Calcium delivery using UV polymerised HEMA:NVP hydrogel in soil

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Abstract

This paper reports results of preliminary testing to use hydrogels impregnated with water-soluble calcium salts as an alternative approach to improve soil sodicity. The polymer hydrogels used in this study were synthesised through the polymerisation of 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl pyrollidinone (NVP) which produced a polymer capable of absorbing water and returning to an original size when completely dehydrated. These HEMA:NVP polymers differ to polyacrylamide or polyglycol ester polymers because they will encapsulate then release incorporated contents under hydrated conditions. Milliequivant proportions to 10 t /ha calcium as calcium nitrate ($Ca(NO_3)_2.4H_2O$) in hydrogel and gypsum ($CaSO_4.2H_2O$) were applied to a silty sand and clay loam soil, with and without addition of recycled organic compost (ROC). Soluble salts as soil EC, exchangeable and soluble cations including Ca^{2+} and Na^+ and colloidal turbidity were compared. Results indicate that hydrogel applications provide a consistent delivery of calcium across all soil treatments and were successful in contributing to reducing exchangeable sodium (as ESP) and soil water turbidity. Aspects of nitrate leaching, concentration rates, timed delivery or biodegradability were not assessed.

Key Words

Soil polymer, HEMA-NVP hydrogels, calcium, controlled-release, sodicity.

Introduction

The polymer hydrogels used in this study were synthesised through the polymerisation of HEMA and NVP under the influence of an ultra violet source (Ng and Swami 2005). Being chemically and structurally different to other polymers polyacrylamide (Sojka *et al*. 2007) and polyglycol esters currently used in soil management to improve soil moisture and reduce erosion (Caufield *et al*. 2002), carry slow release fertilizer (Liu *et al*. 2007) or act as soil wetters (Weil *et al*. 1979); the HEMA:NVP hydrogel polymer are capable of absorbing water and swelling to more than 100 times their original size without being dissolved, retaining structure when completely dehydrated (Ng and Swami 2008). The HEMA:NVP hydrogels have originally been employed for studies in controlled-release in medical applications for delivering embedded drugs to target sites. Using a similar principle, it was possible that water soluble calcium salts could be embedded in neutral hydrogels and then be released when these hydrogels were incorporated in soils. When the soils were hydrated, the hydrogels would expand due to water absorption. The calcium ions that are held in the voids of the hydrogels would then be released into the soils by diffusion process.

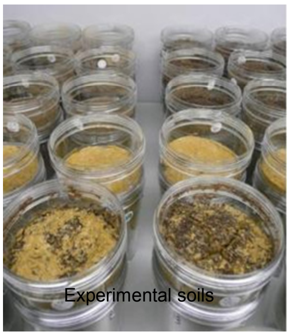
Methods

Preparation of hydrogels

Poly(2-hydroxyethyl methacrylate) (PHEMA) was synthesised from the monomer HEMA, whilst copolymers of HEMA and NVP were prepared with varying amounts of these 2 monomers. Aqueous $Ca(NO_3)_2.4H_2O$ (67% w/w) was added to each of the monomer solutions in a mass ratio of 11:18 in the presence of 0.1% Irgacure 819 (an initiator). The preparation was thoroughly mixed using a mechanical stirrer. 0.5 mL aliquots of the mixture which were introduced into disposable polyethylene graduated Pasteur pipettes, were allowed to be drained into the bulbs and subjected to UV exposure with a 90 W medium pressure mercury lamp model 93110E$_2$ for 10 minutes. All experiments were performed at room temperature. Preparations of hydrogel, as A, B and C had the mole ratio of HEMA:NVP=1:1, 1:0 and 1:3 respectively. Hydrogel A exhibited the optimum hydration capacity and was thus adopted as the hydrogel used in this study. All hydrogel tablets were encapsulated with 1.901 meq Ca^{2+}.

Typical hydrogel used in experiments

Testing comparison with gypsum



Delivery of encapsulated Ca^{2+} into soils was tested with a laboratory scale experiment. Local soils were selected: a dispersive yellowish clay loam of ESP >13, from a Dermosol profile (Jacquier *et al*. 1998) from Richmond NSW and a brown silty sand of ESP 2, of a Leptic Tenosol profile (Jacquier *et al*. 1998) from Penrith NSW. Because of the variable nature of clay soils and their sodic properties the sand was included as a control model.

Bulk experimental soils had been prepared as a stock mix, air dried, crushed and sieved (2 mm) with mixing by coning and quartering. Test soils were prepared in four replicates sets, with and without addition of recycled organic compost (ROC). The ROC was a product of slash pine (Bettergrow Pty Ltd, NSW) mixed with the soil to achieve a total organic carbon content of 3 %.

The hydrogel and gypsum applications were determined for a field application equivalent rate of 10 t /ha calculated for a 450 g soil mix. The hydrogel application consisted of five hydrogel tablets as 9.505 meq and 190.48 mg Ca. The gypsum application, based on an 18.5 % Ca content equated to 9.23 meq and 184.97 mg Ca. Compost had 9 cmol /kg exchangeable Ca^{2+} and although to make up 3 % TOC the addition of 21.3 g dry weight compost equated to 1.917 meq Ca and 38.42 mg Ca, this additional calcium content in ROC was not adjusted in hydrogel and gypsum treatments containing ROC.

Containers were drilled so that leachate from the soil mix could be separately retained. The holes were covered with filter paper and dry soil mixes added. All soil mixes were prepared to a standard weight of 450 g. Additions of hydrogel-encapsulated calcium or gypsum were placed into the surface, top 1 cm of soil for the experimental samples. A watering regime to soil field capacity was undertaken using Ultrapure deionised water and the leached portions retained in a sealed cup. Water applications were typical for each clay, sand or ROC mix. Watered soils in their containers were left open on the laboratory bench for 7d then evaporation losses were recharged. Moisture percentages were calculated.

For analyses only the lower one-third of soil in each container was used. Samples were air-dried and ground to pass a 2 mm sieve. Soil pH and EC were measured in 1:5 soil water extracts (Rayment and Higginson 1992) and exchangeable bases by equilibration with 1M ammonium acetate (CH_3COONH_4) at pH 7.0 at a soil/solution ratio of 1:10 without pretreatment for soluble salts (Rayment and Higginson 1992). Soluble cations and turbidity were determined on the leachate volumes (Rayment and Higginson 1992). Soluble and exchangeable cations were analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and were used to calculate ESP.

Results

The cycle of soil moisture recharge was quantified as moisture percentage (Figure 1). The moisture percentage was the net amount of water including evaporation. Evaporation produced a drying range of 5 % less than field capacity, recharged periodically. For the soils with ROC the ROC addition provided 10 % more moisture holding capacity, and thus a 10 % higher field capacity. This corresponded after experiment completion, to a lower bulk density for the ROC soils, particularly for the sand. Thus for the soils with ROC, their net moisture was the same whether a sand or clay soil.

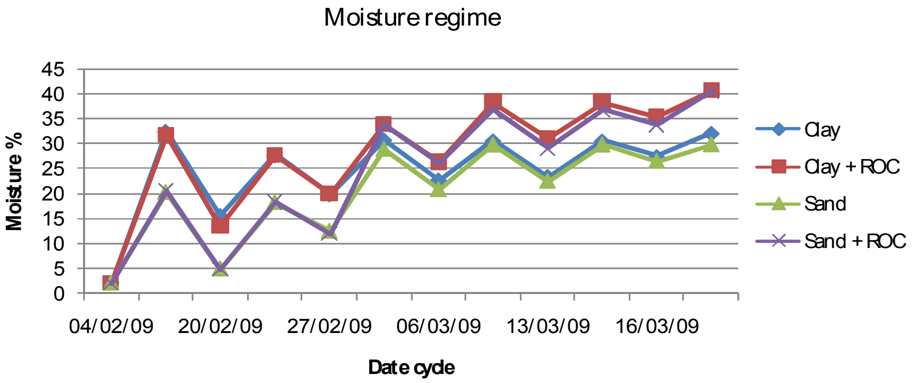


Figure 1. Plot of moisture addition commencing from dry to wetted.

The application of hydrogel and gypsum contributed to an elevated level of salts, being significantly higher than for control soils. EC values were lower for the sand than the clay. In all soil mixes EC values via hydrogel were higher than with gypsum and the level of soluble salts for both were elevated, which significantly reduced colloidal turbidity of the leachate water (Table 1). Further assessment for calcium delivery was determined by ESP comparison. Reductions in ESP were evident for the clay soils with hydrogel but with ROC added, were less evident. For the sand those mixes also responded to a calcium delivery via hydrogel, with ESP values lower than the controls.

Table 1. Soil and leachate properties of salinity and sodicity.

Treatment			Soil EC (dS/m)	95% CI	Leachate Turbidity (mg/L)	95% CI	Soil ESP (%)	95% CI
Clay and Clay Mixes	Clay	Control	0.15	0.01	36.5	27.254	18.1	1.97
		Hydrogel	0.38	0.02	0.7	0.567	15.5	1.58
		Gypsum	0.34	0.10	0.9	0.710	17.5	1.81
	+ ROC	Control	0.16	0.00	20.1	11.166	18.3	1.10
		Hydrogel	0.27	0.02	1.8	1.978	17.6	3.60
		Gypsum	0.23	0.02	2.7	1.245	16.7	1.18
Sand and Sand Mixes	Sand	Control	0.02	0.00	7.5	1.659	11.2	3.22
		Hydrogel	0.22	0.02	0.3	0.202	6.65	1.55
		Gypsum	0.10	0.01	1.2	1.169	8.08	2.32
	+ ROC	Control	0.03	0.00	7.8	7.217	8.18	1.92
		Hydrogel	0.14	0.01	0.2	0.109	6.20	1.67
		Gypsum	0.09	0.02	0.5	0.350	9.50	1.65

A difference between the sand and clay response to calcium delivery was further indicated by a comparison of the proportion of Na^+ and Ca^{2+} ions in leachate solutions (Figure 2 A and B). In the sand mixes hydrogels consistently provided elevated Ca^{2+} over Na^+ (Figure 2A) because the exchange complex did not take up the available calcium. In the clay mixes including the controls, Na^+ was higher than Ca^{2+} (Figure 2B) suggesting leached sodium, but more calcium was retained as an exchangeable cation proportion. Also evident was the lesser amount of soluble Ca^{2+} ion from gypsum, suggesting that Ca^{2+} delivery via hydrogel should be restricted in sandy soils.

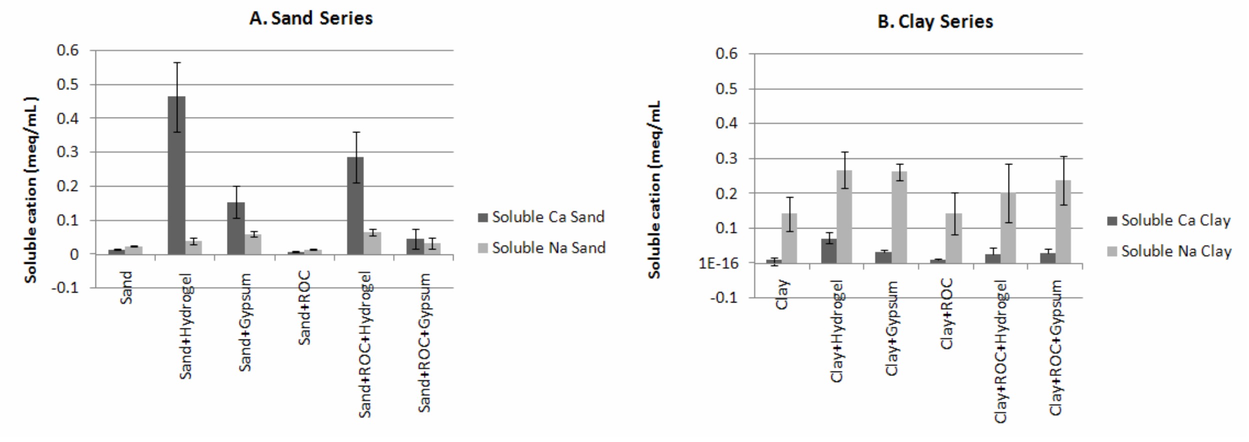


Figure 2. A and B. Soluble Ca and Na for sand and clay soils with hydrogel and gypsum treatments.

The comparison of hydrogel and gypsum application of calcium to the soil as exchangeable Ca^{2+}, over the 40d (6 week) experiment, is illustrated by Figure 3. Soil meq Ca, as delivered, was calculated for each treatment. The efficacy of calcium application via hydrogel compared to that for gypsum suggests the hydrogel provides a consistent delivery to all soil types providing calcium to the exchange complex more efficiently, which for the clay soils was 6 of the possible 9 meq Ca. Alternatively, in all other treatments they provided 4-5 of the possible 9 meq Ca. By comparison, gypsum provided 5 meq Ca to the clay, but less than 2 meq Ca for all other soil mixes. Thus the use of a soluble calcium source with the hydrogel will have benefits that will be immediate, rather than delivery being delayed and more variable via a gypsum application. In both cases not all the applied calcium was accounted for because analysis was only of the lower level soil and leachate.

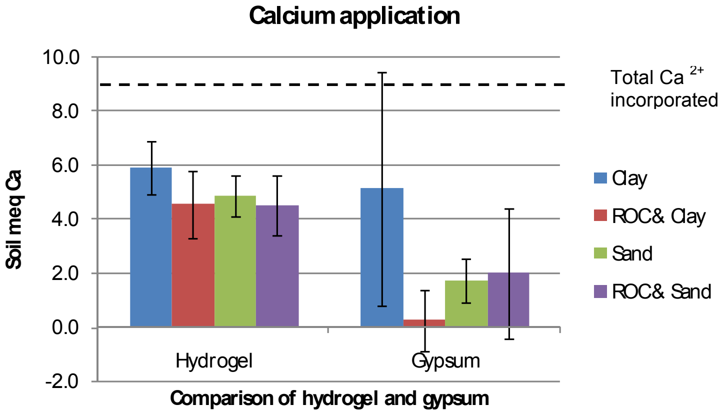


Figure 3. Calcium application hydrogel or gypsum for soils treatments.

In this study hydrogels were prepared with calcium nitrate $Ca(NO_3)_2.4H_2O$, which has a solubility of 138g/100g water (Aylward and Findlay 1971) and a molar ratio of calcium to nitrate ions is 2:1. However the efficacy of applying soluble calcium via hydrogel may be negated by addition of nitrate. As an artificial fertiliser nitrate is useful but is a problem if leached to groundwater (Bond, 1998). Thus a further investigation is required to consider the fate of nitrate as a factor of calcium delivery application via hydrogel. An alternative calcium salt is calcium chloride as $CaCl_2•6H_20$ with solubility of 83g/100g but the calcium to chloride ratio is 1:2 and would not be suitable for soil applications.

Conclusion

Although sustainability factors such as fate of nitrate and polymer biodegradability will require further assessment this study shows that encapsulation and release of soluble calcium via the 1:1 HEMA:NVP polymer-hydrogel, provides a more consistent delivery of calcium than gypsum, across a variety of clay and sand soil mixes with and without incorporated recycled organic compost. The hydrogel was successful in reducing exchangeable sodium (as ESP) and colloidal soil water turbidity. This was achieved with all soils hydrated to field capacity, even those with ROC addition.

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