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UNIVERSITY OF ALBERTA

DEVELOPING THE CONCEPT OF CONTROLLED-RELEASE PHOSPHORUS FERTILIZER

BY

DONALD G. PAULY ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE**

IN

SOIL FERTILITY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

FALL, 1995

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled DEVELOPING THE CONCEPT OF CONTROLLED-RELEASE PHOSPHORUS FERTILIZER submitted by DONALD G. PAULY in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in SOIL FERTILITY.

M. Nyborg
M. Nyborg (Supervisor)

J. A. Robertson

John Hoddinott
J. Hoddinott

T. L. Roberts

Date: August 28, 1995

To Kelly, best friend and life's partner, for love, support, shared dreams, and a happy home, and to Karis for the joy and privilege of being "Dad".

ABSTRACT

The potential benefit of controlled-release phosphorus (P) lies in the incongruity between the availability of applied P fertilizer and plant demand for P; the availability of applied P decreases as plant demand for P increases. The validity of the controlled-release P fertilizer concept was established in a series of greenhouse experiments. Phosphorus solutions applied to the rooting zone of barley every second day or every eleventh day for 44 days, as a simulation of controlled-release P fertilizer, increased P uptake by barley relative to applying all P at sowing (Chapter 2). In a second experiment, P uptake by barley after 45 days was higher with commercial 12-51-0 (MAP) with a thin (1.8% by mass) polymer coating than uncoated MAP (Chapter 3). Apparent fertilizer efficiency with this thin coating was nearly double that of the uncoated MAP. In a third experiment, barley head and total dry matter yield at 90 days were higher when P (31.4 mg P pot^{-1}) was supplied by controlled-release products (thin and thick [2.2% by mass] polymer coating, and shrink-wrap coating [with four pin-holes]) than by uncoated MAP (Chapter 4). Plant harvests at 30, 60, and 90 days indicated that P uptake subsequent to the 30 day harvest increased barley head and total dry matter yield. The pattern of barley dry matter accumulation and P uptake, as well as *in situ* P release characteristics from polymer-coated MAP over 52 days were determined in a fourth experiment (Chapter 5). Phosphorus release was nearly complete within 26 days with the thin coating, and was about 80% complete after 52 days with the thick coating. Barley dry matter yield and P uptake after 13 days were higher with uncoated MAP than with either thin or thick-coated P, but after 52 days controlled-release P sources had greater (thin coating) or similar (thick coating) P uptake and dry matter yield as uncoated P. Controlled-release P sources were found to be capable of supplying growing plants with P when conventional P sources could not, validating the concept of controlled-release P fertilizer.

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CHAPTER 1

PHOSPHORUS FERTILIZER UPTAKE AND EFFICIENCY

1.1 INTRODUCTION

Many soils in western Canada continue to be responsive to phosphorus (P) application even after years of fertilization (McKenzie *et al*, 1994). From a farm perspective, P fertilization is therefore often an economically justifiable cost of production. In spite of the continued importance of P for crop production in western Canada, agronomic research related to P nutrition and fertilization has diminished in recent years. Apparently, both research funders and researchers tended to consider that the knowledge relating to P was reasonably complete for farming situations in western Canada and that anticipated gains from additional research would be small relative to the research investment. However, the recent research by McKenzie *et al* (1994) indicated that the knowledge relating to P may not be as complete as perceived.

1.2 PHOSPHORUS FERTILIZER REACTION PRODUCTS

Phosphorus fertilizer, when applied to soil as a dry granule, draws soil water towards itself by osmotic pressure (Khasawneh *et al*, 1974). The dry granule attracts enough water to become dissolved in a saturated solution (Lindsay, 1979) which can then diffuse away from the application site, contacting and reacting with the soil solution and soil solids as it moves.

The characteristics of the saturated fertilizer solution and the subsequent reactions with soil are dependent upon the original fertilizer source and soil properties. Common fertilizer products and some characteristics of their saturated solutions are given in Table 1.1. Triple super phosphate (TSP) and monoammonium phosphate (MAP) produce solutions that are strongly acidic and capable of dissolving soil solids. In saturated solutions, the phosphate is accompanied by calcium or ammonium ion(s) which can exchange with ions held on the cation exchange complex of the soil. Although diammonium phosphate (DAP), MAP, and TSP have been used in western Canada, MAP is by far the most commonly used form of P fertilizer.

Table 1.1 Saturated solutions of common phosphate fertilizers†

Fertilizer	pH	P (moles L^{-1})	Accompanying Cation	Cation Concentration (moles L^{-1})
$Ca(H_2PO_4)\cdot 2H_2O$ (TSP)	1.48	3.98	Ca^{++}	1.44
$NH_4H_2PO_4$ (MAP)	3.47	2.87	NH_4^+	2.87
$(NH_4)_2HPO_4$ (DAP)	7.98	3.82	NH_4^+	7.64

†from Lindsay *et al*, 1962

Numerous researchers have attempted to identify the reaction products of P fertilization. When MAP or DAP is the source of P, calcium and or magnesium phosphate precipitates usually form (Lindsay *et al*, 1962; Racz and Soper, 1967; Bell and Black, 1970b; Messier, 1990). Magnesium phosphates are most likely to form on alkaline soils containing carbonates of calcium and magnesium, especially when P is applied as DAP (Bell and Black, 1970b; Racz and Soper, 1967). It is estimated that when the ratio of water soluble calcium to magnesium is 1.5:1 or higher, calcium phosphate precipitates form, and when the ratio is less than 1.5:1, magnesium phosphate precipitates form (Racz and Soper, 1967). Brushite ($CaHPO_4\cdot 2H_2O$), which is also known as dibasic calcium phosphate dihydrate or dicalcium phosphate dihydrate (DCPD), is one of the most widely identified P fertilization reaction products (Lindsay *et al*, 1962; Racz and Soper, 1967; Bell and Black, 1970b; Messier, 1990). In some western Canadian soils octacalcium phosphate ($Ca_4H(PO_4)_3\cdot 2.5H_2O$) has also been identified (Racz and Soper; 1967, Messier, 1990).

Brushite and octacalcium phosphate are less soluble than the original P fertilizer but contain P considered labile and readily available for plant uptake. In P fractionation studies, both of these products are included in the resin-P extractable fraction (Messier, 1990; Wagar *et al*, 1986a). In laboratory and field situations brushite and octacalcium phosphate are relatively stable and have not been found to convert to more thermodynamically stable and less soluble forms of phosphate minerals such as apatite (Bell and Black, 1970a, and Sadler and Stewart, 1975). In the field, octacalcium phosphate has been identified as the mineral solid which controlled the soil solution levels of phosphate three years after fertilization with MAP at 50, 100, and 200 kg P ha^{-1} (Ridley and Tayakepisuthe, 1974).

1.3 APPLIED PHOSPHORUS MOBILITY AND SOLUBILITY

The mobility and solubility of applied P is affected by the precipitation of fertilizer reaction products. On calcareous soils most P movement away from a 0.1 g application of MAP occurred within 0.5 days of application (Lewis and Racz, 1969). About 90% of applied MAP remained within 1.5 cm of the application site. Phosphorus did not continue to move because the precipitation of fertilizer reaction products restricted its movement. In the same study, fertilizer applied to a non-calcareous soil continued to be mobile for about three weeks, indicating that the formation of precipitates was slower than on calcareous soils, but most P still remained within 2.5 cm of the application site. In a greenhouse study, Messier (1990) found that almost all applied fertilizer remained within two cm of the application site on non-calcareous soils. Messier's work used point applications of 0.1 g or 0.01 g granules of MAP and P movement was measured after a barley crop had been grown on the soil. In the field, movement of applied P was found to be dependent upon soil properties and application rate with greatest P movement occurring at high P application rates on soils with low P fixing capacity (Eghball *et al*, 1990).

Messier (1990) worked with soil from the Breton plots and found that added P (5000 $\mu g\ P\ g^{-1}$ soil) was in equilibrium with octacalcium phosphate two months after fertilization. Messier's high application rate affected soil properties since he found an equilibrium $H_2PO_4^{-1}$ activity of about 10^{-1} mol L^{-1} following fertilization whereas the unfertilized soil solution would have had a $H_2PO_4^{-1}$ activity of about 10^{-3} mol L^{-1} at the normal soil pH of 6.0 if brushite and octacalcium phosphate were controlling the solubility and activity of $H_2PO_4^{-1}$.

If added P fertilizer did not drastically alter the properties of soil, and if the added P reached equilibrium with a relatively soluble phosphate like octacalcium phosphate, the solubility of added P could be reduced by several orders of magnitude (possibly from the initial activity of about 10^0 to an equilibrium activity of 10^{-2} or 10^{-3} mol L^{-1}). If P fertilizer could be made available to plants in such a way that the formation of fertilizer reaction products was prevented, possibly there could be a plant benefit.

1.4 PLANT USE AND UPTAKE OF PHOSPHORUS

Phosphorus performs structural and functional roles in plants. Structurally, P is an integral part of cell membranes and nucleic acids (both RNA and DNA) (Marschner, 1986). Functionally, P, in the form of adenosine phosphates, is involved in energy transfer reactions within living cells. Phosphorus also is functionally involved in regulating starch synthesis in the chloroplast and sugar translocation in the cytoplasm (Marschner, 1986). Phosphorus deficiencies can result in starch accumulating in chloroplasts (Marschner, 1986; Ozanne, 1980).

It has been suggested that a model plant would contain about 0.004% P as DNA, 0.04% as RNA, 0.03% as lipid, 0.02% as ester, and 0.13% as inorganic P (Ozanne, 1980). Therefore, plants' structural P content, although essential, is relatively low with most P remaining as inorganic P. Since P is associated with numerous structures and functions in the plant, P deficiencies at any time in a plant's life cycle could be detrimental, but the effects would be most harmful if they occurred during periods of rapid growth.

One of the perceived advantages of controlled-release fertilizers is that plant yield and recovery of applied fertilizers can be improved when the release of fertilizer is closely parallel to the plant demand for the nutrient (Dahnke *et al*, 1962; Oertli and Lunt, 1962; Hall and Baker, 1967). Although this seems simple, it may not be easily achieved since various crops have different patterns of P uptake (Kalra and Soper, 1968). Matching release to crop demand may also be difficult because P deficiencies early in wheat growth can severely limit yield (Boatwright and Viets, 1966) and late season uptake may not have any influence on yield (Karamanos, 1989).

When plotted against time, P uptake by annual crops for most of the growing period follows a typical sigmoidal growth curve similar to dry matter accumulation (Kalra and Soper, 1968). In solution culture of constant P concentration, plants take up very little P during the first 28 days of growth but rapidly acquire P between 28 and 42 days (Ningping and Barber, 1985). Unfortunately that report did not indicate which plant growth stages were involved or what amounts of P were taken up after the 42 day harvest when P was still being accumulated at a rapid rate.

Boatwright and Haas (1961) found that wheat acquired most of its P by the time the head emerged from the collar. During grain head development Bauer *et al* (1987) found that P was translocated within the plant from stems and leaves to the spike . It was estimated that translocation from stems and leaves accounted for about 57% of the P in grain (Bauer *et al*, 1987). It is also estimated that 64 to 100% of the total P present in a wheat plant at harvest had been acquired by the plant prior to anthesis (Clarke *et al*, 1990). For many annual crops produced in western Canada, P accumulation during the most rapid phase of vegetative growth (possibly from about 20 to 50 days after seeding depending on growing conditions) to anthesis, most likely plays a crucial role in the health and economic value of the crop.

The Boatwright and Viets (1966) paper will be closely examined here since it has been cited as showing the importance of phosphorus uptake in the first few weeks of growth (Chambers and Yeomans, 1991; Tomasiewicz and Racz, 1993). Boatwright and Viets grew wheat in nutrient solutions that were either deprived of P for 0, 2, 3, 4, or 6 weeks, or solutions where P was supplied for 2, 3, 4, 5, 6, 8, or 10 weeks and later withheld. They found that when P was absent for the first two weeks of growth, significant irreversible damage (lost yield) occurred. They also found that maximum dry matter and grain yield was achieved when P was supplied for 5 weeks (up to heading). Phosphorus uptake after heading had no affect on dry matter or grain yield. The absolute time values presented in this experiment cannot be projected to field situations because of the condensed period for wheat maturation. In this experiment, wheat plants had headed after 5 weeks (35 days) and were apparently mature after 10 weeks (70 days). The growing conditions used in this experiment caused a wheat life cycle that was much shorter than can be expected for field situations. The authors caution against transferring these results to field situations since the whole plant P concentration at heading was three times that experienced for field situations. With this high P concentration, subsequent plant P requirements could be met by P translocation rather than uptake. The results of this experiment indicated that wheat P uptake by heading, and not necessarily 5 weeks, plays an important role in the overall development and yield of the crop.

Plant demand for P and applied fertilizer's ability to supply P are partially incongruous. Fertilizer P becomes less available with time; plant demand for P increases with time. It remains to be determined if there is a crop benefit from adding P to the soil in a manner that prevents or reduces the formation of fertilizer reaction products in order for P to be available later (possibly 20 to 50 days after emergence) in the crop's development.

1.5 PHOSPHORUS FERTILIZER EFFICIENCY

Plants acquire P from the soil through diffusion (Barber, 1980). Therefore any process that affects diffusion such as soil moisture content and soil temperature, (Olsen *et al*, 1961) will affect plant recovery of applied P. The recovery of applied P also depends on the volume of soil fertilized, the likelihood of root interception, and the soil's ability to "fix" added P (Korvar and Barber, 1989). If soil did not fix P, the greater the volume of soil fertilized, the larger the root mass exposed to the fertilizer and the greater the crop recovery of the fertilizer. In western Canada, banding P in a small volume of soil near the seed or placing P with the seed of cereals is usually superior to placing the same amount of P throughout a large volume of soil (Ridley and Tayakepisuthe, 1974; Bailey and Grant, 1990). The efficiency of applied P is also affected by the crop involved (Strong and Soper, 1973), the source of P fertilizer (Soper and Kalra, 1969), and the rate of P application, (Ridley and Tayakepisuthe, 1974).

It has also been found that the recovery of applied P is greatest when the difference between the P concentration at the source of application and the P concentration in soil solution is greatest (Strong and Soper, 1974). There is a direct relationship between the P concentration at the source of fertilization and crop recovery of applied P, and an inverse relationship between soil P levels outside a fertilizer band and crop utilization of the P from the band (Strong and Soper, 1974). Therefore low P fertilization efficiencies are likely to occur if P fertilization reaction products with low solubilties form at the P application site.

Phosphorus recovery by crops in the greenhouse ranged from 4 to 8% for flax, 13 to 20% for wheat, 33 to 56% for buckwheat, and 41 to 58% for rape with the same rate of P application for all four crops (Strong and Soper, 1973). Fertilizer P efficiency values can be affected by increasing or decreasing the P application rate. For example, if a soil was P deficient and a P fertilizer response was likely to occur, P applied at a low rate would be efficiently taken up by a crop, especially if the application rate was equal to or lower than the crop requirement. In the same way, if the P application rate was considerably greater than the crop requirement, the efficiency of the applied fertilizer would most likely be low, even if total P uptake was enhanced relative to lower P application rates.

Phosphorus fertilizer efficiencies for field situations are variable. This author estimates that about 25% of applied P might be recovered in the year of application by an annual crop in western Canada. A 25% recovery of applied P in the year of application has not been a concern of many researchers because the applied P remains "essentially plant-available" for long periods of time (Roberts and Fixen, 1993). In theory applied P remains plant available for long periods because stable, insoluble P fertilization reaction products have not been identified in soil (Bell and Black, 1970a; Sadler and Stewart, 1975). Unlike nitrogen (N) or sulphur (S), P is not subject to leaching losses as are N and S, or losses to the atmosphere as is N. In most soils P is retained near the site of application. Losses of P from the site of application could occur with erosion, but those losses are estimated to be small (Barrow, 1980).

The value of residual P has been well investigated by several researchers (Ridley and Tayakepisuthe, 1974; Wagar *et al*, 1986a and 1986b; Read *et al*, 1977; Bailey *et al*, 1977;

Sadler and Stewart, 1975; Spratt *et al*, 1980; Halvorson and Black, 1985a and 1985b). The experiments measured crop yield and P uptake for several years following broadcast and incorporation of up to 400 kg P ha^{-1}. It was concluded that one-time broadcast applications of P and their residual value can effectively meet crop needs for several years after application. However, the results and conclusions of these experiments need to be placed within the context of the amount of P applied and the amount of P removed over the duration of an experiment. Since P application rates often greatly exceeded P removed through grain harvests during the course of the experiment, the fact that large initial applications were effective for the duration of the experiment does not necessarily indicate that all applied fertilizer was recovered or remained recoverable.

Two of these residual P studies (Read *et al*, 1977, and Spratt *et al*, 1980) appear to be based on the same field results from two sites in Manitoba. The field results were used to calculate actual and projected effectiveness of the one time large applications of P (Spratt *et al*, 1980). Based on average values of the two soils, and assuming (according to Spratt *et al*, 1980) that wheat on the soils would be responsive to P fertilization after the soil reached a $NaHCO_3$-extractable P value of 15 $\mu g\ g^{-1}$, the 100 kg P ha^{-1} application rate would be effective for about 5.5 years (Spratt *et al*, 1980). Higher P application rates (200 and 400 kg P ha^{-1}) were reported to theoretically last 11 and 22 years before again responding to P fertilization, but these projected values were based on the experimental data of the 100 kg P ha^{-1} application rate multiplied two and four times to fit the higher rates (Spratt *et al*, 1980). Measured values for average P uptake for the duration of the experiment carried over the effective time of the residual P, indicated that the residual P was not even close to being 100% plant available (Table 1.2). The long-term effectiveness of previously applied P fertilizer (residual P that might be in the brushite or octacalcium phosphate form) may be similar to the effectiveness of annual P fertilization.

Table 1.2 Long-term effectiveness of broadcast P fertilizer from Read *et al* (1977) and Spratt *et al* (1980)

Rate (kg P ha^{-1})	Average P Uptake (kg P ha^{-1} year^{-1})	Projected Effectiveness (years)	Net P Uptake† (kg P ha^{-1})	Fertilizer Efficiency† (%)
0	5.7	-		
100	10.5	5.5	26.4	26

†calculated based on values reported by Read *et al* (1977)

It has been suggested that controlled-release P is not needed because soil rapidly reverts soluble P to less soluble fertilizer reaction products that are inherently "slow-release" P compounds (Engelstad and Terman, 1980). However, Barrow (1980) reported that P fertilization reaction products have not remained fully effective after application to the soil. Even though stable, insoluble P fertilization reaction products have not been identified following P fertilization, the soil is apparently a sink for applied P. Logically, a mechanism that prevents or limits the reactions between soil and applied P can improve the efficiency of the P fertilizer. Phosphorus fertilizer that is effectively utilized in the year of application would not be subject to the apparent labile P losses that occur with time.

1.6 CONTROLLED-RELEASE PHOSPHORUS FERTILIZERS

The concept of a controlled-release P fertilizer is not new. Hall and Baker (1967) hypothesized that an effective coating on P fertilizer would reduce the diffusion of P into the soil and would extend the period of time that applied P was available. Hall and Baker (1967) coated superphosphate with asphalt amounting to 16% of the total coated fertilizer weight. The coated product did not behave the way they had theorized and was less effective than dicalcium phosphate in increasing plant yield (Hall and Baker, 1967). There were similar failures when P was coated with a sulphur and wax coating (33% by weight) (Terman *et al*, 1970) and a coating of sulphur, wax, and conditioner (14.9% by weight) (Allen and Mays, 1971).

The failures of the tested coated P fertilizer products does not invalidate the concept of coating P fertilizer. Hall and Baker (1967) concluded that the nature of their coating was the problem since it was less effective than low solubility P sources (dicalcium phosphate). The thick coating used by Terman *et al* (1970) had release problems since only 1.1% of the soluble P in the fertilizer dissolved in water at 43^0C after 5 days. The dissolution of P from the thinner coating used by Allen and Mays (1971) was also very slow (5% after 7 days at 43^0C). These experiments failed not because the concept was invalid but rather because the products tested did not accurately control the release of P.

1.7 OBJECTIVES

The purpose was to determine if controlled-release techniques when applied to P fertilizer increased crop growth and recovery of applied P. The hypothesis is that P delivered to a plant over an extended period of time and delivered in a way that reduces soil-fertilizer contact results in higher plant yield and plant P uptake than from an equivalent quantity of fertilizer P applied and immediately soluble at sowing. This hypothesis was tested by periodic applications of P solution to the root zone of a developing barley crop (Chapter 2) and subsequently by the performance of dry forms of controlled-release P fertilizer (Chapters 3 to 5).

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CHAPTER 2

SIMULATION OF CONTROLLED-RELEASE PHOSPHORUS USING SPLIT APPLICATIONS

2.1 INTRODUCTION

The pattern of phosphorus (P) uptake by annual crops is generally similar to crop dry matter accumulation (Bauer *et al*, 1987; Clarke *et al*, 1990; Kalra and Soper, 1968; Ningping and Barber, 1985). Matching P delivery to crop demand has been proposed as a potential benefit of controlled release P fertilizer (Hall and Baker, 1967; Oertli and Lunt, 1962). However, experimental controlled-release P fertilizers made with asphalt or sulphur coatings have failed to improve the efficiency of P fertilizer in the year of application (Allen and Mays, 1971; Hall and Baker, 1967; Terman *et al*, 1970). Since these coated P products did not readily release P into solution it was possible that the concept of controlled-release P fertilizer was rejected on the basis of the failure of specific experimental products.

Split applications of P, where P was applied at sowing and one or two times subsequent to sowing, have improved the efficiency of applied P relative to all P applied at sowing (Karamanos, 1989; Raju *et al*, 1982). Although these split P application experiments were not aimed at the development of controlled-release P fertilizers, the results support the concept of controlled-release P. Furthermore, plant uptake of P and fertilizer efficiency were found to be enhanced when P was applied in split applications over 44 days (Nyborg *et al*, 1995). The literature therefore indicates that the concept of controlled-release P fertilization may be valid and in need of additional investigation.

This experiment was performed to confirm the findings of Nyborg *et al* (1995). The hypothesis was that P applied over 44 days, as a simulation of a controlled-release P fertilizer, would improve plant P uptake and the efficiency of applied P relative to all P applied at sowing.

2.2 MATERIALS AND METHODS

Plastic pots of 2.2 L volume (0.16 m high and 0.14 m diameter) were filled to three cm below the rim with soil taken from the Ellerslie Research Station (Soil 1) or from the Breton Research Plots (Soil 2) (see Appendix 1 for soil characteristics). A fertilizer solution of NH_4NO_3, KCl, and Na_2SO_4 equivalent to 143 kg N ha^{-1} (257 mg N pot^{-1}), 38 kg K ha^{-1} (68.4 mg K pot^{-1}), and 14 kg S ha^{-1} (25.2 mg S pot^{-1}), was thoroughly mixed into the soil from each pot. The mass of soil used was: 2025 g (oven dry basis) for Soil 1, and 2750 g (oven dry basis) for Soil 2. For both soils, the surface area per pot was 0.018 m^2. A volume of dry soil equivalent to 2 cm of soil depth was removed and the pots were watered to field capacity. Twelve barley (*Hordeum vulgare* L. 'Leduc') seeds were placed on the moist soil in groups of 3 seeds arranged in an equilateral triangular pattern at the 3, 6, 9, and 12 o'clock positions. The seeds were then covered with loose, dry soil. Disposable pipette tips (1 mL) were inserted into the soil into the center of each seed grouping so each tip was positioned about 2 cm below seeding depth and was equidistant from each seed at each position. All pots, including controls, had 4 pipette tips (applications sites). Commercial fertilizer grade monoammonium phosphate (12-51-0) (MAP) and diammonium phosphate (18-46-0) (DAP) were used to prepare the treatment solutions. For each phosphorus fertilization, the pipette tips were removed and 0.5 mL of fertilizer solution was injected to the resulting hole. After treatment application, the tips were inserted back into their original holes. The treatments were applied according to Table 2.1.

Treatments No. 2 and 3 received all their P fertilizer on Day 0 (day of seeding: April 29) of the experiment. Phosphorus fertilizer solutions were applied to treatment No. 4 and 5 on Day 1 and every second day until Day 43 (22 applications at each of the 4 sites pot^{-1}). The every 11-day MAP and DAP treatments (No. 6 and 7) were applied on Day 0, 11, 22, and 33 (4 applications at each of the 4 sites pot^{-1}).

Table 2.1 Experiment 1 outline of treatments

No	Treatment Fertilizer	Application	No. Sites Pot^{-1}	Fertilizer Solution P Concentration mM	 ppm	No. of Applications Site^{-1}	Total P mg pot^{-1}
1	None	None	0	0	0	0	0
2	MAP	Day of sowing	4	254	7860	1	15.7
3	DAP	Day of sowing	4	254	7860	1	15.7
4	MAP	Each second day	4	12	357	22	15.7
5	DAP	Each second day	4	12	357	22	15.7
6	MAP	Each eleventh day	4	63	1965	4	15.7
7	DAP	Each eleventh day	4	63	1965	4	15.7

This experiment was conducted from late April to mid June 1992. The experiment was arranged in the greenhouse as a randomized complete block design with 2 soils and 7 treatments replicated four times (56 pots in total). Throughout the experiment the greenhouse was maintained with 16 hours of supplemental light (Sylvania high pressure sodium) and a minimum temperature of 20°C but daytime heating often resulted in temperatures exceeding 25°C. After germination each pot was thinned to 8 plants (about 450 plants m^{-2}) with two plants at each application site. All pots received a second nitrogen application (143 kg N ha^{-1}) on Day 23. Throughout the experiment pots were watered to field capacity about every second day. Watering schedules were adjusted so fertilizer application and watering were on alternate days in order to minimize phosphorus movement away from the application site. All above-ground portions of the barley plants were harvested on Day 46 of the experiment when the heads on most treatments were fully emerged. Harvested plant material was dried for 48 hours at 70°C, weighed, ground, digested (Technicon Industrial Systems, 1975/Revised 1978), and analyzed for P content using an autoanalyzer (Technicon Industrial Systems, 1977).

Net P uptake, the apparent contribution of fertilizer to the plants' total P uptake, was calculated by subtracting the control P uptake from the P uptake value of each treatment that received P in each replicate. The fraction of the total applied P that was represented by the calculated Net P values were used to calculate apparent fertilizer efficiencies (the fraction multiplied by 100 put the apparent fertilizer efficiencies in the percent form). Compared to measured P uptake, Net P was much less precise since the necessary calculations increased variability. Consequently fertilizer efficiencies usually represent trends in treatment effects and are not necessarily statistically significant.

2.3 RESULTS AND DISCUSSION

Barley dry matter yield from all treatments with added P was greater than the control treatment on Soil 1 (Table 2.2) and on Soil 2 (Table 2.3). This yield response to added P was small with no yield differences between any of the treatments with added P on either soil.

Table 2.2 Yield and uptake of added P by barley after 45 days on Soil 1

Fertilizer	P Added mg pot^{-1}	Frequency of P Addition	Yield g pot^{-1}	P Uptake mg pot^{-1}	Recovery of Added P in Plants %
None	0	None	8.77	20.98	
MAP	15.7	Once Only	10.40	22.99	12.8
MAP	15.7	Each 2nd Day	10.87	24.79	24.2
MAP	15.7	Each 11th Day	11.07	25.01	25.6
DAP	15.7	Once Only	10.84	22.22	7.9
DAP	15.7	Each 2nd Day	11.08	23.71	17.4
DAP	15.7	Each 11th Day	11.00	23.66	17.0
LSD (0.05)			0.82	2.76	

Table 2.3 Yield and uptake of added P by barley after 45 days on Soil 2

Fertilizer	P Added mg pot^{-1}	Frequency of P Addition	Yield g pot^{-1}	P Uptake mg pot^{-1}	Recovery of Added P in Plants %
None	0	None	9.77	25.80	
MAP	15.7	Once Only	11.94	28.68	18.3
MAP	15.7	Each 2nd Day	11.78	31.43	35.8
MAP	15.7	Each 11th Day	11.48	30.47	29.7
DAP	15.7	Once Only	11.62	27.97	13.8
DAP	15.7	Each 2nd Day	11.52	31.95	39.1
DAP	15.7	Each 11th Day	11.72	31.40	35.6
LSD (0.05)			0.81	2.05	

The dry matter yield on Soil 2 tended to be slightly greater than Soil 1 (Tables 2.2 and 2.3), possibly due to the greater soil mass and greater extractable P in Soil 2 (see Appendix 1). This effect was more evident with P uptake.

While there were differences in P uptake between the two soils, a significant soil by treatment interaction did not occur (see Appendix 2, Tables A2.5 and A2.6). Combined data therefore indicated the overall effect of the different P fertilizer treatments (Table 2.4). Phosphorus uptake was greater when P was applied every second day or every eleventh day rather than all P applied at seeding. The net effectiveness (trend) of P applied every second day with MAP was double and with DAP was nearly triple the effectiveness of all P applied at seeding. These results were similar to an earlier experiment (Nyborg *et al*, 1995).

These results indicated, but did not prove, that there may be benefit to controlled-release P compared to conventional P fertilizer. The split applications of P, which were intended to simulate controlled-release products, increased P uptake but did not increase dry matter yield. Karamanos (1989) concluded that increased P uptake from split P application was not economically valuable because there was no yield increase. It is possible that controlled-release P fertilizers would deliver P later in the growing season and would not contribute to yield. Dry matter yield results from my experiment would support the conclusion drawn by Karamanos. However, experimental conditions might have minimized the benefits of simulated controlled-release P. In this experiment, barley was not very responsive to P fertilization, at least with the imposed greenhouse conditions. Regular watering to field capacity and soil temperatures greater than 20^0C would have maximized the availability of both soil P and fertilizer P. Furthermore, the high plant densities and low soil volumes would have maximized the contact between roots and soil P and could have minimized the effects of P fertilizer treatments.

Table 2.4 Yield and uptake of P by barley after 45 Days: Soils 1 and 2 data combined

Fertilizer	P Added mg pot^{-1}	Frequency of P Addition	Yield g pot^{-1}	P Uptake mg pot^{-1}	Recovery of Added P in Plants %
None	0	None	9.27	23.39	
MAP	15.7	Once Only	11.17	25.84	15.6
MAP	15.7	Each 2nd Day	11.33	28.11	30.0
MAP	15.7	Each 11th Day	11.28	27.74	27.7
DAP	15.7	Once Only	11.23	25.09	10.8
DAP	15.7	Each 2nd Day	11.30	27.83	28.2
DAP	15.7	Each 11th Day	11.36	27.53	26.3
LSD (0.05)			0.56	1.66	

2.4 CONCLUSIONS

Phosphorus applications as MAP or DAP delivered every second day or every eleventh day increased P uptake by barley and tended to increase the effectiveness of applied P compared to applying all P at sowing. Phosphorus fertilization increased barley yield, but split applications of P did not increase yield over all P applied at sowing. The split applications of P, that were intended to simulate a controlled-release P fertilizer, indicated that the concept of controlled-release P fertilization might find application if suitable products could be manufactured. Future research will need to find if P uptake from controlled-release products will be economically valuable.

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CHAPTER 3

CONTROLLED RELEASE OF PHOSPHORUS FERTILIZERS USING SYNTHETIC COATINGS

3.1 INTRODUCTION

Experiments with P fertilizer solutions evenly applied to barley every two or eleven days for 44 days indicated that the concept of controlled-release P fertilizer was valid (Chapter 2; Nyborg *et al*, 1995). Although periodic additions of solution P were necessary in order to establish the potential benefit of controlled-release P fertilizer, applications of P solutions to the rooting zone of growing crops are not realistic for large-scale crop production. Therefore the potential benefit of controlled-release P must be established with granular fertilizers.

Experimental controlled-release P fertilizers made with asphalt or sulphur coatings have failed to improve the efficiency of P fertilizer in the year of application (Allen and Mays, 1971; Hall and Baker, 1967; Terman *et al*, 1970). The failure of these experimental products was probably due to their extremely slow release characteristics which would have hindered rather than promoted plant recovery of applied P. Since the yield of cereal crops is influenced by P uptake prior to heading (Boatwright and Haas, 1961; Boatwright and Viets, 1966; Bauer *et al*, 1987; Clarke *et al*, 1990) controlled-release P fertilizer must release the majority of its P prior to heading. For greenhouse situations most P should be released by the 40 to 50 day period following sowing of cereal grains depending upon greenhouse conditions and crop growth rate.

Controlled-release urea which utilizes a very thin membranous coating has been commercialized. This thin polymer coating controls the release of urea by restricting the rate of diffusion across the membrane (Zhang, 1993). Diffusion and the rate of release are dependent on the thickness, permeability and integrity of the polymer membrane as well as the size distribution of the coated granules (Feng *et al*, 1994). With urea, the integrity of the membrane appears to be a function of the thickness of the membrane with many defects associated with thin membranes and fewer defects with thick membranes (Feng *et al*, 1994). Although the same polymer can be used to coat either urea or mono-ammonium phosphate (12-51-0), membrane integrity with coated 12-51-0 is probably compromised by granule shape and surface characteristics since the shape of the fertilizer is more irregular than urea. In theory, the more irregular the shape and surface of the granule the greater the potential for a defective membrane. Imperial Oil, Chemicals Division, who by request manufactured experimental product for this and subsequent experiments, expected the coated 12-51-0 MAP fertilizer to be defective.

Dahnke *et al* (1962) determined that controlled-release urea could be made for experimental purposes by sealing individual fertilizer pellets in packaging film and subsequently poking pin-holes in the film. Controlled-release fertilizer of this nature was considered to have more predictable release characteristics than the release from a number of other coating materials.

This experiment was performed to determine if experimental controlled-release P sources were superior to conventional P fertilizer. In this experiment both polymer coated and packaging film coated P fertilizers were utilized. The hypotheses were that synthetically coated P would allow for greater plant uptake of applied P, increased fertilizer efficiency, and increased plant yield relative to uncoated P fertilizer.

3.2 MATERIALS AND METHODS

2.2 L pots were filled to three cm below the rim with soil taken from the Ellerslie Research Station or from the Breton Research Plots (see Appendix 1 for soil characteristics). A fertilizer solution of NH_4NO_3, KCl, and Na_2SO_4 equivalent to 143 kg N ha^{-1} (257 mg N pot^{-1}), 38 kg K ha^{-1} (68.4 mg K pot^{-1}), and 14 kg S ha^{-1} (25.2 mg S pot^{-1}), was thoroughly mixed into the soil from each pot. The mass of soil used was: 2025 g (oven dry basis) for the soil from Ellerslie, and 2750 g (oven dry basis) for the soil from Breton. For both soils, the surface area per pot was 0.018 m^2. A volume of dry soil equivalent to 4 cm of soil depth was removed and the pots were watered to field capacity. Phosphorus fertilizer treatments (Table 3.1) were applied to the wet soil surface. Control treatments received no added P but all other treatments received P at 20 kg P_2O_5 ha^{-1} (15.7 mg P pot^{-1}). For all treatments that received P, four fertilizer granules of approximately equal size were placed in each pot with a granule at each of the 3, 6, 9 and 12 o'clock positions.

The polymer-coated 12-51-0 (MAP) and 18-46-0 (DAP) were prepared in March 1992 by Imperial Oil Chemicals Division, Redwater Alberta, using the same polymer and process used in the preparation of controlled-release urea. Two polymer coatings, 1.8% and 2.2% by weight, will be referred to as thin and thick coatings respectively. Treatments 2 through 7 were prepared by enveloping pre-weighed, uncoated P fertilizer in commercial packaging film. Individual fertilizer granules were sealed in small envelopes of packaging material, which when heated, shrunk tightly against the fertilizer granule. Two, four, or six pin-holes were then poked into this shrink-wrap packaging film on one side of the granule only. Mixture treatments (14 and 15) consisted of 1 uncoated granule, 1 thin coated granule, and 2 thick coated granules, all approximately the same size and mass.

Table 3.1 Granular fertilizer treatments

Treatment	P Source	Properties of Coating
1. Control	none	not applicable
2. SW 1	MAP (12-51-0)	Shrink Wrap packaging film with 2 pin-holes
3. SW 1	DAP (18-46-0)	Shrink Wrap packaging film with 2 pin-holes
4. SW 2	MAP (12-51-0)	Shrink Wrap packaging film with 4 pin-holes
5. SW 2	DAP (18-46-0)	Shrink Wrap packaging film with 4 pin-holes
6. SW 3	MAP (12-51-0)	Shrink Wrap packaging film with 6 pin-holes
7. SW 3	DAP (18-46-0)	Shrink Wrap packaging film with 6 pin-holes
8. Uncoated	MAP (12-51-0)	none
9. Uncoated	DAP (18-46-0)	none
10. Thin	MAP (12-51-0)	1.8% polymer coating by weight
11. Thin	DAP (18-46-0)	1.8% polymer coating by weight
12. Thick	MAP (12-51-0)	2.2% polymer coating by weight
13. Thick	DAP (18-46-0)	2.2% polymer coating by weight
14. Mixture	MAP (12-51-0)	1 granule uncoated, 1 granule 1.8%, 2 granules 2.2%
15. Mixture	DAP (18-46-0)	1 granule uncoated, 1 granule 1.8%, 2 granules 2.2%

MAP: mono-ammonium phosphate (predominantly)
DAP: di-ammonium phosphate

Fertilizers were covered with about two cm of dry soil. Twelve barley (*Hordeum vulgare* L. 'Leduc') seeds were placed on the dry soil in groups of three seeds arranged in an equilateral triangular pattern at the 3, 6, 9, and 12 o'clock positions. With this sowing arrangement, P fertilizer was slightly below and beside the barley seed. The seeds were then covered with the remaining dry soil.

This experiment was conducted from May 1 to June 15, 1992. The experiment was arranged in the greenhouse as a randomized complete block design with two soils and 15 treatments replicated four times (120 pots in total). Throughout the experiment the greenhouse was maintained with 16 hours of supplemental light (Sylvania high pressure sodium) and a minimum temperature of 20^0C but daytime heating often resulted in temperatures exceeding 25^0C. After germination each pot was thinned to 8 plants (about 450 plants m^{-2}) with two plants at each application site. All pots received a second nitrogen application (143 kg N ha^{-1}) on Day 23. Throughout the experiment pots were watered to field capacity as needed. All above-ground portions of the barley plants were harvested on Day 45 of the experiment. Harvested plant material was dried for 48 hours at 70^0C, weighed, ground, digested (Technicon Industrial Systems, 1975/Revised 1978), and analyzed for phosphate content using an autoanalyzer (Technicon Industrial Systems, 1977). Net P uptake and apparent fertilizer efficiencies were calculated in the same manner as Chapter 2.

3.3 RESULTS AND DISCUSSION

At harvest, taken 45 days after sowing, the barley heads had emerged on most treatments. The control treatment was an exception, developmentally lagging behind treatments that had received P. Plant development with the thick polymer coating (especially Treatment 13) was slightly delayed during most of the experiment compared to other treatments with P but was advancing relatively quickly toward the end of the experiment.

Dry matter yield and uptake of P in the control treatment were similar to the yield and P uptake in the control from Chapter 2 (Table 2.4 and Table 3.2). The soil from Breton generally had higher dry matter yield and P uptake than the soil from Ellerslie probably due the greater soil mass and extractable P available for plant growth (see Appendix 1).

With both soils, the addition of fertilizer P increased both P uptake and dry matter yield (Table 3.2). Unlike the solution experiment in Chapter 2, in this experiment there were also significant yield differences between treatments that received P. A significant soil by treatment interaction occurred in the combined soils dry matter yield data (see Table A3.5), hence combined yield data are not reported.

Table 3.2 Barley dry matter yield and P uptake after 45 days

	Ellerslie		Breton		Soils Combined
Treatment	DM† (g pot^{-1})	PUP†† (mg pot^{-1})	DM (g pot^{-1})	PUP (mg pot^{-1})	PUP (mg pot^{-1})
1. Control	8.68	20.60	10.71	25.44	23.02
2. SW 1 MAP	11.20	23.81	12.24	29.31	26.56
3. SW 1 DAP	11.32	22.96	11.38	28.38	25.67
4. SW 2 MAP	11.01	24.70	11.75	28.53	26.61
5. SW 2 DAP	11.13	24.38	11.44	29.60	26.99
6. SW 3 MAP	11.33	22.96	11.87	28.59	25.77
7. SW 3 DAP	11.41	21.56	11.43	29.62	25.59
8. Uncoated MAP	11.41	22.86	11.98	28.36	25.61
9. Uncoated DAP	11.79	23.66	12.33	29.39	26.53
10. Thin MAP	12.26	25.08	12.83	31.20	28.14
11. Thin DAP	12.20	24.21	12.93	27.78	25.99
12. Thick MAP	11.66	24.63	11.69	29.34	26.99
13. Thick DAP	12.19	22.92	12.39	28.52	25.72
14. Mixture MAP	12.66	24.19	12.32	31.39	27.79
15. Mixture DAP	12.49	22.48	12.40	28.24	25.36
LSD (0.05)	0.68	2.39	0.81	2.06	1.74

†Dry Matter
††Phosphorus uptake

With the soil from Ellerslie, treatments that included the polymer coating generally had significantly higher yield than the uncoated or shrink wrap-coated P. The mixture treatments (14 and 15) yielded higher than uncoated MAP or DAP. Furthermore, the yield from the thin-coated MAP (Treatment 10) was greater than from the uncoated MAP. There were no significant yield differences between the thick-coated and uncoated MAP treatments or between the uncoated DAP and either the thin or thick coated DAP.

The yield results with the soil from Breton displayed similar trends as the soil from Ellerslie. Treatments with the polymer coating generally outyielded treatments with shrink-wrap coating. The thick-coated MAP was an exception, with yield equal to the lowest yielding of the shrink-wrap treatments. The thin coating on MAP increased yield relative to the uncoated MAP, but there were no differences between uncoated DAP and any treatments with the polymer coating.

After 45 days of growth, dry matter yield was not necessarily a reflection of P uptake. With the soil from Ellerslie, the thin-coated MAP and the DAP mixture had similar dry matter yield yet different P uptakes (Table 3.2). Similarly, the shrink-wrap-coated MAP with four holes (Treatment 4) and the thin-coated MAP had similar P uptakes but yield was lower with the shrink wrap coating. On the soil from Breton, there were similar occurrences where a treatment had low yield and high P uptake and another treatment had higher yield and similar P uptake (compare Treatments 5 and 11). Generally, the thick-coated MAP or shrink-wrap-coated MAP or DAP had low yield and high P uptake (Table 3.2).

There were instances where controlled-release P fertilizer was of no benefit over conventional P fertilizer (compare treatments 8 and 11 on both soils) but there were indications that an effective controlled-release P source could be superior to conventional P sources. The thin polymer coating on MAP had greater dry matter yield (Ellerslie) and P uptake (Breton and combined data) than uncoated MAP. The thickness of coatings used in this experiment were not established on theoretical or experimental bases but were purely arbitrary. The instances where controlled-release P failed to be superior to conventional P sources may only be due to specific product performance rather than inadequacies with the concept of controlled-release P.

After the 45 day harvest, attempts were made to recover intact controlled-release P fertilizer granules. The thin-coated MAP or DAP granules were usually found as empty shells encircled by a dense mat of crop roots. The thick-coated MAP was often found in a much less dense cluster of roots and generally maintained a spherical shape. These thick-coated MAP granules were elastic and would bounce if dropped, similar to tiny rubber balls. Shrink-wrap-coated granules characteristically were not encircled by dense crop roots and were devoid of observable fertilizer remnants. On the basis of these observations it is possible that the controlled-release P products that failed to outperform uncoated P either were extremely slow in their fertilizer release or the granule physically limited root interception.

The observed root growth around the thin-coated granules indicated that this product released P in such a way that the crop roots were stimulated to proliferate in the vicinity of the granule. It is likely that the P release was in all directions from the spherical granule on the basis of the root growth around the granules. Although the thick-coated MAP product also could have released its P in all directions, the presence of intact granules at the completion of the experiment indicated that the release was slower than the length of the experiment, possibly limiting plant yield. If these granules started to release P fairly rapidly toward the end of the experiment, relatively large amounts of P would become plant available fairly late in the plant development cycle. This could possibly explain why plant uptake was high yet dry matter yield was relatively low. Since the holes on the shrink-wrap-coated granules were only on one side of the granule, P diffusion away from the application site would have been restricted. Roots possibly did not proliferate around the granule because P was not readily available around the entire granule and the relatively large plastic envelope around the granule could have impeded root growth and P interception.

If fertilizer P in the thick-coated MAP and shrink-wrap treatments became plant available toward the end of the experiment, it is uncertain that this P could have produced additional yield. Boatwright and Viets (1966) found that P taken up after heading was luxury consumption and did not contribute to yield. However, in that study tissue P concentrations at heading were about three times the usual concentration (Boatwright and Viets, 1966). In the present experiment, the highest tissue P concentration in any individual treatment was 0.266% with treatment mean tissue concentrations of 0.193% to 0.226% (Appendix 7). Since these tissue P concentrations could be considered to indicate P deficiencies (Tomasiewicz and Racz, 1991) it is possible that late season plant growth could have been affected by late season P uptake if the experiment had continued longer. The single harvest used in this experiment indicated barley dry matter accumulation and tissue P concentration after 45 days but did not reveal when the plant growth or P uptake had occurred and could not give any indication how growth and P uptake would continue after 45 days.

Net P uptake was calculated by subtracting the control P uptake from each treatment uptake within each replicate (Table 3.3). Net P uptake values calculated in this manner indirectly measure the contribution of fertilizer P to total plant P uptake. This method may possibly underestimate the contribution of fertilizer P and may overestimate the contribution of soil P in treatments that received P since P fertilization sometimes reduces plant uptake of soil P (Strong and Soper, 1974). Net Fertilizer Efficiency (NFE) is the apparent percentage of applied fertilizer that is contained in the Net P.

Apparent fertilizer efficiencies of the uncoated MAP and DAP with barley (Table 3.3) were similar to the 13 to 20% range reported elsewhere with wheat (Strong and Soper, 1973). The apparent benefit of the thin polymer coating with MAP was very large. The thin polymer coating on MAP (combined data), which increased plant total (Table 3.2) and net P uptake (Table 3.3) relative to the uncoated MAP, nearly doubled the efficiency of the added fertilizer. Mixing uncoated MAP with thin and thick-coated MAP (combined data) also increased the Net P uptake of barley and increased the efficiency of the fertilizer relative to uncoated MAP used alone. Polymer coatings with DAP, either thin, thick, or mixtures of thin, thick, and uncoated, did not increase net P uptake or fertilizer efficiency. Subsequent P fertilizer release studies with DAP (Appendix 6) indicated that the coatings were doing little to control the release of P.

Controlling the release of P with other synthetic coating tended only to produce occasional modest increases in fertilizer efficiency.

Table 3.3 Net P uptake and fertilizer efficiency after 45 days

	Ellerslie		Breton		Soils Combined	
Treatment	Net P† (mg pot^{-1})	NFE†† (%)	Net P (mg pot^{-1})	NFE (%)	Net P (mg pot^{-1})	NFE (%)
2. SW 1 MAP	3.22	20.5	3.87	24.6	3.54	22.5
3. SW 1 DAP	2.37	15.1	2.93	18.6	2.65	16.9
4. SW 2 MAP	4.10	26.1	3.08	19.6	3.59	22.8
5. SW 2 DAP	3.78	24.0	4.15	24.0	3.97	25.2
6. SW 3 MAP	2.36	15.0	3.14	20.0	2.75	17.5
7. SW 3 DAP	0.96	6.1	4.18	26.6	2.57	16.3
8. Uncoated MAP	2.26	14.4	2.91	18.5	2.59	16.5
9. Uncoated DAP	3.07	19.5	3.95	25.1	3.51	22.3
10. Thin MAP	4.48	28.5	5.76	36.6	5.12	32.6
11. Thin DAP	3.61	23.0	2.34	14.9	2.97	18.9
12. Thick MAP	4.04	25.7	3.90	24.8	3.97	25.3
13. Thick DAP	2.33	14.8	3.08	14.8	2.70	17.2
14. Mixture MAP	3.59	22.8	5.95	37.8	4.77	30.3
15. Mixture DAP	1.89	12.0	2.80	17.8	2.35	14.9
LSD (0.10)	1.81					
LSD (0.05)			2.07		1.69	

†Net P uptake

††Net fertilizer efficiency

3.4 CONCLUSIONS

A 1.8% (thin) polymer coating on MAP significantly increased plant P uptake and the apparent efficiency of applied fertilizer relative to uncoated MAP. A mixture of uncoated, thin-coated, and thick-coated MAP (applied in a 1:1:2 ratio) also significantly increased plant P uptake and calculated fertilizer efficiency. When MAP was coated with a thin polymer membrane or when uncoated MAP was used in combination with thin and thick-coated MAP, the efficiency of the applied fertilizer was nearly doubled. Synthetic coatings failed to improve the efficiency of DAP. Observations made of the fertilizer-soil-plant reaction zone indicated that the thick-coated MAP released its P very slowly. Observations also indicated that the shrink-wrap packaging or arrangement of holes in the packaging material might have been restricting root proliferation around the applied fertilizer. Synthetic coatings which failed to improve the performance of fertilizer P (increased growth or P uptake) after 45 days of growth might have contributed P to plant growth and development later in the growing season.

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CHAPTER 4

THE EFFECT OF CONTROLLED-RELEASE PHOSPHORUS FERTILIZERS ON BARLEY GROWTH AND PHOSPHORUS UPTAKE OVER 90 DAYS

4.1 INTRODUCTION

A previous experiment found that monoammonium phosphate (MAP) applied in solution every other day for 44 days increased the uptake of phosphorus (P) by barley and the efficiency of the fertilizer relative to applying MAP in one application at sowing (Chapter 2). A second experiment found that a thin (1.8% by weight) polymer coating on granular ammonium phosphate (12-51-0) fertilizer increased barley dry matter yield and P uptake compared to uncoated 12-51-0 after 45 days of growth (Chapter 3). These findings indicated that the concept of controlled-release P fertilizer was valid even though previous research by Hall and Baker (1967), Terman *et al* (1970), and Allen and Mays (1971) failed to show any benefit from coating P fertilizer with asphalt or elemental sulphur to control P release.

Observations made in Chapter 3 suggested that a thick polymer coating and shrink-wrap coating on 12-51-0 might have prevented root proliferation in the vicinity of the applied fertilizer granules or might have excessively delayed the release of P from the controlled-release granules. After 45 days of growth, barley that had received P with these coatings often had relatively low dry matter yield and relatively high P uptake suggesting that P was taken up late in the experiment and had no impact on yield (luxury consumption) or that the experiment was harvested before the late uptake could have affected plant growth and yield.

Controlled-release P products that deliver P late in a crop's life cycle apparently are of little importance if they do not increase grain yield. Karamanos (1989) found in the greenhouse that P applied to wheat at tillering, or tillering and boot stage, was effectively taken up but by maturity had no affect on straw or grain yield. Furthermore, P uptake does not necessarily increase yield since P uptake may be in excess of plant requirements (Clarke *et al*, 1990). In a hydroponic experiment, Boatwright and Viets (1966) found maximum dry matter and grain yield was attained when wheat was supplied with P from germination up to heading, but supplying P after heading did not influence yield.

In a prior experiment roots did not proliferate around shrink-wrap-coated P granules (Chapter 3). Possibly having pin-holes only on one side of the fertilizer envelope limited root interception and subsequent proliferation. It is possible that pin-holes on both sides of the granule envelope would still control the release of P but would also allow P to diffuse into a slightly greater soil volume and would increase the chance of root interception.

Results from previous experiments (Chapters 2 and 3) have only been obtained from harvests after 45 days of growth. It is not known at what time prior to harvest P uptake occurred in previous experiments or if dry matter and grain yield would have been influenced by late season P uptake. Periodic harvests over the life cycle of the crop could provide additional information for the development of potential controlled-release P products.

The objective of this experiment was to find if P delivered over an extended period from coated phosphate granules would increase barley dry matter and grain yield as well as P uptake. Another objective was to determine at what period in barley's life cycle grain-yield-influencing P uptake occurred. The hypothesis was that effective controlled-release P fertilizer would increase barley P uptake, grain yield, and dry matter yield over conventional P fertilizer.

4.2 MATERIALS AND METHODS

In 1992 Imperial Oil, Chemicals Division provided commercial 12-51-0 fertilizer that had been coated with the same polymer used in the production of controlled-release urea. Two polymer coatings (% by weight) were used, 1.8% (thin) and 2.2% (thick). Homemade controlled-release 12-51-0 was also constructed somewhat similar to that used by Dahnke *et al* (1962). The 12-51-0 granules were sealed in thin plastic packaging wrap that shrunk tightly against the granule when the plastic was heated (hereafter called shrink-wrap or SW). Pin-holes (two on each side) were then poked in the shrink wrap so water could move in and the fertilizer solution could move out.

2.2 L pots (0.018 m^2 soil surface area) were filled to three cm below the rim with 2275 g (oven dry basis) of a Gray Luvisolic soil (0 to 15 cm depth) that had been taken from a field near Goodfare, Alberta (see Appendix 1 for soil characterization). This field had been in continuous hay (alfalfa, Timothy, and bromegrass mixture) for many years with very low or no fertilizer inputs. Solutions of NH_4NO_3, KCl, and Na_2SO_4 equivalent to 143 kg N ha^{-1}, 38 kg K ha^{-1}, and 14 kg S ha^{-1} were mixed into the soil from each pot prior to the start of the experiment. A volume of soil equal to a 3.5 cm depth was removed from each pot and water was added to bring the 2275 g of soil to field capacity. Phosphorus fertilizer granules for the different treatments were then applied to the surface of the moist soil with each granule about 2.5 cm from the edge of the pot, and were covered with 1.5 cm of dry soil. There were 11 P fertilizer treatments, a control that received no P fertilizer, and 5 types of 12-51-0 fertilizer that were applied at 2 rates, 15.7 and 31.4 mg P pot^{-1}. These 5 types of 12-51-0 were: uncoated; coated with shrink-wrap (SW); thin (1.8%) polymer coating; thick (2.2%) polymer coating; and a mixture that consisted of non-coated, thin-coated, and thick-coated granules in a ratio of 1:1:1 using granules that were approximately of equal mass. Three granules pot^{-1} (3,7 and 11 o'clock positions) were used at the 15.7 mg P pot^{-1} rate and 6 granules pot^{-1} (1,3,5,7,9, and 11 o'clock positions) were used at the 31.4 mg P pot^{-1} rate. Barley (*Hordeum vulgare* L. 'Leduc') seeds were then placed on the dry soil surface and covered with the remaining soil (about two cm of depth). The seeds were positioned so they were slightly above and slightly to the side of the P fertilizer treatments. Five days after emergence the seedlings were thinned to 12 per pot with two plants equidistant from each potential P fertilizer placement position (1,3,5,7,9, and 11 o'clock positions). There were 9 pots of each treatment, with three replicates for each of three harvests (30, 60, and 90 days). The 99 pots were arranged in the greenhouse in a randomized complete block design. The experiment ran from September 1 to November 30,

1992. The greenhouse was maintained at approximately 22°C for the first week of the experiment but for the remainder of the experiment the temperature was maintained at a minimum of 18°C with typical daytime heating up to 25°C. Plants were supplied with 16 hours of supplemental light (Sylvania high pressure sodium) from emergence to harvest. Pots were watered to field capacity as needed for the duration of the experiment. Three additional nitrogen and sulphate additions (surface applied and watered in) equivalent to 143 kg N ha^{-1} and 14 kg S ha^{-1} at each application were applied on Day 20, 50, and 70 of the experiment. At each harvest all above ground portions of plants were harvested, dried at 70°C for 24 hours, weighed, ground, and digested by a Kjeldahl method (Technicon Industrial Systems, 1975/revised 1978). Digests were subsequently analyzed for P using an autoanalyzer (Technicon Industrial Systems, 1977). Net P uptake and apparent fertilizer efficiencies were calculated in the same manner as previous experiments (Chapters 2 and 3). Tillers that had developed beyond Haun stage 1.0 were included in tiller numbers at 30 days.

4.3 RESULTS AND DISCUSSION

At 30 days, pots that had received P were about at Haun growth stage 5.5 (±0.3) and the control was about at growth stage 4.2, indicating that plant development had been curtailed by lack of P. Tiller numbers (not counting mainstems) at 30 days also indicate that the barley was responsive to P fertilization and that added P affected tiller development. Generally tiller numbers were greater with uncoated P than with polymer-coated P. Tiller numbers with the thick polymer coating were lower than any other treatment that received P at the same P application rate, but were still greater than control tiller numbers. At the 30 day harvest the dry matter yield from all treatments that received P was greater than from the control (Table 4.1). The thick-coated P product (Treatments 5 and 10) did not yield as high as other treatments with P at the 30 Day harvest, possibly indicating that the coating prevented P release from the granules. The poor performance of the thick-coated product apparently affected treatment 6 as well since the mixture of controlled-release products and uncoated P yielded less than the uncoated P or thin-coated P at the 15.7 mg P pot^{-1} application rate. After 30 days, there was not much difference in yield between the uncoated, shrink-wrap, and thin-coated treatments at the low P application rate and the corresponding treatment at the high application rate.

At the 60 day harvest, plant yield and development in the control treatment lagged behind that of all other treatments. Generally, day 60 dry matter accumulation was about three to four times greater than it had been at day 30 (Table 4.1). Total dry matter yield at 60 days was also lower for the thick-coated treatments than for all other treatments at the same P application rate. However, the head yield from the thick-coated treatment was equal to that from the uncoated 12-51-0 at either application rate, even though it yielded less than the other controlled-release P products. At 60 days, the uncoated treatments tended to yield less than the highest yielding controlled-release products at the same P application rate. The overall differences in dry matter yield between P application rates increased between the 30 and 60 day harvests.

Table 4.1. Barley yield after 30, 60, and 90 days

		Tillers (pot^{-1})	Yield (g pot^{-1})				
Treatment	P Added (mg P pot^{-1})	30 Days	30 Days	60 Days		90 Days	
			Total	Heads	Total	Heads	Total
1. Control	0	0	1.4	0	7.9	3.9	11.2
2. Uncoated	15.7	12.0	4.7	6.3	16.6	11.1	21.1
3. SW Coat	15.7	14.1	4.6	6.4	17.0	10.7	20.9
4. Thin Coat	15.7	9.6	4.5	6.8	17.6	12.4	23.0
5. Thick Coat	15.7	3.7	3.1	5.7	15.0	9.2	18.5
6. Mixture†	15.7	8.4	3.8	6.6	16.8	12.0	22.4
7. Uncoated	31.4	19.3	5.2	8.9	20.7	13.9	25.7
8. SW Coat	31.4	18.2	5.1	9.3	21.4	16.4	28.6
9. Thin Coat	31.4	14.6	5.0	9.8	21.5	17.5	29.2
10. Thick Coat	31.4	9.6	3.7	8.1	18.8	16.5	27.8
11. Mixture†	31.4	14.3	4.8	9.4	21.1	15.5	26.9
LSD (0.05)		2.1	0.5	1.0	1.5	1.9	2.2

†Mixture of Uncoated, Thin Coat, and Thick Coat in a ratio of 1:1:1 using approximately equal sized granules.

At maturity (90 days) the control yielded much less than any of the treatments that had received P. The average head yield from the 15.7 mg P pot^{-1} treatments was nearly three times the control yield. At this low P rate, the head yield in the thick-coated treatment was lower than the head yield in the thin-coated and mixture treatments. At the high P application rate, the head yield was less with the uncoated 12-51-0 treatment than with any of the three controlled-release P products. Treatment 10 (thick coating) which had lower dry matter (30 and 60 days) and head (60 days) yield than Treatments 8 and 9 had yield equal to these treatments at maturity. Treatment 10 produced head dry matter yield in the 60 to 90 day interval.

After 30 days, P uptake in the control was less than any treatment that received P (Table 4.2). In most cases, treatments at the high P application rate had greater P uptake than treatments at the low application rate. As was the case with dry matter yield, after 30 days the thick coated treatments (5 and 10) and the mixture treatments that contained the thick coating had lower P uptake than the other controlled release sources and the uncoated 12-51-0 treatments. The lower dry matter yield with the thick coating was likely due to low P uptake as a result of slow P release.

Table 4.2 P uptake by barley after 30, 60 and 90 days

Treatment	P Added (mg P pot^{-1})	P Uptake 30 Days	 60 Days (mg P pot^{-1})	 90 Days
1. Control	0	2.2	6.4	7.5
2. Uncoated	15.7	6.9	11.7	13.4
3. SW Coat	15.7	7.8	12.2	13.8
4. Thin Coat	15.7	7.8	13.1	15.4
5. Thick Coat	15.7	5.4	13.2	13.7
6. Mixture†	15.7	6.1	12.5	15.9
7. Uncoated	31.4	10.3	17.7	20.0
8. SW Coat	31.4	11.4	19.1	21.7
9. Thin Coat	31.4	10.9	20.2	22.1
10. Thick Coat	31.4	7.0	16.8	23.0
11. Mixture†	31.4	9.1	19.1	21.6
LSD (0.05)		1.2	1.7	3.3

†Mixture of Uncoated, Thin Coat, and Thick Coat in a ratio of 1:1:1 using approximately equal sized granules.

Tillers that had developed by 30 days usually did not form heads by 60 days or by maturity. Very rarely did any individual pot produce heads on anything other than mainstems. During the day 40 to day 50 time period, it was observed that the lower leaves of many plants were senescing. It is possible that the tiller abortion and premature senescence were due to P translocation from old to new growth. Phosphorus uptake at day 60 was only about two times that found at day 30 (Table 4.2) even though dry matter had increased about four-fold (Table 4.1). This reduction in total plant P concentration (Appendix 7) perhaps indicated that the P application rates used in this experiment were inadequate for plant demand.

At 60 days, P uptake with the thick-coated P was lower than other controlled-release P treatments at the same application rate and was equal to the uncoated P. During the 30 to 60 day interval the P uptake of the uncoated P treatments (2 and 7) did not increase as much as did the thin (4 and 9), thick (5 and 10), or uncoated/thin/thick mixture treatments (6 and 11). Nevertheless, the head yield at the 60 day harvest (Table 4.1) in the uncoated treatments remained nearly as great as in the best of the controlled-release P products at the corresponding P rate. If the experiment had stopped after 60 days it would have been reasonable to conclude that the additional P uptake with the controlled-release P sources at the high rate was merely luxury consumption of no importance for head yield.

Most treatments at both rates continued to acquire P slowly between 60 days and maturity (Table 4.2). Treatment 10 (thick coat) was an exception, taking up about 6.2 mg P pot^{-1} (over 25% of its total P) in the last 30 days of growth which was far more than any other treatment. The late season P uptake in Treatment 10 apparently contributed to the yield increase over the same time interval (Table 4.1). Even though the controlled-release P sources at the high rate increased head yield over uncoated P (Table 4.1), the differences in total P uptake were usually not significant (Table 4.2). Compared to conventional P fertilizer, it would appear that controlled-release P sources can deliver P to plants in a manner or at a time that allows the plants to effectively utilize the fertilizer.

The yield increase in Treatment 10 due to late season P uptake differs from the finding of Boatwright and Viets (1966) that P taken up by wheat after heading did not affect yield. In the work of Boatwright and Viets (1966), wheat P concentration at heading was about three times the usual concentration found in wheat at heading, indicating that there was abundant P for translocation within the plant. In the present work, there was evidence of P translocation prior to heading and P concentrations had already declined by heading. Thus on soils that are P deficient, P uptake after heading might contribute P (affecting head yield) which could not be supplied to the heads by translocation from leaves and stems.

Net P uptake and fertilizer efficiencies were calculated by subtracting the control P uptake from the P uptake for each treatment (Table 4.3). Apparent fertilizer efficiencies at maturity ranged from 37% to 53%. At both P application rates, the uncoated P apparently was the least efficient P source. These fertilizer efficiencies are considerably higher than values reported elsewhere for wheat (Strong and Soper, 1973).

Table 4.3. Net P uptake and recovery of added P after 30, 60, and 90 days

Treatment	P Added	Net Uptake of Added P (mg P pot^{-1})			Net Recovery of Added P (%)		
	(mg P pot^{-1})	30 days	60 days	90 days	30 days	60 days	90 days
2. Uncoated	15.7	4.8	5.3	5.9	30	34	37
3. SW Coat	15.7	5.7	5.8	6.2	36	37	40
4. Thin Coat	15.7	5.6	6.7	7.8	36	43	50
5. Thick Coat	15.7	3.3	6.8	6.1	21	43	39
6. Mixture†	15.7	4.0	6.1	8.3	25	39	53
7. Uncoated	31.4	8.1	11.3	12.5	26	36	40
8. SW Coat	31.4	9.3	12.7	14.2	30	40	45
9. Thin Coat	31.4	8.8	13.8	14.6	28	44	46
10. Thick Coat	31.4	4.8	10.4	15.9	15	33	51
11. Mixture†	31.4	6.9	12.7	14.1	22	40	45
LSD (0.05)		1.3	1.8	2.9			

†Mixture of No Coat, Thin Coat, and Thick Coat in a ratio of 1:1:1 using approximately equal sized granules.

Barley dry matter yield and P uptake were increased by P fertilization on this soil. The soil was probably P deficient (low extractable P) as a result of continuous nutrient removal without nutrient replacement. Strong and Soper (1974) found that there was an inverse relationship between the availability of soil P and the utilization of P from a band or pellet-like application. If available soil P was very low, a growing crop would utilize fertilizer P more effectively than if available soil P was high. The relatively high fertilizer efficiencies in this experiment (Table 4.3) are possibly a product of the severely P deficient nature of the soil.

In Chapter 1 it was argued that if controlled-release P could limit the formation of P fertilizer reaction products it could increase the effectiveness of applied fertilizer P. Dicalcium phosphate dihydrate (DCPD) has often been identified as a P fertilizer reaction product (Lindsay *et al*, 1962; Racz and Soper, 1967; Bell and Black, 1970; Messier, 1990). Strong and Soper (1974) found that DCPD could effectively be utilized by flax, wheat, rape, and buckwheat on soils with low available P. Therefore, with the severely P deficient nature of the soil from Goodfare, it is possible that if DCPD formed as a reaction product following fertilization with uncoated 12-51-0, then barley still could have acquired P from DCPD, maximizing fertilizer effectiveness. Even under these experimental conditions, controlling the release of P with synthetic coatings led to higher head yield (thin, thick, and SW) and total dry matter yield (thin and SW) when P was applied at 31.4 mg P pot^{-1}.

4.4 CONCLUSIONS

The response of barley to P fertilization indicated that the soil used in these greenhouse experiments was very P deficient. Controlled-release P fertilizer sources significantly increased barley head yield over uncoated 12-51-0 P fertilizer when P was applied at 31.4 mg P pot^{-1}. The yield increase occurred with both high technology products (polymer coatings) and crude experimental products (leaky shrink-wrap packages). Coatings that delayed the release of P from the fertilizer granules increased the effectiveness (plant yield) and tended to increase the efficiency (% recovery) and of the applied fertilizer. Differences between fertilizer treatments usually did not occur at the 15.7 mg P pot^{-1} rate. The thick polymer coating appeared to release fertilizer slowly, but P released after 60 days of growth apparently contributed to barley head yield. The hypothesis that effective controlled-release P fertilizer would increase barley P uptake, and grain and dry matter yield over conventional P fertilizer is only partially true. At the 31.4 mg P pot^{-1} P application rate, total P uptake was not increased with controlled release sources. However, controlled-release P sources effectively converted P into higher head yield than was attained with conventional P sources. This experiment indicated that controlled-release phosphorus fertilizers may be superior to conventional P fertilizers.

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Chapter 5

BARLEY YIELD, PHOSPHORUS UPTAKE, AND PHOSPHORUS RELEASE FROM CONTROLLED-RELEASE SOURCES OVER 52 DAYS

5.1 INTRODUCTION

Phosphorus uptake by barley and barley dry matter yield over 45 days (Chapter 3) and barley head yield over 90 days (Chapter 4) indicated that synthetic coatings could increase the benefit of commercial 12-51-0 in experimental situations. Shrink wrap packaging with 4 pin-holes (2 holes on each side of the fertilizer granule), thin (1.8%) polymer coating, and thick (2.2%) polymer coating were found to be effective controlled-release P sources through a trial and error selection process. Inferences on P release characteristics of those controlled-release P sources were drawn from plant P uptake and dry matter yield at periodic plant harvests, but the longevity and detailed direct release characteristics of those controlled-release products have not been determined.

The purpose of this experiment was to determine *in situ* P release characteristics of thin (1.8%) and thick (2.2%) polymer-coated 12-51-0. A secondary purpose was to assess inferences from previous work that indicated controlled-release P sources were more effectively utilized than conventional P fertilizers. The hypothesis was that controlling the release of P fertilizer with synthetic coatings increased the effectiveness (plant P uptake, yield, fertilizer efficiency) of applied P relative to present uncoated commercial fertilizers.

5.2 MATERIALS AND METHODS

2.2 L pots (0.018 m^2 soil surface area) were filled to three cm below the rim with 2275 g (oven dry basis) of a Gray Luvisolic soil (0 to 15 cm depth) that had been taken from a field near Goodfare, Alberta (see Appendix 1 for soil characterization). This field had been in continuous hay (alfalfa, Timothy, and brome mixture) for many years with low or no fertilizer inputs. Solutions of NH_4NO_3, KCl, and Na_2SO_4 equivalent to 143 kg N ha^{-1}, 38 kg K ha^{-1}, and

28 kg S ha^{-1} were mixed into the soil from each pot prior to the start of the experiment. A volume of soil equal to a 3.5 cm depth was removed from each pot and water was added to bring the 2275 g of soil to field capacity. Phosphorus fertilizer treatments were then applied to the surface of the moist soil in a hexagonal arrangement (6 granules pot^{-1} with all granules 2.5 cm from the edge of the pot), and covered with 1.5 cm of dry soil. There were four P fertilizer treatments: a control that received no P fertilizer, uncoated 12-51-0 fertilizer, thin (1.8%) polymer-coated 12-51-0, and thick (2.2%) polymer-coated 12-51-0. Phosphorus was applied at 21.6 mg P pot^{-1} using 6 granules pot^{-1} (1,3,5,7,9, and 11 o'clock positions) for all treatments that received P. Barley (*Hordeum vulgare* L. 'Leduc') seeds were then placed on the dry soil surface and covered with the remaining soil (about two cm of depth). The seeds were positioned so they were slightly above and slightly to the side of the P fertilizer treatments. Five days after emergence seedlings were thinned to 12 per pot with two plants equidistant from each P fertilizer placement position. There were 12 pots of each treatment, with three replicates for each of four harvests (13, 26, 39, and 52 days). The 48 pots were arranged in the greenhouse in a randomized complete block design. The experiment ran from late January to mid March 1993. The greenhouse was maintained at approximately 22^{0}C for one week (during germination) but for the remainder of the experiment the temperature was maintained at a minimum of 18^{0}C. Unlike previous experiments, sunshine had little affect on daytime temperatures. Plants were supplied with 16 hours of supplemental light (Sylvania high pressure sodium) from emergence to harvest. Pots were watered to field capacity as needed for the duration of the experiment, usually daily or every two days. Two additional nitrogen and sulphate additions (surface applied) equivalent to 143 kg N ha^{-1} and 14 kg S ha^{-1} at each application were applied on Day 14 and 27 of the experiment. The second and third nitrogen and sulphur applications also included copper applied at 1 mg copper kg^{-1} soil. At each harvest all above-ground portions of plants were harvested, dried at 70^{0}C for 24 hours, weighed, ground, and digested by a Kjeldahl method (Technicon Industrial Systems,

1975/revised 1978). Digests were analyzed for P using an autoanalyzer (Technicon Industrial Systems, 1977). At each harvest, the polymer-coated fertilizer granules were recovered from the potted soil, cleaned free of soil, placed in deionized water, and cut open. The P remaining in the fertilizer granules was dissolved in the water and then solution P was measured by an ascorbic acid method (Watanabe and Olsen, 1965). Fertilizer P released from controlled-release sources was calculated by the difference between the amount applied initially (21.6 mg P pot^{-1}) and the amount remaining in the fertilizer granules at each harvest. The fertilizer efficiency (FE) of controlled-release P products could be calculated at each harvest interval on the basis of plant P uptake and P released. Net P uptake and apparent fertilizer efficiencies were calculated in the same manner as previous experiments (Chapters 2-4).

5.3 RESULTS AND DISCUSSION

Phosphorus fertilizer treatments were applied on a per pot basis using six approximately equal sized granules. For the P release characterization, all six fertilizer granules pot^{-1} had to be recovered in order to determine the fraction of P released from the coated fertilizer. Unfortunately this was not always possible for all three replicates of each treatment at each harvest. The dark brown color of the coated 12-51-0 was much the same as the color of the moist soil, and consequently recovery of all granules was difficult, especially at the day 13 harvest when root proliferation around the controlled-release P granules had not occurred. For each treatment at each harvest interval the entire six coated granules were recovered from at least two replicates.

The thin and thick-coated P products had different release characteristics (see Appendix 5, Table A5.1). The thin-coated product released over half of its P by 13 days and essentially all of its P by 26 days (Table 5.1). Release from this thin-coated product was exponential (P release = $21.6*(1-e^{-0.08day})$, see Appendix 5, Table A5.2) The thick-coated treatment released its P much more slowly with about 19% of its P remaining in the granule after 52 days. Release from the thick-coated P was linear over the 52 days of this experiment (P release = 4.4 + 0.26day, see Appendix 5, Table A5.3).

The release characteristics of the thick coating indicated that considerable quantities of P would have been available for uptake even after 52 days. In Chapter 4, it was speculated that the thick coated treatment released P late in the growing season producing grain yield after 60 days. Since these results indicate that about 19% of the P remained within the thick coated granules after 52 days, the late season yield improvement in the thick coated treatment in Chapter 4 could very well have been from late season P release from the coated P fertilizer.

Table 5.1 P released from controlled-release sources over 52 days

Treatment	P Released From Coated Fertilizer ($mg\ P\ pot^{-1}$)			
	Day			
	13	26	39	52
Thin	13.2	20.1	20.4	20.8
Thick	7.3	11.7	15.3	17.6

The uncoated 12-51-0 initially (13 days) had higher dry matter yield (Table 5.2) and P uptake (Table 5.3) than did the thin or thick-coated P fertilizer. At 26 days, the thin-coated P had higher P uptake than the uncoated 12-51-0, but the two treatments had similar yield which was higher than with the thick coating. At subsequent harvests (39 and 52 days) the thin-coated P yield and P uptake were higher than either measurement with the thick-coated or uncoated P.

The thick-coated treatment yield and P uptake were lower than the uncoated P for the first two harvests. By the third harvest (39 days) the yield was still higher with the uncoated P but the P uptake in the two treatments were similar. When the experiment was terminated at 52 days P uptake and head yield were similar in uncoated and thick-coated P treatments.

Table 5.2. Barley yield over 52 days

Treatment	Stem and Leaf Yield (g pot^{-1})			Yield After 52 Days (g pot^{-1})		
	Day					
	13	26	39	Stem and Leaf	Head	Total
Control	0.45	1.19	3.19	7.76	0	7.76
Uncoated	0.96	5.32	11.70	15.33	3.63	18.96
Thin	0.71	5.21	13.73	18.07	6.35	24.41
Thick	0.60	3.65	10.12	14.53	4.11	18.64
LSD	0.20	0.82	1.34	2.19	1.7	3.37

Table 5.3. Barley P uptake over 52 days and net fertilizer efficiency and P concentration at 52 days

Treatment	P Uptake (mg P pot^{-1})				NFE† (%)	FE†† (%)	P Concentration at 52 Days (%)	
	Day				Day	Day		
	13	26	39	52	52	52	Stem and Leaf	Head
Control	0.65	1.27	4.15	6.47	n/a*	n/a	0.083	n/a
Uncoated	3.65	6.96	11.18	12.39	27.4	27.4	0.052	0.123
Thin	2.50	8.72	12.76	15.71	42.8	44.4	0.045	0.122
Thick	1.40	5.58	11.08	13.28	31.5	38.7	0.055	0.128
LSD	0.66	0.61	0.83	2.22			0.006	0.010

*n/a: not applicable

†NFE: Net fertilizer efficiency: net P uptake/fertilizer P applied

††FE: Fertilizer efficiency: net P uptake/fertilizer P released. This calculation is included in order for the different P fertilizer products to be compared on the basis of fertilizer released. The apparent fertilizer efficiencies of controlled-release P sources in this calculation are not artificially deflated by P remaining within the coated fertilizer granules.

Apparent P fertilizer efficiencies at 52 days were similar to fertilizer efficiencies at 60 days in Chapter 4 (see Table 4.3 and Table 5.3). The efficiency of the uncoated P treatment was slightly lower than the previous experiment possibly due to the slightly lower greenhouse temperatures and slightly less available fertilizer reaction products, assuming reaction products formed. At 52 days, the fertilizer efficiency (FE) of the thick-coated P tended to be slightly lower than the thin-coated P but both appeared (trend) to be considerably more efficient than the uncoated P. The efficiency (trend) of P fertilizer with the thin polymer coating was over 1.5 times the efficiency of uncoated P.

The pattern of dry matter accumulation and P uptake observed in this experiment was similar to the first 60 days of growth in Chapter 4 (compare Tables 4.2 and 5.3). The similarity in dry matter yield and P uptake in the present 52-day long experiment and previous work suggests that if this experiment had continued, the head yield and P uptake in the thick-coated P treatment might have surpassed that of the uncoated treatment. At the conclusion of this experiment the uncoated and thick-coated treatments had similar head yield, total yield, P uptake, and plant P concentrations in the heads, stems, and leaves. After the 52 day harvest, the uncoated treatment would have been able to draw upon P in the soil and in stems and leaves. After the 52 day harvest, the thick-coated treatment could have drawn upon the same pools of P available to the uncoated P, plus P not yet released from the controlled-release granules.

The inclusion of an early (13 days) harvest revealed that the uncoated 12-51-0 had higher yield and P uptake than controlled-release P sources during the first 13 days of growth. In spite of the increased P uptake and plant growth early in the experiment, uncoated P was not able to maintain this early season advantage over the course of the experiment. Since both the uncoated and thin-coated treatments were applied at the same rate, it is possible that the poor performance of the uncoated treatment later in the experiment was caused by fertilizer P being made less available to plants perhaps through precipitation of fertilizer reaction products.

Tomasiewicz and Racz (1991) found that in several field situations wheat grain yield was often limited by P stress in the first few weeks after emergence. Tomasiewicz and Racz (1991) compared a broadcast treatment of 20 kg P ha^{-1} (P stress early) with a treatment that combined 20 kg (seed-placed) P ha^{-1} and 50 kg (broadcast) P ha^{-1} (ample P throughout the growing season) and found higher tissue P concentrations early in the experiment, and higher yield at maturity, in the ample P treatment than in the broadcast treatment. In subsequent work, however, Tomasiewicz and Racz (1993) included a seed-placed 20 kg P ha^{-1} treatment which had similar yield as the broadcast 20 kg P ha^{-1} treatment and both yielded lower than the combined 20 kg (seed-placed) P ha^{-1} and 50 kg (broadcast) P ha^{-1}. If the broadcast P was an accurate indicator of early P stress, there should have been a difference in yield between 20 kg P ha^{-1} broadcast and seed-placed (assuming seed-placed P alleviated early season P stress). Possibly in the earlier work Tomasiewicz and Racz mistakenly associated timing of P stress to their treatments when they should have associated overall P availability. Broadcast treatments positionally do not support plant P uptake early since roots must randomly grow and intercept fertilizer P. However, broadcast P also has greater soil-fertilizer reaction zone volume than banded or seed-placed P, potentially increasing the chances of P attenuation (precipitation or adsorption) prior to root interception. Although broadcast P fertilizer is positioned for later P uptake, the placement [illegible] can decrease the effectiveness of the fertilizer.

Bailey and [illegible] attributed higher rape yield from banded compared to broadcast P, [illegible] and concentration with the banded P at early growth stages (21 days after emergence). However, at every measured harvest interval (not just 21 days) dry matter yield (and grain yield at maturity) and P uptake were always higher with banded P, possibly indicating that the results were due not to a timing of P uptake but overall availability. This interpretation is supported by the fact that P banded at 20 kg P ha^{-1} (the apparent yield plateau rate) had higher P uptake than P banded at 15 kg P ha^{-1} at every harvest interval including maturity and had higher dry matter (and grain yield) at every harvest interval other than 21 days. Differences between banded P and broadcast P probably indicate differences in overall P availability between the treatments (due to placement) more than differences in the timing of P uptake.

Boatwright and Viets (1966) found that wheat and wheatgrass deprived of P early in their growth and development suffered permanent damage. It must be remembered that Boatwright and Viets were working with hydroponics where the control (nil) P rate was much closer to 0 available P than can be expected in soil. Even with the soil from Goodfare, which was very P deficient, the control treatment still had access to some P (0.65 mg pot^{-1}) by 13 days. Although the thin and thick polymer coatings delayed the release of P, both products were capable of supplying some P to plants early in the experiment (Table 5.1). In this work, controlled-release P treatments were not totally deprived of P early in the experiment and were supplied with P for extended periods of time.

In this experiment the yield-limiting P stress occurred after the first few weeks of growth (since the uncoated P source had the highest P uptake and dry matter yield after 13 days yet was inferior to the thin-coated P fertilizer by the end of the experiment), possibly contradicting what is generally accepted as true regarding P fertility. However apparent discrepancies between these results and those of other researchers are due to the present inclusion of controlled release P sources which were not available before.

5.4 CONCLUSIONS

Polymer coatings on commercial 12-51-0 fertilizer controlled the release of P. Measured *in situ* with soil and growing barley, a 1.8% polymer-coated product (thin) released essentially all P within 26 days of application, and a 2.2% (thick) polymer-coated product released about 80% of its P within 52 days. Uncoated 12-51-0 produced the highest dry matter yield and had the highest P uptake at 13 days. The product with the thin polymer coating initially (13 days) had lower yield and P uptake than the uncoated P, at 26 days the two treatments had similar yield but P uptake was higher with the thin coating, and for subsequent harvests the thin-coated P had higher P uptake, dry matter yield, and head yield (52 days). The thick polymer coating also initially (13 and 26 days) had lower P uptake and yield than the uncoated P, but by the final harvest the two treatments were equal in all measured parameters. At the termination of this experiment the thick-coated treatment had greater potential for growth and P uptake than the uncoated treatment since about 20% of applied P remained as potentially plant available within the controlled release fertilizer. The pattern of P uptake, dry matter yield and grain yield observed with barley on this very P deficient soil also suggested that the P limiting stress did not necessarily occur very early in plant growth and development. Situations may exist where conventional P fertilizers (due to the formation of insoluble fertilizer reaction products or some other attenuation process) may not be able to supply a growing crop with P late in the crop growth cycle when controlled-release P fertilizers are capable of delivering adequate P. The results of this experiment indicate that controlled-release P fertilizer may have benefits over existing conventional P fertilizers.

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CHAPTER 6

SYNTHESIS

Controlled-release P is based on the perception that applied P fertilizer becomes less available as plant demand for P increases. Calcium and or magnesium phosphate precipitates have been identified following application of MAP or DAP (Lindsay *et al*, 1962; Racz and Soper, 1967; Bell and Black, 1970; Messier, 1990). These fertilizer reaction products can reduce the solubility of applied P. The pattern of plant P uptake is somewhat similar to the pattern of dry matter accumulation, with large amounts of P taken up during the most rapid phase of vegetative growth (Kalra and Soper, 1968; Ningping and Barber, 1985). Matching P fertilizer release with plant demand could increase the benefit of applied fertilizer (Dahnke *et al*, 1962). Controlling the release of P could also limit the contact of applied P fertilizer with soil, possibly reducing attenuation processes (precipitation and/or adsorption), and increasing the plant availability of the fertilizer (Hall and Baker, 1967).

The concept of controlled-release P fertilizer is not new. However, to my knowledge, there is no record in the literature that an effective controlled-release P fertilizer product has ever been successfully tested except for work stemming from my research (Nyborg *et al*, 1995; Solberg *et al*, 1995; Pauly *et al*, 1995). Hall and Baker (1967), Terman *et al* (1970) and Allen and Mays (1971) tested controlled-release P products which were ineffective P fertilizers, possibly because P release from these products was much slower than plant demand. Terman *et al* (1970) and Allen and Mays (1971) rejected the concept of controlled-release P fertilizer apparently because their specific experimental products failed to function.

In my experiments, the validity of controlled-release P fertilizer was first established by testing the idea without testing specific experimental P fertilizers. Phosphorus uptake by barley was increased by applying P solutions to the rooting zone of the growing crop every second day or every eleventh day for 44 days relative to applying all P at sowing (Chapter 2). Phosphorus applied in this manner simulated an effective controlled-release P product.

The controlled-release P concept was further evaluated by testing experimental granular controlled-release P products in the greenhouse. Phosphorus uptake after 45 days was higher with commercial 12-51-0 (MAP) prepared with a thin (1.8% by weight) polymer coating than uncoated MAP (Chapter 3). Fertilizer efficiency with this thin polymer coating was nearly double that of the uncoated MAP. Fertilizer (MAP) with a thick (2.2%) polymer coating, or wrapped in shrink-wrap packaging with pin-holes, did not increase P uptake or efficiency over uncoated MAP, possibly because these controlled-release P sources were releasing P excessively late in the crop's life cycle.

In a third experiment, barley head and total dry matter yield at maturity (90 days) were higher when P (31.4 mg P pot-1) was supplied by controlled-release products (thin and thick polymer coating, and shrink-wrap with four holes) than by uncoated MAP (Chapter 4). The plant harvests at 30, 60, and 90 days indicated that P uptake subsequent to the 30 day harvest increased barley head and total dry matter yield. Controlled-release P sources tended to supply more P to barley after 30 days than did conventional (uncoated) P sources. Phosphorus uptake, during the 60 to 90 day interval with the thick polymer coating, accounted for about 25% of this treatment's total P uptake. The efficiency of applied P tended to be higher with controlled-release sources than with uncoated MAP. In this third experiment, barley acquired P from controlled-release P sources when P was apparently less available from uncoated MAP, further validating the concept of controlled release P fertilizer.

The pattern of barley dry matter accumulation and P uptake, as well as the *in situ* P release characteristics from polymer coated MAP over 52 days were determined in a fourth experiment (Chapter 5). Phosphorus was released from the thin-coated P fairly rapidly (about 60% after 13 days and over 93% after 26 days) but was released more slowly from the thick-coated P (33% after 13 days and 81% after 52 days). Barley dry matter yield and P uptake after 13 days were higher with uncoated MAP than with either thin or thick polymer-coated P. Uncoated and thin-coated MAP had similar dry matter yield at 26 days but the thin-coated MAP had higher P uptake (26, 39, and 52 days) and dry matter (39 and 52 days) and head (52 days) yield for most of the experiment. Although the thick-coated MAP had lower P uptake and dry matter yield than uncoated P at 13, 26, and 39 days, the two treatments were equal at 52 days in all measured parameters (P uptake, dry matter yield, head yield). Phosphorus uptake and dry matter accumulation over 52 days as observed in this experiment indicated that controlled-release P sources were capable of supplying growing plants with P longer than conventional P fertilizer sources, again validating the concept of controlled-release P fertilizer.

Controlled-release P products used in the third and fourth experiments were identified through a trial and error process. Although the two polymer-coated P products were found to be effective for the greenhouse conditions and soils that I used, better or more effective controlled-release P products could still be identified. The thin and thick-coated products had different release characteristics, yet both effectively delivered P to barley. Ideally it probably would have been better to have a product that released P evenly until heading (about 40 days after sowing) rather than releasing P over 26 days (thin-coat) or in excess of 52 days (thick-coat). Field research, where soil is not maintained at field capacity, or where soil temperatures are lower than those used in the greenhouse, might find thin or thick, both, or neither of these polymer-coated products to be effective P sources. The controlled-release P sources that I used in my experiments have been instrumental in validating the concept of controlled-release P fertilizer but could possibly be improved.

I approached the concept of controlled-release P fertilization assuming that conventional P fertilizer became less available with time as fertilizer reaction products formed. In my work I have no direct evidence to support this assumption. I also do not have direct evidence indicating that protective coatings on P limit or prevent the formation of fertilizer reaction products. Through my experimental work, however, I have found that barley continues to take up P relatively late (after 60 days) in its life cycle. Based on *in situ* P release characteristics I have found that the thin and thick-coated MAP used in three of my experiments could deliver readily soluble P to growing plants over extended periods. In four greenhouse experiments I have found that simulated or experimental controlled-release P sources were often superior to conventional uncoated P fertilizer on the basis of increased plant P uptake and fertilizer efficiency and/or higher plant (dry matter or head) yield. Controlling the release of P from fertilizer therefore is a valid concept.

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APPENDIX 1

CHARACTERISTICS OF SOILS FROM ELLERSLIE, BRETON, AND GOODFARE

Table A1.1 Soil Characteristics

Origin	Great Group	Texture	pH†	Organic C ($g\ kg^{-1}$)	Total N ($g\ kg^{-1}$)	Total P ($mg\ kg^{-1}$)	Extractable P†† ($mg\ kg^{-1}$)
Ellerslie	Black Chernozem	Silty Loam	5.8	59.4	5.0	800	9.2
Breton	Gray Luvisol	Sandy Clay Loam	6.2	12.3	1.0	370	16.2
Goodfare	Gray Luvisol	Clay Loam	6.0	18.5	1.4	350	5.6

†In water (2 parts water and one part soil)

††Extractable in 0.03 M NH_4F & 0.015 M H_2SO_4

APPENDIX 2

CHAPTER 2 STATISTICS

Table A2.1 ANOVA of phosphorus uptake after 45 days on soil from Ellerslie (Table 2.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	13.0952	4.3651	1.26	0.3169
Treatment	6	48.3987	8.0664	2.33	0.0764
Error	18	62.2189	3.4566		
Total	27	123.7128			

C.V. = 7.97

Table A2.2 ANOVA of dry matter yield after 45 days on soil from Ellerslie (Table 2.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	1.5952	0.5317	1.75	0.1921
Treatment	6	16.5220	2.7537	9.08	0.0001
Error	18	5.4588	0.3033		
Total	27	23.5760			

C.V. = 5.21

Table A2.3 ANOVA of phosphorus uptake after 45 days on soil from Breton (Table 2.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	5.6393	1.8798	0.98	0.4223
Treatment	6	123.0410	20.5068	10.74	0.0001
Error	18	34.3827	1.9102		
Total	27	163.0629			

C.V. = 4.66

Table A2.4 ANOVA of dry matter yield after 45 days on soil from Breton (Table 2.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	2.4868	0.8289	2.78	0.0710
Treatment	6	13.0771	2.1795	7.3	0.0005
Error	18	5.3715	0.2984		
Total	27	20.9353			

C.V. = 4.79

Table A2.5 ANOVA of phosphorus uptake after 45 days on soils from Ellerslie and Breton combined (Table 2.4)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	10.3206	3.4402	1.28	0.2955
Soil	1	562.2909	562.2909	208.82	0.0001
Treatment	6	152.4817	25.4136	9.44	0.0001
Soil*Treatment	6	18.9579	3.1596	1.17	0.3403
Error	39	105.0154	2.6927		
Total	55	849.0666			

C.V. = 6.19

Table A2.6 ANOVA of dry matter yield after 45 days on soils from Ellerslie and Breton combined (Table 2.4)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	2.9729	0.9910	3.24	0.324
Soil	1	9.6065	9.6066	31.38	0.0001
Treatment	6	27.8470	4.6412	15.16	0.0001
Soil*Treatment	6	1.7521	0.2920	0.95	0.4687
Error	39	11.9393	0.3061		
Total	55	54.1179			

C.V. = 5.03

APPENDIX 3
CHAPTER 3 STATISTICS

Table A3.1 ANOVA of barley dry matter yield after 45 days on soil from Ellerslie (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	2.8536	0.9512	4.21	0.0109
Treatment	14	49.7782	3.5556	15.73	0.0001
Error	42	9.4944	0.2260		
Total	59	62.1262			

C.V. = 4.13

Table A3.2 ANOVA of phosphorus uptake by barley after 45 days on soil from Ellerslie (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	46.8015	15.6005	5.58	0.0026
Treatment	14	86.0171	6.1441	2.20	0.0250
Error	42	117.5169	2.7980		
Total	59	250.3355			

C.V. = 7.15

Table A3.3 ANOVA of barley dry matter yield after 45 days on soil from Breton (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	7.0783	2.3594	7.38	0.0004
Treatment	14	19.9411	1.4244	4.45	0.0001
Error	42	13.4318	40.4512		
Total	59	40.4512			

C.V. = 4.72

Table A3.4 ANOVA of phosphorus uptake by barley after 45 days on soil from Breton (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	22.8048	7.6016	3.63	0.0204
Treatment	14	110.7287	7.9092	3.78	0.0004
Error	42	87.9274	2.0935		
Total	59	221.4609			

C.V. = 5.00

Table A3.5 ANOVA of barley dry matter yield after 45 days on both soils combined (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	9.3035	3.1012	11.45	0.0001
Soil	1	6.4293	6.4292	23.75	0.0001
Treatment	14	60.5982	4.3284	15.99	0.0001
Soil*Treatment	14	9.1211	0.6515	2.41	0.0068
Error	87	23.5547	0.2707		
Total	119	109.0067			

C.V. = 4.43

Table A3.6 ANOVA of phosphorus uptake by barley after 45 days on both soils combined (Table 3.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	8.3322	2.7773	0.91	0.4417
Soil	1	911.9202	911.9202	297.46	0.0001
Treatment	14	161.4057	11.5290	3.76	0.0001
Soil*Treatment	14	35.3400	2.5243	0.82	0.6421
Error	87	266.7184	3.0657		
Total	119				

C.V. = 6.69

Table A3.7 ANOVA of net phosphorus uptake by barley after 45 days on soil from Ellerslie (Table 3.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	416.2213	138.7404	60.28	0.0001
Treatment	13	52.3101	4.0239	1.75	0.0888
Error	39	89.7688	2.3018		
Total	55	558.3002			

C.V. = 50.49

Table A3.8 ANOVA of net phosphorus uptake by barley after 45 days on soil from Breton (Table 3.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	91.7915	30.5972	14.59	0.0001
Treatment	13	59.1648	4.5511	2.17	0.0312
Error	39	81.8080	2.0976		
Total	55	232.7643			

C.V. = 38.97

Table A3.9 ANOVA of net phosphorus uptake by barley after 45 days on both soils combined (Table 3.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	447.1955	149.0652	51.96	0.0001
Soil	1	14.1803	14.1803	4.94	0.0290
Treatment	13	77.0802	5.9292	2.07	0.0251
Soil*Treatment	13	34.3947	2.6457	0.92	0.5343
Error	81	232.3941	2.8690		
Total	111	805.2449			

C.V. = 50.40

APPENDIX 4
CHAPTER 4 STATISTICS

Table A4.1 ANOVA of tiller numbers after 30 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	27.7171	13.8586	2.69	0.0738
Treatment	10	3067.3535	306.7354	59.46	0.0001
Error	86	443.6162	5.1583		
Total	98	3538.6869			

C.V. = 20.18

Table A4.2 ANOVA of barley dry matter yield after 30 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.1575	0.0787	1.13	0.3438
Treatment	10	38.3503	3.8350	54.88	0.0001
Error	20	1.3977	0.0699		
Total	32	39.9054			

C.V. = 6.32

Table A4.3 ANOVA of barley head yield after 60 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.6420	0.3210	0.95	0.4029
Treatment	10	225.5633	22.5563	66.88	0.0001
Error	20	6.7457	0.3373		
Total	32	232.9511			

C.V. = 8.27

Table A4.4 ANOVA of barley dry matter (total) yield after 60 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.9461	0.4730	0.63	0.5438
Treatment	10	464.7836	46.4784	61.72	0.0001
Error	20	480.7916	0.7531		
Total	32	480.7916			

C.V. = 4.91

Table A4.5 ANOVA of barley head yield after 90 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	8.7132	4.3566	3.35	0.0555
Treatment	10	472.1647	47.2165	36.35	0.0001
Error	20	25.9820	1.2991		
Total	32	506.8600			

C.V. = 9.01

Table A4.6 ANOVA of barley dry matter yield (total) after 90 days on soil from Goodfare (Table 4.1)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	6.8579	3.4289	2.14	0.1433
Treatment	10	851.6412	85.1641	53.27	0.0001
Error	20	31.9759	1.5989		
Total	32	890.4750			

C.V. = 5.45

Table A4.7 ANOVA of phosphorus uptake by barley after 30 days on soil from Goodfare (Table 4.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.0751	0.0376	0.07	0.9308
Treatment	10	216.6054	21.6605	41.47	0.0001
Error	20	10.4466	0.5223		
Total	32	227.1271			

C.V. = 9.35

Table A4.8 ANOVA of phosphorus uptake by barley after 60 days on soil from Goodfare (Table 4.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	10.3105	5.1552	4.94	0.0180
Treatment	10	526.8415	52.6841	50.50	0.0001
Error	20	20.8660	1.0433		
Total	32	558.0179			

C.V. = 6.93

Table A4.9 ANOVA of phosphorus uptake by barley after 90 days on soil from Goodfare (Table 4.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	11.9926	5.9963	4.48	0.0255
Treatment	10	687.9856	68.7986	51.35	0.0001
Error	19	25.4540	1.3397		
Total	31	725.4322			

C.V. = 6.84

Table A4.10 ANOVA of net phosphorus uptake by barley after 30 days on soil from Goodfare (Table 4.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.4841	0.7420	1.30	0.2982
Treatment	9	114.8983	12.7665	22.29	0.0001
Error	18	10.3117	0.5729		
Total	29	126.6941			

C.V. = 12.39

Table A4.11 ANOVA of net phosphorus uptake by barley after 60 days on soil from Goodfare (Table 4.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	5.7950	2.8975	2.56	0.1047
Treatment	9	297.7066	33.0785	29.27	0.0001
Error	18	20.3392	1.1300		
Total	29	323.8408			

C.V. = 11.60

Table A4.12 ANOVA of net phosphorus uptake by barley after 90 days on soil from Goodfare (Table 4.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	12.6734	6.3367	4.45	0.0278
Treatment	9	396.7623	44.0847	30.98	0.0001
Error	17	24.1878	1.4228		
Total	28	445.6604			

C.V. = 11.50

APPENDIX 5
CHAPTER 5 STATISTICS

Table A5.1 Contrast of phosphorus release characteristics over 52 days from thin and thick-coated MAP

Contrast	DF	Contrast Sum of Squares	Mean Square	F Value	Significance p>F
Thin vs Thick	1	128.3026	128.3026	63.98	0.0001
Error	7	14.0365	2.0052		

Table A5.2 Phosphorus release from thin-coated MAP over 52 days (Non-linear Least Squares Regression)

Source	DF	Sum of Squares	Mean Square
Regression	2	2854.8705	1427.4353
Residual	6	14.3999	2.4000
Uncorrected Total	8	2869.2705	
Corrected Total	7	88.2345	

Parameter	Estimate	Asymptotic Standard Error
b_0	21.5716	1.0280
b_1	0.0801	0.0041

P release = $b_0(1-e^{-b_1 \text{time}})$

Table A5.3 Phosphorus release from thick-coated MAP over 52 days

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	1	117.3456	117.3456	80.109	0.0001
Error	6	8.7890	1.4648		
Total	7	126.1346			

C.V. 9.32 R^2 0.9303

Variable	DF	Estimate	Standard Error	T for H_0	Prob > |T|
Intercept	1	4.4173	1.04815	4.214	0.0056
Day	1	0.2635	0.02944	8.950	0.0001

P release = intercept + Day(time)

Table A5.4 ANOVA of barley stem and leaf yield after 13 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.0416	0.0208	2.12	0.2008
Treatment	3	0.4283	0.1428	14.59	0.0037
Error	6	0.0587	0.0098		
Total	11	0.5286			

C.V. = 14.55

Table A5.5 ANOVA of barley stem and leaf yield after 26 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.6985	0.8492	5.01	0.0525
Treatment	3	33.3520	11.1173	65.58	0.0001
Error	6	1.0171	0.1695		
Total	11	36.0675			

C.V. = 10.71

Table A5.6 ANOVA of barley stem and leaf yield after 39 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	5.5426	2.7713	6.19	0.0348
Treatment	3	188.5282	62.8427	140.29	0.0001
Error	6	2.6878	0.4480		
Total	11	196.7585			

C.V. = 6.91

Table A5.7 ANOVA of barley stem and leaf yield after 52 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.9321	0.9660	0.80	0.4908
Treatment	3	172.4898	57.4966	47.48	0.0001
Error	6	7.2153	1.2025		
Total	11	181.6371			

C.V. = 7.88

Table A5.8 ANOVA of barley head yield after 52 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.6489	0.8244	1.13	0.3823
Treatment	3	62.2219	20.7406	28.52	0.0006
Error	6	4.3638	0.7273		
Total	11	68.2346			

C.V. = 24.22

Table A5.9 ANOVA of barley total yield after 52 days on soil from Goodfare (Table 5.2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	5.0714	2.5357	0.89	0.4584
Treatment	3	438.2165	146.0722	51.31	0.0001
Error	6	17.0805	2.8468		
Total	11	460.3684			

C.V. = [illegible] 7

Table A5.10 ANOVA of phosphorus uptake by barley after 13 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.1266	0.0633	0.58	0.5878
Treatment	3	15.4913	5.1638	47.43	0.0001
Error	6	0.6532	0.1089		
Total	11	16.2711			

C.V. = 16.10

Table A5.11 ANOVA of phosphorus uptake by barley after 26 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.1754	0.0877	0.95	0.4380
Treatment	3	90.8507	30.2836	328.17	0.0001
Error	6	0.5537	0.0923		
Total	11	91.5797			

C.V. = 5.39

Table A5.12 ANOVA of phosphorus uptake by barley after 39 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.2496	0.6248	3.66	0.0913
Treatment	3	132.8334	44.2778	259.59	0.0001
Error	6	1.0234	0.1706		
Total	11	135.1063			

C.V. = 4.22

Table A5.13 ANOVA of phosphorus uptake by barley after 52 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	1.4998	0.7499	0.61	0.5754
Treatment	3	138.3465	46.1155	37.32	0.0003
Error	6	7.4148	1.2358		
Total	11	147.2611			

C.V. = 9.29

Table A5.14 ANOVA of barley stem and leaf tissue P concentration after 52 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000154	0.000077	10.27	0.0116
Treatment	3	0.002603	0.000868	115.77	0.0001
Error	6	0.000045	0.000008		
Total	11	0.002802			

C.V. = 4.66

Table A5.15 ANOVA of barley head tissue P concentration after 52 days on soil from Goodfare (Table 5.3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000250	0.000125	4.60	0.0616
Treatment	3	0.034772	0.011591	425.87	0.0001
Error	6	0.000163	0.000027		
Total	11	0.035185			

C.V. = 5.60

APPENDIX 6
PHOSPHORUS RELEASE RATES IN WATER

Phosphorus release rates were determined in water for uncoated, thin coated and thick coated MAP and DAP. 2.5 g of fertilizer was added to 500 mL of deionized water in a plastic container fitted with a screw-top lid. A 2 mL aliquot was removed from the solution 4 hours after the addition of fertilizer, and once each day thereafter. Prior to removing the aliquot, the solution was gently stirred (only time the solution was agitated). Phosphorus in the aliquot was determined by a colorimetric method (phosphomolybdenum blue complex read at 880 nm wavelength) with a Technicon Autoanalyzer II (Technicon Industrial Systems, 1973). Unlike the original method which used a combined working reagent, the ascorbic acid was added separately (Olsen and Sommers, 1982).

Table A6.1 Release of soluble P (% of applied) into water with time

	MAP			DAP		
Time (hours)	**Uncoated (%)**	**Thin (%)**	**Thick (%)**	**Uncoated (%)**	**Thin (%)**	**Thick (%)**
4	92	4	2	94	44	21
24	97	22	10	98	98	69
48	100	39	19	99	100	91
72	100	54	28	100	100	100
96	100	67	36	100	100	100
144	100	80	49	100	100	100
168	100	88	55	100	100	100
216	100	94	65	100	100	100
288	100	98	67	99	100	100

Uncoated MAP and DAP rapidly were dissolved in water. The thin polymer coating on DAP did little to control the release of P. The thick coating on DAP was marginally more effective than the thin coating. The polymer coatings on MAP were more effective than they were on DAP. MAP was released over 9 days with the thin polymer coating and was still slowly being released after 12 days with the thick coating. DAP with either level of polymer coating does not appear to be much of a controlled release P source.

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APPENDIX 7
TISSUE PHOSPHORUS CONCENTRATIONS

Table A7.1 Phosphorus concentration after 45 days in Chapter 2

Fertilizer	P Added mg pot^{-1}	Frequency of P Addition	Tissue P Concentration (%)		
			Breton	Ellerslie	Combined
None	0	None	0.251	0.226	0.238
MAP	15.7	Once Only	0.227	0.208	0.218
MAP	15.7	Each 2nd Day	0.228	0.194	0.211
MAP	15.7	Each 11th Day	0.252	0.216	0.234
DAP	15.7	Once Only	0.263	0.203	0.233
DAP	15.7	Each 2nd Day	0.251	0.214	0.233
DAP	15.7	Each 11th Day	0.253	0.203	0.228
LSD (0.05)			0.021	n.s.	0.018

n.s.: not significant

Table A7.2 ANOVA of barley tissue P concentration after 45 days on soil from Ellerslie (Chapter 2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.000989	0.000330	0.77	0.5244
Treatment	6	0.002647	0.000441	1.03	0.4360
Error	18	0.007683	0.000427		
Total	27	011320			

C.V. = 9.88

Table A7.3 ANOVA of barley tissue P concentration after 45 days on soil from Breton (Chapter 2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.002942	0.000981	4.81	0.0125
Treatment	6	0.004448	0.000741	3.63	0.0154
Error	18	0.003671	0.000204		
Total	27	0.011062			

C.V. = 5.79

Table A7.4 ANOVA of barley tissue P concentration after 45 days combined data from Ellerslie and Breton (Chapter 2)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.003219	0.001073	3.47	0.0251
Soil	1	0.019762	0.019762	63.87	0.0001
Treatment	6	0.004735	0.000789	2.55	0.0352
Soil*Treatment	6	0.002361	0.000394	1.27	0.2926
Error	39	0.012038	0.000309		
Total	55	0.042145			

C.V. = 7.72

Table A7.5 Barley tissue phosphorus concentrations after 45 days on soils from Ellerslie and Breton (Chapter 3)

Treatment	Tissue Phosphorus Concentration (%)		
	Ellerslie	Breton	Soils Combined
1. Control	0.226	0.226	0.226
2. SW 1 MAP	0.202	0.229	0.215
3. SW 1 DAP	0.193	0.237	0.215
4. SW 2 MAP	0.213	0.230	0.221
5. SW 2 DAP	0.207	0.245	0.226
6. SW 3 MAP	0.192	0.228	0.210
7. SW 3 DAP	0.179	0.246	0.213
8. Uncoated MAP	0.190	0.225	0.207
9. Uncoated DAP	0.189	0.226	0.208
10. Thin MAP	0.193	0.230	0.211
11. Thin DAP	0.187	0.204	0.196
12. Thick MAP	0.200	0.238	0.219
13. Thick DAP	0.178	0.219	0.198
14. Mixture MAP	0.181	0.242	0.211
15. Mixture DAP	0.170	0.216	0.193
LSD (0.05)	0.029	0.023	0.019

Table A7.6 ANOVA of barley tissue P concentration after 45 days on soil from Ellerslie (Chapter 3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.005822	0.001941	4.71	0.0063
Treatment	14	0.011627	0.000830	2.02	0.0403
Error	42	0.017297	0.000412		
Total	59	0.034746			

C.V. = 10.50

Table A7.7 ANOVA of barley tissue P concentration after 45 days on soil from Breton (Chapter 3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.004823	0.001608	6.22	0.0014
Treatment	14	0.007142	0.000510	1.97	0.0450
Error	42	0.010848	0.000258		
Total	59	0.022814			

C.V. = 7.00

Table A7.8 ANOVA of barley tissue P concentration after 45 days combined data from Ellerslie and Breton (Chapter 3)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	3	0.006139	0.002046	5.45	0.0018
Soil	1	0.039060	0.039060	104.07	0.0001
Treatment	14	0.011164	0.000797	2.12	0.0177
Soil*Treatment	14	0.007604	0.000543	1.45	0.1491
Error	87	0.032652	0.000375		
Total	119	0.096620			

C.V. = 9.17

Table A7.9. Barley tissue phosphorus concentrations [illegible] 90 days (Chapter 4)

Treatment	P Added (mg P pot^{-1})	Tissue Phosphorus Concentration (%)				
		30 Days	60 Days		90 Days	
		Stem and leaf	Head	Stem and leaf	Head	Stem and leaf
1. Control	0	0.152	0.000	0.081	0.093	0.052
2. Uncoated	15.7	0.147	0.115	0.045	0.097	0.027
3. SW Coat	15.7	0.169	0.117	0.044	0.102	0.028
4. Thin Coat	15.7	0.173	0.119	0.046	0.099	0.029
5. Thick Coat	15.7	0.175	0.139	0.058	0.108	0.041
6. Mixture†	15.7	0.163	0.118	0.047	0.106	0.031
7. Uncoated	31.4	0.197	0.131	0.051	0.120	0.030
8. SW Coat	31.4	0.222	0.140	0.050	0.110	0.030
9. Thin Coat	31.4	0.217	0.140	0.056	0.107	0.029
10. Thick Coat	31.4	0.190	0.133	0.057	0.101	0.033
11. Mixture†	31.4	0.189	0.140	0.051	0.117	0.030
LSD (0.05)		0.020	0.014	0.006		0.011

Table A7.10 ANOVA of barley stem and leaf tissue P concentration after 30 days on soil from Goodfare (Chapter 4)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000354	0.000177	1.24	0.3117
Treatment	10	0.017835	0.001784	12.47	0.0001
Error	20	0.002861	0.000143		
Total	32	0.021050			

C.V. = 6.59

Table A7.11 ANOVA of barley stem and leaf tissue P concentration after 60 days on soil from Goodfare (Chapter 4)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000120	0.000060	5.35	0.0137
Treatment	10	0.003229	0.000323	28.71	0.0001
Error	20	0.000225	0.000011		
Total	32	0.003574			

C.V. = 6.31

Table A7.12 ANOVA of barley head tissue P concentration after 60 days on soil from Goodfare (Chapter 4)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.007182	0.000359	4.96	0.0179
Treatment	10	0.048768	0.004877	67.31	0.0001
Error	20	0.001449	0.000072		
Total	32	0.050935			

C.V. = 7.25

Table A7.13 **ANOVA of barley stem and leaf tissue P concentration after 90 days on soil from Goodfare (Chapter 4)**

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000252	0.000126	3.23	0.0611
Treatment	10	0.001656	0.000166	4.24	0.0029
Error	20	0.000782	0.000039		
Total	32	0.002690			

C.V. = 19.16

Table A7.14 **ANOVA of barley head tissue P concentration after 90 days on soil from Goodfare (Chapter 4)**

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000440	0.000220	1.85	0.1827
Treatment	10	0.002073	0.000207	1.75	0.1381
Error	20	0.002372	0.000118		
Total	32	0.004884			

C.V. = 10.32

Table A7.15 **Barley tissue phosphorus concentrations over 52 days (Chapter 5)**

	Tissue Phosphorus Concentration (%)				
Treatment	13 Days	26 Days	39 Days	52 Days	
	Stem and leaf	Stem and leaf	Stem and leaf	Heads	Stem and leaf
1. Control	0.145	0.107	0.131	0.000	0.083
2. Uncoated	0.379	0.133	0.096	0.123	0.052
3. Thin Coat	0.358	0.170	0.093	0.122	0.045
4. Thick Coat	0.235	0.153	0.111	0.128	0.055
LSD (0.05)	0.051	0.023	0.011	0.010	0.006

Table A7.16 ANOVA of barley stem and leaf tissue P concentration after 13 days on soil from Goodfare (Chapter 5)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.003341	0.001671	2.60	0.1535
Treatment	3	0.108045	0.036015	56.11	0.0001
Error	6	0.003851	0.000642		
Total	11	0.115238			

C.V. = 9.07

Table A7.17 ANOVA of barley stem and leaf tissue P concentration after 26 days on soil from Goodfare (Chapter 5)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.002402	0.001201	8.81	0.0164
Treatment	3	0.006696	0.002232	16.37	0.0027
Error	6	0.000818	0.000136		
Total	11	0.009916			

C.V. = 8.29

Table A7.18 ANOVA of barley stem and leaf tissue P concentration after 39 days on soil from Goodfare (Chapter 5)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000648	0.000324	11.00	0.0098
Treatment	3	0.002677	0.000892	30.28	0.0005
Error	6	0.000177	0.000029		
Total	11	0.003502			

C.V. = 5.04

Table A7.19 ANOVA of barley stem and leaf tissue P concentration after 52 days on soil from Goodfare (Chapter 5)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000154	0.000077	10.27	0.0116
Treatment	3	0.002603	0.000868	115.77	0.0001
Error	6	0.000045	0.000008		
Total	11	0.002802			

C.V. = 4.66

Table A7.20 ANOVA of barley head tissue P concentration after 52 days on soil from Goodfare (Chapter 5)

Source	DF	Sum of Squares	Mean Square	F Value	Significance p>F
Block	2	0.000250	0.000125	4.60	0.0616
Treatment	3	0.034772	0.011591	425.87	0.0001
Error	[illegible]	0.000163	0.000027		
Total	11	0.035185			

C.V. = 5.60