Biopolymer additives to reduce erosion-induced soil losses during irrigation

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Received 8 April 1999; accepted 25 June 1999

Abstract

A series of biopolymers added to irrigation water were tested for their efficacy in reducing shear-induced erosion in a laboratory-scale mini-furrow. Suspensions of chitosan, starch xanthate, cellulose xanthate, and acid-hydrolyzed cellulose microfibrils, at concentrations of 20, 80, 80, and 120 ppm, respectively, reduced suspended solids by more than 80%. None of these biopolymers, however, exhibited the > 90% runoff sediment reduction shown by the present industry standard, synthetic polyacrylamide polymers, PAM. PAM is effective at concentrations as low as 5 ppm. In field tests, chitosan solutions were only marginally effective in reducing runoff from the end of a 137 m long furrow, with indications that results were dependent on the length of the furrow. Sediment runoff of some clay-rich Northern California soils was reduced by up to 85% by increasing the concentration of exchangeable calcium to > 2.5mM. Calcium improved the sedimentation of the polyelectrolytic polymers in this study. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Erosion; Soil stabilization; Polyacrylamides Chitosan; Xanthate; Biodegradable

1. Introduction

Soil erosion threatens water quality and agricultural productivity through the loss of valuable ‘top-soil’ and runoff of agricultural chemicals. Row-crop farmers in the US lose an average of 5800 kg of soil per acre per year, despite being world leaders in practicing soil conservation. The increasing evidence that chemical toxins readily pass from our waterways into the air (McConnell et al., 1998) increases the need to prevent chemicals, such as pesticides and herbicides, from leaving the field in runoff.

Soil loss is especially significant during furrow irrigation because of the shearing action of flowing irrigation water, and because arid soils often are low in the natural polysaccharides that stabilize soil structure. Farmers could minimize erosion-induced soil losses by stringent use of settling ponds, sodded furrows, straw-bedded furrows, minibasins, soil stabilizers, and buried runoff pipes; however, these techniques are often too cumbersome or costly for adequate adoption.
Recently, an easy and effective tool has been added to these soil conservation measures — adding small quantities of polyacrylamide copolymers (PAM) to the in-flowing water (Mitchell, 1986; Levy et al., 1991; Lentz et al., 1992; Lentz and Sojka, 1994; Wallace and Wallace, 1996). Lentz et al. (1992) added 5–20 ppm of high molecular weight anionic PAM to irrigation water in the first several hours of irrigation, and reduced soil losses of a highly erodible soil up to 97%. This represented an ideological breakthrough in the use of soil conditioners, in which only the soil in contact with irrigation water is modified. For furrow irrigation, this translates to improved soil structure in the 1–5 mm thick layer at the soil/water interface. Consequently, relatively small quantities of polymer are used, approximately 0.5–1.0 kg per hectare per irrigation, with seasonal application totals ranging from 2 to 7 kg of polymer per hectare.

The successful use of PAM in irrigation water raises the question of whether there are other polymers that may have similar benefits. Concerns have arisen about the widespread use of PAM in open agricultural environments — concerns that have been countered by various soil scientists studying PAM. PAM is a synthetic polymer that degrades at rates less than 10% per year via deamination, shear-induced chain scission and photosensitive chain scission (Kawai, 1993; Barvenik et al., 1996; Kay-Shoemake and Watwood, 1996). With such stability, the potential for accumulation exists.

The other environmental concern is the fact that acrylamide, the monomer used to synthesize PAM, is a neurotoxin. Even low levels of monomer impurity in the product must be avoided. This issue has been suitably addressed by suppliers who provide PAM almost devoid of monomer (< 0.05%). Concern that the monomer may occur as a degradation product is countered by studies showing that the most likely route to degradation is early removal of the amine group from the polymer backbone (Kay-Shoemake and Watwood, 1996).

Some of the uncertainties of associated with PAM use could be alleviated by using biopolymers that degrade more readily in the environment. Increasing scientific (Sojka et al., 1998b) and anecdotal evidence implies that PAM efficacy varies drastically with certain soil properties, including sodicity, texture, bulk density, and surface charge-related properties. It would also be beneficial to have a wide array of polymers with potentially different soil-stabilizing mechanisms, applicable to different soil types. Finally, PAM is a synthetic polymer using a non-renewable monomer source from oil refining. It would be advantageous to derive an effective soil amendment from a renewable feedstock, especially from an agricultural waste stream. Not only do natural polymers generally degrade via relatively benign routes; they are often perceived to be safer by the public.

The general objective of this study was to produce and screen a series of biopolymers to quantify their effectiveness as erosion retardants in irrigation water. Natural biopolymers derived from agricultural or natural by-products were selected specifically because of their potential environmental advantages, and because of their similar functional attributes to PAM. Important parameters for PAM are their large size, their affinity to soil, and their easy dispersion/solution in water. PAM obtains an affinity to charged soil particles because it is generally a copolymer of acrylamide and acrylic acid (Scheme 1).

Cellulose and starch xanthates are promising as potential alternatives to PAM, considering that they have been applied as flocculating agents (Maher, 1981; Coltrinari, 1994) and soil stabilizers (Meadows, 1956, 1959; Swanson, et al. 1975; Menefee and Hautala, 1978). Like PAM copolymers, xanthates carry a charge, they dissolve readily in water, and they are available with large molecular weights. The amylpectin component of a starch xanthate derivative is in the tens of

![Scheme 1. PAM: Poly(acrylamide-co-acrylic acid).](image-url)
Scheme 2. Starch or cellulose xanthate.

2. Materials and methods

2.1. Polyacrylamide (PAM)

Polyacrylamides from a variety of sources were used to establish parameters in the mini-furrow test and as a comparison of the biopolymer samples. PAM samples were random copolymers of acrylamide and acrylic acid (Scheme 1), varying in molecular weight, charge type, charge (acrylic acid) content, and relative solubility in water. A series of samples were provided by Cytec Industries of Stamford, CT, with the trademark, Magnifloc, and product codes 835A, 836A, 837A, 846A, 905N, 442C, 492C, and 494C. Cytec also provided several relatively short-chain samples specifically for this project. Samples were also provided by Allied Colloids, Suffolk, VA, and trademarked Percol (product codes 338, E24, and LT25). Additional PAM samples ranging in molecular weight from 40 000 to 15 million were purchased from Aldrich Chemical. Molecular weight and charge data were generally provided by the manufacturers. Stock solutions of PAM with concentrations of 0.2% (w/w) were prepared in tap water and metered into irrigation during laboratory and field test experiments.

2.2. Cellulose and starch xanthates

Cellulose xanthate was produced following the procedure of Menefee and Hautala (1978) using Whatman filter paper #4 as a source of pure cotton cellulose. Starch xanthates were produced according to Maher (1981) with the following starch sources: Midsol 50 wheat starch (Midwest Grain Products, Inc., Atchison, KS), Hylon VII high amylose corn starch (National Starch and Chemical Corp., Bridgewater, NJ), and potato starch (Avebe, Princeton, NJ). The cellulose or starch was swollen by soaking in 20% aqueous NaOH. After decanting off excess NaOH, molar volumes of carbon disulfide were added with mixing, forming an orange, sticky mass. After several hours of stirring, xanthates were diluted to a 2% solution (based on polysaccharide content), which presumably stopped the reaction and facilitated further dilution. The de-
gree of substitution, \( ds \), was estimated using a standard combustion method for sulfur content (Scroggins, 1973). The shelf life of xanthate is generally limited to several days, so samples were tested within 24 h after production.

2.3. Charged cellulose microfibrils

Acid hydrolyzed cellulose microfibril suspensions were formed from cotton fiber (Whatman filter paper #4) following a procedure outlined by Revol et al. (1992). Cellulose fibers were milled in a Wiley Mill to pass through a 40 mesh screen, added at 8% concentrations to 60% sulfuric acid at 60°C, and stirred for 30 min. The reaction was stopped by adding excess water, and the samples were centrifuged and washed repeatedly (at least three times) until free of salts and acid. According to the process of Revol et al. (1992), hydrolysis with sulfuric acid will create sulfate esters \((-\text{O}–\text{SO}_3^–)\) at the surface of the microfibrils. The procedure used here produces crystallites 0.2–0.5 microns in length (Orts et al., 1998), with a sulfonation level of \( \sim 10\% \). That is, the negative charge distribution covers 10% of the surface anhydroglucose units or roughly 0.2 sulfate groups per nm².

2.4. Chitosan

Chitosan was provided by Vanson, Inc., Redmond, WA. In general, chitosan was put into solution at high concentration by adding weak acid to lower the pH below 6.0. Before use, solutions were diluted and the pH was adjusted back to 7.0. This process was not required for a proprietary water-soluble chitosan, Klarify 101, designed by Vanson as a water-soluble, natural flocculating agent. It maintains its affinity to charged soil over a wide range of pH conditions.

2.5. Laboratory-scale mini-furrows

Laboratory-scale furrows were created based on furrows described by Stott et al. (1996). Except where noted, the soil tested in the mini-furrow was a Zacharias gravelly clay loam soil obtained from Patterson, CA, a northern California farming community 150 km south of Sacramento. This soil was chosen because it is typical of California’s Northern Central Valley and because anionic PAM has been particularly effective in controlling its erosion. Soils were dried, sieved and re-moisturized to 18% (w/w) water contents and then formed into miniature furrows roughly 1/100th the size of a full furrow. That is, 1500 g of moist soil was packed flat into a 2.5 × 2.5 cm well cut into a 1 m long bar. A furrow with dimensions 0.63 × 0.63 cm was pressed lengthwise down the center of the packed soil to create a mini-furrow. Test solutions were pumped down the furrow, set at an angle of 5°, at flow rates of 7 ml/min. Water was collected at the lower end of the furrow and tested for solids contents. Sediment concentration was determined by measuring turbidity using a Shimadzu UV-Vis UV1601 spectrophotometer, and calibrating turbidity with those from a set of pre-weighed soil dispersions. The relative suspended solids content was determined for at least five replicates per sample.

Multiple parameters affected the results of the furrow tests, including soil type, water flow rate, furrow slope, furrow length, water purity, and polymer properties. For example, if the flow rate is too high, even PAM is ineffective in clarifying the runoff. The mechanism for creating stable soil/PAM aggregates depends on their affinity, their size, and the presence of other ions, such as divalent calcium.

After some trial and error, conditions were selected for the mini-furrow so that results were reflective of the field tests results of Lentz and Sojka (1996). The results from the mini-furrow test are compared with those from the field (Fig. 1), showing the effect of PAM’s molecular weight, MW, on its efficacy. For the mini-furrow test, >95% solids are removed (relative to control) with no molecular weight dependence above MW = 200,000. A similar trend is seen for field tests results, although the sediment levels are higher and the molecular weight dependence is apparent up to MW = 6 million. Thus, the mini-furrow tests are more ‘sensitive’ than field test results. Such conditions were chosen to reduce the risk of missing polymers with potential (i.e. it was better to have false positive results than false negatives).
The tap water used in these experiments is low in exchangeable calcium and other salts. The electrical conductivity, ECO, is less than 0.2 dSm\(^{-1}\) (at 25°C). Such low calcium levels can result in poor water infiltration into soil and affect the ability of PAM to bind with soil (Wallace and Wallace, 1996). In some experiments where noted, exchangeable calcium was added to polymer stock solutions by dissolving calcium nitrate (Aldrich Scientific) at concentrations ranging up to 2.5 mM.

2.6. Field tests

Field furrow studies were conducted at the USDA-ARS Northwest Irrigation and Soils Research Laboratory at Kimberly, ID. The soil was a highly erodible Portneuf silt loam (coarse-silty, mixed, mesic, Durixerolic Calciorthid). The furrow had a slope of 1.5% and a length of 137 m. Irrigation water was from the Snake River, with an average electrical conductivity of 0.5 dSm\(^{-1}\) and a sodium adsorption ratio (SAR) of 0.6 (Carter et al., 1973). Irrigation water was applied from individually regulated valves on gated pipe to conventionally prepared furrows between rows of silage corn. During the initial advance stage of irrigation, the water inflow rate was set at approximately 23 l/min. Polymer samples were metered into the flow from 0.2% (w/w) stock solutions at the top of each furrow via calibrated peristaltic injection pumps. The final concentration of PAM or chitosan in the furrow was 10 or 20 ppm as noted. Further details of the irrigation and runoff monitoring procedure were described previously (Lentz, et al., 1992; Lentz and Sojka, 1996; Sojka et al., 1998a). Sediment content was measured at the end of furrows by collecting 1 l of sample and measuring sediment using the Imhoff cone technique, and pre-calibrated turbidity measurements (Sojka, et al., 1992; Trout et al., 1995).

Fig. 1. Laboratory-scale furrow results compared with field test results highlighting the effect of molecular weight on the effectiveness of polyacrylamide, PAM, in controlling erosion-induced soil losses. Curves are drawn between data points in order to guide the eye.
3. Results and discussion

3.1. Cellulose and starch derivatives

Results of laboratory-scale furrow tests for cellulose xanthate samples are shown in Fig. 2. Cellulose xanthate (degree of substitution, ds = 1.7) reduces soil runoff by more than 80% when it is applied at 80 ppm or greater. In comparison, PAM under the same conditions effectively reduces runoff at 10 and even 5 ppm to less than 3% of the control (or 97% sediment removal). Thus, PAM is significantly more effective than cellulose xanthate at concentrations only 1/8th those of the xanthates. Similarly high concentrations are required for starch xanthates produced from wheat, corn and potato starch. Interestingly, there is no significant difference between xanthates from wheat, corn or potato, provided the degree of substitution is relatively high (ds > 0.38).

As outlined in Table 1, cellulose microfibrils also reduced the irrigation-induced erosion in mini-furrow experiments. Concentrations of at least 100 ppm were required to exhibit any significant reduction in runoff sediment, with a concentration of 120 ppm resulting in 78% reduction. In contrast, PAM (Cytec Magnifloc 836A) removed 98% of solids at 10 ppm.

It is clear that cellulose and starch derivatives have some potential to reduce soil runoff during irrigation. Whether xanthates or cellulose microfibrils could compete with PAM in the marketplace, however, is unclear. The main commercial use of xanthate is as an intermediate in the viscose production of rayon fiber, with costs less than $2 per kg, compared with PAM at $5.50–11.00 per kg. However, several major drawbacks of xanthate must be overcome. Their relative instability means that they have a shelf life of days or weeks. Meadows (1956, 1959) developed strate-
gies to extend the shelf life by removing the water, by storing at cooler temperatures, by storing in vacuum-sealed packages, and by adding dehydrating agents, such as CaO.

Xanthates themselves may be environmentally benign, or even beneficial; however, xanthate production presents an environmental risk. Xanthate additives would degrade in a relatively benign mode, and may even provide a source of sulfur to highly calcareous soils low in sulfur. However, the Viscose process for producing rayon fibers via xanthates is becoming increasingly obsolete because of the sulfur-based waste products generated during large-scale production. The washing process during production leaves large quantities of sulfur-tainted water.

Similar arguments hold for charged cellulose microfibrils. Although relatively high concentrations of cellulose would be required to effect erosion, microfibrils hold some promise, considering that cellulose microfibrils have been produced industrially at lower prices than PAM. Their performance could be potentially improved by optimizing reaction conditions and by varying the source of cellulose. For example, sugar beet microfibrils are up to 1 μm long and 50 nm in diameter, significantly larger than the fibers derived from cotton (Dufresne and Cavaille, 1999). Larger microfibrils would stabilize larger soil aggregates by spanning between a greater number of particulates. An optimal charge distribution on the outer surface of the microfibrils would likely improve aggregate stability.

Cellulose microfibrils are attractive because they are readily available from various waste agricultural sources, such as wheat and rice straws, sugar beet fiber, and cotton wastes (including recycled cotton). Within the next several years, EPA guidelines and state mandates will prevent farmers in western states from burning rice straw between seasons. Thus, such straws could be a low-cost source of microfibrils.

3.2. Chitosan: laboratory-scale and field tests

Laboratory-scale mini-furrow results outlined in Table 2 show that highly deacetylated chitosan at 20 ppm was as effective as PAM in reducing erosion-induced soil losses. With such favorable mini-furrow results, chitosan was further tested in a series of field tests at the USDA Northwest Irrigation and Soil Research Lab, Kimberly ID. In the field tests, chitosan did not reduce erosion induced soil losses relative to the control (see Table 2). The sediment concentration in the runoff water from chitosan treated furrows was, at best, an order of magnitude higher than that of PAM (although results for the chitosan furrows

<table>
<thead>
<tr>
<th>Additive</th>
<th>Soil conc. in runoff (mg/L)</th>
<th>Soil conc. in runoff (% of control)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (tap water)</td>
<td>51.5 ± 4.2</td>
<td>100</td>
</tr>
<tr>
<td>PAM (Cytec 836A); 10 ppm</td>
<td>0.99 ± 0.54</td>
<td>1.9</td>
</tr>
<tr>
<td>Cellulose xanthate; 80 ppm; (ds = 1.7)</td>
<td>9.8 ± 2.2</td>
<td>19.3</td>
</tr>
<tr>
<td>Wheat starch; 80 ppm; (ds = 0.0)</td>
<td>50.6 ± 6.7</td>
<td>98.6</td>
</tr>
<tr>
<td>Wheat starch xanthate; 80 ppm; (ds = 0.38)</td>
<td>12.9 ± 5.8</td>
<td>25.0</td>
</tr>
<tr>
<td>Wheat starch xanthate; 80 ppm; (ds = 0.54)</td>
<td>9.4 ± 4.9</td>
<td>19.1</td>
</tr>
<tr>
<td>Potato starch xanthate; 80 ppm; (ds = 0.47)</td>
<td>6.7 ± 3.1</td>
<td>12.9</td>
</tr>
<tr>
<td>High amylose corn starch (Hylon VII) xanthate; 80 ppm; (ds = 0.45)</td>
<td>7.5 ± 1.8</td>
<td>14.5</td>
</tr>
<tr>
<td>Cellulose microfibrils; 120 ppm</td>
<td>11.0 ± 4.8</td>
<td>21.3</td>
</tr>
</tbody>
</table>

a The soil used for this study had a pH of 7.5, exchangeable Ca of 7%, and ~5% organics. Calcium nitrate was added to the water, at a concentration of 10 ppm, to ensure ionic bridging.
b Standard deviations are reported based on five replicates per sample.
Table 2
A comparison of polyacrylamide, PAM, (MW ~16 million, 18% anionic) and chitosan solution in controlling irrigation-induced sediment loss in a laboratory-scalea and a field furrow test

<table>
<thead>
<tr>
<th></th>
<th>Control (tap water)</th>
<th>PAM (10 ppm)</th>
<th>Chitosan (10 ppm)</th>
<th>Chitosan (20 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lab mini-furrow resultsb</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids in runoff (mg/l)</td>
<td>48.1a</td>
<td>3.4b</td>
<td>5.5b</td>
<td>4.2b</td>
</tr>
<tr>
<td>Solids in runoff (% of control)</td>
<td>100</td>
<td>7.1</td>
<td>11.4</td>
<td>8.7</td>
</tr>
<tr>
<td><strong>Field test resultsb</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment in runoff (kg/ha)</td>
<td>38745a</td>
<td>268b</td>
<td>18981a</td>
<td>24566a</td>
</tr>
<tr>
<td>Solids in runoff (% of control)</td>
<td>100</td>
<td>0.7</td>
<td>49.0</td>
<td>63.4</td>
</tr>
</tbody>
</table>

a No calcium was added to the irrigation water.
b Results within a row with a different letter are significantly different from each other.

were highly variable). The only results significantly different from controls were for PAM (Cytec Magnifloc 836A), whereby sediment losses were reduced by 99% relative to controls.

Such poor comparative results, however, do not mean that chitosan had no effect on the irrigation. Observations of the chitosan-treated furrows revealed remarkable results in the first ~20 m of the furrow. Chitosan acted as a very effective flocculating agent by removing fine sediments, and even algae from the irrigation water. In the first 20 m, the chitosan-treated furrows became green in color due, presumably, to algae build-up. In contrast, the control furrows or PAM-treated furrows did not attain a greenish hue during irrigation. Apparently, the flocculation aspect of chitosan works at least on a par with that of PAM. One explanation for the inability of chitosan to control erosion in a long furrow is that the chitosan binds so readily with sediment that it flocculates out of solution near the beginning of the furrow and is unavailable to reduce sedimentation losses in the lower end of the furrow. Such an explanation implies that the role of chitosan is dependent on furrow length.

Another explanation is that chitosan, lacking the size of the high molecular weight PAM, does not form a large stable soil/polymer network at the soil surface. Even though chitosan forms stable aggregates, as noted by its effectiveness at removing sediment in the first 20 m of the furrow, that may not be enough. Sojka et al. (1998a) points out that PAM not only forms stable flocs with soil suspended in water, but also interacts with the soil at the water/soil interface to create a protective network of PAM/soil aggregates. In a PAM-treated furrow, very little sediment is stirred up in the water from the outset. Rather, a network forms immediately at the furrow surface that prevents shear forces from disrupting the surface structure and improves water infiltration efficiency. The high molecular weight of PAM allows it to be effective at very low concentrations (5–20 ppm in the irrigation water) by forming large network structures.

3.3. Calcium effects

One of the interesting results of this study was the fact that improvements in soil runoff in the lab furrow test were achieved independent of the presence of PAM. To explore this result further, we utilized a soil from Davis, CA that did not respond well to PAM. The soil was highly calcareous with a pH of 8.4 and a low concentration of soluble, exchangeable calcium. As shown in Fig. 3, calcium alone significantly reduced suspended solids in the runoff from this soil, although PAM and calcium still had a greater effect than calcium alone. A similar result was also reported by Wallace and Wallace (1996), who noted that exchangeable calcium (gypsum) or other ions that improve electrical conductivity (Shainberg et al., 1989, 1990) also reduce erosion losses in clay-rich soils. The results in Fig. 3 confirm their observations in a laboratory environment. It is important to note, though, that the calcium effect would not necessarily be universal.
Fig. 3. The effect of added calcium on suspended solids in soil runoff from a laboratory-scale mini-furrow test for water with (●) and without (▲) PAM. PAM is 18% anionic with MW = 16 million.

Many sources of irrigation water have a much higher electrical conductance or exchangeable calcium than the tap water or canal water found in Northern California. More notably, the benefit from added calcium is short term. Calcium must be added continuously to the irrigation water. In contrast, PAM can be added for a short period during an initial irrigation series, and provide a lasting effect for weeks without additional doses.

4. Conclusions

Different polymer additives in irrigation water were tested for their efficacy in reducing soil losses during irrigation. Starch xanthate, cellulose xanthate, and acid hydrolyzed cellulose microfibrils all appear promising for reducing soil runoff. The effective concentrations of these derivatives, however, were 8–16 times higher than for PAM, and did not match its full effectiveness. Because these polymers are cheaper than the high-purity PAM employed here, they may still be economical.

Tests with chitosan solutions showed that there are some discrepancies between field and laboratory results. In laboratory-scale mini-furrows, chitosan solutions were effective at controlling erosion-induced soil losses at concentrations approaching those used for PAM. However, in field tests, the effectiveness of chitosan was highly variable, with no clear improvement over controls. A likely explanation is that chitosan does not have the molecular size of PAM, preventing it from forming large stable soil/polymer networks at the furrow surface. Another possibility is that chitosan binds too readily with sediment, and settles out of solution near the top of the furrow, an implication that the effectiveness of chitosan depends on the length of the furrow. In conclusion, laboratory tests are useful for screening potentially useful polymers for reducing erosion-induced soil losses, however field tests with longer furrows and potentially higher shear forces are required to assess market readiness.
Interestingly, the addition of calcium nitrate to irrigation water, with or without polymer additive, can reduce the amount of soil runoff for the clay-rich soils and relatively pure water encountered in Northern California. The addition of exchangeable calcium, however, would not have the long-term effect on soil structure exhibited by PAM.

Although biopolymer additives did not reach PAM’s efficacy in these tests, results show that biopolymers can reduce erosion-induced sediment loss, especially if their properties are optimized for their specific application. The performance of the biopolymers may already be in a range of effectiveness to be tried in various other related uses besides furrow irrigation. These include erosion reduction at construction sites and highways, tackifying straw beds (so they stay in place), and hydroseeding. In such applications, the costs of material are not the limiting restriction. The environmental advantages of degradable polymers derived from renewable sources may give these biopolymers an economic advantage over other materials. In addition, all of the biopolymer alternatives to PAM studied here would be considered as a source of polysaccharides to arid soils that generally lack structural polysaccharides. Their addition would generally be regarded as environmentally beneficial, with little concern about long-term accumulation.

Acknowledgements

The authors thank Youngla Nam and Jim Foerster for their superior technical support, and Michael McElhinney, USDA Natural Resources Conservationist, Modesto, CA, for helpful discussions and for supplying characterized soil samples. The authors thank Ray Farinato of Cytec, Inc. for his any helpful insights into the nature of PAM polymers, and for providing characterized samples. This work was partially supported by the Washington and Idaho Wheat Commissions under ARS agreement 58-5325-7-850.

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