UNIVERSIDADE FEDERAL DE LAVRAS

EDUARDO LOPES CANCELLIER

DEVELOPMENT OF BIOBASED COATINGS FOR CONTROLLED RELEASE FERTILIZERS AND PHOSPHORUS USE EFFICIENCY BY WHEAT

LAVRAS – MG

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Orientador

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Coorientador

LAVRAS-MG
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EDUARDO LOPES CANCELLIER

DESENVOLVIMENTO DE REVESTIMENTOS DE BASE BIOLÓGICA PARA FERTILIZANTES DE LIBERAÇÃO CONTROLADA E EFICIÊNCIA NO USO DE FÓSFORO PELO TRIGO

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APROVADA em, 22 de setembro de 2017.

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LAVRAS-MG
2017

Aos meus pais, Geraldo e Sueli pelo apoio e exemplo de vida.

DEDICO.

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GENERAL ABSTRACT

While controlled release nitrogen (N) fertilizers demonstrated to have agronomic and environmental advantages over their fully soluble alternatives, little is known about the effect of controlled release fertilizers (CRF) on phosphorus (P) use efficiency. In spite of these benefits, the use of petroleum-based non-biodegradable coatings is expensive and pollutes soil, rising the demand for new types of coating produced from inexpensive biobased materials. On new coatings research numerous samples need to be tested and methods to determine nutrient release rates from CRF usually rely on chemical analyses, which are time-consuming and/or expensive. Therefore, the goals were to (i) develop an innovative and rapid low-cost method to evaluate nutrient release from CRF using conductometry; (ii) test biobased materials as coatings to produce CRF; and (iii) to investigated the potential of controlled release P fertilizers to reduce P fixation and increase P use efficiency. To achieve that, nutrient release in water was determined by measuring the electric conductivity (EC) over time, with intervals dependent on release rates. For soluble salt fertilizers, EC can be immediately determined and converted to concentration using a calibration curve. In the case of urea, an additional step is needed to convert the EC-neutral urea into ammonium. A validation test demonstrated strong agreement with the release determined using the EC method and analytical techniques. The new method hence offers an easy way to quickly evaluate over time the release of nutrients from CRF. For the coating development, a set of biobased materials was tested as coatings to produce CRF, consisting of combinations of wood resins with lignin and biobased sources of polyols for polyurethane synthesis. The biobased source of polyols demonstrated to be suitable for production of high performance CRF. It reduced MAP and urea release rates to 208 and 34 days respectively using as little as 6% of coating on MAP and 10% on urea. To assess the performance of these fertilizers, three CRF were prepared by coating MAP, with a release time of 7, 37 and 209 days. These fertilizers were incubated in soil for 70 days and chemical analyses of P in the soil and fertilizer were carried out. Also a pot trial with wheat was carried out to assess the agronomic effectiveness, using isotopic ^{33}P tracer. A lower release rate did not decrease P fixation in the calcareous soil, but had an effect in the Oxisol for the fertilizer with 37 days release. In the pot trial, the CRF either had no effect on yield or even decreased the yield in comparison with the control uncoated-MAP, particularly for the fertilizers with the slowest release rate. However, for MAP with 37 days for release, the P uptake was higher than for the control MAP in the Oxisol, indicating that controlled release does have potential to reduce fixation by oxides and hence increase P uptake. Although reduction in fixation was observed to a limited extend, the increase in P uptake was substantial (56%). It evidences that it is possible to improve P use efficiency by controlled release MAP.

Keywords: Polymer coated fertilizers. Phosphorus. Release rate. Labile P. Polyurethane.

RESUMO GERAL

Enquanto fertilizantes nitrogenados de liberação controlada geralmente demonstram vantagens agronômicas e ambientais sobre sua alternativa solúvel, pouco sabe-se a respeito dos fertilizantes fosfatados de liberação controlada. Em contrapartida, o uso de revestimentos derivados de petróleo e não biodegradáveis é caro e polui o solo, demandando assim revestimentos produzidos de materiais biológicos de baixo custo. Na busca por novos revestimentos, numerosas amostras precisam ser testadas. Contudo, os métodos para determinação de taxa de liberação de nutrientes de fertilizantes de liberação controlada (FLC) geralmente são baseadas em análises químicas onerosas e demoradas. Desta forma, objetivou-se (i) desenvolver um método rápido e de baixo custo para avaliar a liberação de nutrientes de FLC usando condutivimetria; (ii) testar materiais biológicos para produção de FLC; e (iii) investigar o potencial de fertilizantes fosfatados de liberação controlada em reduzir fixação e aumentar a eficiência de uso de P. Para isto, a liberação de nutrientes em agua foi determinada através da leitura da condutividade elétrica (CE) no tempo. Para fertilizantes baseados em sais solúveis a CE pode ser imediatamente determinada e convertida para concentração usando uma curva de calibração. No caso da ureia, uma etapa adicional converte ureia em amônio utilizando urease. A validação demonstrou uma alta concordância entre a liberação estimada por técnicas analíticas e através da CE, demonstrando ser uma forma fácil e rápida de avaliar a liberação de nutrientes. Ademais, um conjunto de materiais de base biológica foram testados como revestimento para produção de FLC, consistindo de combinações de resinas com lignina e fontes biológicas de polióis para síntese de poliuretano. As fontes biológicas de polióis foram adequadas para a produção de FLC. Elas reduziram o tempo de liberação do MAP e da ureia para 208 e 34 dias respectivamente usando apenas 6% de revestimento no MAP e 10% na ureia. Para avaliar a performance destes fertilizantes, três FLC foram preparados revestindo-se MAP e obtendo tempos para liberação de 7, 37 e 209 dias. Estes fertilizantes foram incubados no solo por 70 dias e ao final foi feita quantificação do P no solo e fertilizante. Ademais, um experimento em vaso com trigo foi conduzido para avaliar a eficiência agronômica usando traçador isotópico. Menores taxas de liberação não reduziram a fixação do P em solo calcário, entretanto houve um pequeno efeito no Oxisol para o fertilizante com 37 dias para liberação. No experimento em vaso, os FLC não tiveram efeito sobre o crescimento de plantas ou até mesmo reduziu o crescimento em relação ao MAP controle, especialmente para o fertilizante com a menor taxa de liberação. Entretanto, para o MAP com 37 dias para liberação, a absorção de P foi maior do que para o MAP controle no Oxisol, indicando que a liberação lenta pode reduzir a fixação pelos óxidos e assim aumentar a absorção de P. Apesar da redução da fixação ser pequena, o aumento na absorção de P foi expressiva (56%). Isto evidencia uma possibilidade de se aumentar a eficiência no uso de P com MAP de liberação controlada.

Palavras-chave: Fertilizantes revestidos por polímeros. Fósforo. Taxa de liberação. Labilidade do P. Poliuretano.

SUMÁRIO

FIRST PART

1 GENERAL INTRODUCTION

Controlled release fertilizers are fertilizers that release nutrients slower than the soluble reference at a controlled rate over an extended time frame. These fertilizers are claimed to have several advantages over uncoated soluble fertilizers. Controlled release nitrogen fertilizers have been extensively studied and their effects demonstrated. They reduce cost of fertilizer application if a single application is used instead of multiple split applications. They reduce N losses through ammonia volatilization, nitrate leaching and nitrous oxide emissions. They improve synchrony between nutrient supply and plant demand, and as a result often increase agronomic efficiency or yield. Their higher price remains their major limitation for wide adoption by farmers for some crops.

In contrast with N, controlled release P fertilizers have received less attention and little research is published on coated P products. The reduced effectiveness of P fertilization with time is well known and documented. This reduction can be attributed to slow reactions of which the rate depends on soil properties. Given that P effectiveness decreases with time, a shorter time between P application and plant demand may result in less P fixation or “aging”, and hence higher bioavailability and P use efficiency by plants. For that reason I hypothesized that using controlled release P fertilizer would be a good fertilization strategy to increase P use efficiency.

In spite of the possible benefits of using controlled released fertilizers, some drawbacks are expected. The polymers used to produce coatings are majorly petroleum-based and non-biodegradable, which will accumulate in soil causing a new type of soil pollution. Since the cost remains the major limitation for commercialization of controlled release fertilizers (CRFs), the developing of cost-effective environmentally friendly coatings is a research priority. New coatings need be produced using inexpensive and renewable materials rendering a biodegradable coating.

On research seeking to produce coating with the aforementioned characteristics, a large number of samples is generated for testing, modelling release rates, testing blends with other fertilizers or checking longevity claims. The basic test for CRFs demands many measurements over long incubation times of up to one year which is time consuming, costly and not practical for routine laboratory analyses. Therefore, the development of a quick, inexpensive and accurate method to measure released nutrients to the incubation media is highly desirable.

1.1 Research questions, goals and thesis structure

This work was developed in order to answer the question (i) if controlled release of P can reduce P fixation in soil and enhance P availability. To accomplish such task the synthesis of coating with specifically designed properties and release rates were required. This is when I faced a second issue on polymer coatings: the current environmental downside of using petroleum-based raw materials for coating production and their accumulation in soil. So, for that, I needed (ii) to prospect several low cost, plentiful available renewable biobased materials for the production of coatings to control nutrient release from MAP and urea. While working on the coating development, I faced a third issue: the high cost on instrumentation and/or an intensive labor for testing the coating efficacy of experimental polymer coated samples. Hence, it was necessary to (iii) develop a simple, rapid, low-cost, but efficient and accurate method to evaluate nutrient release rates of coated fertilizers using a conductivity meter.

Therefore, the thesis started from the first research question raised on efficacy of controlled-release P. But the development occurred according to the steps necessary to answer this main goal. Therefore PAPER 1 describes the laboratorial procedure of a new method to evaluate N and P release from controlled release urea and MAP using conductometry. The paper details the conditions for sample incubation, preparation of calibration curves, electrical conductivity analysis and calculations. The method was compared to traditional analytical procedure used and possibility of bias and precision is discusses as well as assumptions and limitations of the method. In the PAPER 2, several biobased materials were tested for production of coatings for controlled release fertilizers. The experimental procedure used to produce coatings based on lignin and resin or to synthesized biobased polyurethane is explained. The samples produced had their release rates characterized using the method described on the first paper. Additional coating characterization is described and issues on the coating synthesis and materials are discussed. In the PAPER 3 the coatings were used to control release of MAP and evaluate their efficacy on reducing P fixation. For that coated MAP with three release rates were compared to uncoated MAP in soil incubation and plant growth experiments. Chemical analysis were used to track diffusion and lability of P in soil while isotopic labeling was used to track P uptake in plants. The effect of the release rates of P fixation, agronomic efficacy and implications for environment are discussed. Recommendation for further research is given. The first paper (PAPER 1) was submitted to

Journal of Applied Polymer Science, PAPER 2 will be submitted to Journal of Agricultural Food Chemistry and PAPER 3 to Soil Science Society of America Journal.

The goals of this work were to (i) develop a simple, rapid, low-cost, but efficient and accurate method to evaluate nutrient release rates of coated fertilizers using a conductivity meter; (ii) to prospect several low cost, plentiful available renewable bio-based materials for production of coatings to control nutrient release from MAP and urea; and (iii) assess if controlled release of P can reduce P fixation in soil and enhance P availability to plants.

SECOND PART – PAPERS

This paper was prepared according the guidelines for submission at the Journal of Polymers and the Environment.

PAPER 1 - RAPID AND LOW-COST METHOD FOR EVALUATION OF NUTRIENT RELEASE FROM CONTROLLED-RELEASE FERTILIZERS USING ELECTRICAL CONDUCTIVITY

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RAPID AND LOW-COST METHOD FOR EVALUATION OF NUTRIENT RELEASE FROM CONTROLLED-RELEASE FERTILIZERS USING ELECTRICAL CONDUCTIVITY

Abstract

Methods to determine nutrient release rates of coated fertilizers usually rely on chemical analyses, which often are time-consuming and/or expensive. Our goal was to develop an innovative and rapid low-cost method to evaluate nutrient release from polymer coated MAP or urea using conductometry. The release in water is determined by measuring the electric conductivity (EC) over time, with intervals dependent on release rates. In the case of soluble salt fertilizers, EC can be immediately determined and converted to a concentration using a calibration curve. In the case of urea, an additional step is needed to convert the neutral urea into ammonium. The release rates in water were assessed for a range of commercial and laboratory-coated fertilizers. A validation test demonstrated strong agreement between the nutrient release determined using analytical techniques. The EC method hence offers an easy way to quickly evaluate the time course of release of nutrients from controlled-release fertilizers.

Keywords: urease, polymer coated fertilizers, phosphorus, nitrogen, release rate.

Abbreviations used: EC, Electrical conductivity; N, Nitrogen; P, Phosphorus; CRF, controlled release fertilizers; PCF, polymer coated fertilizers; TKN, total Kjeldahl nitrogen; MAP, monoammonium phosphate.

INTRODUCTION

Increasing concerns about fertilizer use efficiency and environmental impacts of fertilizers have resulted in the development of so-called enhanced efficiency fertilizers [1]. Controlled-release fertilizers (CRF) belong to this group and are said to improve agronomic efficiency by improving synchrony between nutrient supply and plant demand, which in turn reduces losses to the environment. The current high cost of CRFs has provided motivation for the development of new coating formulations aiming to use cheaper materials and reduce environmental impacts with biodegradable polymers [2–4].

A large number of samples is generated for testing when assessing new coating formulations [5], modelling release rates [6, 7], testing blends with other fertilizers [1] or checking longevity claims [8, 9]. The basic test for CRFs demands many measurements over long incubation times [10] of up to one year [11] which is time consuming, costly and not practical for routine laboratory analyses. Therefore, the development of a quick, inexpensive and accurate method to measure released nutrients to the incubation media is highly desirable.

There is no widely accepted standardized method to measure nutrient release rates from CRF, and peer-reviewed articles published on the subject vary widely in the methods and apparatus used. The different approaches include laboratory membrane permeation cells [12], incubation in water [6], in soil [9], in the field and accelerated water incubation methods [8]. All of these methods require nutrient analysis of either the solutions obtained or the incubated granules. The measurement of nutrients is still the highest cost in the evaluation of the release rate, despite the various analytical options available. The current options for nitrogen (N) are (i) Total Kjeldahl N (TKN) [13], (ii) Dumas combustion method [9], (iii) colorimetric determination of NH_4^- or NO_3^- [6], (iv) granule weight loss [10], (v) nitrate and ammonium-specific electrodes [13] and (vi) colorimetric determination of urea in solution [12]. The cost of these techniques was compared and ranged from an average of US$0.18 for the weight loss method to US$12.00 per sample for the most expensive TKN method [13]. However, the weight loss method has the limitation that it is suitable only for polymer-coated urea and it requires incubation of multiple samples, one for each sampling time [10]. Besides its high cost, the TKN method has the inconvenience of dealing with acid digestion using H_2SO_4 at 350°C followed by neutralization with concentrated NaOH which has safety concerns. The Dumas combustion method requires the use of expensive instrumentation. The ammonium ion-specific electrode is a cheap approach and relatively simple once urea has been hydrolysed [13, 14], however, to the best of our knowledge no method has described and calibrated this type of electrode and the preparation of urease for measuring release from coated urea.

The analytical measurements for polymer-coated phosphate fertilizers must employ either (i) ICP-OES, which is also an expensive instrument with relatively complex operation or (ii) the use of a colorimetric methods, such as the molybdate blue colorimetric method [15], which are relatively labor-intensive.

Analysing the release characteristics of CRFs requires measurements at different times and large numbers of samples are generated. High costs, related to labor and/or expensive equipment, may limit the number of samples that can be analyzed. Therefore, our goal was to develop a simple, rapid, low-cost, but efficient and accurate method to evaluate nutrient release rates of coated fertilizers using a conductivity meter. Since the most common fertilizers are either soluble salts or can be hydrolysed into ammonium in the case of urea, we hypothesized that electrical conductivity (EC) measurements could be used to estimate release of nutrients into solution. Electrical conductivity meters are cheap, widely available and easy to operate instruments with a very short response time. We evaluated the use of EC measurements to assess the release of nutrients from polymer-coated monoammonium phosphate (MAP) and urea fertilizers.

EXPERIMENTAL

MAP release test

A calibration curve was prepared using 14 standards from 0 to 50 g L^{-1} of fertilizer grade monoammonium phosphate (MAP) in 10-mL vials to assess the relationship between MAP concentration and EC. For that, ground (< 250 µm) fertilizer grade MAP (The Mosaic Company, USA) was shaken for 24 h before reading the EC. The EC meter (TPS model 2100, Australia, using conductivity sensor of $k = 1.0$) was calibrated using a 0.05 mol L^{-1} KCl solution and the readings were taken at room temperature (23±2°C).

In the release test, three replicates (1.50 g) of three polymer-coated MAP fertilizers with different release rates and coating compositions were incubated in 50 mL of deionized water and kept in an incubator at 25ºC. As a control, uncoated fertilizer grade MAP was incubated under the same conditions. The polymer coated fertilizers were prepared using polyurethane-based compounds as the coating material. Briefly, polyurethane coatings were synthesized on the surface of fertilizer grade MAP by reacting different polyols with isocyanate in a coating drum and appropriately controlling coating thickness and temperature. Samples used for incubation had from 5 to 11% (in weight %) of polyurethane coating. The samples were removed from the incubator periodically (e.g. 2 h, 6 h, 1 d, 3 d, 7 d, 10 d, 14 d, 21 d…), equilibrated to room temperature, and gently hand swirled to homogenise, after which the EC was measured. The EC probe was positioned at nearly 1 cm from the bottom of the container with care not to touch fertilizer particles.

After sample dilution, the P concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Perking Elmer, Optima 7000 DV) for all calibration samples, which were used to establish the calibration curve, and for a set of incubated samples, which were used for validation. Using the calibration curve equation, sample EC values were converted into MAP concentration in solution and then expressed as a percentage of total fertilizer MAP. We also applied a correction factor using linear interpolation to normalize the uncoated MAP control mean to 100% release. This correction step accounts for temperature related variation in EC readings.

Urea release test

Unlike MAP fertilizer, urea does not dissociate into ionic forms when solubilized in water and therefore has negligible effect on solution EC. To overcome this, a urea hydrolysis step was added to the method previously described for MAP. The urea hydrolysis, which is catalyzed by urease, occurs as follows:

$$(NH_2)_2CO+2\,H_2O \xrightarrow{\text{Urease}} NH_4^+ + NH_3 + HCO_3^-$$

The production of ionic species upon hydrolysis of urea results in an increase in the EC. Most commercially available urease products are purified from Jack Bean (*Canavalia ensiformis*). Jack Bean urease activity is specified in units, with one urease unit (U) defined as the amount of urease that will release one µmol of NH_3 from urea per min under optimal conditions (pH 7.0, at 25°C, no inhibitors). However, for the conditions described here, the hydrolysis rate may be affected by self-inhibition (high NH_4^+ concentrations), a rise in pH and the presence of contaminants in the fertilizer such as metallic ions [16, 17]. Therefore, a preliminary experiment was carried out to measure the hydrolysis rate for our conditions using fertilizer grade urea (Incitec Pivot, Australia) under unbuffered conditions. Solutions were prepared using a factorial combination of three urea concentrations (2, 5 or 15 g L^{-1}) and three urease (Jack Bean urease, Sigma-Aldrich, USA) rates (1.5, 5 or 17 kU L^{-1}), resulting in urease to urea ratios ranging from 6 to 511 U $mmol^{-1}$. The EC was measured over time up to 20 h to assess the rate of hydrolysis.

For the release test, samples (3 g) of polyurethane-coated urea (PCU) were incubated in 50 mL of deionized water and kept at 25°C in an incubator. At given incubation times, the

N released from PCU was quantified by EC measurement on a diluted subsample after urea hydrolysis. For that, a 0.25-mL sample from the incubation solution was transferred into a 10-mL vial, and 0.25 mL of urease solution containing 50 U of urease together with 4.5 mL of deionized water was added. These diluted samples were kept in a horizontal shaker at 25ºC for a minimum of 1 h to attain complete hydrolysis, after which the EC was determined.

Two calibration curves were developed using fertilizer and analytical grade urea (Sigma-Aldrich, CAS Number 9002-13-5) to make sure the urease hydrolysis performance or EC readings were not affected by impurities in the fertilizer. The calibration curves were set up in 10-mL vials and were shaken for 24 h using 14 sample concentrations from 0 to 60 g L^{-1}. After this equilibration, urease was added to a diluted subsample as described above and the EC was determined after 1 h of equilibration. The same urea fertilizer was used to prepare both the calibration curve samples and the coated samples.

In order to validate the method, the hydrolysed samples were analysed for ammoniacal nitrogen (NH_4-N) in solution using the traditional colorimetric method. Ammoniacal N was determined reacting the sample with sodium salicylate and sodium nitroprusside followed by reaction with dichloroisocyanurate solution and colorimetric detection at 660 nm using an automated flow injection analyzer (Lachat QuikChem 8500 series 2) [18].

Data analysis

Parameters of a quadratic regression between EC and urea or MAP concentration from calibration curves were used to estimate the concentration of released N or P in solution. From this concentration the release was calculated using the following equation:

$$\mathrm{FR}_t = \frac{\mathrm{C}_t}{\mathrm{SL} \cdot (1-\mathrm{CR}) \cdot \mathrm{R}_t} \cdot 100 \qquad \text{Equation 1.}$$

where:

FR_t is the fertilizer release at a given time (t) of incubation in % of total fertilizer mass,

C_t is the fertilizer concentration in g L^{-1} in the incubation solution, estimated from the calibration curve, at a given time,

CR is the coating rate in g g^{-1},

SL is the solid to liquid ratio used for incubation in g L^{-1} (for our conditions is 30 and 60 g L^{-1} for coated MAP and coated urea, respectively),

R_t is the mean recovery for uncoated fertilizer control (MAP or urea) at a given time in g g^{-1}.

The factor (1-CR) is used to correct for weight of the coating of the fertilizer. The factor R_t corrects for possible drifts in EC readings that may occur due to differences in solution temperature and EC-meter conditions. For MAP, we observed values from 72 to 101% with a mean of 90%. For urea, recoveries ranged from 82 to 112% with a mean of 103.3%.

To compare the results of the EC method with those of the chemical analyses, a linear regression was fitted and the hypotheses of slope = 1 and intercept = 0 was tested using t-tests with level of significance at $p = 0.05$. All plots and statistical tests were programmed in the R environment [19].

RESULTS

MAP calibration and validation

For the calibration curve, a second order polynomial regression was fitted relating the EC to the MAP concentration (Figure 1a) which showed a significant quadratic component ($p \leq 0.001$). The calibration point of 40 g L^{-1} of MAP exceeded the maximum reading range of the EC meter, therefore limiting the maximum solid to liquid ratio to be used in the incubation to 30 g L^{-1}. The EC of analytical grade MAP was on average 28% higher than that one of the fertilizer grade for the range of concentrations used. This difference is due the presence of insoluble impurities in fertilizer grade MAP. The concentrations of MAP determined based on EC agreed well with those measured using ICP-OES (Figure 1b). Observing samples individually, the biggest difference between methods was 3.7% and a high accuracy was indicated by the R^2 of 99.6%. The slope was 0.98, not differing from the ideal value of 1 ($p > 0.05$) and the intercept was 2.26%, differing in small magnitude from zero (95% confidence interval is from 0.28 to 4.25%). These parameters demonstrate that there is very good agreement between both methods with no clear evidence of proportional or fixed bias of P release measurement using the EC method.

< Figure 1 >

FIGURE 1 Relationship between the concentration of fertilizer grade MAP and electrical conductivity (a) and correlation between release of coated MAP determined by the EC method and conventional P measurement using ICP-OES (b).

Urea calibration and validation

1.1.1 Selection of urease to urea ratio

The rate of hydrolysis increased with increasing urease to urea ratio (Fig. 2a). The data were modelled using the ratio of EC to maximum EC achieved for that urea concentration, representing the fraction of substrate hydrolyzed. For the urea solutions with 33, 83 and 250 mmol L^{-1}, the maximum EC values were 3.8, 8.3 and 18.4 mS cm^{-1}, respectively. The increase in the fraction hydrolyzed over time could be well described with a first order kinetics model ($y = 1 - e^{(-kt)}$). The rate constant parameter (k) was fitted for each of the nine solutions, and showed a strong positive relationship with the urease to urea ratio (Fig 2b, $k = 0.00306x^{1.326}$). To reach near-full hydrolysis within 1 h, the rate constant k should be at least 3 h^{-1}, or the urease to urea ratio at least 180 U $mmol^{-1}$. Hence, in the release measurements, 50 U of urease was added to the subsample which contains at most (after full release) 15 mg or 0.25 mmol urea, resulting in a minimal urease to urea ratio of 200 U mmol^{-1}. This guarantees that no less than 97% of the urea will be hydrolyzed in the worst case scenario, which is after urea has been fully released.

< Figure 2 >

FIGURE 2 Ratio of electrical conductivity relative to maximal electrical conductivity (EC) after full hydrolysis of urea as a function of time for different ratios of urease units to urea concentrations, ranging from 6 to 510 U mmol^{-1} urea (a) and the hydrolysis rate parameter per urease urea ratio (b). In plot (a), the dashed red line represents the chosen urea to urease ratio. Another measurement of solution EC was taken at 20 h, which was used for modelling but omitted from plot a.

1.1.2 Validation of nitrogen release by the urease-EC method

The relationship between EC and urea concentration in the diluted sample after hydrolysis fitted a quadratic model well (Fig. 3a). The equation had an intercept of 0.29 mS cm^{-1}, significantly different from zero ($p < 0.001$), which can be attributed to the conductivity of the urease solution itself as indicated by EC measurements of the urease solution in deionized water without added fertilizer. The relationship was very similar for analytical-grade urea, but with a slightly higher (1-2.5%) EC at the same concentration. This difference can be attributed to a higher N content of analytical grade urea (>99% purity), while fertilizer grade urea contains various levels of impurities. These including biuret (usually < 1.5%), which is not readily hydrolyzed by urease and other additives such as anticaking agents and hydrophobic coatings.

The agreement between the urea release determined by the EC method or through chemical analysis was very good, indicating high accuracy (Fig. 3b) ($R^2 = 0.998$). The intercept of the regression line was not significantly different from zero ($p = 0.07$) and the slope not different from 1 (p = 0.93), again demonstrating that there is no evidence of proportional or fixed bias of N release measurement using the EC method.

< Figure 3 >

FIGURE 3 Calibration curve relating electrical conductivity (EC) and concentration of fertilizer urea after urease hydrolysis (a). Correlation between the release of urea from controlled release fertilizers as determined by the EC method or using the conventional colorimetric ammoniacal N method (b).

Application of the method for coated fertilizers

After the methods for MAP and urea were calibrated, we evaluated the complete release curve of selected polymer-coated MAP and urea formulations produced in our laboratory (Fig. 4). Measurements of EC were taken regularly until the samples reached complete release or only very small changes were observed over time. The estimates of release over time were consistent and very precise as evident from the small error bars (Fig. 4). For the six samples in triplicate and multiple measurements in time in Fig. 4, despite the relatively small sample size for each replicate (1.5 g for coated MAP and 3 g for coated urea), the average standard error was only 1.1%. This small standard error does not only include the analytical error but also the intrinsic sample variation between replicates.

< Figure 4 >

FIGURE 4 Release curves of several polyurethane-coated MAP fertilizers as determined by the EC-method and polyurethane-coated urea fertilizers as determined by the urease-EC-method. For the MAP fertilizers, coating rates on fertilizer are from 5.6 to 11.5% and for urea from 8 to 10%. Error bars are SE (*n* = 3). The lines are fitted curves using first order kinetics $\widehat{y} = y_0 + a - e^{(-kt)}$.

DISCUSSION

Soluble salt fertilizers

Electrical conductivity can be used as a measure of dissolved salts. Therefore, the release of soluble salts from controlled release fertilizers can be estimated based on the EC, by means of a calibration curve. The assumption is made that the coating itself is inert and therefore does not influence EC, which is the case of most if not all polymer-coated fertilizers.

The relationship between EC and fertilizer concentration was a second order polynomial. In very dilute solutions with EC < 0.01 mS cm^{-1}, EC responds linearly to ion concentration, however at higher concentrations, ion-ion interaction becomes significant and the molar conductivity (EC divided by mole concentration) decreases [20].

Because of the high salt concentration in our method, possible interferences on the EC, such as CO_2 in solution and water dissociation, are negligible. Since the EC readings are not ion-selective, any ion in solution will contribute to the EC. For this reason, the calibration curve must be prepared using the same fertilizer as the base material of the coated formulation. Phosphate fertilizers produced from different mineral sources, industrial processes, and the presence of additives will lead to different contents of soluble P and impurities, the latter being either soluble or insoluble. Therefore a calibration curve for one coated fertilizer may not be completely accurate for other coated fertilizers produced from a different core material. However, even if the uncoated base material is not available, a calibration curve can still be established, by simply puncturing or damaging the coating so that the soluble fertilizer is immediately released, and using this fertilizer with damaged coating to establish the calibration curve. In that case, the factor (1-CR) in Equation 1 must be omitted, as the fertilizer used for the calibration has the same coating rate as the sample.

Because EC is a non-selective measurement, there are some limitations to this method. This method may not be accurate for evaluation of multi-element coated fertilizers in which different salts are used as the core. Broschat [21] demonstrated that for Osmocote (The Scotts

Co., Marysville, Ohio) with the formulation 15N–3.9P–10K, 81% of the N (as both NO_3^- and NH_4^+), 75% of K, and 54% of P was released after seven months of incubation. Heterogeneous release rates of elements in multi-nutrient fertilizers are also reported for other fertilizers and by other authors [6, 22–24]. The granule weight loss method is also inappropriate for mixed salt fertilizers [13]. In the case of coated MAP, the matrix is constituted by a single salt, so we assumed that both nutrients (N and P) are released simultaneously in order to maintain charge balance. Moreover there are limitations related to the incubation of fertilizer in water, regardless of analytical method used for P or N determination. This type of incubation is not suitable for measuring release of slow release fertilizers based on low solubility materials such as struvite, phosphate rock, double layered hydroxides and insoluble N forms. The P release rate of these fertilizers is strongly affected by the presence of the soil solid phase, which acts as a sink for dissolved ions and buffers the pH [25–28], which is not provided by our in-solution incubation.

The above proposed technique would also be suitable for polymer-coated fertilizers where the soluble core is based on monocalcium phosphate, ammonium nitrate, ammonium sulphate, potassium chloride, calcium nitrate and any other mono-salt based fertilizer.

Electrical conductivity of a solution is easily and quickly measured, giving consistent results with very good reproducibility at nearly zero consumable cost with no hazardous waste generation. EC-meters are relatively cheap instruments already available in most research laboratories. This instrument is easily operated with only a few potential and easily controllable interferences. The alternative methods to determine release from P fertilizers will either involve expensive and relatively complex use of ICP-OES, which is costly in terms of consumables, maintenance and other associated costs. Another option is the use of the molybdate-blue colorimetric method which is labor intensive and demands a skilled analyst and results in the production of potentially toxic chemical waste. In some methods [29] p-nitrophenol is used and it is known to be highly hazardous to human health.

Urea

All the concepts about EC mentioned in the previous section are valid for the evaluation of release curves of polymer-coated urea. The only difference between these two methods is the additional step necessary for urea hydrolysis into ammonium. Our goal was to hydrolyze urea under non-optimal condition where pH was not buffered at optimal values and in the presence of enzyme inhibitors, especially ammonium, until nearly full hydrolysis of the substrate is achieved. The term “near full hydrolysis” is adopted because the hydrolysis rate decreases as the substrate asymptotically approaches full conversion. The product concentration tends to the initial substrate concentration as time tends to infinity, therefore full hydrolysis is never achieved.

We found that 50 U of urease was needed to obtain near full hydrolysis within 1 h for a subsample which contains at most 15 mg urea. The cost of urease is currently around US$ 2.00 per kU, hence the cost of the urease needed for a single sample amounts to only US$0.10.

Urea fertilizers can, in some cases, be treated with urease inhibitors which could interfere with the performance of the EC method to measure nutrient release from polymer-coated granules. The extent to which the inhibitor will affect hydrolysis rate depends on many factors and can be considered unpredictable, so validation of the method would be needed if it were to be used for this kind of fertilizer. This method is also not suitable for slow-release N fertilizers based on low solubility molecules such as isobutyledene-diurea and urea-formaldehyde. These molecules require soil microbial decomposition to hydrolyse their N chain, which cannot be predicted in solution [25, 26].

CONCLUSIONS

A novel inexpensive, quick and accurate method to evaluate the release of nutrients from controlled release MAP and urea fertilizers was developed. This method allows the screening of many controlled release fertilizers with minimum demand of analyst time using a conductivity meter. No hazardous chemical waste is generated and the cost is much lower than any other conventional methods based on chemical analysis and/or sophisticated instrumentation.

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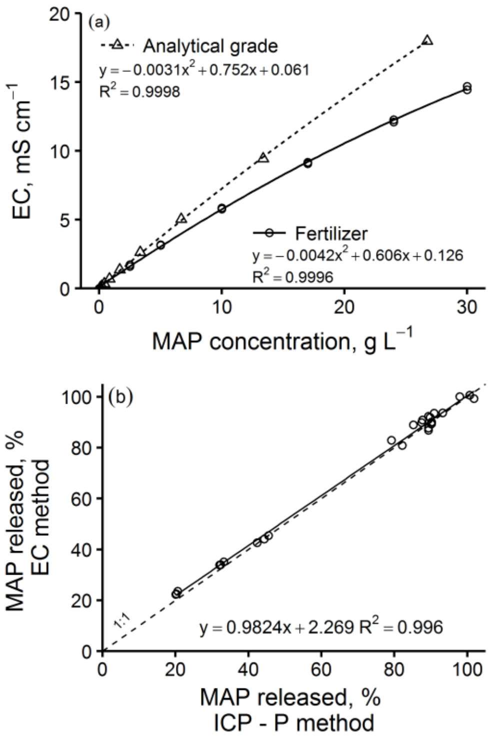

FIGURE 1 Relationship between the concentration of fertilizer grade MAP and electrical conductivity (a) and correlation between release of coated MAP determined by the EC method and conventional P measurement using ICP-OES (b).

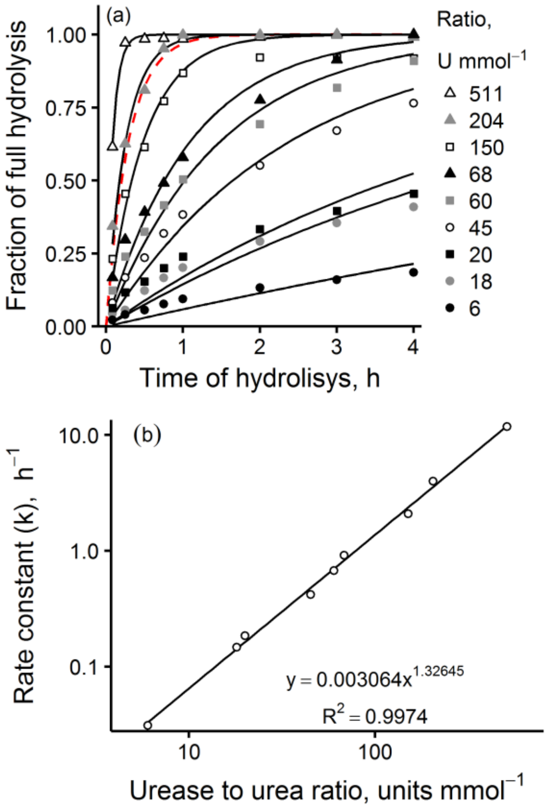

FIGURE 2 Ratio of electrical conductivity relative to maximal electrical conductivity (EC) after full hydrolysis of urea as a function of time for different ratios of urease units to urea concentrations, ranging from 6 to 510 U mmol^{-1} urea (a) and the hydrolysis rate parameter per urease urea ratio (b). In plot (a), the dashed red line represents the chosen urea to urease ratio. Another measurement of solution EC was taken at 20 h, which was used for modelling but omitted from plot a.

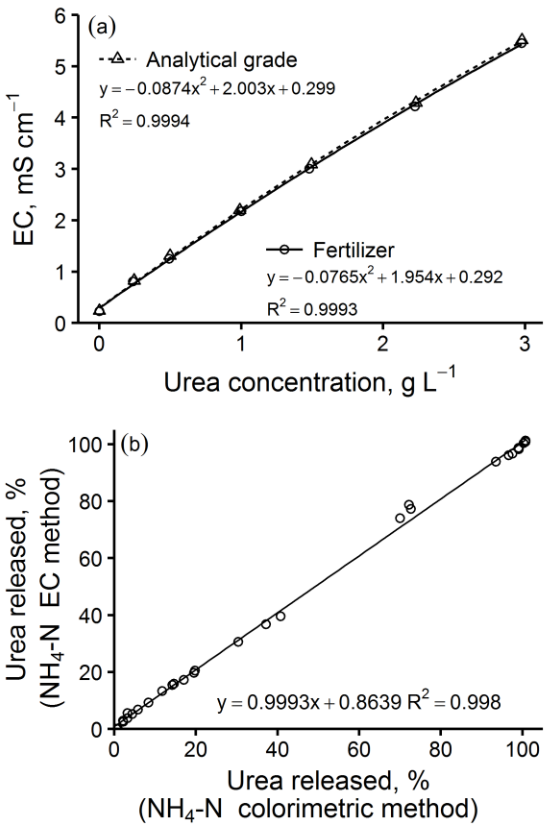

FIGURE 3 Calibration curve relating electrical conductivity (EC) and concentration of urea after hydrolysis by urease (a). Correlation between the release of urea from controlled release urea as determined by the EC method or using colorimetric ammoniacal N method (b).

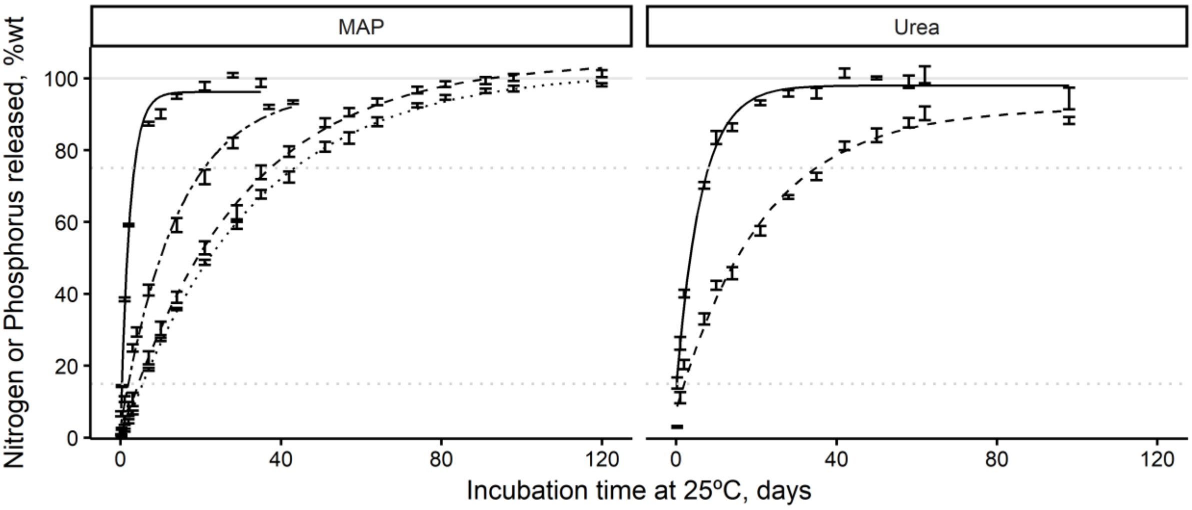

FIGURE 4 Release curves of several polyurethane-coated MAP as determined by the EC-method and polyurethane-coated urea as determined by the urease-EC-method. For the MAP, coating rates are from 5.6 to 11.5% and for urea from 8 to 10%. Error bars are SE (*n* = 3). The lines are fitted curves using first order kinetics $\hat{y} = y_0 + a - e^{(-kt)}$.

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PAPER 2 - PRODUCTION OF CONTROLLED RELEASE FERTILIZERS USING BIOBASED MATERIALS

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Abstract

The use of petroleum-based non-biodegradable coatings for controlled release fertilizers is expensive and repetitive use may potentially result in soil pollution, hence creating a need for coatings produced from inexpensive biobased materials. We are presenting several low cost, readily available renewable biobased materials for production of coatings to control nutrient release from MAP and urea. The biobased materials consisted of combinations of modified wood resins with lignin and biobased sources of polyols for polyurethane synthesis. While the resins and lignin failed to form an impermeable coating, the biobased source of polyols demonstrated to be suitable for production of high performance CRF. It reduced MAP and urea release rates to 208 and 34 days respectively using as little as 6% of coating on MAP and 10% on urea. The vegetal based coatings allows to substitute part of the petroleum based products used on coating production.

Keywords: polyurethane, bio-polyol, castor oil, wheat straw.

1 INTRODUCTION

Nitrogen and phosphorus fertilizers have low plant use efficiency in agriculture. For N, typically less than 50% is assimilated by plants [1] and usually 10 to 15% of applied P [2] is taken up by plants in soils with high P fixing potential in the year of application. Several chemical pathways render the nutrients unavailable to plants and therefore decrease fertilizer use efficiency [3].

Controlled release fertilizers (CRFs) are those which better meet the plants needs by either delaying the nutrient availability or extending its availability significantly longer than a rapidly available fertilizer, such as urea and monoammonium phosphate. One mechanism used to control the release is to coat a semipermeable barrier which limits the dissolution of the soluble core by water, hence, the nutrient is released slower than its soluble reference [4,5]. CRFs often increase crop yield, reduce ammonia volatilization and nitrous oxide emissions, nitrate leaching and labor required for application [3,5–7]. Therefore, they increase nutrient use efficiency and provide a more environmentally responsible alternative than soluble fertilizers. So far, CRFs are mostly used in high value crops due to their elevated cost which allows them only a small market share [7].

Current controlled release products are based primarily on polyolefins, polystyrene, dicyclopentadiene, polysulfone, polyurethane and glycerol ester [5,6,8]. All of these petroleum-based polymers are made from non-renewable resources and are very slowly-biodegradable [9–11] which results in accumulation in soil. In addition to the importance of soil conditions, such as temperature and moisture interacting with the coating, the chemistry at the coating/ core granule interface is important for coating tenacity and release rates as they interact chemically. Watanabe et al. (2009) observed a higher permeation of urea through a coating produced from glycerol monooleate compared with castor oil due to the chemical reaction with urea resulting in unsaturation in the glycerol monooleate chain.

Therefore, the marrying of production method with chemical characteristics of both core granule and coating are important.

Since the cost remains the major impediment for commercialization of CRFs, the development of cost-effective environmentally friendly coatings is a research priority. New coatings need to be produced using inexpensive and renewable materials. They should also render a biodegradable coating which can control release of one or more fertilizer matrices, like urea and MAP. So far, the majority of coating technologies have focused on urea, while very few studies have been published on the production of phosphate-based CRF [13–18].

There is a diverse range of materials which have been used industrially for the production of slowly permeable coatings[19,20]. Some could meet the above mentioned requirements yet they have not been considered as fertilizer coatings or their evaluation has been limited. One option would be the use of a lignin bulk coating using natural and modified wood resins as adhesives [21] which would be non-toxic and likely biodegradable. These resins are frequently used and are readily available, derived from pine trees and can be easily modified to obtain a wide variety of chemical and physical characteristics [22,23]. Another option is drying oils, which have been used to treat lignocellulosic material for protection sealing surfaces, forming an impermeable coating notably as varnishes for wood [19].

Another alternative is to use biological sources of polyols for the synthesis of polyurethanes [24]. Polyurethanes are copolymers formed by the reaction of a monomer containing hydroxyl groups (polyol) with an isocyanate (-N=C=O). Castor oil is a natural oil derived from the castor-oil plant (*Ricinus communis*) containing 85-95% of ricinoleic acid [25] and has the unique characteristic among natural oils to have reactive hydroxyl groups in its structure, being therefore suitable for polyurethane synthesis without any prior treatment. Moreover, ricinoleic acid contains ester bonds which are known to render a molecule more easily biologically hydrolysable [26,27]. However, the suitability of castor oil for production of controlled release fertilizers still has not been demonstrated. Another possible source of biopolyols is through liquefaction of lignocellulosic material [24]. In that case, materials like crop stover (the leaves and stalks of crops left in the field after harvest), which are low-cost, widely available and in plentiful supply, can be turned into polymers for polyurethane synthesis for fertilizer coatings. Coatings based on liquefied corn stover have been produced for urea coating with other additives incorporated such as superabsorbent composites [28]. However up until now no biobased polyurethane coatings have been synthesized for coating of phosphates. Therefore, we are presenting several low cost, readily available renewable biobased materials for production of coatings to control nutrient release from MAP and urea.

2 MATERIAL AND METHODS

2.1 Coating materials

Wheat stover (WS) was collected in the field at harvest stage. Spikes were removed and the material was dried and ground to < 0.25 mm. Four wood resin samples (referred to as Resin A, B, C and D) were supplied by Pinova Inc. (Pinova Inc., Brunswick, GA, USA). The term resin is used in its broad definition[20], which includes rosins, their solid derivate obtained with removal of volatile compounds. **Pexalyn Ester 10 (Resin A)**, a glycerol ester of partially dimerized rosin, is a hard, pale, thermoplastic resin with a higher softening point than typical glycerol esters of wood or gum resin. **Pentalyn FC (Resin B**), a pentaerythritol ester of maleic anhydride-modified wood rosin, is a pale, high softening point, high acid number, thermoplastic resin. **Foral AX (Resin C)** is a thermoplastic, acidic resin produced by hydrogenating wood rosin to a high degree. **Staybelite Ester 3 (Resin D)** is a triethylene glycol ester of partially hydrogenated wood rosin. Except for Resin D, which is a highly viscous liquid, all the resins were ground to < 200 μm. All the other chemicals and materials were used as received. **4,4'-diphenylmethane diisocyanate (MDI)** contains isomers and oligomers of high functionality, product supplied under the commercial name Lupranate

M20S (BASF Polyurethanes, Lemfrode, Germany). It has a NCO content of 31.5% with an average functionality of 2.7. **Lignin powder** is a purified form of kraft pine lignin, insoluble in water, supplied under the commercial name Indulin AT (Ingevity Corp, North Charleston, US). **Linseed oil** with added drying agent was obtained from Recochem Inc. (Recochem, Montreal, Canada) which is supplied under the commercial name Diggers Pale Boiled Linseed oil. **Ethyl acetate** HPLC grade (EA), **Ethylene glycol** (EG), **Ethylene carbonate** (EC), **Diethylenetriamine** (DETA), **Diethylene glycol** (DEG), **Triethanolamine** (TEA) and **Castor oil** (CO) were obtained from Sigma-Aldrich.

Liquefied wheat stover (LWS) was prepared as a source of polyol for polyurethane synthesis. The liquefaction of crops residues has been extensively investigated [24,29,30] and the appropriate reaction times and solvent proportions optimized. The process used can be described as follows: a three-neck round-bottom flask was set up with a thermometer and a reflux condenser in an oil bath. Ethylene carbonate (80 g), ethylene glycol (20 mL) and sulfuric acid (2.5 mL) as a catalyst were added and preheated to 160ºC with mechanical stirring [24]. Wheat stover powder was slowly poured into the solution while stirring and the reaction was kept stirring for 60 minutes and then cooled down in a water bath [24,28].

2.2 Fertilizer matrix and pre-treatment

Fertilizer grade urea (Incitec Pivot Fertilizers, Southbank, Australia) was sieved to obtain the 2.8 to 3.35 mm fraction. Fertilizer grade monoammonium phosphate (The Mosaic Company, Plymouth, USA) supplied without dust suppression coating was used as the material core for the production of controlled-release P fertilizers. The sphericity of these core granules was highly variable and given that poor sphericity affects the homogeneity of the coating, increases the granule surface area to volume ratio and increases the amount of coating material required, two pre-treatments were undertaken.

In the first instance commercial MAP was re-granulated in the laboratory drum to produce granules more closely sized and with improved sphericity. The MAP was ground and sieved to pass a 250 µm screen. The powder was granulated in a granulating pan using a water atomizer, to produce granules between 2.8 mm and 3.35 mm, by sieving and recycling undersized and drying at 80°C until constant weight. We can observe the higher sphericity and smoother surface of re-granulated MAP (Figure 1A) in comparison with commercially available MAP (Figure 1B). The porosity of these granules, however, was much higher than the commercial product due to the significantly lower pressures and tumbling bed weights in the lab drum cf. production drums. Problems with these granules emerged concerning coating efficacy and it failed to produce a good quality product (see results). Therefore, in addition to re-granulating we developed a physical treatment for commercial MAP to break off sharp angles and increase sphericity without changing the porosity of the granules. In this treatment the fertilizer was firstly placed in a container, filled to about 20% of its capacity, and loaded onto a high energy mixer/mill (SPEX mixer/mill 8000M, Metuchen, USA) activated for 40 seconds (720 cycles). After this, the granules were screened to obtain those with a diameter between 2.8 to 3.35 mm and were loaded into a coating drum and sprayed using a water atomizer until the powder on surface and outer granule surface dissolved. With drum rolling and cascading forces, surface smoothing occurred due to the filling of surface voids during re-crystallization. The granules were then oven dried at 60°C. The granules obtained were smooth surfaced, powder free, high-density MAP to which all the coatings described below were also applied. The resulting product can be seen in Figure 1C.

< Figure 1 >

2.3 Pine resins and Kraft-lignin as coating for controlled release fertilizer

A range of high softening point thermoplastic pine resins were tested as lignin adhesives with a linseed oil sealing as coat for MAP. We also tested a coating based on a mixture of all resins in equal proportions using Resins ABCD described in the materials section. For the coating preparation, powdered resins were dissolved in ethyl acetate at 200 g L^{-1} in a glass vial. Linseed oil was added to this solution at 4.15 mL L^{-1} and was mixed using a vortex shaker. Lignin powder is a water insoluble material and was used to form the bulk of the coating. Linseed oil was used as a sealing agent to fill up pores forming a protective impermeable hydrophobic coating layer.

For the coating procedure, 40 g of fertilizer granules (MAP or urea) was loaded in the coating drum which was kept at room temperature. A spraying system, consisting of a peristaltic pump coupled to an ICP nebulizer, was used to spray the solvent-resin-oil solution directly over the moving granules in the coating pan. As granules were getting moist and sticky by spraying the solution, lignin powder was slowly sprinkled over the wet rotating flow of granules using a spatula. The coating pan was kept inside a fume hood. Due to the air flow and the high volatility of ethyl acetate, granules dried quickly depending on the spraying rate while allowing lignin to stick onto the granules' surface. The lignin and solution were added in three batches of 1/3 of total coating amount, to ensure a homogenous ratio of lignin/resin across the coating layer. The ratio lignin/resin/oil in the final coating composition was 10:6:1 (w:w:v). To coat 40 g of raw fertilizers, 2.91 g of lignin /1.74 g of resin / 0.29 mL of linseed oil and 8.72 mL of ethyl acetate were used.

2.4 Polyurethane coatings

2.4.1 Coating process for LWS as polyol for polyurethane synthesis (LWS-PU)

The polyurethane prepared from LWS was coated on 40 g of fertilizers granules, urea or re-granulated MAP. The granules were loaded into a coating drum inside a fume hood and were preheated to 75 ± 3°C using a heat gun set at between 150°C and 200°C and aimed directly at the granules. The granule temperature was frequently monitored using a non-contact infrared thermometer (Digitech QM7221). Liquefied wheat stover and MDI were preheated to 50ºC using a hot plate and were individually pipetted and slowly dispensed across the bed of rotating granules in amounts equivalent to 1.1 wt% (0.247 g of LWS and 0.247 g of MDI) for each addition. This process was repeated 10 times allowing about 12 minutes between each addition. Two mL of a DETA solution diluted to 1% v/v in ethanol was sprayed over the granules after the 7th and 9th layer to speed up the curing reaction, reduce tackiness and minimize potential losses to the drum. Ethanol was expected to volatilize before contact with granules due to strong air flow and temperature therefore eliminating the risk of pores forming in the coating. A peristaltic pump with ICP nebulizer was used for this addition (Figure S1, Supplementary material). Granules were left to cure on a paper lined tray avoiding contact between granules and preventing formation of agglomerates such as in Figure S2 (Supplementary material).

2.4.2 Coating process for Castor oil as polyol for polyurethane synthesis (CO-PU)

The coating procedure was as described above for LWS-PU by pipetting the polyol and the MDI over granules. A DETA solution was sprayed on granules as described for LWS coating preparation. To allow for the complete curing reaction granules were left overnight on a paper lined tray.

2.4.3 Coating process for Diethylene glycol (DEG) and triethanolamine (TEA) as petroleum based polyurethane (DEG/TEA-PU)

A stock solution was prepared by homogeneously mixing TEA in DEG at 22.2 wt%. This proportion represents an ideal stoichiometric ratio to produce a highly crosslinked tack free rigid polyurethane [31]. The procedure to synthesize the polyurethane coating was similar to those described for LWS coating, however, instead of LWS solution, a DEG/TEA solution was added as a source of polyol. The mixing ratio between MDI to DEG/TEA solution was 2:1. To coat 40 g of fertilizer 1.29 mL of DEG, 0.37 mL of TEA and 3.28 mL of MDI was used, with no addition of DETA catalyst or other curing agent. The DEG/TEA polyurethane was produced in order to be used as a conventional petroleum-based polyurethane coating for comparison with the biobased polyurethanes. All coatings mentioned above were calculated to account for 10% wt of final coated fertilizers and an extra 1% wt was added to account for losses on the coating pan.

*2.4.4 **Coating physically amended MAP***

The re-granulated MAP was highly porous causing problems during coating synthesis (see results). Therefore, the physically amended MAP described previously was coated and required some modifications from the method described. Instead of spraying DETA individually for synthesis of LWS-PU and CO-PU, this catalyst was mixed at a ratio of 20 g L^{-1} with the polyols. The mixing with the polyols ease the distribution of the catalyst on the bulk of fertilizer. Fertilizers were then left to cure on a paper lined tray overnight between every addition of 2 wt% of coating rate.

*2.4.5 **Coating rate***

Given that a considerable amount of coating material sticks to the coating pan, it cannot be assumed that the granules have the same coating rate as calculated by the amount of PU added. Therefore, the coating rate was determined gravimetrically. For MAP, a 2-g sample was weighed out in a mortar and the coating of the granules was broken using a pestle. The sample was then transferred into a vial to which was added 20 mL of water and 10 mL of concentrated HNO_3, which dissolved completely the MAP matrix, including impurities. An uncoated MAP was used to check for the complete dissolution of the fertilizer. Samples were shaken overnight and filtered. The filter residue consisted entirely of PU coating, which was dried and weighed. The coating rate was calculated as a weight percentage of the original sample mass. For coated urea fertilizer, the same procedure described above was used. However, instead of the diluted acid, 40 mL water was used to dissolve the sample.

2.5 Nutrient release rates

A nutrient release test method previously developed (Cancellier et al. 2017) [32] was used to assess the release kinetics from these coated fertilizers. The method consists of incubating fertilizer samples at 25ºC in water and measuring electrical conductivity (EC) periodically. For MAP, the EC was determined directly on the fertilizer suspension, and converted to percentage release using a calibration curve. For urea, the EC was determined after hydrolysis of a subsample. To do so, a subsample was taken from the fertilizer suspension periodically, the aliquot was diluted, urease was added and the EC was determined after one hour of equilibration. From the EC, the nutrient release was calculated based on a calibration curve.

Since the method is based on EC measurements, we checked whether our newly developed coating influenced EC to avoid any measurement bias. To that end, we synthesized the coatings inside incubation vials, with the solid liquid ratio kept identical as in the conditions for release test (30 g L^{-1}).

2.6 Coating characteristics

2.6.1 ***Preparation of coated slides and contact angle measurement***

A series of evaluations were performed to characterize the coatings. Coated glass slides were used to investigate the properties of the coating and remove the influences of the fertilizer core. In the preparation of slides, polyols and MDI solutions were preheated to 50ºC and pipetted in the same proportion and conditions as used to prepare fertilizers coatings. Polyols and MDI were well mixed and approximately 0.25 mL of polyurethane solution was immediately pipetted onto a 70ºC preheated microscope slide. The PU solution was manually spread over the slide using a cover slip and then left to cure for at least 48 h prior to evaluation. In the case of wood resins, the resins were dissolved in EA and pipetted onto slides surface and left to air dry. The process was repeated 3 times to obtain a thicker resin coating.

To evaluate the coatings for hydrophobicity, also called wettability, the water contact angle was measured on the coated microscope slides using a 3 µL drop. Contact angle was evaluated using a contact angle meter (Attension Theta, Biolin Scientific, Stockholm, Sweden).

2.6.2 Microscope Imaging

The coated fertilizers were inspected under the microscope to check coating homogeneity, quality and distribution on the granule. The surface was observed as well as a cut cross-sections of the granules. Images were captured using an Infinity 4 digital camera with 11 MP resolution (Lumenera Corporation, Ottawa, Canada) coupled to a Wild M420 microscope (Leica Microsystems GmbH, Wetzlar, Germany). A 1 mm Olympus stage micrometer was used for calibration prior to measurements. Acquiring and processing of the microscope images was done using Infinity analyze software (Lumenera Corporation, Ottawa, Canada).

2.6.3 FT-IR characterization

All precursors and reaction products were scanned using Fourier transform infrared spectroscopy (FTIR). Liquid samples were scanned using a Bruker alpha equipped with a Multireflection-Attenuated total reflection (ATR) sampling module, while the PU powder sample required the same equipment equipped with a Platinum ATR sampling module. Wheat stover was scanned using a PerkinElmer Frontier fitted with a Diffuse Reflectance Infrared

Fourier Transform (DRIFT) sampling accessory. All samples were scanned for absorbance for 60 s from 4000 to 375 cm^{-1} with resolution of 4 cm^{-1}. Spectra were transformed into ATR units. When necessary, baseline correction was also applied. Spectra were acquired and processed using OPUS and R software.

2.7 Data analysis

In the release tests, the parameters of a quadratic regression between EC and urea or MAP concentration from calibration curves were used to estimate the concentration of released fertilizer in solution. For the contact angle measurements, means were compared by Tukey's LSD at 5% significance. All nutrient release curves were fitted to the model $y = y_0 + a - e^{(-kt)}$ using a non-linear least squares method. The longevity was determined as the time needed for release of 75% of the nutrients using the release equation. All statistical analysis and plotting of graphs were performed in R environment [33].

3 RESULTS and DISCUSSION

3.1 MAP release from re-granulated MAP

The resin-lignin coating did little to controll the release of phosphorus from MAP, releasing all the nutrient within 24 h (Figure 3). Coatings produced from Resin A, B and the mixture of all resins (ABCD) had some control over initial release, but they still released 86, 69 and 85% of nutrients within the first 2 h of incubation and all of them released over 97% of nutrients in 24 h. Coated Resins C and D did not have any effect over MAP dissolution with 94 and 96% of P released within 2 h. The European Committee for Standardization [34] suggests a definition for controlled release fertilizers stating they must have no more than 15% of nutrient released in 24 h and no more than 75% of nutrient released in 28 days. None of the resin coated products met these criteria.

The association of different natural resins, drying oils and related products has been long used in industry to produce varnishes for impermeable coatings for wood protection [19]. However we failed to produce an effective water impermeable coating layer on fertilizers. The microscope images demonstrated a heterogeneous coating, in which the small clearer spots presumably have a thinner lignin layer (Figure 2 A and B). Although the lignin was firmly adhered to the granules, the coating was soft and could be easily removed when the surface was scratched with a spatula. This could possibly be due to the lack of compaction since our coating pan has the diameter of 20 cm on an angle of 39.2 Deg and provides a shallow granule bed and hence smaller surface forces. Alternatively it is also possible that the combination of the chosen materials did not provide conditions for crosslinking and so did not render a hard surface coat.

< Figure 2 >

The biobased-polyurethanes, demonstrated a degree of control over nutrient release. The CO-PU and LWS-PU had a release of 38 and 25% in 24 h and a longevity of 3.5 and 7 days respectively (Figure 3). This was better than the petroleum based DEG/TEA-PU which released 49% in 24 h. They still do not meet the CRF criteria mentioned above.

< Figure 3 >

The polyurethane coated fertilizers controlled the release more than the lignin based ones, but the release was still relatively fast and unlikely to have an agronomic effect. We believe that the high porosity of granulated MAP is the main cause for poor performance of the coatings. The high porosity allowed polyurethane precursors (polyols and MDI) to penetrate inside the granule, which can be clearly seen in Figures 2 and 4. The LWS-PU was the best performing coating and therefore likely the one with the least penetration, yet, we calculated that the PU precursors mixed throughout most of the MAP matrix (Figure 4). Ideally the MDI and polyols should not penetrate the granule. The penetration of PU precursors into the granule hindered a homogenous mixing and synthesis of an external polyurethane layer.

< Figure 4 >

3.2 Phosphorus release from smoothened commercial MAP

Given the lack of evidence supporting the formation of a quality coating using resin and lignin and that the failure could not be directly related to the MAP porosity, we did not use these materials for the further trials. Only the polyurethane coatings were coated on the smoothened commercial granules. The performance of the PU coatings for controlling P release improved significantly for these treated granules while also using less coating material (Figure 5 and Table 1). All MAP coatings achieved a P release smaller than 11% in 24 h, with only 0.3% release for the CO-PU coating. The longevities of the controlled-release MAP products were 21, 146 and 209 days for LWS-PU, DEG/TEA-PU and CO-PU respectively. No PU penetration in the fertilizer core could be observed using microscopy (Figure 6 A, C, E). The castor oil based polyurethane had a much higher control of the release than the petroleum based-DEG/TEA-PU. Therefore the new bio-polyurethane coating promotes a better control of release and/or allows for a reduction in coating rate, reducing costs and the environmental impact. It renders this new fertilizer coating a more economically and environmentally friendly product than current commercially available coatings.

< Figure 5 >

< Table 1 >

< Figure 6 >

3.3 Urea release

Similar as observed for the coated re-granulated MAP, none of the resin and lignin based coatings effectively prevented fast dissolution of urea and therefore none of them can be considered controlled release fertilizers according to CEN standards. All of the lignin-resin coated urea released over 85% in the first 6 hours. The “solid” non-porous structure of urea does not allow penetration of liquids into the granule structure (Figure 7). The ineffectiveness of resin-lignin coatings on urea supports the hypothesis that the ineffectiveness of this coating is not related to the porosity of granules.

< Figure 7 >

The polyurethane coated urea products performed well in the release test. None of the PU coated urea released more than 15% within the first 6 h of incubation (Figure 8). It demonstrated an efficient coating process where a small percentage of granules presented release failure. The best performance for controlling release was from DEG/TEA-PU and CO-PU which had longevities of 34 and 37 days respectively. As also observed for the smoothened MAP granules, the LWS-PU performed the worst among polyurethanes, with a longevity of 8 days. LWS-PU was the only PU which increased electrical conductivity significantly when incubated in water (Figure 9). This suggests the polymerization reaction was incomplete, resulting in an excess of LWS. In the IR spectrum (Figure 11D), no evidence was found of unreacted isocyanate groups based on the absence of the NCO peak at 2260 cm^{-1} in the LWS-PU. Therefore a coating with unreacted fractions is likely the reason for the faster release of fertilizers coated with this material. The electrical conductivity of the PU coating incubation was not changed in the CO-PU and DEG/TEA-PU, indicating the coating insolubility which is backed up by the higher control of release from these two (Figure 9).

< Figure 8 >

< Figure 9 >

3.4 Coating hydrophobicity

The hydrophobicity of PU coatings, measured by the water contact angle on a flat coating surface, seems to be playing a role in the nutrient release control. We observed that the more hydrophobic coating CO-PU (Contact angle: 89°) was the one with the longest longevity. The LWS-PU coating with the shortest longevity for both urea and MAP had a lower hydrophobicity (Contact angles: 74°) (Figures 5, 8 and 10). The high hydrophobicity of castor oil based PU is probably due to the inherent non-polar structure of ricinoleic acid, an unsaturated fatty acid which is the major component of castor oil [25]. Contact angle measurements confirmed the highly hydrophobic nature of the resin with a contact angle of up to 94°.

< Figure 10 >

The reduction of urea permeation through a PU membrane with increased castor oil content was observed by Watanabe et al.[12] . These authors observed that urea permeation is lower when the PU side chain is longer. The longer side chain conformation in CO is conferred by the molecule structure, hydroxyl group position and the length of alkyl side chain after the hydroxyl. For DEG/TEA-PU, the hydroxyl is always in the terminal position of the monomers carbon chain, suggesting a higher permeability for this type of polymer. Additionally, DEG/TEA-PU also has a lower urethane content, which was also observed to be negatively correlated to permeability [12].

3.5 Synthesis validation using FT-IR

The spectrum for LWS showed absorption peaks characteristic of cellulose and hemicellulose, the main components in wheat stover. We observed a broad peak for -OH stretching at 3362 cm^{-1} (Fig. 11a), ester C=O stretching at 1722 cm^{-1} and C=C stretching vibrations at 1452 cm^{-1} and absorption at 1122 cm^{-1} related to stretching of C-O bonds. The wheat straw liquefaction consists of turning cellulose and hemicellulose into a biopolymer rich in free OH groups, the reactive group used for PU synthesis. The high and broad absorption peak of LWS at 3362 cm^{-1} is indicative of the high presence of -OH groups in this compound.

Both the DEG and TEA present strong absorption bands at 3341 and 3317 cm^{-1} from their high -OH content (Fig. 11b). The absorbance peak at 2260 cm^{-1}, which can be attributed to the isocyanate group, was absent in the DEG/TEA-PU, demonstrating the complete urethane polymerization. The peak at 3290 cm^{-1} in the DEG/TEA-PU, which was not present in the precursors, was attributed to –NH stretching vibrations present in the urethane links. Furthermore, three other absorption peaks were observed at 1701, 1597 and 1515 cm^{-1} which were attributed to the carbonyl C=O, βNH- and the aromatic C=C stretching from the isocyanate molecule respectively.

The peaks in CO and CO-PU at 2853, 2925 and 3010 cm^{-1} (Fig. 11c) were attributed to the symmetric and antisymmetric vibrations of CH_2 from CO structure, making up the polymer backbone and part of the side chains. The peak at 1742 cm^{-1} was attributed to C=O stretching in the ester groups of CO, which shifted to 1719 cm^{-1} in the CO-PU. The absorption peak at 2274 cm^{-1} was attributed to free NCO groups demonstrating an incomplete crosslinking reaction and unreacted isocyanate. It has been demonstrated that the higher ability for hydrolysis of ester groups makes the free isocyanate groups to be the first group attacked by microorganisms for degradation [27].

3.6 Environmental considerations

The use of renewable materials in the polyurethane industry is highly attractive, not only due to the low cost of the materials, but also due to cuts on consumption of petroleum-based products to decrease greenhouse gases emissions. Controlled release N fertilizers have been demonstrated to reduce emissions of greenhouse gases from soil [35] and now have the additional benefit of be produced from vegetal C instead of petroleum C. The use of vegetal raw materials can be an effective way forward to improve the carbon balance in agriculture, as the carbon in the coating was captured into plant biomass through photosynthesis [11].

Moreover the bio-polymers eliminate one of the biggest concerns associated with the use of polymer coated fertilizers, which is the accumulation of non-biodegradable material in soil [11]. The CO-PU is hydrolytically degradable due to hydrolysable ester bonds in its molecule [26] and wheat stover material is long known to be biologically degradable [36,37]. The use of bio-polymers for the production of controlled release fertilizers may help to reduce production costs and environmental contamination while increasing fertilizer use efficiency, therefore, contributing to more environmentally friendly and sustainable agriculture.

Although some authors claim that crop-stover-based coatings can also benefit crops by releasing nutrients to soil [28], this effect can be considered negligible. Considering the proportion and nutrient content (Table Sx, Supplementary material) of wheat stover in the coating composition, it would supply for example only 28 g ha^{-1} of K and 1.3 g ha^{-1} of P for common application rates, which is far from rates demanded by plants.

Although part of the chemicals in the urethane being biobased, it still requires the crosslinking with isocyanate, which is petroleum-based. Other 100% biobased materials have been tested for controlled release and are not fit for purpose or show little effect on release rates, with longevities generally less than 24 h [7,28,38,39].

In conclusion, the bio-polyols were proven to be a suitable alternative for production of polyurethane coated CRFs based on urea and MAP. The CO-PU demonstrated a very slow MAP release rate, with longevity of 208 days while using only a 6.1% coating rate. This polymer was also able to control urea release, indicating its versatility to coat more than one type of fertilizer matrix.

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Notes

The authors declare no competing financial interest.

5 SUPPORTING INFORMATION DESCRIPTION (OPTIONAL)

Table Sx. Raw wheat stover nutrient content prior to liquefaction. Values represent average of tree replications ± standard error.

Ca	K	Mg	P	S	Zn	Cu	Mn	Fe	B
--- mg kg^{-1} ---									
1809 ± 22	7614 ± 41	761 ± 3	352 ± 1	1136 ± 7	22 ± 0.37	3 ± 0.18	17 ± 0.07	243 ± 1.23	23 ± 0.28

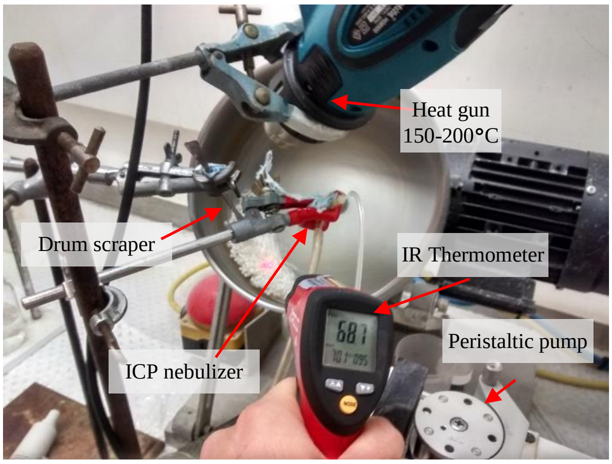

Figure S1. Laboratory coating pan and controlling devices.

Figure S2. Agglomerated granules showing coating damage.

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7 TABLES

Table 1. Coating rate (weight %) determined by gravimetric method of bio-polyurethane coatings. For the MAP fertilizers, the coatings were either applied on lab-granulated granules or smoothened commercial granules.

	MAP		
Coating	Lab-granulated	Smoothened	Urea
CO	10.6	6.1	10.2
DEG/TEA	9.4	8.8	8.0
LWS	9.3	5.6	8.0
Resin A	9.4	-	8.2
Resin B	10.9	-	8.5
Resin C	9.8	-	8.1
Resin D	9.6	-	8.0
Resin ABCD	9.9	-	7.9

8 FIGURES

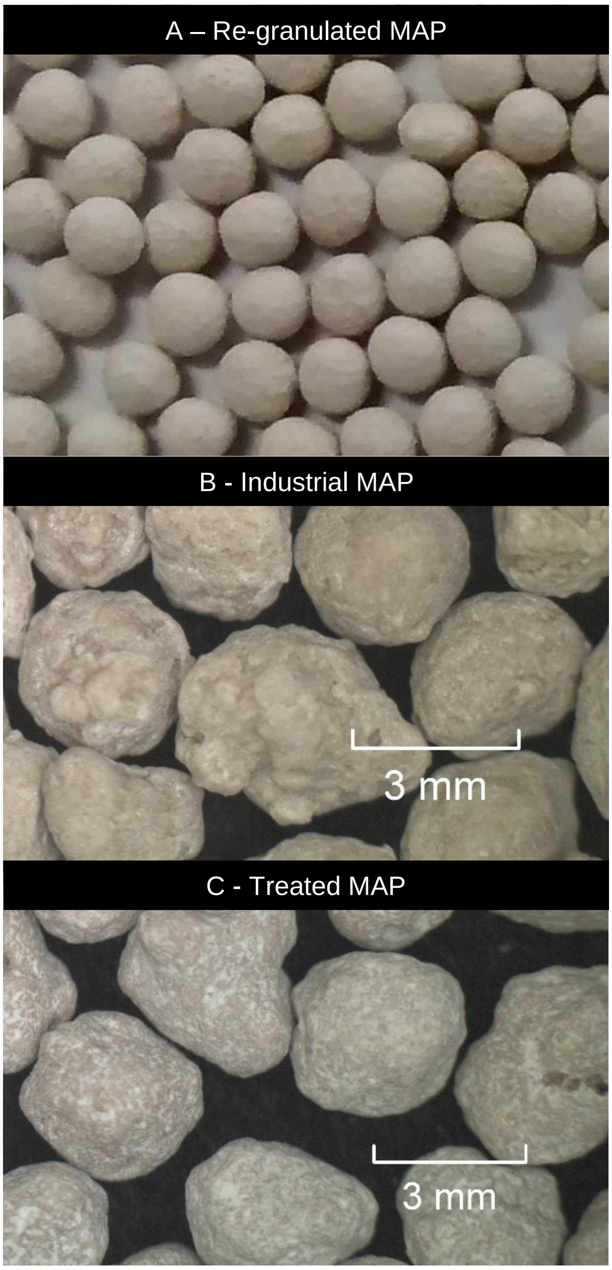

Figure 1. Treatment of fertilizer grade MAP. A – Re-granulated MAP from powdered commercial fertilizer. B – Commercial granules (as received). C –Smoothened commercial granules.

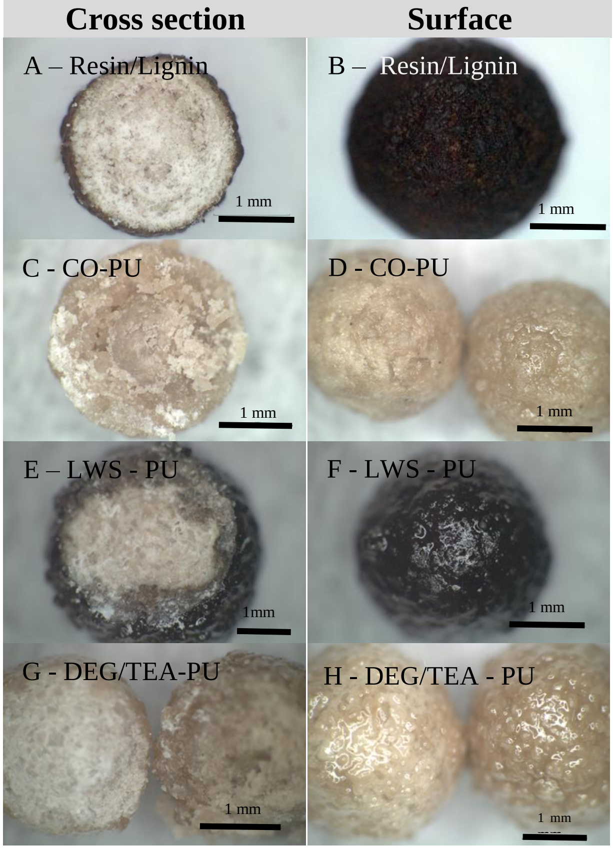

Figure 2. Microscope images of biobased coatings on re-granulated MAP granules. Left column show fertilizers in cross section and the right column shows coating surface. Panels A&B show Resin B, which represents all visually similar resin coats. Panels C and D are MAP coated with Castor oils based polyurethane. Panels E and F are liquefied wheat stover based polyurethane coatings and panels G and H are the diethylene glycol and triethanolamine based polyurethane coating as reference of coatings produced fully from petroleum.

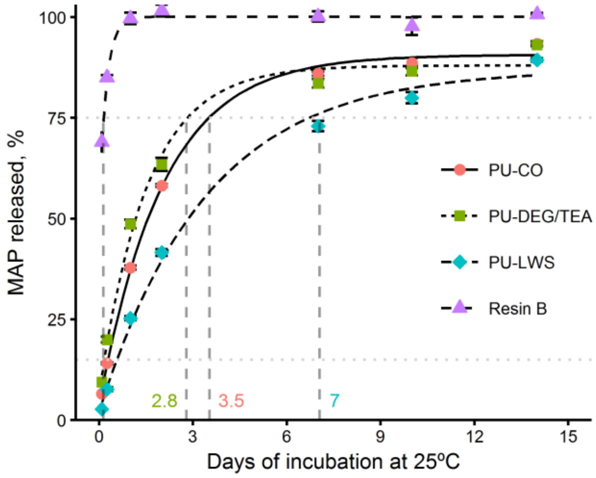

Figure 3. Monoammonium phosphate released from re-granulated spherical MAP coated fertilizers incubated at 25ºC in water. Numbers over the x-axis are the longevities (time for 75% release) of each fertilizer. Lines are fitted models to $y = y_0 + a - e^{-kt}$. Vertical error bars indicate SE (n = 3). Fertilizers which had no effective control over nutrient release were not plotted (Resin A, Resin C, Resin D and Resin ABCD).

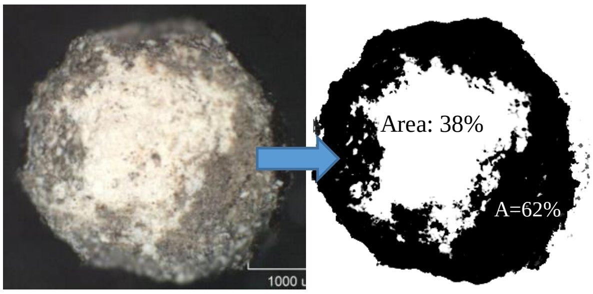

Figure 4. The image is from a granule cross section of LWS-PU “coated” granule after complete release in water. The dissolution of the MAP core renders it white, providing good contrast with the black LWS-PU. The image was processed in GIMP software applying a color threshold allowing the measurement of the unaffected vs LWS-PU affected area. Through pixels counting in the 2d image we found that the polyurethane precursors mixed with 67% of the area.

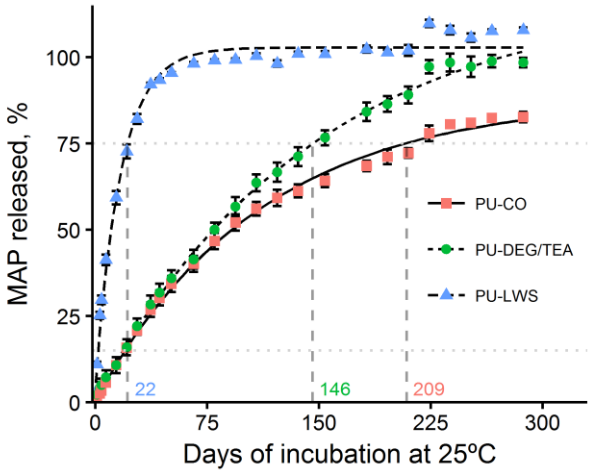

Figure 5. Monoammonium phosphate release rate from smoothened commercial MAP coated with bio-polyurethanes and DEG/TEA-PU. Numbers over the x-axis are the longevities (time for 75% release) of each fertilizer. Lines are fitted models to $y = y_0 + a - e^{-kt}$. Vertical error bars indicate SE (n = 3).

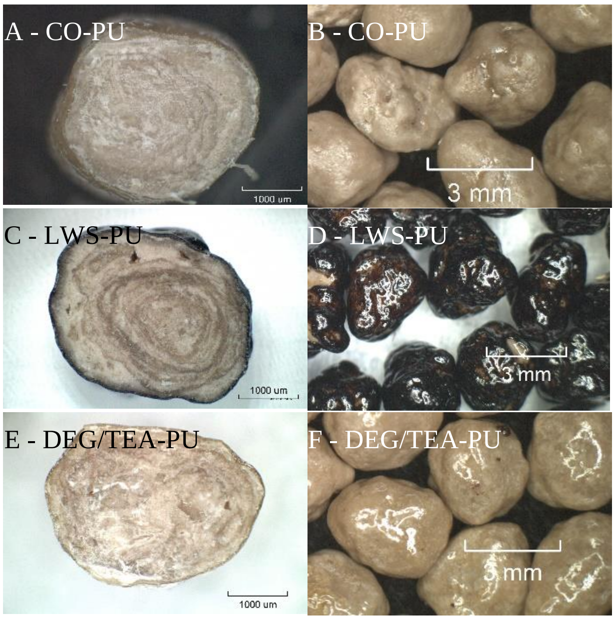

Figure 6. Biobased polyurethane coatings on smoothened commercial MAP granules (left: cross-section; right: whole granules). A and B are the castor oil based PU coating, C and D are the liquefied wheat stover based PU coating and The E and F are the diethylene glycol and trietanolamene based PU representing the petroleum based PUs.

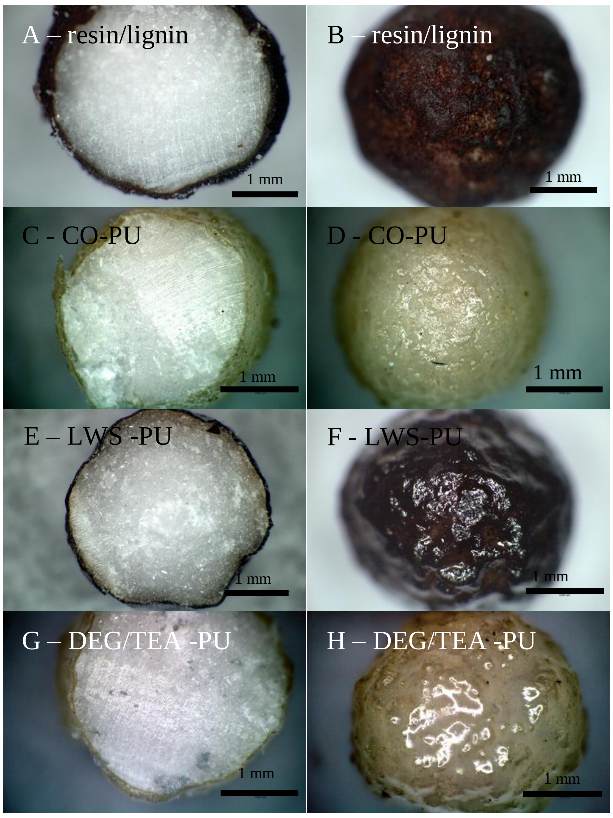

Figure 7. Polyurethane coatings on urea fertilizer (left: cross-section; right: whole granule). All resin-lignin based coatings are visually similar, resin B is depicted to represent them all (Images A and B).

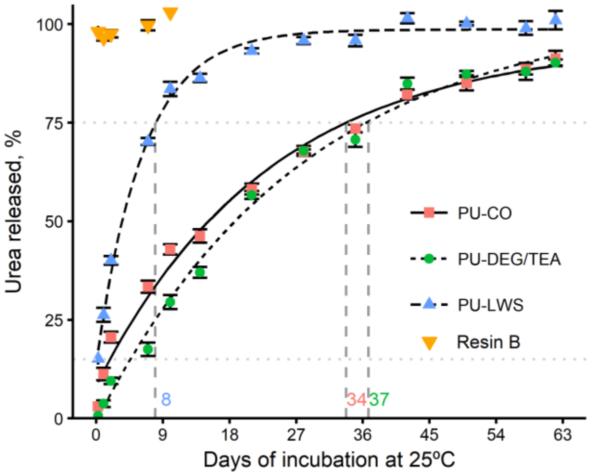

Figure 8. Urea released from controlled release fertilizers incubated at 25ºC in water. Vertical error bars indicate standard deviation (*n* = 3). Resin based coatings failed completely on controlling release and were omitted from the plot.

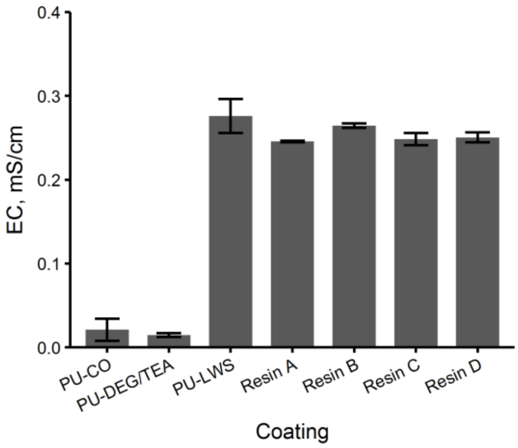

Figure 9. Effect of coating on the EC (mS/cm) at 7 days after incubation. Error bars are SE.

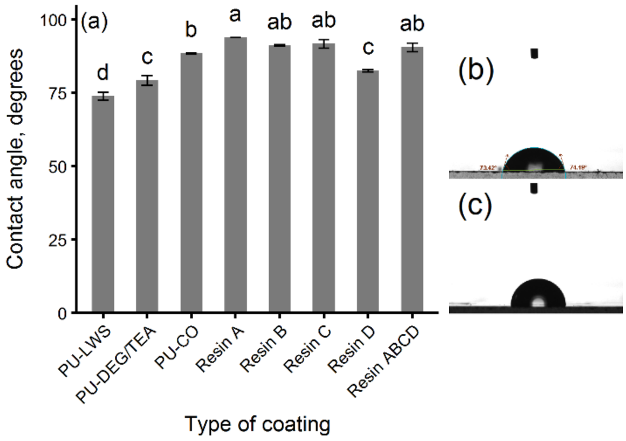

Figure 10. Water droplet contact angle for polyurethane coating materials (a). Sample pictures of contact angle measurement for PU-LWS (b) and Resin B (c). Different letters above the bars indicate significant differences (P≤0.05) according to the Tukey test.

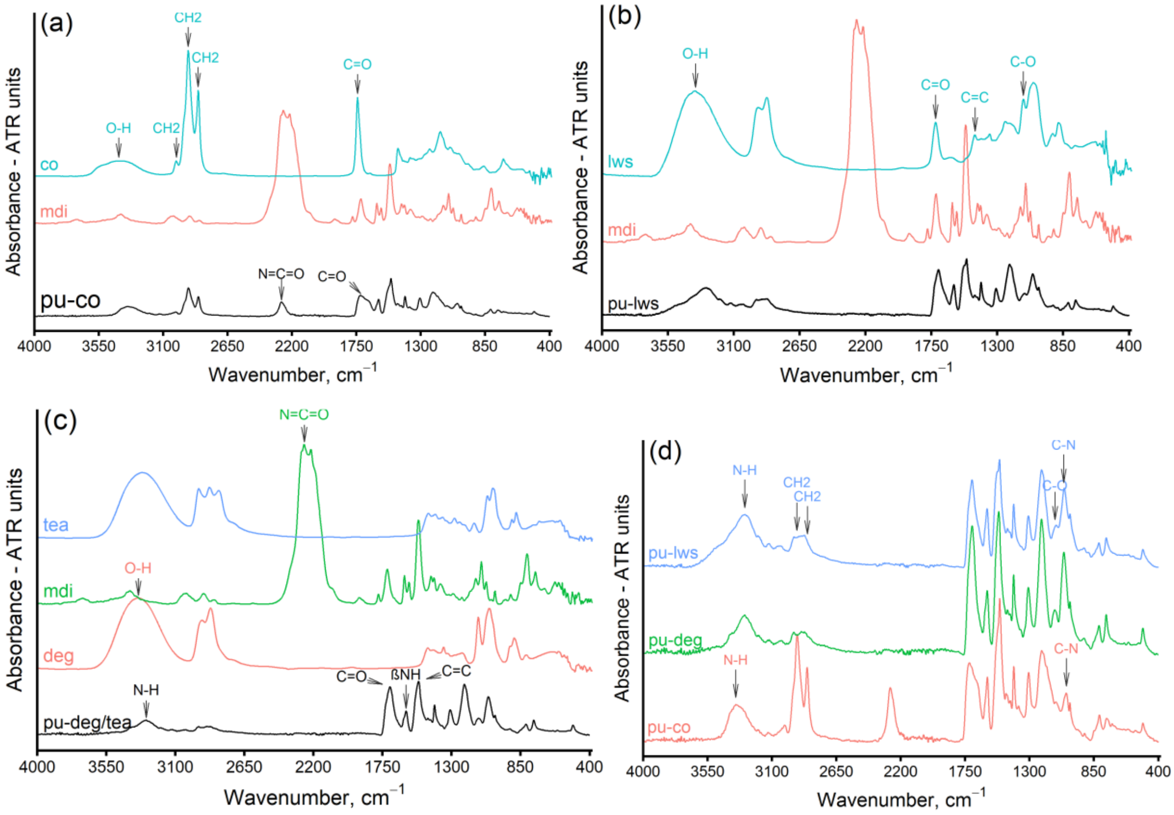

Figure 11. IR-ATR spectra of polyurethanes synthesized for coatings. Y axis is absorbance transformed to ATR and baseline correction. (a) The PU-CO and its precursors, (b) The PU-LWS and its precursors, (c) The PU-DEG/TEA and its precursors, (d) All PU samples.

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PAPER 3 CONTROLLED RELEASE PHOSPHATES: LIMITED INCREASE IN FERTILIZER USE EFFICIENCY FOR ANNUAL CROPS.

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9 Abstract

Controlled release fertilizers (CRFs) for N delivery are well known but few studies investigated the effect of CRFs on P use efficiency. Therefore, we investigated the potential of P-based CRFs to reduce P fixation and increase P use efficiency by wheat in two soils, a calcareous soil and an Oxisol with high P fixation capacity. Three CRFs were prepared by coating MAP, with a release time of 7, 37 and 209 days. These fertilizers were incubated in soil and P diffusion was visualized at different times. After 70-days of incubation, chemical analyses of P in the soils and fertilizer was carried out. Also a pot trial assessed the agronomic effectiveness and employed the isotopic dilution to quantify the fertilizer contribution. A lower release rate did not decrease P fixation in the calcareous soil, but had a small effect in the Oxisol for the fertilizer with 37 days release. In the pot trial, the CRFs either had no effect on plant growth in comparison with the control (uncoated) MAP or even decreased growth, particularly for the fertilizers with the slowest release. However, for MAP with 37 days for release, the P uptake was higher than for the control MAP in the Oxisol, indicating that CRFs do have potential to reduce fixation by oxides and hence increase P uptake. Although reduction in fixation was observed to a limited extend, the increase in P uptake was substantial (56%). It evidences that it is possible to improve P use efficiency by controlled release MAP.

Keywords: polymer coated P; P lability; controlled release P; P use efficiency; P sorption; isotopic labelling.

10 Highlights

- No increase in plant growth with controlled release P due to limited initial growth.
- No increase in P lability, plant growth or P diffusion in high Ca soil.
- Higher P lability and plant P uptake in oxidic soil using controlled release P.

Controlled release fertilizers (CRF) are fertilizers that release nutrients slower than the soluble reference at a controlled rate over an extended time frame (Trenkel, 2010; ISO, 2016). These fertilizers are claimed to have several advantages over uncoated soluble fertilizers (Trenkel, 2010). Controlled release nitrogen (N) fertilizers have been extensively studied and their effects demonstrated (Shaviv, 2001; Chien et al., 2009; Thapa et al., 2016). They reduce cost of fertilizer application if a single application is used instead of multiple split applications

(Guertal, 2000; Chagas et al., 2016). They reduce N losses through ammonia volatilization (Wang et al., 2016; Cancellier et al., 2016), nitrate leaching (Entry and Sojka, 2010; Peng et al., 2011) and nitrous oxide emission (Halvorson et al., 2014; Thapa et al., 2016). They also improve synchrony between nutrient supply and plant demand, and as a result often increase agronomic efficiency or yield. Their higher price remains their major limitation for wide adoption by farmers for some crops (Azeem et al., 2014).

In contrast with N, controlled release P fertilizers have received little attention and little research is published on coated P products. These two nutrients largely differ in how they react in soil. Nitrogen is highly mobile, is incorporated into organic matter and can volatilize. In contrast, P is strongly sorbed in most soils, is mostly in inorganic form in cropping soils and does not volatilize. As a result, there is little loss of P from soil, but the reactions with the soil solid phase (precipitation or strong adsorption) may strongly reduce fertilizer effectiveness. The reduced effectiveness of P fertilization with time is well known and documented (Barrow, 1983a; b, Torrent et al., 1992, 1994). This reduction can be attributed to slow reactions of which the rate depends on soil properties (Barrow, 1983a, 2015).

In current fertilization practices, soluble P fertilizers are applied at sowing when P uptake rate by crops is minimal. Although the early P supply is critical for plant development, the rate of P uptake is proportional to growth rate. Therefore the highest P uptake rate occurs at later stages, typically around 1 month after emergence for annual crops (Bender et al., 2013, 2015), when part of the added P would have penetrated into less-labile pools. The better match between plant demand and freshly released P from CRF would theoretically result in a better nutrient use efficiency. Despite the frequently claimed benefit of supply and demand synchrony, the concept of controlled release soluble P fertilizers to enhance P use efficiency has only been tested in a few studies and the results are inconsistent (García et al., 1997; Nyborg et al., 1998; Pauly et al., 2002). Pauly et al. (2002) found significant increases in P use efficiency and barley dry matter yield. However, these authors did not relate their results with soil properties and P lability which are major factors affecting P use efficiency and response to fertilizer. García et al. (1997) evaluated ryegrass growth in calcareous soils and tested coatings on DAP and TSP. The reduced release rate of the coated fertilizers did not improve P uptake for any of the fertilizers tested.

Given that P effectiveness decreases with time, a shorter time between P application and plant demand may result in less P fixation or “ageing”, and hence higher bioavailability and P use efficiency by plants. For that reason we hypothesized that using controlled release P fertilizer would be a good fertilization strategy to increase P use efficiency. To our knowledge, the hypothesis of improved P use efficiency for coated soluble P fertilizers in annual crops has not yet been appropriately tested and related to soil properties. Our aim in this study was to assess if controlled release of P can reduce P fixation in soil and enhance P availability. For that purpose, we coated MAP with a new type of biopolymer coating material using renewable materials to make more environmentally friendly fertilizers. The effect of the controlled release on P lability and P use efficiency was tested in incubation and pot trial experiments using an isotopic tracer technique.

11 MATERIAL AND METHODS

11.1 Fertilizers

Treatments for two independent experiments consisted of unfertilized control, uncoated MAP (unc-MAP, 224 g P kg^{-1}) and three coated MAP with different release rates (7, 37, 209 days for 75% release, denominated 7d-MAP, 37d-MAP and 209d-MAP respectively). The release rate was determined by incubating 1.5 g of fertilizer in water with regular determination of P release by measuring electrical conductivity as described in the first chapter. The time for release was adopted to be the time to reach 75% P release (ISO, 2016), as modelled by first order kinetics model (Fig. 1). An uncoated commercial grade (2.8 - 3.35 mm) MAP fertilizer was used as the reference fully soluble treatment. This fertilizer was also used as the matrix for the production of the controlled release coated MAP. To make the coated MAP, new types of biobased polyurethane coatings were used employing vegetable oil and crop stover residues as raw materials. These polymers were chosen in order to produce more environmentally friendly coatings and a detailed description of the manufacturing process is described in the second chapter. The three coated MAP fertilizers selected for this study differ in their release rate (Fig. 1), coating composition and coating rate (9.3, 11.5 and 6.1% of coating rate for 7, 37 and 209 respectively). Differences between these samples in terms of their reactions in soil are assumed to be entirely due to different release rates rather than a direct effect of coating composition as they are inert polymers.

< Figure 1 >

11.2 Soil selection

Three soils (0-20 cm layer) were selected due to their highly contrasting attributes (Table 1). Kingaroy is an Oxisol (Soil Taxonomy, USA). Black Point is a sandy loam high-Ca non-calcareous surface soil which is calcareous at depth, classified as Inceptisol (Soil Taxonomy, USA). Monarto soil is a sandy Alfisol (Soil Taxonomy, USA). In Kingaroy, a decrease in P availability would likely occur due to high energy sorption on Al and Fe oxides, while in Black Point precipitation of Ca-P forms would likely be dominant process. Monarto is a weakly P sorbing soil where high diffusion is expected (Degryse and McLaughlin, 2014).

< Table 1 >

11.3 Incubation experiment

11.3.1 Experiment set-up

A Petri dish experiment was carried out in order to compare the P diffusion and lability from coated and uncoated MAP. Petri dishes with 27.5 cm radius and 10 mm height were filled with 33, 35 and 30 g of equivalent dry soil, which led to an approximate bulk density of 1.4, 1.48 and 1.25 g cm^{-3} for Black Point, Monarto and Kingaroy soils, respectively. Soils were previously moistened to 130% of gravimetric moisture at -10 kPa (field capacity) using deionized water. After packing the soil, MAP granules containing 5.6 mg of P were placed at the center of each Petri dish 3 mm below surface. To do so, a small hole was made in the center of the dish where the granule was placed and the hole was carefully closed with soil. Finally, the Petri dishes were closed, sealed and incubated at 25ºC in the dark. Also a control treatment without fertilizer addition was included. Four replicates were prepared for unc-MAP and 5 for coated MAP.

11.3.2 Phosphorus diffusion and lability

At 1, 3, 7, 14, 21, 33, 45, 57 and 70 days after addition of MAP, the Petri dishes were opened, the water content was adjusted and the P diffusion was evaluated by a visualization technique (Degryse and McLaughlin, 2014). This technique consists of deploying an iron oxide-impregnated paper on soil surface. The iron oxide paper, which acts as a sink, adsorbs P from the soil solution. After removal from the soil, the filter paper is submitted to a color development process using ammonium molybdate and malachite green. Finally, the iron oxide is dissolved using sulfuric acid to clean the paper which is further dried and scanned for analysis with image manipulation software (GIMP Development Team, GNU Image Manipulation Program, v2.8.14) to determine the radius of the high-P diffusion zone around the granule (Rdiff).

After the last visualization on the 70th day of incubation, the incubated granules were carefully uncovered with a spatula and collected using tweezers. We made an effort to bring a minimum of soil attached which was rinsed off with deionized water, except in case of the uncoated MAP. The coated granules could be recovered physically intact, while unc-MAP was recovered as a paste containing visually a certain level of soil contamination and possibly small loss of MAP left in the soil. Granules were dried in oven at 60ºC before recording their weight and transferred into a 15-mL centrifuge tube. Inside the tube, the coating of the coated granules was ruptured using a stainless steel rod before adding a 20% v/v HNO_3 extractant solution. Samples were kept overnight in an end-over-end shaker, centrifuged, filtered (Whatman No. 1) and analysed for their remaining P content that was not released in the soil during the incubation, by inductively coupled plasma optical emission spectroscopy ICP-OES (Perking Elmer, Optima 7000 DV).

After granule removal, two concentric sections of soil were collected. The inner soil section, comprising soil from fertilizer placement to 7 mm radius and the outer section with the remaining soil, from 7 to 27.5 mm radius. The inner soil section was sampled using a steel cylinder driven into the soil and both sections were oven dried at 60ºC. The samples were homogenised in a high-energy Spex mixer for 1 minute. The pseudo-total P concentration was determined by extraction with 20% v/v HNO_3 for 24 h followed by ICP-OES analysis of the extract. For the Kingaroy soil, extraction with 50% v/v HNO_3 at 80°C for 48 h was used in order to obtain full recovery of the added P. Another subsample was taken to measure labile P using the isotopic dilution method (E-value) (Hamon and McLaughlin, 2002). For that, 1 g of soil was placed in a 15-mL centrifuge tube and 10 mL of deionized water was added. To inhibit microbial activity, 10 µL of toluene was added. Samples were kept in an end-over end shaker for 24 h for equilibration, after which the pH and EC was measured and carrier free ^{33}P (10 kBq per sample for Monarto and 70 kBq for Black Point and Kingaroy) was added. The samples were equilibrated for a further 24 h, centrifuged at 4658 g for 30 min and then filtered over a 0.2-µm syringe filter (Sartorius) and analysed for orthophosphate-P using the Murphy and Riley (1962) colorimetric method. The ^{33}P activity was measured after mixing 1 mL of filtrate with 4 mL of liquid scintillation cocktail (Ultima Gold AB, PerkingElmer) using a Liquid Scintilation Analyzer (Tri-Carb 3110 TR, PerkingElmer). Spiked and non-spiked blank controls without soil were included to measure the activity added per sample. Labile P (E-value) was calculated according to Hamon and McLaughlin (2002) as follows:

$$E = R \cdot \left(\frac{C_s \cdot V}{r \cdot W} \right) \qquad [1]$$

where E is the amount of isotopically exchangeable P (mg P kg^{-1}), R is the amount of radioactivity added to the sample (Bq), C_s is the concentration of P in solution (mg P L^{-1}), r is the amount of radioactivity (Bq) in solution after 24 h of exchange, V is the solution volume (L), and W the mass of soil (kg).

The distribution of P in soil rings was calculated as:

$$P_i = 100 \cdot \frac{(Px_i - Pc) \cdot W_i}{Pfert} \qquad [2]$$

where P_i is the % of recovered P in section i (i.e. inner or outer); Px_i is the acid extracted P in the section i (mg P kg^{-1}) of the relevant treatment; Pc is the measured P in the in the control treatment (mg P kg^{-1}); W_i is the weight of soil in section i (kg); and $Pfert$ is the sum of the amount of P recovered in the inner and outer section (mg).

The percentage of labile P in each section relative to the added P was calculated as:

$$Plab_i = 100 \cdot \frac{(E_i - Ec) \cdot W_i}{Padd} \qquad [3]$$

where $Plab_i$ is the percentage of added P in section i which remained in the labile form (isotopically exchangeable); $Padd$ is the amount of P added (mg); E_i is the E value in section i; and Ec that of the control soil (mg). The amount of labile P was divided by the added P rather than recovered P to avoid the variation imposed by recovery variations in the acid extraction.

The percentage of labile P relative to amount of P released in soil (*Plab.rel*) was calculated as:

$$Plab.rel = 100 \cdot \frac{\sum_{i=1}^{n} (E_i - Ec) \cdot W}{Padd - Pgr} \qquad [4]$$

where Pgr is the amount of P recovered in the granule after incubation (mg).

11.4 Plant growth and phosphorus uptake

11.4.1 Soils preparation

In the pot trial, wheat (*Triticum aestivum* cv. Axe) was grown on the Kingaroy (oxidic) and Black Point (high-Ca) soils using the same controlled-release fertilizers as in the incubation experiment. A treatment with uncoated MAP was included as a positive control and a treatment without P as a negative control.

The soils were air dried and sieved to < 4 mm. In order to measure the contribution of fertilizers to P uptake, an indirect isotopic labeling technique was used (Frossard et al., 2011).

The soils were labeled with carrier-free ^{33}P at a rate of 150 kBq kg^{-1} of dry soil using a hand sprayer and were well homogenized. After mixing in the isotope, the soil was left to equilibrate for 11 days inside a sealed plastic bag. After the incubation, plastic-lined pots were filled with soil equivalent to 2 kg air dry soil.

11.4.2 Treatment application and plant growth

Fertilizer granules were placed in five equidistant holes six cm below the soil surface. These holes were partially filled with soil and sowed with three wheat seeds per hole at two cm depth. Basal fertilization was applied on soil surface in both soils at rates of 60, 50, 100, 14, 12, 8, and 1 mg kg^{-1} of N, K, Mg, Zn, Mn, Cu and B respectively. From using sulphate salts, the dose of S was 180 mg kg^{-1}. In the 3rd and 4th week after sowing, an additional 50 mg of K and N kg^{-1} were supplied in each application so the total dose of N was 160 mg kg^{-1}. An additional 4.2 mg N kg^{-1} was supplied to the control treatment, to balance the N supplied with the P from MAP. Differences in N availability due to controlled release of N in the coated MAP was considered negligent due to the small quantity supplied through MAP. Fertilizer treatments were applied at a rate of 35 mg P kg^{-1}. This rate was chosen based on previous P-response trials in both soil where this rate was 60 and 77% of maximum plant response for Kingaroy and Black Point respectively.

Soil moisture was kept at 80% of field capacity (-10 kPa) using deionized water. Plants were grown in a constant environment room at a temperature of 23ºC at day and 15°C at night in a 12 h day/night cycle at 65% of relative humidity under a photosynthetic photon flux density of 210 µmol m^{-2} s^{-1}. Ten days after fertilizer addition, plants were thinned to one plant per position, resulting in 5 plants per pot. Wheat seeds ($\cong$ 31 mg each) used in this experiment were analyzed to account for P contribution, which was found to be 106 ± 5 µg P $seed^{-1}$.

11.4.3 Plant analysis

One plant per pot was harvested at 21, 33, 45, 57 and 70 days after sowing and MAP application, matching the times of the P visualization analysis in the incubation trial. When plants were heterogeneous, the smallest plant per pot was harvested. The plant material was dried, weighted, ground and digested using a mixture of HNO_3 and H_2O_2 (Wheal et al., 2011). Digestion extracts were diluted and centrifuged for P quantification by ICP-OES. For determination of ^{33}P activity, 4 mL of the diluted plant extract was transferred into a scintillation vial and mixed with 16 mL of liquid scintillation cocktail (OptiPhase HiSafe 3, PerkingElmer). The activity was measured in a liquid scintillation analyzer (Tri-Carb 3110 TR, PerkingElmer). All ^{33}P counts were corrected for dilutions and radioactivity decay.

The percentage of P derived from MAP was calculated as follows (adapted from Frossard et al., 2011):

$$\%P_{dff} = 100 \cdot (1 - SA / SA_c) \quad [5]$$

where: $\%P_{dff}$ is the percentage of P in the plant that is derived from the fertilizer, *SA* is the specific activity of the plant grown in presence of a fertilizer tratment (Bq mg^{-1} P); and *SAc* is the specific activity of the plant grown in in absence of the P fertilizer (Bq mg^{-1} P). Specific activity is the ratio between the amount of radioactive P recovered in the plant and the amount of P taken up by the plant.

11.5 Data analysis

In the incubation experiment, the design was a completely randomized factorial scheme of 3 soils × 5 fertilizer treatments. For the visualization method, there were 9 repeated measurements in time. The statistical modelling was performed using a linear mixed-effects model (Zuur et al., 2009). This model was used to appropriately address the covariance in repeated measures of visualization and special dependence in sections of Petri dish in P distribution and lability. The heteroscedasticity and normality assumptions were not met therefore a variance structure was used.

In the plant growth experiment, the design was randomized blocks in a factorial scheme of 2 soils × 5 fertilizers in 5 replications with 5 repeated measurements in time. Dry mass yield was log transformed and percentage of P derived from fertilizer was transformed to $\arcsin(x^4/100)$ to normalize residuals.

Model validation and assumptions were tested using graphical and numerical tools. Pairwise comparisons of coated treatments with unc-MAP were performed using Dunnett-style contrasts. For those procedures the packages nlme (Pinheiro et al., 2016) and lsmeans (Lenth, 2016) were used in R environment (R Core Team, 2016).

12 RESULTS

12.1 Incubation

12.1.1 Visualization of P diffusion from MAP granule

For the unc-MAP treatment, the diffusion radius increased quickly within the first 24 h after which there was little change in the Black Point and Kingaroy soils (Fig. 2). This is usually seen with soluble P fertilizers in strongly sorbing soils and can be explained by initially fast diffusion because the sorption sites are oversaturated followed by slow diffusion as adsorption and fixation comes into play. In Monarto, the Rdiff was higher than the other soils and increased up to 21 days, which can be explained by the weaker sorption in that soil. For the coated MAP, the increase in the diffusion zone was slower and more gradual.

< Figure 2 >

To estimate the release of P from the coated granule under soil conditions, the amount of “fertilized soil” in the coated and uncoated MAP was compared, using the same approach as used to estimate P release from struvite fertilizer (Degryse et al., 2017):

$$\%\text{Released} = 100 \cdot \frac{A}{A_{\text{unc-MAP}}} \tag{5}$$

where A and $A_{\text{unc-MAP}}$ are the area of the high-P diffusion zone for the coated MAP treatment and uncoated MAP treatment respectively. For a given coated MAP, the estimated release over time was similar for the three soils (Fig. 3). For the 209d-MAP fertilizer, a lag phase was observed with no release before day 7. This lag phase likely corresponds to the time necessary for water do penetrate the coating and trigger the release process under soil conditions. This lag phase was not observed in water incubation, but otherwise, the release in water corresponded quite well with the estimated release under soil conditions (Fig. 3).

< Figure 3 >

12.1.2 Distribution of fertilizer phosphorus

After 70 days of incubation, the residual MAP granules were collected and the soil was sampled in two sections and analyzed to account for the amount of P released. As to be expected, the amount of P remaining in the granule increased as the time to release the fertilizer increased (Fig. 4). For the uncoated MAP, 9% of added P was still left in the granule, which can likely be attributed to insoluble P impurities in the MAP. For the 37d-MAP, the P left in granule was accounted for 19.9% of the added P. For the 209d-MAP, about 85% of the P was still left in the fertilizer.

The total recovery of the added P across the two soil sections and the granule ranged from 79 to 101%, with an average of 89%. Due to differences in recoveries among treatments, the data was scaled to 100% for easier interpretation. For the inner soil section, differences were found among unc-MAP, 7d-MAP and 37d-MAP with significantly lower values for 209d-MAP in all soils (Fig. 4). The average P recovery in the inner section was much lower for Monarto soil due to its high diffusion potential which allowed P to diffuse into outer section. In the Kingaroy soil, P recoveries in the inner circle were the highest. This decreasing order of diffusion was also observed using the visualization technique for P diffusion as shown above. A high content of fertilizer P was found in the soil < 7 mm from granule, 1380 mg P kg^{-1} for Kingaroy, 976 mg P kg^{-1} for Black Point and 267 mg P kg^{-1} for Monarto, reflecting the different sorption capacities of these soils. As the soil section close to granule is near P sorption saturation, except for 209d-MAP, there were only small differences between fertilizer treatments for the inner section. Differences in P release between fertilizer are more likely to be observed in the outer section.

< Figure 4 >

The P distribution in soil was in good agreement with the P diffusion visualization. The sequence of diffusion in soils is in agreement with adsorption capacity of the soils, ranging Kingaroy > Black Point > Monarto (see Freundlich parameter k in Table 1). There was a consistent decrease in the fraction of P in the outer section and increase in fraction of P still in the granule with slower release rates.

12.1.3 Lability of fertilizer P

Values for labile P in the outer section of 209d-MAP in Kingaroy and Black Point were very close to control, with overlapping standard errors. As a result, zero and negative values for percentage of recovered P were obtained when applying Eq. [3], therefore values for these treatments were considered to be below quantification limit.

The amount of labile P was compared both to total added P (Eq. 3) and to the amount of P released from the granule (Eq. 4). Since the former equation considers all P applied with the fertilizers, the result indicates the overall capacity of fertilizer to supply P to plants within the experiment time period (70 d). The latter equation only considers released P and the results hence reflect the reaction of soil with the released P. None of the coated fertilizer treatments increased the amount of labile P (as % of added) in soil over the unc-MAP (Table

2). The 37d-MAP treatment had lower labile P than unc-MAP in Black Point and did not differ in Kingaroy (p = 0.12), while much lower added labile P for 209d-MAP was observed in all soils, which can be explained by much of the P still being retained in the granule (Figure 4). However, when only the P released from granule is considered, the treatment 37d-MAP in Kingaroy and 7d-MAP in Monarto increased significantly the P lability over unc-MAP (p = 0.03 and 0.01). These results suggest lower fixation of the released P in those treatments and therefore a potential to increase P lability through use of controlled release phosphate.

< Table 2 >

12.2 Plant growth

12.2.1 Dry mass yield

There was no significant difference in dry mass yield between soils, so the average values for both soils is used for discussion. There was a significant difference in DMY between fertilizer treatments at all sampling times. The unc-MAP treatment had a significantly higher yield at the first two harvest times (21 and 33 days after sowing). However, at the later sampling times, the 7d and 37d controlled release treatments caught up with the unc-MAP. There was no difference in yield between the 7d-MAP and unc-MAP from day 45 onwards, and no difference between 37d-MAP and unc-MAP in the last harvest at day 70 (Fig. 5).

< Figure 5 >

The treatment 209d-MAP did not differ from the control in the two first harvests. This fertilizer treatment was severely P deficient due to a lag-phase in release, followed by a slow initial release rate as indicated by the P diffusion assay (Fig. 2). In this treatment, plant growth was higher than the control only at the day 57 and day 70 harvests.

From the plant growth experiment, the overall observation is that controlled release rates of P led to slower initial plant development. Nevertheless, except for the 209d-MAP, plants grown with controlled release P formulations were still able to achieve similar DMY as those grown with unc-MAP by the end of the 70-d pot trial. This is in very good agreement with the incubation experiment, where similar amounts of labile P were found for the unc-MAP, 7d-MAP and 37d-MAP treatments, but much lower amounts for the 209d-MAP due to little release.

12.2.2 Uptake of P derived from fertilizer

The contribution of P derived from fertilizer (Pdff) to the total plant P uptake was high in both soils (ratio of Fertilizer P to total P content, Fig 6). Excluding the 209d-MAP, the contribution of Pdff ranged from 86 to 91% at day 21, increasing to 91-94% of Pdff at day 70 in the Black Point soil. For Kingaroy, the Pdff was between 56 to 65% on day 21 and increased to 89-93% at day 70. The lowest percentage of Pdff was for the 209d-MAP treatment, with values ranging from ~25 to 70%.

The treatment 7d-MAP had similar uptake of fertilizer P as the unc-MAP in all soils and at all sampling dates (Fig. 6). In the Black Point soil, the 37d-MAP treatment had a lower uptake of fertilizer P than unc-MAP only at the first sampling date, but there was no difference at the later sampling dates. In the Kingaroy soil, the uptake of fertilizer P was lower for 37d-MAP than unc-MAP at the two first sampling dates. However, the 37d-MAP treatment showed a 13% higher P uptake than unc-MAP at day 57 and a 56% higher uptake than unc-MAP at the last harvest (day 70). The 209d-MAP treatment showed little fertilizer P uptake (Fig. 6), with the uptake significantly lower than the reference unc-MAP in all soils and sampling dates.

In most cases (17 out of 20), there was higher uptake of P derived from fertilizers in Black Point than in Kingaroy. This is probably due the higher sorption potential of Kingaroy, as also indicated by the k parameter from the sorption isotherm and the higher P dose needed to obtain maximum yield as observed in preliminary experiments (data not shown). The only case with significantly higher P uptake in Kingaroy than Black Point was for the 37d-MAP at day 70.

< Figure 6 >

13 DISCUSSION

13.1 Agreement between release in soil and solution

Three coated MAP were included for this study, with release times in water determined to be 7d, 37d and 209d. By comparing the high P diffusion zone around the coated MAP granule with that around an uncoated granule, we estimated the release from the granule over time in soil. The estimated release in time corresponded quite well with the release rate determined in water (Fig. 3), indicating that a release test in water can be used to predict the release behavior under soil conditions. This agrees with literature results for polymer-coated urea, which generally have found a good correspondence between the urea release rate in water or in soil (e.g. Salman et al., 1989), as the nutrient release through a polymer membrane is not significantly affected by soil properties (Trenkel, 2010). This contrasts with the behavior of slow-release fertilizer based on sparingly soluble compounds such as struvite. For low-solubility P compounds, the solubility in water does not indicate their release rate in soil, as the rate of dissolution is strongly affected by soil properties, such as pH and P buffering capacity (Cabeza et al., 2011; Degryse et al., 2017).

13.2 Agreement between soil incubation and plant growth

We evaluated the release, diffusion, lability and availability to plants using batch, incubation and pot trial experiments. The results of these independent experiments were in good agreement. Reducing the release rate of MAP resulted in a slower increase of the high P zone around the granule. Once the P of the coated MAP was released to the same extent as uncoated MAP, the P diffusion radius was the same. Sampling and chemical analysis at the end of the incubation experiment confirmed that the coated MAP samples reached the same P distribution around the granule when the P was quasi fully released from the granule, which was the case for the 7d- and 37d-MAP. The much slower release for the 209d-MAP resulted in a smaller high-P zone and lower P concentrations around the granule. The lability measurements indicated that the controlled release of the 37d-MAP had resulted in slightly less fixation and hence higher lability than for uncoated MAP in the Kingaroy soil. The 37d-MAP treatment in the Kingaroy soil showed a higher P uptake than the uncoated treatment. This higher P uptake however, did not turn into a higher dry mass production. This was probably due to limited initial plant development caused by P deficiency in the first couple of weeks.

13.3 Effect of coatings on fixation and availability

No evidence was found of reduction in P fixation or increase in P uptake in the high Ca soil Black Point. It is known that in this type of soil significant losses can occur by Ca-P precipitation. This process occurs due to influx of high Ca soil solution into the hygroscopic granule which results in oversaturation and precipitation of Ca-P compounds (Lombi et al., 2005, 2006). Since the polymer coating could limit the influx of Ca into the granule, we believed the fertilizer coating might result in less P precipitation and hence have a beneficial effect on P availability. However, evidence of such effect was not observed since the coated MAP products did not outperform unc-MAP in Black Point, or even performed worse in case of the fertilizer with slowest release. This suggests that precipitation still occurred to the same extent, likely in the soil surrounding the granule.

Little effect of controlled release P treatments was expected for the Monarto soil. In this soil, the adsorption capacity is low as indicated by the low clay content and Fe_{ox} and Al_{ox} which also indicates a limited extent of slow sorption reactions. Therefore, P was maintained in a labile form and had higher diffusion with low binding energy sorption as dominating process. There was a 6% increase in the labile fraction of released P for treatment 7d-MAP in this soil, which is of small magnitude. This soil was not included in the pot trial, as there was little reason to expect a beneficial effect of coating on P availability.

For Kingaroy, the amount of labile P was not significantly increased due to non-released P within the granule (lock-off effect, discussed further); however, the increase of 7.9% in labile P relative to released P in 37d-MAP demonstrates a reduction in fixation of the released P. Additionally, in this same treatment, the plant P uptake was considerably higher than for the unc-MAP treatment at day 70 (Figure 6). This is likely result of the shorter contact time between P release in soil and active plant uptake, demonstrating the effect of improved synchrony between supply and demand. Similar results with higher plant growth or P uptake than soluble phosphate have also been observed using partially acidulated phosphate rock (PAPR) in acidic soils (McLean and Logan, 1970). These authors also observed that the higher the fixation potential of soils the higher was the response to PAPR, which can be considered one form of slow release P. However, in our experiment, the higher P uptake did not translate in higher yield. We hypothesize that this is due to the lower P availability at the start for the 37-d MAP treatment, which resulted in initially slower growth. A combination of unc-MAP, to ensure sufficient P at the start, with 37-d MAP, to still supply P later on, might potentially result in a yield benefit over unc-MAP, but this remains to be proven.

The Kingaroy soil has a high clay, Fe_{ox} and Al_{ox} content and therefore a highly amorphous surface, which was found to be correlated with the rate of the slow P reactions (Torrent et al., 1992). Therefore we believe that Kingaroy would have a high rate of slow P reaction when compared to other soils and therefore positive response to controlled release P are more likely in this type of soil. Additionally, high responses are necessary to make the use of high-cost polymer-coated fertilizers economically feasible. Given that only small responses were obtained in a controlled release P responsive soil, we believe that controlled release phosphate may not significantly enhance P use efficiency for annual crops.

13.4 Lock-off effect

Lock-off effect refers to the amount of nutrient that is not released from the fertilizer during the active uptake time by the current crop cycle (Shaviv, 2001; Trenkel, 2010) and therefore is agronomically ineffective during that cycle. We observed that after reaction with soil around 9% of the P from unc-MAP remains in the soil as insoluble P forms or soil-fertilizer reaction products. However, due to the coating barrier, a higher P content was found inside granules with a clear increase of "locked-in P" as the release rate decreases (Fig. 4). It can happen when the fertilizer longevity is inappropriate for the crop growth cycle, such as the treatment 209d-MAP. At the end of active plant uptake this treatment contained most of its P while still in the period of linear release. It is also a case of lock-off when a fraction of the granules release the nutrient at a significantly longer longevity than the average of the bulk of granules.

To potentially reduce P fixation, the P release rate should be sufficiently low; however, this increases the risk of P still being locked in the granule, and hence ineffective, at the end of the crop season. In contrast, faster release rates, as for the 7d-MAP fertilizer used in this study, reduce the risk of lock-off, but may not bring about any benefits on fixation or uptake. The locked-in P is undesirable as it reduces the fertilizer economic cost effectiveness, nutrient use efficiency and increase chances of environmental contamination (Shaviv, 2001). The locked-in P could harm the environment because P-containing granules could be carried away in runoff water into water bodies and contribute to eutrophication.

13.5 Comparison with other literature results

Results from other authors studying coated MAP corroborate our results in some points. Pauly et al. (2002) also observed limited growth in early development stages using coated MAP. However, at 45 days of growth, higher DMY was obtained for one coated MAP treatment. These authors also did not observe differences in release rates between different soils. However, they found a much more pronounced and consistent increase in barley growth using coated vs uncoated MAP in three soils. They also tested coated DAP, but did not find any consistent improvement in barley yield. García et al. (1997) evaluated coated TSP and DAP against their uncoated controls in two highly calcareous soils (> 40% $CaCO_3$) where large losses though Ca-P are reported. No increase in ryegrass DMY was observed. This result is in agreement with our observations, as we also did not find any increase in DMY or P uptake for the coated fertilizers in the calcareous soil.

13.6 Agronomic benefit of coatings for P vs N

It has clearly been shown in the literature that controlled release N can have substantial agronomical and environmental benefits (Shaviv, 2001); yet, little is known about controlled release P. This study suggests that the agronomic benefits for P are small at best. The difference between the two elements can be related to their chemistry in soil. For N, the main losses are leaching, volatilization and denitrification. Controlled release may reduce these losses by: (1) better synchronization between plant demand and supply; (2) reducing urea content in soil and hence limiting the pH rise around the granule and hence volatilization; (3) allowing time for urea to be incorporated into the soil through rainfall action, hence also decreasing volatilization; (4) reducing ammonia toxicity and salinity to seedlings; (5) reducing leaching. Among these effects, only the synchrony between supply and demand is important for P fertilizers. Leaching is generally not relevant for P, except in a limited range of soil and climate conditions in which case controlled release P may potentially be more beneficial.

For P, in general there are not much actual losses (i.e. P does not get lost from the root zone compartment), but only a reduction in availability over time due to fixation. When recovery of P is calculated over many years, in most cases high recoveries are obtained since P is not irreversibly sorbed (Barrow, 2015). Therefore even when P is not taken up in the first days or seasons, it can be taken up later. Johnston and Seyers (2009) argued that for most soil near the critical level of P, the replacement of the removed P each year from the harvested crop usually has recoveries higher than 90% if measured by the balance method. Therefore, the only mechanism to increase fertilizer performance is to reduce “true P fixation” (P locked up in precipitates or oxides). Evidence of a reduction in P fixation was observed in treatment 37d-MAP in Kingaroy, for which also higher P uptake was observed, but the overall effect was limited. Therefore, in contrast to N, our results suggest that controlled release P has limited potential benefit, as it is expected to only increase P availability in (i) strongly P-fixing soils with low P status and (ii) very sandy soils in high-rainfall environments for which P leaching is an issue.

13.7 Environmental aspects

Although the potential agronomic benefits of controlled-release N fertilizer have been well reported in literature, there are also many studies that did not find any agronomic benefit of controlled release N, which may be related to soil and weather conditions (Chen et al., 2008; Thapa et al., 2016; Cancellier et al., 2016). However, even when there is no agronomic response, several environmental advantages are observed which justifies their use. Most likely, controlled released P would also have environmental benefits. It would potentially reduce the risk of contamination of water bodies through P runoff and through P leaching in coarse-textured soils (Lewis et al., 1987; Hart et al., 2004; Entry and Sojka, 2010; McLaughlin et al., 2011). Nevertheless, the use of these coatings either for environmental advantages or limited agronomic benefits is likely to be limited by their high cost, as also has been the case for polymer-coated N fertilizers. Their future adoption will highly depend on the value of crops and environmental contamination vulnerability (Chalk et al., 2015), as well as public policies to promote the use of such products.

13.8 Future research

The benefit of controlled release P relies on the shorter contact of fertilizers with soil and plant uptake. This effect could be observed in relatively short contact times, as in 37d-MAP with 70 days incubation. Therefore, it is probable that greater benefit of coated over uncoated will be observed for longer contact time and longevities, which would likely be appropriate for fertilization of perennial crops. This hypothesis is yet to be tested and is recommended as future research. In our experiment, the plant development in early growth stages was severely limited by P deficiency for the 37-d MAP treatment, but the plants were still able to achieve the same plant yield and higher P uptake, despite the initial nutritional stress. Therefore, we also believe that using a “starter” P rate by addition of uncoated MAP may provide enough P for initial development and allow higher growth and P uptake in the coated MAP treatments. This alternative treatment is also recommended for further testing. Today, the high cost of coating is still one of the biggest limitations for adoption of controlled release N fertilizers. Even if higher P use efficiency or reduction in environmental impact is demonstrated, the cost will likely still limit the use of polymer coated P. Hence, it is essential to develop low cost and environmentally friendly coatings to turn controlled release P into an affordable alternative to soluble P sources.

14 CONCLUSIONS

The lower release rate of polymer coated MAP was verified and demonstrated. Release rates too slow, such as 209d-MAP, have the burden of keeping P unavailable as lock-off effect, which reduces agronomic, environmental and economic effectiveness of this fertilizer. On the other hand, the fertilizer with negligible lock-off effect released the P too fast and therefore did not increase P uptake.

Good agreement was observed between the incubation and plant growth experiment. The controlled release fertilizer did not decrease sorption or increase uptake in the high Ca soil. In the Oxisol, the full substitution of soluble P fertilizer at sowing in P deficient soil by controlled release P was not an efficient fertilization strategy, however, an appropriate release rate did reduce P fixation and increase P uptake. Although reduction in fixation was observed to a limited extend, the increase in P uptake was substantial. It evidences that it is possible to improve P use efficiency by controlled release MAP.

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17 TABLES

Table 1. Attributes of selected soils for evaluation of controlled release MAP.

Soil location	pH	Organic C	Ca	HCO_3-P†	Total P	Fe_{ox}	Al_{ox}	CEC	Clay	FC‡	Freundlich k§	Freundlich n
	(H_2O)	g kg^{-1}	$cmol_c$ kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	$cmol_c$ kg^{-1}	g kg^{-1}	g g^{-1}	mg^{1-n} kg^{-1} L^n	
Black Point	7.06	13.5	9.3	4.2	85	580	1115	16.3	198	0.20	96.8	0.432
Kingaroy	5.53	11.8	5.2	11.7	310	2560	2350	17.2	626	0.30	424	0.261
Monarto	6.35	8.4	3	4.0	107	236	345	6.2	75.7	0.12	19.6	0.518

†Colwell P; ‡ moisture content at field capacity (-10 kPa); §Freundlich equation: $s = kc^n$ with s in mg kg^{-1} for s and c in mg L^{-1}). Al_{ox}, Fe_{ox}: ammonium oxalate extractable Al and Fe. Total P, Fe_{ox} and Al_{ox} were obtained from previously published work by Degryse and McLaughlin (2014) using these soils.

Table 2. Isotopically exchangeable soil P (Labile P) after 70 days of incubation of controlled release phosphate fertilizers. Inner section is the soil up to 7 mm from granule and outer section is the soil > 7 mm of distance from granule.

Soil	Fertilizer	Labile P			
		Inner	Outer	Total	Total
		% of added P†			% of released P‡
Black point	unc-MAP	20.7	16.1	36.7	40.5
	7d-MAP	20.7	13.3	34.1	38.7
	37d-MAP	23.4	5.8*	29.2*	34.3
	209d-MAP	4.7*	<LQ[§]	4.7*	31*
Kingaroy	unc-MAP	24.8	6	30.8	34.2
	7d-MAP	23.5	8.6	32.1	36.3
	37d-MAP	25.6	8.9	34.5	44.2*
	209d-MAP	6.2*	<LQ	6.2*	33.6
Monarto	unc-MAP	5.9	37.5	43.4	47.1
	7d-MAP	6.3	39.1	45.5	53.1*
	37d-MAP	6.6	34.1*	40.7	51.3
	209d-MAP	1.6*	0.7*	2.3*	18.0*

†normalized by the amount of P added through the granule per Petri dish. ‡ normalized by amount of P released from granules. [§]lower than limit of quantification. * statistically different from unc-MAP at 5% of significance in Dunnet-style contrast.

18 FIGURES

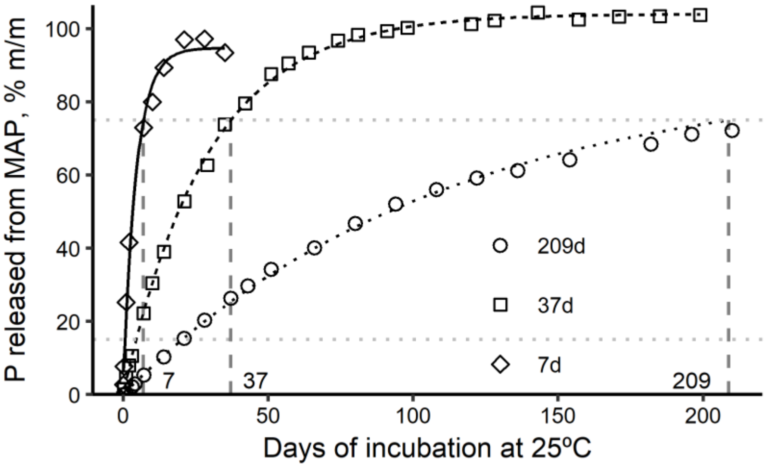

Figure 1. Phosphorus release curve from coated MAP incubated in water at 25ºC. Numbers represent the longevity of coated MAP in days. Models were fitted to first order kinetics y = y_0 + a - exp(-kt). The time to reach 75% release is indicated on the x-axis.

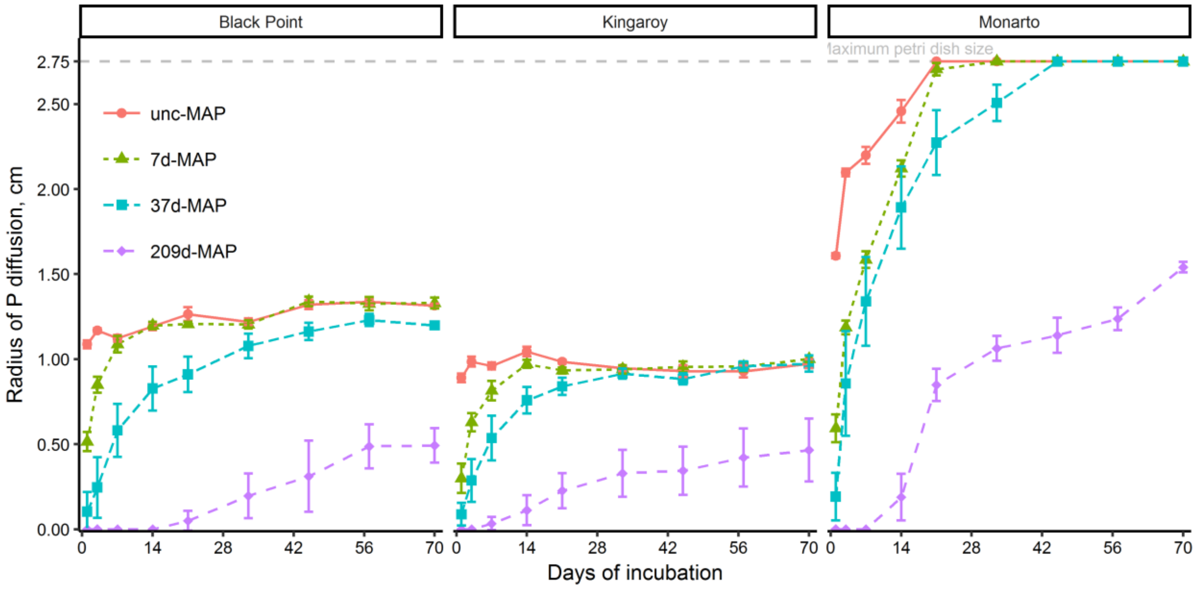

Figure 2. Radius of P diffusion from granules of controlled release P in Petri dish incubated soils. Maximum radius was 2.75 cm corresponding to Petri dish size therefore values of 2.75 should be interpreted as > 2.75 cm. Error bars represent standard error (SE), n = 4 for MAP and 5 for others.

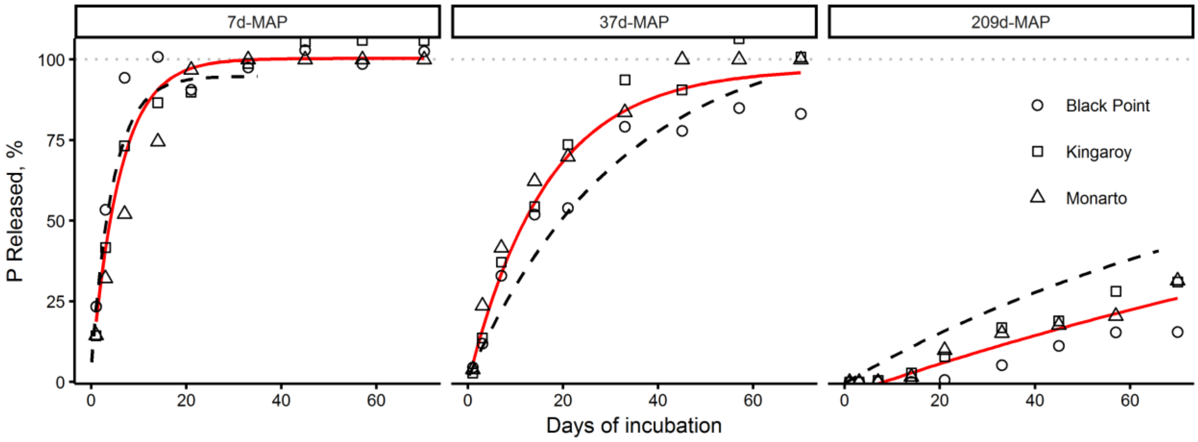

Figure 3. Phosphorus release from the coated MAP granules as a function of time in water and in the 3 soils (symbols). The release in soil was estimated from the high P zone around the granule in comparison to that around an uncoated granule. The red line shows the estimated release in soil (first-order release curve fitted to the data of all three soils) and the dashed black line the release in water.

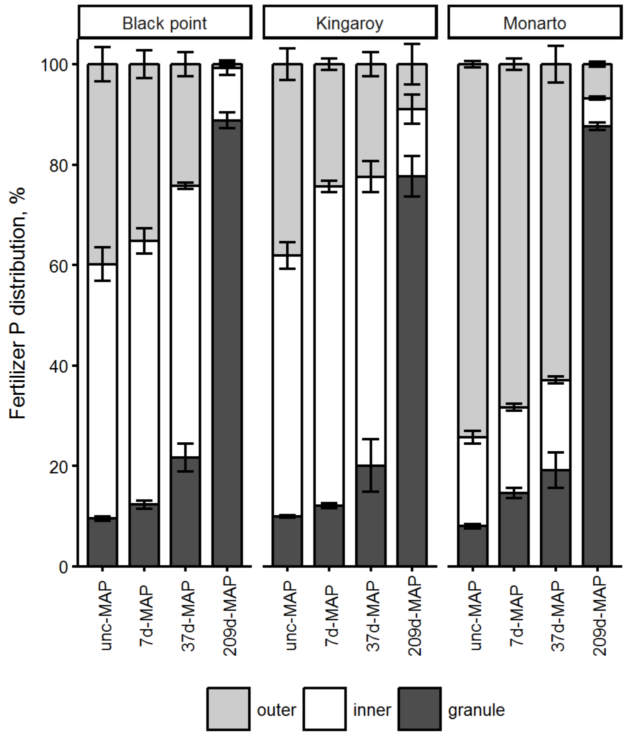

Figure 4. Distribution of P added by MAP and from controlled release MAP after 70 d of incubation in different soils. Added P was obtained by strong acid extraction of soil P (Eq.[2]) or cold digestion of granules. Inner section is the soil up to 7 mm from granule and outer section is the soil > 7 mm of distance from granule. Error bars represent SE of each individual section calculated after scaling to 100%, n = 4 for unc-MAP and 5 for others.

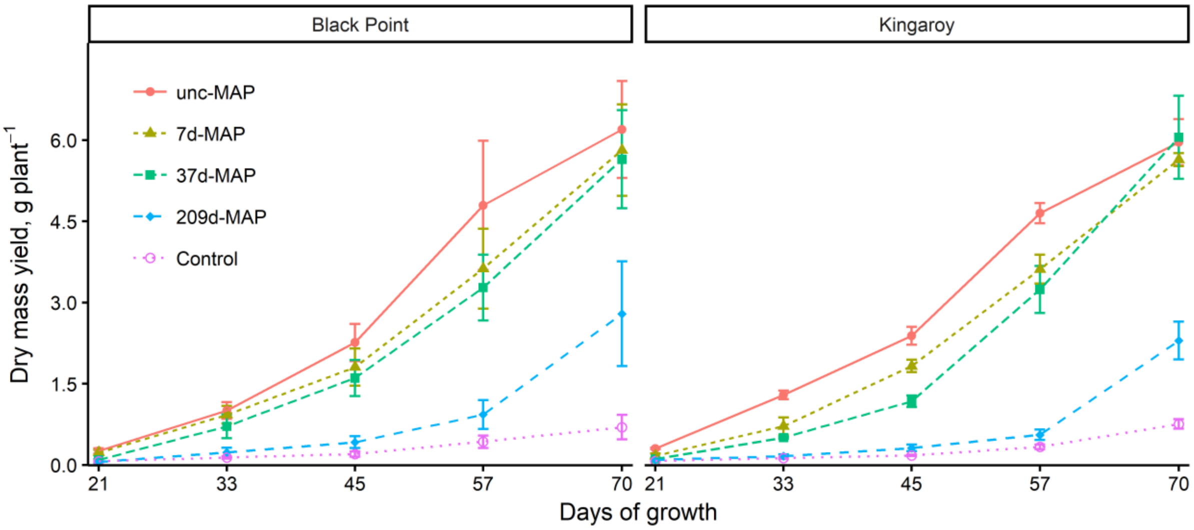

Figure 5. Dry mass yield of wheat plants grown with increasing P release rates from controlled released MAP in two contrasting soils. Error bars represent SE, *n* = 5.

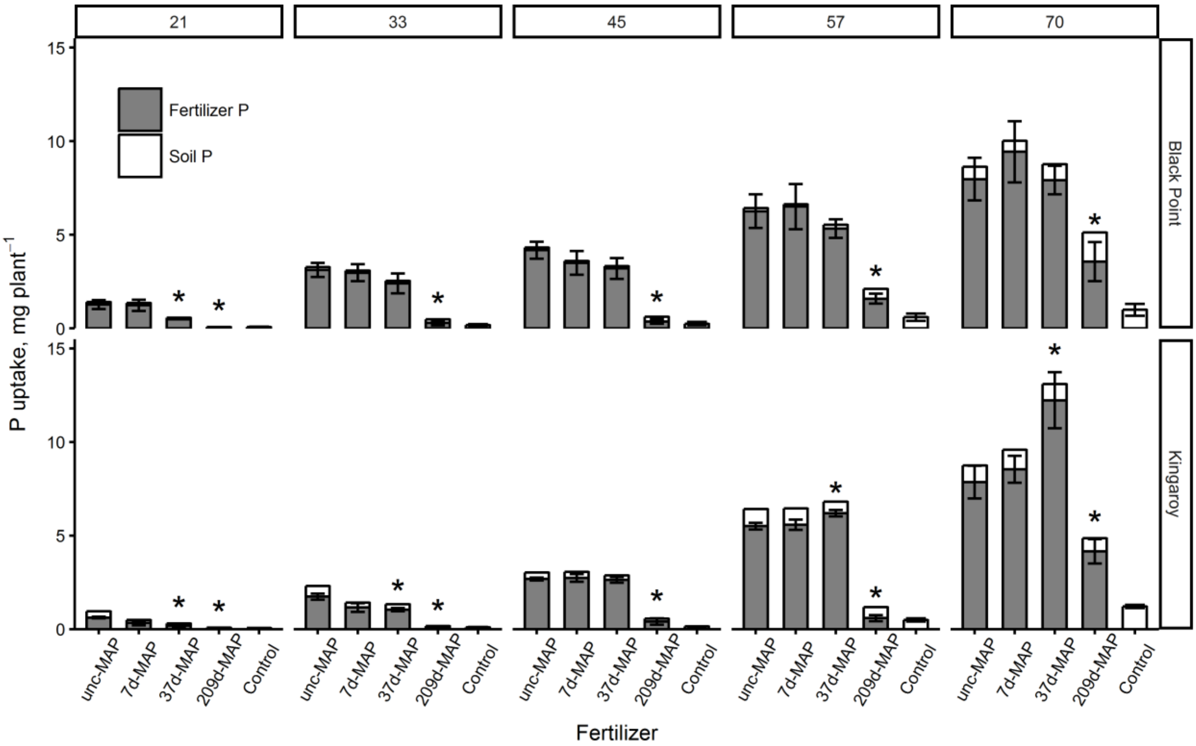

Figure 6. Phosphorus uptake from soil and fertilizer by wheat grown in a high Ca soil (Black Point, top) or an Oxisol (Kingaroy, bottom) at different harvest times for the different fertilizer treatments: uncoated MAP (unc-MAP), coated MAP with various release rates or no P fertilizer (control). * represents a significant difference ($p<0.05$) in fertilizer P uptake from the unc-MAP treatment within the same sampling date. Error bars represent SE of P derived from fertilizer, *n* = 5.