# Materials for Sustained and Controlled Release of Nutrients and Molecules To Support Plant Growth

Drew Davidson<sup>†</sup> and Frank X. Gu\*,<sup>‡</sup>

<sup>†</sup>Department of Chemical Engineering and <sup>‡</sup>Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

**ABSTRACT:** Controlled release fertilizers (CRFs) are a branch of materials that are designed to improve the soil release kinetics of chemical fertilizers to address problems stemming losses from runoff or other factors. Current CRFs are used but only in a limited market due to relatively high costs and doubts about their abilities to result in higher yields and increased profitability for agricultural businesses. New technologies are emerging that promise to improve the efficacy of CRFs to add additional functionality and reduce cost to make CRFs a more viable alternative to traditional chemical fertilizer treatment. CRFs that offer ways of reducing air and water pollution from fertilizer treatments, improving the ability of plants to access required nutrients, improving water retention to increase drought resistance, and reducing the amount of fertilizer needed to provide maximum crop yields are under development. A wide variety of different strategies are being considered to tackle this problem, and each approach offers different advantages and drawbacks. Agricultural industries will soon be forced to move toward more efficient and sustainable practices to respond to increasing fertilizer cost and desire for sustainable growing practices. CRFs have the potential to solve many problems in agriculture and help enable this shift while maintaining profitability.

**KEYWORDS:** controlled release fertilizer, nutrients, phosphate, nitrate, agriculture

## INTRODUCTION

Potential for Controlled Release Fertilizers (CRFs) in Improving Agricultural Efficiency. Industrial agriculture around the world has been increasing at a rapid pace to keep up with the growing population. As a result, global application of chemical fertilizer, specifically nitrogen, phosphorus, and potassium (N, P, and K), increased dramatically in the last half of the 20th century<sup>1</sup> and is forecast to rise significantly around the world at a rate of 2.5 million metric tonnes per year.<sup>2</sup> Demands for fertilizers are increasing as both the fertilizer use per hectare of many staple crops such as corn, palm kernel, and sugar beet increases along with crop area used for growing. Increasing fertilizer use is driven largely by China, the United States, and India. China possesses an agriculture industry characterized by intensive use of fertilizer as well as large crop areas. India is a more modest user of fertilizer per hectare, but very large crop areas result in it being a large consumer of fertilizer regardless. By 2030 fertilizer applications in these regions are expected to increase by 54.6% in Asia and 49.9% in North and Central America with less extreme but significant increases in other regions.<sup>2</sup>

Nitrogen application in particular rose by 15 times over the 40 year period before 1990.<sup>1</sup> Whereas fertilizer application increased, the amount of nutrients recovered by crops has not kept the same pace, only tripling over the same period as N increased by 15 times,<sup>1,3</sup> signifying that much of the nutrients from fertilizers are not utilized by plants and are lost to the environment.<sup>3</sup> Current fertilizer use models predict that use will continue a significant sustained rise over the next 10 years of 18.1%.<sup>2</sup>

Fertilizer costs are already rising significantly and will continue to rise in the future. These increases in price are caused by factors such as the increasing cost of fossil fuel energy used to mine and transport mineral fertilizers and the depletion of natural stocks of fertilizers, especially phosphorus, as well as increased demand for fertilizers from an increasing biofuel market.<sup>4</sup> The food crisis in 2008 had its roots in a 5-7-fold increase in P cost at the time.<sup>4</sup> Phosphorus is the most pressing of the three major nutrients because it is a nonrenewable resource that has no alternative source other than mining except for recycling.<sup>4</sup> It is expected that peak phosphorus production will be hit around 2030 at the current rate of P usage.<sup>5</sup> Use of controlled release fertilizers allows the release of nutrients to be better matched with the life cycle of the plant<sup>3,6</sup> to increase the efficiency of nutrient uptake by plants. Furthermore, the nutrient demands of the plant can be met more closely by designing an appropriate controlled release system to increase efficiency and reduce the risk of overdosing the plant.<sup>6</sup> Controlled release fertilizers also prevent fertilizers from being leached from the soil and decrease costs for agriculture by reducing the amount of fertilizer needed and the labor and fuel costs associated with repeated applications of fertilizers.<sup>3,7,8</sup> There is also evidence that different nutrients and micronutrients can influence the ability of plants to utilize other nutrients effectively. $^{3,9-11}$  Development of a system to administer these synergistic nutrients would allow plants to more efficiently utilize the fertilizers applied, resulting in less waste and cost.

CRFs are able to address problems such as fertilizers lost due to runoff, chemical reaction, leaching, or other issues that reduce the amount of fertilizers available for plant growth and

Received:	October 8, 2011
<b>Revised:</b>	December 20, 2011
Accepted:	December 22, 2011

which de December 22, 2011

Published: December 22, 2011

increase the amount of pollution resulting from agricultural activity. CRFs incorporate a physical barrier to immobilize fertilizers in the soil and protect them from degradation from microorganisms such as algae. Immobilization of the fertilizers prevents solubilization of the mineral fertilizers, which can lead to runoff and groundwater leaching depending on weather conditions. CRFs also offer potential in tuning nutrient application to the growth requirements of different crops according to growth timeline and nutrient requirements, which has the potential to improve plant yield while requiring less fertilizer application.

Environmental Benefits from the Use of CRFs. In addition to benefitting agriculture in terms of increased efficiency and reduced cost of fertilizer use, CRFs offer many ecological benefits as well. The sustainability of agriculture and the pollution caused by it are of great concern to the public. Studies have been commissioned to look at the environmental impacts and potential solutions to problems such as ground-water leaching<sup>12</sup> and sustainable growing practices.<sup>13</sup> Conventional fertilizers can be lost through a variety of means, mostly by leaching, volatilization, breakdown by microorganisms, and chemical processes such as hydrolysis or precipitation.<sup>3,7</sup> The products of these various processes often have adverse effects on the environment. Leaching and runoff of fertilizers can lead to algal blooms and contamination of groundwater,<sup>3,14</sup> whereas volatilization and metabolism by microorganisms can release products such as nitrous oxide in large volumes.<sup>7</sup> Nitrous oxide release into the environment causes destruction of atmospheric ozone and, when transformed into nitrogen dioxide and nitric acid, contributes to acid rain and acidification of the environment.' Eliminating nutrient loss is especially important for phosphorus as this element has no renewable sources, and new phosphorus must be mined from ore.

Excessive nitrogen concentration as a result of fertilizer application is of concern to farmers due to not only the risk of crop destruction but also potential health problems in humans and livestock due to excessive levels of these compounds being present in the plants consumed.<sup>3</sup> Traditional salt-based fertilizers also have adverse effects on the soil to which they are applied. Repeated applications of chemical fertilizers can alter the soil composition, increasing the salinity and concentration of heavy metals, and can also result in increased leaching of other nutrients and minerals that are critical for plant growth.<sup>3</sup> Large concentrations of fertilizer in soil can also cause the formation of algal crusts in the soil, which disrupt the aeration of soil and reduce water penetration into the soil.<sup>3</sup>

There are many strategies being considered for improving the efficiency of fertilizer use to combat both the increasing demand for fertilizer and looming problems of supply shortfalls such as peak phosphorus. Losses of nutrients can be reduced by maintaining lower levels of nutrients in the soil so that less is leached into groundwater or lost through chemical and biological processes; however, reducing the nutrient content of the soil will lead to lower crop yield. Strategies for optimizing land use in conjunction with lower nutrient level soils would allow crop yields to be maintained while increasing the efficiency of fertilizer usage.<sup>15</sup> Example of this type of management strategy are the current agricultural strategies in India, which use more land but relatively less fertilizer than other regions such as China and the United States. This strategy has the obvious drawback of increasing land use for agriculture; alternatively, nutrient losses can be reduced by implementing measures to reduce the erosion of the soil such

as shallower tilling of the soil, mulching of unused plant matter into the soil, and planting grasses or trees around crop fields to stabilize soil and reduce the amount of nutrients lost to erosion from wind and precipitation.<sup>15</sup> Improving the efficiency of nutrient usage by crops can also be achieved by optimizing the relative amounts of nutrients in the soil. Optimizing fertilizer applications for plant growth is another viable strategy for increasing fertilizer use efficiency. For nutrients to be properly utilized by crops, the plants must be able to access the nutrients in the soil, and different crops require different ratios of nutrients. For example, crops with shallow root systems grown in rows will be able to access only nutrients such as phosphorus present at shallow soil depths in limited areas of the field.<sup>15</sup> Altering the nutrient use characteristics of crops is also being looked at as a strategy for reducing nutrient losses and agricultural pollution through the engineering of crops that are better able to extract and utilize nutrients in the soil<sup>16</sup> or by using symbiotic organisms such asarbuscular mycorrhizal fungi, which retain nutrients at soil depths accessible to crops.<sup>15</sup> New technologies that utilize gene insertion to allow crops to ward off pests to reduce losses and advanced tracking of soil quality using GPS and computer-aided modeling also have potential to increase agricultural efficiency.<sup>17</sup> By addressing many of the root causes of nutrient loss, controlled release fertilizers have shown potential for reducing or eliminating the environmental issues associated with application of fertilizers to agricultural fields. Controlled release fertilizers are able to reduce losses through regulation of fertilizer release in areas of the soil and on a timeline most accessible to the plant and by stabilizing the N, P, and K compounds, preventing degradation or physical removal from the soil.  $^{3,6,7}$ 

## MOLECULES AND NUTRIENTS OF INTEREST FOR SUSTAINED RELEASE

Major nutrients for plant growth are the largest components of any commercial fertilizer: N, P, and K. $^{3,6,7,12}$  These nutrients are most commonly applied in salt forms, which are vulnerable to losses through a variety of processes such as degradation, leaching, runoff, volatilization, absorption, or soil immobilization.<sup>18</sup> The prevention of these losses is a major driving force behind the development of sustained and CRFs.<sup>7,12,18</sup> Techniques that are used for sustained or controlled release include polymer-coated pellets, the most common method and commercially available, and others such as polymer films,<sup>18</sup> using insoluble forms of  $N-P-K^{19}$  or hydrogel matrices.<sup>20,21</sup> Polymer coating of large fertilizer granules is the most common controlled release mechanism and relies on the biodegradation of the polymer coating to release fertilizers over a sustained period. Coating the fertilizers with a polymer serves to help immobilize the fertilizer pellets and hence make them resistant to runoff and leaching;<sup>22</sup> various degrees of leaching resistance have been observed depending on the type of controlled release fertilizer used. In one experiment, it was observed that polyolefin-coated urea resulted in improved immobilization of nitrogen, whereas other CRFs including isobutyridene diurea, oxamide, and an organic nitrogen source (rapeseed meal) did not effectively immobilize the nitrogen, resulting in only small reductions in nitrogen leaching.<sup>22</sup> The encapsulation also serves to lower the exposure of fertilizers to environmental degradation from microorganisms or chemical reactions and also lengthens the amount of time plants have to absorb the fertilizer.<sup>23</sup> In one study, use of a polymer-coated urea substantially increased nitrogen use efficiency of onion

crops.<sup>24</sup> However, these types of CRF are vulnerable to changes in the soil type, moisture content, and other factors that can affect the release rate.<sup>25</sup> These complications can lead to fertilizer release not being synchronized with plant demand and may create situations in which the plants are starved of nutrients or unable to use the fertilizer released. These reasons may be why the use of current CRFs takes up a relatively low market share of total fertilizer use.<sup>3</sup>

Avoiding Nutrient Burn. Nutrient burn is a term used by those in agriculture to describe overdose of plants of major nutrients.<sup>18</sup> Excessive levels of fertilizers in a field can cause plants to sicken or die because of this effect. In addition, nutrient demand is specific to each crop and strain, necessitating that farmers adjust the amount of fertilizer applied depending on the crop. The distribution of nutrients in a field is dictated by a variety of mechanisms, not just how the fertilizers are applied by the farmer. Soil conditions, leaching, rainfall, and other factors may cause large local concentrations of fertilizers, which can harm plants and reduce the efficiency of fertilizer absorption. An experiment using a large sealed tank sandy sediment showed significantly heterogeneous distribution of nitrogen fertilizer applied in aqueous solution both before and after simulated rainfall.<sup>26</sup> Use of CRFs prevents nutrient overdose by extending the period over which fertilizer is released into the soil.<sup>18</sup> This prevents overdose of the plant from occurring as the amount of fertilizer released from the system is closer to the demand of the crop plants.<sup>3</sup> CRFs also anchor the fertilizers in position, which helps prevent local concentrations of fertilizer from occurring due to migration of the fertilizer after application.<sup>3</sup>

Prevention of Salt Buildup. Depending on the soil type and composition, the application of chemical fertilizers and irrigation water can cause increased salinity of the soil.<sup>27</sup> Increased salinity of the soil can cause adverse effects for crop health, growth, and yield and is a major problem in many areas.<sup>28</sup> Chemical fertilizers can contain traces of ions from the rock they are initially mined from; phosphate fertilizer can contain traces of thorium, uranium, aluminum, iron, and other ions,<sup>29</sup> which can negatively affect plant growth. This is of particular concern in Third World countries or in areas that must support their agriculture with large amounts of water due to a dry climate.<sup>27</sup> One alternative to chemical fertilizers that has less risk of increasing salt buildup is using natural fertilizers such as either fresh or composted manure.<sup>30</sup> There are some concerns over using natural fertilizers due to both supply issues and health risks, which may be part of the reason that chemical fertilizers still make up the overwhelming bulk of those used in agriculture today. To help prevent the degradation of soil, CRFs can be used to reduce the amount of chemical fertilizer that is applied to the soil and also make the fertilizer more accessible to plants to keep it from remaining in the soil afterward. 3,6,7,18

**Micronutrients.** Plants rely on a number of micronutrients to optimize growth and yield. These micronutrients are not present in all soils in sufficient amounts. Common micronutrients that are critical for plant growth include calcium, magnesium, iron, manganese, and zinc, among others.<sup>31,32</sup> Micronutrients are critical for plant growth in small concentrations, but like the macronutrients discussed above, excessive levels of micronutrients, such as iron, can result in toxicity to the plant, which can be detrimental to growth and yield of crops.<sup>33</sup> In addition, deficiencies of micronutrients can not only stunt plant growth but also exacerbate the toxic effects

of other nutrient overdoses and make the plant vulnerable to other stresses as well.<sup>33</sup> It has been documented as well that introducing micronutrients along with macronutrients will increase the efficiency of nutrient absorption of the plant.<sup>3,34</sup> Most chemical fertilizers contain a mix of micro- and macronutrients in salt forms; however, applying a mixture in this state assumes that the different ions will migrate through the soil in the same way, which may not be the case. Using a controlled release system to anchor the mixture of nutrients in the soil will enable the application of a specific, controlled mixture of nutrients designed to maximize plant yield while at the same time ensuring that the mixture remains in the soil in the desired concentrations.<sup>3</sup> The release of fertilizers from a CRF system can be modeled using computer-aided modeling to design a system for specific crops and desired release profiles.<sup>35</sup>

Application of Pesticides, Herbicides, and Fungicides. Pests that target crop plants are a devastating problem for agriculture, requiring large amounts of pesticides to ensure that crops provide optimal yields.<sup>36</sup> The large volumes of different types of pesticides that are being used in agricultural crops today are of great concern in terms of people's health and environmental risk.<sup>36</sup> In much the same way, controlled release can be used to reap additional benefits from lower volumes of fertilizer, and similar systems have been proposed for pesticide agents to reduce the amounts of these chemicals needed to achieve a crop protective effect and reduce the amount of chemicals released into the surrounding environment<sup>36</sup> or provide better systemic application.<sup>37,38</sup> Controlled release systems are most useful as antifungals and to address soilborne pests that affect seeds, roots, and early plant growth because these problems can be targeted using a soil-based release system.<sup>36,39</sup>

It has been suggested that using pesticides in this way could have benefits for both efficiency of fertilizer applications and reduction of the possible toxic effects to the surrounding environment. In response to this need there have been recently developed methods for the encapsulation and controlled release of different varieties of pesticides to both provide higher efficacy and reduce the amount of pesticide released into the environment.<sup>40</sup> A polyacrylamide-methylcellulose hydrogel showed sustained release of paraquat pesticide over a period of 45 days and was speculated to have further use as a method of improving water retention qualities of soil.<sup>40</sup> Herbicides are an important part of reducing crop losses due to competition between crop plants and weeds. Herbicides are typically deployed in large doses in spray form, and this method results in large percentages of herbicide being lost to the environment.<sup>41</sup> Hexagonal mesoporous silica modified with carboxylic acid obtained by a sol-gel process was able to release herbicides at a constant rate for a period of 30 days, which would allow sufficient amounts of herbicide to reduce weed infiltration while significantly reducing the amounts of herbicide needed and released to surrounding areas.<sup>42</sup> Another herbicide release mechanism employing magnesium/aluminum layered double hydroxides was also shown to be able to encapsulate and release hydrophobic herbicides in early trials.<sup>43</sup> Unfortunately, the double hydroxide mechanism was not as long-lasting as the mesoporous silica, reaching a maximum release of herbicide in 8 days as opposed to 20 days for the  $silica.^{42}$ 

**Improvement of Water Retention.** Water retention of soil is an important growth factor for crops that determines their resistance to drought events. It is desirable for soil to keep

water at root level for as long as possible so the water is accessible to plants for growth before it drains to groundwater or evaporates into the air. Of particular concern as well is the depletion of freshwater reserves that may result in the necessary use of more sodic or saline soils that are less optimal for plant growth and introduce salts into the soil.<sup>28</sup> Systems for improving the water retention of soil have been researched to develop novel materials such as hydrogel matrices that will reduce the amount of water needed to support crops and increase drought resistance.<sup>44</sup> However, for this technology to become more widely applicable, there remain concerns regarding the affordability of these novel materials and their ability to provide adequate hydration to plants in different kinds of soils. Commercially available hydrogel materials remain unreliable under the demands of real agricultural conditions.<sup>44</sup> Optimally, a system will be developed that will mitigate this cost through combining the demand for CRF systems with that of a water retention matrix to offer a lower cost solution to both problems for commercial agriculture.

#### MATERIALS FOR SUSTAINED RELEASE

**Commercially Available and Emerging Products.** There are a few types of CRFs that are available to agriculture currently and more are under development; those that are discussed in this review are summarized in Table 1. There are a

 Table 1. Available Controlled Release Devices for

 Agricultural Applications

	water retention	fertilizers	pesticides
commercially available	none	paraffin wax polyolefin coatings polyethylene coatings	none
in development	polyvinyl alco- hol/chitosan hydrogel	curdlan carboxymethyl cellu- lose calcium alginate polylactic acid phosphate glass pectin insoluble NPK (nitro- gen-phosphorus- potassium)	polyacrylamide— methylcellulose hydrogel hexagonal mesopo- rous silica magnesium—alumi- num double-layer hydroxide

number of strategies among currently available CRFs. The first method is to use materials that protect fertilizer granules using a physical barrier such as a polymer coating or matrix that will allow fertilizers to gradually diffuse outward. A second method involves using inorganic fertilizers that will only slowly become solubilized and available to plants and will not easily migrate due to water flows in the soil. Another method is to use materials that are made available as fertilizer only after chemical or biological degradation; one example of this material is known as ureaform. Another common method is to use a coating of a material that gradually decomposes and releases the stored material such as paraffin wax, polyolefins, or polyethylene.<sup>3,18</sup> The longevity of organic-coated fertilizers depends on the thickness of the polymer coating.45 Coated fertilizer releases nutrients through the penetration of water, which creates a nutrient-rich solution from the solid fertilizer, which then diffuses out. The release of nutrients from the particles is increased as more of the solid nutrient is solubilized. Release kinetics experiments show that coated fertilizers have a linear increase in the amount of fertilizer released over time, releasing fertilizer more rapidly as time increases,45 and because CRFs are applied during seeding, this means that more fertilizer is released as plants grow. However, some fertilizer is still released in the earliest stages of plant growth, whereas traditional fertilizers are not applied until later.

Emerging materials for CRFs include materials that have novel properties designed to improve plant growth through added features such as improved water retention or ability to apply specific release profiles of different nutrients to address plant needs.<sup>35,46</sup> Some materials are able to apply a greater variety of materials to plants such as beneficial microorganisms as well.<sup>47</sup> These materials also include materials designed to be more environmentally friendly than current formulations by reducing the need for organic solvents that many of the current polymer-based materials rely on.<sup>18</sup> Other formulations promise better control over nutrient release, ability to load multiple materials into the particle such as micronutrients and pesticides, and reduced-cost materials.<sup>3,7,18,25,48</sup> Many newer CRF materials are based on existing drug delivery systems because it is already known that these materials are able to release small molecules in a controlled way. Materials such as Curdlan, carboxymethyl cellulose, and other polysaccharides that have classically been used as drug delivery mechanisms or encapsulation agents are finding use as CRF materials,<sup>20,21</sup> as well as coating and granulation processes such as fluidized bed.<sup>18</sup> The challenge in adapting these new materials lies in determining if the release rates can be adjusted to be useful for fertilizer applications and whether these materials can stand up to outdoor environments. Additional materials such as calcium alginate and polylactic acid are able fulfill roles similar to the

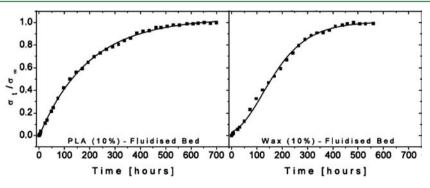


Figure 1. Release kinetics of urea coated with polylactic acid (left) and wax (right). Reprinted with permission from ref 58. Copyright 2002 Elsevier.<sup>58</sup>

#### Journal of Agricultural and Food Chemistry

traditional polymer coating materials but do not require organic solvents and are readily derived from plants and can also be used to encapsulate a wider variety of fertilizer materials such as beneficial bacteria.<sup>49,50</sup> Polylactic acid is applied as a polymer in solution by spray-coating or fluidized bed to coat fertilizer particles much in the same way as traditional polymer coatings, the main difference being that polylactic acid is less toxic. Polylactic acid particles release fertilizer on a time scale that is comparable to traditional wax-coated CRFs; a comparison is shown in Figure 1.

Calcium alginate is made through the addition of calcium chloride to sodium alginate, which causes the material to crosslink into gel beads typically around 4 mm in diameter.<sup>50,51</sup> However, the kinetics associated with calcium alginate gel are not a sustained release but instead exhibit a burst release of encapsulated material that accompanies the release of water from the gel followed by a slow release of the remaining encapsulated substance.<sup>51</sup> This problem has been addressed by coating the gel beads with polymer (Figure 2) or through

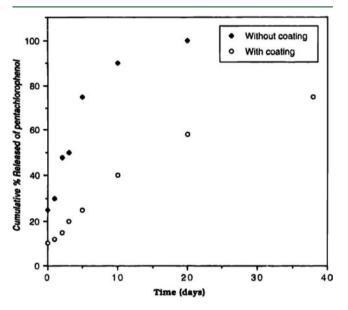


Figure 2. Release of pentachlorophenol herbicide from calcium alginate gel beads with and without polyethylene imine coating. Reprinted with permission from ref 51.<sup>51</sup>

modifying the gels through the incorporation of other materials such as cellulose or gelatin to create gels with a more sustained release and was shown to be an effective medium for controlled release of bacterial fertilizer.<sup>50,51</sup>

Phosphate glass is a material made by converting crystalline phosphate doped with potassium, calcium, magnesium, or silicon oxides to an amorphous glass material under high temperature. This material is made up entirely of nutrients that can be utilized by plants once dissolved and is completely nontoxic.<sup>52</sup> The material degrades through hydrolysis of phosphorus oxygen bonds of the glass, which results in a soluble form of phosphate that can be taken up by plant roots. The kinetics of release from this glass material depends strongly on a number of factors including temperature, granule size, moisture content of the soil, and concentrations of dopants in the material.<sup>52</sup> Theoretically these phosphate glasses are capable of tunable solubility, allowing complete dissolution between days and 4 years, but the unpredictable impact of

degradation due to soil moisture content and other factors may limit its usefulness.  $^{\rm 53}$ 

Pectin, carboxymethyl cellulose, and other similar hydrogels are naturally sourced materials and as such are nontoxic and biodegradable. The hydrogels are made through dissolution of the polymers in water and addition of a cross-linking agent or heating of the solution, which causes a hydrogel to form.<sup>21</sup> The gel characteristics can be altered by changing the parameters of the cross-linking reaction to alter the material properties and release kinetics of the hydrogel. Materials are encapsulated in the gel by mixing before cross-linking to physically trap the molecules by the cross-linked gel. These hydrogels have been shown to exhibit other functions that are useful to crop growers in addition to the sustained release of nutrients such as improving the water retention of the soil and uptake of harmful heavy metals.<sup>21</sup> Due to the mechanism for nutrient release from the hydrogel as well as hydrogel degradation, the release kinetics of these hydrogels depends heavily on the moisture content of the soil.

Insoluble NPK rhizosphere-controlled fertilizer (RCF) consists of insoluble NPK compounds that are made available to the plant only through reaction of the compounds with plant-produced carboxylic acids to form soluble fertilizer compounds, which can be absorbed by the plant roots. A phosphorus form of this material was made by using a matrix of double-metal (Mg, Zn) phosphates.<sup>19</sup> This type of fertilizer promises to solve many of the current issues with CRFs by preventing the fertilizer-bearing compounds from becoming soluble until activated by citric or other carboxylic acids produced by plants. This type of CRF was shown to decrease the leaching and volatilization of the phosphorus compounds in soil while maintaining plant availability of the nutrient.<sup>11</sup> However, the same study showed that the RCF compound was pH-sensitive in soil, altering the amount of nutrients released on the basis of soil acidity and suggesting that the compound is not completely protected from environmental effects that degrade its performance. Fertilizer release from this type of CRF is slowed significantly, so much so that it must be coupled with soluble nutrient sources to supply the plant until the RCF has had time to be activated and start releasing nutrients. The pH sensitivity of the RCF compounds results in much more water-soluble fertilizers having to be added to RCF placed in alkaline soil due to the further reduction of the speed of nutrient release from the RCF compound.<sup>54</sup> Overall, RCF and other insoluble NPK sources are promising in addressing many problems with commercial fertilizer application but have limitations on their use, such as limited efficiency in alkaline soil, which may limit their market penetration and usefulness.

The development of these materials and other new materials for CRFs is important because there are a number of issues preventing widespread adoption of sustained or controlled release materials in their current state. Slow release materials have been and continue to be a relatively small market when compared to typical chemical fertilizers.<sup>3</sup> The major limitations of current CRFs are primarily their high cost, which can range between 2.5 tand 8 times that of regular chemical fertilizers, representing a cost increase of up to \$64 per acre depending on the type of crop and controlled release system, and a lack of data regarding the release kinetics of CRF in various types of soil and environmental conditions of interest to the agriculture industry.<sup>8</sup> Current CRFs are vulnerable to changes in temperature, ambient moisture, bioactivity of the soil, and wetting and drying cycles of the soil. Changes in any of these

## Journal of Agricultural and Food Chemistry

conditions will make the release rate of the fertilizers unpredictable and will negatively affect the efficiency of the fertilizer release, especially if the release rate has been calibrated for a specific kind of crop. In addition, CRFs do not respond directly to the plant's demand for nutrients and release nutrients at the same rate regardless of whether a plant is demanding more nutrients or none at all.<sup>3</sup> The emerging products currently under development address some of these issues, but whether this will be enough to outweigh the costs enough for the agricultural industry to undergo a major adoption of these products is unknown.

## CROPS OF MAJOR INTEREST FOR CONTROLLED RELEASE FERTILIZERS

The main beneficiary of better CRF technology will be the agriculture industry, which will be able to use this technology to reap improved yields and fewer losses of crops. Of greatest interest for CRFs are crops that are typically fertilizer intensive due to needing a great deal of chemical fertilizer application to achieve optimal growth, because these have the greatest potential for efficiency gain. These crops rapidly deplete soil of major nutrients such as nitrogen and require large amounts of fertilizer or crop rotation with leguminous crops capable of nitrogen fixation to restore nitrogen to the soil.55 However, crops used to restore nitrogen in this way are much less profitable than cash crops, and this practice can reduce the profitability of land due to lost growing time for profitable crops. These crops are also typically the most in demand for crop growers because they make up the majority of the feed for livestock as well as being used extensively for human consumption and, in the case of corn, biofuels.

The crops that CRFs have the potential to benefit most are common agricultural crops such as wheat, corn, soy, tomatoes,<sup>31</sup> and potatoes<sup>12</sup> and other crops that also require large amounts of fertilizer or very rich soil to grow well. Materials that are used for improving water retention would also be most useful for plants that have weak drought resistance or shallow root systems<sup>56</sup> such as rice<sup>57</sup> and wheat grasses for foliage or lawns.

Overall, as the push for agriculture to become more sustainable becomes stronger due to the development of a green mentality among the public, industrial agriculture will need new solutions to help reduce the amount of resources consumed by the production of food. In addition, the pressures of increasing fertilizer cost and the possibility for climate shifts resulting in drought or water shortages will make the development of new solutions even more pressing and necessary to reduce costs and improve efficiency. CRFs offer solutions to many of the problems that are on the horizon for agriculture. Solutions in development promise to reduce air and water pollution from fertilizer, increase the efficiency of fertilizer absorption and plant growth, and improve the water retention properties of the soil to reduce water need and increase drought resistance. Due to the additional cost required to deploy CRFs, the materials currently available have not been able to develop a large market share. If the materials in development are to succeed, they will need to offer better value to growers by reducing the cost of fertilizer application, reducing the amount of fertilizer needed, and increasing crop yield or reducing crop losses.

# AUTHOR INFORMATION

### **Corresponding Author**

\*Phone: (519) 888-4567, ext. 38605. E-mail: frank.gu@ uwaterloo.ca.

### REFERENCES

(1) Peters, G. H. A hundred years of British food and farming – a statistical survey. J. Agric. Econ. **1989**, 40, 407–408.

(2) Zhang, W. J.; Zhang, X. Y. A forecast analysis on fertilizers consumption worldwide. *Environ. Monit. Assess.* 2007, 133, 427–434.
(3) Shaviv, A.; Mikkelsen, R. L. Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation – a review. *Fert. Res.* 1993, 35, 1–12.

(4) Childers, D. L.; Corman, J.; Edwards, M.; Elser, J. J. Sustainability challenges of phosphorus and food: solutions from closing the human phosphorus cycle. *Bioscience* **2011**, *61*, 117–124.

(5) Cordell, D.; Drangert, J. O.; White, S. The story of phosphorus: global food security and food for thought. *Global Environ. Change* **2009**, *19*, 292–305.

(6) Malhi, S. S.; Soon, Y. K.; Grant, C. A.; Lemke, R.; Lupwayi, N. Influence of controlled-release urea on seed yield and N concentration, and N use efficiency of small grain crops grown on Dark Gray Luvisols. *Can. J. Soil Sci.* **2010**, *90*, 363–372.

(7) Akiyama, H.; Yan, X. Y.; Yagi, K. Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for  $N_2O$  and NO emissions from agricultural soils: meta-analysis. *Global Change Biol.* **2010**, *16*, 1837–1846.

(8) Simonne, E. H.; Hutchinson, C. M. Controlled-release fertilizers for vegetable production in the era of best management practices: teaching new tricks to an old dog. *HorTechnology* **2005**, *15*, 36–46.

(9) Barak, P.; Chen, Y. The evaluation of iron-deficiency using a bioassay-type test. *Soil Sci. Soc. Am. J.* **1982**, *46*, 1019–1022.

(10) Kafkafi, U.; Neumann, R. G. Correction of iron chlorosis in peanut (arachis-hypogea-shulamit) by ammonium-sulfate and nitrification inhibitor. *J. Plant Nutr.* **1985**, *8*, 303–309.

(11) Clarkson, D. T.; Hanson, J. B. The mineral-nutrition of higherplants. *Annu. Rev. Plant Phys.* **1980**, *31*, 239–298.

(12) Shrestha, R. K.; Cooperband, L. R.; MacGuidwin, A. E. Strategies to reduce nitrate leaching into groundwater in potato grown in sandy soils: case study from North Central USA. *Am. J. Potato Res.* **2010**, *87*, 229–244.

(13) Dennis, J. R.; Lopez, R. G.; Behe, B. K.; Hall, C. R.; Yue, C. Y.; Campbell, B. L. Sustainable production practices adopted by greenhouse and nursery plant growers. *HortScience* **2010**, *45*, 1232–1237.

(14) Li, X. X.; Hu, C. S.; Delgado, J. A.; Zhang, Y. M.; Ouyang, Z. Y. Increased nitrogen use efficiencies as a key mitigation alternative to reduce nitrate leaching in north China plain. *Agric. Water Manage.* **2007**, *89*, 137–147.

(15) Schroder, J. J.; Smit, A. L.; Cordell, D.; Rosemarin, A. Improved phosphorus use efficiency in agriculture: a key requirement for its sustainable use. *Chemosphere* **2011**, *84*, 822–831.

(16) Hakeem, K. R.; Ahmad, A.; Iqbal, M.; Gucel, S.; Ozturk, M. Nitrogen-efficient rice cultivars can reduce nitrate pollution. *Environ. Sci. Pollut. Res. Int.* **2011**, *18*, 1184–1193.

(17) Rains, G. C.; Olson, D. M.; Lewis, W. J. Redirecting technology to support sustainable farm management practices. *Agric. Syst.* **2011**, *104*, 365–370.

(18) Zhao, C.; Shen, Y. Z.; Du, C. W.; Zhou, J. M.; Wang, H. Y.; Chen, X. Y. Evaluation of waterborne coating for controlled-release fertilizer using wurster fluidized bed. *Ind. Eng. Chem. Res.* **2010**, *49*, 9644–9647.

(19) Erro, J.; Baigorri, R.; Yvin, J. C.; Garcia-Mina, J. M. <sup>31</sup>P NMR characterization and efficiency of new types of water-insoluble phosphate fertilizers to supply plant-available phosphorus in diverse soil types. *J. Agric. Food Chem.* **2011**, *59*, 1900–1908.

(20) Lehtovaara, B. C.; Gu, F. X. Pharmacological, structural, and drug delivery properties and applications of  $1,3-\beta$ -glucans. J. Agric. Food Chem. **2011**, 59, 6813–6828.

(21) Guilherme, M. R.; Reis, A. V.; Paulino, A. T.; Moia, T. A.; Mattoso, L. H. C.; Tambourgi, E. B. Pectin-based polymer hydrogel as a carrier for release of agricultural nutrients and removal of heavy metals from wastewater. *J. Appl. Polym. Sci.* **2010**, *117*, 3146–3154.

(22) Morita, A.; Takano, H.; Oota, M.; Yoneyama, T. Nitrification and denitrification in an acidic soil of tea (*Camellia sinensis* L.) field estimated by delta N-15 values of leached nitrogen from the soil columns treated with ammonium nitrate in the presence or absence of a nitrification inhibitor and with slow-release fertilizers. *Soil Sci. Plant Nutr.* **2002**, *48*, 585–593.

(23) Tian, X. H.; Saigusa, M. Response of tomato plants to a new application method of polyolefin-coated fertilizer. *Pedosphere* **2005**, *15*, 491–498.

(24) Drost, D.; Koenig, R.; Tindall, T. Nitrogen use efficiency and onion yield increased with a polymer-coated nitrogen source. *HortScience* **2002**, *37*, 338–342.

(25) Chen, D.; Suter, H.; Islam, A.; Edis, R.; Freney, J. R.; Walker, C. N. prospects of improving efficiency of fertiliser nitrogen in australian agriculture: a review of enhanced efficiency fertilisers. *Aust. J. Soil Res.* **2008**, *46*, 289–301.

(26) Mastrocicco, M.; Colombani, N.; Palpacelli, S.; Castaldelli, G. Large tank experiment on nitrate fate and transport: the role of permeability distribution. *Environ. Earth Sci.* **2011**, *63*, 903–914.

(27) Al-Hurban, A. Preliminary assessment of the effects of fertilizers on soil properties in farming areas, southern Kuwait. *Manage. Environ. Qual.* **2003**, *17*, 258–274.

(28) Yaduvanshi, N. P. S.; Swarup, A. Effect of continuous use of sodic irrigation water with and without gypsum, farmyard manure, pressmud and fertilizer on soil properties and yields of rice and wheat in a long term experiment. *Nutr. Cycl. Agroecosyst.* **2005**, *73*, 111–118.

(29) Kamel, N. H. M.; Hegazy, W. S.; Navratil, J. D. Solubility and sorption properties of some phosphate fertilizer components on soils. *J. Radioanal. Nucl. Chem.* **2010**, *284*, 653–658.

(30) Miller, J. J.; Beasley, B. W.; Larney, F. J.; Olson, B. M. Soil salinity and sodicity after application of fresh and composted manure with straw or wood-chips. *Can. J. Soil Sci.* **2005**, *85*, 427–438.

(31) Kang, Y. I.; Park, J. M.; Kim, S. H.; Kang, N. J.; Park, K. S.; Lee, S. Y.; Jeong, B. R. Effects of root zone pH and nutrient concentration on the growth and nutrient uptake of tomato seedlings. *J. Plant Nutr.* **2011**, *34*, 640–652.

(32) Welch, R. M. Micronutrient nutrition of plants. *Crit. Rev. Plant Sci.* 1995, 14, 49–82.

(33) Sahrawat, K. L.; Mulbah, C. K.; Diatta, S.; Delaune, R. D.; Patrick, W. H.; Singh, B. N.; Jones, M. P. The role of tolerant genotypes and plant nutrients in the management of iron toxicity in lowland rice. J. Agr. Sci. **1996**, *126*, 143–149.

(34) Malakouti, M. J. The effect of micronutrients in ensuring efficient use of macronutrients. *Turk. J. Agric. For.* **2008**, 32, 215–220.

(35) Shaviv, A.; Raban, S.; Zaidel, E. Modeling controlled nutrient release from a population of polymer coated fertilizers: statistically based model for diffusion release. *Environ. Sci. Technol.* **2003**, *37*, 2257–2261.

(36) Damalas, C. A.; Eleftherohorinos, I. G. pesticide exposure, safety issues, and risk assessment indicators. *Int. J. Environ. Res. Public Health* **2011**, *8*, 1402–1419.

(37) Kimoto, N.; Takahashi, A.; Inubushi, K. Design and release profile of timed-release coated granules of systemic insecticide. *J. Pestic. Sci.* **2007**, *32*, 402–406.

(38) Kimoto, N.; Kutsuzawa, Y.; Inubushi, K. Design and release profile of timed-release coated granules of herbicide. *J. Pestic. Sci.* 2007, 32, 243–248.

(39) Tabarant, P.; Villenave, C.; Risede, J. M.; Roger-Estrade, J.; Dorel, M. Effects of organic amendments on plant-parasitic nematode populations, root damage, and banana plant growth. *Biol. Fert. Soils* **2011**, 47, 341–347. (40) Aouada, F. A.; de Moura, M. R.; Orts, W. J.; Mattoso, L. H. C. Polyacrylamide and methylcellulose hydrogel as delivery vehicle for the controlled release of paraquat pesticide. *J. Mater. Sci.* **2010**, *45*, 4977–4985.

(41) Vieira, E. M.; do Prado, A. G. S.; Landgraf, M. D.; Rezende, M. O. D. Study of adsorption desorption of herbicide 2,4D in soil. *Quim. Nova* **1999**, *22*, 305–308.

(42) Prado, A. G. S.; Moura, A. O.; Nunes, A. R. Nanosized silica modified with carboxylic acid as support for controlled release of herbicides. *J. Agric. Food Chem.* **2011**, *59*, 8847–8852.

(43) Touloupakis, E.; Margelou, A.; Ghanotakis, D. F. Intercalation of the herbicide atrazine in layered double hydroxides for controlled-release applications. *Pest Manag. Sci.* **2011**, *67*, 837–841.

(44) Singh, A.; Sarkar, D. J.; Singh, A. K.; Parsad, R.; Kumar, A.; Parmar, B. S. Studies on novel nanosuperabsorbent composites: swelling behavior in different environments and effect on water absorption and retention properties of sandy loam soil and soil-less medium. J. Appl. Polym. Sci. 2011, 120, 1448–1458.

(45) Xiong, Y. S.; Yuan, J. F.; Hu, R. G. Characteristics of nutrient release kinetics for organic polymer-coated fertilizers. *J. Food Agric. Environ.* **2010**, *8*, 733–735.

(46) Cahill, S.; Osmond, D.; Weisz, R.; Heiniger, R. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. *Agron. J.* **2010**, *102*, 1226–1236.

(47) Wu, Z. S.; Zhao, Y. F.; Kaleem, I.; Li, C. Preparation of calciumalginate microcapsuled microbial fertilizer coating *Klebsiella oxytoca* Rs-5 and its performance under salinity stress. *Eur. J. Soil Biol.* **2011**, 47, 152–159.

(48) Qian, P. Y.; Schoenau, J. Effects of conventional and controlled release phosphorus fertilizer on crop emergence and growth response under controlled environment conditions. *J. Plant Nutr.* **2010**, *33*, 1253–1263.

(49) Wu, C. S. Characterizing biodegradation of PLA and PLA-g-AA/starch films using a phosphate-solubilizing bacillus species. *Macromol. Biosci.* 2008, *8*, 560–567.

(50) Liu, C. H.; Wu, J. Y.; Chang, J. S. Diffusion characteristics and controlled release of bacterial fertilizers from modified calcium alginate capsules. *Bioresour. Technol.* **2008**, *99*, 1904–1910.

(51) Kenawy, E. R.; Sakran, M. A. Controlled release formulations of agrochemicals from calcium alginate. *Ind. Eng. Chem. Res.* **1996**, *35*, 3726–3729.

(52) Karapetyan, K. G.; Senichenkov, V. A.; Zenin, G. S.; Ryabova, M. N. Kinetics of dissolution of glassy fertilizers. *Russ. J. Appl. Chem.* **2005**, *78*, 1383–1385.

(53) Ivanenko, V.; Karapetyan, G.; Lipovskii, A.; Maksimov, L.; Rusan, V.; Tagantsev, D.; Tatarintsev, B.; Fleckenstein, J.; Schnug, E. Principal studies on phosphate glasses for fertilizers. *Landbauforsch. Volk.* **2007**, *57*, 323–332.

(54) Mullins, G. L.; Sikora, F. J. Effect of soil-pH on the requirement for water-soluble phosphorus in triple superphosphate fertilizers. *Fert. Res.* **1995**, *40*, 207–214.

(55) Tonitto, C.; David, M. B.; Drinkwater, L. E. Replacing bare fallows with cover crops in fertilizer-intensive cropping systems: a meta-analysis of crop yield and N dynamics. *Agr. Ecosyst. Environ.* **2006**, *112*, 58–72.

(56) Padilla, F. M.; Pugnaire, F. I. Rooting depth and soil moisture control mediterranean woody seedling survival during drought. *Funct. Ecol.* **2007**, *21*, 489–495.

(57) Kato, Y.; Kamoshita, A.; Yamagishi, J. Evaluating the resistance of six rice cultivars to drought: restriction of deep rooting and the use of raised beds. *Plant Soil* **2007**, *300*, 149–161.

(58) Devassine, M.; Henry, F.; Guerin, P.; Briand, X. Coating of fertilizers by degradable polymers. *Int. J. Pharm.* **2002**, *242*, 399–404.