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THE UNIVERSITY OF ALBERTA

Polymer-coated urea: N release rate and N uptake by barley

BY

Mingchu Zhang ©

A thesis submitted to the Faculty of Graduate and research in partial fulfillment of the requirement for the degree of DOCTOR OF PHILOSOPHY

Department of Soil Science

EDMONTON, ALBERTA

Spring 1994

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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 POLYMER-COATED UREA: N RELEASE RATE AND N UPTAKE BY BARLEY submitted by Mingchu Zhang in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Soil Science.

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A thesis dedicated to my family for their love and support

During the time I was a graduate student, I was also a worshiper of Lord, a husband, a father, a son, and a friend to others.

Through this study, I feel I were a child picking up stones along a sea shore and making them into a picture.

We all want to contribute our wisdom and knowledge to this world so that it can be better, but somehow the problems in this world if not all are caused by our wisdom and knowledge.

Abstract

Encapsulating granular N fertilizers by a polymeric membrane is a new approach to improve N uptake to crops and to reduce the potential of pollution by N fertilization. Experiments ranging from laboratory to field scale were conducted to determine permeability of a polymer coating to urea, urea release rate from polymer-coated urea (PCU) in soil and N uptake from PCU under field conditions. Polymer-coated urea was provided by Imperial Oil Chemicals Division. An apparatus was constructed in order to determine permeability of the polymer to urea and activation energy of the permeability. In the laboratory, two batches of PCU with varied coating thickness were incubated for 15, 30 and 60 days in an Orthic Black Chernozem and a Dark Gray Chernozem to relate coating thickness, soil temperature, water content and texture to urea release rate. Field experiments were conducted in the same two soils and another soil (Gray Luvisol) in Alberta for two consecutive years (Sept. 1989-Sept. 1991). The release rate of urea from PCU was determined in cold and frozen soil. Nitrogen uptake by barley from PCU and conventional urea was compared with contrasting methods of application in spring and fall, including constricted band and point application.

The membrane permeability to urea was $1.4 \pm 0.5 \times 10^{-14}$ m^2 s^{-1} at 12°C and $3.5 \pm 1.5 \times 10^{-14}$ m^2 s^{-1} at 31°C. The activation energy of the permeability was 350 kJ mol^{-1}. Using the permeability and activation energy of the permeability, maximum flux (J_{max}) of urea was calculated with different temperature and coating thicknesses. PCU on incubation showed soil temperature and coating thicknesses had a remarkable influence on the urea release rate. By comparing urea flux in flowing water with that in soil at the same temperature, the flux in soil was only 10% of the J_{max} in water. High N uptake by barley was found with PCU banded in fall and non-coated urea banded in spring. To explain water moving in and out of the membrane, a two-step release model was proposed; the key feature of the model was the existence of a

boundary layer around the coated granule. The simulated points fell within the standard error of the actual urea release 66% of the time in fertilizer-soil incubations. In conclusion, this dissertation provided a systematic approach for evaluating controlled release fertilizers. Encapsulation is a useful way to promote the efficiency of nutrient supply from conventional fertilizers to crops, but the constricted band or point application still retains an unchallenged position in fulfilling such a task. Combining these two is a more powerful mean for attaining prescribed fertilizer release patterns.

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Chapter 1. Introduction

Controlled release technology is a recent scientific discipline. Both the theory and the practical application of controlled release are actively applied in controlling the release of drugs, fertilizers, pesticides and herbicides. In the 1950's and 1960's, ways were found of slowing the release rate of drugs or bioactive agents for plants, but the release rates of those products were often affected by external factors. For example, the amount of N released from isobutylidene diurea (IBDU), a slow release fertilizer, is controlled by the hydrolysis rate of the compound, which is dependent on the soil water content [16]. Strictly speaking, such products are not within the catalogue of controlled release. They have a sustained or delayed release. A controlled release formulation, by definition, is a system where the release rate of an active agent is determined by design. The principal interest of this dissertation is controlled release fertilizers (CRF).

There are many coating materials used to control the release rate of fertilizers. Those materials can be either inorganic or organic. The well known sulfur-coated urea (SCU) from Tennessee Valley Authority is an example of inorganic coating. Organic materials are mainly polymers. They can be further divided into two groups, thermoplastic and thermosetting polymers. Most recently a hydrophilic polymer neither thermoplastic nor thermosetting has been used in controlled release [27]. If based on the mechanisms of controlled release formulations, controlled release fertilizers can be categorized as: membrane encapsulating devices, such as Polyon®, Meister® and Osmocote®; matrix devices (urea-rubber matrix, for example [14]); or swelling membrane devices using a hydrophilic polymer. From an agronomic point of view, controlled release fertilizers are classified as those releasing macro nutrients of nitrogen or phosphorous, or those releasing micro nutrients such as zinc [19,20,21].

Research on controlled release fertilizers has focused on: 1) influence of environmental factors on the nutrient release rate; 2) field assessment of controlled release fertilizers for different kinds of plants; 3) release characteristics of nutrients; 4) mathematical modeling of nutrient release rate; 5) methods of evaluating fertilizers in the laboratory.

Factors affecting nutrient release from controlled release fertilizers

Soil temperature, water content, texture, pH, microorganism activity, and labile carbon content of soil have been studied for their effect on release rate of nutrient from controlled release fertilizers. Earlier investigations with SCU showed that the openings of diffusion channels in S coatings were partly dependent on soil microbial activity [26], implying that any factor closely related to soil microorganism activity would modify the release rate of N from SCU. High soil pH and soil labile carbon content stimulated N release from SCU [13,30]. Conversely, soil sterilization retarded N release [1]. In contrast to S coating, plastic coatings, with the exception of soil temperature, were less affected by environment factors. Research on Osmocote® showed that soil water content between wilting point and field capacity had little relation to urea release rate, whereas it was closely related to temperature and coating thickness [24,28]. Later studies on different polymer-coated N fertilizers gave similar results [6,22].

Hauck [15] proposed a release model for coated fertilizers applied to soil. It included: 1) vapor diffussion through the coating and dissolution of the salts inside to build up osmotic potential; 2) diffusion of dissolved nutrients through the coating; 3) slow degradation of the coating by microbial, chemical, or physical actions. Since relative humidity in soil changes little from -0.033 to -10 MPa water potential [18], water moving into the granule as vapor can explain the limited effect of soil water content on nutrient release. Gambash *et al.* [11] incubated coated KNO_3 on filter paper held in a petri dish and concluded that vapor was the form of water moving into the coating, and the rate of vapor movement into the granule was the rate-limiting step for diffusion of KNO_3 out of the coating. Christianson [6] found N release rate from reactive layer coated urea incubated in soil at -0.033 MPa water potential was constant regardless of drying rates.

Temperature promotes nutrient release from coating through solubility and diffusivity. Urea solubility exponentially increases with temperature [31], and the higher the urea concentration gradient existing across the coating, the more urea moves out of the coating. Diffusivity also increases with temperature [32].

When a nutrient is released from an encapsulated fertilizer in soil, it becomes a reactant or substrate for chemical or biochemical reaction. If that reaction rate is faster than the nutrient diffusion rate through coating, the release rate of the nutrient is dependent on the rate of diffusion, or *vice versa*. Because the urea hydrolysis rate can be as high as 95 μg urea hydrolyzed g^{-1} soil h^{-1} [37], it was assumed that the amount of urea released from coated urea into soil was simultaneously hydrolyzed. Therefore, the urea release rate was only controlled by the diffusion rate through coating [6].

Efficiency of controlled release N to crops

Promoting fertilizer N efficiency has been a research subject for many years. Higher N uptake by crops was achieved through changing or spliting of time and methods of application. For example, in western Canada, greater yield and N recovery in barley grain was found with band application of urea or ammonium nitrate, and with spring application [25]. These practices, however, required special equipment and extra time for application. Therefore, controlled release might be an effective and acceptable technique both to academicians and to farmers. But reports on the efficiency of controlled release N to crops are scarce. Top dressing of polyolefin coated urea (POCU) on rice showed 26% higher N recovery than did top dressing of ammonium sulfate in later growing season [12]. Good N uptake with POCU was also found in corn, wheat and soybean [12]. Apart from field crops, studies on use of controlled release fertilizers have been made on horticultural crops, turf grasses, and ornamental trees. A combination of reactive layer coated urea with uncoated urea generated a higher quality of bermudagrass [29]. Positive results of coated N fertilizers were shown on greenhouse-grown strawberries and ornamental crops [34], but not on watermelon, field-grown pepper and tomato [8,17].

Release characteristics and boundary layer effect

The release pattern of an encapsulated controlled-release drug, fertilizer, and pesticide, or herbicide usually has three stages: transition release, steady state release and declining release (Fig.1-1). Depending on the time of storage of an encapsulated product, the release rate during the transitional stage can be either a burst effect or a time lag. If a coated agent is dispersed into a membrane, a burst effect will likely take place. In contrast, a newly coated product always has a time lag effect [10]. The

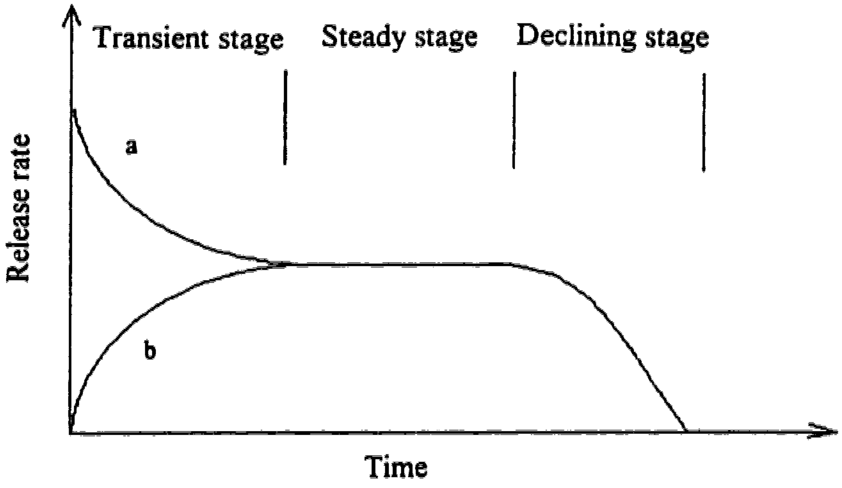

Fig.1-1 Release pattern of encapsulated bioactive agent, a: burst effect and b: time lag.

steady release stage is the result of the coexistence of solid and liquid phases in the core zone. As depletion of the solid core held in the membrane occurs, the concentration profile decreases with time resulting in decreased release rate. Mathematical equations have been derived to depict the release processes in the three stages for the encapsulated device in different forms. Trigonometric and exponential series were major constituents of the transitional stage, and a mass balance equation was used for steady or declining release stages [7,10,35,36].

In the laboratory, encapsulated granules have been tested in stirred water so that the surface concentration of the membrane was kept close to zero and a maximum flux of a coated agent was attained. But in reality, such as in the human body or soil, water movement is limited. Under these circumstances, a zero concentration at the outer surface of the membrane is hard to achieve and the assumption of a zero outer surface concentration is not valid. A static water layer thereafter possibly exists around the outer surface of the membrane. This water layer is termed stagnant layer, unstirred layer, or boundary layer. Burnette [5] used an approach based on Fick's equations to derive a mass transport equation considering stagnant layers at both sides of the membrane. Crank [7] used an error function to describe built-up concentration of a diffusant released into a confined volume of unstirred fluid. Another equation was introduced by Baker [3], in which diffusivity of the diffusant in the boundary layer was assumed to be the same as that in free water; thickness of the boundary layer or mass transport across the membrane and the boundary layer was then calculated.

Mathematical modeling

Mathematical models have been developed in the simulation of bioreactive agents released from controlled release products with varying geometry and devices. A detailed list of those models was made by Fan and Singh [10]. Of particular interest were the models by Fan *et al.* [9], Tojo and Fan [35], Tojo and Miyanami [36], and Lu and Lee [23], which involved membrane encapsulated urea. Fan *et al.* [9] used a mass balance equation and incorporated the Mechaelis-Menten equation into the model to measure the decay of the active agent. They also incorporated a heat balance equation into the model to adjust rates for varying temperatures. The release rate of an active agent and concentration profile were simulated [9]. Improvement of the model was made by introducing a dispersion factor, which referred to the uniform distribution of solid in the core zone [35]. Later the authors compared the predicted N release rate from the model with published results [36]. Unfortunately the values of the parameters in the model, such as void fraction of the membrane or rate constants in the mass balance equation and Mechaelis-Menten's equation, were not given.

Lu and Lee [23] simulated release of urea from latex-coated urea in a finite volume of water, using a three-stage release model. The diffusion coefficient of urea through the latex film was experimentally determined in an agitated water apparatus, and based on the diffusion coefficient, urea release rate was simulated. The release pattern of latex-coated urea had three phases: an initial slow release stage during the time required to build up the concentration profile; a steady state stage where the release rate was constant due to the existence of solid urea in the core zone; and a ' tailing off ' stage after the solid urea was depleted in the core zone, during which the urea concentration gradient decreased with time and gradually approached zero. They used Crank's equation [7] in the first stage, and a mass balance equation with constant and variable urea concentrations in the core zone for the steady and 'tailing off' stages, respectively. The results predicted by the model matched experimental urea release. The model, however, did not consider non-isothermal conditions.

Evaluation of controlled release fertilizers in the laboratory

Oertli and Lunt [28] were the first to incubate CRF in soil at varying temperatures and moisture contents to determine nutrient release rate. Since then, this approach has been commonly used for each newly-invented CRF. Savant *et al.* [33], among others, used a modified approach by placing CRF in a plastic bag, incubating it in soil, and calculating the percentage nutrient released into soil based on the recovery of CRF in the bag. Another way used to assess CRF was to incubate fertilizer granules in water of differing ionic strengths, made by adding different amounts of NaCl and NaH_2PO_4, or $CaCl_2$. The solution was static or agitated [14,26,28]. A method used in industry for SCU evaluation is known as the 7-day dissolution method, and consists of placing 50 g SCU in 250 mL water at 38°C in each of a series of beakers with subsequent daily determination of SCU mass for 7 days [4]. In pharmaceuticals, however, the release rate of controlled release drugs is estimated by determining permeability or diffusivity of drugs through a membrane matrix using a saturated diffusion cell [2].

Objectives of this dissertation

The main objectives of this study were to find the release mechanisms of polymer-coated urea (PCU), and to determine N uptake efficiency by barley from the fertilizer with different times and methods of application.

In Chapter 2, permeability of a polymer coating to urea will be determined and urea release rate from PCU in flowing water will be compared with that in static water. In Chapter 3, urea release rate from PCU in soil will be related to soil temperature, water content and texture. In Chapter 4, N uptake by barley from PCU in the field will be related to time and methods of PCU application. In Chapter 5, the existence of a boundary layer around the PCU granule in soil will be verified. In Chapter 6 urea release rate from PCU will be simulated in non-isothermal conditions. Chapter 7 will be a synthesis of the main discoveries of this dissertation with projections into the future.

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Chapter 2. Determining permeability of coatings of polymer-coated urea†

Introduction

A variety of methods have been used to assess behavior of slow- or controlled-release fertilizers. For example, Lunt and Oertli [10] determined mineral-N content in soil after incubating a fertilizer-soil mixture for several days. Savant *et al.* [14] suggested placing the coated fertilizer in plastic bags inserted into soil for incubation. Attoe *et al.* [1] determined the amount of nutrient left in the coated fertilizer after incubation in soil.

Blouin [3] proposed a '7-day dissolution rate' method, in which 50 g of S-coated urea (SCU) was immersed in 250 mL water, and urea concentration was measured every day for 7 d. This has become the conventional way of evaluating SCU and polymer-coated urea [5,13]. Nevertheless, the concentration of urea in water increases with time, impeding the movement of urea through the coats. Although the technique can roughly estimate the effectiveness of coatings with varied thicknesses, there is no theoretical basis from which to extrapolate the existing results involving different thicknesses. Recently, Hassan *et al.* [7] measured the diffusivity of urea in urea-rubber matrices. But diffusivity is not sufficient to evaluate membrane encapsulated fertilizers. Mathematical approaches used to predict the release rate of an encapsulated fertilizer in water and soil involved parameters which were difficult to measure [9,15].

Our hypothesis for this study was that the accumulation of urea in elusion medium slowed the urea diffusion rate through polymer coating; therefore, the release

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† A version of this chapter has been submitted for publication. Zhang M, Nyborg M and Ryan JT (1994) Fert Res

rate of urea from the coated granules was higher in flowing water than in static water. To test this hypothesis, urea release rates of the two conditions were compared. The urea release rate in flowing water was obtained by measuring coating permeability in a device described below, and the urea release rate in static water was determined by the 7-d dissolution rate method.

Theory

Diffusion of a membrane encapsulated bioreactive agent across a membrane in hydraulic medium can be treated as a binary diffusion system. In this system, one side is the solid agent and the other pure water; between them is the membrane. Due to the differences in water potential, water moves across the membrane to dissolve the solid agent on the one side, and the dissolved agent diffuses into water on the other. The apparent rate of diffusion for the agent can be described by Eq.(1) [4,6]

$$J = -\frac{K_m D(C_2 - C_1)}{L} \qquad (1)$$

in which J is the flux of a solute across a membrane (mg m^{-2} s^{-1}). Km, the non-dimensional partition coefficient, is a ratio of a solute concentration in the membrane to bulk solution at equilibrium. D is the binary diffusivity of a solute in the membrane (m^2 s^{-1}). C_1 and C_2 (Mg m^{-3}) are the solute concentrations at the inner and outer surface of the membrane, respectively. L is the thickness of the membrane (m). The product of Km and D is termed permeability (P). Hence, Eq.(1) becomes:

$$J = -\frac{P(C_2 - C_1)}{L} \qquad (2)$$

Solubility of urea in water is high and increases with temperature [11]. It was assumed that urea was saturated at the inner surface of the membrane. If the outer surface concentration of urea can be reduced to near zero, then the concentration gradient is known (C_2 - C_1). The thickness of coating (L) can be determined using a scanning electron microscope (SEM). If the flux was obtained experimentally, permeability was calculated by Eq.(2).

Rogers [12] proposed an Arhennius-type equation to calculate the activation energy (E_p) for permeability at different temperatures:

$$P=P_o\exp(-E_p/RT) \qquad (3)$$

where P and P_o were permeabilities at two different temperatures, and R is universal gas constant and T is absolute temperature. Using the permeabilities at the two temperatures (12 and 31°C in this study) and using Eq.(3), E_p is calculated based on the assumption that permeability has a logarithmic linear relation to temperature within the test temperature range. In turn, E_p was used to calculate the permeability at any temperature within the ranges of 12 to 31°C.

Materials and methods

Two batches of a polymer-coated urea from Imperial Oil Chemicals Division (Edmonton, Canada) were sieved to a 2- to 3-mm diameter (Table 2-1). The granules were sliced in half and attached to aluminum stubs and examined with a Cambridge 250 SEM. The thicknesses of coating were measured, based on the scale in the SEM photographs (Fig. 2-1).

Table 2-1 Characteristics of the coated fertilizers

Coated urea	Total N	Mass/100 granules	Coat thickness
	g kg^{-1}	g	m
Thin coating	457	1.31±0.07	$8.8\pm1.7\times10^{-6}$
Thick coating	455	1.34±0.09	$14.7\pm3.9\times10^{-6}$

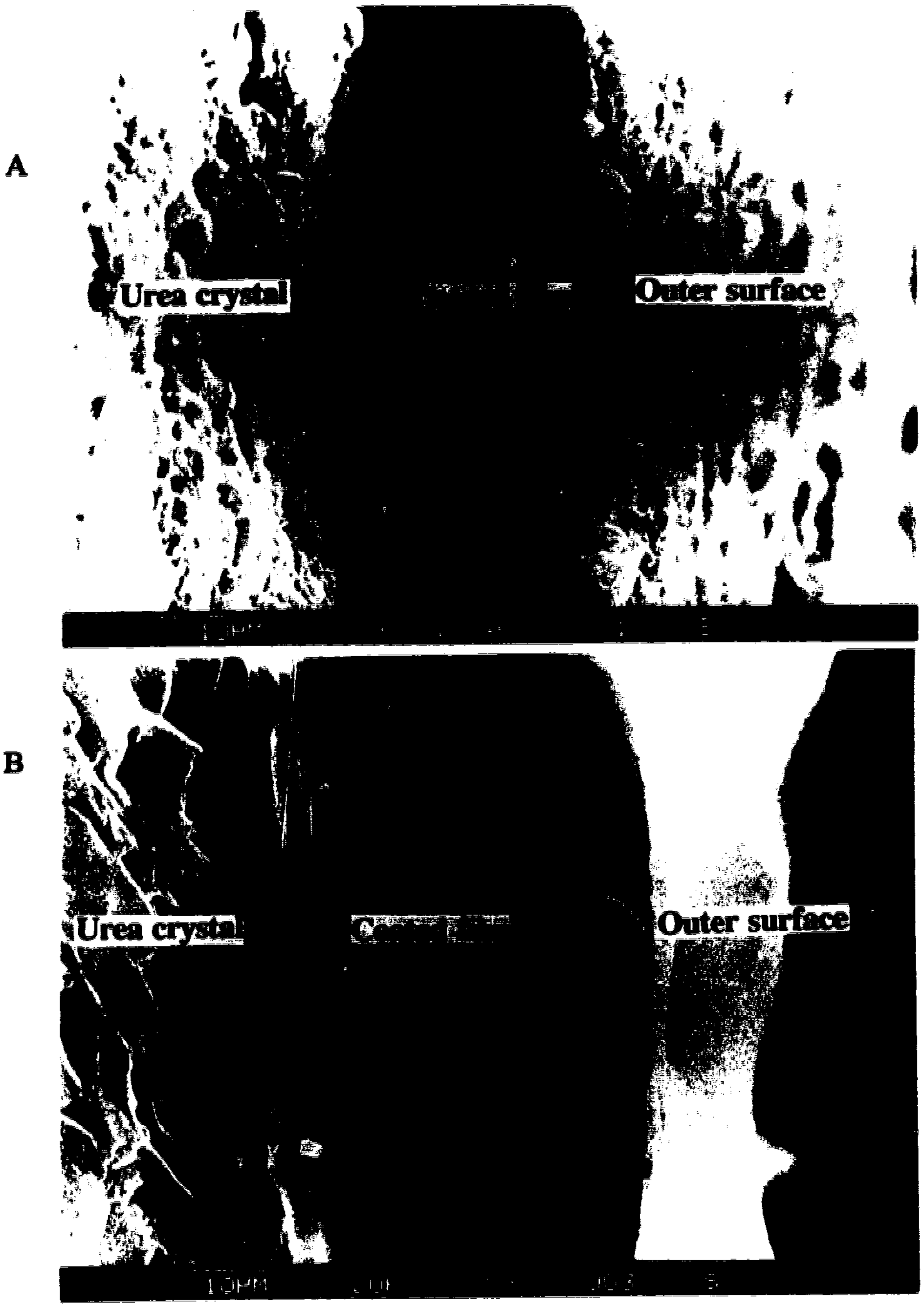

Fig.2-1 SEM images of sliced polymer-coated urea, a: thin coating and b: thick coating.

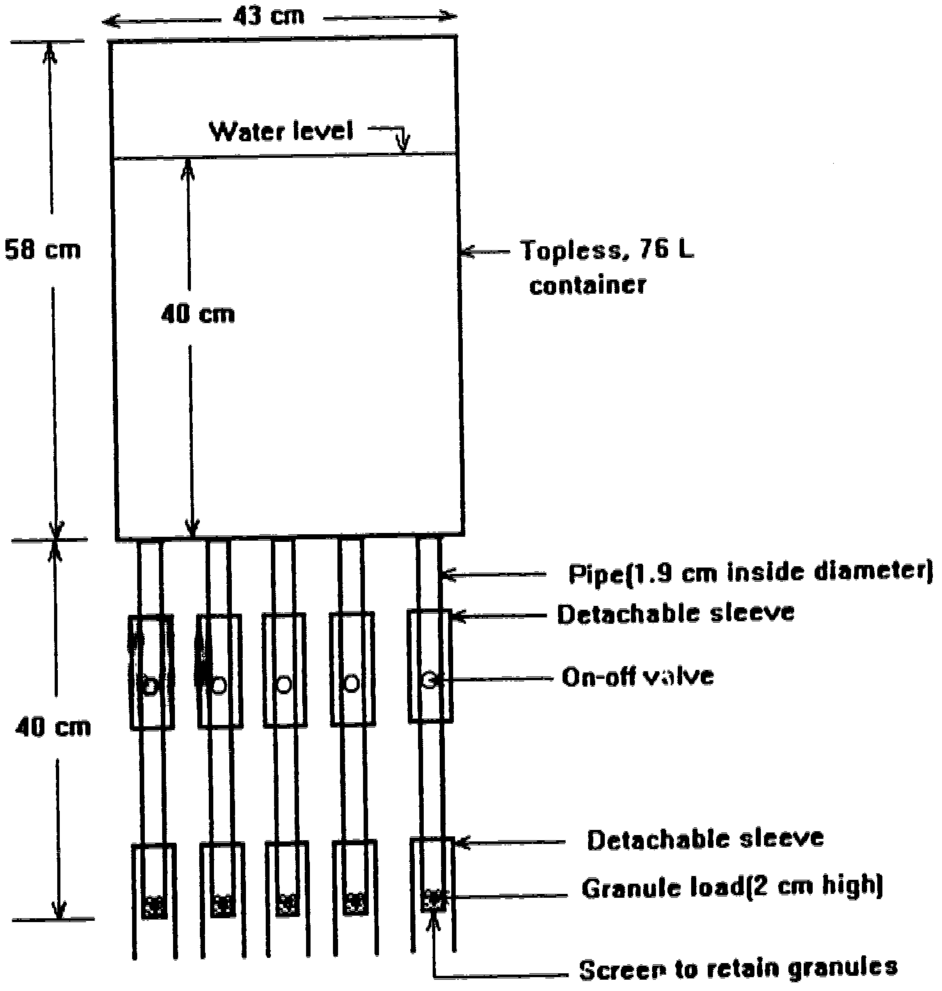

Fig.2-2 Device used in determination of the permeability of coated granules.

A device was constructed to determine the maximum flux of urea across the coating membrane. The device consisted of a cylindrical container (43-cm diam, 58-cm height) and 10 round acrylic pipes (1:9-cm diam) attached to the holes of the floor of the container (Fig.2-2). The coated granular urea products were loosely packed (2 cm deep) in the bottom end of each pipe. Water table was maintained at a height of 80 cm and water flowed turbulently (48.5 mL/s per pipe) over the granules (Appendix 1), so that there was no urea accumulation at the outer surface of the coatings. The granules were held by a screen (1 x 1 mm) fastened by a sleeve. Another sleeve accommodated an on-off valve for water flow and loading and removal of granules.

The experiment used urea granules with either of two thicknesses of coating, two water temperatures (12 and 31°C), and 19 (or 26) periods of time for exposure of granules to running water. The time of exposure to water was increased from 3- or 5-min to 30- or 60-min intervals, and the longest exposure was 5 h at 31°C and 15 h at 12°C. After removal, granules were placed on toweling to eliminate excess water, dried at 60°C for 48 h, then weighed and discarded. The urea mass loss at each load was calculated as mass loss per unit area of the granular surface (g cm^{-2}).

The urea release rate in static water was determined by the 7-d dissolution rate method at 23°C. The experiment used coated urea with either of two thicknesses of coating, seven exposure times (1, 2, 3, 4, 5, 6 and 7 days) and three replicates of each set of variables. Ten g of coated urea and 50 mL of distilled water were placed in a series of 100-mL containers (the ratio of mass of coated urea to volume of water was the same as used by Blouin [3]). Each day, six of the coated urea-solution mixtures were filtered (Whatman No.40 paper). The granules were dried at 60°C for 48 h, and weighed.

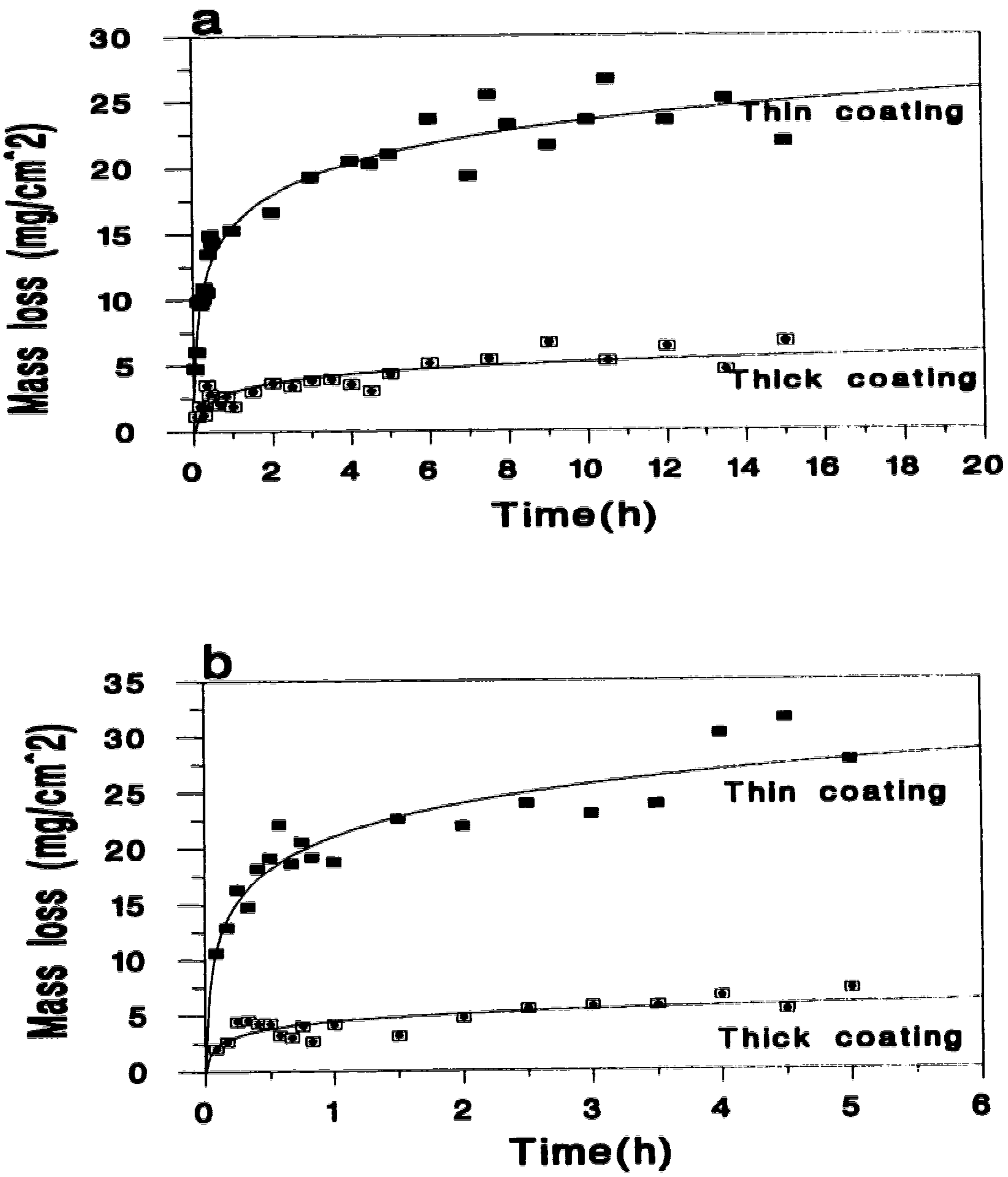

Fig.2-3 Mass loss of urea from coated urea with time at 12°C(a) and 31°C(b).

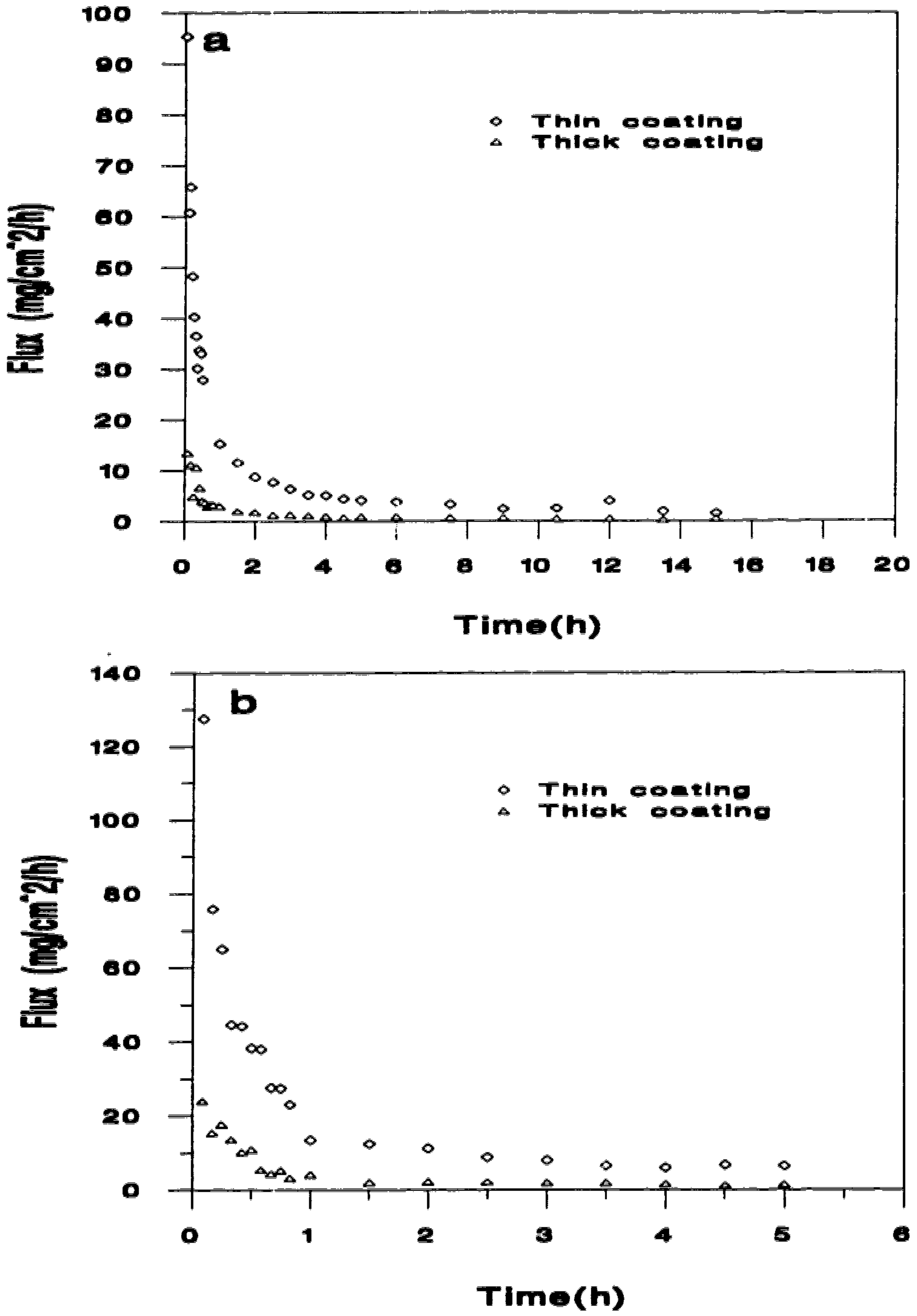

Fig.2-4 Flux of urea from coated urea with time at 12°C(a) and 31°C(b).

Results and discussion

For the flowing water system, urea losses over the test period followed a logarithmic pattern (Figs.2-3a, 2-3b). The curves clearly showed two stages of release, a fast release stage (transient state) followed by a steady release rate. In the first hour of the test, the cumulative mass loss of urea at 12°C increased from 0 to 3.0 or 15.5 mg cm^{-2} for thick and thin coatings, respectively, but in the second hour, the values were 3.7 and 17.9 respectively. The net increments were only 0.7 and 2.4 mg cm^{-2}. The two stages of release were illustrated as urea flux (mg cm^{-2} h^{-1}) plotted against time (Figs.2-4a, 2-4b).

Baker [2] and Fan and Singh [6] indicated two types of release phenomena for encapsulated pharmaceuticals in the transient state: 'time lag' or 'burst effect'. The first has a slow release rate, the latter has a fast release rate. If a coated product is stored before use, a burst effect occurs on its application because the membrane becomes saturated with the active agent during storage. The coated urea was stored for 33 months before the test. In addition, defects in some coated granules may have contributed to the burst effect. Occasional membranes were observed to be emptied of urea after only 3-min exposure to water. At a constant concentration gradient, the flux in a steady state should be a constant [8], but in this study it continued to decrease at a very low rate (Figs.2-4a, 2-4b). This might be caused by variations of the coating thickness.

To obtain a constant flux, the mass loss per unit area against time after 1 h of testing was linearized. The slope of each regression line was the flux of the thin- or thick-coated urea. The flux together with other parameters were used in Eq.(2) to calculate the permeability (Table 2-2).

The activation energy calculated from Eq.(3) was 350 KJ mol^{-1}, and the permeability at 23°C was 2.4×10^{-14} m^2 s^{-1}. In order to compare the percentage of urea released by the 7-d dissolution method at 23°C, we used the permeability of

23°C to calculate the amount of urea release in the steady state by Eq.(2). Nearly 100 h was required to obtain 100% release (transient + steady) for the thick coating but only 45 h for the thin coating (Fig.2-5). The 7-d dissolution rate showed that only 49.6% of urea was released by 168 h with the thin coating, and 20% with the thick coating (Fig.2-6a). The restrictions to urea release in the 7-d dissolution method come from two resistances, the polymer membrane itself and the elution medium around the granule. In the flowing water, the only restriction to diffusion of urea was the polymer coating because the urea concentration in the elution medium was reduced to be negligible; consequently, the time needed for 100% release was much shorter. The concentration of urea in the solution in the 7-d dissolution method increased with each day (Fig.2-6b). The driving force for diffusion, therefore, is expected to be decreased with time, thereby contributing to the smaller percentage of release in the 7-d dissolution.

Table 2-2 Parameters in calculation of permeability

Designation	Temp.	Flux	C1*	C2**	Permeability	Mean
		mg m^{-2} s^{-1}	Mg m^{-3}		------ m^2 s^{-1} -----	
Thin coating	12±2°C	1.54±0.73	0.87	0	$1.5\pm0.8\times10^{-14}$	$1.4\pm0.5\times10^{-14}$
Thick coating	12±2°C	0.73±0.28	0.87	0	$1.2\pm0.6\times10^{-14}$	
Thin coating	31±2°C	7.36±3.74	1.35	0	$4.7\pm2.5\times10^{-14}$	$3.5\pm1.5\times10^{-14}$
Thick coating	31±2°C	2.10±1.20	1.35	0	$2.3\pm1.4\times10^{-14}$	

* Urea concentration at the inner surface of the membrane
** Urea concentration at the outer surface of the membrane

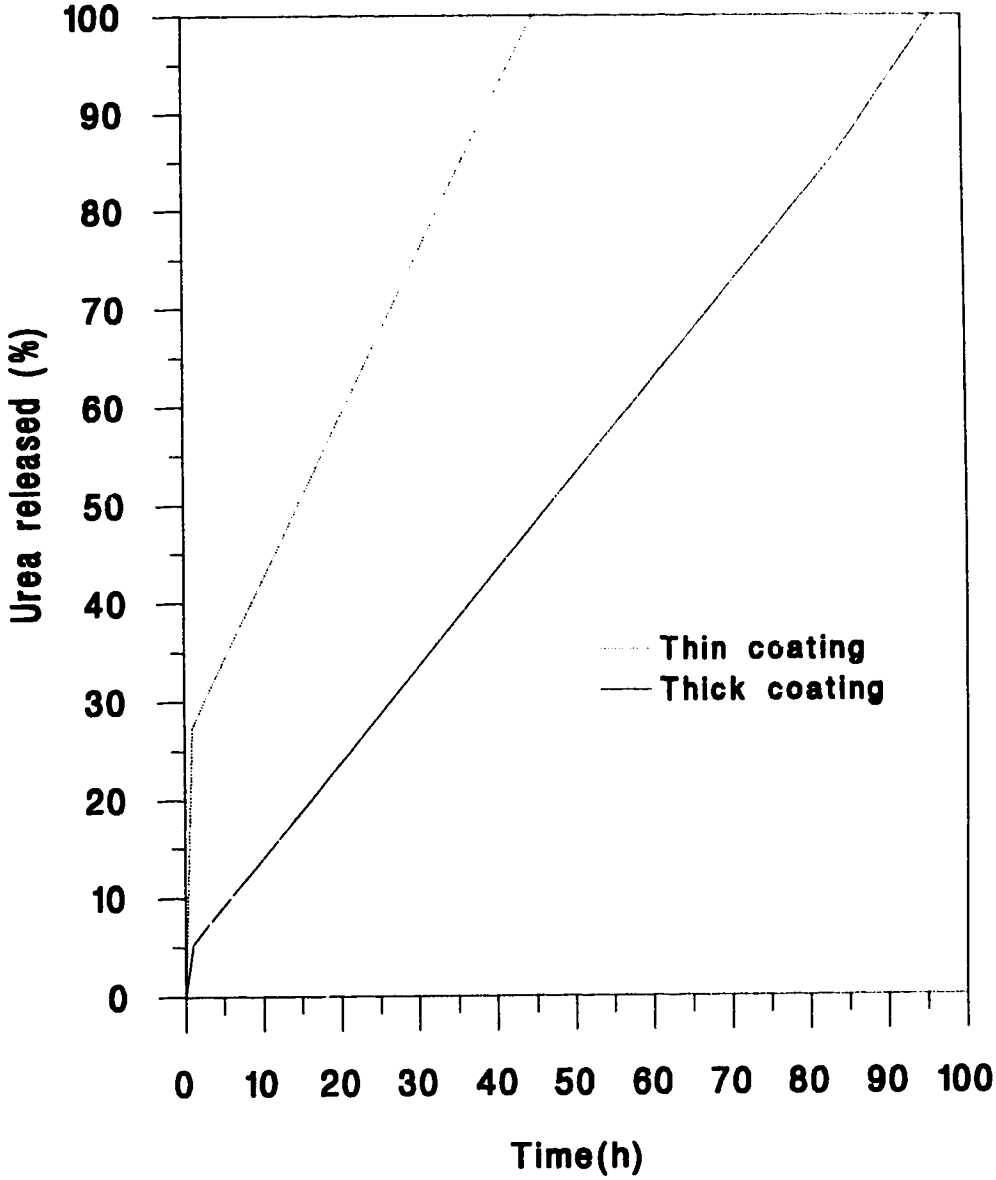

Fig.2-5 Predicted urea release at 23°C by Eq.(2).

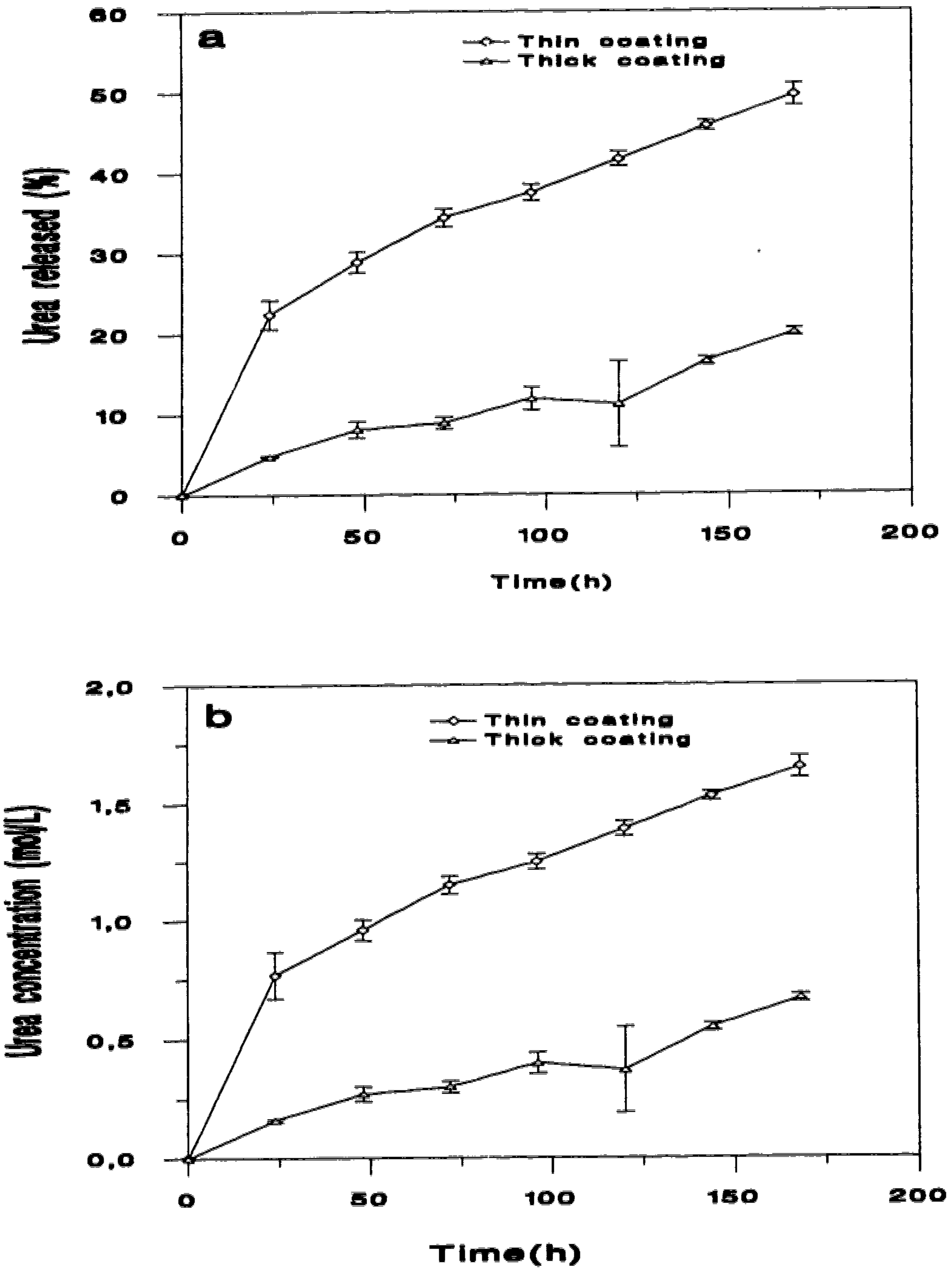

Fig.2-6 Percentage of coated urea released(a) and urea concentration in the solution(b) by the 7-day dissolution rate method.

Even though the urea release rate in flowing water was faster than that in the static water, the release pattern (shape of the curves in Fig.2-3 and Fig.2-6) was similar, *i.e.* a quick release stage at the beginning followed by a steady release. If the permeability can be calculated from a constant flux with a fixed concentration gradient in the flowing water, it should also be calculated from a variable flux with a variable concentration gradient in static water, provided that there is a viable mathematical approach. If so, the flowing water method in turn can be used to justify the mathematical approach.

The time required for 100% release by the two methods differred greatly. In flowing water, a zero outer surface concentration was obtained, but in practice, the outer surface concentration may not be as low as zero. The next step is to find the surface concentration of urea in soil under different conditions, such as soil temperature and water content, so that the release rate in soil can be predicted.

Conclusions

The urea release rate determined in flowing water was much greater than with the 7-day dissolution rate. It was inferred that increasing urea concentration in the elution medium in static water slowed diffusion.

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Chapter 3. Mineral-N release from polymer coated urea in soil

Introduction

Most commercial N fertilizers are readily soluble in water. Consequently, they are susceptible to denitrification, leaching, volatilization or fixation in soil. Numerous researches have been undertaken to minimize the N loss from the above pathways. These include methods of application such as banding or split applications of fertilizers; using less soluble N sources like ureaform; and applying inhibitors of nitrification. However, the successes of these methods have been limited. Encapsulation of granular N fertilizers with membranes is another technique. This newly emerged technology, often called 'controlled-release technologies', has been widely used in pharmaceutical science.

Either inorganic or organic membranes are used to encapsulate fertilizers [15]. Representatives of the two groups are sulfur-coated urea (SCU) and resin-coated ureas (e.g. Osmocote®). Nutrient release from resin-coated fertilizers is related to soil temperature more than to soil water content [8,9]. The Imperial Oil Chemicals Division (Edmonton, Canada) has recently developed a polymer coating for granular urea; this product was used for the present report. This is the same product used as described in Chapter 2 to determine coating permeability and urea release calculated by the diffusion equation at a given outer surface concentration of urea. The objective of the present study was to find urea release rates in soils with different temperatures, water contents and textures so that urea concentration at the outer surface of the coating could be derived. Thus, we could estimate urea release rate of the polymer-coated urea in soil.

Materials and methods

Two coated granular ureas were prepared by the Imperial Oil Chemicals Division. The two differed in coating thickness and seven day dissolution rate (Table 3-1). Granules of 2- to 3-mm diameter were incubated in two soils: either the Dark Gray Chernozem or the Orthic Black Chenozem (Table 3-2). A factorial experiment in three replicates was conducted on each soil as follows: four treatments (nil, uncoated urea, thin-coated urea, thick-coated urea), two temperatures (10 and 23°C), two soil water contents (-0.10 and -0.29 MPa water potential), and three incubation periods (15, 30, and 60 days). Plastic containers (115 mm diam. and 77-mm height) with perforated lids received 400 g soil and 80 mg of fertilizer N (200 mg N kg^{-1} soil) placed 25 mm deep. The number of granules varied from 13 to 14 to supply 80 mg N. Water content of soils was maintained by periodic addition. Soils in containers at 15, 30 or 60 d were air-dried, sieved (2-mm), and any intact granules were removed. NH_4-N and NO_3-N were extracted by 2 M KCl solution in a 1:5 soil:solution ratio, and their concentrations were determined with a Technicon AutoAnalyzer II [12,13].

Effect of coating on extractable mineral N ($NH_4^+ + NO_3^-$) at 23°C and -0.10 MPa were studied using a randomized complete block design followed by calculation of LSD at $P<0.05$. The effects of temperature and soil water potential on N release from the coated urea products were tested by ANOVA (split-plot design). Results from the two soils were compared with a T-test.

Results and discussion

Effect of coating

Gradual increase in mineral N concentration in the soil with time indicated the slow release of N from coated urea (Figs.3-1A and 3-1C). The amount of the urea left inside the membrane coats decreased with each sampling time (Figs.3-1B and 3-1D). Nitrogen released from the coated urea during the first 15 d of incubation was greater

Table 3-1 Basic properties of coated ureas

Urea	Total N	Coating thickness	7-day dissolution rate
	g kg^{-1}	m	%
Thin coating	457	$8.8 \pm 1.7 \times 10^{-6}$	49.6 ± 1.4
Thick coating	455	$14.7 \pm 3.9 \times 10^{-6}$	20.0 ± 0.5

Table 3-2 Selected soil properties

Soils	Classification*	Total N	Total C	Mineral N	Texture	Water content at -0.033MPa	pHw
		---- g kg^{-1} ----		mg kg^{-1}		g kg^{-1}	
Soil 2	Dark Gray Chernozem	3.5	42	25	sandy loam	306	6.8
Soil 3	Orthic Black Chernozem	5.2	63	20	clay loam	402	6.1

* Canadian Soil Classification System

with the thin rather than thick coating, but this difference disappeared at 60 d (Figs.3-1A and 3-1C). The influence of coating thickness on the N release rate was reported by Christianson [1] using reactive-layer coated urea. Average N release rate (mg N kg^{-1} soil d^{-1}) for the two soils was 9.4 and 5.8 during the first 15 d for the thin and thick coating, respectively. Then it slowed to an average of 4.9 and 4.3 mg N kg^{-1} soil d^{-1} during 30 d. The release rate was apparently governed by the urea concentration gradient across the membrane. As solid urea was depleted inside the

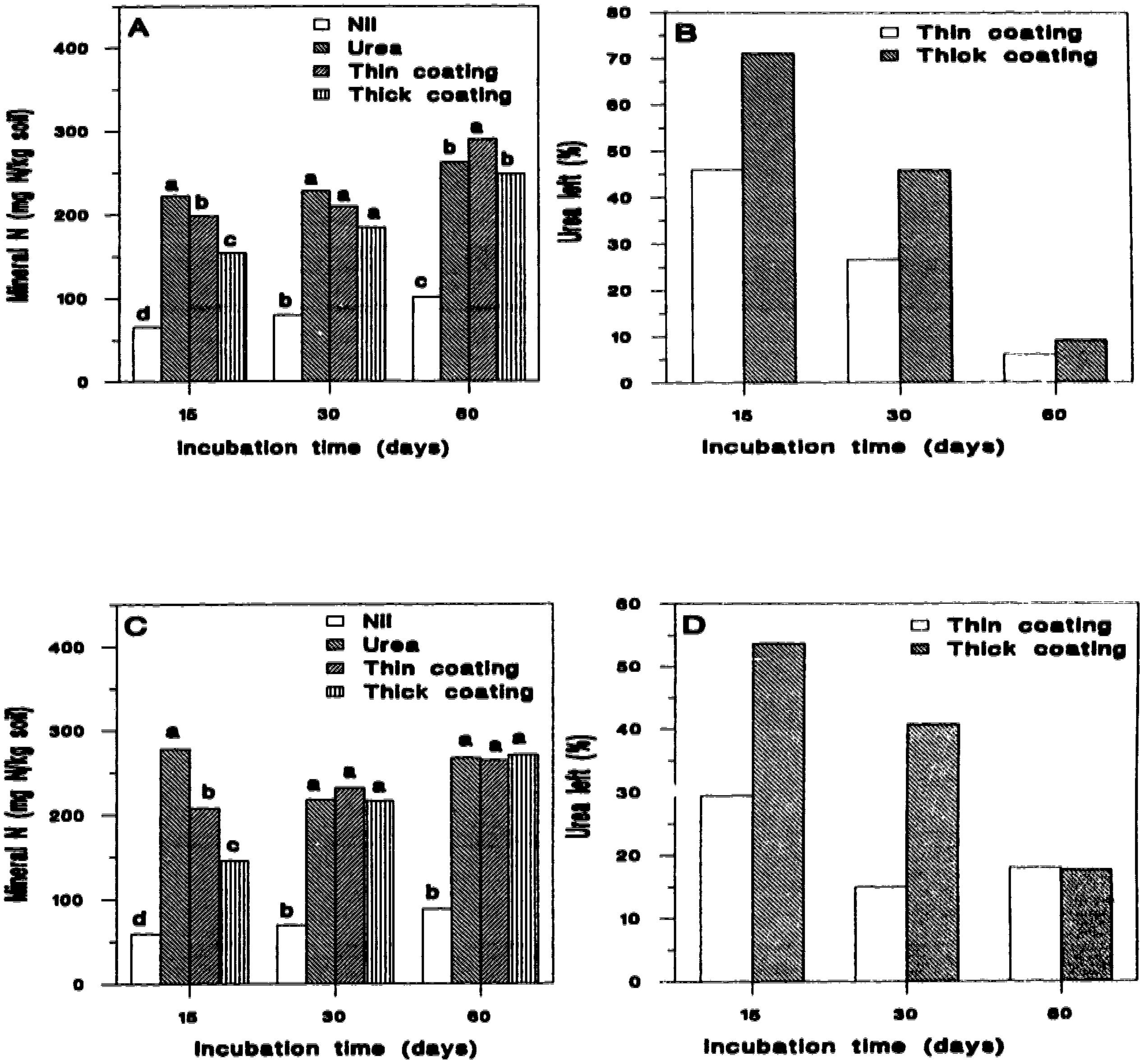

Fig.3-1 Mineral N and % urea in soil 2 (A, B) and soil 3 (C, D) after incubation of coated urea at 23°C and -0.10 MPa water potential. Differences are statistically significant($P<0.05$) where lower case letters differ within a group of bars.

membrane, the concentration gradient decreased with a subsequent decrease in release rate into the soil. Jarrell and Boersma [5] described a similar urea release pattern for SCU. For a perfect and uniform coating, urea concentration should stay in saturation if there exists solid urea inside the coating [2,14]. The release rate at this stage is steady, and it has been described as zero order release [2,14]. But in the manufacture of coated urea, both uniform and defect-free coatings are difficult to obtain. If defects exist in coated granules during incubation, a high release rate likely occurs before the first sampling time.

Soil water content and temperature effects

Net mineral N (N with fertilizer treatments minus N in Nil) varied with the soil water contents (Fig.3-2) and soil temperature (Fig.3-3). Nitrogen recovery in both soils was largely independent of soil water content, but dependent on soil temperature (Table 3-3). Kochba *et al.* [7] found that N diffusing from polymer-coated KNO_3 was not responsive to the change of soil water content from 50 to 100% field capacity. Similar results were also obtained by Lunt and Oertli [8] and Christianson [1].

We had hypothesized that the greater the soil water content, the greater the surface area of the fertilizer granule which would be in contact with water, and therefore the higher the release rate. Our results did not support this hypothesis. Hauck [4] hypothesized that water vapor moved into coated urea granules and dissolved the urea. As the pressure increased, dissolved urea began leaking to the outside of the coated granules. Kochba *et al.* [7] and Gambash *et al.* [3] tested this hypothesis with the coated KNO_3, and they suggested that movement of water vapor was the limiting factor for the N release from the coated KNO_3. Results reported in the previous experiment with water running around granules of thin- and thick-coated urea indicated that liquid water also penetrated into the polymer coating (Chapter 2).

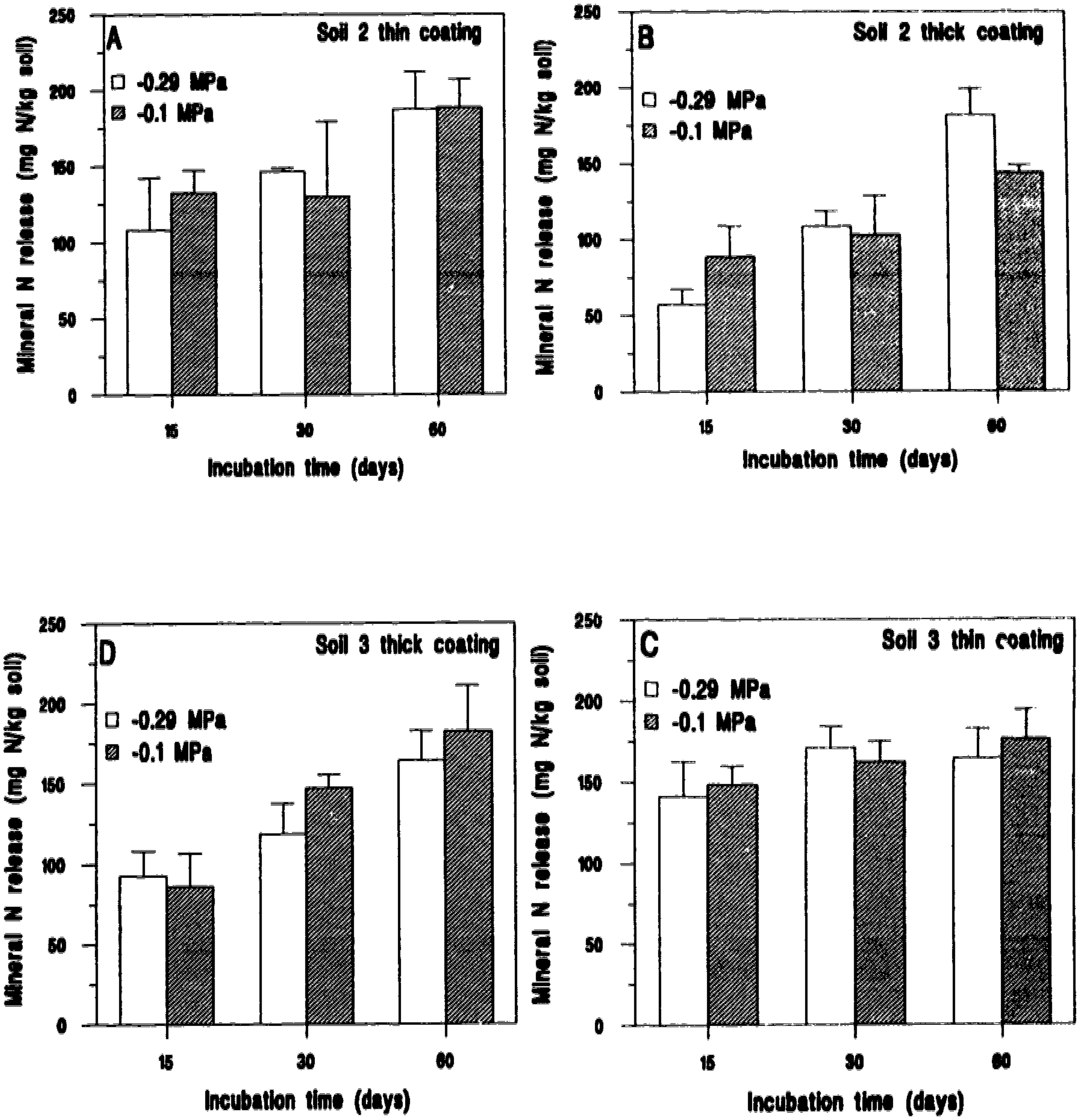

Fig.3-2 Net mineral N release at -0.10 and -0.29 MPa soil water potential with 23°C from coated ureas in soils. Means are given with standard errors(n=3).

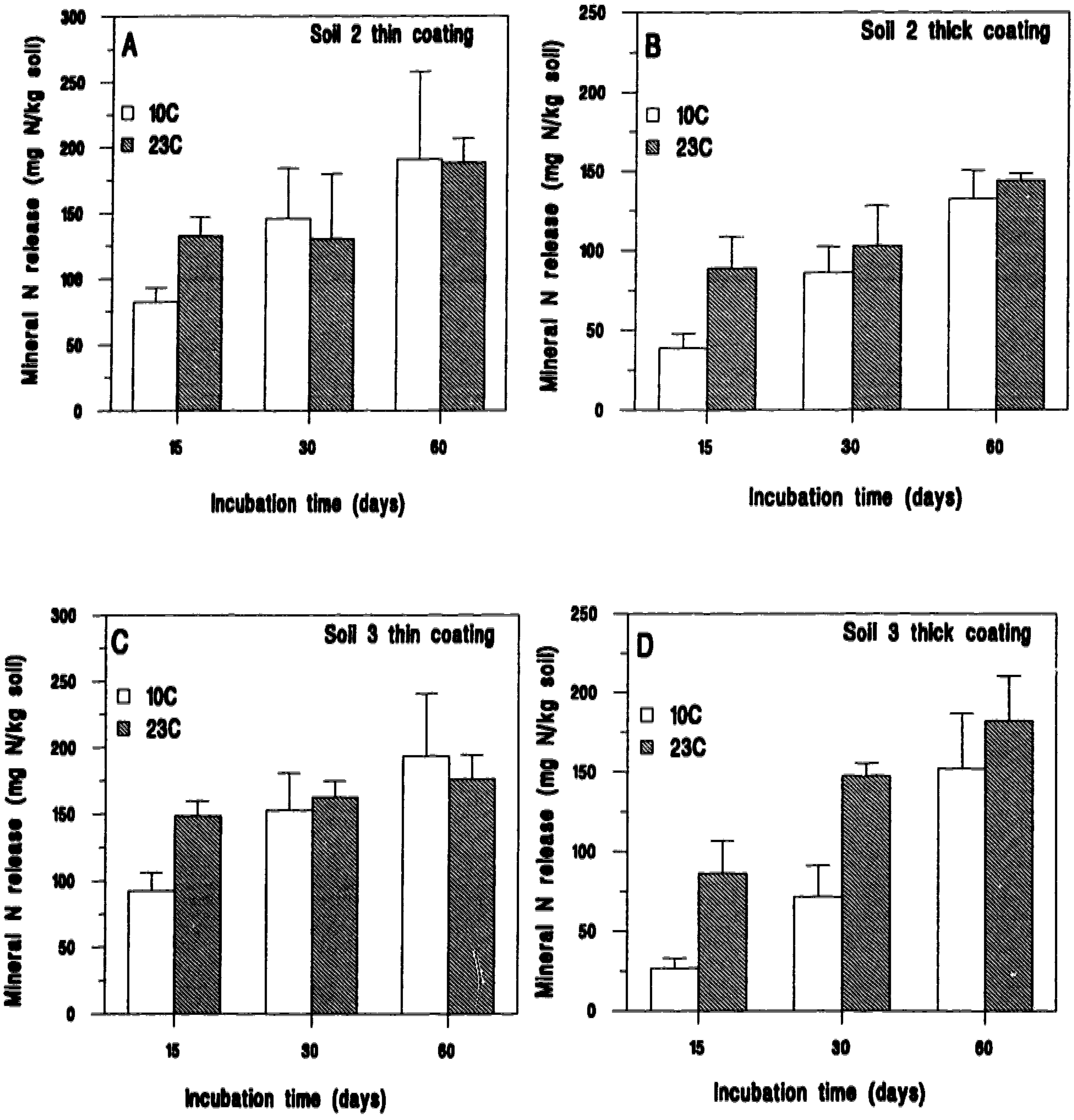

Fig.3-3 Net mineral N release at 10 and 23°C at -0.10 MPa from coated ureas in soils. Means are given with standard errors(n=3).

Table 3-3 Statistics of incubation experiments in soil 2 and soil 3 with urea coating temperature and water contents

Soil	Urea	Source	Probability (F test)		
			15 d	30 d	60 d
Soil 2	No coating	Temperature(T)	0.0002	0.60	0.80
		Water content(W)	0.22	0.78	0.78
		T x W	0.40	0.40	0.19
	Thin coating	Temperature(T)	0.076	0.74	0.39
		Water content(W)	0.59	0.77	0.32
		T x W	0.17	0.31	0.34
	Thick coating	Temperature(T)	0.002	0.076	0.04
		Water content(W)	0.06	0.93	0.17
		T x W	0.04	0.55	0.02
Soil 3	No coating	Temperature(T)	0.002	0.93	0.41
		Water content(W)	0.013	0.38	0.49
		T x W	0.028	0.05	0.27
	Thin coating	Temperature(T)	0.003	0.034	0.63
		Water content(W)	0.53	0.36	0.12
		T x W	0.96	0.12	0.38
	Thick coating	Temperature(T)	0.0004	0.0004	0.03
		Water content(W)	0.31	0.07	0.13
		T x W	0.30	0.37	0.77

Even if the medium for diffusion of a dissolved nutrient is liquid water, there is still one question remaining with Hauck's proposition, namely, can water vapor still enter the inside of a membrane when its pores are filled with water and dissolved nutrients? As a complement to Hauck's hypothesis, we suggest a two-step release model of encapsulated urea in soil. It is based on the present work with soil and on the work reported in Chapter 2 with running water. First, water vapor penetrates the coating and begins dissolution of urea. As the dissolved urea diffuses across the membrane, a thin liquid film is formed on the outer surface of the granule. This film is an exchange medium to condense water vapor into liquid. Then this liquid water diffuses into the inside of the membrane. Salts in the film create a water vapor gradient between the film and its surrounding medium, causing the water vapor to move toward the granule. Hillel [5] found that relative humidity is stable at soil water potential of 0 to -10 MPa. Consequently, the release rate of the coated fertilizers is not expected to be responsive to the change of soil water content.

In contrast to the soil water content, soil temperature had a definite influence on the N release rate from coated urea. The net mineral N found in the soils was lower at 10 than that at 23°C (Fig.3-3, Table 3-3). The release rate of N from encapsulated fertilizers is sensitive to temperature [1,7,9,11]. Kochba *et al.* [7] used first-order kinetics to describe release of encapsulated KNO_3. Others reported that both urea solubility and diffusivity were functions of temperature [6,11].

There are three diffusion processes in membrane-coated urea: diffusion of dissolved urea to the inner surface of the membrane; urea diffusion across the membrane; and diffusion of urea from the membrane outer surface to the elution medium. The diffusion coefficients of all three processes theoretically are affected by temperature. Urea solubility decreased from 1,123 to 830 g kg^{-1} water as temperature changed from 23 to 10°C [10]. Because more urea was dissolved inside the membrane at the higher temperature, the urea concentration gradient was greater, which apparently resulted in a higher release rate.

Effects of soil texture on release rate

As we have shown, water contents of the two soils at -0.033 MPa water potential were different by 9.6% (Table 3-2). The N released from the coated urea at -0.10 MPa and 23°C were similar with both soils (Fig.3-4). The original hypothesis was that the contact area of the granular surface with water was greater in the fine-textured soil, and therefore, a higher release rate would be found. The results, however, did not support such a hypothesis. This further confirms that water vapor is the major form of water movement toward coated granular urea in soil.

Conclusions

Among the environmental factors soil temperature, water content and texture, only temperature significantly influenced N release rate of the polymer-coated urea. The limited influence of soil water content and texture suggested that water moved toward the surface of the coated granular urea predominantly in the form of vapor. To explain the movement of water into and out from the coated urea, a two-step release model was proposed. This included water vapor penetration into the granule to initiate dissolution solid urea, and then the formation of a thin liquid water film on the outer surface of the coating as diffusion of urea occurred. Upon that thin film, water vapor was condensed into liquid and diffused inside of the coating to further dissolve urea.

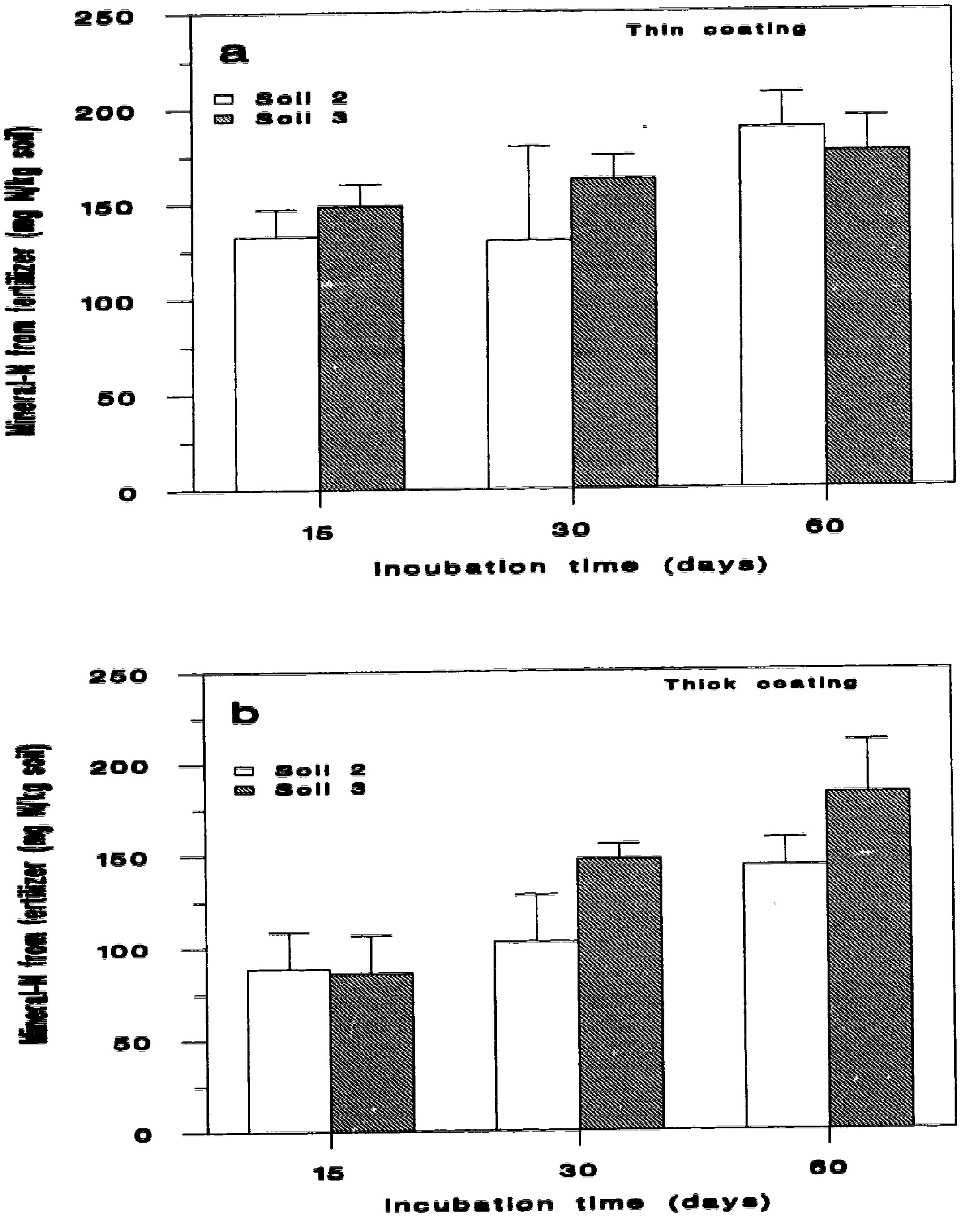

Fig.3-4 Net mineral N released in the soils after incubation of coated urea at 23^{o}C with -0.10 MPa water potential. Means are given with standard errors(n=3).

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Chapter 4. Polymer-coated urea in the field: mineralization, nitrification, and barley yield and nitrogen uptake

Introduction

The short growing season (80-120 d) of the Prairie Provinces of Canada forces most farmers to produce spring-sown cereal grains or oilseeds. The effective management of N fertilizers in the Prairie Provinces is crucial if profitable yields are to be produced. Nevertheless, some 30-50% of the fertilizer N is applied the previous fall instead of at spring sowing. The fall-applied practice is used in the Prairie Provinces and into the northern USA. Fall-application is motivated by tradition, advertisement, and avoiding the drying of the seedbed by deep placement of spring-applied N fertilizers. When compared to spring application, fall application of N resulted in only 55% as much yield increase (average of 44 experiments, range 23-94%) [11]. The usual inferiority of fall application is masked by heavy application of N or only slight response to N. The poor response to fall application is most striking when application is early rather than late in the fall [5], and early application favors near complete nitrification [8]. In the Prairie Provinces the poor performance of fall application is closely connected with nitrification and subsequently with denitrification in saturated topsoil perched on frozen subsoil in late winter or early spring [3, 10].

We found that slowing of nitrification of fall-applied fertilizers and increasing the efficiency of fertilizer N use were possible by different approaches: banding [7] or placement as large pellets or constricted nests [4, 12]; delaying application [5]; using nitrification inhibitors, e.g. thiourea, ATC, or N-Serve [6a]; or combinations of these approaches [6b]. Use of polymer coatings of urea [13] is still another approach, and has the advantage of controlled release of N to a crop.

Our objectives were: (1) find the rates of mineralization and nitrification of urea from polymer-coated granular urea of two coating thicknesses during a period extending from October through April; (2) compare the crop yield and N uptake of coated urea to those of non-coated urea for fall and spring application; (3) find whether the coating was as effective as banding and point injection placement of urea or as guanidine sulphate-ammonium sulphate mixture.

Materials and methods

Field experiments were conducted at 3 sites within 100 km of Edmonton, Alberta (54°N 114°W). Typically, the area had frozen soil November to March, and the average annual precipitation is 500 mm. Soil characteristics are given in Table 4-1.

Table 4-1. Soil characteristics of experimental sites.

Site No.	Place name	Soil Great Group†	Soil external drainage	Texture	Organic carbon	Total nitrogen	pH (1:2)
					- - - -	g kg^{-1} - - -	-
1	Breton	Gray Luvisol	Good	Loam	16	1.4	6.2
2	Smoky Lake	Dark Gray Chernozem	Moderate	Sandy Loam	42	3.5	6.8
3	Ellerslie	Black Chernozem	Good	Clay	63	5.2	6.1

† Canadian Soil Classification System

Field experiments consisted of 10 treatments each made in either fall or spring. Fall treatments were: (1) no N; (2) urea, incorporated (incorp.); (3) urea, band; (4) thin-coated urea, incorp.; (5) thin-coated urea, band; (6) thick-coated urea, incorp.; (7) thick-coated urea, band; (8) guanidine sulphate-ammonium sulphate mixture (GS) with 75% of nitrogen as GS by weight, incorp.; (9) GS mixture, band; and (10) urea solution injected at points, half in fall and half post-sowing. Spring treatments (No. 11-20) were applied at sowing, except that the urea solution was applied half at sowing and half post-sowing. Treatments Nos. 8 and 18 (GS, incorp.) were not included at Site 1. The urea used was a commercial fertilizer. Two experimental polymer-coated urea products were those described in Chapter 2. Near-saturated urea solution was point injected (points 2 cm dia. set at 8 cm depth, each point separated from the next by 23-cm row spacing and 25 cm in row) with a prototype spoke injector.

Nitrogen fertilizer was incorporated by spreading the fertilizers on the soil surface and rototilling to a depth of 12 cm. Band placement of N fertilizers was achieved using an engine-powered plot seeder with narrow hoe openers. The bands were 1 cm wide at a 10 to 12 cm depth with a row-spacing of 46 cm. The individual plots were 2.7 by 7.3 m in area and treatments were replicated 4 times in a randomized complete block design.

All treatments were sown to barley (Hordeum vulgare cv. Leduc) at 100 kg ha^{-1}. There were 12 rows in each plot with 23-cm row spacing. The mature barley plants were harvested in September from 5-m long central rows. Samples were dried at 60°C, threshed and weighed. The grain and straw were analyzed for total N by a Kjeldahl method [2] or by Near Infrared Reflectance spectroscopy [9].

Daily precipitation at each site in both years was recorded. The soil and plant data were subjected to ANOVA. Data were not combined from the sites, nor were the mineral N values from different soil sampling times.

Experiment 1. Release of mineral N from fall-applied fertilizers

Mineral-N content of soil in fall-applied treatments was determined periodically from fall, 1989, to spring, 1990 (Table 4-2). Subsequently, barley was grown with determination of N-uptake in mature crop accompanied by a final soil sampling for mineral N. Fall-application treatments (No. 1-10) received 127 kg N ha^{-1} on 15 Oct., 1989, 24 Oct., 1989, and 10 Oct., 1989, at Sites 1, 2, and 3, respectively. The experiments were sown in 1990 on 2 June, 5 June and 20 May at Sites 1, 2, and 3, respectively, and in the same order they were harvested on 15, 10 and 26 September.

Soil sampling of the incorporation treatments was made using a 2-cm diameter coring tube when the soil was not frozen in the fall of 1989. Ten cores were taken from each plot and composited. When the soil was frozen, 2 blocks of soil (46 by 23 cm area and 15 cm deep) were taken from each plot using heavy chisels. In the spring of 1990, the banded treatments as well as the incorporation treatments were soil sampled. The bands had been marked during application the previous fall so that soil blocks could be placed exactly on the band. Both incorporation and banding treatments were sampled in fall of 1990 using the 2-cm diameter corer. Soil samples were thinly spread and dried at room temperature. Soil was crushed to pass a 2-mm sieve, and 20 g samples were extracted in 100 mL 2M KCl solution. The concentrations of NH_4-N and NO_3-N in the extract were determined with a Technicon Auto Analyzer II [14, 15]. Soil bulk density was determined at each site and mineral N was expressed as mass per area (kg ha^{-1}).

Results of mineral N in October and November, 1989, and soil samplings at Sites 1, 2 and 3 (Table 4-2) were converted to net % recovery for urea, thin-coated urea and thick-coated treatments (Table 4-3). Daily average soil temperature at the 5 cm depth was recorded at the Ellerslie Meteorological Station [1], that station being 200 m from Site 3. In addition, non-fertilized soil from Sites 2 and 3 received granules of urea, thin-coated urea and thick coated urea (200 mg N kg^{-1}) in the laboratory; soils were incubated (10°C; 0.10 kPa water content) for 15 and 30 d. Details of the incubation procedure are given in Chapter 3. The mineral-N results at 15 and 30 d (Table 4-3) were given as net % recovery of fertilizer-N.

Experiment 2. Crop yield and N uptake in 1990 and 1991

The 1990 crop received an unusually heavy application of N (127 kg ha^{-1}) , but the yield and N-uptake results are given for Site 1 (Table 4-4) because the crop showed visual N-stress differences among treatments. Rate of fertilizer N was decreased to 50 kg ha^{-1} for the next experimental year, October 1990 to September 1991. At Sites 2 and 3 the experiments were reset immediately adjacent to those in 1989 to 1990, but the experiment at Site 1 was not moved. Fall treatments (No. 1-10) received N on 24, 30 and 20 October, respectively for Sites 1, 2 and 3. Spring treatments (No. 10-20) received N on 5 June, 4 June, 31 May, respectively, for Sites 1, 2 and 3. The crop was sown during the first week of June and harvested in September.

Results

Experiment 1. Release of mineral N from fall-applied fertilizer

Total mineral N and nitrate-N from fall to spring

Incorporation treatments were sampled to follow the total mineral-N (NH_4^+ + NO_3^-) and NO_3-N content in soil during the fall to spring period (Table 4-2). The treatments with coated urea had less total mineral N and NO_3-N than with non-coated urea. Table 4-2 displayed gross values, but calculated net apparent values (after deduction of nil treatment) showed changes with time. At the October or November samplings, net release values of mineral N were far less for thin-coated urea, and especially thick-coated urea, than for non-coated urea. The thick-coated urea tended to retain its slow release effect even with the spring sampling. For example, the net mineral N values at spring sampling were 16, 25 and 36 kg N ha^{-1} less with thick-coated urea than with non-coated urea for Sites 1, 2 and 3, respectively.

Release of mineral N from coated urea continued in October and November although the soil was cold (at 5 cm depth 8°C on 10 October with a steady decrease to 1°C on 14 November). Nevertheless, % release of coated urea in the field during that cold period was much the same as the % release on incubation at 10°C in the laboratory for 15 or 30 d (Table 4-3). The substrate concentration used in the laboratory studies was 2.5 times greater than that used in the field, but presumably the concentration would not have an appreciable effect on percent N release, because urea release through the polymer coating was a physical and not biological process. Both field and laboratory results were obtained from Sites 2 and 3 but only field results were obtained from Site 1 (Table 4-3). Further, the timing of soil sampling in the field did not exactly match the timing of sampling during the incubation studies. Essentially, % release in the field was approximately as great as in the laboratory, even though the average soil temperatures were 5.7 to 2.3°C, and 39% of thick-coated urea was released after 42 or 43 d.

The nitrification of released mineral N lagged in the fall, but the proportion of NO_3-N found in the released mineral N did not differ with either urea, thin-coated urea or thick-coated urea (Table 4-2). Nitrate loss had occurred by the time of the February sampling at Site 1, and such loss in frozen soil has been found before [10]. Nitrate accumulation from net released mineral N increased at the 3 sites by April sampling, but the proportion of NO_3-N to mineral N was less from thick-coated urea as compared with uncoated urea. While the net NO_3-N found with uncoated urea treatment was 54, 74 and 76 kg N ha^{-1} at Sites 1, 2 and 3, respectively, the corresponding values for the thick-coated urea treatment were lower by 28, 31 and 25 kg N ha^{-1}.

Less NO_3-N was found in the spring in soil to which urea was banded-applied (treatment No. 3) than with incorporated urea (treatment No. 2) at Sites 2 and 3 (Table 4-2). The differences were 31 and 39 kg NO_3-N ha^{-1}, respectively. This difference between banding and incorporating urea was not observed at Site 1, apparently because of the NO_3-N loss during the winter in the incorporation as indicated by the February sampling. At the spring sampling, less of the total mineral N

Table 4-2. Mineral N in soil at Site 1,2 and 3 from Fall 1989 to Spring 1990 after fall application of N fertilizer (127 kg N ha^{-1}) on October 15, 1989, and the crop N plus soil mineral N in September 1990[+].

Treatment								Crop total N + mineral N in soil
Site	No.	Fertilizer	Placement	Mineral N (NO_3-N in brackets) as kg N ha^{-1}				as kg N ha^{-1}
				26/10/89	**26/11/89**	**28/02/90**	**04/05/90**	**Sept. 90**
1	1	None		15(9)	28(14)	22(1)	41(14)	47
	2	Urea	Incorp.[†]	109(29)	156(41)	133(5)	120(68)	84
	3	Urea	Band[‡]				197(74)	92
	4	Thin coat	Incorp.	68(25)	116(37)	104(8)	107(53)	71
	5	Thin coat	Band				176(82)	86
	6	Thick coat	Incorp.	32(15)	78(23)	72(5)	104(40)	81
	7	Thick coat	Band				172(58)	94
	9	GS	Band				96(29)	109
	LSD (0.05)			14(4)	37(20)	28(3)	47(21)	19
				06/11/89	**26/02/90**		**22/04/90**	**Sept. 90**
2	1	None		19(14)	37(25)		69(37)	91
	2	Urea	Incorp.[†]	81(49)	158(64)		150(111)	155
	3	Urea	Band[‡]				186(80)	152
	4	Thin coat	Incorp.	65(25)	130(42)		147(88)	157
	5	Thin coat	Band				180(84)	171
	6	Thick coat	Incorp.	49(32)	82(40)		125(81)	160
	7	Thick coat	Band				149(78)	170
	8	GS	incorp.	54(30)	62(28)		99(56)	181
	9	GS	Band				113(70)	224
	LSD (0.05)			20(8)	33(11)		46(19)	31
				28/10/89	**26/11/89**	**22/02/90**	**26/04/90**	**Sept. 90**
3	1	None		37(26)	50(34)	65(28)	96(62)	83
	2	Urea	Incorp.[†]	141(58)	198(73)	223(64)	255(133)	157
	3	Urea	Band[‡]				228(94)	168
	4	Thin coat	Incorp.	96(44)	153(53)	§	209(106)	149
	5	Thin coat	Band				215(95)	151
	6	Thick coat	Incorp.	71(39)	105(46)	160(39)	219(108)	155
	7	Thick coat	Band				187(87)	163
	8	GS	Incorp.	74(45)	101(54)	98(38)	154(93)	154
	9	GS	Band				147(89)	173
	LSD (0.05)			65(5)	37(12)	57(22)	53(19)	16

[+] Soil sampling depth was 0 to 60 cm in spring and at harvest, but previous samplings were 0 to 5 cm deep

[†] Incorporation to a depth of 12 cm; [‡] Placement in narrow band at 10 to 12 cm deep; § Missing

Table 4-3. Net release of mineral N from field-applied urea and coated urea in Fall 1989 and from laboratory incubation at 10°C of the same materials.

		Days	Soil tem+	Net release (%) of mineral N from application[§]			
Site	Condition		°C	Urea	Thin Coat	Thick Coat	LSD (0.05)
2	Laboratory[†]	15	10.0	63	41	20	9
	Field(24/10 to 6/11)	13	3.8	47	36	24	11
3	Laboratory[†]	15	10.8	68	63	13	21
	Field(10/10 to 28/10)	18	5.7	75	42	24	12
	Laboratory[†]	30	10.0	93	76	37	19
	Field(10/10 to 22/11)	43	3.2	106	74	39	30
1[‡]	Field(15/10 to 26/10)	11	5.4	74	42	14	14
	Field(15/10 to 26/11)	42	2.3	99	70	39	26

[†] Soils used for laboratory experiment were taken from Sites 2 and 3.

[‡] Site 1 soil was not used in the laboratory.

[§] Application was 200 mg N kg^{-1} in laboratory and 127 kg N ha^{-1} in the field.

was found as NO_3-N from banded rather than incorporated urea. This trend was observed at all sites regardless of whether the urea was coated, but the banding effect was greater with uncoated urea.

Mineral N and crop N uptake from spring to fall

At Site 1, from either coated or uncoated urea the mineral-N release during the spring was notably greater in the band treatments than in the incorporation treatments (Table 4-2). The same trend was observed at Site 2, but not at Site 3. Because banding may slow nitrification [8], more rapid nitrification and loss of NO_3-N from incorporated urea may have had occurred at Site 1 during the winter.

Total N in the grain and straw + soil mineral N (0- to 60-cm depth) at crop harvest during September 1990 at Site 1 showed recovery of less than one-half of the 127 kg N ha^{-1} application made in October 1989. The recoveries were greater at Site 2 and at Site 3, but fell well short of the 127 kg N ha^{-1} application with the exception of the banded GS treatment. Most of the N recovered was found in the grain and straw rather than as soil mineral N.

The net N recoveries of the fall-applied fertilizers found at the late April sampling are depicted in Fig. 4-1, as well as the net fertilizer N in crop at harvest plus apparent residual fertilizer N found in the soil as mineral N after harvest. Recovery of mineral N in spring was greater than the net crop N uptake plus residual N for the urea and coated urea treatments; GS followed the opposite pattern. The superiority of banding instead of incorporation at Site 1 coincided with the low recovery of fall application and heavy rainfall in June and July (precipitation totalled 284 mm during these two months). Fall-applied, banded GS produced the least amount of mineral N in the subsequent spring, but at all three sites, the greatest recoveries of N were obtained from banded GS applied a year before. Guanidine sulfate, especially when banded, has recently been found to be a slow-release material in the laboratory [16].

Experiment 2. Crop yield and N uptake in 1990 and 1991

Grain yields in 1990, from N applications in the fall of 1989, did not differ significantly among the fertilizer treatments at Site 1 (Table 4-4). However, the banding effect was significant ($p = 0.05$) for total N uptake in grain + straw. Total N uptake in grain and straw from GS and point-injected urea tended to be only slightly

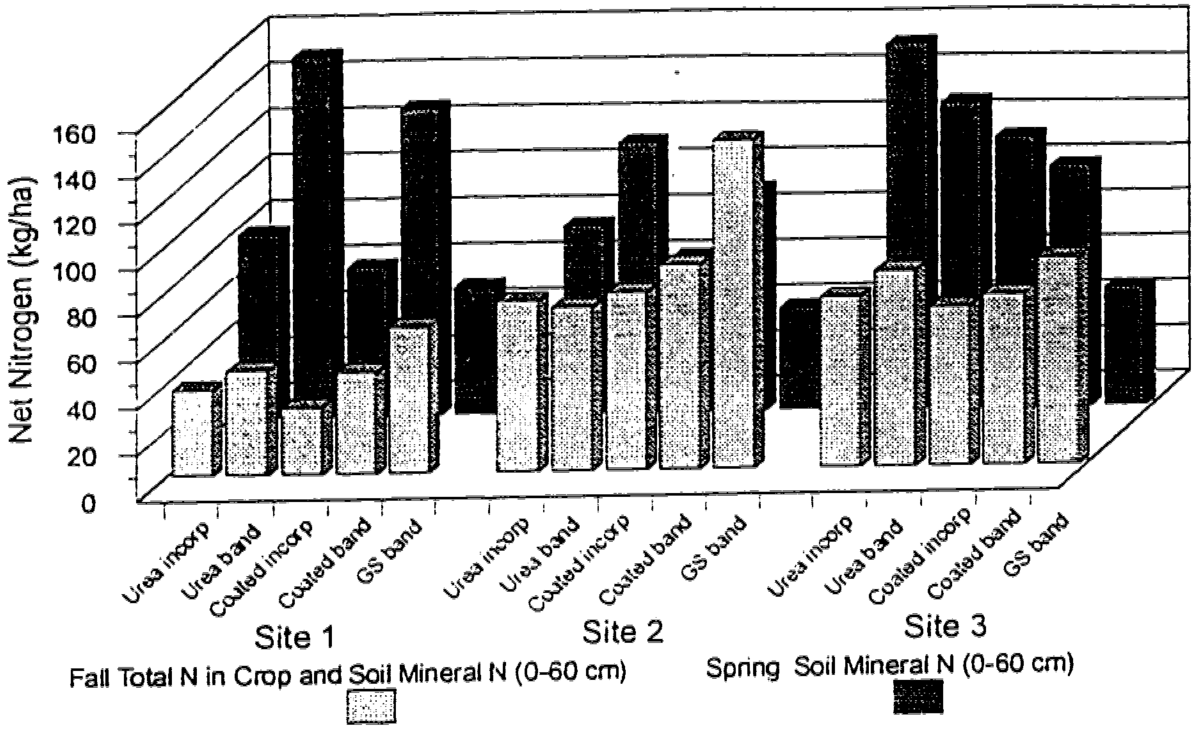

Fig.4-1 Net recovery of fall (September) applied fertilizer N at 3 sites in 1990.

greater than with banding. Spring application (treatments 12 to 20) showed a different pattern. The total N uptake of grain + straw was less for incorporated urea (and banded GS) than for the remaining fertilizer treatments. This 1990 experiment received 127 kg N ha^{-1}, a rate usually high enough in the Prairie Provinces to mask differences of yield and N uptake among treatments. However, Site 1 had unusually large N denitrification losses to explain the differences among our treatments.

In 1991 the rate of N was 50 kg N ha^{-1}. Even so, Sites 2 and 3 were low-responsive to applied N in 1991. Data for these sites, therefore, are not presented. However, Site 1 was markedly N responsive (Table 4-5). The yield and N-uptake from fall applications were greater with banding than with incorporation and GS generally had values similar to the other banded treatments. The point injection treatment was one of the higher in yield and N uptake. Heavy precipitation in early April accompanied by soil saturation at Site 1 suggests the occurrence of denitrification and the tendency for benefit from fall banding, polymer-coated granules, GS, or point injection.

Heavy rainfall in May and June (240 mm) laid the pattern of N uptake for spring treatments (treatments No. 12 to 20). The urea incorporation treatment resulted in the least N uptake, but banding increased N uptake as did incorporation of coated urea. The point injection treatment tended to have the greatest N uptake value. Less N was taken up from GS than from the other materials which were band-application.

Discussion

Mineralization and accumulation of NO_3-N was markedly slower for fall-applied polymer-coated urea. During periods in October and into November, the N release rate from coated urea in the field was similar to that obtained during laboratory incubation (10°C), even though mean daily soil temperatures in the field ranged from 1 to 8°C. Thick-coated urea when compared to non-coated urea produced 24% less net mineral-N and 42% less net NO_3-N, about 6 or 6.5 months (4 with frozen soil) after the October application. Considering the greater effectiveness of thick-coated urea (15 μm coat) compared to thin-coated urea (9 μm coat), a further increase in coating thickness probably would reduce NO_3-N accumulation.

As with incorporation, the banding of thick-coated urea tended to result less mineral N than banding of non-coated urea. Banding, either non-coated urea or coated urea resulted in accumulation of far more mineral-N than incorporation of these

Table 4-4. Yield and N uptake, September 1990, at Site 1 after fertilizer N application (127 kg N ha^{-1}) made October 15, 1989, or May 24, 1990.

Treatment				Yield		N uptake	
No.	Fertilizer	Time	Placement	Grain	Grain + straw	Grain	Grain + straw
				-- t ha^{-1} --		-- kg N ha^{-1} --	
1	None			2.12	4.19	30.3	39.7
2	Urea	Fall	Incorp.‡	3.54	6.90	60.3	77.4
3	Urea	Fall	Band§	3.81	7.27	66.1	86.4
4	Thin coat	Fall	Incorp.	3.42	6.79	51.0	65.9
5	Thin coat	Fall	Band	3.28	7.34	55.0	80.6
6	Thick coat	Fall	Incorp.	3.70	7.24	58.4	74.9
7	Thick coat	Fall	Band	3.58	7.49	63.3	87.8
9†	GS	Fall	Band	3.50	7.06	64.9	91.6
10	Urea	1/2 Fall, 1/2 in crop	Point	3.40	6.96	66.2	88.9
11	None			2.24	4.63	34.2	43.9
12	Urea	Spring	Incorp.	3.66	7.29	63.2	82.2
13	Urea	Spring	Band	3.67	7.34	73.6	100.8
14	Thin coat	Spring	Incorp.	4.32	8.11	78.9	100.5
15	Thin coat	Spring	Band	3.33	7.08	69.1	99.4
16	Thick coat	Spring	Incorp.	3.62	7.43	71.5	100.6
17	Thick coat	Spring	Band	3.39	7.22	71.4	100.9
19	GS	Spring	Band	2.52	5.27	53.4	76.7
20†	Urea	1/2 Spring, 1/2 in crop	Point	3.50	7.08	74.1	101.0
LSD (0.05)				0.78	1.25	15.8	18.7

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† Urea solution injected at points.

‡ Incorporation to a depth of 12 cm.

§ Placement in narrow bands at 10 to 12 cm deep.

Table 4-5. Yield and N uptake, September 1991, at Site 1 after fertilizer N application (50 kg N ha^{-1}) made October 24, 1990, or June 5, 1991.

Treatment				Yield		N uptake	
No.	Fertilizer	Time	Placement	Grain	Grain + straw	Grain	Grain + straw
				- - t ha^{-1}	- - -	- - kg N ha^{-1}	- -
1	None			1.49	3.17	25.7	43.2
2	Urea	Fall	Incorp.‡	1.79	3.95	28.8	48.7
3	Urea	Fall	Band§	1.97	4.31	30.2	54.5
4	Thin coat	Fall	Incorp.	1.67	3.59	26.8	47.7
5	Thin coat	Fall	Band	2.45	5.41	39.8	70.1
6	Thick coat	Fall	Incorp.	1.79	3.61	31.0	51.0
7	Thick coat	Fall	Band	2.05	4.40	34.3	60.3
9†	GS	Fall	Band	2.09	4.58	34.2	62.2
10	Urea	1/2 Fall, 1/2 in crop	Point	2.25	4.71	38.2	67.6
11	None			1.48	3.11	24.3	40.9
12	Urea	Spring	Incorp.	2.15	4.47	33.7	55.5
13	Urea	Spring	Band	2.80	5.94	46.9	80.8
14	Thin coat	Spring	Incorp.	2.39	5.43	36.6	67.1
15	Thin coat	Spring	Band	2.28	5.45	39.6	76.7
16	Thick coat	Spring	Incorp.	2.94	5.95	49.1	79.0
17	Thick coat	Spring	Band	2.43	5.45	42.7	82.8
19	GS	Spring	Band	2.35	4.97	40.4	72.3
20†	Urea	1/2 Spring, 1/2 in crop	Point	2.69	5.52	47.6	85.9
LSD (0.05)				0.48	0.89	7.9	12.1

† Dry urea nest in Fall, urea solution injected at points in the crop.

‡ Incorporation to a depth of 12 cm.

§ Placement in narrow bands at 10 to 12 cm deep.

materials at 2 sites. In other research, applying fall-applied fertilizer in constricted bands or nests had conserved mineral-N at spring [7] and reduced denitrification or immobilization [4].

The amount of net recovery of mineral-N at the spring sampling was greater than crop N-uptake + soil mineral-N at harvest. The exception was fall-applied, banded GS mixture, with little mineral N in spring but greatest N-uptake + mineral N at harvest. The banded GS mixture apparently fitted a 1-yr long pattern of release. Spring application of banded GS was too late because N recovery from this treatment was less than that from banded urea. Guanidine sulfate mineralizes N more quickly when incorporated into soil rather than when placed in constricted bands in the laboratory [16].

In Experiment 1 we applied a heavy rate of N (127 kg N ha^{-1}) for dryland cropping in the Prairie Provinces, and a typical rate (50 kg N ha^{-1}) was applied in the second year. Even so, a clear N fertilizer response was obtained both years at Site 1. The patterns of crop response differed with fall-and spring-application. With one exception, the crop N uptake response from fall application was due to banding, and not coating. With spring application, crop N uptake response was to banding or to coating. In other work, fall applications have been improved by banding [7], banding with nitrification inhibitors [6a, 7], and more still by nesting [7, 12]. The efficiency of spring-applied fertilizer N has been improved less by these techniques [7], depending on the occurrence of intense rainfall early in the growing season [10]. Nevertheless, the present results indicated that the polymer-coated urea applied in spring increased crop N uptake and, since fall-applied coated urea showed a slowed release of mineral-N during the winter, an increase in thickness of coat would delay release until needed by the spring sown crop.

In conclusion, the polymer-coating of fall-applied urea resulted in decreased accumulation of NO_3-N by late winter or spring, and coated urea applied in spring tended to increase crop N uptake. Placement of fertilizer N in narrow bands seemed a more powerful technique, as did point injection of urea or use of GS. Polymer coating, point injection, and GS can now be added to the list of techniques for decreasing NO_3-N accumulation and decreasing N loss from fertilizers; it is now a matter of refinement in the use of these techniques separately or in combination.

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Chapter 5. Delayed release of polymer-coated urea in soil: the existence of a boundary layer at the coat surface

Introduction

Coating fertilizers with polymeric membranes is an effective approach to control the release rate of conventional fertilizers [6, 10]. Incubating coated N fertilizers in soil at different temperature and water potentials indicated that water content of a soil (50 to 100% field capacity) had little effect on the release rate [8, 10]. Hauck [6] hypothesized that water vapor moves into the coating and then dissolves the nutrients held inside the coated granule, and when the osmotic pressure is established, nutrients begin to diffuse. Gambash *et al.*[5] suggested that vapor diffusion in soil was a rate-limiting step for nutrient release. Since vapor pressure changes little from 0 to -10 MPa [7], the effect of soil water on the release rate of nutrients was minimal.

Release rate of encapsulated drugs somehow was faster in *vitro* than in *vivo*. Baker and Lansdale [1] attributed the difference to the existence of a boundary layer around the outer surface of the membrane. A theoretical approach was used by Burnette [2] to analyze mass transport across the boundary layer. The thickness of boundary layers and their impact on the release rate of an encapsulated bioactive agent were studied mathematically. However, the boundary layer on coated fertilizer granules in soil has not been reported.

Chapter 2 reported a new approach to determine the membrane permeability of coated urea in running water, where urea concentration in the outer surface of the granule was negligible. The same product was also incubated in soils with different water contents and temperature (Chapter 3). Even though water content had little effect on the release rate of urea, the life span of two coated products lasted as long as 60 d, depending on coating thickness and temperature.

Hauck [6] proposed that water moving into the coat was in vapor form. If the medium of diffusion for a dissolved nutrient is liquid water, one question remained with Hauck's hypothesis; namely, whether water vapor still passes through a membrane when the its pores are filled with water and dissolved nutrients. In Chapter 3, a two-step release model was made to complement Hauck's proposition, *i.e.* when a dry-coated urea granule is placed in soil of 100% relative humility, water vapor begins to penetrate the coating and condenses on the surface of the encapsulated urea. Urea dissolves as it makes contact with the water. Water vapor continuously moves through the coat, but has no chance to make direct contact with the solid phase, condensing at the solution-air interface. Consequently, urea concentration is lower in the solution-air interface than the solution-solid interface, and so urea diffuses within the solution. As these processes continue, the frontier of the liquid phase progressively moves outward through the pores of the coat, but stops when its vapor pressure equals that of the surrounding medium. Consequently, a thin liquid film is formed around the coated granule. This liquid film acts as an exchange medium upon which water vapor is converted into liquid, diffusing back into the inside of the coat by the pores to further dissolve urea; simultaneously or intermittently (depending on uniformity of coat) the urea diffuses out of the coating. Urea diffused to the coat surface is subject to hydrolysis. The basis of the model would be the existence of a thin water film around the coated granule. The objective of this study was to test the existence of the film.

Hypothesis

If a thin film existed around the coated granule in soil, and if urea concentration within the film was much greater than the K_m of urease, then trace amounts of urea would be detected in soil incubated with coated urea. Consequently, urea release rate would be slower in soil than in a system where water flowed around the coated particles to remove urea at the outer surface of coating, because the urea concentration at the outer surface of the coating is not negligible (*i.e.* is not being continually removed) in incubated soil.

Test of the hypothesis

Outlines of Chapter 2 and 3

As discussed in Chapter 2, coated urea was exposed to flowing water at 12 and 31°C , therefore, there was no urea accumulation on the outer surface of the membrane. A maximum flux was obtained. The permeability (P) at each temperature was calculated by

$$J_{\max} = \frac{-P(C2 - C1)}{L}$$

where J_{max} is the flux , and C_1 and C_2 are urea concentration at the inner and outer surface of the coating, respectively. In the experiment, C_1 is the urea concentration in saturation at a given temperature, and C_2 is zero. L is the thickness of the coating, determined by a scanning electron microscope. The activation energy of the permeability was calculated by an Arhennius-type equation [11], which can be used to calculate any permeability within a given temperature range. The maximum flux is thereafter calculated. In the study, maximum flux of urea was calculated at 10 and 23°C.

As reported in Chapter 3, coated urea was incubated together with non-coated urea in two soils of different texture. The incubation was conducted at two soil temperatures (10 and 23°C) and two soil water potentials (-0.10 and -0.29 MPa). Soil mineral N (NH_4^+ + NO_3^-) was extracted at 15, 30 or 60 d of incubation. The experimental results indicated that temperature had a significant influence on urea release rate. Soil water content and soil texture only have limited effects on the release rate of urea. In addition to determining the mineral N in soil, urea was also extracted from soil after 15 d of incubation, using KCl-Phenylmercury solution; urea was determined by a colorimetric method [4]. Results of this determination are given below. As indicated earlies, the amount of mineral N released at 15, 30 or 60 d was calculated as urea flux in soil (mg urea m^{-2} s^{-1}).

Evidence

Urea hydrolysis in soil is a rapid process, and its rate can be as high as 95 ug urea hydrolyzed g^{-1} soil h^{-1}[12]. The average concentration of urea found in the two soils varied from 0.9 to 10.2 mg kg^{-1} soil considering all treatments and ranges of soil temperature and water content (Table 5-1). Compared with the amount of mineral-N extracted at the same time, the quantity of urea present in soil was trivial (Fig.5-1). However, this provided evidence of a small portion of urea in soil which was not hydrolyzed. The hydrolysis of urea follows the Mechaelis-Menten equation [9]. As the enzyme becomes saturated at higher substrate concentration, the reaction rate is

Table 5-1 Urea concentration in soil after urea and coated urea incubated for 15 days

	10°C		23°C	
	-0.29 MPa	-0.10 MPa	-0.29 MPa	-0.10 MPa
	······················mg urea kg^{-1} soil························			
<u>Soil 2</u>				
Urea	3.1±0.2	3.9±0.2	0.9±0.7	1.3±0.8
Thin coating	6.9±1.5	4.4±0.6	8.4±5.9	3.8±2.9
Thick coating	5.9±0.2	3.8±1.1	5.2±0.2	4.1±1.5
<u>Soil 3</u>				
Urea	3.1±0.1	2.4±0.6	2.1±1.1	1.2±0.1
Thin coating	7.8±3.1	8.3±1.4	10.2±4.8	7.1±2.6
Thick coating	4.7±3.5	4.6±1.3	7.3±3.0	6.5±5.7

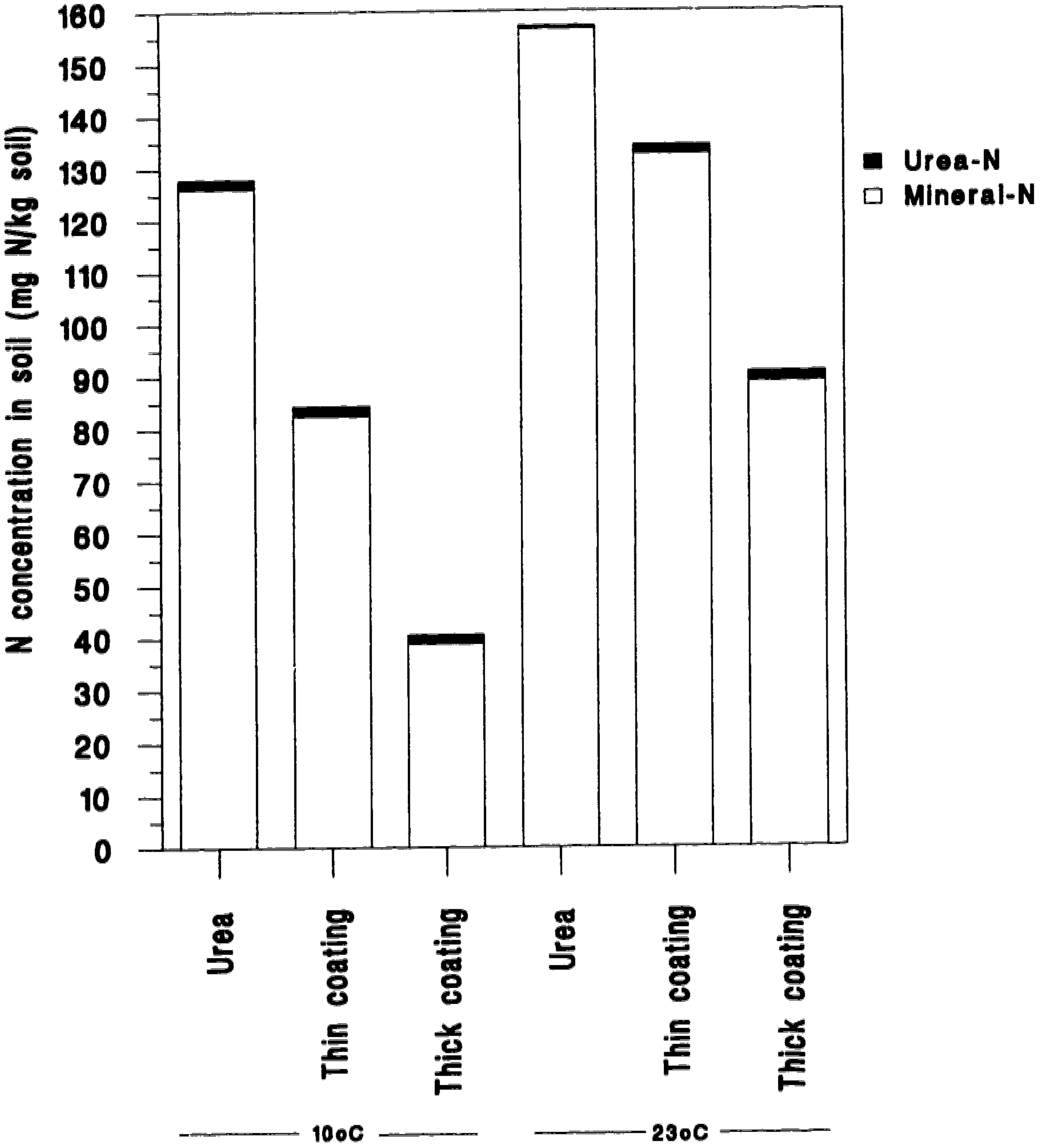

Fig.5-1 Comparison of mineral N released from fertilizers with N extracted as urea.

thereafter restrained by concentration of the enzyme. For a granule 2.5 mm in diameter, the maximum contact area in relation to soil is 19.6 mm^2. In this confined zone, urease concentration is limited and ready to be saturated by urea diffused out of the membrane. In addition, high ionic strength caused by urea in this zone could also inhibit the activity of urease. Deductively, this extracted urea possibly originated from the adjacent area of the outer surface of the membrane. The existence of urea in soil indicated that urea concentration in soil, more precisely at the outer surface of the membrane, was not zero.

In the experiment with running water, we reduced urea concentration at the outer surface of the membrane to zero. The average time required for 100% release was 1.9 and 4.2 days for the materials with thin and thick coatings, respectively. However, when the same products were incubated in soil, the time needed for 100% release was more than 30 days, regardless of coating thickness. If, as was assumed by Christianson [3], urea diffusing out of the membrane was instantaneously hydrolyzed or removed, the time required for 100% release in soil should be the same as that in running water because urea concentration at the outer surface of the coating was zero. But in our comparison, urea release rate in soil was much slower than that in the flowing water (Table 5-2). Clearly, this demonstrated that in addition to the

Table 5-2 Flux in soil and water

Coated Fertilizers	Temperature	Water	Soil		
			15d	30d	60d
	°C	mg m^{-2} s^{-1}			
Thin coating	10	1.54	0.24	0.18	0.11
	23	3.11	0.34	0.20	0.12
Thick coating	10	0.81	0.10	0.10	0.09
	23	1.85	0.21	0.16	0.11

restriction of diffusion by the membrane, there was another factor constraining urea diffusion, *i.e.* the thin film around the outer surface of a coated granule. Commonly, this film is termed the boundary layer. The high disagreement of release rates of encapsulated pharmaceuticals between *vivo* and *vitro* was caused by this boundary layer [1].

The boundary layer and urea release rate: Soil Retardation Factor

An equation (Eq.(2)) was proposed to assess the effect of the boundary layer on the release rate [1]. In Eq.(2), J_t is flux in unstirred elusion media, J_{max} is the maximum flux attained in a stirred elution media, D is the diffusion coefficient of an active agent in the boundary layer, λ is the thickness of the boundary layer, and C_s is the concentration of active agent in saturation.

$$\frac{J_t}{J_{max}} = \frac{1}{1+\frac{\lambda J_{max}}{DC_s}} \qquad (2)$$

To predict the flux of an active agent with the existence of a boundary layer, one has to calculate the thickness of the boundary layer, and a diffusivity, D, in water of 2×10^{-6} cm^2 s^{-1}, is assumed. In this study, it was assumed that the boundary layer was thin enough so that the influence of soil porosity and tortuosity on diffusivity of urea in the boundary layer can be neglected. Stokes-Einstein's equation was used to calculate diffusivity of urea in water (1.7×10^{-5} cm^2 s^{-1}) [2], and thickness of the boundary layer was calculated by using urea flux in running water (J_{max}) and in soil (J_t). The thickness of the calculated boundary layer at 23^{o}C varied from 6.71 to 11.29 m. Obviously this was quite unrealistic in soil, which implied that there was a 6.71 or 11.29 m water-saturated zone around granule. If the influence of soil porosity and tortuosity on urea diffusivity in the boundary layer was considered, the calculated boundary layer thickness from Eq.(2) ranged from 4.7 to 8.0 cm, which was still considerably thicker. The value for the boundary layer (i.e. thick layer) resulted from use of diffusion coefficients for urea movement through the membrane and within the boundary layer that differed by a factor 10^2 to 10^5. One possibility was that we overestimated diffusivity of urea by using Stokes-Einstein's equation. The urea molecule has a platy structure, while the Stokes-Einstein equation is valid for use with spherical particles. Using the equation to calculate diffusivity of non-spherical molecules may result in an error as high as 120% [2]. The other possibility was that electro-static charges existed at the surface of the membrane. Urea is a polar molecule; the surface charge imposed an attractive force to resist urea diffusion. Under these circumstances, diffusivity of urea at the surface should not be as same as that in free water.

Instead of obtaining the urea diffusivity through a more sophisticated determination, we introduced a new parameter, S_b, Soil Retardation Factor, into Eq.(2) to modify J_t as follows:

$$J_t = J_{max} S_b \qquad (3)$$

S_b was calculated from the ratio of J_t/J_{max} . In Chapter 2, maximum flux was determined in running water; increasing coating thickness slowed down urea flux (Table 5-2). In Chapter 3, two coated urea fertilizers were incubated in two soils with different soil temperature and water contents. The urea flux was related to coating thickness and soil temperature, but not soil water content and texture. Therefore, the mean release rate of urea at different times and temperatures were tabulated (Table 5-2). Steady flux was found with the thick coating, and was more prominent at the lower temperature. Combining results presented in Chapters 2 and 3, the ratio of J_t/J_{max} was derived (Table 5-3). Even though the flux obtained under different conditions varied dramatically, S_b was rather similar at a given sampling time. As we have discussed before, the slower release rate of urea in soil was caused by the existence of a boundary layer around the granule. The thickness of the layer somehow

Table 5-3 Soil retardation factor

Coated Fertilizers	Temperature °C	S_b 15d	30d	60d	Average
Thin coating	10	0.16	0.12	0.07	0.12
	23	0.11	0.06	0.04	0.07
Thick coating	10	0.12	0.12	0.11	0.12
	23	0.11	0.09	0.06	0.09
Average		0.13	0.10	0.07	0.10

was related to the affinity of the membrane to water. Thickness of boundary layer should not be related to coating thickness. In Chapter 2, a fast release rate of urea was reported for the two products used during the first hour of exposure to running water. A similar phenomenon was found in soil. Since J_{max} was a constant, values of S_b reflected the changes of urea flux in soil. S_b was found higher in the first 15 d, and then declined in 30 and 60 d. This effect was found to be more pronouned in the thin coatings (Table 5-3). To avoid the burst effect at the beginning, we arbitrarily chose an average S_b in 30 d: 0.1. Therefore, urea release rate can be predicted by

$$J_t = 0.1 \times J_{max} \qquad (3a)$$

J_{max} is a function of urea concentration. It should remain constant as long as there is solid urea inside the coating. After depletion of solid urea, urea concentration declines. J_{max}, thereby, decreases.

Conclusions

Evidence is given to support the existence of a boundary layer, the basis of the proposed two-step release model. Existence of a boundary layer around a granule in a static system is an important factor in the estimation of nutrient release in soil from coated fertilizers. The newly introduced S_b, Soil Retardation Factor, provides a refinement to the existing model estimating.

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Chapter 6. Predicting urea release rate from membrane encapsulated urea

Introduction

Simulation of controlled release bioactive agents has been developed through a variety of approaches. With controlled-release pharmaceuticals, Higuchi [3] made a pseudo-steady state assumption in predicting release rate of a drug across a membrane, *i.e.* the rate of mass transfer through the membrane remains constant while the rate of disappearance of the agent in the core zone is in a transient state. This assumption was widely used in simulating drug release rate [5]. Fan *et al.* [2], Tojo and Fan [7], and Tojo and Miyanami [8] used a different approach to derive a model in which the release rate of an encapsulated agent could be changed as a function of temperature, decay rate, and dispersion of a coated agent in the core zone. Nitrogen release rate of sulfur-coated urea was predicted at two temperatures by this model, but the authors did not indicate how to obtain the parameters listed in the model. Lu and Lee [4] developed a model based on constant core concentration-variable extraction medium concentration and variable core concentration-variable extraction medium concentration. They used this model to compare analytical data with the experimental results obtained with latex-coated urea. The diffusivity used in their model was calculated from the experimental data determined in continously stirred water, and the simulation results were compared with the cumulative urea release from the experiment.

The release rate of an encapsulated agent ingested by a human somehow is slower than in stirred water because of the existence of a boundary layer on the coating surface [1]. But the effect of this layer on the release rate of coated fertilizer in water or soil has not been reported. The present research used the equation proposed in Chapter 5 to predict N release of membrane-encapsulated urea in soil. The precision of the model was tested under non-isothermal conditions.

Analysis

When a membrane-encapsulated urea granule is placed into soil, water vapor penetrates the coating and dissolves urea. Urea diffusion occurrs, and consequently a boundary layer is established around the granule (Chapter 5). The unknown thickness of the boundary is indicated by x (Fig.6-1), and its effect is represented by S_b, the Soil Retardation Factor. It is assumed that urea diffused out of the boundary layer is completely hydrolyzed, its concentration reducing to zero, $C = 0$. The diameter of a polymer-coated urea ball and urea granule are a and b, respectively. The thickness of coating is a-b. Urea is highly soluble in water, hence it is assumed that the urea concentration in the core zone is in saturation (C_s) as long as the solid urea exists. The time required for depleting solid urea is defined as t_{sat}. When $t > t_{sat}$, urea concentration in the core zone varies with time. Because the difference in release rate between transient and steady stage is only 0.03 (Chapter 5), only two release stages were simulated, *i.e.* a linear release stage as long as the solid urea existed in the core zone, and a declining release stage as the solid urea is depleted in the core zone.

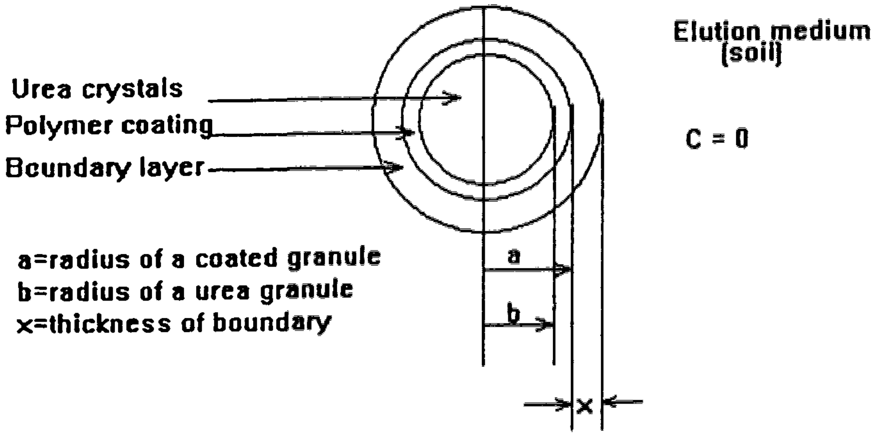

Fig.6-1 The schematic of coated urea applied in soil with coating thickness of a-b and boundary layer thickness, x.

The governing equation for simulation was

$$J_t = S_b J_{\max} \qquad (1)$$

where, J_t is urea flux in soil, mg m^{-2} s^{-1}; J_{max} is urea flux in running water, mg m^{-2} s^{-1}, which is the maximum flux of urea across the membrane; S_b is the Soil Retardation Factor, dimensionless. Considering the cumulative release of urea , Eq.(1) can be written as

$$M_t = tJ_{\max} S_b \qquad (2)$$

where Mt is the total amount of urea released in time t. J_{max} is calculated by

$$J_{\max} = -\frac{PC_s}{a-b}$$

P is the permeability of a membrane, m^2 s^{-1}; C_s is urea concentration at saturation, Mg m^{-3}; a-b (total diameter minus core diameter of coated particle) is the thickness of the membrane, m. Urea concentration before and after solid urea is depleted in the core zone is

$t < t_{sat}$ $\qquad C = C_s$

$t > t_{sat}$ $\qquad C = C_i$

C_i is the concentration at a given time after solid urea is depleted in the core zone.

Methods of computation

1. Saturated urea concentration is varied with temperature and calculated from the regression equation, $y = 65.08 \times 10^{0.101x}$ (r^2=0.996), based on the data reported by Pratt [6], where y is the solubility of urea (urea g/100 g H_2O) and x is temperature. The data was limited to temperatures above 0^oC; any urea concentration below zero was an extrapolation from the above equation. When $t > t_{sat}$, urea concentration was calculated by $\frac{W_0 - W_i}{V}$, where W_o was the initial mass of a granule, W_i was the

amount of mass released at time *i*, and V was the volume of the core zone. Since the coating was very thin, the volume of a coated granule was used as that of the core zone.

2. The average diameter of the coated urea was 2.5 mm; the surface area and volume were 19.6 mm^2 and 8.18 mm^3, respectively. Mass per 100 granules for thin or thick coatings was 1.31 and 1.34 g, respectively.

3. Thickness of coating was 8.7×10^{-6} m and 14.6×10^{-6} m for thin and thick coating, respectively (Chapter 2).

4. Time step for simulation was 24 hours.

5. Permeability at 31°C was $3.5\pm1.5\times10^{-14}$ m^2 s^{-1}. Permeability at a given temperature was calculated from $\frac{Ln\ P_2}{Ln\ P_1} = \frac{Ea}{R}(\frac{T_2 - T_1}{T_1 T_2})$, where P_2 and P_1 are permeabilities at temperature T_1 and T_2, respectively. E_a is activation energy, 350 kJ mol^{-1}, and R is the universal gas constant, 8.314 J mol^{-1} K^{-1}.

6. $t < t_{sat}$, urea concentration was C_s, and J_{max} was constant, $t > t_{sat}$, J_{max} was a function of urea concentration. Urea concentration was calculated based on the amount of urea left divided by the volume of the granule after each time step of simulation.

7. All computations were made using the Microsoft Excel for Windows, V3.0a.

8. S_b was 0.1 .

Results and discussion

The cumulative urea release over time showed two stages, linear release as $t < t_{sat}$, resulting from constant flux and a curvature release when $t > t_{sat}$ (Fig. 6-2). The increment of cumulative urea release was proportional to time. After the time reached

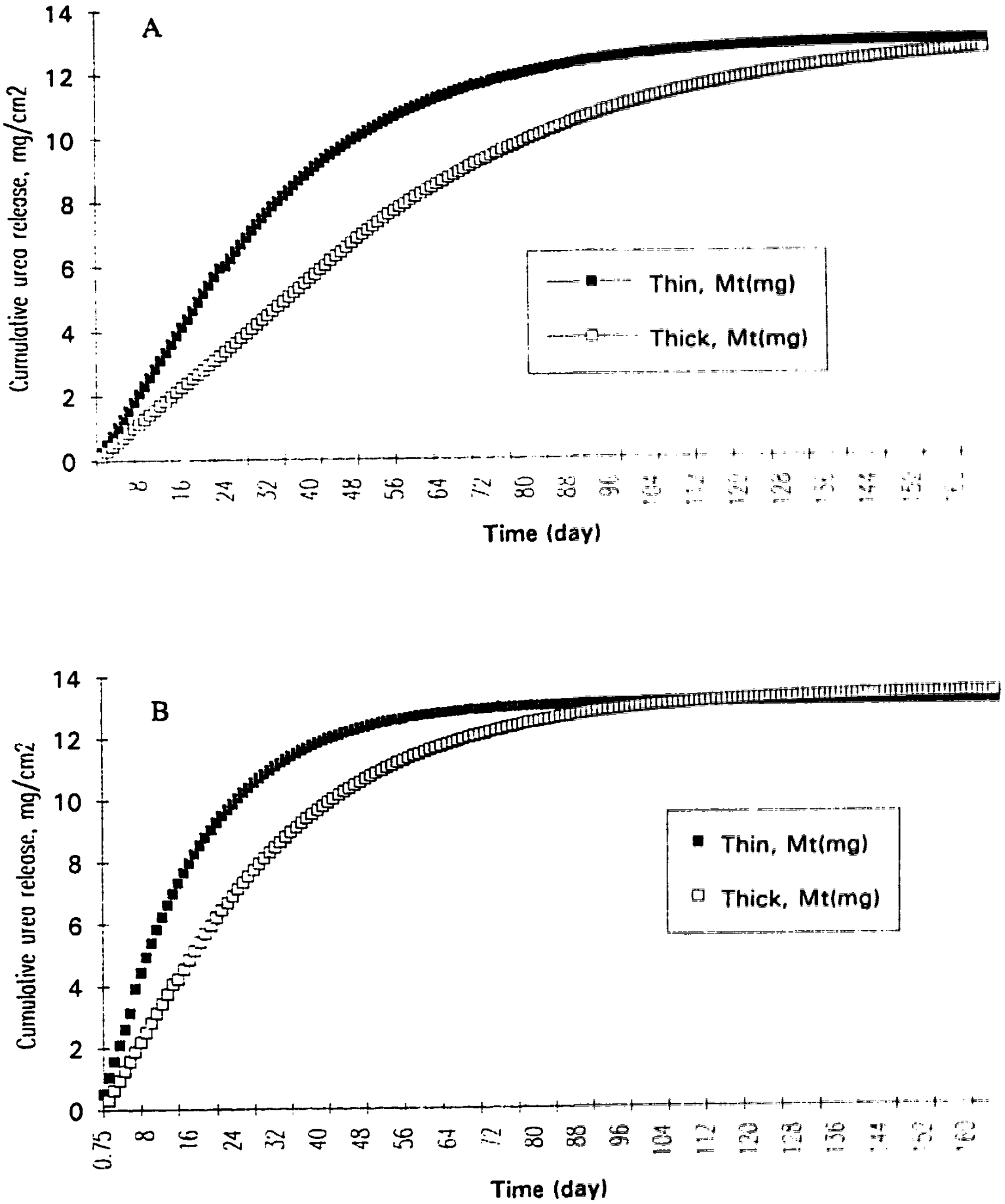

Fig.6-2 Predicted urea release at a constant temperature, A, 10°C and B, 23°C.

t_{sat}, linear release changed to a curvature release. In this stage, the cumulative release slowed and gradually leveled. This decrease in urea release at each time interval was caused by a declining urea concentration in the core zone. Lu and Lee [4] described a similar release pattern for latex-coated urea. But when $t > t_{sat}$, they used an exponential function.

The number of days required to reach the t_{sat} varied with temperature and coating thickness (Table 6-1). For the same temperature, the thick coating had a greater t_{sat} than the thin one. Also, a lower temperature resulted in a longer t_{sat} as compared with high temperature for the same coating. Urea release rate, in fact, dictated t_{sat}. The higher the release rate, the shorter the t_{sat}. The higher temperature and thinner coating resulted in a faster release rate, therefore, a shorter t_{sat}. Even with the same temperature and thickness of coating, as the elution medium changed, the release rate was proportionally only 10% in soil to that in dynamic water. As a result, the t_{sat} in soil was 10 times higher than that in the water.

Table 6-1 Comparison of t_{sat} in water and soil

	Soil		Water	
Temperature	Thin coating	Thick coating	Thin coating	Thick coating
°C	………………	……………… h	………………	………………
10	558	1080	55	108
23	180	325	18	32

Both urea solubility and membrane permeability were affected by temperature (Chapter 2). To evaluate sensitivity of these two parameters to temperature, *i.e.* which of the two parameters contributed more to flux as a result of temperature change, we kept one of the parameters constant and calculated urea flux change as affected by temperature. When permeability changed alone from 31°C to 10°C, flux decreased from 5.43 to 2.16 mg m^{-2} s^{-1} for thin coating: a 60% decrease. For the same coating and temperature range, when urea solubility alone changed, urea flux dropped from 5.43 to 3.47 mg m^{-2} s^{-1}, a 36% decrease in flux. The same percentage decrease resulted from the sensitivity analysis for the thick coating. The analysis clearly indicated that as temperature varied, change in permeability contributed more to flux change.

The cumulative N release predicted by Eq.(1) was contrasted with the actual amount of N released in an experiment with thin- and thick-coated urea incubated in soil. The mineral N was extracted from soil at 15, 30 or 60 days (Chapter 3). The mean amount of urea released from soil during 15, 30 and 60 days of incubation (two soils and two soil water contents) was 67% of that predicted by the simulation model (Table 6-2). Simulated data also were compared with results of the field experiments, where two coated ureas were incorporated in the three Alberta soils in fall of 1989, with soil samples being taken in October, November, December, February and April (Chapter 4). It was found that 52% of the predicted N release matched that actually found in the field soils (Table 6-3). The percentage match varied with location. At Site 3, where the temperature was recorded and used in this simulation, the predicted release in each instance fell within the standard error of the apparent N release as found in the soil samples. But at the other two sites which were 100 to 150 km away from Site 3, the match of simulated to experimental values was poor. Because Site 1 and Site 2 were distant from Site 3, the average temperatures at Site 3 may not have represented the temperature at the other two sites. Because urea release rate is sensitive to temperature (Fig.6-3), using a Site 3 average temperature to calculate the release rates occurring at Sites 1 and 2 may not have been valid. Further, the soil mineral N content at Site 1 and 2 tended to decrease during the period of the last two samplings (Table 6-3), indicating possible N loss through denitrification.

In summary, this study provided a simple simulation approach to predict urea release rate from coating in situ. The parameters in the model were clearly defined and experimentally determined, yet the model could predict most N release either in soil incubated at a constant temperature, or in soil in the field at dynamic temperatures.

Table 6-2 Comparison of calculated cumulative urea release with the amount urea found in soil of incubation

Temperature	Coating	Predicted amount			Apparent urea released in soil		
		15d	30d	60d	15d	30d	60d
°C		………… mg urea cm^{-2} …………					
10	Thin	19.9	37.2	56.1	29.4±3.0	42.7±6.1	54.6±5.4
	Thick	10.2	21.4	41.3	12.2±2.6	25.3±3.2	43.2±7.5
23	Thin	37.2	54.6	64.8	40.5±7.4	48.3±7.2	55.9±1.4
	Thick	23.0	41.3	58.7	24.7±4.5	36.2±7.9	52.9±7.5

Table 6-3 Comparison predicted N released from model with the apparent N recoverd from soil samples in the field

	Days after application	Predicted N release		Apparent N release	
		Thin	Thick	Thin	Thick
		………… kg N ha^{-1} …………			
Site 1	12	29.4	18.1	52.9±10.0	17.1±4.5
	45	80.3	50.0	88.4±39.5	50.1±23.8
	135	114.4	90.3	89.3±13.0	50.0±15.6
	200	122.8	108.2	66.8±14.1	63.5±21.7
Site 2	17	35.1	21.6	45.5±9.6	31.0±8.6
	126	109.2	80.2	82.4±21.7	47.3±10.0
	179	119.4	99.1	78.1±24.1	54.8±5.7
Site 3	18	42.8	26.3	56.1±20.1	30.6±4.4
	43	82.0	52.0	93.8±34.2	50.0±7.3
	134	115.7	92.9	§	87.234.3
	190	122.5	107.4	137.7±25.1	138.9±29.0

§ Missing data

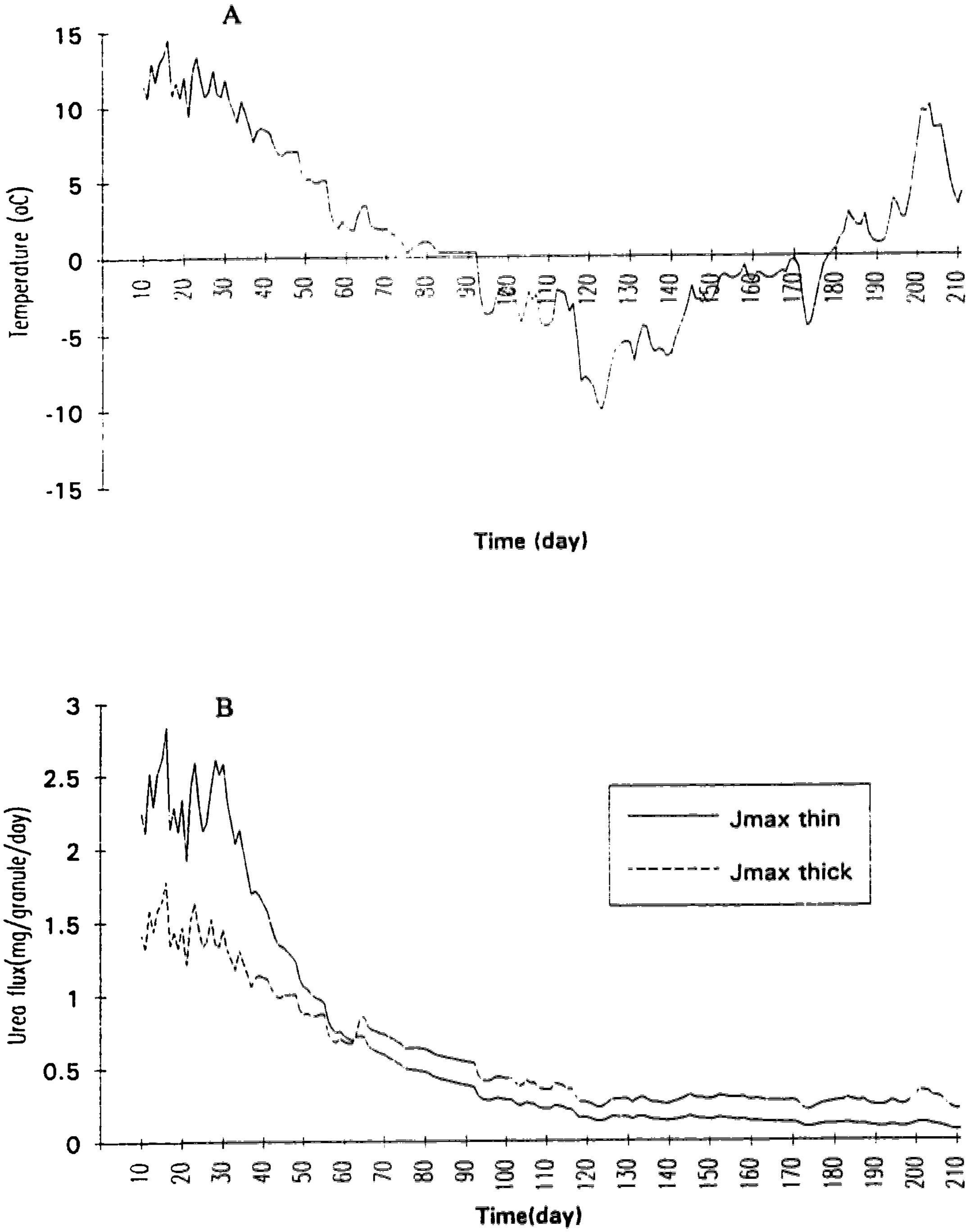

Fig.6-3 Urea flux over time with changing soil temperature. A, soil temperature during 210 days, B, urea flux.

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Chapter 7. Synthesis

Summary

The overall objectives of the work reported in dissertation was to find the release mechanisms of polymer-coated urea and N uptake efficiency by barley from the fertilizer with different times and methods of application. The study was made at four levels: laboratory study including thickness, permeability to urea in water and activation energy of permeability; incubation in 0.5 L containers of coated urea in soils to assess the influence of environmental factors on the urea release rate; field experiments with individual plots of 20 m^2 to evaluate urea release rate and N uptake efficiency by barley from different N sources and methods of placements in the three soils and a simulation model for predicting release rate in non-isothermal conditions. In laboratory, it was found that urea release rate across the polymer was faster in flowing water than in static water. The difference indicated that the concentration in the elution medium strongly influenced diffusion. The results from the incubation demonstrated that among the environmental factors soil temperature, water content and texture, only temperature had an effect on N release rate of the coated urea. The coating thickness, the artificially manipulated factor, influenced N release rate from polymer coating. Therefore, one can change the coating thickness to achieve a desired N release rate for a particular crop. In the field, the greatest N uptake by barley was obtained with thin-polymer coated urea banded in fall, but it was with non-coated urea banded in spring that a conventional N rate (50 kg N ha^{-1}) was applied. It indicated that coating conventional fertilizers was one of the approaches to promote N efficiency to crops and reduce any potential pollution caused by fertilizers. The modeling approach was developed based on the binary diffusion equation, and simulated points fell within the standard error of the actual urea release 66% of the time in the fertilizer-soil incubation.

A two-step release model was proposed in the course of study to explain water moving in and out of the coating. The key of the two-step release model was the existence of a thin water film or boundary layer around the coated fertilizer granule, and was verified by the existence of trace amounts of urea in the fertilizer-soil incubation, and by slower urea release rate in soil, in comparison with that in flowing water. The effect of this layer on urea release rate in soil was reflected by the newly introduced parameter, S_b, Soil Retardation Factor, into the release model. Through this factor, urea release rate was simulated in isothermal and non-isothermal conditions.

Contribution to knowledge

The 7-day dissolution method is the predominate procedure in determining release rate of coated fertilizers in the laboratory. In this dissertation, the method was shown not to be a true measure of urea release rate because the increased urea concentration in static water slowed the urea release rate. Hence it was necessary to determine coating thickness and permeability if one wanted to estimate the release rate of a nutrient from a coated fertilizer. This dissertation further confirmed Hauck's proposition that water vapor was the form of the water moving toward a coated granule in soil. However, a complement was made to Hauck's proposition, that is, the existence of a boundary layer around a coated granule in soil. This boundary layer was a medium for vapor and liquid water exchange, and was an extra barrier to urea diffusion. The theoretical existence of a boundary layer has been reported for injested pharmaceuticals, but the boundary layer has not previously been reported with coated fertilizers in soil. In this research a new factor, S_b, Soil Retardation Factor, was introduced for the estimation of urea release rate in soil, by which the prediction of urea release rate in the field became simplified. This dissertation also provided evidence that coating of conventional urea was one approach to improve urea N uptake by crop.

Interrelationship of soil science and other disciplines

Soil science is a relatively young science. Following its development, three trends can be seen. First, as a sub-discipline under agronomy, namely studying the relationship of soil to crop. Increasing crop yield and improving nutrient efficiencies is the center of research. Second, soil classification or taxonomy: categorizing soils so that a group of soil reflects the particular environment in which it develops. Third, the development of soil chemistry, soil biochemistry, soil physics, soil mineralogy and soil microbiology are driven by the aspiration for a thorough understanding of soil. Research activities in such areas are diverse and intense. They have a tendency to divorce themselves from traditional soil science and have more in common with other scientific disciplines. For example, nutrient transport and delivery to plant roots involves a controlled-release concept. The controlled release concept has proliferated in such diverse fields as chemical engineering, weed and insect control, medicine, pharmacology, biotechnology, and even perfumery. The research in these areas often focuses on delivering a substrate to a target in a designed system, with a given reaction rate and duration. Such a device can promote the efficiency of the substrate and simultaneously alleviate cumbersome administration of the system. Another example is mass transport in porous media. It is a subject in soil physics, chemical engineering, geophysics and other disciplines. In soil physics, understanding movement of pollutants in soil is crucial to conserving ground water free from contamination. In chemical engineering, understanding mass transport in a porous-media reaction bed is critical for designing a system. In geophysics, movement of oil and gas in porous media is important in the productivity of oil and gas fields, and characteristics of wave transfer in porous media has already become a major technique for detecting oil and minerals, or determining basic properties of porous media. Soil microbiology and biochemistry use porous media technology in fermentation and the design and operation of bioreactors.

The common research aim of soil science and other scientific disciplines has resulted in the formation of a new scientific discipline, namely, the science of porous medium. We already know that chemical reactions occurring in soil are different kinetically and thermal-dynamically to those in bulk solutions, but for some reason we still use the rules derived from examination of non-porous medium in soil. Earlier studies have indicated that mass transport of ions in the particle surface follows the Nernst-Plank equation better than Fick's diffusion laws [2]. Therefore, we need more studies into the uniqueness of the porous medium itself to develop rules adequate to this medium. The development of such a scientific discipline will benefit not only soil science but other disciplines as well.

Controlled-release fertilizers

Controlled-release fertilizer has so far shown positive signs of increasing fertilizer efficiency and reducing pollution fertilizer application. The database, however, is too scarce to address academic, environmental, social and political concerns. Further research should focus on the following issues so that the results can be used as guidelines for government legislation, farmers, and consumers.

1) Mechanisms of nutrient movement in soil-solution-root continuum. We are not completely sure how nutrients move in soil although three theories are now employed to explain the movement of nutrients to plant roots: mass flow, diffusion and root interception [4]. Following this concept, nitrogen moves by mass flow, phosphorus by diffusion and potassium 20% by mass flow, 78% by diffusion and 2% by root interception [1]. The concept was derived simply by comparing calculations of solution concentration in soil with the evaporation rate of plants. Detractors argue

that mass flow and diffusion are inseparable processes in the soil-solution-root continuum [3]. Putting aside the academic argument, if N and P movement in soil is different, should we use the same polymer and device for controlling N and P release rate in the soil?

2) Mass balance of N^{15}-labeled N from CRF. Studies have been conducted on the N uptake efficiency of crops from CRF, but we do not know the fate of residual N left from CRF.

3) Environmental assessment of polymers or other materials using CRF's. Increasing applications of CRF's may result in accumulation of coating materials in soil. The presently used or envisioned coating materials range from fast (starch) to inert (clay) with respect to biodegradability; the residence time of these materials has not been investigated

4) Use of CRF's under different crop and management systems. A given controlled-release N fertilizer may be suitable for some crops, but not for others. The factors which come into play are the type of crop, crop residue and intensity, tillage, length of growing season, soil temperature, rainfall distribution or irrigation, yield goal and the nitrate-loss allowable. CRFs have not been developed for particular crops and conditions to perfect synchronization of supply with crop need. As well, near-perfect recovery of CRF's by crops is envisioned. The question is whether there will be extensive use of CRF. The answer will depend on international developments (e.g human population, N-fixation by grain crops, level of global warming, fission versus fossil fuels). But in the meantime, research on "porous media-CRF-plant uptake-nutrient non-leakage" will hopefully be conducted as one closely integrated subject.

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Appendices

Appendix 1 Calculation used to design the apparatus used in the determination of permeability of polymer-coated urea

Equations

Reynolds Number

$$R_{p,m} = \frac{D_p V_s \rho}{\mu(1-\varepsilon)}$$

$R_{p.m}$ - Reynolds's number
V_s - superficial velocity
Vs = Q/A
Q: discharge rate cm^3/s
A: area of the pipe cm^2
ρ - density of the liquid, g cm^3
μ - viscosity of the liquid, g cm^{-1} S^{-1}
D_p - diameter of particles, cm
ε - porosity

Burke-Plumber equation

$$f = 1.75 \frac{\Delta X V_s^2}{D_p} \times \frac{1-\varepsilon}{\varepsilon^3}$$

f - friction heating per unit mass, J kg^{-1}
ΔX - height of porous media, cm

Bernoulli's equation

$$\frac{P}{\rho} + g\,\Delta Z = f$$

P - pressure, Pa
ρ - density of liquid, g/cm^3
ΔZ - total height, cm
g - 980 cm S^{-2}

If there is no extra pressure in the system, P = 0, then
integrating Burke's equation and Bernoulli's equation

$$\frac{\Delta Z}{\Delta X} = 1.75\frac{Vs^2}{gD_p} \times \frac{1-\varepsilon}{\varepsilon^3}$$

Choose Reynolds number, determine the ratio of total height to the height of the porous media.

Reynolds' No.	Vs(cm/s)	ΔZ/ΔX cm	ΔX cm	ΔZ cm
1000	21.44	61.15	2	122.3
500	10.72	15.30	2	30.6

So the designed total height should be between 30.6-122.3 cm

Choosing

total height: 80 cm
porous media height: 2 cm

then the Vs = 17.3 cm

Rp.m = 807

Testing the apparatus

loading 2 cm in height of 2.5 cm (diam.) polymer-coated granules in the device, keep water in the designed level, measure the discharge rate from each pipe in 5-second interval

n= 59 Q = 56.3 ± 2.6 ml/s

discharge rate in design: Q = 48.5 mL/s

Appendix 2 Yield results (grain + straw) and N uptake(grain + straw) by barley in Site 2 and Site 3

		1990†		1991†	
Treatment	Application	Yield	N uptake	Yield	N uptake
		………… kg ha^{-1} …………			
Site 2					
fall application					
None		6265.6±238.4	75.6±5.8	5352.1±621.1	54.5±14.3
Urea	incorp	7668.5±568.3	123.8±12.9	6559.7±453.7	83.1±17.1
Urea	band	6776.0±916.8	110.0±16.2	6262.3±739.3	83.9±17.2
Thin coat	incorp	8102.2±726.4	127.1±11.5	6331.2±563.4	78.6±14.2
Thin coat	band	6571.1±973.5	115.4±8.1	6073.6±960.8	80.4±13.5
Thick coat	incorp	6952.3±923.2	112.7±9.6	6507.8±614.2	84.1±12.2
Thick coat	band	6819.0±280.5	114.3±9.6	6815.2±329.3	88.9±13.4
GS	incorp	7880.0±901.8	137.3±18.6	6551.5±542.9	77.3±12.3
GS	band	8491.7±1387	144.8±29.3	5388.3±851.8	76.4±13.2
urea(liquid)	spoke	7534.4±1439	131.1±20.7	6572.3±624.3	84.4±7.5
spring application					
None		5964.7±327	71.2±7.3	5544.8±924.6	65.3±7.9
Urea	incorp	8114.5±812.3	133.5±10.1	6386.0±226.4	74.7±3.3
Urea	band	6446.2±677.6	109.9±12.7	5896.1±1362.0	74.9±3.3
Thin coat	incorp	6707.5±401.2	114.2±6.4	6395.0±945.5	89.8±17.5
Thin coat	band	6911.2±1033	102.9±26.1	6528.5±775.2	78.7±10.4
Thick coat	incorp	8213.5±768.5	137.1±12.8	6463.7±362.8	76.2±16.1
Thick coat	band	7375.7±1080	121.5±13.1	6408.4±683.6	85.6±18.2
GS	incorp	6947.2±805.2	117.7±11.2	6533.4±801.6	82.4±12.8
GS	band	7088.4±1477	112.6±18.8	6447.9±593.0	84.2±10.8
urea(liquid)	spoke	7512.7±597.0	133.1±8.5	7277.0±552.3	89.2±7.4

† Rate of N in 1990 and 1991 was 127 and 50 kg N ha^{-1}.

Appendix 2 continued

		1990		1991	
Treatment	Application	Yield	N uptake	Yield	N uptake
		………………… kg ha^{-1}		…………………	
Site 3					
fall application					
None		6051.4±937.3	63.7±13.4	4999.4±319.4	67.8±3.4
Urea	incorp	9372.6±914.3	133.9±14.8	5792.0±1054.7	88.4±16.1
Urea	band	9257.5±431.6	144.4±6.3	5988.7±430.2	90.3±9.8
Thin coat	incorp	9055.1±866.8	133.3±10.3	5180.0±505.5	81.4±11.5
Thin coat	band	9500.2±248.4	142.2±13.3	5466.9±560.0	85.4±10.5
Thick coat	incorp	9063.1±680.9	131.5±8.8	5718.8±441.8	87.8±8.5
Thick coat	band	9395.6±566.7	131.4±17.7	5745.7±874.9	89.4±12.1
GS	incorp	9554.8±339.2	135.3±11.6	5866.1±561.6	96.9±14.6
GS	band	8867.0±732.2	138.0±8.4	5505.7±289.4	80.2±7.7
urea(liquid)	spoke	7979.5±334.2	121.0±9.6	5936.5±460.5	92.3±4.4
spring application					
None		5509.3±910.3	53.0±10.6	4525.1±306.0	58.9±4.5
Urea	incorp	9778.1±611.7	163.2±8.8	5320.1±1000.4	76.0±22.1
Urea	band	8400.1±295.6	135.9±12.7	5908.5±170.4	96.8±7.0
Thin coat	incorp	9641.5±169.1	155.4±3.8	5523.0±361.2	90.1±6.8
Thin coat	band	8638.5±572.6	135.1±14.3	5299.7±778.6	82.7±7.2
Thick coat	incorp	9901.9±906.9	155.9±7.4	5665.4±430.0	81.9±13.5
Thick coat	band	8779.0±187.8	137.1±9.3	5429.1±497.8	87.5±7.4
GS	incorp	8588.2±687.3	139.6±3.8	5715.3±559.5	86.0±7.6
GS	band	8175.6±705.1	110.0±14.8	5935.4±325.2	94.6±5.6
urea(liquid)	spoke	8912.5±942.4	136.4±14.2	5870.4±1092.8	98.0±19.0

Appendix 3 Mineral-N found in the incubation experiments with soil saturated by water at 7.5- or 15-day intervals

	Mineral N					
	7.5 day intervals†			15 day intervals†		
Treatment	15d	30d	60d	15d	30d	60d
	ug N g soil^{-1}					
Site 2						
Nil	35.7±1.4	37.8±4.0	99.6±13.5	70.0±2.5	41.7±7.5	20.2±1.5
urea	191.2±0.7	214.9±9.1	192.1±7.6	216.5±18.7	189.8±51	171.9±21.6
thin coat	155.4±12.5	197.5±21.2	187.9±21	178.6±28.3	179.6±2.7	192.6±22.7
thick coat	98.9±19.5	144.4±28.2	152.0±16.4	127.7±21.5	137.2±34.9	173.0±17.3
GS	54.0±1.0	141.6±45.2	188.3±7.9	115.7±24.1	72.4±9.5	138.3±10.7
Site 3						
Nil	missing	43.1±0.6	49.9±7.9	62.5±1.5	25.9±3.3	22.7±1.9
urea	158.5±6.5	203.9±18	200.0±3.7	272.8±81.4	216.6±41.5	171.4±19.9
thin coat	149.5±7.8	197.2±23.5	209.5±21.7	231.6±8.7	153.0±36.2	113.4±5.4
thick coat	93.2±12.5	139.5±11.2	194.0±4.5	146.3±31.0	87.9±29.2	171.8±17.0
GS	32.1±6.9	64.5±6.6	174.0±4.2	124.3±29.2	56.8±6.3	128.4±29.2

† Soil was in saturation and filed capacity in 7.5 or 15 days intervals.