely to resist in-field losses of nitrogen. This increase in the charge-bound form of ammonium may also prevent ammonia volatilisation if bentonite is used as a bedding material or additive in-shed.

Implications for industry

The results of the trials met or exceeded the research team's expectations and suggests that with further development, the litter fertiliser formulation may compete very well on the current domestic/household fertiliser market. Rising fertiliser costs and proof of the formulation's high plant nutrient use efficiency will further close the gap between the product's cost (approximate manufacturing+materials costs of around \$561 tonne⁻¹) and its comparative bulk nutrient value for horticulture and forage production. The current crude price of the nutrient content is about \$400 tonne⁻¹, considering nitrogen, phosphorus, and potassium. If plant nutrient uptake of 90% was demonstrated then the relative bulk fertiliser value would be around \$720 tonne⁻¹.

Full development of this "smart" sorber/fertiliser technology is a potential pathway to increased value and demand for spent litter, which is currently seen as a waste product. Additionally, sorber additions

will support ongoing sustainable industry expansion by decreasing nutrient losses to the environment when spent litter is land applied as a fertiliser.

Recommendations for the industry representatives and the Poultry CRC

The results of this proof of concept trial were very encouraging, but the technology needs further development in order to contribute to an improved ability of the industry to expand. These needs include:

- 1. Quantification of the nutrient use efficiency benefits of the fertiliser formulation through laboratory, greenhouse, and field trials.
- 2. Development of final fertiliser formulations for the target markets.
- 3. Full evaluation of the potential benefits of the application of bentonite as a bedding material (laboratory and pilot scale shed trials).
- 4. Evaluation of the greenhouse gas emission benefits of the spent poultry litter formulation relative to inorganic fertilisers (which tend to cause emissions). Life cycle analysis has a clear role in this area.
- 5. Characterisation of the carbon sequestration behaviour of the fertiliser carbon content, and the potential for soil improvement due to the clay content of the fertiliser formulations.
- 6. Development of management techniques to integrate the fertiliser formulations into agricultural management.
- 7. Evaluation of the economics of the range of target uses.
- 8. Participatory research trials with the fertiliser's potential end users and poultry farmers to ensure the technology is practical and provide technology transfer.

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Introduction

Global population is set to increase by one third before 2050 (United Nations figures). 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 fertilizers that, unlike soluble synthetic fertilizers, produce environmentally sustainable outcomes. Spent poultry litter products can be part of this solution.

The nutrient use efficiency of conventional fertiliser products (e.g. urea or superphosphate) is very poor. Despite decades of agricultural effort, conventional fertiliser applications result in less than 40 to 60 % plant uptake of the target nutrients (Bolland and Gilkes 1998; David and Gentry 2000; Galloway and Cowling 2002; Van der Molen et al. 1998: as reviewed by Drinkwater and Snapp 2007). 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 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. Such oversupply increases the potential for environmental contamination of waterways through run-off. 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 GHG emissions, and exacerbating the nitrogen to phosphorus imbalance.

However, we propose that poultry litter is a nutrient source with potential to deliver significant agricultural benefits beyond those provided by conventional inorganic fertilisers. This project is a first step in improving the ability to reduce environmental contamination and to more fully realise the full fertiliser and soil amendment value of spent litter. The project aimed to establish some of the initial proof-of-concept for the possibility of on-demand supply of nutrients to plants, achieved whilst minimising nutrient losses.

An additional advantage of this approach is the very low embodied greenhouse gas emissions of a nitrogen and phosphorus fertiliser prepared from waste products and used close to its source. This contrasts dramatically with conventional fertilisers like urea-nitrogen, every kilogram of which requires the equivalent of 3 to 3.5 kg of carbon dioxide to manufacture and distribute (pers. comm. Dr Stewart Ledgard, AgResearch NZ).

The value of the phosphorus and nitrogen content of this fertiliser source is set to rise as other costs rise – as evidenced by price spikes over the past few years. Supplies of rock-phosphate are finite (Cordell *et al.* 2009), and increasingly contain cadmium, a very persistent regulated contaminant in soil.

Whilst the natural tendency of applied spent litter is to steadily release nutrients over time, the rate of supply of these nutrients from spent litter has never been matched to the growth requirements of crops and pastures. Yet the potential of spent litter as a tailored/slow release fertiliser is high.

Tailoring the concentration of nutrients in plant available water in soils, and the replenishment of these nutrient ions to solution, is the key to controlling nutrient losses and plant availability. Realistically priced ion exchangers are potentially viable tools in this role (Gillman and Noble 2005), and a suite of such materials are available. These materials tend to maintain solution concentrations and respond to plant uptake by steadily replenishing soil solution from an exchange pool. Solution concentrations are never high enough to result in substantial nutrient losses.

A range of litter additives have been studied for use in-shed (e.g. alum, zeolite, and sodium bisulphite) to decrease the volatilisation of ammonia into the shed atmosphere — where it can have health repercussions for staff or birds (Li *et al.* 2008). Several additives (alum, liquid alum, ferric sulphate) also decrease the vulnerability of litter-phosphorus to loss via run-off or leaching when the litter is land applied as a fertiliser (Li *et al.* 2008; Warren *et al.* 2008), but also tend to decrease the fertiliser value of the spent litter (as discussed below).

We have completed initial testing of a combination of bentonite and hydrotalcite (a clay, rare in natural occurrence, but readily manufactured from recycled materials and previously reported in Gillman and Noble 2005). This combination is theoretically capable of retaining ammonium, nitrate, and phosphate in plant available forms:

- Bentonite will retain ammonium cations in exchangeable forms (forms that are reversibly attached to surface negative charge).
- Hydrotalcite has a very large capacity to preferentially retain phosphate in plant available forms, and a lesser preference (but large capacity) for nitrate. This sorption is reversible and exchangeable, with these negatively charged ions being retained in clay interlayer sites.

This combination of functionality differs considerably from that offered by previously published formulations for poultry litter. Most significantly, other tested amendments tend to retain phosphorus in non-plant available forms. Alum is believed to retain phosphorus through a combination of several mechanisms:

- Alum additions to litter form amorphous aluminium hydroxide (Al(OH)₃) which adsorbs inorganic P (Hunger *et al.* 2004; Peak *et al.* 2002).
- Phosphorus may be retained as poorly formed wavellite (Hunger *et al.* 2004; wavellite is an aluminium phosphate mineral).
- Alum addition inhibits organic P mineralisation during storage, retaining much of it in the phytate form (Warren *et al.* 2008).

Likewise, ferric sulphate retains phosphorus through the formation of chemical bonds (chemisorption) in sesquioxide complexes or possibly through precipitation (though the latter may be less important as it has been found for P-fixation by Aluminium, Peak *et al.* 2002; Zvomuya *et al.* 2006).

Not only are these phosphorus forms highly insoluble, but they are also largely unavailable to pastures, crops, and other plants. The fertiliser value of the product has therefore been degraded.

Bentonite exchangeably retains ammonium, in a similar manner to zeolite. This mechanism is also likely to retain ammonium after application to land, where it may be exposed to leaching and runoff water. Bentonite has the added advantage of being capable of mopping up moisture; up to several multiples of its own mass. Alum and ferric sulphate treatments retain ammonium dominantly by lowering the pH and decreasing the tendency for ammonia volatilisation. This mechanism will not prevent dissolution and loss in water once the acidified litter is land applied.

If the proposed benefits of bentonite are supported by experimentation, it may be possible to use bentonite as a replacement bedding material rather than merely a post-shed litter additive. This is dependent on economics and operational considerations.

The combination of bentonite and hydrotalcite in fertiliser formulations has previously been published in the literature, using piggery pond sludge as a nutrient source (Gillman and Noble 2005; Gillman 2006). The use of hydrotalcite with poultry manure was also proposed (Gillman 2006). This technology is therefore in the public domain and available for exploration on behalf of the poultry industry.

The projected fertilizer product will be very beneficial as a soil amendment when added to lighttextured soils, because each application will result in an increase in clay content, giving the soil increasing capacity to retain nutrients and water.

The ultimate targets of this research are: value added spent litter products that are more appealing to the agricultural and home fertiliser markets; greater returns to poultry producers; decreased potential for nutrient losses to water resources and decreased GHG emissions.

Therefore, this study sought to explore several hypotheses that have not previously been addressed in the literature:

- Bentonite additions to litter under likely shed conditions results in a high proportion of mineral N being retained in exchangeable form, and less volatilisation than from untreated litter.
- Hydrotalcite addition to litter stabilises P against leaching and runoff losses but maintains this storage in an exchangeable form.
- The retention of P and N via bentonite+hydrotalcite treatment to minimise runoff, leaching, and volatilisation is superior or equivalent to that achievable through the use of alum treatment.

Objectives

This pilot trial sought to establish initial proof-of-concept that cation and anion sorber additions to spent litter can:

- Prevent losses via volatilisation or transport to water resources, and yet allow steady ongoing nutrient release.
- Exceed the performance of conventional approaches to volatilisation and P oversupply such as the use of alum or lime.

This work will enable value adding solutions that meet the CRC II commitments to:

- "Increase the productivity of crops grown with fertiliser derived from poultry production";
- "Increase the nutrient value of litter and manure for downstream resource management";
- "Improve the use of poultry litter on crops...[adding] to its value, creating additional income for poultry producers"; and
- "Enhance carbon sequestration in soil through efficient nutrient cycling".

Methods

Materials

Litter was obtained from a meat chicken production unit in south-east Queensland, 25 days into the production cycle. Hardwood shavings to a depth of 50 mm had been introduced to the shed at the commencement of the production cycle as a part of routine management. Forty kilograms of litter was collected from the shed. This bulked litter sample was representative of the full depth of litter, and was collected from below drinkers, around feeders, and from the space between (Figure 1). The litter was immediately transported to a cold room, mixed thoroughly, and stored at 4°C until used.

Sodium bentonite was obtained from the Ebeneezer Coal Mine located at Ipswich, Queensland. It was industrial grade material containing traces of coal (< 1%). It was ground and sieved to 0.5 to 2 mm diameter for use in the studies (Figure 2). The bentonite was characterised *via* X-ray diffraction and spectrographic analysis.



Figure 1. The poultry shed immediately prior to litter collection.



Figure 2. Bentonite was ground and sieved to between 0.5 to 2 mm (left). An example of the pelletised litter fertiliser with bentonite and hydrotalcite is on the right. All experimentation was conducted with 0.5 to 2mm pellets.

Technical-grade hydrotalcite was obtained as described in Gillman and Noble (2005) and Gillman and Noble (2006) from a colleague's completed research project. The material was characterised *via* X-ray diffraction and spectrographic analysis.

Analytical reagent grade alum (Al₂(SO4)₃.18H₂O) was used wherever alum is specified in the following methods.

Litter and bentonite were both subjected to analysis for: pH (1:5 ratio of sample to water Rayment and Higginson 1992), total-nitrogen (Kjeldahl nitrogen, method 7A1 Rayment and Higginson 1992), total-phosphorus (Crosland *et al.* 1995), Colwell-phosphorus (bicarbonate extractable phosphorus, method 9B2 Rayment and Higginson 1992), total-potassium, soluble and exchangeable bases, and cation exchange capacity (aqueous ethanol for soluble cations, ammonium chloride extract for exchangeable ions of potassium, magnessium, sodium, calcium, method 15C1, Rayment and Higginson 1992), total carbon (high frequency induction furnace, method 6B2 Rayment and Higginson 1992), and organic carbon (Walkley and Black 1934).

The hydrotalcite's sorption characteristics were determined via batch sorption according to Rayment and Higginson (1992; method 9J1), however pure aqueous solutions of potassium dihydrogen orthophosphate were used (0,1.5, 3, 6, 12, 17, 22 μ g phosphorus ml⁻¹) at a solution to sorber ratio of 4150:1.

Extracts of litter and the sorber formulations for subsequent water soluble ammonia and nitrate analysis were collected by three sequential 1:9 sample to water extracts on the same sample. Two samples of each treatment (3 g oven dry equivalent) were weighed into two 50 ml centrifuge tubes, and 27 ml of deionised water dispensed into each tube. The samples were shaken for 5 minutes, end over end, then centrifuged for 30 minutes. The two supernatants were decanted into a single 250 ml volumetric flask, and the extraction process repeated. Following three such successive extractions of the same two samples, the total volume of liquid in the volumetric flask was made to 250 ml with deionised water.

Extracts with 2 M potassium chloride were collected in an essentially similar fashion, though an initial 1 hour shaking period was conducted with the first extraction cycle.

Several analytical techniques were applied through out the studies described. Ammonia and nitrate+nitrite analysis was conducted via steam distillation using magnesium oxide and Devarda's alloy (Mulvaney 1996). Molybdate reactive phosphorus (MRP; these include phosphates, orthophosphate, and readily acid-hydrolysable phosphorus forms) was determined via the ascorbic acid colorimetric technique (Murphy and Riley 1962). Oven dry moisture contents of bentonite were performed at 105°C for 18 hours, while spent litter moisture determinations were conducted at a lower temperature (70°C) to prevent organic matter loss.

A persulfate digest technique (Koroleff 1983) was also applied to selected eluent and runoff samples. Persulfate digestion does not break down phytate compounds (Benson *et al.* 1996), but will transform less recalcitrant non-molybdate reactive phosphorus forms into phosphorus forms detectable by that technique. The digested solutions were adjusted to pH 5.0 with 0.01 N hydrochloric acid, and molybdate reactive phosphorus determined.

Except where explicitly stated otherwise, all water used in these trials was purified to >18 M Ω .cm (using a MilliQ Academic reverse osmosis unit), and contained sub-detection limit concentrations of ammonium-N (< 1.1µg ml⁻¹), nitrate+nitrite-N (< 1.1µg ml⁻¹), and molybdate reactive phosphorus (<0.02 µg ml⁻¹).

Experiment 1: Ammonium retention through bentonite treatment

This experiment sought to establish if bentonite additions to litter under likely shed conditions could adsorb a high proportion of the litter's mineral N in exchangeable form. Experimental conditions sought to duplicate the worst-case scenario for ammonium generation in the shed: the conditions that may occur in the litter beneath a leaky drinker. These conditions were simulated *via* laboratory incubation and analysis.

Samples of spent litter (135 g oven dry equivalent) were treated with varied rates of sodium bentonite (0, 43, 86, 171, and 214 g oven dry equivalent). Five replicate treated samples were prepared at each rate.

The samples and treatments were thoroughly mixed, wet to saturation water content, and incubated at 25°C in open, wide-mouth, 1 L polyethylene bottles. Five and 10 days following the commencement of incubation the samples were re-wet to the initial moisture content. After a total period of 14 days, water and 2 M potassium chloride extracts of the incubated samples were collected and analysed for ammonium and nitrate+nitrite (as described in the previous analytical methods section).

Experiment 2: Peristaltic leaching of P from hydrotalcite treatments

This column leaching trial sought to establish if hydrotalcite additions to litter (at seven rates) were capable of preventing leaching losses of phosphorus from spent litter material.

The five replicates of the 171 g bentonite treatment from experiment 1 were combined, re-saturated with water, and thoroughly mixed. Seven sub-samples (100g wet weight; each contained 13.7 g of oven dry equivalent spent litter and 17.3 g of oven dry equivalent bentonite) were transferred to 150 ml polystyrene, wide-mouth bottles, and treated with different rates of hydrotalcite (0, 5, 10, 20,

30, 40, and 50% of the oven dry equivalent litter mass). These samples were tightly capped and incubated for 9 days at 25°C. The bottles were weighed on a daily basis to ensure a constant moisture content was maintained (minor water additions were necessary), and gas pressure build-up relieved.

The samples were then pressed through a kitchen, hand-held noodle-making device, and oven dried at 70°C. These dry "noodles" were then crushed with the minimum force required to cause them to pass through a 2 mm mesh sieve. The small quantity of material capable of passing through a 0.5 mm sieve was discarded (80% of the material was retained).

A sub-sample of 17.8 g of each sample was mixed with a volume of polyethylene beads equivalent to three times that of the pelletised litter sub-sample (66.8 g). Individual leaching columns (glass, 25 ml internal diameter) were prepared by (figure 3):

- 1. Pressing a plug of washed glass wool into their base;
- 2. Packing the columns with a prepared pelletised litter/polyethylene bead sub-sample;
- 3. Inserting a second plug of washed glass wool; and
- 4. Installing the column end-cap.

The pore volume of each packed column was determined by metering water into the columns with a peristaltic pump until the litter and polyethylene beads were saturated. The average pore volume of all columns was used in the subsequent leaching events.

A total of 33 pore volumes of deionised water were leached through the columns with a multi-channel peristaltic pump at a flow rate of 0.7 ml minute⁻¹, over a total period of 11 days. Two leaching events were conducted daily (Figure 4):

- A volume of deionised water equivalent to 1.5 pore volumes was pumped into the columns from the column base (pumping into the base helps fill column voids). Eluent exiting the upper outlet of the column was collected.
- The columns were then inverted, and air was pumped with the peristaltic pump into the columns (through the same inlet as the water was injected) until the volume of eluent collected in this step and the previous step totalled 1.5 pore volumes. Air injection minimises the development of anaerobic conditions.
- Samples were passed through a membrane filter ($<0.45 \mu m$ pore diameter) within 24 hours.
- All filtered samples were analysed for molybdate reactive phosphorus within 48 hours.

A persulfate digest technique (Koroleff 1983) was also applied to the filtered samples from the first three pore volumes.



Figure 3. Columns prepared for the leaching trial. Note the 3:1 volume ratio of polyethylene beads to pelletised litter treatments. The admixture of beads prevents blockage and allows effective daily drainage to prevent development of anaerobic conditions.

One further leaching step was conducted to establish the exchangeability of the phosphorus retained by the hydrotalcite. Two days after the final water leaching, 1.5 pore volumes of 0.1 M sodium carbonate was pumped into the base of each column, and the solution eluent collected from the upper outlet of the column. The lower outlet of the column was then plugged, and the columns were allowed to stand overnight. Additional 0.1 M sodium carbonate was pumped into each column until a total of 3 pore volumes of eluent was collected from each column. These samples were then filtered (<0.45 μ m pore diameter membrane filter), and analysed for molybdate reactive phosphorus. This carbonate leaching process was subsequently repeated with 1 M sodium carbonate.



Figure 4. Leaching in-progress using a multi-channel peristaltic pump.

The equations fitted to the cumulative leaching data were:

$$loss = Asymptote a \times b^{Vol}$$
, Equation 1

where *loss* represents the leaching loss of phosphorus (μg), *Vol* is the volume eluted through the column (pore volumes); *Asymptote*, *a*, and, *b* are fitted parameters. Alternatively, a similar linear plus exponential equation was fitted:

$$loss = Asymptote a \times b^{Vol} + c \times Vol,$$
 Equation 2

where c is an additional linear fitted parameter.

The relationship between cumulative leached phosphorus and hydrotalcite rate was characterised with the logistic equation:

$$loss = L + \frac{C}{(1 + e^{b(R-M)})},$$
 Equation 3

Where *loss* represents the leaching loss of phosphorus (μ g), *R* is the rate of hydrotalcite treatment (a proportion); *L* (the lower limit to leaching losses), *C*, *b*, and *M* are fitted parameters.

Experiment 3: Flume rainfall simulation and runoff nutrient trial

A matrix of litter treatments, including alum, bentonite, and hydrotalcite were prepared and incubated for three weeks under saturated conditions at 25° C in a tightly sealed polyethylene bottle (Table 1). These treatments can be summarised as follows:

- Untreated, water saturated litter.
- A range of hydrotalcite treatment rates with a fixed rate of bentonite addition.
- A range of bentonite treatment rates with a fixed rate of hydrotalcite addition.
- A range of alum $(Al_2(SO4)_3.18H_2O)$ treatment rates.

Each of these treatments was extruded through a hole in the corner of a plastic bag, directly onto the treatment plots immediately before rainfall simulation.

A rainfall simulator built to published specifications (Humphry *et al.* 2002; Figure 5) was stationed over a flume (as described in Redding *et al.* 2008). For each treatment, a section of cut, homogenous kikuyu turf (0.400 m by 2.1 m, 0.04 mm deep) was spread out in a tray constructed to match these dimensions, and placed on the flume assembly, sloping towards the collection flume at 2.5°. The turf was wet with 8 litres of water.

The treatment was then applied to the turf, leaving an untreated 0.30 mm buffer immediately up-slope of the collection flume:

- The upper 1.8m length of turf was divided into quarters with string lines.
- The litter treatment was divided into 4 equal portions.
- A quarter of the treatment was applied separately to each quarter of the turf area. The application pattern was a series of tight zig-zags overlain at 90° to each other. This ensured homogenous application.

Rainfall simulation was conducted at a nozzle pressure of 28 KPa (the design pressure required to deliver an intensity of 70 mm h^{-1}) and a duration of 20 minutes. The apparatus used allowed evaluation of two turf sections and their treatments simultaneously.

A composite sample of the water exiting the flume of each treatment was automatically collected (Global Water, WS750 water sampler) at the commencement of flow and every subsequent 5 minutes (100 ml aliquot composited for each 5 minute collection event). Irrigating water was sampled in a catch pot during each simulation run.

Each sample collected was analysed for molybdate reactive phosphorus (after passing the sample through a membrane filter, $<0.45~\mu m$).

Treatment	Alum	Bentonite	Hydrotalcite
	g	g oven dry equivalent	g oven dry equivalent
Litter 1	0	0	0
Litter 2	0	0	0
Litter 3	0	0	0
Litter 4	0	0	0
Hydrotalcite/bentonite 0	0	633	0
Hydrotalcite/bentonite 1	0	633	50
Hydrotalcite/bentonite 2	0	633	100
Hydrotalcite/bentonite 3	0	633	150
Hydrotalcite/bentonite 4	0	633	200
Hydrotalcite/bentonite 5	0	633	250
Bentonite 0	0	0	150
Bentonite 1	0	158	150
Bentonite 2	0	316	150
Bentonite 3	0	474	150

Table 1. The matrix of 0.5 kg litter treatments incubated for the rainfall/runoff simulation. The treatments were extruded directly onto the treatment plots.

Bentonite 4	0	633	150
Bentonite 5	0	791	150
Alum 0	0	0	0
Alum 1	11	0	0
Alum 2	22	0	0
Alum 3	33	0	0
Alum 4	44	0	0
Alum 5	55	0	0



Figure 5. Rainfall simulator assembled over a the dual flume apparatus.

Experiment 4: Head-space ammonia volatilisation trial

This experiment sought to investigate the effect of bentonite treatment on ammonia volatilisation and compare these results to treatment with alum. Three treatments were prepared including: a control, a bentonite treatment (127 g of bentonite [100 g spent litter]⁻¹, representing the use of bentonite as a bedding material), and a moderate alum treatment (6.6 g of bentonite [100 g spent litter]⁻¹) selected from literature (Choi and Moore 2008; Warren *et al.* 2008). Each field moist litter sample (200 g oven dry equivalent) was mixed thoroughly with the treatment, wet to saturation, and stored in a polyethylene bottle.

Sub-samples of each treatment (equivalent to 37.5 g of oven dry litter) were transferred to 200 ml Erlenmeyer flasks. Each flask was fitted with a bung, with two glass tubes allowing air-flow through the head-space above the litter treatments. Nitrogen was pumped through the headspace (0.7 ml minute⁻¹) using a peristaltic pump, conducted via teflon tubing to first one, then a second glass impinger, then exhausted to the air (figure 6). The impingers were each filled with 50 ml of 0.25 N sulphuric acid.

These headspace assemblies were incubated at 22°C for a period of three weeks. Every 2 to 3 days the impinger fluid was replaced with fresh 0.25 N sulphuric acid, and the spent impinger fluid analysed for dissolved ammonia via steam distillation.

The trial was conducted as a blocked design — a single flask of each treatment plus one blank (empty) flask was tested at a time, and the process replicated four times for a total trial length of 12 weeks.

Total ammonia volatilisation from a replicate was calculated as the sum of ammonia captured in each impinger.

Table 2.	Treatment matrix for the ammonia volatilisation trial	l. These treatments were applied to 200g of
litter (ov	en dry equivalent).	

Treatment	Alum	Bentonite
	g	g
Untreated litter	0	0
Bentonite	0	253
Alum	13.2	0



Figure 6. The ammonia headspace apparatus in use for technique development. Two impingers, filled with 50 ml of 0.25 M sulphuric acid are connected to the ammonia source, with a constant flow of air from the source through the impingers.

Statistical techniques

Three statistical techniques were employed throughout the trial: non-linear regression was conducted using the non-linear least squares (NLS) procedure of R, one-way analysis of variance (ANOVA and LM procedures), and paired T-tests (R Core Team 2006).

Ammonium retention through bentonite treatment

Under the worst case scenario of damp litter beneath a leaky drinker, bentonite bedding (economically viable if later formulated as a profitable fertiliser) could adsorb a large proportion of the litter's ammonium, helping to prevent volatilisation. Bentonite additions also probably led to a substantial increase in the fertiliser value of the litter through an increase in the proportion held in a form which is likely to decrease in-field losses of nitrogen (increases from 75 to 189 % compared to untreated litter).

As collected, one third of the litter total-N (6.0 % Total-N; Table 1) was in the form of mineral-N and was dominated by ammonium.

Any soluble ammonium-N in the litter is vulnerable to loss by leaching and volatilisation (in high-pH micro-pockets). We found that about 81 % of mineral-N in the spent litter was in this vulnerable form.

As organic nitrogen continues to be mineralised, it is likely that the soluble form will continue to dominate the untreated spent-litter. Major, on-going loss of fertiliser value is likely.

Bentonite additions steadily decreased this vulnerable, soluble mineral-N percentage from about 81 % to less than 50 % (Table 1; concentrations plotted in Figure 5), the difference being the result of an increase in exchangeable N. The proportion of mineral N retained in exchangeable form rose from 19 (no bentonite) to 54 % (maximum bentonite rate; Table 1, concentrations plotted in Figure 6).

Between 28 and 81 % of the bentonite's cation exchange sites were occupied by ammonium, a value that tended to decrease as application rate increased (total cation exchange capacity was 82.6 cmol kg¹). This data suggests that there is capacity to retain further ammonium on exchange sites.

The effect of bentonite treatment on volatilisation was not directly measured in this experiment, nor was bentonite effect on nitrogen mineralisation rate determined. For this reason the interactions may be more complex than the suggested transfer of soluble ammonia to the exchangeable pool. Volatilisation effects were directly investigated in a separate experiment reported elsewhere.

Nitrate analysis indicated that there was little or no nitrate in the initial litter, or in any of the incubated treatments (nitrate-N values were uniformly below or at the detection limit concentration, less than 6% of the ammonium-N concentration). As a cation exchanger, bentonite is an ideal material to capture nitrogen where a system is dominated by ammonium, the cationic nitrogen form.



Figure 7. There was a strong relationship between exchangeable ammonium and the bentonite treatment rate, and bentonite treatment resulted in significantly more ammonia-N being exchangeably retained (p < 0.001).



Figure 8. A relationship between bentonite soluble ammonium and bentonite treatment rate was present (analysis of variance, p < 0.05, Table 1), but the regression relationship was not strong.

Bentonite Rate	So	luble Ammo	onium-N	Excha	angeable A	mmonium-N	Total A	Ammonium-N
Multiple of litter			mg a	ammonium-	N [g oven	dry litter] ⁻¹		
0.00	16.3	с	81 %	3.78	а	19 %	20.1	а
0.37	14.4	b,c	69 %	6.59	b	31 %	21.0	a
0.74	15.0	b,c	64 %	8.47	с	36 %	23.5	a
1.48	13.0	b	56 %	10.5	d	45 %	23.4	а
1.85	9.72	a	47 %	11.2	d	54 %	20.9	а

Table 3. Bentonite effects on soluble and exchangeable ammonium. Means followed by the same letter are not significantly different (p < 0.05).

Peristaltic leaching of P from hydrotalcite treatments

- 1. Hydrotalcite additions to litter prevent P leaching.
- 2. Additions equivalent to 20 and 30% of the mass of dried litter resulted in 60 and 90% decreases in the quantity of P leached from the litter.
- 3. The study and previously published literature indicate that the P retained by hydrotalcite is not permanently bound and is therefore likely to be available to plants.
- 4. In the longer term, pelletised litter without hydrotalcite released 190 μ g [day]⁻¹ [g litter]⁻¹ on an on-going basis under the experimental conditions. Hydrotalcite treatment of the litter tends to prevent this on-going leaching behaviour.

The leaching trial sought to:

- 1. Establish if hydrotalcite additions to litter were capable of retaining P against leaching processes.
- 2. Determine what rate of hydrotalcite addition is required to achieve a specified degree of P retention. Crops and pastures may or may not require an intense and immediate availability of P. This trial demonstrates how this initial soluble P can be tailored to requirements.
- 3. Demonstrate the exchangeable nature of P retained by hydrotalcite.
- 4. Measure the on-going release of P from the treated litter systems.

The study was successful in each of these aims, with strong differentiation between hydrotalcite treatments in the columns (Figure 7):

- Total cumulative P leaching losses were decreased by up to 99 % with hydrotalcite treatment;
- An 88 % decrease in leaching was achieved with a 30 % treatment with hydrotalcite (dry basis. On a wet basis, this amounts to an addition of 16% of the mass of spent litter; Figure 8);
- The ultimate potential loss to solution from the highest rate hydrotalcite treatment was estimated to be around 2% of that from the untreated pelletised litter (refer to the asymptote value, Table 2); and
- A 71% decrease in loss to solution was possible with a 20% rate of hydrotalcite (about an 11% treatment on a wet litter basis; determined by fitting asymptotic curves to the data; Table 2).

It should be noted that this predicted release is dependent on the experimental conditions and may be different in a soil system where bio-geochemical conditions differ. While the pelletised litter without

hydrotalcite displayed a pattern of on-going release (94.8 μ g [pore volume]⁻¹ [g litter]⁻¹, or 190 μ g [day]⁻¹ [g litter]⁻¹) the higher rates of hydrotalcite treatment displayed negligible on-going release to leaching (cumulative leaching was well-represented by an asymptote parallel to the x-axis; Table 2).



Figure 9. Cumulative phosphorus leached from the columns displaying clear differentiation between treatments. The quantity of phosphorus likely to be initially soluble from the litter system, and hydrotalcite treatment rate can be selected to meet requirements.

	1				
Treatment	Asymptote	a	b	c	\mathbf{R}^2
	µg P [g litter] ⁻¹				
Pelletised litter	7064±76	6789±92	$0.784 \pm .006$	94.8±2.9	100.0
Pelletised litter+5% hydrotalcite	8418±79	7684±186	0.871±0.006	-	99.3
Pelletised litter+10% hydrotalcite	6406±67	5800±123	0.887±0.006	-	99.4
Pelletised litter+20% hydrotalcite	2960±26	3315±39	0.899±0.003	-	99.8
Pelletised litter+30% hydrotalcite	1287±24	1353±19	0.932±0.003	-	99.7
Pelletised litter+40% hydrotalcite	433±14	461±11	0.936±0.005	-	99.3
Pelletised litter+50% hydrotalcite	245±112	225±110	0.987±0.008	-	98.2

Table 4. Asymptotic curves fitted to the cumulative phosphorus release data allow an estimate of the potential loss from on-going leaching (loss=Asymptote- $a*b^{Vol}+C*Vol$, where vol is the volume in pore volumes leached). Note that potential loss from the highest rate hydrotalcite treatments is around 1% of that from the untreated litter pellets.



Figure 10. This plot can be used to determine the rate of hydrotalcite to use for the experimental conditions. Since it is unlikely that the absence of soluble phosphorus would be the goal of fertiliser formulation it is likely that a hydrotalcite rate of less than 30% would be required. Total leached phosphorus is fitted with Equation 1.

It is possible to determine the hydrotalcite treatment rate required to provide a specified soluble P availability. There is a fairly smooth progression in retention with treatment rate (Figure 7), and the cumulative loss data was well characterised by the logistic equation (Figure 8):

$$\log = \frac{13705 \pm 648}{(1 + e^{(0.117 \pm 0.006)(R - [8.84 \pm 0.81])})} - 31.9 \pm 83.4, R^2 = 100.0\%$$
 Equation 4

where *loss* (μ g [g litter]⁻¹) is dependent on the treatment rate (*R*; %) and parameter estimates are followed by standard errors. Logistic curves are often associated with biological systems where the population of an organism is plotted versus time. Initially organism growth is limited by the rate of reproduction, while later resource scarcity limits further population growth. This may be an analogue to the experimental system, where sorption is initially limited by diffusion path lengths and the amount of hydrotalcite present. At higher rates of hydrotalcite, the lack of unsorbed phosphorus limits further sorption.

The treatment rates required to achieve retention are substantially less than those reported by Gillman and Noble (2006). They found that a rate of about 91 % hydrotalcite addition (as a proportion of piggery pond sludge solids) was required to decrease soluble P to comparable concentrations to those observed here for the 50 % treatment.

The efficiency of P retention in our experiments exceeded the 2.6 % level reported in Gillman and Noble (2006). Maximal P sorption as a proportion of hydrotalcite mass varied between 2.0 and 3.7 %, peaking in the 10% hydrotalcite treatment. This figure is probably controlled by diffusion rates in the litter and the interaction between kinetics and the hydrotalcite treatment rate. These factors are in turn controlled by moisture content, temperature, litter character, ionic composition, and contact time. The optimisation of each of these factors should be investigated further to ensure the most efficient fertiliser manufacturing process.

It is evident that as P continues to be released from organic molecules in the litter of the higher rate hydrotalcite treatments, the hydrotalcite will continue to "mop it up". This is suggested by the observation that P retention as a proportion of hydrotalcite mass peaked in the 10% treatment, at a

sorption rate greatly below the maximal sorption (3.7 % compared to about 6 % maximum sorption in the sorption characterisation).

A proportion of the phosphorus retained by the hydrotalcite in exchangeable forms was extracted by the 6 pore volumes of carbonate solution. Between 2 and 17 % of the phosphorus retained due to hydrotalcite treatment (despite water leaching) was extracted with the sodium carbonate leaching procedure. This is in common with other trials (Gillman and Noble, 2005), and it is likely that with a more extensive carbonate leaching most of the phosphorus would be extracted.

Nutrient retention under simulated rainfall



Figure 11. Summary of the effect of treatments on molybdate reactive phosphorus losses.

Hydrotalcite, at all rates investigated (contained in both the hydrotalcite and bentonite treatments), decreased the loss of molybdate reactive phosphorus to background concentrations (t-Test, p < 0.05). This means that where 10% or more hydrotalcite was applied, losses were equivalent to those from the unfertilised turf. The following system of logistic equations represented the alum and hydrotalcite treatments well (R²=95.6 %) and demonstrated that the two treatments were significantly different (p < 0.001):

Loss from HT treated fertiliser =
$$\frac{2.428E11}{(1 + e^{(21.97 \pm 3.31)(R + (1 \pm 1206))})} + 58.04$$
, Equation 5

Loss from Alum treated fertiliser =
$$\frac{2.863E11}{(1 + e^{(21.97 \pm 3.31)(R + (1 \pm 1206))})} + 265.0$$
, Equation 6

where R is the rate of application (kg/kg of dry litter), and all HT treatments contain a constant rate of bentonite addition (1.27 kg/kg of dry litter). The latter bentonite addition had only a small effect on phosphorus losses in runoff (Figure 11), an expected result since bentonite is not considered a strong phosphorus sorber.

The rates of alum addition used are representative of the range of rates of addition in literature. The rates of HT addition selected are clearly superior at retaining phosphorus under simulated rainfall.

Mineral nitrogen data (ammonium and nitrate) for the rainfall simulation was inconclusive. This was largely due to the experimental design being focused on measuring phosphorus losses. The incubation procedure led to greater initial ammonium attached to the charged surfaces of the bentonite (as expected from the results of experiment 1), leading to higher initial ammonium concentrations in the bentonite treatments. This tended to confound the results in terms of ammonium data.

Measured rainfall intensities were 56 ± 3 mm hour⁻¹ (mean±standard deviation).

Head-space ammonia volatilisation trial

Due to the low initial pH of the litter investigated (5.4) no detectable volatilisation (< 0.004 mg [g litter]⁻¹) occurred from any of the treatments during two weeks of anaerobic incubation. An alternative litter with a pH more representative of the industry median is currently being sourced to re-run this trial.

Economics of bentonite and hydrotalcite treatment

- The litter/bentonite/hydrotalcite formulation is likely to compete very well on the current domestic/household fertiliser market and may be a superior nutrient supplier to plants.
- Rising fertiliser costs and the probable high plant nutrient use efficiency of the litter formulation will close the gap between the litter formulation's cost (estimated manufacturing costs of around \$561 tonne⁻¹) and its comparative bulk nutrient value (current crude price, about \$400 tonne⁻¹ of product; nitrogen, phosphorus, and potassium accounted for).
- Nutrient use efficiency of conventional fertilisers is very poor (40 to 60%). Proving the advantages of the bentonite/hydrotalcite formulation is critical to obtaining the full potential monetary value of the product. For example if plant nutrient uptake of 90 % was demonstrated for a formulation then the relative bulk fertiliser value would be around \$720 tonne⁻¹.
- A full analysis of manufacturing and distribution costs is not possible with the current data and is beyond the scope of this project.

Without further trials, it is not possible to complete a full assessment of the economics of the formulation of precision nutrient supply fertiliser products from poultry litter. However, input costs on some aspects of the manufacturing process are available. Inputs included in this estimate are: the hydrotalcite, bentonite, haulage of these materials to the poultry farm (80 km at \$27.50 m⁻³ [100 km]⁻¹), drying costs (\$27.50 [tonne water]⁻¹; based on 25 % inflation of the Gillman and Noble, 2006 costs), a cost offset related to replacing wood shaving bedding (valued at \$2800 shed⁻¹ cycle⁻¹) with bentonite (\$4010 shed⁻¹ cycle⁻¹); and fortification of the product with urea to balance the N:P ratio (8:1 required, Sharpley *et al.* 2007). The output product would contain about: 8 % nitrogen, 1 % phosphorus, 1 % potassium.

Without consideration of its additional functionality, the litter product is likely to be competitive with several popular domestic garden fertilisers (Table 3). However, functionality should not be discounted, as the bentonite/hydrotalcite combination is capable of precision nutrient supply that conventional, "organic", and slow release fertilisers are not — leading to great potential for improved nutrient use efficiency.

Nutrient use efficiency of conventional fertiliser products (e.g. urea or superphosphate) is woeful. Additions of these transient nutrient forms, despite decades of management development, result in less than 40 to 60 % plant uptake of the target nutrients (Bolland and Gilkes 1998; David and Gentry 2000; Galloway and Cowling 2002; Van der Molen et al. 1998: as reviewed by Drinkwater and Snapp 2007).

Previous research with fertiliser formulations of hydrotalcite and bentonite addition suggest that higher yields can be achieved with equivalent nutrient applications (Gillman and Noble 2005). Though these previous studies did not measure nutrient use efficiency directly, it is probable that such formulations result in increases in this parameter. This is an important target for research.

Not only is improved nutrient use efficiency likely, but increasing conventional fertiliser costs (Figure 9) will continue to increase the attractiveness of our formulation. Some commentators are suggesting a dramatic increase in the cost of phosphorus to producers in the mid term: peak phosphorus production is predicted around 2030 (Cordell *et al.* 2009). Ultimately, precision nutrient supply formulations are likely to compete with conventional fertilisers on a price basis, but are already superior on an environmental basis (decreased losses to the environment).

It may also be advantageous to "fortify" a spent litter/bentonite/hydrotalcite product with other nutrients (macronutrients, micronutrients, trace elements) to form a truly balanced fertiliser product. While this will increase the cost of manufacture, it may provide disproportionate additional value in some markets. For example, other successful domestic fertiliser products supply a wide range of nutrients and trace elements at a premium cost (e.g. Osmacote). This approach would also provide returns for the range of other beneficial elements contained in spent poultry litter (for example, potassium).

Table 5. Comparison of the value for money of the modified poultry litter to conventional fertiliser and two popular household products. These values are compared with the sum of known input costs for the litter product or to retail prices for the two household fertilisers.

	Modified		Dynamic
	Litter	Osmacote	Lifter
	\$ [tonne of product] ⁻¹		
Conventional N Value	285	251	58
Conventional P Value	80	175	130
Conventional K Value	34	143	23
Total	399	569	211
Retail Price/Input Costs			
Comparison	561	15833	1667



Figure 12. Australian fertiliser prices are rising (Australian Bureau of Agricultural Resource Economics 2009).

Discussion

This trial sought to increase the fertiliser value of the litter through addition of an anion-sorber (hydrotalcite) to decrease phosphorus losses to the environment, yet ensure its continued availability to pastures and crops.

Additionally, this trial sought to determine if bentonite had potential as a:

- Litter additive to increase the fertiliser effectiveness of spent poultry litter; and
- Bedding material to decrease in-housing atmospheric ammonia concentrations.

The observations collected have all supported the potential of these materials in these roles.

Under the worst case scenario of damp litter beneath a leaky drinker, bentonite addition was found to capture a large proportion of the litter's ammonium on its charged surfaces. This will probably help prevent ammonia volatilisation.

A head-space volatilisation trial (being conducted separately) is in progress and will serve to answer the remaining questions regarding this potential. This trial will also compare effectiveness with the use of alum in a similar role.

Bentonite additions also led to a substantial increase in the fertiliser value of the litter through an increase in the proportion of nitrogen (increases of 75 to 189 % compared to untreated litter) held in a form which is likely to decrease in-field losses of nitrogen.

The combination of bentonite and hydrotalcite is not simply a competitor to alum treatment — it allows the production of a fertiliser that competes with some of the market's highest value precision fertilisers. Alum treatment of litter is capable of decreasing both ammonia volatilisation and the risk of phosphorus losses *via* run-off or leaching. However, such treatment ties up litter phosphorus in forms largely unavailable to plants.

In contrast, hydrotalcite retains phosphorus even in leaching or high intensity run-off conditions (based on evidence from Experiment 2). Additions equivalent to 10% of the mass of dried litter resulted in phosphorus losses from spent litter being decreased to negligible levels during rainfall simulations. This exceeded the performance of the range of alum treatment rates reported in literature.

The retention by hydrotalcite is in exchangeable form (reversibly bound to surface charge) and other researchers have shown that this exchangeable phosphorus is plant available (Gillman and Noble 2005).

A full analysis of manufacturing and distribution costs is not possible with the current data and is beyond the scope of this project. However, the data available suggests that the litter fertiliser formulation may compete very well on the current domestic/household fertiliser market. This product may also more precisely supply plant nutrients than conventional and even slow-release fertilisers.

At first glance, the formulation appears expensive relative to more broad-acre fertiliser products. However, conventional fertiliser costs are increasing and the bentonite/hydrotalcite formulation will probably be found to have a much higher plant nutrient use efficiency than conventional fertilisers (which are very poor: 40 to 60 % uptake of applied nitrogen and phosphorus). These likely events will tend to close the gap between the litter formulation's cost (incomplete manufacturing costs of around \$561 tonne⁻¹) and its current comparative bulk nutrient value (current crude price, about \$400).

To correctly represent the true value of the bentonite/hydrotalcite formulation, an evaluation is required of the effect of these additives on:

- Nutrient use efficiency;
- Nutrient losses to the environment; and
- The potential for ammonium retention in bentonite to decrease nitrous oxide losses. Nitrous oxide is a potent greenhouse gas, and a major contributor to agricultural emissions.

Implications

The research conducted and that previously published (Gillman and Noble 2005; Gillman 2006) indicates that a fertiliser formulation of spent litter, bentonite, and hydrotalcite may have a range of agronomic advantages. It appears likely that such a product could immediately be priced competitively for the household garden market. In addition, such formulations may well become economically competitive for horticultural and forage production applications (and later for other broad-acre uses) as the cost of nutrients rise, or as community environmental expectations become more stringent.

Such a fertiliser formulation would not be patentable. The technology for sorber/fertiliser formulations, and indeed bentonite/hydrotalcite/nutrient or organic waste formulations, has already been released to the public domain *via* a range of publications (including, but not limited to Gillman and Noble 2005; Gillman 2006). On the other hand, the technology appears unencumbered by patents held by other organisations.

Full development of this "smart" sorber/fertiliser technology will promote higher profit products manufactured from an industry waste — increasing the demand for this material. In turn, an increased demand for the industry's waste product and lower environmental losses from its application to land will facilitate continued industry expansion.

Bentonite used as a bedding material may also prove capable of decreasing in-shed atmospheric ammonia. However, this is only likely to prove economically feasible where the spent litter is then processed as a fertiliser.

The research conducted by our team and others indicates that these formulations have great promise. Further research is required to demonstrate the nutrient use efficiency advantages of these fertilisers, to determine how best to formulate and use them for real agronomic scenarios, and to overcome any contaminant issues (for example any toxic trace element content).

Widely publicising the results of such research would best meet industry goals of promoting the value of litter and enabling wider responsible use. A campaign to enable technology uptake and to make the technology more useable to industry managers will be required.

A continued work program with this technology will enable value adding solutions that meet the CRC II commitments to:

- "Increase the productivity of crops grown with fertiliser derived from poultry production";
- "Increase the nutrient value of litter and manure for downstream resource management";
- "Improve the use of poultry litter on crops...[adding] to its value, creating additional income for poultry producers"; and
- "Enhance carbon sequestration in soil through efficient nutrient cycling".

Further technologies of a more patentable nature are likely to be developed around manufacturing techniques where challenges may well be encountered.

Recommendations

Further research is required to:

- Establish the nutrient use efficiency advantages of the litter/bentonite/hydrotalcite formulation;
- Determine how to use these formulations to best agronomic advantage (e.g. to determine how much initial soluble nitrogen and phosphorus is required);
- Investigate whether bentonite can effectively be used as bedding;
- Develop manufacturing processes for the on-farm or industrial scale; and
- To extend the technologies to end users.

Since the bentonite/hydrotalcite fertiliser formulation appears public domain (and un-patentable) industry and community advantage is best served by widely publicising any proven advances in most of these research areas.

The results of this proof of concept trial met or exceeded all of the research team's expectations, but needs further work to achieve outcomes and to contribute to an improved ability of the industry to expand. We have submitted a subsequent proposal designed to achieve these outcomes (CRC II proposal "Maximising spent litter fertiliser returns through nutrient and carbon management").

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References

Australian Bureau of Agricultural Resource Economics (2009) Australian commodity statistics. (Australian Government). http://www.abare.gov.au/interactive/09acs_dec/.

Benson RL, McKelvie ID, Hart BT, Truong YB, Hamilton IC (1996) Determination of total phosphorus in waters and wastewaters by on-line UV/thermal induced digestion and flow injection analysis. *Analytica Chimica Acta* **326**, 29-39.

Bolland MDA, Gilkes RJ (1998) The chemistry and agronomic effectiveness of phosphate fertilizers. *Journal of Crop Production* **1**, 139-163.

Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* **8**, 559-568.

Choi IH, Moore PA (2008) Effect of Various Litter Amendments on Ammonia Volatilization and Nitrogen Content of Poultry Litter. *Journal of Applied Poultry Research* **17**, 454-462.

Cordell D, Drangert JO, White S (2009) The story of phosphorus: Global food security and food for thought. *Global Environmental Change-Human and Policy Dimensions* **19**, 292-305.

Crosland AR, Zhao FJ, McGrath SP, Lane PW (1995) Comparison of aqua-regia digestion with sodium-carbonate fusion for the determination of total phosphorus in soils by inductively-coupled plasma-atomic emission-spectroscopy (icp). *Communications in Soil Science and Plant Analysis* **26**, 1357-1368.

David MB, Gentry LE (2000) Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. *Journal of Environmental Quality* **29**, 494-508.

Drinkwater LE, Snapp SS (2007) Nutrients in Agroecosystems: Rethinking the Management Paradigm. *Advances in Agronomy* **92**, 163-186.

Galloway JN, Cowling EB (2002) Reactive nitrogen and the world: 200 years of change. *Ambio* **31**, 64-71.

Gillman G, Noble A (2005) Environmentally manageable fertilizers: A new approach. *Environmental Quality Management* **15**, 59-70.

Gillman GP (2006) Converting feedlot waste to fertilizer using charged clays: Environmental and economic benefits. *Environmental Quality Management* **16**, 73-80.

Humphry JB, Daniel TC, Edwards DR, Sharpley AN (2002) A portable rainfall simulator for plot-scale runoff studies. *Applied Engineering in Agriculture* **18**, 199-204.

Hunger S, Cho H, Sims JT, Sparks DL (2004) Direct speciation of phosphorus in alumamended poultry litter: Solid-state P-31 NMR investigation. *Environmental Science & Technology* **38**, 674-681. Koroleff F (1983) Simultaneous oxidation of nitrogen and phosphorus compounds by persulfate. In 'Methods of seawater analysis'. (Eds K Grasshoff, M Everhardt, K Kremling) pp. 168-169. (Verlag Chmie: Weinheimer, Germany).

Li H, Xin H, Liang Y, Burns RT (2008) Reduction of Ammonia Emissions from Stored Laying Hen Manure Through Topical Application of Zeolite, Al+ Clear, Ferix-3, or Poultry Litter Treatment. *Journal of Applied Poultry Research* **17**, 421-431.

Mulvaney RL (1996) Nitrogen-inorganic forms. In 'Methods of soil analysis'. (Eds DL Sparks, AL Page, PA Helmke, RH Loeppert, PN Soltanpour, MA Tabatabai, CT Johnston, ME Sumner) pp. 1123-1184.

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**, 31-36.

Peak D, Sims JT, Sparks DL (2002) Solid-state speciation of natural and alum-amended poultry litter using XANES spectroscopy. *Environmental Science & Technology* **36**, 4253-4261.

R Core Team (2006) R: a Language and Environment. (Gnu Software License: http://www.gnu.org/software/r/R.html).

Rayment GE, Higginson FR (1992) 'Australian Laboratory Handbook of Soil and Water Chemical Methods.' (Inkata Press: Melbourne, Australia).

Redding MR, Welten B, Kear M (2008) Enhancing the P trapping of pasture filter strips: successes and pitfalls in the use of water supply residue and polyacrylamide. *European Journal of Soil Science* **59**, 257-264.

Sharpley AN, Herron S, Daniel T (2007) Overcoming the challenges of phosphorus-based management in poultry farming. *Journal of Soil and Water Conservation* **62**, 375-389.

Van der Molen D, T., Breeuwsma A, Boers PCM (1998) Agricultural nutrient losses to surface water in the Netherlands: impact, strategies, and perspectives. *Journal of Environmental Quality* 27, 4.

Walkley A, Black I (1934) An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* **37**, 29-38.

Warren JG, Penn CJ, McGrath JM, Sistani K (2008) The impact of alum addition on organic P transformations in poultry litter and litter-amended soil. *Journal of Environmental Quality* **37**, 469-476.

Zvomuya F, Rosen CJ, Gupta SC (2006) Phosphorus Sequestration by Chemical Amendments to Reduce Leaching from Wastewater Applications. *Journal of Environmental Quality* **35**, 207-215.