

# Macroreticular Hydrogel Effects on Dissolution Rate of Controlled-Release Fertilizers

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The effects of cross-linked sulfonated polystyrene granules (soil conditioner) with three different absorptions of deionized water were investigated on the dissolution of three different  $K_2SO_4$  fertilizers. One of the fertilizers used was water soluble, whereas the other two were controlled-release fertilizers with differing nutrient release rates. Soil columns regularly rinsed with water for a period of 3 months were used for testing. It was found for water-soluble fertilizer that the quantities of K leached from the columns increased with the absorption capacity of the polymers. In the case of application of the polymer with the highest absorption capacity ( $100 \text{ g of water g}^{-1}$  dry polymer), the water-soluble K leached was 188% more than that leached from controlled-release formulations. It was found also that the presence of hydrogels in soil increased dissolution of controlled-release fertilizers. Yet, this increase was relatively small and did not depend significantly on absorption.

**Keywords:** *Controlled-release fertilizers; gel; macroreticular polymers; soil columns; soil conditioners*

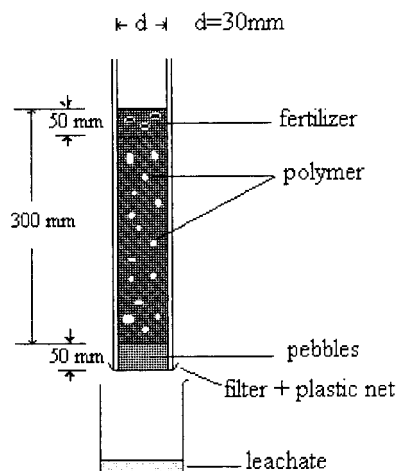
## INTRODUCTION

Hydrophilic network polymers (hydrogels) are used as soil conditioners due to their capacity to absorb a large quantity of water that is subsequently liberated to plants. For container mixes, alternatively to incorporation of organic matter or careful selection of soil materials, these polymers are also used. In field agriculture, the use of polymers is only limited by their relatively high cost, which has restricted their use mainly in light and medium soils with high sand content. These soils are characterized by limited field capacities and high losses of nutrient elements to deeper layers due to their high hydraulic conductivity. The increased soil moisture, however, results in enhanced dissolution of fertilizers during the stage of water release (desorption) from polymers (Prasad, 1976; Kochba et al., 1990; Chatzoudis and Valkanas, 1995), thus worsening environmental problems due to this leaching (Puchades et al., 1984; Boman, 1993). Optimized application of combined polymeric soil conditioners and controlled-release fertilizers may improve nutrition of plants, mitigating at the same time the environmental impact from draining water-soluble fertilizers (Chatzoudis and Valkanas, 1995; Abraham et al., 1996) and reducing consumption of good quality water for agricultural purposes due to reduction of evaporation losses resulting from lower frequency of irrigation when polymers are used (Rigas et al., 1991a). Furthermore, these materials may improve soil for cultivation with regard to better soil aeration and friability and soil erosion prevention (Rigas et al., 1991b).

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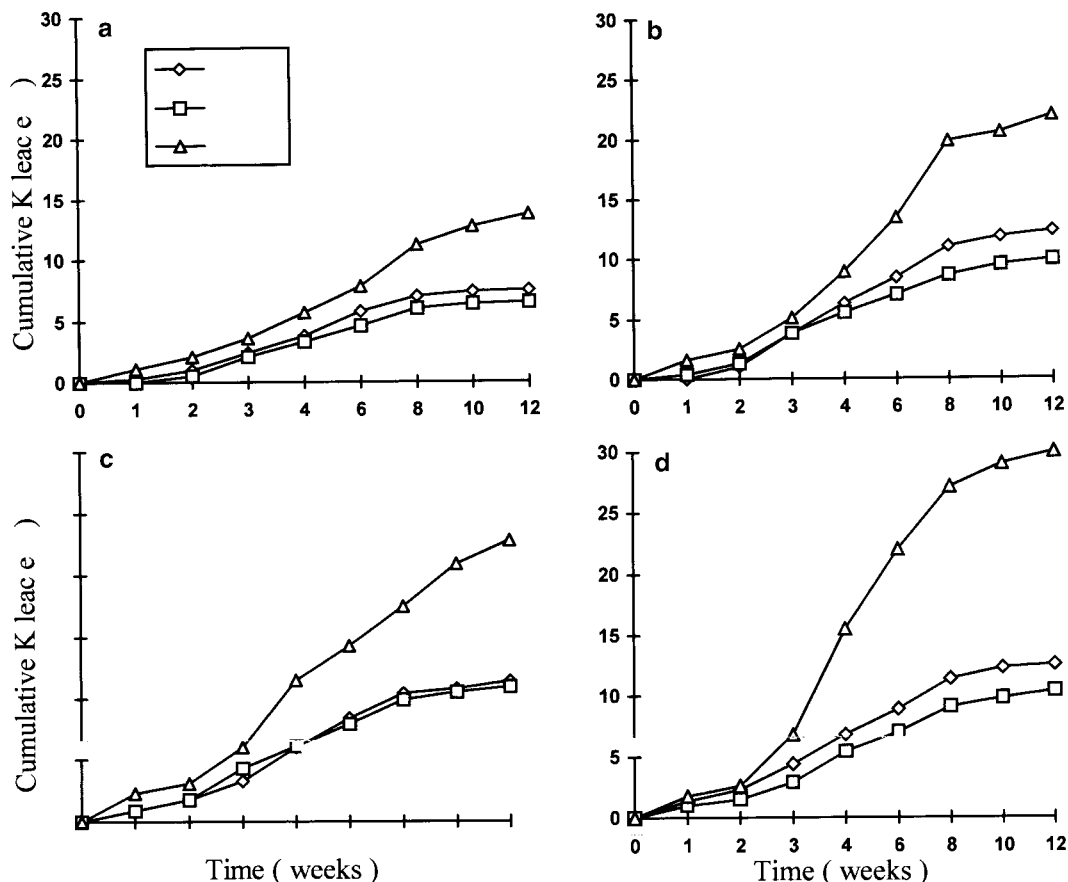
**Figure 1.** Soil column used.

**Table 1.** Characteristics of the Fertilizers Studied

type of fertilizer	fertilizer contents (%)				nutrient release rate (%) 7 days (20 °C)
	paraffinic wax	modified rosin	poly-ethylene	nutrient	
CRF1	28	1.75	5.25	65	47
CRF2	25	5	0	70	28

Among various controlled-release fertilizers (CRF), sulfur-coated urea (Blouin et al., 1971), coated superphosphate (Subrahmanyam and Dixit, 1988), and urea–formaldehyde condensates (Prasad et al., 1971) are typical examples.

In this laboratory study, polystyrene-based soil conditioners and both water-soluble and controlled-release fertilizers were investigated in soil columns. A sandy clay loam with medium fertility and water retention capacity was selected as a testing soil. Dissolution of two controlled-release fertilizers and their corresponding



**Figure 2.** Dependence of cumulative K leached from soil columns on various types of polymers and fertilizers. CRF1 and CRF2 stand for two types of CRFs and WSF is the corresponding water-soluble fertilizer. PSC1, PSC2, and PSC3 are three types of polymeric hydrogels with absorption of water 25, 65, and 100 (w/w), respectively. (a) No polymer; (b) polymer PSC1, (c) polymer PSC2, (d) polymer PSC3.

water-soluble fertilizers was studied in the presence and in absence of three polymeric soil conditioners differing in their absorption capacity of deionized water.

#### MATERIALS AND METHODS

The macroreticular soil conditioners and the controlled-release fertilizers used in this work were prepared in the Laboratory of Organic Chemical Technology of National Technical University of Athens (NTUA), according to methods found in the literature (Theodoropoulos et al., 1992; Kakoulides and Valkanas, 1994). Fertilizer draining experiments were performed in the laboratories of the National Agricultural Research Foundation (NAGREF).

**Soil Conditioners Preparation.** The matrix of the soil conditioner used in the experiments was prepared by post-polymerization cross-linking of atactic polystyrene using 1,4-dichloromethyl-2,5-dimethylbenzene as a cross-linking agent and sulfuric acid as a catalyst. The nonionic network produced was subsequently sulfonated, resulting in ionic networks possessing three different absorption capacities of deionized water: 25, 65, and 100 g of equilibrium water/g of dry polymer. These tailor-made soil conditioners were represented as PSC1, PSC2, and PSC3, respectively. It is stressed that these were various types of the same polymeric network, differing only in the mean molecular weight per cross-link.

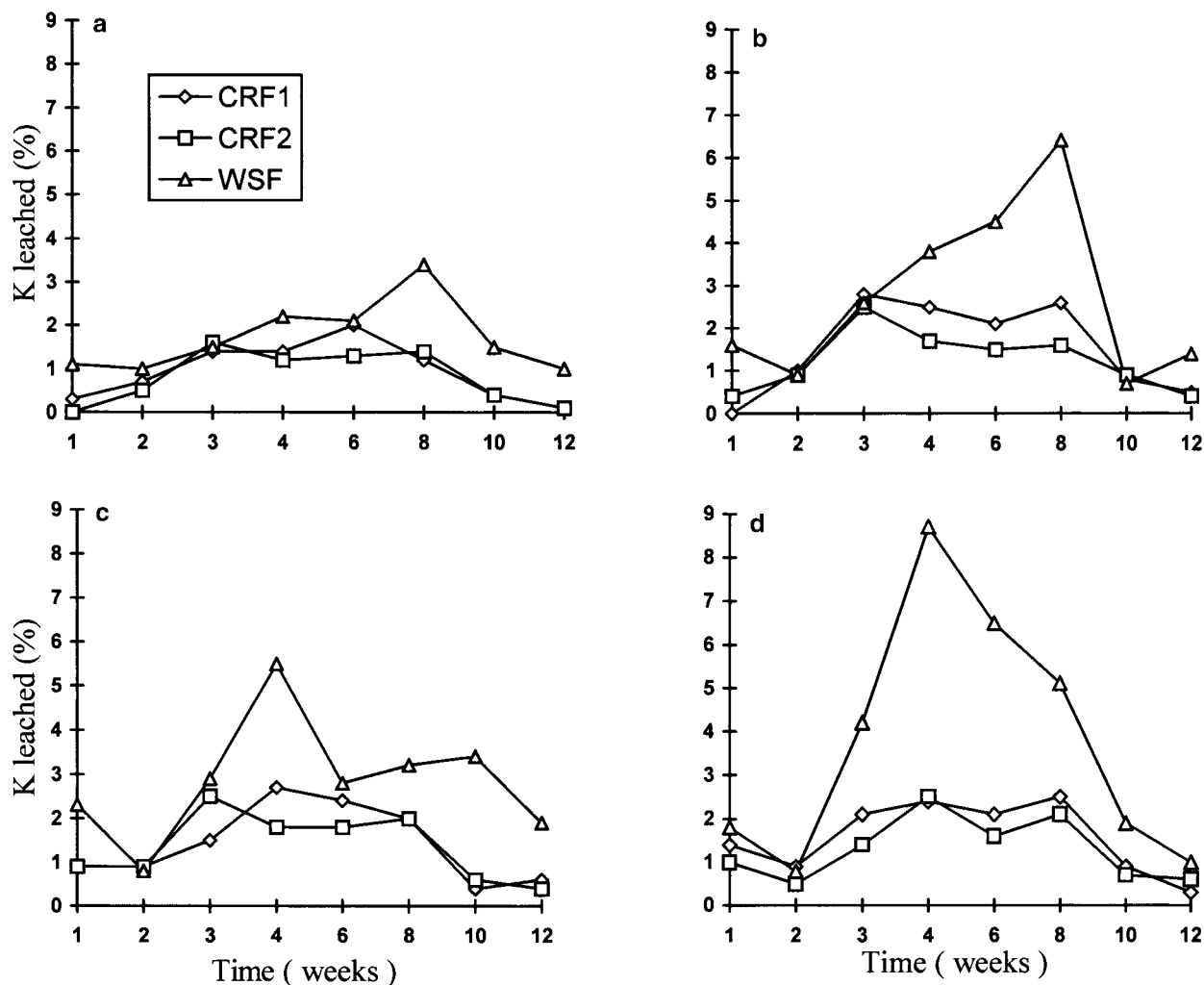
**Controlled-Release Fertilizers Fabrication.** CRFs were prepared by mixing paraffinic wax, modified rosin (dimer), and the active substance, i.e., the fertilizer. Two types of fertilizers were fabricated, the second type containing low molecular weight polyethylene in addition to the above materials. The characteristics of these CRFs and their symbolic names are shown in Table 1. CRFs were shaped by compression to small cylindrical pills of 6 mm diameter and 3 mm height.

**Table 2. Total K Recovered from 80 mg for Various Combinations of Fertilizers and Polymeric Soil Conditioners**

treatment	total K recovered in each leaching (mg)								total K <sup>c</sup> (mg)
	1st <sup>e</sup>	2nd <sup>e</sup>	3rd <sup>e</sup>	4th <sup>e</sup>	6th <sup>e</sup>	8th <sup>e</sup>	10th <sup>e</sup>	12th <sup>e</sup>	
Without Polymer in Soil									
control	2.0	0.5	0.8	0.7	0.3	0.7	0.5	0.6	6.1a
CRF1 <sup>a</sup>	2.2	1.1	1.9	1.8	1.9	1.7	0.8	0.7	12.1c
CRF2 <sup>a</sup>	2.0	0.9	2.1	1.6	1.4	1.8	0.8	0.7	11.3c
WSF <sup>b</sup>	2.9	1.3	2.0	2.4	2.0	3.4	1.7	1.4	17.1de
With Polymer PSC1 <sup>d</sup> in Soil									
control	2.9	0.7	1.3	1.2	0.5	0.9	0.7	0.8	9.0b
CRF1	2.9	1.5	3.5	3.2	2.2	3.0	1.3	1.2	18.8f
CRF2	3.2	1.4	3.3	2.6	1.7	2.2	1.4	1.1	16.9d
WSF	4.2	1.4	3.4	4.2	4.1	6.0	1.3	1.9	26.5g
With Polymer PSC2 <sup>d</sup> in Soil									
control	3.2	0.6	1.4	1.2	0.4	1.1	0.7	0.7	9.3b
CRF1	3.9	1.3	2.6	3.4	2.3	2.7	1.0	1.2	18.4ef
CRF2	3.9	1.3	3.4	2.7	1.8	2.7	1.2	1.0	18.0def
WSF	5.0	1.3	3.7	5.6	2.6	3.7	3.4	2.2	27.5g
With Polymer PSC3 <sup>d</sup> in Soil									
control	3.1	0.5	1.3	1.0	0.4	0.8	0.7	0.8	8.6b
CRF1	4.2	1.2	3.0	2.9	2.1	2.8	1.4	1.1	18.7f
CRF2	3.9	0.9	2.4	3.0	1.7	2.5	1.2	1.3	16.9d
WSF	4.5	1.2	4.6	8.0	5.6	4.9	2.2	1.6	32.6h

<sup>a</sup> Two different types of controlled-release fertilizers. <sup>b</sup> Water soluble fertilizer. <sup>c</sup> Means followed by the same letter within a column are not significantly different at 0.05 significance level. <sup>d</sup> Hydrogels with three different absorption capacities: 25, 65, and 100 g of water g<sup>-1</sup> dry polymer, at a soil content equal to 0.2% (w/w) (in cases these were used). <sup>e</sup> Leaching time in weeks.

**Soil Characteristics.** The soil used is characterized as sandy clay loam (SCL). It contained 19.2% (w/w) CaCO<sub>3</sub>, organic matter 1.4% (w/w), available phosphorus 22.9 mg kg<sup>-1</sup>



**Figure 3.** Dependence of K leached in every leaching of soil columns on time for various types of soil conditioners and fertilizers (CRF) in comparison with control (WSF). (a) No polymer, (b) polymer PSC1, (c) polymer PSC2, polymer PSC3.

dry soil, and exchangeable potassium  $0.88 \text{ mequiv } 100 \text{ g}^{-1}$  dry soil. Its pH was 8.04, its total cation exchange capacity (CEC) was  $17.5 \text{ mequiv } 100 \text{ g}^{-1}$  dry soil, and its water holding capacity was 33.8% (w/w).

**Experiments in Soil Columns.** The three fertilizers, the two types of CRFs and the corresponding water-soluble (powdered  $\text{K}_2\text{SO}_4$  with no binder), were combined with the three polymers at the 0% and 0.2% (w/w) levels. Four control treatments were installed, one of which contained only soil and the other three containing in addition each type of polymer.

PVC pipe of 30 mm internal diameter was cut into 500 mm length to hold soil. Each pipe was filled with 400 g of air-dried soil sieved to less than 2 mm to form a soil column of about 300 mm. In treatments where a polymer was used, a quantity of swollen polymer corresponding to 8 g of dry polymer was mixed with the above quantity of soil before placing into the PVC pipe. Fertilizers were put on the top layer of the soil columns and mixed intimately with soil to a depth equal to 50 mm. At the bottom of columns, a 50 mm layer of thin pebbles was placed below the soil. The materials in the columns were held by common filter paper supported by a plastic net (Figure 1).

With the exception of control treatments, in each column, 200 mg of K as  $\text{K}_2\text{SO}_4 \text{ kg}^{-1}$  dry soil was added for each type of fertilizer. Water was added after water saturation, and the columns were kept in a controlled temperature room at  $20 \pm 1 \text{ }^\circ\text{C}$ . Rinsing with 35 mm of deionized water 1, 2, 3, 4, 6, 8, 10, and 12 weeks after their installation resulted in a leachate of 15–25 mm water each time, from which K was determined

by the aid of a flame photometer. Values of K leached were corrected by deducting K values of control columns.

A completely randomized design was used for all experiments, with three replicates per treatment. Data were analyzed by analysis of variance and means were separated by LSD.

## RESULTS AND DISCUSSION

The K leached from the columns after each leaching was significantly greater when a polymeric soil conditioner was incorporated in soil (Table 2).

Measuring the rate of absorption of polymers, it was found that these gained 75% of their water capacity in 5 min. Upon mixing with soil, polymers were fully swollen, but during the 1–2 weeks intervals between subsequent rinses the deswelling process began in which water moved from polymer to soil. The polymers returned to their equilibrium water capacities during rinses.

The increased moisture content of soil, due to the presence of polymer, resulted in enhanced dissolution of CRFs and especially of water-soluble fertilizers (WSF). This increase in dissolution ranged from 59% to 117% for WSF in a 3 month period, whereas this ranged from 52% to 68% for CRF1 and CRF2 (Table 2).

The absorption capacity of gels seems to significantly affect this process only in the case of water-soluble K

(Table 2). It is obvious from this table that leached quantities of K increase with the absorption of water by polymers. In case of CRFs a small increase of leached K is also observed, but this is not significantly affected by the absorption of water. In polymers with high absorption of water (65 and 100 g of water g<sup>-1</sup> dry polymer), no increase in dissolution of CRFs fertilizers was observed in relation to that with absorption of water equal to 25 g g<sup>-1</sup>. This seems strange, but a deeper look in the dissolution mechanism of CRFs could offer some explanation. Thus, this mechanism may be devised in three stages (Figure 3). During the first stage, lasting about 2 weeks, soaking and penetration of water vapor into the pores of fertilizer takes place. This stage is characterized by a slow-release rate of nutrient elements. Yet, the reduced concentrations of K measured at the outflow of the column did not depend exclusively on the slow dissolution rate of fertilizers. The most significant factor in this effect seems to be the partial retention of K by the soil clay. This was confirmed by the reduced outflow concentrations of K observed also for the WSF during the first 2 weeks (Figure 3). The second stage (from second to tenth week) was characterized by a steady-state release of significant quantities of nutrient elements. During the third stage (from tenth week to the end of experiment), dissolution rate diminished significantly due to the limited ability of water vapor to open new pores in fertilizer granules. As clearly demonstrated in Figure 3, this stage is the slowest and is not affected at all by the absorption of water by polymer. The dissolution mechanism of these fertilizers in water was investigated by Kakoulides and Valkanas (1994). These authors found that the release rate of nutrient elements is almost totally controlled by the diffusion of water vapor inward and outward of fertilizer granules.

In this experiment, 85–90% of leached K came from the first two dissolution stages, requiring further investigation. The presence of polymers resulted in higher dissolution rates as compared to the cases without polymer, regardless the type of polymer (Figure 3). The dissolution rate of fertilizer granules was mainly affected by the porosity and tortuosity of matrix, as well as by the water content of soil (Kakoulides and Valkanas, 1994). Considering that the first two of these factors were constant in each type of fertilizer, the effect of soil moisture was investigated. The dissolution mechanism of these CRFs was based on the diffusion of water vapor from the surrounding soil through the pores into the granules (Hauk, 1972). On the other hand, increasing the moisture content within the range of field capacity does not have a marked effect on the vapor pressure of water in the soil (Parker, 1986). Thus, the increased moisture content caused by the polymers PSC2 and PSC3 did not affect significantly the dissolution rate of CRFs (Figure 2c,d) in relation to the case with use of polymer PSC1 (Figure 2b). Kochba et al. (1990) investigated the dissolution rate of four types of CRFs, selecting four levels of moisture content in soil (namely, 25, 50, 75, and 100% of field capacity). They found that no significant change of dissolution rate of CRFs occurred for moisture contents above 50% of field capacity. Prasad (1976) investigated the dissolution of sulfur-coated urea (SCU) in two soil types and three water contents. He found that, in one type of soil, dissolution of SCU increased with soil moisture. He also

observed a slight reduction of dissolution of SCU at the highest soil moisture in relation to the medium level.

Comparing under identical conditions the three types of fertilizers prepared, it was found that K leached from WSF is much more than that of CRFs fertilizers. Thus, leached K was from 84% to 112% more in WSF as compared to CRFs in the case of soil without polymer (Figure 2a). The highest relative increase in leached K (138–188%) relative to entrapped fertilizer was observed in the case of incorporation of polymer PSC3 in soil (Figure 2d).

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Received for review November 12, 1997. Accepted April 9, 1998.

JF970969F