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Long-term water retention increases in degraded soils amended with cross-linked polyacrylamide

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Abstract

Cross-linked polymer hydrogels, polyacrylamide co-polymer (XPAM), and K-polyacrylate (XPAA) increase soil water availability under drought, but their long-term effects are unknown despite the importance of such knowledge in assessing economic feasibility. This 9-yr outdoor pot study evaluated a one-time addition of XPAM or XPAA at 0.25 or 0.5% dry weight (5.6 or 11.2 Mg ha^{-1}) in a degraded calcareous silt loam. Controls included an unamended degraded soil and an unamended nondegraded soil (topsoil). Soil water retention and plant available water (PAW, g water g^{-1} dry $soil^{-1}$) were measured in soil samples collected in spring for seven of the nine years. Across all years, the 0.5% XPAM produced the greatest PAW (0.318) and the PAW of other treatments followed in the order: 0.5% XPAM > 0.25% XPAM > Topsoil > 0.5% XPAA > 0.25% XPAA = control (0.224). In all years, the 0.25% XPAM and 0.5% XPAM treatments increased soil PAW relative to the control, that is, their PAW ratios exceeded unity. Topsoil PAW exceeded that of the control in six of the seven years measured. The PAW of 0.25% XPAM and 0.5% XPAM peaked in Year 1 after application and declined linearly with time ($P < .03$), at $-0.0036\ yr^{-1}$ and $-0.0044\ yr^{-1}$, respectively. Hence, the mean residence time the XPAM-related water-retention benefit is 24–29 yr. In this study, soil water-retention benefits from XPAM amendments exceeded projections proposed by the industry (5 yr) and suggests that the cost-benefits of field-level XPAM applications might be more favorable than previously anticipated.

1 | INTRODUCTION

Critical components of soil health and productivity are a soil's ability to absorb and retain water for use by growing crops. Past cropping and irrigation practices and soil erosion in semiarid farmlands have substantially compromised soils by removing top soil and decreasing the soil's organic matter content, which decreases soil aggregate stability, infiltration rate, and water-holding capacity (Khaleel, Reddy, & Overcash, 1981; Larney & Angers, 2012; Lentz, Lehrsch, Brown, Johnson-Maynard, & Leytem, 2011; Robbins, Mackey, & Freeborn, 1997). A reduction in rainfall in some areas in response to a warming global climate likely will intensify the negative effects of this soil degradation (Trenberth, 2011).

The potential of superabsorbent polymer hydrogels for increasing the water retention of soils and water supply of plants has been known since the early 1980's. Related research was reviewed by Kazanskii and Dubrovskii (1992). More recently, Hüttermann, Orikiriza, and Agaba (2009) reviewed literature addressing hydrogel use for improving

Abbreviations: MRT, mean residence time; PAW, plant available water; PR, penetration resistance; XPAA, crosslinked K-polyacrylate; XPAM, crosslinked polyacrylamide co-polymer.

degraded lands. Cross-linked, high molecular-weight anionic polyacrylamide (XPAM) or hydrogel amendments have been shown to increase soil water retention and potentially mitigate effects of drying climates and water stress (Agaba et al., 2010; Choudhary, Shalaby, & Al-Omran, 1995; Duarte, Contreras, Contreras, Carvajal, & Ramirez, 2019; Hüttermann, Zommorodi, & Reise, 1999; Kalhapure, Kumar, Singh, & Pandey, 2016; Liu & Chan, 2015; Narjaryk, Aggarwal, Singh, Chakraborty, & Singh, 2012; Nirmala & Guvvali, 2019; Riad, Youssef, Nashwa, El-Azm, & Ahmed, 2018; Woodhouse & Johnson, 1991). A 0.4–0.5% (w/w) addition of XPAM to a sandy soil prolonged time to wilting of crop and tree seedlings by three to five times compared to untreated soil (Hüttermann et al., 1999; Woodhouse & Johnson, 1991). An application of 0.6% (w/w) XPAM or XPAA increased the water holding capacity two- to four-fold over the control in sand and loam soils with pH of 7 to 8, and XPAM was the most effective treatment (Choudhary et al., 1995). The addition of 0.4% (w/w) K-XPAA increased plant available water (PAW) by up to three-fold in sand, two-fold in silt loam, and 1.5-fold in loamy and clayey soils, compared to the controls (Agaba et al., 2010). The XPAM and XPAA had no significant effect on soil PAW when applied at rates <0.2% (w/w; Sivapalan, 2006; Leciejewski, 2009; Taban & Naeini, 2006).

The crosslinked polymers also influence other soil physical properties. Choudhary et al. (1995) reported that evaporation from sand and loam soils declined as XPAM and XPAA treatment rates increased from 0 to 0.6%. Hayat and Ali (2004) observed an 8% decrease in the bulk density of a sandy loam when amended with 0.5% (w/w) XPAM. When applied at 0.003% (w/w) to a sandy loam, neither XPAM nor XPAA measurably affected soil bulk density, but both significantly decreased soil penetration resistance (Xu, Zhang, McLaughlin, Mi, & Chen, 2015).

Manufacturers of XPAM estimate that the product has a useable life in soil of 3 to 5 yr (Chen, Zommorodi, Fritz, Wang, & Hüttermann, 2004), but this claim has not been demonstrated with published research. The majority of XPAM and XPAA studies were conducted in the laboratory or greenhouse over a period of 5 mo or less. Of the field studies, observations were made over periods of 8 mo or less. Thus, few (if any) field studies were designed to evaluate the long-term persistence of hydrogel effects on soil or growing crops (Xu et al., 2015). A 72-mo tree-seedling survival study in a revegetated slate quarry evaluated XPAM (1 g L^{-1} substrate^{-1}) for increasing water retention (Williamson et al., 2002). The XPAM gel samples collected from soil at 18, 43, and 72 mo were dried at 60 C then rehydrated in distilled water. By the eighteenth month, the field-conditioned XPAM absorbed only 15% of the water it did when fresh (Holliman, Clark, Williamson, & Jones, 2005).

The degradation of XPAM and XPAA in the soil appears to be a multi-stage process (Stahl, Cameron, Haselbach, & Aust, 2000). Unpolymerized monomers and low molecular-weight oligomer contaminants in the products, and hydrogel cross-linkages are most susceptible to breakdown and mineralization (Cook, Bloom, and Halbach (1997). Degradation of the cross-linkages results in the breakdown of gel's three-dimensional structure and release of linear polymers, which are solubilized by the soil solution (Cook et al., 1997; Stahl et al., 2000). The degradation of polymer cross-linkages can occur relatively rapidly in soil, though reports are conflicting. Cook et al. (1997) reported rapid solubilization of XPAA gel particles during incubation in simulated municipal solid waste, with gels no longer visible after 3 d. Others found that XPAM and XPAA gel structure persisted in soils for months or years (Holliman et al., 2005; Oksi ska, Magnucka, Lejcu , & Pietr, 2016, 2019; Stahl et al., 2000). Oksi ska et al. (2016, 2019) reported that the rate of solubilization differs with polymer type, being more rapid for XPAA (100% yr^{-1}) than for XPAM (41% yr^{-1}). Solubilization of the hydrogel molecule exposes interior linear components to degradation processes. The mineralization rate of the linear polymer can be two- to six-times greater than that for the gel (Cook et al., 1997; Stahl et al., 2000).

The degradation of hydrogel cross-linkages results in the breakdown of the gel structure that is responsible for its water absorbing and retention functionality. This long-term outdoor pot experiment targets a gap in the hydrogel literature, addresses conflicting reports of the hydrogel's persistence in soil, and provides economic information applicable to field-level management. The study treated a degraded soil with a single application of either XPAM or XPAA hydrogel and measured their effect on soil water retention in the following nine years.

2 | MATERIALS AND METHODS

2.1 | Site, soils, and amendments

Soil for the study was collected from 0- to 15-cm depth in an artificially eroded Portneuf silt loam (coarse-silty, mixed superactive, mesic Durinodic Xeric Haplocalcids) in early Spring 2009. The field source near Kimberly, ID (42E 31 N, 114E 22 W, elevation of 1,190 m) had been stripped of topsoil in Spring 1991 to expose the calcareous Bk horizon and simulate erosion (Robbins et al., 1997). Topsoil from a Portneuf silt loam in an adjacent field, which was not subject to artificial erosion, was sampled using the same procedure as that for the eroded Portneuf. Soil properties are reported in Table 1.

The XPAM treatment used is a commonly available anionic cross-linked K-acrylate-polyacrylamide copolymer (Stockosorb Agro-S, Evonik Stockhausen, Greensboro, NC). The XPAM was manufactured by cross-linking linear

TABLE 1 Selected properties of soils. Particle size analysis was done by hydrometer method after removal of organic material. Electrical conductivity (EC) and pH were determined on saturated extract. Calcium carbonate equivalent ($CaCO_3$) was determined using a pressure calcimeter (Sherrod, Dunn, Peterson, & Kolberg, 2002). Organic carbon (OC) was determined by dry combustion after pretreatment to remove inorganic carbon (Shimadzu Total Carbon Analyzer)

Material	Sand	Silt	Clay	EC	pH	$CaCO_3$	OC	C[a]	N[a]	C:N
	g kg^{-1}			dS m^{-1}		%	g kg^{-1}			
Subsoil	220	600	180	0.45	8.0	23.5	5.8	34.3	0.7	49.0
Topsoil	240	560	200	0.58	7.8	9.6	8.4	20.0	0.9	22.0

[a]Total C and total N of soil were determined on a freeze-dried sample with a Thermo-Finnigan FlashEA1112 CN analyzer (CE Elantech, Lakewood, NJ).

polyacrylamide copolymer molecules with an anionic charge density of 27 to 35% and a molecular weight of 12 to 15 Mg mol^{-1}. The XPAA hydrogel is a crosslinked, high molecular-weight polyacrylic acid-potassium salt (Stockosorb 660, Evonik Stockhausen, Greensboro, NC). Both hydrogel chemistries incorporated K counterions and both were crystalline, with granule diameters ranging from 0.8 to 2.0 mm. Waters with different electrical conductivities (EC) strongly influence hydrogel performance (Johnson, 1984). We compared the water absorbing characteristics of the two hydrogels in water alone to show how the effects of tap water used in the experiment are related to those of differing water qualities. The water absorbance of the hydrogels was determined by inundating a 0.5-g sample (previously dried at 60 C.) in deionized water adjusted to ECs of 0, 0.6, or 0.12 dS m^{-1} with $CaCl_2$, or simulated irrigation water (2.5 mmol$_c$ L^{-1} Ca^{+2} as $CaCl_2$, 3.0 mmol$_c$ L^{-1} Na^+ as NaCl, and 2.5 mmol$_c$ L^{-1} Mg^{+2} as $MgCl_2$). After 72 h, the hydrogel was drained on filter paper before weighing. The trial included three replicates.

2.2 | Experimental design

The experimental design was completely randomized with four replicates. The full design comprised six treatments: two XPAM rates, two XPAA rates, an untreated control, and an untreated topsoil. The XPAM and XPAA were applied at 0.25 or 0.5% (w/w) a.i. rates. The 0.25% rate was selected to ensure a measurable effect on soil water retention and was doubled in the second rate to give equally spaced treatments. An untreated control and topsoil received no amendments. The 0.25 and 0.5% treatments are roughly equivalent to 5.6 and 11.2 Mg a.i. ha^{-1} (dry weight), respectively. A planting pot (14-L volume, 26-cm diameter, and 26-cm depth) represented one experimental unit.

Treated soils were prepared on 17 April 2009. Weed barrier cloth was used to line the pot bottom, followed by a base-layer of 5 cm of wet sand. An appropriate mass of air-dried amendment material was mixed with 13.2 kg of air-dried Portneuf subsoil and packed into each pot by firmly tapping the vessel on the concrete floor five times.

Soil pots were moved outdoors on 2 July 2009 to start the current study, where they remained except for 3 to 4 d each spring when they were moved under cover to perform leaching measurements (not reported here). All other sampling and measurements were conducted in the field. Pots were arranged in a shallow trench with straw packing around pot sidewalls to insulate them from surface heating and/or cooling effects. The straw was replaced by bark-chip mulch in subsequent years.

A series of locally cultivated crops were grown in pot soils from 2009 to 2018 to simulate farm conditions (Table 2). We did not attempt to duplicate local rotations because the pots did not lend themselves well to root or corn (Zea mays) crops (although one corn crop was included). Prior to planting each year, we sampled the pot soil using a 20-mm diameter probe. Three samples to 15-cm depth were collected and composited, 100 g was retained, and the excess was returned to the pot. We then tilled pots manually to simulate annual tillage, inverting and mixing the soils to 15-cm depth. Conventional tillage is a common practice in this irrigated tract. Crop planting and harvest information and soil sampling dates are given in Table 2. An automated flow-emitter system supplied irrigation water to all pots equally to meet estimated crop evapotranspiration requirements. Irrigation water was supplied from local groundwater with an electrical conductivity of 0.94 dS m^{-1} and pH of 7.3. At harvest, the entire aboveground crop tissue was harvested from each pot. The crop roots remained in pot soils except for the corn root crown, which was removed at planting the following year. Pot surface soils were left fallow and uncovered during the nongrowing season.

2.3 | Soil water retention

Soil samples were collected from pot soils in 2009–2011, 2013, and 2015–2018. Water retention was measured on the samples using a pressure plate apparatus which determined soil water retention at matric potentials of 0, −10, −20, −33, −50, −100, −300, −500, and −1,500 kPa (Dane & Hopmans,

TABLE 2 The type and number of crop plants grown, fertilizer applied, and dates of planting, harvest, and soil sampling during each year of the study

Year	Crop	N as NH_4NO_3	P_2O_5 as KH_2PO_4	K_2O as KH_2PO_4, KCl	Fertilizer applied	Planting date	Number of plants per pot [a]	Harvest date	Date soil sampled
		kg ha^{-1}							
2009	Bean (Phaseolus vulgaris L.)	100	22.4	59.6	23 Apr.	6 July[b]	2	30 Sept.	17 Apr.
2010	Barley (Hordeum vulgare L.)	277[b]	–	–	18 May	14 May	11	3 Aug.	19 Apr.
2011	Pea (Pisum sativum)	–	–	–	–	17 May	2	2 Aug.	11 May
2012	Bean	–	–	–	–	1 June	4	14 Sept.	4 May [c]
2013	Sweet Corn (Zea mays L.)	200	22.4	37.2	27 June[d] 12 July	31 May	1	22 Aug.	10 May
2014	Barley	50	5.6	9.3	1 Apr.	19 May	2	31 July	5 May[c]
2015	Bean	–	–	–	–	19 May	4	21 Sept.	5 May
2016	Pea	–	–	–	–	18 May	4	–	3 May
2017	Oat (Avena sativa)	100	22.4	8.9	15 May	5 May	5	9 Aug.	2 May

[a] Surplus seeds were planted and the seedlings were later thinned to this target number.
[b] In 2009, the topsoil pots were added after the other treatments, prepared and sampled on 28 July, and planted on 29 July.
[c] Soil water retention not measured in soil samples this year.
[d] Split application.

2002; Reynolds & Topp, 2008). Because the surface soil structure is disrupted substantially through tillage each year, we determined water retention on repacked soil samples, reasoning that this approach would be representative of agricultural surface soils at the start of each growing season. This technique also allowed the use of smaller sample volumes and shorter equilibration times, which was convenient given the limited soil volume available in pots and large numbers of samples to be processed in a given year (Klute, 1986). The air-dried soil samples were crushed and passed through a 2-mm sieve, roots were removed, and subsamples were oven-dried to determine water content. The air-dried soil was packed into 48-mm diameter, 19-mm long brass rings with nylon cloth bottom to a bulk density of 1.16 g cm^{-3}. Soil rings were saturated with a de-aerated 0.005-M $CaSO_4$ solution and sequentially equilibrated at the nine pressure heads. Water retention was measured in a constant temperature room to minimize changing temperature effects on soil water characteristics (Bachmann, Horton, Grant, & Van der Ploeg, 2002). Plant available water was estimated as the soil water retained between −10 and −1,500 kPa (Johnson & Veltkamp, 1985; Sivapalan, 2006; Hardie, Clothier, Bound, Oliver, & Close, 2014).

2.4 | Retention fractions and pore size interval classes

The soil water retention measured at each soil matric potential was reported as g water g^{-1} oven-dried soil^{-1}. The retention fraction (a) is the difference in water retained between two adjacent soil matric potential stages; (b) represents the water held in an equivalent pore-size range class (as determined by the capillary rise equation); and (c) when resolved across all included matric potentials, provides a measure of soil pore size distribution (Flint & Flint, 2002). For example, the soil water retained at −1,500 kPa was held in pores with an equivalent pore diameter of 0.19 m. The equivalent pore diameters for other matric potential stages in the series from −500 to −10 kPa are 0.58, 0.97, 2.92, 5.84, 8.85, 14.6, and 29.2 m. Therefore, the retention fraction for the matric potential interval −1,500 to −500 kPa represents water held by equivalent pores in the size interval from 0.19 to 0.58 m diameter, and so on. The −10 to 0 kPa matric interval would include soil water held in pores >29.2 m diameter, but since soil rings contained repacked soils, this pore size class range was estimated to be 29.2- to 300- m diameter.

2.5 | Soil penetration resistance

We assessed the strength of treated pot soils 4 yr after amendments were applied (15 May 2013) and again, on 9 April 2018, 9 yr after application. The surface soil penetration resistance (Lowery & Morrison, 2002) was measured using a Carter-type ASAE standard recording cone penetrometer with a 13-mm diameter, 30 solid angle cone-tipped probe. The hand-operated device, with a 600-mm-long measuring depth, electronic load cell, and distance sensor, measured soil unconfined compressive strength as kilograms of force. Pot soils

were brought to field capacity and shielded from rainfall for 10 d prior to the determination. We measured the in-situ penetration resistance (PR) of undisturbed soil three times in each pot by probing vertically downward from the soil surface to 150 mm at about 30 mm s^{-1}. The instrument integrated PR over 25-mm depth intervals. We used the arithmetic average of the three probings in a pot and individual depth intervals to give a mean PR for 0- to 50-, 50- to 100-, and 100- to 150-mm depths.

2.6 | Calculations and statistical analysis

To simplify comparisons among amendments across years, a PAW ratio was computed by normalizing treatment PAW measurements, that is, PAW values were divided by the mean control PAW value for the corresponding year. A PAW ratio greater than one indicates that the amendment increased soil PAW relative to the untreated, eroded, control soil. For the same reason, we also calculated a retention fraction ratio for each pore size range class, that is, treatment retention fraction values were divided by the mean control retention fraction value for the corresponding year. The mean residence time (MRT) of XPAM in the soil, relative to its water retention benefit, was calculated from:

$$\mathrm{MRT} = \frac{\mathrm{PAW}_0}{k} \quad (1)$$

where $\mathrm{PAW}_0 = \mathrm{PAW}_{\mathrm{control}} - \mathrm{PAW}_{\mathrm{XPAM}}$, $\mathrm{PAW}_{\mathrm{control}}$ is the overall mean, $\mathrm{PAW}_{\mathrm{XPAM}}$ is the value at time zero (i.e., 2009), and k is the slope of the PAW vs. year regression.

The means and standard errors of the mean for the XPAM and XPAA water absorption data were calculated using PROC Means in SAS (SAS Institute, 2012). We examined soil water retention for each pore size range, the PAW, and the PAW ratio via analysis of variance (ANOVA), PROC Mixed in SAS (SAS Institute, 2012). The statistical model employed a repeated measures statement (Repeated year/type = ARMA(1,1) subject = trt*rep;), included treatment (trt), year, and their interaction as fixed effects, and block and year × block as the random effect. Note that, if significant, the effect of year on responses is not strictly temporal, but represents the combined influence of time, climate, crop, and other factors. Regression analysis (PROC Reg) computed PAW vs. year relationships among treatments. We compared regression lines among treatments (trt) using PROC GLM and the solution option (model PAW = year trt year*trt/solution). The treatment effects on PR responses were analyzed separately for 2013 and 2018. We used a completely randomized model in PROC Mixed with a contrast statement to evaluate the effect of hydrogel application rate. Statistical analyses were conducted using a significance probability of .05.

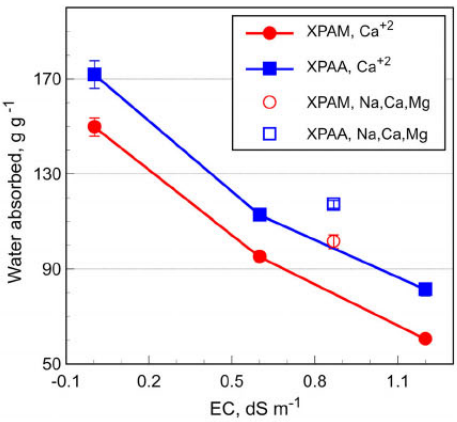

FIGURE 1 Water absorbed (per gram dry hydrogel) by crosslinked polyacrylamide co-polymer (XPAM) and crosslinked polyacrylate (XPAA) when saturated for 72 h in solutions of varying electrical conductivity (EC), adjusted by adding $CaCl_2$ (solid symbols) and in simulated irrigation water containing Na^+, Ca^{+2}, and Mg^{+2} cations (open symbols). Each leg of the error bars equals one standard error of the mean (n = 3)

3 | RESULTS AND DISCUSSION

3.1 | Hydrogel water absorbance

The expanded, water-saturated hydrogel exhibits a porous honeycomb-like structure with well-defined cells and a homogeneous pore-size distribution (Aouada, de Moura, Orts, & Mattoso, 2010; Johnson & Veltkamp, 1985). Water is retained within the cells and the cell walls. The XPAA absorbed 1.2 to 1.4 times more water from solutions than XPAM (Figure 1), which may result from molecular differences between hydrogels, such as the type and concentration of monomer components, and the degree of crosslinking (Aouada et al., 2010). Note that absorbed water declined substantially with increased EC but increased when the proportion of single-valence cations in the saturating solution increased (Figure 1). The monovalent-sodium effect on hydrogel water absorption is consistent with increased soil-swelling observed in XPAM-amended silt loams treated with increasing NaCl additions (Lentz, 2007). The hydrated anionic polymer coil diameter shrinks with increasing solution cation concentration, with multivalent cations having a greater effect than monovalent cations (Lakatos, Lakatos-Szabó, & Tóth, 1981). The shrunken molecular structure retains less water.

3.2 | Plant available water

Treatment, year, and their interaction all influenced soil PAW (Table 3). The progression of PAW values across the years

TABLE 3 The influence of treatment, year, and year × treatment interaction on retention fraction, i.e. water retained between soil matric potential stages (and corresponding soil pore size class ranges); plant available water (PAW); and PAW ratio (computed by dividing the treatment PAW by the average control PAW values for the corresponding year) for 2009 to 2017. Table includes P-values from an analysis of variance for factor effects

	Retention fraction								PAW	PAW ratio
Soil matric potential range, kPa	−500 to −1500	−300 to −500	−100 to −300	−50 to −100	−33 to −50	−20 to −33	−10 to −20	0 to −10	−10 to −1,500	–
Approx. soil pore size class, mm	0.2–0.6	0.6–1	1–3	3–6	6–9	9–15	15–30	>30	0.2–30	–
	P-values									
Source of variation										
Treatment	ns[a]	ns	***	***	***	***	***	***	***	***
Year	***	ns	***	***	***	***	***	***	***	***
Treatment × Year	ns	ns	***	***	***	**	***	***	***	***

**Significant at the .01 probability level.
***Significant at the .001 probability level.
[a]ns, not significant.

differed with treatment; XPAM values declined with time, whereas XPAA, topsoil, and control values remained relatively constant (Figure 2a). Differences between the treatments were consistent over time (Figure 2a). When averaged across all years (Table 4), the 0.5% XPAM produced the greatest PAW (0.318) and the PAW of other treatments followed in the order: 0.5% XPAM > 0.25% XPAM > topsoil > 0.5% XPAA > 0.25% XPAA = control (0.224). Following this same order, the mean treatment PAW ratios were [0.5% XPAM] 1.42 > 1.22 > 1.11 > 1.04 > 1.01 = 1.00 [control] (Figure 2b). These long-term PAW ratios are in the lower range of values reported in the literature for short-term studies with similar soils (loam or silt loam) and application rates (Table 5).

Variation in PAW ratios between studies can result from the differences in polymers or soils, or both, and chemistry of applied water. Hydrogel water adsorption properties vary with crosslink density, concentrations and molecular weights of nonionic and ionic monomer components, and type of counterion (Bai, Zhang, Liu, Wu, & Song, 2010; Okay, 2010). The water absorption capacity of hydrogels in soil, as measured by soil swelling index, varies as a function of XPAM application rate, soil texture (silt), and sodium adsorption ratio (Lentz, 2007). The chemistry of irrigation water can influence the chemistry of the soil solution and thus, the amount of water absorbed by hydrogel particles. Choudhary et al. (1995) applied deionized water to amended soils and measured water retention ratios at the high end of ranges given above, suggesting that the diluted soil solution increased hydrogel absorbance (Figure 1). In the current study, the overall smaller XPAM PAW ratio values are at least partially due to the declining effectiveness of hydrogels with time.

The overall mean long-term PAW ratio for the 0.5% XPAA treatment was much smaller than the published average value (1.03 vs. 2.1, Table 5), indicating that it was only marginally effective for increasing PAW values in this degraded soil. Of the XPAA treatments, only the 0.5% rate increased PAW and only in 2010 and 2011 ($P < .02$), so its effect appeared to be delayed, limited in magnitude, and limited in duration compared to XPAM. In contrast, previous research showed that XPAA produced an immediate and substantial increase in soil water retention for both calcareous and acidic soils (Choudhary et al., 1995; Leciejewski, 2009, Agaba et al., 2010). Some of these previous experiments used irrigation water or soils with lower ECs than those used in the current study (Choudhary et al., 1995; Agaba et al., 2010). This potentially could have reduced water absorption of XPAA in the current study relative to others (Johnson, 1984). Differences in soil pH between studies also may have influenced retention outcomes (Johnson, 1984). Soil EC tends to decrease with decreasing soil pH, which implies that hydrogel water absorption in soils with successively declining pH should increase (Johnson, 1984). However, this is not necessarily the case because water absorption by hydrogels is also influenced by other factors such as the soil solution sodium adsorption ratio and soil texture (Johnson, 1984; Lentz, 2007). The effects of EC and pH on water retention appear to be relatively conservative and probably do not fully explain XPAA's near failure to increase water retention. It seems more likely that XPAA's poor performance was due to the destruction of polymer cross-linkages and the altering of its macro-molecular structure (see discussion in following subsection).

TABLE 4 Treatment effects on the plant available water (PAW) and PAW ratio (computed by dividing the treatment PAW by the average control PAW values for the corresponding year) averaged across years

Treatment	Control	Topsoil	0.25% XPAM [a]	0.5% XPAM	0.25% XPAA	0.5% XPAA
PAW, g H_2O g^{-1} dry soil $^{-1}$	0.224e[b]	0.248c	0.272b	0.318a	0.226e	0.232d
Paw ratio	1.00e	1.11c	1.22b	1.42a	1.01e	1.04d

[a]XPAM, crosslinked polyacrylamide co-polymer; XPAA, crosslinked polyacrylate.

[b]For each treatment category, means followed by the same letter are not significantly different ($P < .05$).

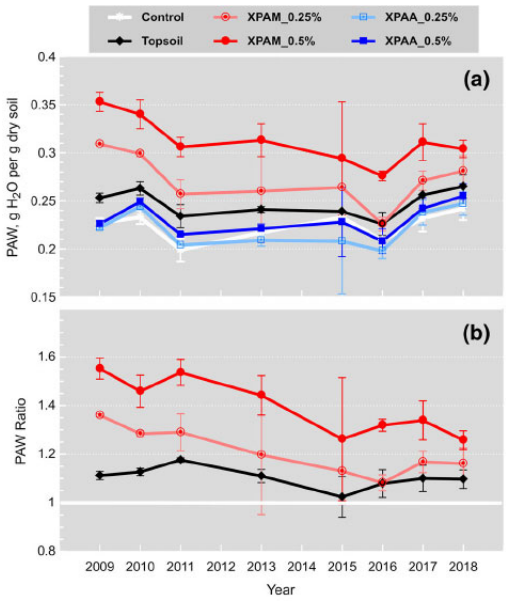

FIGURE 2 Plant available water (PAW, the water retained between potentials of −10 and −1,500 kPa) in soil as a function of treatment (XPAM, crosslinked polyacrylamide co-polymer; XPAA, crosslinked polyacrylate; % concentration w/w) and year measured (a). The influence of treatment and year on the soil PAW ratio, computed as the treatment value divided by the mean control value in the corresponding year (b). A PAW ratio value >1 indicates that the PAW in the treated soil exceeds that of the control. The XPAA treatments typically did not differ from controls and therefore were excluded in panel (b). Each leg of the error bars represents one standard error of the mean (n = 4).

3.3 | Degradation rate of water retention benefit

The water retention benefit described by the PAW ratio, as for PAW values, slowly decreased with time for XPAM, but was relatively constant for XPAA and other treatments (Figure 2a, 2b). Regression analyses indicate that PAW values for 0.25% XPAM and 0.5% XPAM treatments declined linearly with time ($P < .03$, Table 6), whereas those for topsoil, control, and the two XPAA rates were constant with time ($P > .26$). The slopes of the two XPAM regressions were not different ($P = .69$), indicating that PAW values decline equally with time, regardless of application rate, by an average 0.004 yr^{-1}, or 0.4% yr^{-1}. This rate was one-fourth the XPAM mineralization rate observed in a 76-d, soil-incubation study, that is, 1.7% yr^{-1} (Stahl et al., 2000), and about one-twentieth the rate estimated for the molecular degradation of linear polyacrylamide co-polymer (PAM) in soil (Entry, Sojka, & Hicks, 2008). The increased, apparent persistence of XPAM in soil relative to linear PAM may be expected because crosslinked polymers are better able to resist changes resulting from mechanical forces, heat, and attack by solvents (Maitra & Shukla, 2014). Assuming the useful life of the material may be estimated by its mean residence time, the useful life of the 0.25% XPAM application in the irrigated soil may be as long as 24 yr and that of 0.5% XPAM as long as 29 yr.

The limited effect of XPAA on water retention in the current study suggests that this hydrogel was rapidly solubilized after application. Hydrogel structure is degraded in soils due to abiotic effects of UV radiation, mechanical forces such as tillage or freeze-thaw cycles, chemical attack (oxidizing agents), or biologic activity, either through mineralization of component molecules or destruction of cross-linkages. The breaking of cross-linking bonds promotes breakdown by exposing linear polymers to forces of degradation. The UV radiation (limited to surface soil) and mechanical forces can break the linear polymer chain into smaller oligomers, which can then be assimilated by microbes (El-Mamouni, Frigon, Hawari, Marroni, & Guiot, 2002).

Biodegradation studies indicated that the mineralization rate of the main chain (linear backbone) for XPAM and XPAA in agricultural soils ranges from 0.5% yr^{-1} to 1.7% yr^{-1} (Stahl et al., 2000; Wilske et al., 2014; Wolter et al., 2002). The mineralization of XPAA cross-linkages by soil biotic processes and resulting solubilization occurs more quickly than for XPAM; the former's degradation rate varies from 1% yr^{-1} to 100% yr^{-1} (Cook et al., 1997; Stahl et al., 2000; Oksi ska et al., 2019). The solubilization rate for XPAA in eroded Portneuf soil appears closer to the 100% yr^{-1} rate. White-rot fungus Phanerochaete chrysosporium can completely solubilize these hydrogels in <18 d (Sutherland, Haselbach, & Aust, 1997), but it degrades XPAM more readily than XPAA (Stahl et al., 2000). The fungus accomplishes this via production of extracellular secondary metabolites, which their system

TABLE 5 Hydrogel effect on soil plant available water relative to an untreated control (PAW ratio, computed by treated-soil divided by control-soil values) in silt loam or loam soils. Values were measured within four months of application and reported as the ratio. Mean increase values were interpolated from rates used in experiments reported in the literature

Hydrogel	Application Rate	Approximate range of increase [a]	Mean increase [a]
	% (w/w)		
XPAM [b]	0.25	1.0–2.1	1.4
	0.5	1.4–3.2	2.2
XPAA	0.25	1.0–2.1	1.4
	0.5	1.3–3.5	2.1

[a]From Abedi-Koupai, Sohrab, & Swarbrick, 2008; Agaba et al., 2010; Chen et al., 2004; Choudhary et al., 1995.
[b]XPAM, crosslinked polyacrylamide co-polymer; XPAA, crosslinked polyacrylate.

TABLE 6 Fitted linear regression models (n = 32) for control, topsoil, and crosslinked polyacrylamide co-polymer (XPAM) treatments

Treatment	Regression Equation	R^2	P-value
Control	Paw = 0.001 yr − 2.45	.07	.14
Topsoil	Paw = 0.000 yr − 0.13	.00	.82
0.25% XPAM	Paw = −0.0036 yr + 7.54	.14	.001
0.5% XPAM	Paw = −0.0044 yr + 9.25	.27	.0005

produces only under nitrogen limiting conditions uncommon in agricultural soils (Sutherland et al., 1997; Wilske et al., 2014). The XPAM was stable in our soil, suggesting that Phanerochaete chrysosporium had little influence on hydrogel degradation.

3.4 | Soil water retention fractions

When averaged by treatment across all years for each pore size class, the mean retention fraction ratios show that the XPAM amendments increased retained water in pore sizes from 0.6 to >30 m (Figure 3). The water retained in these size classes was increased an average 1.25-fold by 0.25% XPAM and 1.5-fold by 0.5% XPAM relative to the unamended, degraded soil. The greatest increases in retained water were in 1- to 3- and > 9- m pores (Figure 3). The mean annual XPAM retention fraction values were greatest during the first four years after application, up to 2.6 for 1-3- m pores and up to 1.7 for > 9- m pores and declined with time (data not shown). Note that the topsoil pore size classes having the greatest retained water coincided with those size classes that received the greatest increase in retained water under XPAM, relative to the control (Figure 3). This suggests that XPAM's water retention benefits may parallel those produced by increased organic matter in topsoil.

The XPAA produced only a small increase in water from 1- to 3- m pores, indicating a different mode of action than that of XPAM, which would be expected if XPAA cross-linkages had been largely eliminated. Leciejewski (2009) reported that XPAA increased water held in pore sizes with diameters <6 m and >10 m, with the greatest increase in the larger pores. Abedi-Koupai, Sohrab, and Swarbrick (2008) found that XPAM and XPAA both increased soil water retained across the entire soil water potential range (0 to −1500 kPa), with slightly greater increases occurring at potentials >−100 kPa, that is, in pore size classes >9- m diameter. These results contrast starkly with those of the current study, further suggesting that XPAA cross-linkages degraded rapidly after application.

3.5 | Penetration resistance

The treatments influenced measured soil PR by altering both soil matrix strength and soil water content, where PR decreases with increasing water content in these soils (Sojka, Busscher, & Lehrsch, 2001). The PR test provides a measure of the soil resistance that growing roots would experience in the field shortly after soils had been irrigated (Bengough & Mullis, 1990).

Four years after amendments were applied (2013), treatment effects on PR were found at each soil depth interval ($P < .0001$, Table 7). The PR of hydrogels as a group decreased with increasing application rate ($P < .02$), except in the 0- to 50-mm soil layer ($P = .15$). When averaged over the three depths, the 0.5% XPAM produced the least soil PR on average (0.46 MPa) and other treatments generally followed in the order: 0.5% XPAM < 0.25% XPAM < topsoil < 0.5% XPAA = 0.25% XPAA < control (1.62 MPa). Relative to the control four years after hydrogel application, the 0.5% XPAM reduced PR by an average 71% across the three depths, while topsoil produced a 43% reduction, and 0.5% XPAA, a 19% reduction (Table 7). Nine years after amendments were applied (2018), only the topsoil and 0.5% XPAM treatments continued to influence soil PR. Topsoil was most effective, reducing PR by an average 46% (3 depths) vs. a 21% reduction for 0.5% XPAM, compared to the control. The lesser influence of XPAA on PR relative to XPAM is consistent with increased solubilization.

Penetration resistance in soils is related to soil organic carbon, silt + clay content, mean weight diameter, total porosity, bulk density, and water content (Gülser & Candmir, 2012; Pabin, Lipiec, Wlodek, Biskupski, & Kaus, 1998; Sojka et al., 2001). Xu et al. (2015) reported that both XPAM and XPAA reduced soil PR by 20 to 50% in a calcareous sandy loam in the first year after applying only 45 kg hydrogel ha^{-1}. Both

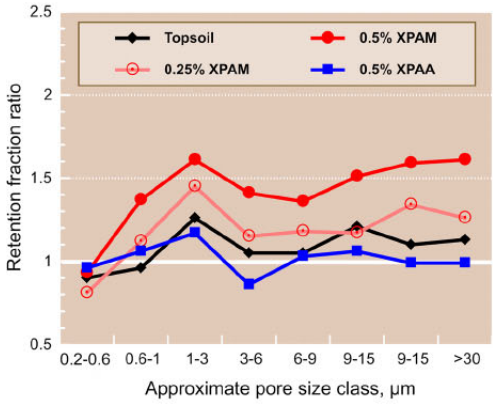

FIGURE 3 The mean retention ratio averaged across all years for each treatment (XPAM, crosslinked polyacrylamide co-polymer; XPAA, crosslinked polyacrylate; % concentration w/w), as a function of pore size class. The retention ratio is the difference in water retained between two adjacent soil matric potentials (and hence pore size classes) divided by the mean control value. Treatment 0.25% PAA differed little from the control and was excluded for clarity

TABLE 7 The mean soil penetrometer resistance for three depths in potted soils for 4 (15 May 2013) and 9 yr (9 Apr. 2018) after application

Soil depth	Treatment	2013	2018
		MPa	
0–50 mm	Control	1.39a[a]	0.96a
	0.25% XPAM	0.59c	0.93a
	0.5% XPAM	0.42d	0.76b
	0.25% XPAA	1.50a	0.89ab
	0.5% XPAA	1.28a	0.82ab
	Topsoil	0.82b	0.48c
50–100 mm	Control	2.14a	1.02a
	0.25% XPAM	0.70d	0.89a
	0.5% XPAM	0.53e	0.74b
	0.25% XPAA	1.69b	0.96a
	0.5% XPAA	1.25b	1.03a
	Topsoil	0.87c	0.61c
100–150 mm	Control	1.99a	1.17a
	0.25% XPAM	0.64d	0.96b
	0.5% XPAM	0.45e	0.80bc
	0.25% XPAA	1.52b	1.15a
	0.5% XPAA	1.24b	1.19a
	Topsoil	0.97c	0.66c

[a]For each year and soil depth increment, 'treatment' means followed by the same letter are not significantly different ($P < .05$).

hydrogels increased the mass of large macro-aggregates in the treated soil at the expense of micro-aggregates mass (Xu et al., 2015). The current study applied almost two orders of magnitude more XPAM than Xu et al. (2015) to a calcareous silt loam, which continued to influence soil penetration resistance nine years after application. Gülser and Candmir (2012) concluded that the greatest direct effect of organic amendments on soil PR can be attributed to increases in the soil's total porosity.

4 | CONCLUSIONS

One-time XPAM or XPAA applications to an eroded soil in cropped, outdoor pots influenced long-term, soil PAW differently depending on the type and rate of hydrogel added and year measured. The XPAM increased soil PAW more effectively than XPAA and produced PAW values greater than those of the uneroded topsoil. The XPAM PAW enhancement persisted for the entire 9-yr study. Thus, of the two hydrogels, XPAM should prove most effective for delivering extended soil water retention benefits.

Compared to XPAM, XPAA had minimal influence on soil PAW, PR, and soil water fractions, which was unexpected because previous, relatively short-term studies in the literature have reported substantial effects. This suggests that crosslinking bonds in the XPAA were rapidly degraded in the soil. In contrast, cross-linkages in XPAM were relatively stable and degraded only slowly over time. A better understanding of soil factors influencing XPAA degradation could be productive.

The XPAM's capability for increasing soil water retention was unexpectantly long lasting, with a mean residence time of 24 to 29 yr. While its persistence in the field makes XPAM application more economical, it is also possible that any potentially negative consequences of XPAM use might be equally persistent, such as reduction in yield under adequate irrigation (El-Hady, Pieh, & Osman, 1990; Islam et al., 2011), increased extractable Cu (de Varennes & Torres, 1999), and increases in pH and soluble Na (Falatah, 1998). Using XPAM in humid regions where precipitation is inconsistent could be a challenge. Years when rainfall exceeds crop needs could result in lower yields (El-Hady et al., 1990; Islam et al., 2011). Increased water retention could slow soil drying and warming in the spring, and delay tillage and planting. Also, during periods of surplus precipitation, increased water retention could exacerbate problems associated with reduced soil gas transport. The use of XPAM in arid-land, irrigated agriculture may provide the most benefits because water deliveries to fields in these areas can be limited or delayed. Problems caused by excessive water inputs would be less likely because irrigation water applications are intensively managed. Additional field

research is advised to sort out potential concerns, particularly long-term effects of hydrogel application on soil nutrient status.

Finally, the magnitude of XPAM's soil water retention increase and its longevity in the field can be altered by adjusting its application rate. This suggests a means of adapting applications for individual fields and circumstances.

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