Estimating Polyacrylamide Concentration in Irrigation Water

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ABSTRACT

One practice used to control irrigation-induced erosion amends irrigation furrow inflows with water-soluble, anionic polyacrylamide (PAM) at low concentrations (0.25–10 mg L^{-1}). Researchers wish to determine the fate of PAM, once added to furrow water streams. We developed and tested an instrumented flocculation test for quantifying PAM concentration in irrigation water. A kaolinite mineral standard is mixed with a PAM-amended water sample, agitated, then placed in a spectrophotometer. The PAM concentration in the suspension was correlated with settling-related transmittance changes. One highly correlated (r = 0.91–0.98) parameter, the time needed to initiate suspension clearing (clarity-shift inflection, CSI), was used as the procedure endpoint. The procedure was sensitive to variations in the amount of kaolinite added, and sample volume, water salinity, and original sediment content. A 10% change in these factors altered measured CSIs by 10 to 50%. The sediment affected CSI by increasing the sample's dissolved organic C concentration. The procedure detected as little as 0.1 mg L^{-1} PAM dissolved in irrigation water; in samples containing >4 mL settled sediment per liter, the PAM detection limit was approximately 0.25 mg L^{-1}. Precision ranged from ±0.06 to 0.11 mg L^{-1} for 0 to 2.5 mg L^{-1} PAM and ±0.39 to 0.86 mg L^{-1} for 2.5 to 10.0 mg L^{-1} PAM. The PAM concentration in runoff from irrigated furrows equaled that of the inflow stream after 3 h continuous treatment at 10 mg L^{-1}. The CSI test provides a simple and accurate method of determining polyacrylamide in surface waters.

WATER SOLUBLE anionic polyacrylamide (PAM) dissolved in irrigation water dramatically reduces furrow irrigation–induced soil losses (Lentz et al., 1992). The PAM technology has great potential for solving critical soil erosion and return-flow water-quality problems associated with furrow irrigation (Lentz and Sojka, 1994). By summer of 1994, PAM was labeled as a soil amendment for use in several western states. In January 1995 the National Resource Conservation Service approved an interim conservation practice standard for the western USA, which specifies the addition of water-soluble anionic polyacrylamide, 18% charge density, 12 to 15 Mg mol^{-1} to irrigation water at 10 mg L^{-1} during the furrow advance phase. The PAM was applied on approximately 20 000 ha in the western USA during the 1995 growing season. The practice is very effective, nonintrusive, and economical; its use is expected to expand dramatically in coming years in both USA and international agriculture. Extensive research has examined field-scale application of PAM via irrigation water (Lentz et al., 1992, 1993; Lentz and Sojka, 1994; Trout et al., 1995), yet no studies have evaluated the fate of PAM once it enters irrigation flows.

Several important practical and environmental questions need to be answered. For example: Does PAM concentration in treated inflows decrease with distance downstream in furrows or wastewater ditches? If so, how rapidly does it decline? What is the potential for PAM losses from furrows and wastewater ditches into return flows and receiving waters? Such research would be greatly facilitated if a more simple and rapid procedure for accurately measuring PAM concentration were available, and its field-application performance documented.

Chemical methods employed to quantify aqueous PAM concentration have included: (i) bromine oxidation of amide functional groups, where the amide product is measured via oxidation of an iodide–starch complex (Scoggins and Miller, 1975, 1979); (ii) PAM digestion and use of Nessler's reagent to determine organic N (Crummett and Hummel, 1963); (iii) polyelectrolyte (colloid) titration using conductometry (Toei and Kohara, 1976), color indicator (Terayama, 1952), fluorescent indicator (Tanaka and Sakamoto, 1993), or turbidimetric methods (Toei and Sawada, 1977); (iv) hydrolyzed PAM reacted with Hyamine 1622 to form a colloidally suspended complex, that is measured tubidimetrically (Wimberley and Jordan, 1971); and (v) methods based on organic carbon content. These methods require a well-equipped laboratory, expensive analytical instruments, and complicated analytical protocols. Some employ costly reagents containing heavy metals that have environmental concerns. The precision of these chemical methods ranges from ±0.2 to 1.0 mg L^{-1}. The precision of some protocols declines at very dilute PAM concentration because of interfering salt or organic components. Often, chemical methods do not selectively measure PAM alone, but also respond to other organic substances in the solution. An analytical procedure based on PAM's potent flocculating capabilities could yield a relatively simple protocol and preclude the use of expensive analytical equipment.

Gregory (1989) reviewed the topic of flocculation. Low molecular weight biopolymers can increase stability of inorganic colloids, possibly through steric stabilization. High molecular weight polymers (>10^6 g mol^{-1}) can increase flocculation by bridging between particles, although, at higher concentrations, excess polymer adsorbed to particles produces steric repulsion, which stabilizes the colloid suspension. Hence, an optimum polymer dosage provides maximum bridging flocculation, although this dosage varies with particle concentration.

Gregory (1983) reviewed nonchemical methods that evaluate efficacy of flocculating-agents at varying concentrations. These procedures measure rates of settling zone boundary rise, final supernatant turbidity, or permeability of flocculated sediment. Few have been adapted for measurement of PAM concentration, and those that have are too cumbersome to use for repeated analyses.

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Received 27 Nov. 1995.

Published in J. Environ. Qual. 25:1015–1024 (1996).

Abbreviations: PAM, water soluble anionic polyacrylamide; SAR, sodium adsorption ratio; ESP, exchangeable sodium percentage; CSI, clarity shift inflection; LSD, least significant difference; DOC, dissolved organic carbon; RCS, relative centrifugal force.

A procedure based on the observed flocculation in a sequence of sample dilutions was used to determine PAM content in sample waters (E.E. Miller, 1994, personal communication). Its main disadvantages were its protracted protocol, limited precision, and undocumented applicability for irrigation water. Our objective was to develop a simple flocculation test that accurately determined PAM concentration (0–10 mg L^{-1}) in furrow and waste-ditch water samples. First, we established a measurable, flocculation-based parameter highly correlated with aqueous PAM concentration, then evaluated its robustness when used in a laboratory procedure (sensitivity analysis). Since the primary change occurring in irrigation water as it flows down-furrow is a change in sediment content, we next determined potential impacts of sediment on the assay results. Stability of stored samples was then investigated, and lastly, the precision and bias of the finalized assay procedure was ascertained.

METHODS

Irrigation Stream Sampling, Storage, and Assay

The sampling and assay protocol developed here (Table 1) included several optional pathways and a decision structure (Fig. 1) that allowed for different sample storage requirements and output precision needs. Details of the protocol follow. Keep in mind that these procedures incorporate knowledge gained through experiments described later in this paper, thus we have in some respects placed the cart before the horse. To avoid potential confusion, note that sediment collected with the irrigation stream sample had two important impacts on the assay: (i) If not removed, sediment reduced aqueous PAM concentration in the sample over time; (ii) Dissolved organics derived from the suspended sediments potentially reduced assay precision. Procedural options were added to address these two problems. To account for dissolved organics effects and increase assay precision, additional sets of PAM standards were prepared using irrigation water containing varying concentrations of sediment (Table 1, Options 1 and 2). The assay procedure also differed depending on the PAM concentration of the sample (see Test Procedure subsection). Greater sample and flocculation substrate additions were used when sample PAM concentrations were <2.5 mg L^{-1}, compared with additions used for high-PAM samples.

Apparatus. A Milton Roy Spectronic[1] 21 spectrophotometer (Rochester, NY) was used with 10-mm pathlength, 7-mL test-tube cuvettes. The analog output from the spectrophotometer was read and displayed in real time on an IBM AT compatible 286 computer via a Keithley DAS8 A/O (Taunton, MA) data acquisition board using an author-written program. Scientific Industries Model G-560 (Bohemia, NY) vortex mixer, 3000 rpm, was used to disperse the flocculation substrate in samples. A refrigerated circulating bath ensured that samples and standards were analyzed at equivalent temperatures.

Flocculation Substrate Preparation. The substrate used in the flocculation procedure was a kaolin clay mineral (hydrite UF, Georgia Kaolin Co. or Sigma). Mineral particles were dispersed in a 0.1 *M* NaOH solution and the <2-μm size fraction was separated using centrifugation (500 RCF[1], 10 min, 22°C). Clay exchange sites of the <2-μm size fraction were saturated with metal cations by washing with a 1 mol_c L^{-1} solution (SAR = 6) consisting of 0.219 *M* $CaCl_2$, 0.219 *M* $MgCl_2$, and 0.125 *M* NaCl. The clay salt content was subsequently reduced via dialysis in a 0.014 mol_c L^{-1} solution (SAR = 6; 0.00119 *M* $CaCl_2$, 0.00119 *M* $MgCl_2$, and 0.00925 *M* NaCl) until bath EC stabilized. The clay slurry was then frozen and dehydrated in a freeze dryer, and stored in a desiccator over calcium carbonate.

Test Procedure. The assay was designed to test dilute solutions having PAM concentrations ≤ 10 mg L^{-1}. Very dilute samples, i.e., ≤ 2.5 mg L^{-1} required greater additions of sample and substrate to accurately estimate PAM concentration. That is, a 5-mL water sample was added to 0.1 g substrate. When samples contained >2.5 mg L^{-1} PAM, these amounts were halved, i.e. a 2.5-mL water sample was added to 0.05 g substrate. Initial determinations should be done on samples that represent a range of sampling conditions. These data will help the operator decide whether to run a given sample using the low- or high-PAM range procedure. In general, if PAM is being injected into furrow inflows at rates >4 mg L^{-1}, the PAM concentration in the furrow stream will likely exceed 2.5 mg L^{-1}; but if PAM injection has been stopped for >1 h, the furrow-stream PAM concentration will likely be <2.5 mg L^{-1}.

In the first step, the kaolin substrate was weighed (±0.001 g) into a test tube cuvette and stoppered. When a determination was made, the water sample volume was pipetted into a cuvette preloaded with kaolin, and the mixture was immediately vortex mixed at maximum speed for 120 s. When agitation was complete, the cuvette was promptly placed (within 4 s) into the spectrophotometer, and sample transmittance (560 nm) measured during the next 2 to 6 min. Shorter measurement periods were needed at higher PAM concentrations. Results were averaged over three to five runs.

Floccules formed during agitation began to settle immediately after the cuvette was removed from the vortex mixer, although PAM continued to promote flocculation of dispersed kaolinite particles. Sample transmittance remained very low during this first phase and either remained constant or increased very slightly. The flocculation rate and the length of Phase 1 was largely a function of a sample's PAM content. Shortly after floccules started settling, the suspension began to clear and sample transmittance increased abruptly. The time (s) at which transmittance increased abruptly (Fig. 2) was called the clarity shift inflection (CSI), and it marked the beginning of Phase 2. Most of the kaolin suspension settled during Phase 2, and sample transmittance increased rapidly. As the bulk of kaolin first settled through the cuvette, the descending flocs intercepted any dispersed particles. This sweeping action effectively cleared that part of the sample intersected by the light path just below the cuvette midline. The increased sample clarity produced a correspondingly distinct transmittance peak in the duration curve (Fig. 2). Typically, sample transmittance then declined slightly as smaller floccules and remaining dispersed particles higher in the cuvette drifted downward through the light path. In the final phase, the remaining suspended kaolinite slowly settled out of suspension and transmittance gradually increased. Convection currents produced by warming of the sample, mostly from the impinging light, often destabilized the descent of finer colloids, resulting in a variable, but generally rising transmittance trace in Phase 3.

Flocculation Test Parameter. An author-written PC program (FLOCS) assisted the operator. It timed the vortex mixing step, accessed spectrophotometer analog output, and displayed in real time the transmittance duration curve, a graph of transmittance vs. time (Fig. 2). The program also computed the CSI duration curve parameter, which was defined as the

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[1] Mention of trademarks, proprietary products, or vendors does not constitute a guarantee or warranty of the product by the University of Idaho or USDA-ARS and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

Table 1. Summary of the flocculation-based irrigation stream sampling and PAM assay protocol (optional steps increase precision).

Apparatus

A
1. Milton Roy Spectronic 21 or equivalent spectrophotometer.
2. IBM/clone PC with Keithley DAS8 A/O data acquisition board and FLOCS software (other spectrophotometers may use the computer's RS-232 port for data input, preempting the need for the data acquisition board).
3. Scientific industries Model G-560 vortex mixer (3000 rpm max.).

Reagents

B
1. Boric acid and *n*-propanol (sample stabilizer additives).
2. Kaolin flocculation substrate (requires preparation).

Procedures: Steps in Options 1 and 2 are in addition to those in the general protocol (except G)

	General	Option 1	Option 2
Sampling			
C1	Obtain samples of in-flowing irrigation water for standard's preparation at each irrigation, or every 2 wk during the sampling period.	Collect samples of untreated furrow tailwater with varying sediment levels, for additional standard's preparation.	Collect samples of untreated furrow tailwater with varying sediment levels, for additional standard's preparation.
C2	Collect PAM-treated furrow water samples. If samples are to be stored for more than 2 d, sediment should be excluded by centrifuging or by allowing the sample to sit undisturbed for 28 h and resampling the supernatant.		Measure sediment levels in each sample.
Storage			
D1	If storage period >4 wk, add solution stabilizers: 1 mL boric acid stock and 2 mL 2-propanol stock per 100 mL sample solution		
D2	Store at room temperature away from UV light sources.		
Standards			
E1	Prepare a 500 mg L^{-1} primary standard and let equilibrate for 36 h.		
E2	Prepare a single set of low (0.0, 0.1, 0.5, 1.0, 2.5 mg L^{-1}) and high (2.5, 5.0, 7.5, 10 mg L^{-1}) PAM concentration standards using irrigation inflow water.	Make up additional standard sets for each of the three to four sediment-bearing tailwaters collected in step C1, Option 1.	Make up additional standard sets for each of the three to four sediment-bearing tailwaters collected in step C1, Option 2.
Testing			
F1	Add kaolin flocculation substrate to spectrophotometer test tube cuvette: To Low-PAM samples ($\le$2.5 mg L^{-1}): Add 0.1 g kaolin To High-PAM samples (>2.5 mg L^{-1}): Add 0.05 g kaolin.		Ensure that the lag time between creation and measurement of sample and standard is identical for both.
F2	Add irrigation water sample to cuvette: To Low-PAM samples ($\le$2.5 mg L^{-1}): Add 5 mL sample To High-PAM samples (>2.5 mg L^{-1}): Add 2.5 mL sample		
F3	Promptly stopper and mix sample for 2 min with a vortex mixer.		
F4	After mixing, immediately insert tube into spectrophotometer and record sample transmittance at 560 nm for 6 min, or until CSI is determined.		
F5	Repeat steps E1-E4 three to five times and compute mean CSI for each sample and standard.		
Compute PAM conc.			
G	Use mean CSI to calculate sample PAM concentration from appropriate standard curves.	Average standards curves from waters with varying sediment content into a single composite function (one each for the for low- and high-PAM concentration ranges). Use the composite function to compute all sample PAM concentrations.	From the calibration curves for waters with varying sediment content, select one or two having sediment levels most similar to that of the sample. Compute sample PAM concentration using one function, or by interpolating between two calibration functions.
Precision			
H	$\le$2.5 mg PAM L^{-1}: ±40% (±1 mg L^{-1}) >2.5 mg PAM L^{-1}: ±10% (±0.6 mg L^{-1}	$\le$2.5 mg PAM L^{-1}: ±10% >2.5 mg PAM L^{-1}: ±3%	$\le$2.5 mg PAM L^{-1}: ±3% >2.5 mg PAM L^{-1}: ±6%

time (s) after tube insertion, when the slope of the highest ascending transmittance-curve segment first exceeded 0.10 (Fig. 2). The CSI could be obtained manually, either by viewing and timing the spectrophotometer readings or by using a recorder trace, but neither of these methods are practical when analyzing large numbers of samples. Correlation coefficients relating PAM concentration to transmittance curve parameters were calculated with SAS statistical software (SAS Inst., 1990). Of 12 transmittance-curve parameters analyzed, CSI was best correlated with sample PAM concentration. The overall correlation was −0.92, with a significance value of $P = 0.0001$ ($n = 57$). Hence its use in assessing sample PAM concentration.

Preparation of Standards. Standard solutions were prepared from untreated irrigation inflow water collected just

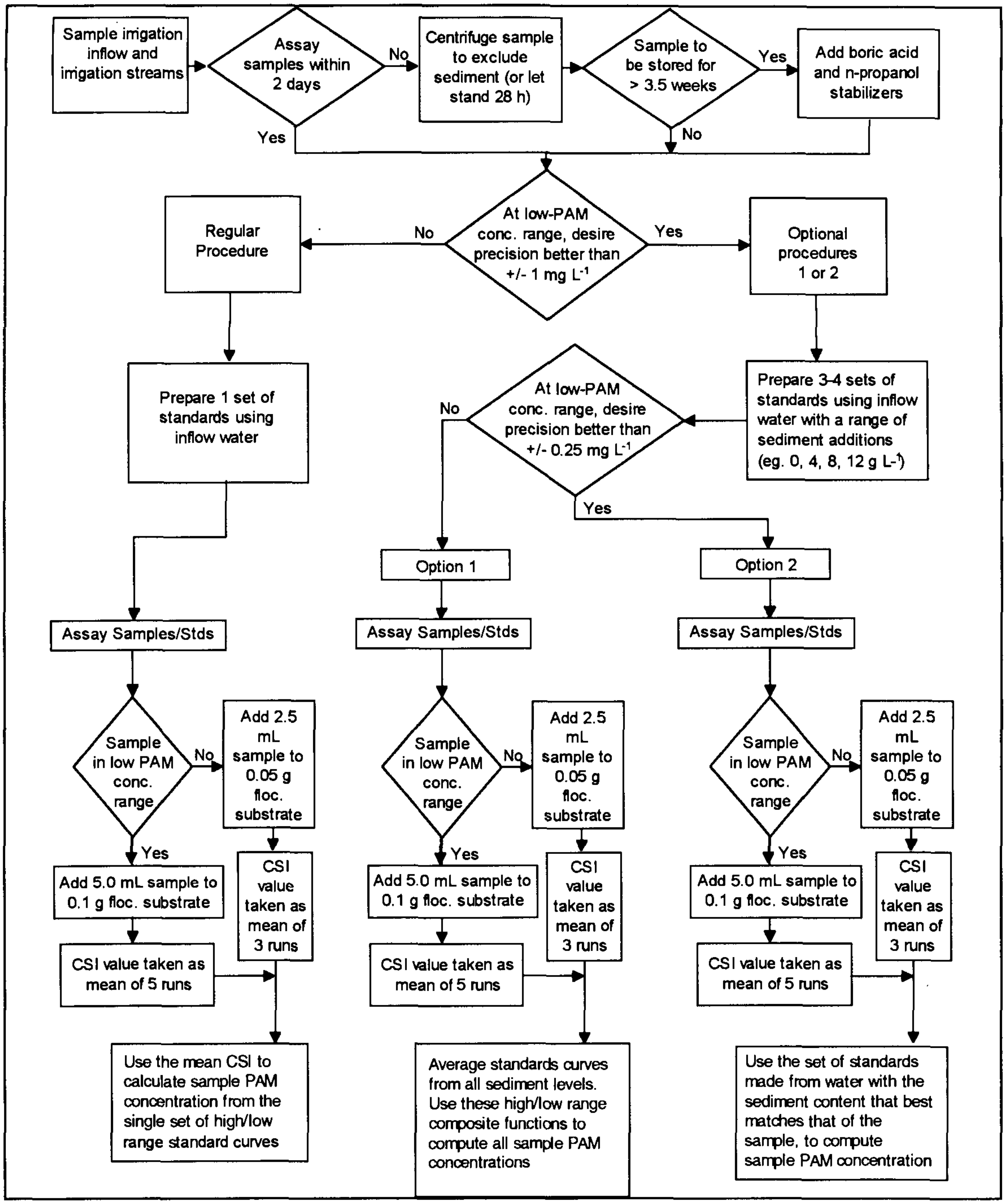

Fig. 1. Flow chart showing decision structure of sampling, storage, and PAM assay procedures.

before, or together with treated samples to be analyzed. The irrigation water was centrifuged (10.2K RCF, 10 min, 10°C) to exclude sediment. If needed, solution stabilizers (boric acid and 2-propanol, see Table 1, D1) were added to this supply. A 500 mg L^{-1} PAM primary stock solution was prepared by slowly adding PAM crystals to a volumetric flask nearly filled with distilled water. A magnetic stir bar, turning at the minimum speed required to form a vortex in the solution, provided mixing during PAM addition. After 10 to 15 min of mixing, the stir bar was removed and the flask filled to volume with distilled water. The stir bar was replaced and agitation continued for 1 to 2 h. After mixing, the solution was allowed to stand for 36 h to ensure adequate PAM dissolution and dispersion. Standards for both the low and high concentration ranges were prepared: The low range included 0.0, 0.1, 0.25, 0.5, 1.0, and 2.5 mg L^{-1}. The high range included 2.5, 5.0, 7.5, and 10 mg L^{-1} standards. These were mixed, as was the primary stock solution, and allowed to stand 12 h before use to ensure complete dispersion. Accuracy of the PAM concentration estimate was improved by preparing and utilizing additional sets of standards. These were prepared similarly to those above, except that untreated irrigation tailwater with varying sediment concentrations was used in the solutions. We prepared a minimum of two additional standard sets, made with irrigation water containing 1 to 4 and 5 to 8 g L^{-1} sediment, depending on the sediment loads observed in PAM-treated furrows sampled in a given irrigation. Although sediment loads in control furrow tailwater commonly exceeded 8 g L^{-1}, those in PAM-

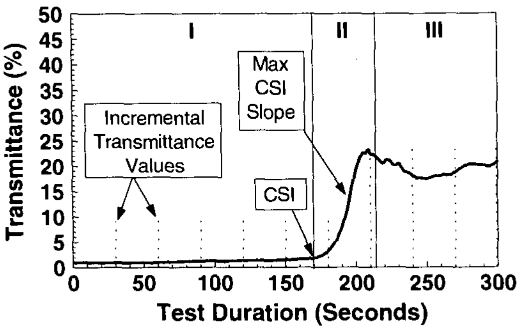

Fig. 2. Transmittance duration curve and curve parameters, including clarity shift inflection (CSI), maximum slope on CSI peak, and 10 uniformly spaced incremental transmittance values. Duration phases are labeled in Roman numerals.

treated furrows rarely did so. Hence, the use of 8 g L^{-1} was used as an upper limit. These standards were assayed, and calibration functions devised just as was done for the original set (Fig. 3). Their use in computing sample PAM concentrations is outlined in Table 1.

Evaluation of the Flocculation Assay

Sensitivity Analysis. This experiment determined sensitivity of measured test values to small changes in protocol or sample factors for samples at two PAM concentrations, 0.1 and 2.5 mg L^{-1}. The multifactorial experimental design and calculations were discussed in detail by Youden and Steiner (1975, p. 33-36, 50-55). Seven factors were included; each was tested at two levels. The seven protocol and sample solution factors were defined for each test in such a way, that the entire analysis required only eight determinations or tests (Table 2). When all determinations were completed, the bilevel impacts of any single factor could be calculated by comparing the average result from a given pertinent group of four determinations with that of the remaining four (Youden and Steiner, 1975).

Factor values for each determination are listed in Table 2. The soil-treatment factor was introduced to examine the potential impact of dissolved organic and inorganic components incorporated from sediment that was detached and mixed into water running down the furrow. Soil was taken from the surface horizon of Portneuf silt loam (coarse-silty, mixed, mesic Durixerollic Calciorthids); Portneuf characteristics are listed in Table 3. The added soil was combined with the water, mixed at maximum speed for 60 s, allowed to settle for 120 s, then removed by centrifuging. The EC and SAR of water samples was modified by adding appropriate amounts of KCL or NaCL. The EC, SAR, and soil treatments were applied to the water before PAM was incorporated into the solutions. Test results for each CSI determination were reported as the average of five assays.

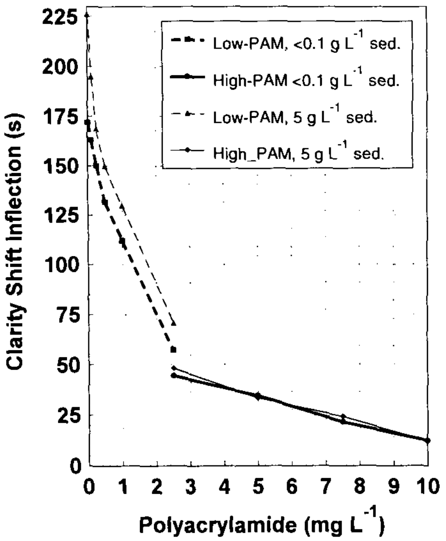

Fig. 3. Two standard curve sets for both polyacrylamide concentration ranges, prepared using irrigation water with initial sediment loads of <0.1 and 5 g L^{-1}.

Sediment Impacts on Water Quality. To ascertain how admixed sediment might influence chemistry and PAM assay of furrow water, samples of 0, 25, or 50 g L^{-1} Portneuf topsoil (bulked surface soil from a 0- to 5-cm depth at five locations across the field) were mixed with irrigation water (Table 4). The treatments were replicated three times. Mixtures were agitated in a reciprocating shaker for 15 min (to simulate postadvance flow in furrows) and sediment was removed by centrifuging (10.2K RCF, 10 min, 10°C). Supernatants were separated. The EC and pH of supernatants were measured with conductivity and pH meters. Soluble Na, Ca, and Mg concentrations were determined by atomic absorption spectrophotometry. Total organic C in the supernatant was measured with a Dohrmann DC-180 (Santa Clara) C analyzer. The supernatant series was then spiked with 1 mg L^{-1} PAM, mixed thoroughly, and the CSI measured with the flocculation test. Regression analysis was used to test for relationships between water quality parameters and soil treatments (Neter et al., 1983; SAS Inst., 1990).

Effects of Sample Retained Sediment on Sample Test Values. This study evaluated residual sediment effects on sample test values. Polyacrylamide was applied at 1 and 5 mg

Table 2. Factor levels included in multifactorial determinations. These same factor levels were used for both PAM solutions tested (0.1 and 2.5 mg L^{-1}).

	Factor values						
Determination no.	Kaolin substrate mass	Water sample volume	Max rpm vortex time	Initial† sediment conc.	Initial sample temp.	Sample EC	Sample SAR
	g	mL	s	g L^{-1}	°C	dS m^{-1}	$mmol_c$ L^{-1}
1	0.10	5.0	120	0	20	0.6	0.6
2	0.10	5.0	60	0	25	0.9	1.2
3	0.10	4.0	120	10	25	0.6	1.2
4	0.10	4.0	60	10	20	0.9	0.6
5	0.05	5.0	120	10	25	0.9	0.6
6	0.05	5.0	60	10	20	0.6	1.2
7	0.05	4.0	120	0	20	0.9	1.2
8	0.05	4.0	60	0	25	0.6	0.6

† Soil was mixed into irrigation water sample before centrifuging (add soil, mix 1 min, let settle 2 min, centrifuge).

Table 3. Properties of Portneuf soil (plow layer).

Texture	Particle-size distrib.			Dominant clay minerals†	CEC	EC‡	Exchangeable sodium percentage	pH	OM‡	$CaCO_3$ equivalent
	Sand	Silt	Clay							
	g kg^{-1}				$cmol_c\ kg^{-1}$	dS m^{-1}	%		g kg^{-1}	%
Silt loam	100–170	650–700	180–200	I>>K = M>V	18–20	0.5–0.7	1.6–1.8	7.9–8.2	10–17	2–8

† Coarse clay fraction. I = illite, K = kaolinite, M = montmorillonite, V = vermiculite.

‡ EC = electrical conductivity (saturated paste extract); OM = organic matter.

L^{-1} to in-flowing water at the head of the three furrows. Irrigation inflow rate was 23 L min^{-1}. Water was sampled from furrows 11.6 m from the furrow head during the PAM application. Boric acid and 2-propanol were added to the samples (see section below) as stabilizers. Each sample was split using a magnetic stirrer to maintain uniform sediment distribution while a siphon withdrew half the sample volume. A centrifuging process (10.2 RCF, 10 min, 10°C) removed sediment from one-half of the sample. The CSI of each solution was measured (average of three to five runs) every 5 to 7 d during the ensuing month. The difference between treatments (sediment − no-sediment) was reported as a percentage of the no-sediment value. Finally, sediment retained in samples was measured via filtration.

A regression analysis evaluated the relationship between time (independent variable) and CSI difference (dependent variable). The latter was given as a log transform of CSI difference plus 40 s to stabilize variance (adding 40 s eliminated negative values). Independent variables included were days since preparation (T_1), days×days (T_2), included in case the relationship was nonlinear, and replicate (T_3, a class variable). The model fitted was

$$C = \beta_0 + \beta_1 T_1 + \beta_2 T_2 + \beta_3 T_3 + \varepsilon_i$$

where C was log(% CSI difference + 40 s), T_i were the independent variables, and β_i were the parameter coefficients. The Durbin-Watson statistic verified that errors were not correlated, i.e., nonautocorrelation assumption, and that the regression was valid for this data (Neter et al., 1983). Confidence limits were computed as 95% prediction intervals.

Sample Stability. In this study, we determined whether a biocide (boric acid) and/or a polymer stabilizing (2-propanol) additive prevented drift of the measured CSI response for stored PAM solutions. A preliminary experiment examined the impact of different sample handling techniques on CSI of PAM solutions with time. Freezing the sample, with or without residual sediment, and thawing before measurement produced the most erratic results, particularly during the first 15 d of storage. The biocide and polymer stabilizer treatments showed greater promise, so a more detailed study included only these alternatives.

The biocide stock solution was prepared by dissolving 6.2 g H_3BO_3 in distilled water and bringing to 100 mL volume. The polymer stabilizer was 2-propanol (Kulicke et al., 1982), a technical-grade solution that contained 70% n-propanol by volume. Sediment-free irrigation water was used to prepare four solutions of equal PAM content (~1 mg L^{-1}). Four treatments were applied: (i) no additive; (ii) 1 mL boric acid stock per 100 mL solution; (iii) 2 mL 2-propanol stock per 100 mL solution; and (iv) boric acid + 2-propanol. Three replicates were included. The CSI of solutions was measured (mean of three to five runs) every few days (intervening interval varied in length), beginning 16 h after preparation. Solutions were stored in clear, glass flasks at room temperature, and were left exposed to the room's fluorescent lighting. Statistical analysis employed repeated measures using a univariate, split-plot approach and the Huynh-Feldt adjustment for nonsphericity (Littell et al., 1991). Separations for treatments-within-time, and time-within-treatment comparisons were evaluated with the LSD statistic. Calculations were done in SAS, and included a 5% significance level with an experiment-wise Bonferroni correction (Snedecor and Cochran, 1980).

Method Detection Limit, Precision, and Bias. This study determined the CSI-test's detection limit and evaluated the bias (systematic error) and single operator precision (repeatability) of the method (Greenberg et al., 1992). Three sets of low- and high-range standards were prepared using irrigation water containing initial sediment contents of <0.1, 1.0, and 5.0 g L^{-1}. Sediment was added as in Exp. 2, except that soil was shaken with the irrigation water for 15 min before separation. Four *unknowns* (to operator) were prepared for each of the three sediment levels employed (0.1, 0.3, 0.6, and 6.5 mg L^{-1}). Eight aliquots of the unknown were prepared as replicates. The method detection limit was taken as the product of [standard deviation of the 0.1 mg L^{-1} unknown determinations] and [the one-sided *t*-distribution value at the 99% level, where d.f. = 8-1] (Greenberg et al., 1992, p. 1-11), and was averaged over the three sets of unknowns having varying initial sediment content. Precision and bias were calculated with (Greenberg et al., 1992, p. 1-13):

$$\text{Precision} = \sqrt{\frac{\sum_{i=1}^{n} (A - M_i)^2}{n - 1}} \qquad [1]$$

$$\text{Bias} = \frac{\sum_{i=1}^{n} (A - M_i)}{n} \qquad [2]$$

where A is actual concentration of the prepared PAM unknown sample (mg L^{-1}); M is the measured unknown PAM concentration (mg L^{-1}); for n replications. Precision was converted to percent by dividing precision values by the maximum PAM concentration in each test range and multiplying by 100.

Field Study. We measured PAM concentration in runoff from treated irrigated furrows using the highest precision, Option 2 procedure. The soil was Portneuf silt loam, the crop was field beans, planted in rows spaced 0.66 m apart and 164 m long. Control and PAM-treated furrows were arranged in

Table 4. Composition of untreated Snake River water.

Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	EC	SAR	pH
m $mol_c\ L^{-1}$							dS m^{-1}	m $mol_c\ L^{-1}$	
2.30	1.44	1.13	0.12	2.95	0.81	0.78	0.42	0.82	8.3

Table 5. Mean CSI differences between factor levels (high − low) of two PAM-solution concentrations, and CSI differences normalized to reflect a uniform 10% change for the factors.

Factor	Factor level		Mean CSI difference		CSI difference for 10% factor adjustment†	
	High	Low	0.1 mg L^{-1}	2.5 mg L^{-1}	0.1 mg L^{-1}	2.5 mg L^{-1}
Kaolinite substrate, g	0.1	0.05	103.6	76.4	20.7	15.3
Water sample, mL	5	4	−41.9	−25.6	−21.0	−12.8
Sample EC, dS m^{-1}	0.9	0.6	−46.2	6.1	−14.0	1.8
Soil treatment conc., g L^{-1}	10	0	97.9	64.2	9.8	6.4
Sample SAR, m mol_c L^{-1}	1.2	0.6	44.8	−16.6	9.0	−3.3
Vortex time @ max. rpm, s	120	60	37.2	14.8	7.4	3.0
Sample temp., °C	25	20	8.1	−24.7	4.1	−12.4

† Computed using: $0.1 \times [(H-L) \times H^{-1}]^{-1} \times D$; were H = high factor level, L = low factor level, and D = mean CSI difference.

a randomized block design. A PAM stock solution was pumped into the head of each furrow using a positive displacement pump (Lentz et al., 1992), at a rate selected to obtain a 10 mg L^{-1} target PAM concentration in the furrow stream. Irrigation inflow rate was 23 L min^{-1}. Tailwater samples were collected from flumes located at the furrow ends, centrifuged, treated with stabilizers, and stored until determinations could be made. Test lag times for standards and samples were the same (Table 1, F1, Option 2).

RESULTS AND DISCUSSION

Sensitivity Analysis

Average CSI differences between factor levels in the sensitivity analysis are presented in Table 5. The generally smaller differences noted for the 2.5 mg L^{-1} PAM solution indicated that factor-level changes had the greatest impact on the more dilute PAM samples. A relative comparison between factor effects was obtained when average factor-level differences in Table 5 were normalized so that each corresponded to a 10% adjustment in factor status. Measured CSI was most sensitive to a 10% variation in added kaolin substrate and sample amounts, especially when PAM solutions were very dilute. Operators must be particularly careful when dispensing these components to obtain best analytical precision. Compared with kaolin and sample amount factors, measured CSI was somewhat less sensitive to a 10% change in the added-soil treatment and EC of the water sample (Table 5). The effect of sample SAR was less than that of EC-induced CSI variations, probably because the kaolin's relatively high ESP buffered the sample-water's influence. The EC and SAR of sample water influenced kaolin flocculation through effects on clay dispersion (Velasco-Molina et al., 1971), polymer conformation (Lakatos et al., 1981), rheology (Tam and Tiu, 1993), and polymer adsorption (Lakatos et al., 1981). Soil additions to the water may have affected kaolinite flocculation by increasing levels of dissolved organic compounds. This hypothesis was tested below.

Sediment Impacts on Water Quality

Regression analyses indicated that solution EC and SAR were unaffected, but pH, total DOC, and CSI (1 mg PAM L^{-1}) changed with increasing soil treatments (Table 6). The regression functions indicated that increasing the soil addition from 0 to 10 mg L^{-1} would only slightly decrease solution pH, but notably increase both solution DOC and CSI (Table 6). The pattern of increasing DOC better paralleled that of the CSI, suggesting that admixing sediment affects measured CSI mainly by increasing DOC concentration of the water. Adsorbed natural biopolymers are known to increase colloidal stability of kaolinite suspensions (Kretzschmar et al., 1993). In general, our data indicate that analytical precision was compromised if standards were prepared with a nonmatching irrigation water supply. Greatest precision required several sets of standards to account for the range of sediment contents present in sampled water. These should be updated throughout the season if irrigation water quality is known to vary significantly.

Effects of Retained Sediment on Sample Test Values

The regression model fit for CSI difference (sediment − no-sediment) was significant for ~1 mg L^{-1} PAM samples (R^2 = 0.85, P = 0.0003), but nonsignificant (P = 0.60) for ~5 mg L^{-1} PAM samples (Fig. 4). Hence, sediment retained in furrow water significantly increased measured CSI of ~1 mg L^{-1} samples with time, while residual sediment had no significant effect on ~5 mg L^{-1} samples. To test whether the amount of retained sediment influenced the CSI-increase, we regressed log(CSI difference + 40) against independent variables, days×days, and sample sediment content. Both parameter coefficients in the regression were significant ($P < 0.003$, R^2 = 0.85). Therefore, when compared with sediment-free samples, the CSI of very dilute PAM solutions increased both with time after solution creation and amount of retained sediment. Measured CSI of samples with very dilute PAM content changed significantly between one and 6 d after solution creation

Table 6. Regression analysis relating admixed soil amounts to resulting solution characteristics (n = 9), including the parameter variation predicted when sediment addition changes from 0 to 10 g L^{-1}.

Parameter	Intercept (P-value)	Slope (P-value)	R^2	Predicted change, adding 10 g L^{-1} soil
Electrical conductivity	0.646 (0.0001)	0.014 (0.212)	0.21	0
Sodium adsorption ratio	1.117 (0.0001)	0.005 (0.180)	0.24	0
pH	8.229 (0.0001)	−0.002 (0.0001)	0.93	−0.02
Dissolved organic carbon	2.797 (0.0001)	0.174 (0.0001)	0.99	1.74
CSI of 1 mg L^{-1} solution	113.022 (0.0001)	1.784 (0.0001)	0.96	17.84

(Fig. 4). Hence, samples that are to be stored for more than 2 to 3 d should be centrifuged to remove sediment. If a centrifuge is not available, samples may be allowed to stand undisturbed for at least 28 h. The supernatant in the upper 10 cm can then be resampled and should then be clear enough to sample and analyze, although this procedure is untested.

Average sediment content in all furrow-stream samples was 1.5 g L^{-1}. The CSI increase caused by residual sample sediment was approximately 15% wk^{-1} for the first 3 wk, but jumped to 75% wk^{-1} in the last 2 wk (Fig. 4). Since biocide and PAM stabilizer additives prevented PAM degradation, it is likely that the aqueous PAM concentration diminished with time as a result of its adsorption onto residual sediment. The increasing slope of the fitted curve is probably a function of nonlinearity in the PAM concentration/CSI calibration curve, i.e., when PAM concentration falls below 1 mg L^{-1}, the slope of the calibration function changes more rapidly as sample PAM content declines (Fig. 3).

The process of polyelectrolyte-particle adsorption can be slow, taking days, weeks, months, or longer to attain equilibrium (van de Ven, 1994). Mortensen (1962) reported that even under vigorous mixing, the adsorption of polyelectrolyte by kaolinite and other clay minerals continued beyond 8 h, depending on the cation exchange species. The presence of multivalent cations can extend the adsorption period (Mortensen, 1962; Theng, 1982). In a freshly collected furrow water sample, initial adsorption rate is relatively rapid, as suspended sediment settles through the solution, intercepting aqueous polymers. Once the sediment settled to the container bottom, however, its availability to dissolved PAM molecules would decrease. The adsorption process would slow, becoming essentially diffusion dependent, and can continue for several weeks. Resuspension of the sediment during storage would be expected to accelerate polymer adsorption.

Sample Stability

The effect of sample storage on measured response is a concern when determinations cannot be done promptly. Measured CSI of PAM solutions changed significantly during the 109-d study. Although a similar pattern of CSI fluctuations occurred among all treatments during the first 14 d, the magnitude of these fluctuations was relatively small (standard deviation, 1.8-4.4 s). Statistical analysis indicated no significant effect of time (within treatment) on measured CSI during the initial 4-wk period. Similarly, treatment did not significantly affect CSI during this interval. Significant changes in measured CSI did occur with time for all treatments after Day 28.

Assuming CSI measurements taken during the first 2 wk produced the more accurate values, we evaluated the treatments by plotting the absolute difference between the 2 through 14-d mean CSI and measured CSI for each assay day. The measured CSI for all treatments did not differ significantly from the 2 through 14-d mean during the first 4 wk (Fig. 5). Subsequently, measured CSI for all but the combined boric acid and 2-propanol treatment exceeded that of the 2 through 14-d mean. For this combination treatment only, CSI test values for the entire 109-d storage interval remained identical to the initial 2 through 14-d mean. Hence, samples and standards should be treated with both boric acid and 2-propanol if they are to be stored for more than 4 wk. The small CSI shifts occurring early in the storage period were remarkably consistent for the different PAM solutions (data not shown). This suggested that analytical precision could be further optimized by ensuring that the lag time between solution creation and measurement is identical for both the standards and samples. If equivalent lag times cannot be maintained during testing, we recommend that standards and samples be measured within 2 wk of solution creation, since the least variation occurs during this period (Fig. 5).

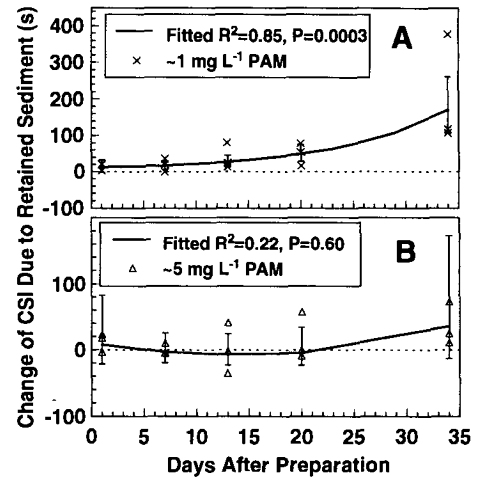

Fig. 4. Increase in sample CSI with time, when sediment is retained in (*A*) ~1 mg L^{-1} PAM sample and (*B*) ~5 mg L^{-1} PAM sample. Fitted line is quadratic model of log(CSI difference + 40), and includes independent variables, days, days×days, and rep (class variable).

Method Detection Limit, Precision, and Bias

The method detection limit of the flocculation test was approximately 0.1 mg L^{-1}. Single-operator precision varied somewhat with the test method employed, ranging

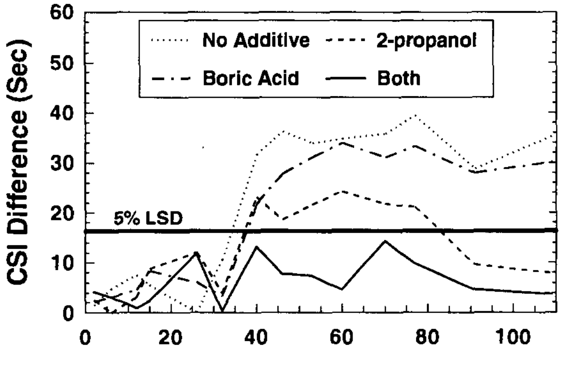

Fig. 5. Stability of measured sample CSI with time. Absolute difference between measured CSI and the treatment's 2 through 14-d mean. The 2 through 14-d mean CSI is significantly different from a given days's CSI if the difference exceeds the 5% LSD.

Table 7. Bias and precision of the flocculation test for two different PAM concentration ranges and three initial sediment levels.

Initial sediment content	0-2.5 mg L^{-1} test range		2.5-10 mg L^{-1} test range	
	Bias	Precision	Bias	Precision
g soil L^{-1}	mg L^{-1}			
0	0.08†	±0.11	0.32	±0.39
1	0.05	±0.08	−0.69	±0.86
5	−0.03	±0.06	0.16	±0.42

† A positive bias indicates underestimation and a negative bias indicates overestimation of PAM content.

from ±0.06 to ±0.11 mg L^{-1} for the low-PAM procedure, and from ±0.39 to ±0.86 mg L^{-1} for the high-PAM procedure (Table 7). This accuracy compared favorably with wet-chemistry methods (±0.2-1.0 mg L^{-1}). The bias analysis indicated that the flocculation test may slightly underestimate PAM concentrations (by 0.03 mg L^{-1}) in the low-PAM protocol, and overestimate PAM concentration (by 0.07 mg L^{-1}) in the high-PAM protocol (Table 7). Bias results may not be consistent if averaged over several analyses conducted by different operators.

When three different operators analyzed several unknowns, mean PAM amounts recovered were within two standard deviations of the actual value of the standard (Table 8), an acceptable accuracy (Greenberg et al., 1992). Operator errors were not consistently negative or positive, suggesting that the flocculation test is not consistently biased, and that accuracy may be better than indicated by results of the single bias analysis reported above.

Field Study

The Option-2 procedure was used successfully in a field study to measure PAM concentration in furrow runoff. However, careful attention to initial scheduling of field and laboratory efforts was necessary to ensure that test lag times were equal for both samples and standards (Table 1, F1). Early in the irrigation, runoff PAM concentration was 3.9 mg L^{-1} (SD = 0.4), one-third to one-half that of the 10 mg L^{-1} irrigation inflow concentration. Over time, however, tailwater PAM concentration increased to 8.9 mg L^{-1} (SD = 1.6), nearly duplicating that of the inflow streams. An unusual calibration curve was occasionally produced when preparing standards from tailwater containing >4 mL L^{-1} settled sediment after 0.5 h settling time in Imhoff cones (Sojka et al., 1992). In these cases, the 0.1 mg L^{-1}, PAM standards displayed an uncharacteristically high flocculation capacity (low CSI), although the 0.0 mg L^{-1} and >0.25 mg L^{-1} PAM standards behaved normally. Obviously, such a calibration curve could not reliably predict PAM concentration below 0.25 mg L^{-1}. For sediment levels >4 g L^{-1}, 0.25 mg L^{-1} PAM was the practical method detection limit. We suspect a DOC/PAM interaction produced this phenomenon. This result might indicate that a different procedure (combination of sample volume and kaolin) is required to accurately test for dissolved PAM at low concentrations.

Table 8. Test errors associated with independent analyses of standards that are unknown to operators.

Unknown	Analytical error† Operator 1	Operator 2	Operator 3
A	1.95	2.40	−1.29
B	−1.43	0.49	0.15
C	−1.18	1.87	−1.40

† Error = mean (measured − actual)/standard deviation of measured values.

CONCLUSIONS

Application of polyacrylamide to irrigation water to control furrow infiltration and erosion is a rapidly expanding practice in the western USA. A convenient method of testing for PAM concentration in surface waters is needed to determine the fate of applied PAM in furrow tailwater and in return flows. The flocculation (CSI) test described here provides a relatively simple, rapid, and accurate method of determining polyacrylamide in irrigation streams. The general procedure outlined in Table 1 is simpler and faster than either of the optional methods, but its accuracy, ±1 mg L^{-1} (±40% for the low range and ±10% for the high range determination), is less than the ±0.25 mg L^{-1} achievable with the optional methods. If inorganic and non-PAM organic components in the water remained constant during the sampling period, the precision of the general procedure would equal that of Option 2. Unfortunately, that is unlikely to be the case in most irrigation water applications. Hence, to improve the method's precision, one can account for water quality effects by preparing optional sets of standards using irrigation water having different sediment contents. These standard sets are used to improve the method's precision during field applications. The best precision was obtained using Option 2 (Table 1), ±3% for 0 to 2.5 mg L^{-1} PAM range, and ±6% for the 2.5 to 10.0 mg L^{-1} PAM range. Option 2 requires sample sediment concentration be known. For most field applications Option 1 provided a reasonable compromise between protocol simplicity and precision, giving a low-range accuracy of ±10% (±0.25 mg L^{-1}), and a high range of ±3% (±0.3 mg L^{-1}). Option 1 does not require data on sample sediment concentration. A preliminary field study indicated that PAM concentrations in uninterupted 10 mg L^{-1} PAM-treated furrow runoff equaled that of the inflow when PAM was applied for as long as 3 h.

ACKNOWLEDGMENTS

The authors thank Dr. David Laird for supplying processed clay mineral substrate; Ms. Barbara Prater, Mr. Ronald Peckenpaugh, and Ms. Emily Aston for their invaluable laboratory and field assistance; Dr. Frank Barvenik, Dr. John Letey, and Dr. Dale Westermann, and three anonymous reviewers, for their helpful comments on an earlier draft of this manuscript. This work was supported in part by the Cooperative Research and Development Agreement with CYTEC Industries under contract 58-3K95-4-216.

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