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SYNTHETIC- AND BIO-POLYMER USE FOR RUNOFF WATER QUALITY MANAGEMENT IN IRRIGATED AGRICULTURE

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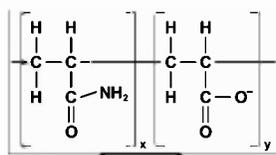
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Abstract: Low concentrations of synthetic- or bio-polymers in irrigation water can nearly eliminate sediment, N, ortho- and total-P, DOM, pesticides, micro-organisms, and weed seed from runoff. These environmentally safe polymers are employed in various sensitive uses including food processing, animal feeds, and potable water purification. The most common synthetic polymer is anionic, high purity polyacrylamide (PAM), which typically provides 70-90% contaminant elimination. Excellent results are achieved adding only 10 ppm PAM to irrigation water, applying 1-2 kg ha⁻¹ per irrigation, costing \$4-\$12 kg⁻¹. Biopolymers are less effective, but show promise; they include starch co-polymers, microfibril suspensions, chitin, polysaccharides and protein derivatives. Using twice or higher concentrations, existing biopolymers are ~60% effective as PAM, at 2-3 times the cost kg⁻¹. A half million ha of US irrigated land use PAM for erosion control and runoff protection. The practice is spreading rapidly in the US and worldwide. Interest in development of biopolymer surrogates for PAM is high. If the supply of cheap natural gas (raw material for PAM synthesis) diminishes, industries may seek alternative polymers. Also “green” perceptions and preferences favor biopolymers for certain applications. More complete history, user/technical information and bibliography are found at <<http://www.nwisrl.ars.usda.gov/pampage.shtml>>.

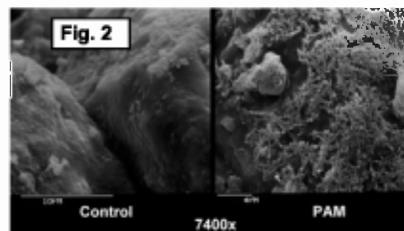
KEYWORDS: PAM, TMDL, Pollution, Erosion, Sediment, Contaminant

Introduction: Polyacrylamide and the acronym PAM refer to a class of polymers, varying in chain length and number or kinds of functional group substitutions. In PAMs used for, erosion control, the polyacrylamide homopolymer is copolymerized. Typically one if five PAM amide functional groups are replaced by groups containing sodium ions or protons that dissociate in water, providing negative charge sites in those chain segments (Fig. 1). Coulombic and Van der Waals forces attract soil particles to PAM (Orts et al., 1999, 2000). The surface attractions stabilize soil structure by enhancing particle cohesion, increasing resistance to shear-induced detachment



and transport. Figure 2 is a scanning electron micrograph showing mesh-like PAM strands binding silt sized soil particles. A minute amount of Ca⁺⁺ in water shrinks the electrical double layer surrounding particles, bridging the particle-PAM surfaces, enabling flocculation (Wallace and Wallace, 1996; Orts et al., 2001).

The large Na⁺ hydrated radius prevents ion bridging, causing dispersion of solids. PAM performance declined when irrigation water SAR rose from 0.7 to 9.0 [m mol_c L⁻¹]^{0.5} (Lentz and Sojka, 1996). PAM formulations for erosion control are water soluble (not gel-forming, cross-linked or super absorbent) anionic polymers with molecular weight of 12-15 Mg mole⁻¹ (≥150,000 monomer units per molecule). They are “off the shelf” industrial flocculents used in mining, biosolids dewatering, paper production, clarifying refined sugar and fruit juices and to thicken animal feeds. In the 1990s PAM was shown to be an effective erosion-preventing and infiltration-enhancing polymer for furrow irrigation of fine to medium textured soils (Lentz and Sojka, 1994; Sojka and Lentz, 1997; Sojka et al., 1998a,b). The US Natural Resource Conservation Service issued PAM-use standards (NRCS, 2001). PAM is now also used for construction site and road cut protection (Roa et al., 2000), and interest is growing worldwide. Several biopolymers perform similar to PAM but have yet to achieve sufficient efficacy at low enough rates or costs to displace PAM for most uses (Orts et al., 1999, 2000).



Methods: Our paper summarizes several related studies using similar methods. PAM or biopolymers were dissolved in water at typical concentrations of 1-10 ppm. The effects of water and PAM solutions flowing over or sprinkled onto sloping soil surfaces (1-2%) were compared for runoff constituents and amount (or infiltration). Some studies applied PAM granules as a powder “patch” to the soil surface in the 1-2 m immediately below furrow inflow points, allowing PAM to dissolve into the flowing water. Some were field studies; others were laboratory studies using soil bins or soil columns. Column studies monitored effects of PAM solutions on hydraulic conductivity and leaching.

Detailed methods and results for all the studies discussed in this paper are available at <http://www.nwisrl.ars.usda.gov/publist.shtml>. We focus on our more recent findings.

Results and Discussion: *Sediment and Nutrients:* PAM, applied in furrows as a powder patch, reduced sediment in runoff 37, 97 and 98% for 7.5, 15.0 and 22.5 L min⁻¹ flows from a 40 m field (Entry and Sojka, 2003). Low control treatment erosion at the 7.5 L min⁻¹ flow rate accounted for the greater relative erosion reduction at higher flows. Table 1 gives nutrient and sediment losses in surface runoff with PAM treatment for three flow rates as percent of mass loss from control plots.

L min ⁻¹	Kjeldahl N	NO ₃	NH ₄	Dissolved Reactive P	K
7.5	5.7*	30.0*	133.3	8.7*	52.6*
15.0	20.0*	21.7*	138.4	6.3*	48.9
22.5	5.7*	31.8*	144.4*	7.7*	49.1*

* Differs from control at P≤0.05 for a given flow rate. Export of DOC, Ca, Mg, Fe, Cu, B, and Zn in PAM-treated runoff is statistically same as controls. Data adapted from Entry & Sojka (2003).

Table 2 gives sediment and elemental losses in surface runoff of PAM-treated plots (dissolved plus adsorbed on sediment), for three flow rates (expressed as percent of mass loss from control plots).

L min ⁻¹	Sediment	C	N	P	K	Ca	Mg	Mn	Fe	Cu	B	Zn
7.5	63.5	70.7	63.5	63.6	63.5	63.9	62.9	64.0	63.4	64.1	75.0	71.4
15.0	3.1*	3.0*	3.1*	3.1*	3.1*	3.1*	3.1*	3.1*	3.1*	<0.1*	<0.1*	3.1*
22.5	2.5*	2.5*	2.3*	2.5*	2.4*	2.4*	2.5*	2.5*	2.5*	<0.1*	0.2*	0.2*

* Differs from control at P≤0.05 for a given flow rate. Data adapted from Entry and Sojka (2003).

For all but one case, whether as dissolved water components or as nutrients in transported sediment, there was either substantial removal of contaminants from the runoff stream or no statistically significant effect of PAM treatment. Export of dissolved NH₄ increased at the highest flow rate. While a large percentile increase, there was only 2.6 mg ha⁻¹ total export of NH₄ and only 0.8 mg ha⁻¹ increase over the control at the same flow rate. It is not entirely clear how NH₄ was elevated by PAM treatment; the data may simply represent Type II statistical error. It is also conceivable that the small amount of urea included in commercial PAM formulations may have affected the NH₄ balance in the furrow stream. Overall, these data show PAM's ability to nearly prevent erosion and thereby greatly reduce sediment and nutrient contamination of irrigation runoff and return flows that pollute riparian waters. Table 2 shows that total nutrient losses are dominated by sediment-adsorbed nutrients. These data agree with and expand upon studies from the 1990s that showed reduced sediment and nutrient contents of furrow irrigation runoff with PAM treatment.

Microorganisms and Weeds: Sojka and Entry (2000) showed that microorganisms were also effectively removed from furrow irrigation streams when PAM was used to control erosion (Table 3). In this case microorganisms were not killed, but merely sequestered via the same kind of flocculation process that held mineral particles. This result has important implications for the epidemiology of soil- and water-borne phyto-pathogens affecting crop production. The potential for pathogen spread both within fields in furrow irrigation water and to neighboring fields via re-used runoff water are reduced. This in turn has implications for environmental protection because of potential reduced application of disease controlling agrichemicals. There are also potential public hygiene impacts via reduced coliform losses from manure-treated fields into public waters. These points have been documented in detail in a series of studies examining microbial losses in a variety of irrigated agricultural settings (Entry and Sojka, 2000; Entry et al., 2002; Spackman et al., 2003). Column studies also demonstrated PAM's ability to reduce transmission of coliform bacteria to groundwater via leaching (Entry et al., 2000, 2003). PAM's ability to sequester microbes can be enhanced by mixing it with Al₂SO₄ or CaO (Entry and Sojka, 2000; Entry et al., 2003).

Table 3. Microbial biomass (as $\mu\text{g C ml}^{-1}$) in PAM-treated runoff, at 3 flow rates, as % of controls.

L min ⁻¹	Active Fungi	Active Bacteria	Total Fungi	Total Bacteria	Algae	Active Microbes	Total Microbes
7.5	<0.1*	40.4	0.8*	9.8*	8.2*	2.6*	10.4*
15.0	10.8*	31.9*	6.8*	38.1*	9.1*	25.1*	11.1*
22.5	12.3*	61.6*	4.0*	42.9*	11.0*	41.6*	26.7*

* Differs from control at $P \leq 0.05$ for a given flow rate. Data adapted from Sojka and Entry (2000).

Weed seed is also sequestered by PAM treatment of furrow irrigation. Sojka et al. (2003), applying PAM either as a powder patch or dissolved as a 10 ppm solution in the water first crossing the field (only), found weed seed reductions in runoff as high as 99.9% among six weed species (Table 4). Their data showed that PAM-treated furrows had greater weed emergence because seed was not lost in runoff and emerging seedlings were not excavated before taking root. Where soil was treated with preplant incorporated herbicides, although more seeds emerged with PAM treatment, they grew poorly producing greatly reduced biomass, or did not survive through the season.

Table 4. Seed of 6 weed species in patch or dissolved PAM-treated runoff as % of controls in 2 yrs.

Species	Kochia		Lambs-quarters		Redroot Pigweed		Hairy Nightshade		Barnyard Grass		Common Mallow		Total	
	97	98	97	98	97	98	97	98	97	98	97	98	97	98
Soln.PAM	37.1	4.1*	24.6*	8.6*	36.2*	8.9*	33.8*	5.7*	<0.1*	<0.1*	82.1	<0.1*	31.0*	7.7*
Patch PAM	29.5	7.6*	36.8*	15.6*	58.1*	4.3*	30.2*	7.0*	<0.1*	62.2*	16.7	<0.1*	45.4*	12.3*
PAM Avg	33.3	5.9*	30.7*	12.1*	47.2*	6.6*	32.0*	6.4*	<0.1*	31.1*	49.4	<0.1*	38.2*	10.0*

* Differs from control at $P \leq 0.05$ for a given treatment. Data adapted from Sojka et al. (2003). Latin names, respectively: *Kochia scoparia* L., *Chenopodium album* L., *Amaranthus retroflexus* L., *Solanum sarrachoides* L. Sendtner, *Echinochloa crus-galli* L., *Malva neglecta* Wallr.

Reduced weed seed numbers in runoff has significant production, environmental and hygiene implications. Reduced seed migration across a field reduces the spread of weeds and related herbicide application needs and costs. Because return flows are often collected and used downstream, reduced seed numbers in return flows reduces the spread of weeds among neighboring fields and further reduces the cost and environmental consequences of herbicide use, as well as potential human exposure during herbicide application and from herbicide contained in runoff entering riparian or recreational waters. In recent years, interest in the use of PAM to control erosion on road cuts and at construction sites has increased (Roa et al, 2000). Some contractors use PAM in hydroseeding mixes; the Sojka et al. (2003) data verify PAM's efficacy for holding planted seed in place against erosion while soil is bare, allowing germination and ground cover establishment as a permanent protection against erosion.

Soil Porosity and Infiltration: Because polymers used in irrigation water to control erosion do so by affects on soil surface structure and solution viscosity, they also affect infiltration characteristics. PAM infiltration effects are a balance between surface seal prevention and increased apparent viscosity in soil pores. In pore diameters >10 mm, PAM effect on viscosity was negligible at 15 and 30 C (Bjorneberg, 1998) and only rose substantially after PAM exceeded 400 kg ML⁻¹. But in small pores, apparent viscosity increases greatly, even at low concentrations used for erosion control (Malik and Letey, 1992). The more significant effect in medium to fine textured soils, is seal prevention. Figure 3 shows a furrow after irrigation with untreated water on the left, with a slick sealed surface,

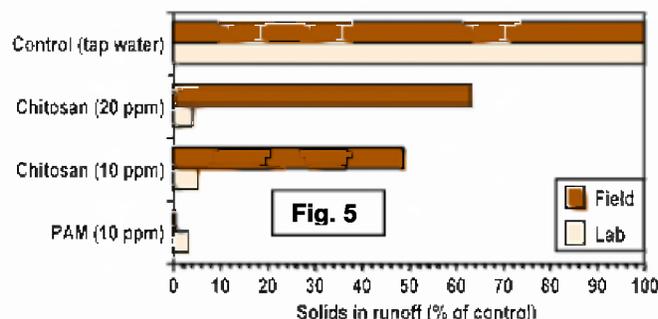
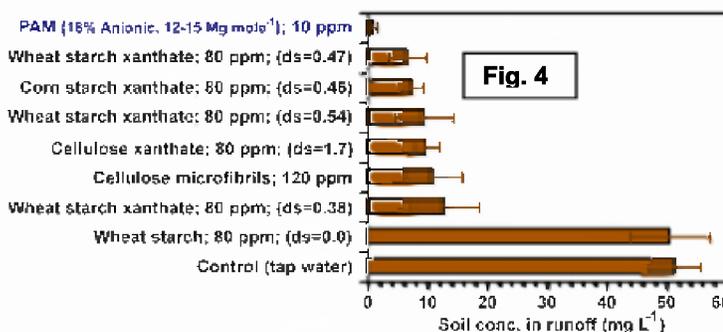


contrasted to the PAM treated furrow on the right where pores are open to the surface because structure was stabilized. In coarse textured soils (sands), where sealing is not an issue, PAM may induce no infiltration effect or may slightly decrease infiltration, particularly above 20 kg ML⁻¹ concentration (Sojka et al., 1998a). Recent column studies and water retention measurements have shown changes in saturated hydraulic conductivity and shifts in water retention consistent with expectations based on viscosity increases (Horne and Sojka, unpublished data).

When PAM is used, furrow stream advance is usually slower, especially on new or cultivated furrows (Sojka et al., 1998a,b). Infiltration rate of PAM-treated furrows on medium to fine textured soil is usually faster than on untreated furrows because PAM prevents formation of surface seals that block surface pores and reduce infiltration rates. For equal inflows, net infiltration on PAM-treated new furrows in silt loam soils is typically 15% more, compared to untreated water; on clay, infiltration can increase 50% (Sojka et al., 1998a). Pore continuity is maintained when aggregates are stabilized by PAM. Sojka et al. (1998a) reported that infiltration at 40 mm tension varied among irrigations between 12.9 and 31.8 mm hr⁻¹ for controls and 26.7 to 52.2 mm hr⁻¹ for PAM-treated furrows; infiltration at 100 mm tension ranged from 12.3 to 29.1 mm hr⁻¹ for controls and 22.3 to 42.4 mm hr⁻¹ for PAM-treated furrows. Because PAM prevents erosion of furrow bottoms and sealing of the wetted perimeter, lateral water movement in silt loam soils is greater for PAM treated furrows than for non-treated furrows. This can be a significant water conserving effect for early irrigations. Recent research quantified the ability of PAM, applied via sprinkler systems, to reduce soil surface seal formation, reduce runoff and increase infiltration on steeply ridged planting beds in Portneuf silt loam soil. Soil surface seals atop beds, sprinkled with untreated water, infiltrated at 22 and 30 mm hr⁻¹ for 100 and 40 mm tensions, respectively, whereas beds sprinkled with PAM-treated water infiltrated at 38 and 61 mm hr⁻¹ respectively for 100 and 40 mm tensions. Over four consecutive irrigations these seal-induced infiltration differences resulted sequentially in approximately 50% more water entering beds irrigated with PAM-treated water, compared to un-amended water (Horne, Sojka, and Bjerneberg, unpublished data).

Biopolymers: PAM or related polymers have been the dominant synthetic polymers developed for the uses described in our paper. Indeed, only anionic high purity PAMs are endorsed for these uses to date by NRCS. There is interest by farmers, environmentalists, the polymer industry and other industries producing recalcitrant organic waste streams regarding the possibility of producing bio-polymer surrogates of PAM and related synthetic polymers. The rationale is multifaceted. PAM is cheap because the chief raw material currently used to synthesize PAM is natural gas. Natural gas may not always be as cheap or available as it is today. Because so many industrial and food processing activities depend on PAM-like polymers there is interest in guaranteeing the future availability of suitable polymers. Biopolymer development is seen as a way to assure future availability of suitable polymers. There is also a perception among some environmentalists that biopolymers would be a more sustainable and environmentally friendly basis for industrial and environmental technology. Research has begun to develop bio polymers synthesized from organic byproducts of crop agriculture and shell fish food processing. These biopolymers may supplement PAM for certain uses where enhanced biodegradability is needed or where bio-based chemistry is perceived to be an environmental benefit (Orts et al., 1999, 2000, 2001, 2002).

Orts and colleagues tested biopolymer surrogates of PAM for furrow irrigation erosion control and infiltration enhancement both in small laboratory soil bins and in field plots. Their work shows that surrogates can likely be developed, although current options are less effective or more expensive than PAM. Figure 4 shows the relative efficacy of surrogates for PAM based on starch xanthate and/or microfibril suspensions tested on small bins; degree of substitution (ds) is the number of hydroxyls per glucose molecule (max of 3) replaced with a xanthate [CS₂] group. While several biopolymer combinations reduce erosion significantly compared to controls, PAM is still five to six times more effective at a much lower concentration. A similar result was seen for both field and lab bin tests of chitosan-based polymers although efficacy was achieved at much lower concentrations (Figure 5). These data also show the difficulty of drawing conclusions based solely on lab studies. Earlier studies with polysaccharides and with cheese whey for furrow irrigation erosion control have also been promising, fueling optimism that commercially viable PAM surrogates may eventually be developed (Brown et al., 1998; Shainberg and Levy, 1994).



Environmental Aspects: Environmental and safety considerations of anionic PAMs have been thoroughly reviewed (Barvenik, 1994; Bologna et al., 1999; Deskin, 1996). While comprehensive assessments of surrogate compounds have yet to be made, impacts - other than direct effects of the specific chemistries - are thought to be similar to anionic PAM within the context of erosion prevention and water contamination control. The most significant environmental effect of these polymers is erosion reduction, protecting surface waters from sediment and other contaminants washed from eroding fields. PAM greatly reduces nutrients, pesticides, biological oxygen demand (BOD), micro-organisms, and weed seed loads of irrigation return flows (Agassi et al., 1995; Lentz et al., 1998, 2001; Sojka and Entry 2000; Entry et al., 2003; Sojka et al. 2003). In Australia, sediment, nutrient, and pesticide reductions using PAM exceeded those achieved by conservation farming methods (Waters et al., 1999a,b). There are issues related to PAM charge type and purity. Used at prescribed rates, anionic PAMs are environmentally safe. Cationic and neutral PAMs have toxicities warranting caution or preclusion from sensitive environmental uses. NRCS specifies anionic PAMs for controlling erosion. PAMs are used worldwide for potable water treatment, sewage sludge dewatering, washing and lye peeling of produce, clarification of fruit juice and sugar liquor, as animal feed thickeners, in cosmetics, for paper manufacturing, for mining and drilling applications and other sensitive uses. Negative impacts have not been documented for aquatic macrofauna, edaphic microorganisms, or crop species for properly applied anionic PAMs used for erosion control Kay-Shoemaker (1998a,b). Even at high concentrations, when PAMs are introduced into waters containing sediments, humic acids etc., PAM effects on biota are greatly buffered via adsorption on suspended impurities (Buchholz, 1992; Goodrich et al., 1991).

An important environmental and applicator safety consideration is the need to use PAMs that contain <0.05% acrylamide monomer (AMD). AMD is a neurotoxin, but PAMs below these AMD contents are safe, when used as directed at low concentrations. Mixed into soil, PAM bio-degrades at rates of at least 10% per year (Tolstikh, et al. 1992; Wallace et al. 1986; Azzam et al. 1983). Because PAM is highly susceptible to UV degradation, its breakdown when applied at the soil surface for erosion control may be faster than the 10% per year rate. PAM does not revert to AMD upon degradation (Mac Williams, 1978). Furthermore, AMD is easily metabolized by microorganisms in soil and biologically active waters, with a half life in tens of hours (Lande et al, 1979; Shanker et al., 1990). Bologna et al. (1999) showed that AMD is not absorbed by plant tissues, and apparently breaks down rapidly even when injected into living plant tissue. While anionic PAMs are safe if used as directed, prolonged overexposure can inflame or irritate skin and mucus membranes. Users should read label cautions and take reasonable care not to breathe PAM dust and to avoid exposure to eyes and other mucus membranes. Practical user considerations are numerous. Labels, websites and available extension information should be consulted before embarking upon use of PAM or other polymers for erosion control or water pollution prevention.

Because of PAM's high affinity for suspended sediments and soil, only 3-5% of PAM applied via furrow irrigation leaves fields in runoff. Furthermore, the PAM has been shown to only migrate 100 to 500 m in waste ditches before being adsorbed on sediments in the flow or onto ditch surfaces (Lentz and Sojka, 1996). Ferguson (1997) reported on a watershed scale PAM test, where over 1,600 ha were irrigated using PAM-treated water for two weeks. On any given day, about half of the 40 farms in the study contributed runoff to the drainage, which collected in Conway Gulch, a Boise River tributary. About half of the water in the drain was field runoff. PAM was detected in drain water samples only twice (< 0.8 kg ML⁻¹) during monitoring. PAM was deemed an effective sediment control, was well liked by farmers, improved water quality and did not harm the drain.

Conclusions: Synthetic- and bio-polymers offer a safe, environmentally friendly, inexpensive and highly effective new alternative for erosion control, runoff reduction and water quality protection for runoff and percolated water from irrigated agriculture. Farmers find the use of polymers easy to integrate into their standard irrigated farming practices without the degree of disruption or equipment cost typically associated with more traditional conservation practices that rely primarily on maintenance of vegetative covers, or surface residue, which can be problematic in surface irrigation. Continued work is needed to identify cost effective biopolymer surrogates for PAM which, currently is the chief synthetic polymer used for erosion control.

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