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Release Characteristics of Nutrients from Polymer-coated Compound Controlled Release Fertilizers

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Abstract Reliable information regarding release characteristics of nutrients from a polymer-coated controlled release fertilizer (CRF) is essential for beneficial agronomic and environmental results. Significant knowledge regarding nitrogen release from polymer-coated urea was gained while the information regarding the release of the different nutrients contained in polymer-coated compound N–P–K CRF remains limited. An experiment in which major factors affecting the differential release of nutrients from two coated compound CRF was performed in free water, water saturated sand and sand at field capacity. In general, nitrate release was the fastest, followed by ammonium and potassium whereas phosphate was significantly slower, with a rate of linear release in free water 45–70% slower than that of nitrate. Little differences were obtained for the lag periods of nitrate, ammonium and potassium release (2–10 days) under the experimental conditions, whereas for P they were one order of magnitude larger. The main factor slowing the release was assumed to be the lower solubility of ions with P being the least soluble. Release into free water was, expectedly, somewhat faster than that into saturated sand and significantly faster as compared to sand at field capacity and particularly so for P. Raising the temperature from 20 °C to 40 °C increased the rate of linear

release of the different nutrients. The energy of activation, EA_{rel} , estimated for the linear release, of the different nutrients, was narrow ranging between 37 to 46 (KJ mol⁻¹) whereas the mean values obtained for the two CRF, differing by 50% in coating thickness, was non-significant. However, EA_{rel} was significantly different in different media. The complex effect of temperature on the lag period and nutrient interactions during release deserve further investigation.

Keywords Polymer · Controlled release · Nutrients · Medium · Model

Introduction

Polymers are versatile materials in a most promising and comprehensive field, and one useful application is in controlled release fertilizers (CRFs), which are called polymer-coated fertilizers. Polymer-coated fertilizers, the most promising section in CRFs, have the potential of optimal supply of nutrients during growth period of crops, and their application should benefit the environmental and economic aspect [1–3]. Significant progress in explaining the mechanisms and quantifying the release from urea based (or other single fertilizers) polymer-coated CRFs were made in the recent years [4–6]. The release course consists of 3 three distinct stages [5]: (1) the initial stage during which almost no release is observed (lag period), (2) a constant-release stage, and (3) a stage of gradual decay of release rate. It was assumed that the duration of the lag period was linked to the time needed for the internal voids of a coated granule to fill with a critical amount of water and thus induce good contact of the

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solution with the inner side of coating, after which a steady state between water penetrating into the granule and nutrients leaving it is attained. The stage of linear (constant rate) release lasts as long as there is solid fertilizer in the granule and thus a constant gradient between the granule and medium solutions is, practically, maintained. Mathematical mechanistic models were proposed for urea (and possibly for similar single fertilizer CRFs) enabling prediction of the release by utilizing chemo-physical parameters [5, 7]. A theoretical mathematical model was also made by Du et al. [8], but only considering simple nutrient CRF, and less attention was devoted to the release of nutrients from compound N–P–K coated CRFs, in which case the processes are expected to be more complex than with a single fertilizer/nutrient. The release of each nutrient/ion in such case is expected to depend on its own solubility in solution, diffusivity/permeability through the polymer coating, interactions between ions as well as temperature, water content and medium type effects.

Wilson and Chem [9] in their critical review, related to release characteristics of slow release fertilizers (SRFs), drew attention to compound N–P–K fertilizers from which the fractional rate of release of N was greater than that of K, and even more so than the release rate of P. Shoji and Gandeza [10] demonstrated this phenomenon with polyolefin-coated CRFs. Huett and Gogel [11] tested release from 17 coated CRFs and reported a consistent trend in nutrient release periods across all CRFs with $P > K > N$ and with differences of around 10% (only) in duration between nutrients. Shaviv [1, 4] mentioned such a common trend for polymer-coated CRFs stressing the significantly lower rates of release of P as compared to K and N. Several other recent reports examined the release from compound CRFs but did not emphasize the unique characteristics of the differential release of the different nutrients and their dependence on environmental conditions [12–14]. Gandeza et al. [15] made an effort to model the temperature effect on nitrogen release from a polyolefin coated CRF but used an empirical (polynomial) expression for this purpose. Jarrel and Boersama [16] suggested an Arrhenius type expression for modeling the effect of temperature on nitrogen release from Sulfur Coated Urea (SCU). Since their model was specifically developed for the release from SCU, it was considered questionable for predicting release from polymer-coated CRFs [4, 5].

This paper examined the differential release rates and patterns of nitrate, ammonium, potassium and phosphate from two polymer-coated compound CRFs and the effects of temperature and water content (or type of release medium) on it. Special emphasis was

put on the changes in the linear release rates and the lag periods for each nutrient/ion as affected by the above-mentioned factors. Differences in the rates of linear release into free water at 3 different temperatures were used to estimate the activation energy of the release EA_{rel} .

Theoretical Considerations

Shaviv et al. [5] proposed the following, rather simplified, expression for the duration of the lag period, t^{lag} , for a single granule of a polymer-coated CRF:

$$t^{lag} = \frac{\gamma r l}{3 P_h \Delta P} \quad (1)$$

Where P_h is water permeability ($\text{cm}^2 \text{d}^{-1} \text{Pa}$), l is coating thickness (cm), r is granule radius (cm), ΔP is the difference between vapor pressure of water and saturated urea solution (Pa) and γ is the critical volume fraction of voids filled with water. The water potential gradient, ΔP , is not expected to change greatly when water content changes from field capacity to saturation or free water in a vessel and thus P_h remains the main temperature dependent factor, which affects the lag.

The lag period was significantly different for different nutrient in the same polymer-coated granule, and this difference couldn't be reflected in above model. Based on the Shaviv's model Du et al. [17] deduced a little more complex one considering the dissolving time of nutrients as following:

$$t^{lag} = \frac{\gamma r}{3} \left(\frac{l}{P_h \Delta P} + \frac{1}{D \phi} \right) \quad (2)$$

Where D is dissolving coefficient, ϕ is mass ratio of a certain nutrient in total granule mass. This model gave a better modeling of lag period for nutrients release from polymer-coated compound CRFs but need further verification.

For the linear period ($t^* - t^{lag}$) the following rate equation was proposed for a single polymer-coated granule:

$$R_{lin}(r, l, t) = \frac{3 P_s C_{sat}}{r l \rho_s} (t - t^{lag}), t^{lag} \leq t \leq t^* \quad (3)$$

where, P_s stands for solute permeability ($\text{cm}^2 \text{d}^{-1}$), C_{sat} – saturation concentration (g cm^{-3}) standing for the difference between solute concentration within the granule, $C_{in} = C_{sat}$, and outside the coated granule, $C_{out} = 0$, ρ_s is fertilizer density (g cm^{-3}) and t^* is the time when the linear release ends. According to Shaviv

et al. [6], such an expression can also be used for a population of granules provided that a narrow range of granule coating thickness and radii is used.

To account for the overall dependence of the release on temperature an Arrhenius type relation is offered, which should allow the estimation of the overall activation energy of the release from a coated granule during the linear period of release. Two parameters in Eq. 3 are likely to be temperature dependent: the permeability P_s , and the saturation concentration C_{sat} . Therefore the following temperature dependence of R_{lin} is proposed:

$$R_{lin} \propto C_{sat} \times P_s = C_{sat}^0 \exp\left(-\frac{EA_C}{RT}\right) \times P_s^0 \exp\left(-\frac{EA_{ps}}{RT}\right) \quad (4)$$

Where, C_{sat}^0 and P_s^0 are reference (standard) values of the solubility and permeability respectively, EA_C [KJ mol⁻¹] is the energy of activation associated with the solubilization of the fertilizer and EA_{ps} , the energy of activation of its permeation through the membrane. By rearranging, one gets:

$$R_{lin} \propto C_{sat}^0 \times P_s^0 \exp\left(-\frac{EA_{ps} + EA_C}{RT}\right) \quad (5)$$

Plotting $\ln R_{lin}$ against $1/RT$ for experimental data in which the temperature is changed, should thus allow the estimation of the overall energy of activation of the release $EA_{rel} = EA_C + EA_{ps}$.

Experimental

Materials

Two polymer-coated fertilizers ("polyurethane-like" coating, provided by Haifa Chemical Co. Ltd, and the commercial name was Multicote): F₁, 19:6:13 (N: P₂O₅: K₂O), with a coating thickness of 0.0065 cm and F₂, 18:6:12 (N: P₂O₅: K₂O), with a coating thickness of 0.0096 cm were used. The fertilizer core was the same but with different coated thickness for these 2 fertilizers, which made it possible to comparing the effect of membrane thickness on the release characteristics of nutrients release.

Nutrients Release in Different Mediums

Release was tested in three different systems: I. Free water (common procedure [4]); II. Water saturated sand packed in columns; and III. Sand at field capacity moisture.

Release in system I. A quantity of 5 g polymer-coated fertilizers was immersed in 33.3 ml water, which was then incubated at three different temperatures (20, 30 and 40 °C). Each treatment was in four replicates. The supernatant solutions were sampled at predetermined time intervals (2 days interval in the first 20 days, then followed 5 days interval) and replaced by fresh de-ionized water. Nutrients in the samples were determined by a Lachat auto-analyzer (nitrate, ammonium, phosphate) and an Optima 1000 ICP (potassium).

Release in system II. A glass column (2.8 cm in inner diameter, and 16 cm in height) with a funnel-shaped bottom was packed with 125 g silica sand (passing 160 mesh sieve). The sand was uniformly mixed with 5 g polymer-coated fertilizer and carefully placed in the column to which 33.3 ml of de-ionized water were added to saturate the sand. A plastic tube connected to the funnel-shaped bottom was used to keep the water level at the surface of the sand. The samples were then incubated at the three temperatures like those of system I. The columns were rinsed with 100 ml de-ionized water every few days (2 days interval in the first 20 days, then followed 5 days interval) and nutrient concentrations determined like in system I. Each treatment was run in four replicates.

Release in system III. A quantity of 5 g polymer-coated fertilizer was uniformly mixed with 125 g silica sand (passing 160 mesh sieve) and placed in a 200 ml plastic jar with a wide cover to which 20 ml distilled water was added to bring it to a moisture content slightly above field capacity (FC). The incubation was performed at 30 °C. About 5 g of the moist sand was gently sampled every few days (2 days interval in the first 20 days, then followed by 5 days interval), extracted in de-ionized water and used for determination of nutrient concentration like in system I. On day 50 of the incubation the remaining sand was washed by adding 200 ml solution to remove the accumulated nutrients in the sand, after which the sand was separated from the solution, re-dried to FC and the incubation continued. To standardize the estimation of the duration of the lag periods of release for each nutrient, the lag was defined as the time at which the fractional release was less than 1%.

Calculation of Activation Energy

The energy of activation of the release, EA_{rel} , was calculated on the basis of estimates of the rate of the release (% released per day) during the linear period obtained from the release curves for the best fits to a

straight line with $R^2 = 0.99$ (considering that the lines start at the end of the lag period).

Results and Discussion

Release of Individual Nutrients

Table 1 showed the individual rates of release of the different ions for the linear period and the 3 different temperatures. Table 1 and Fig. 1 clearly showed the differences in the release rates among different nutrients. Nitrate release was the fastest, followed by ammonium and potassium and phosphate was significantly slower. The rate of P release into water was in most cases 45–70% as compared to nitrate and it reduced to 35–50% in the saturated sand. The differences were even more striking when comparing the lag periods (Table 2). Little differences were obtained for nitrate, ammonium and potassium all ranging between 2 and 10 days under the varying experimental conditions, whereas for P they were almost one order of magnitude larger, ranging between 10 and 40 days. It was noteworthy that the differences in the lag period increased with temperature.

Considering the fact that the volume of available water in the granule is limited [5], it was thus expected that the first ions to dissolve were those with higher solubility. Since the phosphates in the mixture have the lowest solubility, it was expected that they would start dissolving only after a significant proportion of the other ions (particularly nitrate and ammonium) had been released leaving in the granule more available water for P dissolution. In another aspect, there were interactions among nutrients and accompanying ions on P saturated concentration, which might decrease P saturated concentration in the granule, thus decreasing the diffusion force of P across the coated membrane. Therefore, the P release showed a long lag period and lower release rate.

Such differences in the lag and particularly for P indicated that in early stages of plant growth, particularly under lower temperatures, the supply of this nutrient may be too slow and thus more available sources should be added (e.g., a fraction of non coated P or a thinly coated source with fast release of P, like coated mono-ammonium-phosphate). Furthermore, in soils and medium with significant K sorption/fixation capacity one should consider applying a significant proportion of soluble forms not only of P but also of K.

Effect of Release Medium

Figure 2 demonstrated the basic differences in the release between the three different media: free water, saturated sand in columns and sand at FC. Expectedly, the release into the free water was the fastest and that into the sand at FC the slowest. The rates of the linear release of nitrate, potassium and ammonium were generally about 5–20% slower in the saturated soil as compared to those in free water (Table 1). For phosphate the reduction was much more significant ranging between 25 and 55% (Table 1).

Interestingly, in case of the sand at FC the relative reduction in the rates of nitrate, ammonium and potassium (e.g., Fig. 2) in the first 2–3 weeks was small. As the release goes on the rate significantly slows, as expected from the accumulation of the nutrients in the medium causing a significant reduction in the driving force of the release (i.e., Eq. 3, when the assumption $C_{out} \sim 0$ is no more valid).

In case of P, the reduction in the release rate was large (25–55%) when shifting from free water to water saturated sand and very drastic for FC conditions.

The effect of the medium, or eventually the degree of saturation or water availability, on the lag was relatively small (Fig. 2). This was acceptable considering that the total water potential difference between free water to sand at FC was not expected to change significantly. Therefore, the driving force for water entry (ΔP in

Table 1 Release rates (% per day) during the linear period, obtained for CRFs F_1 and F_2 ; four different nutrients (nitrate, ammonium, potassium and phosphate), three temperatures (20, 30, 40 °C) and two release media (free water and water saturated sand in columns)

Nutrients	Release medium	CRF- F_1			CRF- F_2		
		20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
NO ₃ -N	Sand column	1.05 ± 0.03	1.62 ± 0.05	2.08 ± 0.09	0.81 ± 0.02	1.16 ± 0.03	1.77 ± 0.05
	Water	1.04 ± 0.02	2.04 ± 0.04	3.32 ± 0.06	0.76 ± 0.02	1.35 ± 0.02	2.24 ± 0.04
NH ₄ -N	Sand column	0.85 ± 0.02	1.55 ± 0.06	2.83 ± 0.02	0.67 ± 0.03	1.16 ± 0.03	2.01 ± 0.06
	Water	0.98 ± 0.02	1.85 ± 0.03	3.26 ± 0.02	0.75 ± 0.02	1.49 ± 0.02	2.24 ± 0.05
K	Sand column	0.67 ± 0.02	1.12 ± 0.02	1.92 ± 0.04	0.44 ± 0.02	0.77 ± 0.04	1.22 ± 0.04
	Water	0.75 ± 0.02	1.43 ± 0.04	2.59 ± 0.05	0.51 ± 0.01	0.93 ± 0.03	1.56 ± 0.04
P	Sand column	0.39 ± 0.01	0.63 ± 0.03	0.91 ± 0.03	0.28 ± 0.01	0.49 ± 0.02	0.84 ± 0.03
	Water	0.77 ± 0.02	0.89 ± 0.03	2.1 ± 0.02	0.32 ± 0.01	0.65 ± 0.01	1.03 ± 0.02

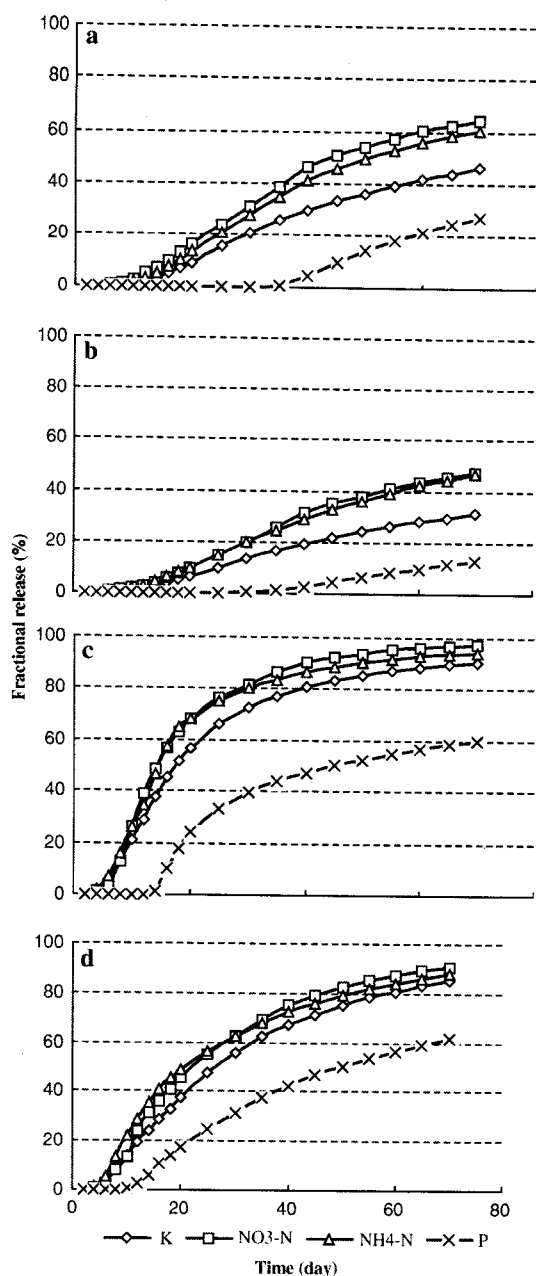


Fig. 1 Release of potassium, nitrate, ammonium and phosphate from CRF (a: CRF-F₁ at 20 °C; b: CRF-F₂ at 20 °C; c: CRF-F₁ at 40 °C; d: CRF-F₂ at 40 °C)

Eq. 1), which was a major factor to affect the lag, is not expected to change significantly between the media.

Effect of Coating Thickness on Release Characteristics

The average release rates into free water for all ions of CRF-F₁ were 0.89, 1.55 and 2.82 (% nutrient per day)

for 20, 30 and 40 °C, respectively, and only 0.59, 1.11 and 1.77 for CRF-F₂ at 20, 30 and 40 °C, respectively. The ratios between the rates obtained from CRF-F₂: CRF-F₁ range between 0.63 and 0.73 and agreed well with the expected from equation 2 for the inverse-ratio of the coating thickness l ($l_{F_1}: l_{F_2}$) corresponding with 0.68. The ratio slightly increased to 0.73–0.75 in case of the release into the water saturated sand and farther increases to 0.75–0.84 in the sand at FC. This indicated that in those cases the release was also affected by the medium or external factors that impede it. Nutrient accumulation outside the granules, when leaching or diffusion away from the granule become restricted was expected to impede the release as shown and discussed in the previous section and thus the effect of the coating thickness was slightly reduced.

The lag period (Table 2) seemed to be almost non-affected by the coating thickness, which didn't conform with Eq. 1, and indicated that the assumptions used for modeling the lag from a single coated fertilizer (i.e., urea) might not be valid for the more complex system of a compound N–P–K fertilizer. On the other hand, nutrient type and temperature had a significant impact on the lag, reiterating that solubility and/or solubilization might have a profound role in this case (Eq. 2).

Temperature Effect on Release

Overall, the reduction in the lag period and the increase in linear rate of release with increasing of temperature could be clearly seen in Fig. 3. Table 1 showed the specific linear rates as obtained for each ion for CRF F₁ and F₂ when releasing into free water and water saturated sand. Table 2 did the same for the lag period. The increase in the average rates of all four ions where the temperature raised from 20 to 40 °C was 3.2 and 3.0 times for the free water and the water saturated sand, respectively. Between 20 and 30 °C, which would be a common range of the rhizosphere temperature for many crops, the increase of the rate with temperature is 1.8–2.0 times for the free water and the water saturated sand, respectively. This conforms to the Q_{10} factor of the release (the change in release rate at an increase of 10 °C, which matches plant nutrient uptake) presented by Shoji et al. [18], and further discussed by Shaviv [4].

Plotting in R_{lin} against $1/RT$ (Eq. 5) for the data in Table 1 allowed the estimation of the overall energy of activation of the release EA_{rel} shown in Table 3. EA_{rel} was an important parameter which demonstrated the temperature sensibility of nutrients release rate.

Table 2 Lag periods estimated for CRF-F₁ and CRF-F₂ (day): four different nutrients (nitrate, ammonium, potassium and phosphate), three temperatures (20, 30, 40 °C) and two release media (free water and water saturated sand in columns)

Nutrients	Temperature (°C)	CRF-F ₁		CRF-F ₂	
		Water saturated sand	Water	Water saturated sand	Water
NO ₃ -N	20	6(0)	6(0)	8(0)	6(0)
	30	4(0)	4(0)	4(0)	4(0)
	40	4(0)	2(0)	4(0)	4(0)
K	20	10(0)	8(0)	10(0)	8(0)
	30	4(0)	4(0)	4(0)	4(0)
	40	2(0)	2(0)	2(0)	2(0)
NH ₄ -N	20	8(0)	8(0)	8(0)	8(0)
	30	4(0)	4(0)	4(0)	4(0)
	40	2(0)	2(0)	2(0)	2(0)
P	20	40(0)	35(0)	35(0)	35(0)
	30	18(0)	20(0)	14(0)	16(0)
	40	14(0)	14(0)	10(0)	10(0)

Note: numbers in parentheses are standard deviations ($n = 4$)

Through controlling the parameter the nutrients release could have a better matching with nutrients requirement of crops during a whole growth stage.

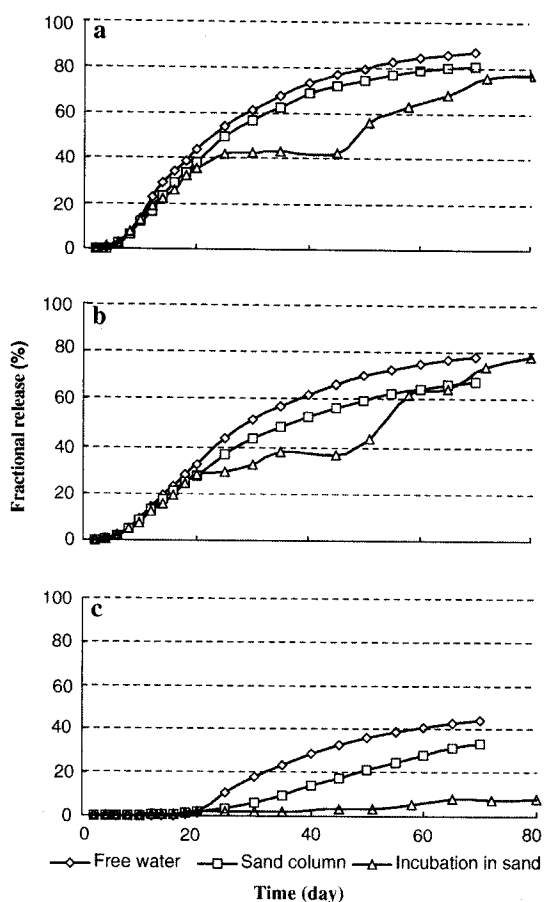


Fig. 2 Release of nitrate (a), potassium (b), and phosphate (c) from CRF-F₁ at 30 °C into free water, water saturated sand (in column) and sand at field capacity

The values obtained for the release into free water were close to the ones obtained by Raban [19] for urea with a similar type of coating. The values obtained for the water saturated sand were about 15–20% lower, which meant that the nutrients release was easily influenced by temperature. This was assumed to further indicate that in this case the temperature effect on the release through the membrane and the dissolution might have been hindered by the medium itself (i.e. tortuosity, lower water content and thermal capacity) and the slower transport of the ions in it. The hindered effects of medium on nutrients release were significantly different among nutrients. The biggest effect was on nitrate, followed by P, ammonium and potassium. Since the mechanism of release prevailing during the decay period were assumed to be the same as for the linear release the energy of activation estimated above should thus apply for the decay period as well.

The temperature also significantly affected the lag period: expectedly, the lag got shorter as the temperature increased. However, there were differences between the different ions and particularly when comparing nitrate, ammonium and potassium to phosphate. In case of the release from a compound N–P–K fertilizer the processes controlling the lag were expected to be more complex as compared to the release of a nutrient from a single coated fertilizer (e.g., Eq. 2). Interactions between ions and particularly the competition on water for solubilization were not accounted for in the simplified model (Eq. 1) and therefore it was felt pre-mature to try and model temperature effects and estimate the energy of activation at this stage.

Ongoing work, which extends the number of tested CRFs and examines the release under various condi-

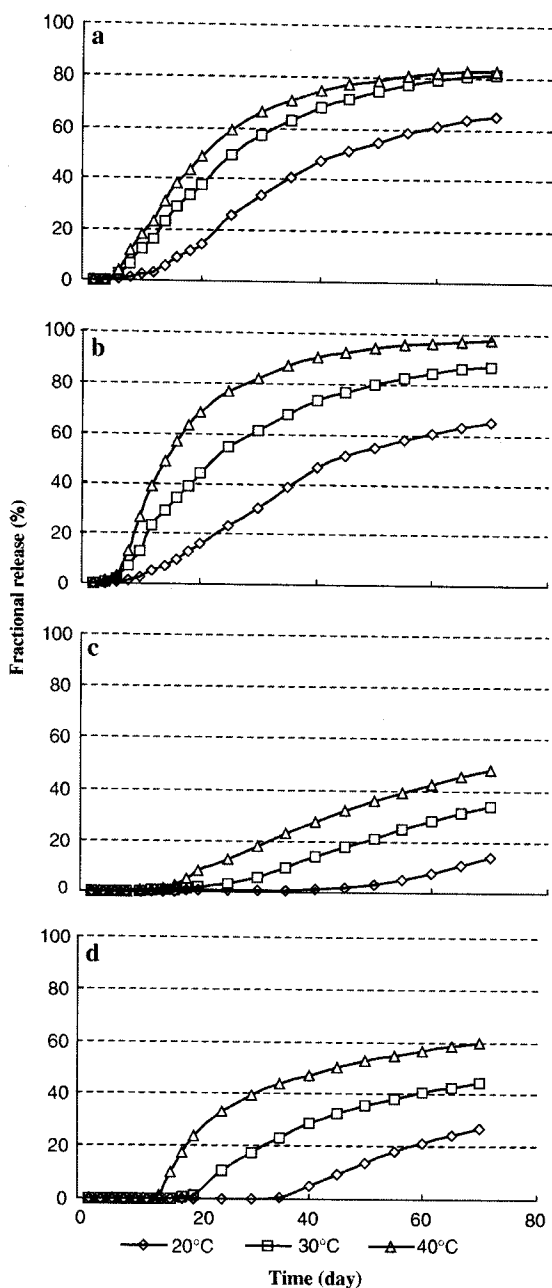


Fig. 3 Release of nitrate and phosphate from CRF-F₁ into free water and water saturated sand as affected by temperature (a: nitrate into water saturated sand; b: nitrate into free water; c: phosphate into water saturated sand; d: phosphate into free water)

tions are performing now in our laboratory aiming at better understanding of the complex mechanism of release from compound coated-CRFs, and special emphasis will be focused on the interaction of ions in the granule. The results are expected to allow modeling

and prediction of multi-nutrient release from compound CRFs.

Conclusions

Nutrients release from polymer-coated CRF was mainly controlled by diffusion mechanism. The temperature and coated membrane thickness were the most important factors that influenced the diffusion coefficient. Lower temperature and thicker membrane made a lower diffusion coefficient of coated membrane, which slowed the nutrients release rate. Nutrients release rate was different in different medium, the fastest release rate was in water, then water saturated sand, and the last was in sand at field capacity. Nutrient release in water was less sensitive to temperature compared with other release medium and was commonly used to evaluate the nutrients release profile from polymer-coated fertilizer. Nutrients release profile from polymer-coated CRF could be described by three stages: lag period, linear stage and decay period. The lag period of P was significantly longer than other nutrients, which indicated that there were strong interactions among nutrients in the fertilizer granule, especially on nutrient solubility, and these interactions deserved further research.

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