INFLUENCE OF STRUCTURE AND FORMULATION ON THE EFFICACY OF POLYACRYLAMIDES AS SOIL STABILISERS

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The use of high M.W. anionic polyacrylamides (PAMs) to prevent soil erosion in furrow irrigation is now well established *(Lentz and Sojka 1994)*. Field studies have, of necessity, concentrated on the gross benefits of PAM treatment by measuring the reduction of soil-loss from the field and the consequent improvement in tail-water quality.

It is recognized, however, that PAM can reduce soil erosion by two distinct mechanisms: improving the stability of the soil aggregates and flocculating suspended solids, thus aiding their deposition in the furrow.

Letey (1994) clearly demonstrated that PAM's were adsorbed essentially irreversibly onto the surface of wet soil aggregates giving them greater mechanical strength. There was little penetration of the soil aggregate so that if it were broken subsequently, by water impact for example, then the interior may be exposed and be susceptible to dispersion.

Flocculation, by physical linking of particles by polymers, is well known and has been extensively reviewed *(Akers 1975, Gregory 1984)*. High M.W. PAMs are known to act as flocculants for clay particles. Formation of flocs which separate out in the furrow will also reduce soil run-off from the field.

Clearly, in a field situation, the extent to which each mechanism contributes to the overall stabilization may vary dramatically. It will be influenced by soil type, cultivation practice, polymer structure, polymer concentration and water velocity. It is further complicated by the fact that the latter two parameters will vary along the furrow during the advance time. Well aggregated soil in low water flows (near the field bottom)

may be stabilized largely by aggregation, whilst flocculation is likely to be an essential mechanism for poorly structured soils at the field top.

Of the two mechanisms, improving aggregate stability would seem the preferred method both practically and theoretically. The soil aggregate remains in place, and treating the surface of aggregates should require less polymer.

Flocculation will dramatically reduce, but not prevent, soil movement. It is also known that the floc structure can be affected by polymer structure and dosage, making flocs more or less permeable to water. Thus a large number of flocs may have an influence on infiltration of water into the soil.

It is well-known that soil aggregate stability can be improved by PAMs of various M.W. from low ($< 10^5$g mole^{-1}) to high ($> 10^7$g mole^{-1}). Letey's work was carried out with very high M.W. products. However, a low M.W. product has a chain length of the same approximate dimensions as a small soil pore. Thus penetration of the aggregates may be increased.

Flocculation, by contrast, requires a very high M.W. polymer. Thus the products currently in use are of high M.W. as these represent the best single option.

The objective of our laboratory work was to quantify the relative contributions of the two possible mechanisms. The technique chosen was to study the effects of mixes of a high and low M.W. PAM on soil stability. It is well known that the latter can stabilise aggregates but has very poor efficiency as a flocculant. The high M.W. PAM is effective by both mechanisms.

Materials

Two polymers were chosen for the experiments. The high molecular weight anionic polyacrylamide (H-PAM) was a solid product ($> 95\%$ active) with M.W. 16 million g mol^{-1}, and had substitution of acrylamide by acrylic acid to the extent of 15%, followed by conversion to the sodium salt. The polymer is known to be an excellent flocculant for clays and to improve aggregate stability of soils.

The low molecular weight product (L-PAM) was an aqueous solution (20% active) with M.W. 100,000g mol^{-1} with substitution of acrylamide by acrylic acid of 36%, followed by neutralisation. The polymer is known to improve aggregate stability of soils.

The soil chosen for the experiment was a sandy silt loam, containing 2.6% organic matter, pH 7.45. The soil is extremely poorly structured, and taken from a field in Lincolnshire, UK, with a history of crusting and slumping. Visually, addition of water to dry crumbs with gentle agitation leads to rapid breakdown.

Soil samples were air-dried on an open bed for 1 week with periodic manual breaking of any larger clods. A fraction of soil crumbs in the range 2-2.8mm was obtained by sieving. A fraction of soil fines of $< 500\mu$m was obtained by grinding and sieving.

Methods

The experiments were designed to simulate, as far as possible, the field situation, i.e. aqueous solutions of polymers were added directly to dried soil and the effects were measured directly, with no opportunity for subsequent drying of the polymer onto the soil.

▼ **Preparation of Polymer Solutions.** Aqueous solutions of each of the two polymers were prepared containing 50ppm dry polymer in each case.

These were used throughout the experiments to prepare solutions of mixed high and low M.W. polymers in a range of 2-18ppm total dry polymer.

▼ **Experimental Design.** A central composite box ('star point') design of experiments was chosen. Polymer compositions tested were arranged in two blocks which allows the work to be performed in two stages (e.g. at separate time stages or with different operators). Subsequent statistical analysis (see below) would allow testing of main effects, interaction and whether curvature was present. Repeating central points would allow estimation of replication error.

Six series of experiments were carried out using mixtures of the high

and low M.W. polymers on soil fines and crumbs over a range of polymer concentrations, as detailed below.

▼ **Experiment 1 Flocculation at Low Polymer Concentration.** Soil fines (20g) were placed in a 1 l measuring cylinder. Water was added to the 1 l mark, the cylinder closed, and shaken vigorously for 30 sec. to disperse the soil fully.

Mixed polymer solution (10ml) was added. The cylinder was inverted 10 times, then allowed to stand before withdrawal of samples for analysis. The experiment was repeated with other mixed polymer solutions.

▼ **Experiment 2A Soil Fines/Low Polymer Concentration.** The experimental series was carried out identically to that of 1 above, except that the polymer solutions were added to the soil suspension prior to vigorous shaking for 30 seconds.

▼ **Experiment 2B Soil Fines/High Polymer Concentration.** Mixed polymer solution was added to soil fines (20g) in the measuring cylinder, to a volume of 1 litre. The suspensions were shaken vigorously for 30 sec., then inverted 10 times and allowed to stand before sampling.

▼ **Experiment 3A Soil Crumbs/Low Polymer Concentration.** Soil crumbs (20g) were gently placed in the cylinder. Water was slowly run down the side of the sloping cylinder to the 1 litre mark. Care was taken throughout to prevent break-up of the crumbs. Mixed polymer solution (10ml) was added, the cylinder was inverted 10 times, and then allowed to stand before sampling.

▼ **Experiment 3B Soil Crumbs/High Polymer Concentration.** Mixed polymer solution was run gently down the side of the sloping cylinder onto the soil crumbs, and made up to the 1 litre mark.

The cylinder was inverted 10 times as above.

▼ **Experiment 4 Soil Crumbs/Initial High Polymer Concentration.** Mixed polymer solution (10ml) was run gently down the side of the cylinder from a pipette onto the soil

crumbs. This volume of solution was sufficient to 'wet-up' the aggregates.

The soil was allowed to stand for 2 mins., then water was added gently to the 1 L mark. The cylinder was inverted 10 times as above.

▼ **Sampling.** In all the experiments above, sampling was carried out as follows. After 3 mins. standing, the cylinder was opened, and an automatic Finn pipette was introduced to an exact depth of 5cm below the surface and 10ml liquid was withdrawn.
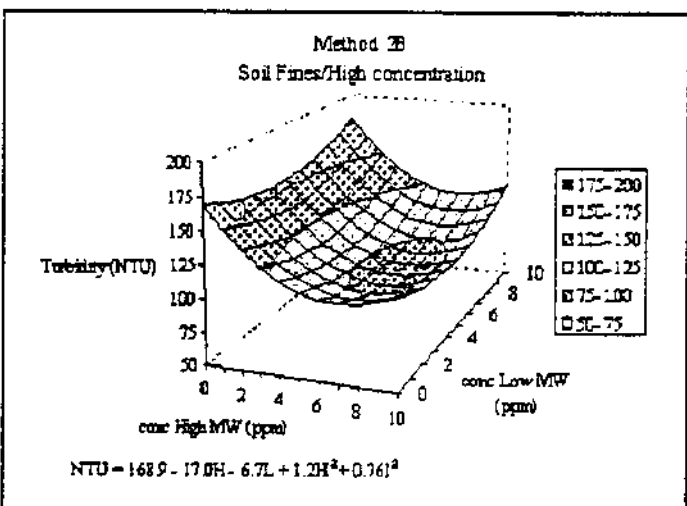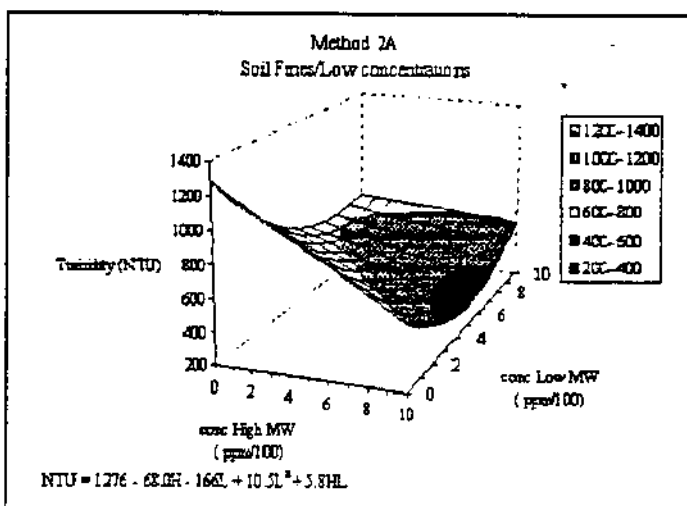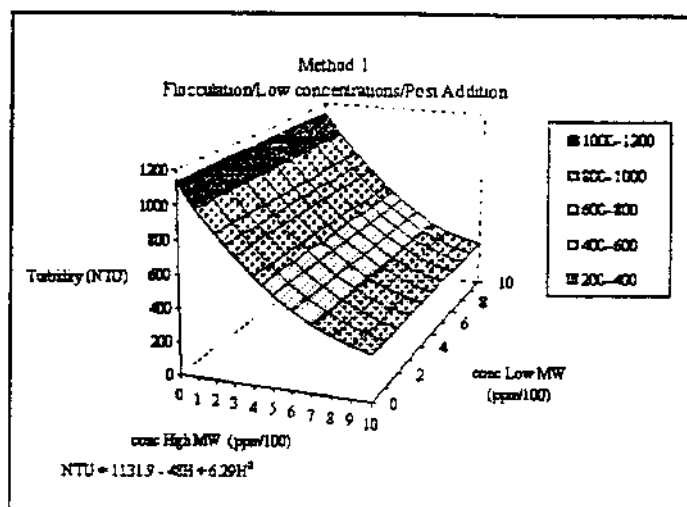
This was added to a cell containing 5ml distilled water. The cell was sealed, dried, agitated, and placed in a Hach 2100P Turbidimeter. Turbidity was determined automatically. Duplicate readings were taken.

▼ **Statistical Analysis.** Regression analysis of the turbidity readings was performed using Minitab statistical software to allow separation of effects due to H-PAM (H), L-PAM (L), H^2, L^2 and HL. Block effects were taken into account where applicable. Only terms with probabilities greater than 90% were used to generate regression equations. These were plotted using Microsoft Excel.

Results and Discussion

As the experiments did not allow any drying of soil, any effects observed should be relevant to a single irrigation in a field situation. Effects may arise between irrigations because of polymer drying onto the soil and becoming irreversibly bound (Letey 1994) but these have been ignored in this study. The results are summarised in the 3-D surface plots.

It should be noted that the polymer concentrations shown on the axes refer to the theoretical level of polymer in aqueous solution, no correction has been made for polymer bound to soil.

Method 1
Flocculation/Low concentrations/Post Addition

Turbidity (NTU)
conc Low MW (ppm/100)
conc High MW (ppm/100)
NTU = 1131.9 - 42H + 6.29H²

Method 2A
Soil Fines/Low concentrations

Turbidity (NTU)
conc Low MW (ppm/100)
conc High MW (ppm/100)
NTU = 1276 - 68.0H - 166L + 10.5L² + 5.8HL

Method 3B
Soil Fines/High concentration

Turbidity (NTU)
conc Low MW (ppm)
conc High MW (ppm)
NTU = 168.9 - 17.0H - 6.7L + 1.2H² + 0.36L²

In Experiment 1, vigorous agitation of the soil fines ensured that maximum breakdown of any soil structure was achieved prior to addition of PAM. Not surprisingly, the results are entirely consistent with a

flocculation effect at low polymer dosage. There is a strongly beneficial effect of H-PAM over the dose range 0.01-0.1ppm polymer, whilst L-PAM had no detectable effect.

In contrast Experiment 2A showed a large beneficial effect of low concentration of L-PAM, even in the absence of H-PAM. The only difference between this experiment and the previous is that the vigorous agitation took place in presence of the mixed polymer. Since L-PAM has no flocculation effect, the likely explanation is that even low dosages of polymer (> 0.05ppm) give some residual stability to soil structures, even during vigorous agitation. In presence of H-PAM, the contribution of L-PAM to the observed effect becomes less important.

A similar effect is detected in Experiment 2B where polymer is applied at higher dosages to soil fines prior to dispersion. The higher dosages lead to less clay left in suspension. Both L- and H-PAM exhibit beneficial effects, suggesting that both aggregate stabilization and flocculation are contributing mechanisms.

Both polymers exhibit a detrimental effect at higher polymer dosages. The 'bowl-shape' to the graph is typical of many flocculation processes, where an increase in solution viscosity can reduce the rate of sedimentation of suspended solids.

In the first experiment with soil crumbs (3A), one conclusion is immediately obvious. Even though the crumbs had been treated with water alone, prior to the addition of any
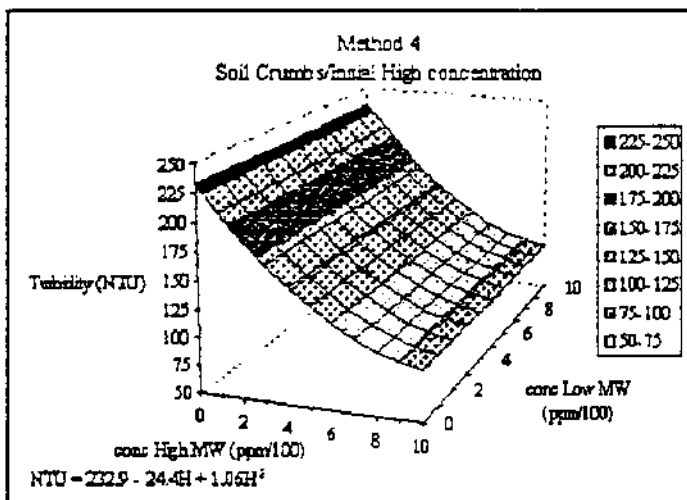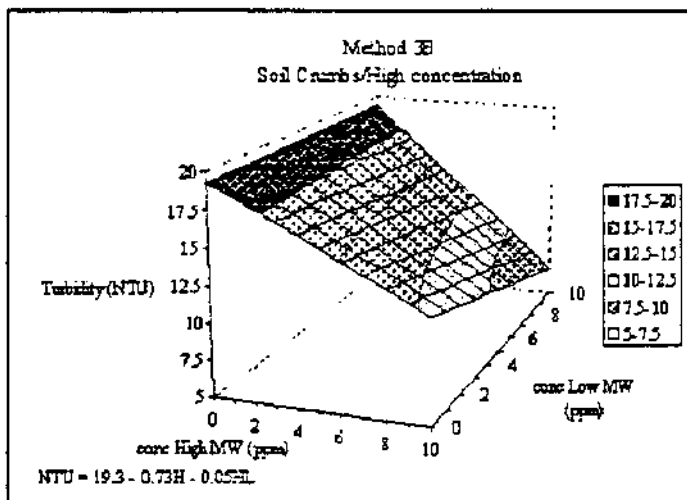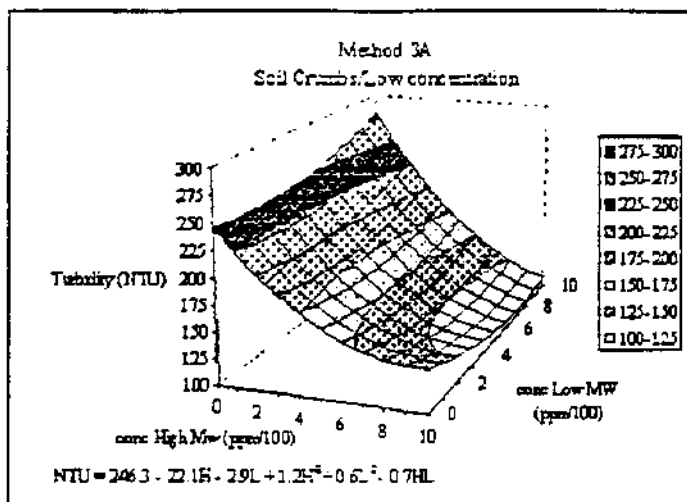
polymer, all the turbidity readings were much lower that those observed in Experiments 1 and 2A.

We can thus conclude that breakdown of the structure into fines, followed by stabilization and/or flocculation plays a minor role in the reduction in turbidity achieved. Thus, significant stabilization of large aggregates can be achieved by very low concentrations of polymer in solution (0.01-0.1ppm).

In Experiment 3B, polymer was applied to soil crumbs at levels typical of those used in the field. Excellent stabilization of the aggregates occurred, giving turbidity readings typical of 'clean' water. Once again, comparison with 2B confirms that breakdown of crumbs into fines followed by stabilisation/flocculation plays an insignificant part in the process.

Comparison of 3A and 3B shows, unsurprisingly, that higher concentrations of polymer give greater aggregate stability. It may be anticipated that higher polymer levels in solution can bring about higher polymer levels on the polymer surface, leading to greater stabilization.

Some insight was provided into this hypothesis by Experiment 4. Small amounts of mixed polymer solutions, sufficient to wet-up the soil crumbs, were added and allowed to stand for two minutes. Thus, the crumbs were subjected to a solution concentration of polymer typical of those used in Experiment 3B. On subsequent addition of water, the overall polymer dosage was typical of those used in Experiment 3A.

Method 3A
Soil Crumbs/Low concentration

$$NTU = 246.3 - 22.1H - 2.9L + 1.2H^2 - 0.6L^2 - 0.7HL$$

Method 3B
Soil Crumbs/High concentration

$$NTU = 19.3 - 0.73H - 0.05HL$$

Method 4
Soil Crumbs/initial High concentration

$$NTU = 232.9 - 24.4H + 1.06H^2$$

The results of Experiment 4 show a remarkable similarity to those of Experiment 3A, as shown by the equations derived from the regression analysis. We thus conclude that we are observing essentially the same phenomenon. Despite the fact that,

in one case the crumbs were soaked in water, then treated with dilute polymer, and in the other case, the crumbs were soaked in higher concentrations of polymer, the final result is that similar dosages of polymer produce similar effects, regardless of methods of addition.

One simple explanation is that there is a very rapid dynamic equilibrium between polymer bound to the soil and polymer in solution, so that a constant surface dosage is maintained.

This is, however, inconsistent with the observation that high M.W. PAM does not desorb from soil aggregates when wet.

Thus, the likely explanation is that there is an excess of polymer compared to binding sites in the soil surface. These are saturated rapidly and the excess polymer is in the aqueous phase. Thus, in both 3A and 4, the same distribution of polymer between soil surface and solution is achieved rapidly.

The explanation that more polymer is bound to the surface in Experiment 3B therefore looks less likely, if we argue that binding sites are saturated.

The alternative explanation is that of surface repair. Any breakdown of the stabilized crumbs exposes new surfaces but these are stabilized rapidly in presence of polymer. The process is naturally faster at higher polymer concentrations.

All the results suggest that a 'classical' flocculation mechanism: complete dispersion of particles into water, followed by flocculation of suspended clay by polymer has a small role to play. The relatively small effects of L-PAM in presence of H-PAM are interesting. It is hypothesized (Letey 1994) that there is a very low probability that large molecular size, multi-segmented, and flexible polymer segments can simul-

taneously be detached and moved back into bulk solution. However, binding and detachment of individual segments is believed to be a dynamic process. It is feasible that an L-PAM molecule may detach, or may be displaced from binding sites by H-PAM.

Summary and Conclusion

The results of this study on a poorly structured soil suggest that even under vigorous agitation (as may be found at the water inlet), total breakdown of soil aggregates is unlikely. On gentle application of polymer solutions, even at very low dosage (0.01-0.1ppm) aggregate stability is increased significantly. Thus, during the advance time, stabilisation by the water-front can be achieved, even if the polymer concentration has been depleted significantly. The speed with which polymer binds to soil surfaces, even at very low dilution suggests that a 'repair' mechanism, i.e. stabilization of newly exposed surfaces before significant breakdown is a key feature.

This mechanism is consistant with the observation (*Lentz and Sojka 1994*) that a high initial dosage of PAM (10ppm) during one to two advance times was more effective than 0.25ppm PAM applied throughout. The high initial dosage will protect the existing surfaces of the soil, together with those generated by the loss of easily detached soil particles early in the irrigation.

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