**Agronomy Journal**

**ARTICLE**

**Agronomy, Soils, and Environmental Quality**

# Cross-linked polymers increase nutrient sorption in degraded soils

**Rodrick D. Lentz[1]** | **James A. Ippolito[2]**

[1] Northwest Irrigation and Soils Research Laboratory, USDA-ARS, 3793 N 3600 E, Kimberly, ID 83341, USA

[2] Soil and Crop Science Dep., Colorado State Univ., 307 University Ave., Fort Collins, CO 80523-1170, USA

**Correspondence**
Rodrick D. Lentz, Northwest Irrigation and Soils Research Laboratory, USDA-ARS, 3793 N 3600 E, Kimberly, ID 83341, USA.
Email: rick.lentz@usda.gov

**Abstract**

Cross-linked polymer hydrogels, polyacrylamide co-polymer (XPAM) or polyacrylate (XPAA) offer potential solutions for soil degradation, declines in soil resilience, and poor productivity in marginal soils. However, little is known about their long-term effect on soil nutrient availability. This 9-yr, irrigated, outdoor, cropped pot study evaluated a single, one-time addition of XPAM or XPAA at 0.25 or 0.5% dry wt. (5.6 or 11.2 Mg ha$^{-1}$) in a degraded (artificially eroded) soil. Controls included an unamended degraded soil and an unamended, non-degraded soil (i.e., topsoil). We measured nutrients in soil and leachate water each year, and in the first 5 yr, crop yields and nutrient uptake. Both hydrogels increased average soil pH and electrical conductivity (EC), soil extractable K, Na, and total organic carbon (TOC), and decreased soil extractable Mg relative to the control. Unlike XPAM, XPAA produced a greater increase in soil extractable K, increased extractable Fe, Zn, Mn, and Cu, increased Olsen P, and decreased total inorganic carbon (TIC). Neither hydrogel affected crop yields but XPAA increased K and Zn and decreased Mg and Na uptake in crops compared to controls. Relative to the control, both hydrogels decreased cumulative Ca, Mg, and S leaching mass losses and increased mean EC of leachate. Unlike XPAM, XPAA increased cumulative leaching mass losses of K, P, NO$_3$–N, and NH$_4$–N relative to the control. The hydrogels' soil effects persisted for $\geq$7 yr, differing as a function of the quantity of included counterions and the stability of the gel structure after soil placement.

## 1 | INTRODUCTION

The current global-warming trend is predicted to reduce general rainfall or increase the likelihood of serious drought occurring in different cropped regions around the world (Trenberth, 2011). Resulting crop water stress will be exacerbated in these areas by the negative effects of soil erosion and degradation. Past cropping and irrigation practices and soil erosion in semiarid, farmlands have substantially compromised soils by removing topsoil and decreasing the soil organic matter content, which decreases soil aggregate stability, infiltration rate, and water-holding capacity (Khaleel et al., 1981). It is particularly important to improve soil water retention of degraded soils in semiarid regions, where water availability may be limiting.

Water retention capacity of degraded soils can be increased using superabsorbent polymer hydrogels (Choudhary et al., 1995; Hüttermann et al., 2009; Hüttermann et al., 1999; Woodhouse & Johnson, 1991). In particular, cross-linked, high molecular-weight anionic polyacrylamide (XPAM) and

**Abbreviations:** DOC, dissolved organic carbon; EC, electrical conductivity; PAA, linear polyacrylate polymer; PAM, linear acrylamide-acrylate polymer; TC, total carbon; TIC, total inorganic carbon; TOC, total organic carbon; XPAA, crosslinked polyacrylate; XPAM, crosslinked acrylamide-acrylate co-polymer.

cross-linked, high molecular-weight Na-polyacrylate (XPAA) hydrogels are reported to increase soil $H_2O$ retention and potentially mitigate effects of drying climates and water stress (Choudhary et al., 1995; Hüttermann et al., 1999; Woodhouse & Johnson, 1991).

In addition to alleviating water stress, hydrogel amendments potentially can increase crop yields, reduce nutrient-leaching losses, and alter soil chemistry. Under various crops, a 0.2% hydrogel application increased biomass yields 2.2-to-9.2-fold relative to a control (Hüttermann et al., 1999; Woodhouse & Johnson, 1991). In some studies, hydrogel applications of 0.01–0.2% have increased yields of corn (*Zea mays* L.) biomass 2.3-fold and in others, hydrogel additions as small as 0.001% have increased potato (*Solanum tuberosum* L.) tuber yield or corn biomass by 1.12- to 1.5-fold compared to untreated soil (Mao et al., 2011). Most of the hydrogel studies evaluated coarse-textured soils, hence, yield benefits were attributed primarily to increased water and fertilizer use efficiency (Islam, Mao, et al., 2011). By increasing soil water retention, XPAM can decrease water seepage and $NO_3$–N and $NH_4$–N leaching losses and, in some cases, increase plant N uptake (Mikkelsen et al., 1993).

Fewer studies have examined hydrogel effects on soil chemical properties. In calcareous soils, both hydrogels increased soil pH and electrical conductivity (EC) and increased soluble Na (the hydrogel counterion), while XPAM decreased soluble Ca and Mg, and decreased extractable micronutrients in soil (Falatah, 1998; Falatah & Al-Omran, 1995). In acid soils, XPAA decreased or had no effect on soil pH, increased extractable soil Na, and decreased extractable K and P (De Varennes et al., 1999). The counterions present in hydrogels readily enter the soil solution (Bowman & Evans, 1991) and influence the associated content in amended soils (De Varennes et al., 1999; Falatah, 1998). Furthermore, the release of these hydrogel counterions have been shown to increase uptake of these ions in plants (Liu et al., 2013; Silverbush et al., 1993). In saline soil conditions, hydrogels commonly decrease Na and Cl uptake by plants relative to the control, with variable effects on Ca and Mg uptake (Chen et al., 2004; El-Kady & Borham, 2014).

Few if any of these hydrogel studies were designed to evaluate the long-term persistence of hydrogel effects on soil or growing crops. Yet, longevity information is needed by farm managers to evaluate the practical and economic ramifications of farm-scale hydrogel applications. In this study, we applied a single XPAM or XPAA application to a degraded silt loam soil and measured crop yields, soil nutrient leaching, and nutrient availability in the following 5–9 yr. A companion paper from this research reported treatment effects on long-term soil water retention characteristics (Lentz, 2020).

---

**Core Ideas**

- Compared 9-yr effects of crosslinked co-polymer (XPAM) and polyacrylate (XPAA).
- Hydrogel counterions and stability in soil influenced long-term nutrient conditions.
- Hydrogels increased soil pH, EC, TOC, and extractable K and Na but decreased Mg.
- Unlike XPAM, XPAA increased extractable soil Fe, Zn, Mn, and Cu and decreased TIC.
- XPAM can reduce leaching losses and increase nitrate and salt accumulation in soils.

---

## 2 | MATERIALS AND METHODS

The soils and amendments employed were described in detail by Lentz (2020). Briefly, the soil was obtained near Kimberly, ID, (42°31′ N, 114°22′ W, elevation of 1,190 m) and was collected from the 0-to-15-cm depth in an artificially eroded Portneuf silt loam (coarse-silty, mixed superactive, mesic Durinodic Xeric Haplocalcids) in early spring 2009. Topsoil from a Portneuf silt loam in an adjacent field not subject to artificial erosion was also collected from the 0-to-15-cm depth. Soil properties of the two soils are reported in Table 1. The soil's coarse clay fraction is dominated by weathered or hydrous mica (50–60%) and includes 10–20% kaolinite and 10–15% montmorillonite (McDole & Maxwell, 1966). The XPAM hydrogel is an anionic cross-linked K-acrylate-polyacrylamide copolymer (Stockosorb Agro-S, Evonik Stockhausen Inc.), containing 90% a.i. and 10% water. On a mass basis, the XPAM molecule comprises approximately 35% C, 30% O, 18% K, 14% N, and 3% H. The XPAA hydrogel is an anionic crosslinked, high molecular-weight polyacrylic acid-potassium salt (Stockosorb 660, Evonik Stockhausen Inc.), containing 94% a.i. and ∼6% water. On a mass basis, the XPAA molecule comprises approximately 34% C, 32% O, 31% K, 3% H, and 0% N. Both hydrogel chemistries incorporated K counterions and have a pH between 7.5 and 8.1. The original materials were crystalline with granule sizes ranging from 0.8- to 2.0-mm in diameter.

### 2.1 | Experimental design

The experimental design was completely randomized with four replicates. The full design comprised six treatments: two XPAM rates and two XPAA rates applied to the degraded Portneuf soil; an untreated, degraded Portneuf (control); and an untreated, nondegraded Portneuf (topsoil), for a total of

**TABLE 1**   Selected properties of subsoil and topsoil (0-to-15-cm depth) prior to adding amendments

| Material | Sand[a] | Silt[a] | Clay[a] | EC[b] | CEC[b] | pH[b] | CaCO$_3$[c] | OC[c] | C[d] | N[d] | C/N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | —————g kg$^{-1}$ dS m$^{-1}$——— | | | | mol$_c$ kg$^{-1}$ | | % | ———————g kg$^{-1}$——— | | | |
| Subsoil | 220 | 600 | 180 | 0.45 | 0.21 | 8.0 | 28 | 5.8 | 34.3 | 0.7 | 49.0 |
| Topsoil | 240 | 560 | 200 | 0.62 | 0.20 | 7.8 | 11 | 8.4 | 20.0 | 0.9 | 22.0 |

*Note.* EC, electrical conductivity; CEC, cation exchange capacity; OC, organic carbon.
[a]Particle size analysis: hydrometer method applied after removal of organic matter.
[b]Electrical conductivity and pH was determined on a saturated extract of the soil.
[c]CaCO$_3$ = calcium carbonate equivalent, determined total inorganic C using a pressure-calcimeter (Sherrod et al., 2002). Organic C, determined by dry combustion after pretreatment to remove inorganic C (Shimadzu Total Carbon Analyzer).
[d]Total C and total N of soil were determined on a freeze-dried sample with a Thermo-Finnigan FlashEA1112 CN analyzer (CE Elantech Inc.).

**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$_4$NO$_3$ | P$_2$O$_5$ as KH$_2$PO$_4$ | K$_2$O as KH$_2$PO$_4$, KCl | Fertilizers 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.[b] | 6 July[b] | 2 | 30 Sept. | 17 Apr.[b] |
| 2010 | Barley (*Hordeum vulgare* L.) | 277[b] | – | – | 18 May | 14 May | 11 | 3 Aug. | 19 Apr. |
| 2011 | Pea (*Pisum sativum* L.) | – | – | – | – | 17 May | 2 | 2 Aug. | 11 May |
| 2012 | Bean | – | – | – | – | 1 June | 4 | 14 Sept. | 4 May |
| 2013 | Sweet corn (*Zea mays* L.) | 200 | 22.4 | 37.2 | 27 June[c], 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 |
| 2015 | Bean | – | – | – | – | 19 May | 4 | 21 Sept. | 5 May |
| 2016 | Pea | – | – | – | – | 18 May | 4 | – | 3 May |
| 2017 | Oat (*Avena* sativa L.) | 100 | 22.4 | 8.9 | 15 May | 5 May | 5 | 9 Aug. | 2 May |

[a]For each crop, surplus seeds were planted and the seedlings were later thinned to this target number.
[b]In 2009, the late-added topsoil pots were prepared and sampled on 28 July, planted on 29 July, and the first leaching was after harvest.
[c]Split application.

24 experimental units). The XPAM and XPAA were applied at 0.25 or 0.5% a.i. w/w rates. The 0.25% rate was selected to ensure a measurable impact on soil water retention and was doubled in the second rate to give equally spaced treatments. The 0.25 and 0.5% treatments are roughly equivalent to 5.6 and 11.2 Mg a.i. ha$^{-1}$ (dry wt.), respectively. The topsoil treatment was not included in the initial design but was added to the experiment in mid-summer the first year (details below). Treated soils were prepared on 17 Apr. 2009 (topsoil on 22 July 2009). Fourteen-liter planting pots, 26-cm diam. by 26-cm deep, each an experimental unit, were prepared by lining the bottom of the pot with weed barrier cloth followed by a base layer of ca. 5 cm of wet sand. The designated mass of air-dried amendment 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, giving a nominal dry bulk density of 1.4 g cm$^{-3}$.

Potted soils were fertilized (Table 2) and kept moist (25–40% by volume) in a greenhouse for several weeks. The pots were moved outdoors on 2 July 2009 to start the current study, where they remained except for 3–4 d each spring when they were moved under cover to perform leaching measurements (see below). All other sampling and measurements were conducted outdoors. Pots were arranged in a shallow trench with straw packing around pot sidewalls to insulate them from surface heating/cooling effects. The straw was replaced by bark-chip mulch in subsequent years (Supplemental Figure S1). A series of locally cultivated crops were grown in pot soils from 2009 through 2017 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 crops (although one corn crop was included). Each spring we tilled pots manually to simulate annual tillage, inverting and mixing the soils to 15-cm depth, as conventional tillage is a common practice in this area of the United States. Crop planting, harvest information, and soil sampling dates are given in Table 2. Pots were irrigated using an automated flow-emitter system that supplied an equal volume to all pots to meet estimated crop evapotranspiration requirements. Irrigation water was supplied from local groundwater with an average EC of 0.80 dS m$^{-1}$, pH of 7.3, and mean concentrations (mg L$^{-1}$): Ca = 55, K = 4.8, Mg = 29, Na = 59, S = 22, Cl = 27, NO$_3$– N = 4.5, NH$_4$–N = 0.12, P = 0.07. At harvest, the entire above ground 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 non-growing season.

## 2.2 | Soil nutrients

Soil nutrient concentrations were determined in soil samples collected from pots prior to planting each year (2010–2017; Table 2). Three, 0-to-15-cm depth samples were collected and composited, approximately 100 g was retained, and the excess was returned to the pot. Samples were air-dried at 35 ˚C and crushed to pass a 2-mm mesh screen. Soil EC and pH were determined on a saturated soil extract. Soil NO$_3$–N and NH$_4$–N were extracted using 2 M KCl and measured within 6 h of extraction with an automated flow injection analyzer (Lachat Instruments). Soil available P was determined using the Olsen-P method (Method S-4.10; Gavlak et al., 2003). Availability of soil K, Na, Mg, Zn, Mn, Cu, and Fe was estimated by extracting with diethylenetriaminepentaacetic acid (DTPA) (Method S-6.10; Gavlak et al., 2003) and analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Soil total carbon (TC) and total nitrogen (TN) were determined by combustion using a Thermo-Finnigan FlashEA1112 CN analyzer, total inorganic carbon (TIC) using a pressure-calcimeter (Sherrod et al., 2002), and total organic carbon (TOC) by difference.

## 2.3 | Plant yield and nutrient uptake

Plant yields were measured and aboveground biomass collected for elemental analysis in 2009 through 2013. Standing, aboveground biomass yields from pots were measured by hand-clipping plants at a 10 mm height above the soil surface. The sample was weighed, dried at 65 ˚C, and ground in a Thomas Wiley mill to pass an 865-µm mesh screen. Total C and total N of the ground sample were determined on a

Thermo-Finnigan FlashEA1112 CN analyzer (CE Elantech Inc.). A 0.50-g subsample was placed in a 100-ml beaker and dry ashed at 500 ˚C for 5 h. The samples were cooled, weighed, and 10 ml of 1 M HNO$_3$ added. The acid solutions were heated on a hot plate until condensation no longer occurred on the inside of the beaker, the remainder was brought to a 50 ml final volume by weight with de-ionized H$_2$O, stirred, and filtered through Whatman no. 50 filter paper. The filtered solution was analyzed for P, K, Ca, Na, Mg, S, and trace elements by ICP-AES.

## 2.4 | Nutrient leaching losses

Nutrient losses in soil drainage water were evaluated by leaching the pot soils prior to planting each spring between mid-April and the 1st week in May from 2009 to 2017. The one exception to this was in Year 2009, when all pots except those from the late-added topsoil treatment were leached on 5 July 2009, and topsoil pots were leached after harvest in 2009. In addition, a "fall" leaching event was conducted each year between mid-September and mid-December from 2009 to 2013. Initiation of drainage typically required the application of >25 mm water, and because irrigation and precipitation events rarely exceeded that volume, little leaching occurred during other times of the year. The one exception occurred on 6 Aug. 2014, when a thunderstorm produced a rare 51-mm rainfall.

Just prior to leaching, the pots were moved to a covered location and placed on individual collection devices that funneled seepage water from pot drains into 2.4-L, foil-capped, glass bottles. Where necessary, we compressed surface soil against pot sidewalls to prevent bypass flow. Irrigation (tap) water was added in 250-to-700-ml portions over 12–24 h until drainage began, then decreasing volumes until leaching was completed. The pots were moved back outdoors after completing the leaching procedure.

During each leaching event in the first 5 yr (2009–2013), we applied nearly equal input water volumes to each pot (leaching regime I). For most pots, we collected between 600 and 850 ml of leachate during each leaching event, varying with year. However, the XPAM-treated soils retained substantially more water than others, thus their drainage water volumes were notably smaller, or lacking entirely relative to non-XPAM treatments. Therefore, during the last 4 yr (2014–2017), we adjusted water inputs to produce similar drainage water volumes among all treatments (leaching regime II). This would simulate a field scenario where applied irrigation included a similar annual leaching requirement across all soils. Typically, an extra 750-to-1500-ml water was added to XPAM pots to meet the percolation volume target. Consequently, leachate volumes across all treatments were nearly equivalent in 2014, and equivalent in 2015–2017.

The collected leachate samples were thoroughly mixed, one subsample was collected for pH and EC determinations, and a second subsample was filtered through a <45-micron Millipore membrane, stabilized with a saturated $H_3BO_3$ solution (1 ml per 100-ml sample), and stored at 4 °C. The filtered sample was analyzed by the following: an automatic, colorimetric flow injection analyzer (Lachat Instruments) determined concentrations of $NO_3$–N, $NH_4$–N and Cl; ICP-AES determined Ca, K, Mg, Na, P, S, Fe, Zn, Mn, and Al; and a Shimadzu TOC-5050A instrument (Shimadzu Scientific Instruments) measured dissolved organic carbon (DOC, as non-purgeable organic C).

## 2.5 | Calculations and statistical analysis

We examined the influence of treatment and year on soil nutrient, plant uptake, and leaching responses via ANOVA using PROC Mixed in SAS version 9.4 (SAS Institute, 2012). The spring leaching event data was used to analyze treatment and year effects on leachate concentration and mass-loss analyses, since this data spanned the entire experimental period. The statistical model employed a repeated measures statement (Repeated Yr/type = ARMA(1,1) subject = TRT×Rep;), included treatment, year, and their interaction as fixed effects, and Rep and year×Rep as random effects. Where needed to resolve nonconstant variance or improve distribution, responses were transformed prior to analysis, primarily using common logs, and means were back-transformed to original units for reporting. The overall treatment means for nutrient leachate concentrations were computed by averaging values across years then analyzed using ANOVA and PROC Mixed, with Rep as the random effect. A similar SAS program analyzed cumulative leachate mass-loss responses, which were summed across all spring and fall leaching events. Contrasts were included in ANOVAs to compare treatment classes to each other or to the control, for example, XPAM vs. control; XPAM vs. XPAA; etc. Statistical analyses were conducted using a significance probability (P) of .05.

## 3 | RESULTS

### 3.1 | Soil nutrients

Treatment and year influenced each measured soil nutrient property (P < .002), while their interaction influenced all properties (P < .03) except TIC and TOC (P > .09). Thus, in most cases, the effects of individual treatments on late-spring soil nutrient status varied from year to year in response to either: (a) waning treatment influence; (b) the changed leaching regime for XPAM instigated in 2014; or (c) annual differences in fertilizer application, crop type, and climatic conditions. Soil pH trended downward from 2010 to 2016 for all treatments except topsoil, followed by a recovery in 2017 (Figure 1a). However, the decline was gradual and consistent for XPAA, steepest for the control, and more erratic for XPAM. Control and hydrogel-treated soil pH values were identical in 2009 on average, but by 2013, control soil pH was 0.16 units less than hydrogel soil mean (Supplemental Table S1). Like pH, the soil EC values trended slightly lower over time, except for control and 0.25%XPAA treatments (Figure 1b). The two XPAM rates and the 0.5%XPAA treatment increased soil EC, relative to the control, particularly in Years 2010–2014, and differences decreased with time. As treatment classes compared to the control, XPAM and XPAA produced similar 1.01-fold increases in overall (across years) mean soil pH (Table 3); however, XPAM produced a greater overall average increase in soil EC, 1.6x, than XPAA, 1.1x (Table 3).

Both hydrogels increased extractable soil K and Na and decreased extractable soil Mg relative to the control; XPAA produced a greater increase in K (6.2x) and larger decrease in Mg (13%) than XPAM, while XPAM produced a greater mean increase in Na (1.9x) than XPAA (1.2x), compared to the control (Figure 1c, 1d; Table 3). Like soil EC, treatment differences decreased with time; gradually for K, but sharply for Na after 2014, when the leaching procedure changed (Figure 1c, 1d, Supplemental Table S1). Only the XPAA treatments increased 8-yr mean soil micronutrient concentrations as compared to the control. When averaged across both XPAA rates, Zn was 3.7x, Fe was 1.5x, Cu was 1.4x, and Mn was 1.1x that of the control (Figure 1f; Table 3). Again, the differences between control and XPAA micronutrient means decreased with time, most notably for Zn and Fe.

Polymers affected soil C and N differently depending on type. Compared to the control, both polymers increased overall TOC 1.2-fold, but XPAM increased overall TC 1.04-fold and did not change overall TIC, whereas XPAA decreased both TC (3%) and TIC (7.7%) (Table 3). This suggests that XPAA reduced the carbonate content of the soil. By contrast, XPAM increased overall soil TN by 1.4- and 1.9-fold relative to the control, while XPAA did not influence soil TN (Table 3).

Finally, the unusually heavy topsoil nitrate-N concentrations in 2010 were due to carry-over fertilizer. These soils were collected from a field border that apparently had been fertilized, but not cropped, the year previous to sampling.

### 3.2 | Biomass yield and nutrient uptake

Year and the treatment × year interaction significantly influenced aboveground biomass yields (P < .0001) during 2009–2013 growing seasons. In most years, yields were similar among treatments and no consistent treatment effect was
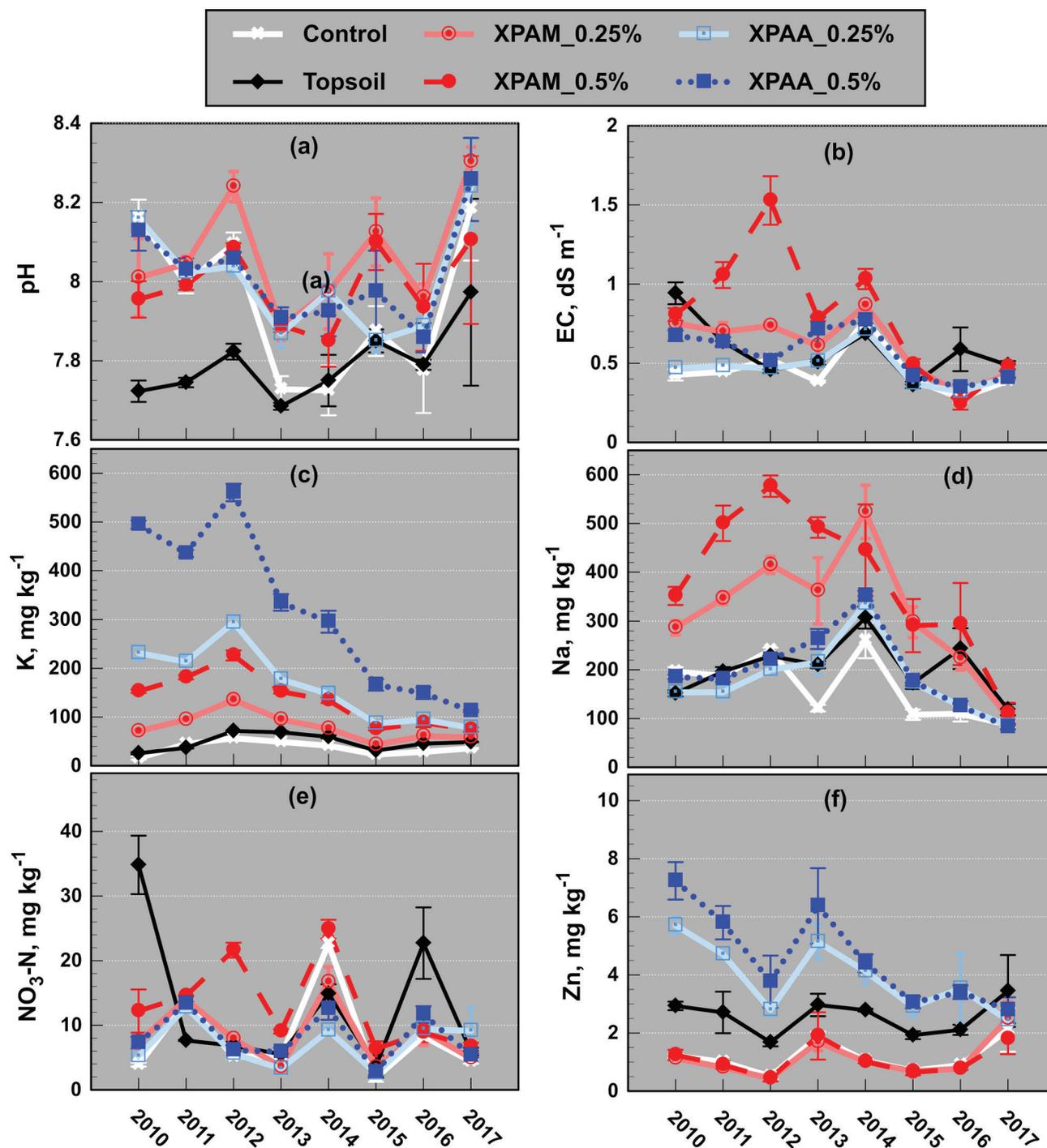
**FIGURE 1** Treatment and year effects on (a) soil pH, (b) soil electrical conductivity (EC), (c) diethylenetriaminepentaacetic acid (DTPA) DTPA extractable K (d) DTPA-extractable Na, (e) nitrate-N, and (f) DTPA-extractable Zn. Symbols represent arithmetic averages of soil samples collected in spring each year from 2010 to 2017. Error bars represent one standard error of the mean ($n = 4$)

apparent from 1 yr to the next (Supplemental Table S2). For example, relative to the control, 0.5%XPAM increased biomass yields in 2009 and decreased biomass in 2011 but had no effect in other years (Supplemental Table S2). Yield results in 2011 differed dramatically from other years in that control biomass yields exceeded those of all other treatments. In 2011, the control mean was strongly influenced by single replicate having a biomass yield nearly twice that of the

other three. The overall, cumulative biomass yields (across all years) reflect the general paucity of annual yield effects, as treatment responses did not differ (Table 4). The XPAA had a more consistent effect on nutrient uptake in biomass than XPAM (Supplemental Table S3), which is manifested in the cumulative nutrient uptake data (Table 4). Relative to the control, XPAA treatments as a class increased overall cumulative uptake of K an average 1.25-fold, increased Zn by an

**TABLE 3** Treatment effects on the soil nutrient properties. Included are the *P* values testing for equivalence between the control (C) and each crosslinked acrylamide-acrylate co-polymer (XPAM) or crosslinked polyacrylate (XPAA) treatment class. Values are averages of soil samples collected in spring each year from 2010 to 2017 (*n* = 4)

| Treatment | C | Topsoil (Top) | 0.25%XPAM | 0.5%XPAM | 0.25%XPAA | 0.5%XPAA | Contrasts C vs. XPAM | C vs. XPAA |
|---|---|---|---|---|---|---|---|---|
| TC, % | 3.42 c[a] | 1.99 d | 3.53 b | 3.61 a | 3.31 b | 3.34 b | ***[c] | **$^*$ |
| TIC, % | 2.85 a | 1.15 c | 2.85 a | 2.85 a | 2.61 b | 2.65 b | ns | *** |
| TOC, % | 0.57 c | 0.84 a | 0.68 b | 0.76 b | 0.69 b | 0.69 b | *** | ** |
| TN, % | 0.07 d | 0.09 c | 0.10 bc | 0.13 a | 0.07 d | 0.07 d | *** | ns |
| Olsen P, mg kg$^{-1}$ | 18.3 b | 21.0 a | 18.2 b | 19.1 b | 21.9 a | 21.5 a | ns | *** |
| NO$_3$-N, mg kg$^{-1}$ | 8.11 b | 12.74 a | 8.4 b | 13.0 a | 7.14 c | 8.12 b | *** | ** |
| NH$_4$-N, mg kg$^{-1}$ | 2.69 a | 2.37 b | 2.63 a | 2.54 ab | 2.54 ab | 2.42 ab | Ns | ns |
| DTPA K, mg kg$^{-1}$ | 33.8 e | 45.5 d | 74.3 c | 125 b | 148 b | 274 a | *** | *** |
| DTPA Mg, mg kg$^{-1}$ | 457 a | 384 c | 437 b | 429 bc | 414 c | 382 d | *** | *** |
| DTPA Na, mg kg$^{-1}$ | 138 e | 185 c | 252 b | 271 a | 154 d | 159 d | *** | *** |
| DTPA Fe, mg kg$^{-1}$ | 3.04 d | 5.33 a | 3.03 d | 2.80 d | 4.55 b | 3.82 c | ns | *** |
| DTPA Zn, mg kg$^{-1}$ | 1.17 d | 2.57 c | 1.13 d | 1.09 d | 3.92 b | 4.60 a | ns | *** |
| DTPA Mn, mg kg$^{-1}$ | 5.01 c | 6.33 a | 5.03 c | 4.61 d | 5.64 b | 5.36 b | ns | *** |
| DTPA Cu, mg kg$^{-1}$ | 1.12 c | 1.62 a | 1.17 c | 1.06 c | 1.52 b | 1.49 b | ns | *** |
| pH | 7.94 b | 7.79 c | 8.07 a | 7.99 a | 8.01 a | 8.02 a | ** | ** |
| EC, dS m$^{-1}$ | 0.45 c | 0.58 b | 0.61 b | 0.80 a | 0.47 c | 0.56 b | *** | ** |

*Note.* TC, total carbon; TIC, total inorganic carbon; TOC, total inorganic carbon; TN, total nitrogen; ns, not significant; DTPA, diethylenetriaminepenataacetic acid extraction; EC, electrical conductivity.

[a]Treatment means followed by the same letter are not significantly different (*P* < .05).

[b]*P* values of contrasts comparing the control with each hydrogel class.

*Significant at the .05 probability level.

**Significant at the .01 probability level.

***Significant at the .001 probability level.

average 1.72-fold, and reduced Mg and Na uptake by an average of 20%, while of the two XPAM rates, only the 0.5%XPAM treatment produced a slight increase in TN, K, S, and Fe relative to the control (Table 4). The XPAA treatments, particularly 0.5%XPAA, produced cumulative nutrient uptake results that were most like that of topsoil, and in addition provided increased cumulative K, S, and Zn uptake relative to the topsoil (Table 4).

## 3.3 | Nutrient leaching

### 3.3.1 | Spring leaching events

Percolation (leachate) volumes generally did not differ among treatments in a given year, except for XPAM treatments during leaching regime I (Figure 2). When all pots received equivalent water inputs during 2009–2013 leaching events, the 0.25%XPAM reduced mean drainage losses by 63% and 0.5%XPAM reduced drainage losses by 98% compared to the control (Figure 2). In 2009 the topsoil also appeared to retain more water than the control (Figure 2). The smaller perco-

lation volume for topsoil in 2009 was probably an artifact caused by its autumn leaching date, given that the topsoil water content prior to leaching was less than that of soils leached in spring 2009. Iron, Mn, Zn, and Al leachate concentrations were low and often below detection limits. Relative to the control, XPAM treatments as a group increased mean spring leachate concentrations for all nutrients (*P* < .003) except Zn (*P* = .7) (Supplemental Table S4). This was probably caused by XPAM's overall smaller leachate volumes compared to other treatments, since solutes in collected leachate are diluted with increasing drainage volume. In contrast, mean spring leachate nutrient concentrations for XPAA treatments as a group generally did not differ from those of controls (*P* > .08), except that K and NO$_3$–N concentrations were generally greater (*P* < .0001, *P* < .03, respectively) and Ca was less (*P* < .0001) than that of the control (Supplemental Table S4).

The pattern of nutrient mass losses across years typically differed between hydrogel types but the two rates within each type tended to influence most nutrients similarly (Figures 3 and 4; Supplemental Table S5). Hydrogel effects on annual, spring, mass losses in leachate produced four basic patterns

**TABLE 4** Treatment effects on cumulative biomass yield and plant elemental uptake. Included are the *P* values testing for equivalence between the control (C) and each crosslinked acrylamide-acrylate co-polymer (XPAM) or crosslinked polyacrylate (XPAA) treatment class. Values for each treatment are summed across Years 2009–2013 (*n* = 4)

| Treatment | C | Topsoil | 0.25%XPAM | 0.5%XPAM | 0.25%XPAA | 0.5%XPAA | C vs. XPAM | C vs. XPAA |
|---|---|---|---|---|---|---|---|---|
| Biomass, Mg ha$^{-1}$ | 35.0[a] | 32.6 | 33.20 | 37.8 | 35.7 | 33.3 | ns[b] | ns[b] |
| TC, Mg ha$^{-1}$ | 13.6 ab | 12.8 b | 13.1 b | 14.9 a | 14.1 ab | 13.1 b | ns | ns |
| TN, Mg ha$^{-1}$ | 0.476 b | 0.458 b | 0.479 b | 0.506 a | 0.548 a | 0.470 b | ns | ns |
| Ca, kg ha$^{-1}$ | 150 ab | 141 ab | 131 b | 146 b | 162 a | 131 b | ns | ns |
| K, kg ha$^{-1}$ | 588 c | 551 c | 590 c | 712 ab | 728 a | 748 a | ns | *** |
| Mg, kg ha$^{-1}$ | 109 a | 82.3 c | 91.7 bc | 98.4 ab | 96.4 b | 80.3 c | ns | ** |
| Na, kg ha$^{-1}$ | 53.3 a | 32.4 c | 51.0 ab | 54.8 a | 42.7 bc | 42.4 bc | ns | * |
| P, kg ha$^{-1}$ | 64.2 ab | 48.0 c | 58.6 abc | 66.4 a | 60.7 ab | 52.3 bc | ns | ns |
| S, kg ha$^{-1}$ | 41.0 b | 25.4 d | 38.4 b | 46.6 a | 39.7 b | 32.8 c | ns | ns |
| Fe, kg ha$^{-1}$ | 2.10 b | 2.34 ab | 2.18 b | 2.83 a | 2.54 ab | 2.28 ab | ns | ns |
| Zn, kg ha$^{-1}$ | 0.86 bc | 0.96 b | 0.81 bc | 0.87 c | 1.47 a | 1.49 a | ns | *** |
| Mn, kg ha$^{-1}$ | 1.33 | 1.29 | 1.20 | 1.40 | 1.26 | 1.23 | ns | ns |
| Al, kg ha$^{-1}$ | 2.23 b | 2.59 ab | 2.35 ab | 2.88 ab | 3.13 a | 2.59 ab | ns | ns |

*Note.* ns, not significant.

[a]For each treatment category, means followed by the same letter are not significantly different (*P* < .05). No letters are shown if treatment values were not significantly different.

[b]*P* values of contrasts comparing the control with each hydrogel class.

*Significant at the .05 probability level.

**Significant at the .01 probability level.

***Significant at the .001 probability level.

relative to the control (Table 5): (a) XPAM often reduced or eliminated mass losses during 2009 (for all nutrients except K, but particularly for Ca, Na, Cl, DOC, and P) but often increased mass losses from 2014 to 2017; (b) The XPAA also reduced nutrient mass losses in 2009, but thereafter had no effect or increased losses (particularly Cl, P, Na); (c) The XPAA increased K mass losses each spring in each year of the experiment; (d) The XPAM commonly reduced Mg mass losses over the entire 2009 to 2017 period.

Thus, hydrogel effects on K and Mg differed from that of most other nutrients. The effect of XPAA on spring leachate K losses was unique in that K losses: (a) were consistently greater than that of the control; (b) increased with XPAA rate; and (c) declined over time (Figure 3b). Overall, the K losses from XPAA were 5.4-fold greater than those of XPAM (Figure 3b). This indicates that XPAA was shedding molecular K into the soil solution. The pattern of Mg losses was unique in that both XPAM and XPAA Mg losses were less than or equal to control values throughout the 8 yr. This suggest that factors influencing Mg chemistry in the amended soils may differ from those affecting other cations. Again, the elevated topsoil nitrate-N concentrations and mass losses in the first 2 yr resulted from excess N fertilization in the collected topsoil samples.

### 3.3.2 | Cross-year cumulative and mean values

When leachate mass losses were summed across all years and all leaching events, results were like those of the annual results. The XPAM treatments as a group reduced cumulative Na, Ca, Mg, S, and Al mass losses by 34–43% compared to the control, and XPAA as a group, increased cumulative K losses sixfold, increased P, $NO_3$–N, and $NH_4$–N losses 1.3- to 1.5-fold, reduced Ca, Mg, and Zn losses by 47–59%, and reduced S losses by 15% relative to the control (Table 6). Since leachate volumes were similar among control and XPAA pots (Figure 2), values in Table 6 and Figures 3 and 4 represent the direct effect of the XPAA treatment on soil chemical status. The two hydrogel groups increased the overall mean EC of soil leachate relative the control, mirroring the results for mean soil EC values (Tables 3 and 6). The XPAA increased the mean pH of leachate compared to the control, analogous to its soil property effect; however, the XPAM group decreased mean leachate pH relative to the control, the opposite of its effect on the soil matrix (Table 6).
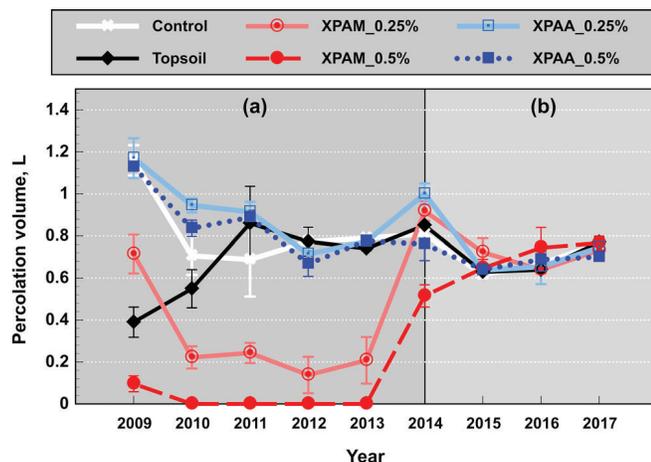
**FIGURE 2** Treatment and year effects on percolation volume collected during spring leaching events (a) in 2009–2013 under leaching regime I (dark gray background), where input water volumes were applied nearly equally to all pots and (b) in 2014–2017 under regime II (light gray), where input water amounts were varied to produce nearly equal percolation volumes in all pots. Symbols represent arithmetic averages of percolation volumes and error bars represent one standard error of the mean ($n = 4$)

## 3.4 | Qualitative summary of results

The two hydrogels behaved similarly in that, relative to the control, they: (a) increased soil pH and EC; (b) increased soil extractable K, Na, and TOC; (c) decreased soil extractable Mg; (d) decreased cumulative Ca, Mg, and S leaching mass losses; (e) and increased mean EC of leachate.

The XPAA differed from XPAM in that, relative to the control, it: (a) increased extractable soil Fe, Zn, Mn, and Cu; (b) decreased soil TC and TIC; (c) had no effect on soil TN, while XPAM increased TN; (d) increased soil Olsen P; (e) increased overall mean crop uptake of K and Zn and decreased uptake of Mg and Na; (f) increased cumulative leaching mass losses of K, P, $NO_3$–N, and $NH_4$–N; and (g) increased average pH of leachate, whereas XPAM decreased leachate pH.

## 4 | DISCUSSION

### 4.1 | How hydrogels affect soil nutrients

The results suggest that the hydrogel's effects on soil nutrient status were derived from their expanding, porous structure and associated negative charges and K counterions, which engender water retention, cation-supplying, and/or cation-binding and absorption capabilities. These capabilities differed between the two hydrogels, producing results unique to each. For example, water retention measurements in these soils reported in the companion paper (Lentz, 2020) revealed that XPAM increased mean 9-yr plant available
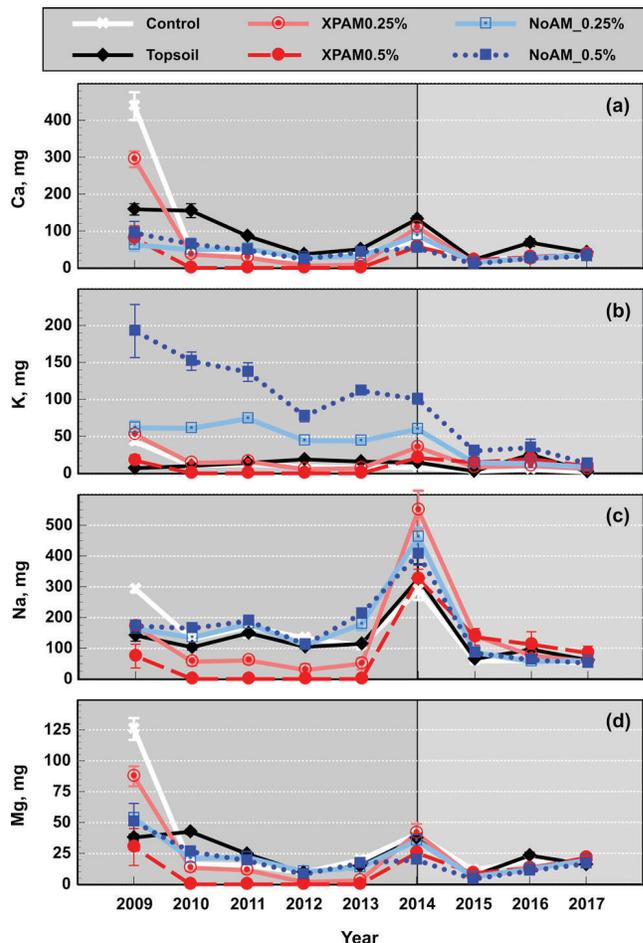


**FIGURE 3** Treatment and year effects on percolation mass losses during spring leaching events, (a) Ca, (b) K, (c) Na, and (d) Mg under leaching regime I, equal inputs (dark gray background), and leaching regime II, equal percolation volumes (light gray). Symbols represent arithmetic averages of mass losses and error bars represent one standard error of the mean ($n = 4$)

water 1.11- to 1.22-fold over that of the control, whereas XPAA produced only a ≤1.04-fold increase. For reasons not well understood, the XPAA molecular crosslinkages degraded rapidly in the soil, which liberated individual linear polymers (PAA), and solubilized the gel mass within 2 yr of application (Lentz, 2020). The released PAA then becomes bound to soil particles (Sojka et al., 2007). The breakdown in XPAA gel structure: (a) reduced the material's capacity to retain water; (b) limited its ability to absorb and potentially sequester soil nutrients; and (c) directly exposed the polymer's anionic functional groups and counter ions to the soil environment.

Both hydrogels supplied organic C and K to soils and XPAM also supplied N. In total, the two XPAM rates supplied an approximate equivalent of 2 and 4 Mg ha$^{-1}$ C to the soil and 1 and 2 Mg ha$^{-1}$ of both K and N, while XPAA supplied 2 and 4 Mg ha$^{-1}$ C and similar amounts of K. The XPAA's greater K content, coupled with its rapid
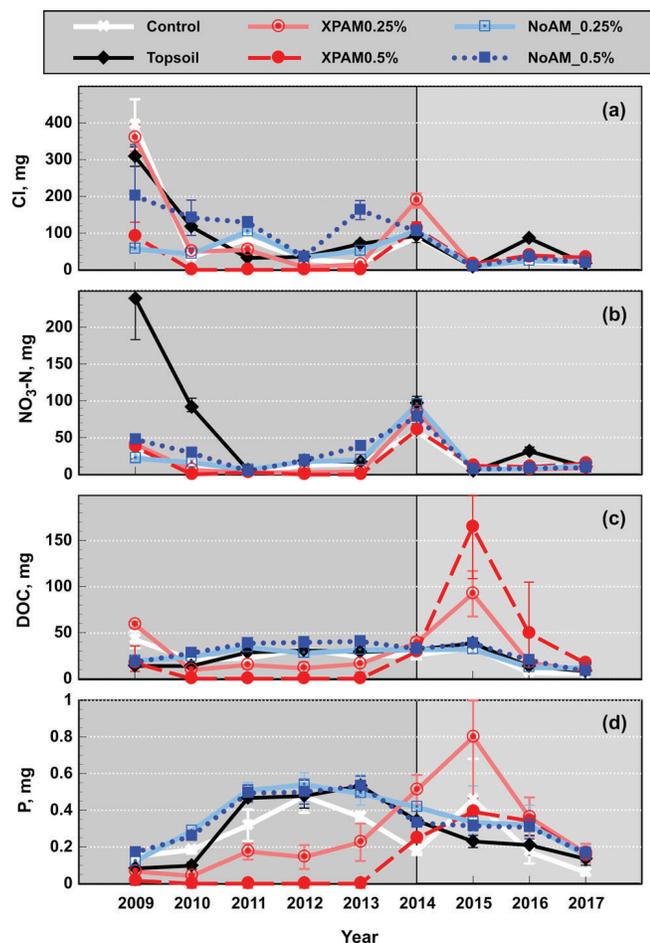
**FIGURE 4** Treatment and year effects on percolation mass losses during spring leaching events, (a) Cl, (b) NO$_3$–N, (c) dissolved organic carbon (DOC), and (d) P. Symbols represent arithmetic averages of percolation volumes and error bars represent one standard error of the mean ($n = 4$)

**TABLE 5** Hydrogel effect on qualitative changes in nutrient mass losses relative to the control during spring-leaching events, 2009–2017. Nutrients most strongly influenced are listed in parentheses

| | | Period | | |
|---|---|---|---|---|
| **Annualpattern** | **Hydrogel** | **2009** | **2010– 2013** | **2014– 2017** |
| 1 | XPAM | ≤ | ≤ or eliminated | ≥ |
| | | (Ca, Na, Cl, P, DOC) | (Na, DOC, P) | (Na, Cl, DOC, P) |
| 2 | XPAA | ≤ | ≥ | ≥ |
| | | (Ca, Na, Cl, P, DOC) | (Cl, P) | (Na, DOC) |
| 3 | XPAA | > | > | > |
| | | (K) | (K) | (K) |
| 4 | Both | ≤ | ≤ | ≤ |
| | | (Mg) | (Mg) | (Mg) |

*Note*. XPAM, crosslinked acrylamide-acrylate co-polymer; XPAA,crosslinked polyacrylate; DOC, dissolved organic carbon.

structural breakdown, amplified K release into the soil relative to that of XPAM. The amide functional group in XPAM is utilized as an N source by soil bacteria through an enzyme-mediated (amidase) reaction (Kay-Shoemake et al., 1998). However, the C in both crosslinked and linear polymers is probably not readily available to soil microorganisms, depending on the type of bacteria and fungi present (Lentz, 2020).

Both XPAM and XPAA increased soil pH and EC, confirming results reported in several studies, though hydrogels with K counterions used in the current study produced smaller pH increases (1.01x) than Na-based gels (>1.03x) used in other studies (Falatah, 1998; Falatah & Al-Omran, 1995). The increase presumably was due to: (a) increased alkalinity from K or Na additions (Falatah & Al-Omran, 1995); (b) increase in base saturation of the soil due to the addition of the K-saturated cation exchange capacity (CEC) contributed by the hydrogel; and (c) a change in sodium absorption ratio (SAR)

of the soil solution due to altered extractable Ca, Mg, and Na concentrations (Table 3).

The hydrogels' anionic character increases the CEC of the soil, for example, by 24 and 48 times for XPAM (El-Hady, El-Kader, & Shafi, 2009). Within 24 h, cations can migrate from the soil solution into the gel matrix (Martin et al., 1993). The gels absorb cations through coulombic attraction or binding of cations, the latter through formation of polydentate chelation complexes with polymer carboxyl ligands (Tomida et al., 2001). Cations are absorbed preferentially by XPAM and XPAA. The cation selectivity of hydrogel differs only slightly from that of the Portneuf-soil CEC: Ca > Mg > K > Na, that is, 74, 20, 4.5, and 1.5% of the total CEC, respectively, and Ca is held so strongly that it can be only partially desorbed (Bowman & Evans, 1991; Li et al., 2002; Martin et al., 1993; McDole & Maxwell, 1966).

Linear PAA and PAM, when released upon degradation of gel crosslinkages, also complex preferentially with cations, though PAM is less effective than PAA (Rivas & Moreno-Villoslada, 1998). The preference for complex formation decreases in the order: Cu > Pb > > Zn > Ni = Co > Mn > Ca > Mg, with only weak molecular species (complexes) formed with Na and K (Tomida et al., 2001). If the concentration of one cation exceeds that of others in solution, mass action will favor formation of its complex over that of dilute cations (De Stefano et al., 2003).

## 4.2 | Soil nutrient properties

### 4.2.1 | Soil pH

Soil pH varied by 0.5 pH units during the 9-yr period, possibly in response to annual fluctuations in spring precipitation and temperature conditions (Supplemental Figure S2), which influence microbiological activity and the $H^+$ budget (Conyers et al., 1997). Annual pH fluctuations in the control soil were larger than in gel-treated soils, indicating that the hydrogel had a buffering effect on pH change likely due to its elevated CEC and capacity to absorb H ions (Mitchell & Atkinson, 1992).

### 4.2.2 | Nitrogen

The XPAM-induced increase in overall soil TN was primarily supplied from N within the XPAM molecule itself and hence the reason N-free, XPAA had little effect on soil TN (Table 3). However, the increase in overall soil $NO_3$–N in 0.5%XPAM soils suggested that XPAM reduced soil nitrate-leaching losses, primarily by decreasing water percolation losses, particularly during leaching regime I (Table 3, Figure 1e). Islam, Mao, et al. (2011) also reported that XPAM minimized nitrate leaching in a loamy sand.

### 4.2.3 | Potassium, magnesium, and sodium

The added hydrogel increased mean soil extractable K through the addition of K counterions, which also displaced Na from the soil exchange complex, leading to increased mean soil extractable Na (Table 3). An increase in soil availability of the hydrogel counterion has been commonly observed (Falatah, 1998; Islam, Ren, et al., 2011). The decreased soil-extractable Mg for hydrogel treatments confirms short-term results reported by Falatah (1998) and was attributed to Mg-cation binding by the polymers.

### 4.2.4 | Phosphorus

The XPAM treatment had little effect on overall mean soil Olsen P, whereas XPAA increased Olsen P (Table 3). This is consistent with previous research that found no effect of XPAM on soil P availability at similar rates (Falatah & Al-Omran, 1995; Hayat & Ali, 2004; Islam, Ren, et al., 2011). Phosphate availability in this soil is largely controlled by its adsorption on amorphous and organically complexed metals and adsorption/precipitation with Ca carbonates (Ippolito et al., 2019; Leytem & Westermann, 2003). An increase in soil pH can desorb phosphate from the sorbents and poten-

tially increase available P. This does not appear to explain our results because both XPAA and XPAM increased soil pH (Table 3). The differing effect of XPAA may be related to its solubilization and/or the release of linear polymer or K cations. Two mechanisms may be involved. In the first, the liberated linear PAA may act much like native soil organic polymers. The organics decrease the proportion of high-energy P-binding sites by slowing the conversion of amorphous calcium phosphate to hydroxyapatite, and thus, increasing the proportion of labile P on the low energy sites (Inskeep & Silvertooth, 1988). In the second, mass action exchanges the surplus K with Ca, Mg, and Na on the soil exchange complex and the excess Ca in the soil solution triggers the sorption of solution and labile phosphate onto solid phases (Akinremi & Cho, 1991). When the soil is leached with water having low K concentrations, such as irrigation water or rainfall, soil-solution K concentration drops precipitously and exchangeable K on the CEC complex is displaced by Ca and Mg from the soil solution. The decline in soil solution Ca and Mg concentrations increases the solubility of calcium phosphates reintroducing phosphate into the solution (Lentz, 2006). In similarly treated Portneuf soil, Lentz (2006) observed elevated phosphate levels in drainage water for several days after the start of irrigation.

### 4.2.5 | Micronutrients

The XPAM treatments either had no effect on, or decreased, soil-extractable micronutrients, in accordance with results of short-term (<180 d) XPAM and XPAA incubation studies (De Varennes & Torres, 1999; Falatah & Al-Omran, 1995). A reduction in micronutrient availability may result from the associated increase in soil pH and iron precipitation or by the binding and sequestering metal cations in the gel (Li et al., 2002; Mengel & Kirkby., 1982). That XPAA treatment increased soil-extractable Fe, Zn, Mn, and Cu, was attributed to gel solublization and release of linear PAA, which formed chelation complexes with the metals (Tomida et al., 2001).

### 4.2.6 | Carbon

While XPAM and XPAA as classes increased soil TOC, one 3-mo-long study on a calcareous sandy loam detected no change in soil TOC even when XPAM was applied at up to 1.5% rate (Hayat & Ali, 2004). The decrease in soil TC and TIC caused by XPAA was not anticipated but may have resulted either from increased leaching of bicarbonate ($HCO_3^-$) or the degassing of $CO_2$ produced during the formation of pedogenic calcium or magnesium carbonates (Monger et al., 2015). Soil bicarbonate concentrations are positively related to pH and DOC concentrations in the soil solution

**TABLE 6** Treatment effect on cumulative leachate volume, mean pH, and electrical conductivity (EC), and nutrient mass losses computed across all leaching events and years. Included are the $P$ values testing for equivalence between the control (C) and linear acrylamide-acrylate polymer (PAM) or crosslinked polyacrylate (XPAA) treatment classes. Values are total losses summed across all leaching events performed from 2009 to 2017 ($n = 4$)

| | | | | | | | Contrasts | |
| | | | | | | | C vs. | C vs. |
| Treatment | C | Topsoil | 0.25%XPAM | 0.5%XPAM | 0.25%XPAA | 0.5%XPAA | XPAM | XPAA |
|---|---|---|---|---|---|---|---|---|
| Drain volume, L | 10.1 a[a] | 8.94 b | 6.63 c | 3.61 d | 10.5 a | 9.73 a | *** | ns |
| Na, g | 2.31 b | 1.92 c | 2.02 c | 1.02 d | 2.42 ab | 2.62 a | *** | ns |
| Ca, mg | 1199 a | 1244 a | 991 b | 351 d | 688 c | 745 c | *** | *** |
| K, mg | 164 d | 171 d | 261 c | 140 d | 620 b | 1330 a | ns | *** |
| Mg, mg | 432 a | 340 b | 348 b | 148 d | 312 bc | 294 c | *** | *** |
| P, mg | 3.28 b | 4.02 ab | 3.67 b | 1.75 c | 4.79 a | 4.47 a | ns | *** |
| S, mg | 1307 a | 1144 b | 1144 b | 425 d | 976 c | 1243a | *** | * |
| $NO_3$–N, mg | 273 d | 832 a | 260 d | 163 cd | 350 c | 463 b | ns | * |
| $NH_4$–N, mg | 1.87 c | 2.69 a | 1.86 bc | 1.12 d | 2.23 bc | 2.64 ab | ns | * |
| Cl, g | 1.82 b | 1.72 b | 2.63 a | 0.79 c | 1.37 b | 2.20 b | ns | ns |
| DOC, mg | 308 bc | 322 c | 393 ab | 344 bc | 340 abc | 421 a | ns | ns |
| Fe, mg | 0.24 b | 0.35 ab | 0.40 a | 0.28 ab | 0.24 b | 0.24 b | ns | ns |
| Zn, mg | 0.11 a | 0.03 b | 0.08 ab | 0.06 b | 0.03 b | 0.04 b | ns | ** |
| Mn, mg | 0.04 ab | 0.05 a | 0.03 ab | 0.04 b | 0.02 bc | 0.03 b | ns | ns |
| Al, mg | 0.58 a | 0.27 d | 0.47 ab | 0.30 bcd | 0.55 ab | 0.52 ab | * | ns |
| pH | 7.93 b | 7.83 c | 7.88 c | 7.78 d | 8.01 a | 8.01 a | *** | *** |
| EC, dS m$^{-1}$ | 1.68 c | 2.46 b | 2.72 a | 3.30 a | 1.70 bc | 2.47 b | *** | * |

*Note.* XPAM, crosslinked acrylamide-acrylate co-polymer; ns, not significant.

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

*Significant at the .05 probability level.

**Significant at the .01 probability level.

***Significant at the .001 probability level.

(Olsen, Watanabe, & Cole, 1960; Pannkuk et al., 2011). Since the average pH of XPAA leachate and mean DOC concentration of 0.5%XPAA leachate exceeded that of the control (Table 6), we conclude that the XPAA treatment increased bicarbonate leaching.

## 4.3 | Nutrient uptake in aboveground biomass

The release of counterions from the hydrogels (K in the current study) can produce an increase in the ion's uptake in crop tissue (Liu et al., 2013). Our results confirm this effect, although less consistently for XPAM than for XPAA (Table 4). The increased K availability and uptake likely caused the reduction in Mg and Na uptake by our crops (Mengel & Kirkby, 1982; Silverbush et al., 1993). It is interesting that P uptake did not increase in crops growing in XPAA-amended soils, though Olsen-P values were greater there (Tables 3 and 4). The greater pH in the XPAA soil solution (Table 6) may have slowed phosphate uptake relative to that in the other lower pH soils (Mengel & Kirkby, 1982).

The enhancement of crop Zn uptake by both XPAA rates over those of other treatments is consistent with the solubilization of XPAA, release of PAA, and the chelation and increased availability of Zn (Tomida et al., 2001). The improved Fe uptake in 0.5%XPAM treatments may be related to XPAM's low-to-moderate capacity to bind Fe (Li et al., 2002) or simply to XPAM's capacity to retain more water containing soluble Fe (Mikkelsen et al., 1993).

## 4.4 | Leaching losses

The polymers' propensity to reduce cumulative Ca and Mg leaching mass losses, the XPAM-associated decrease in cumulative Na, P, $NH_4$–N, S, Cl leached, and the XPAA-induced decrease in Zn-leaching losses (Table 6) are presumably due to the capacity of XPAM, XPAA, and PAA to bind them (Li et al., 2002; Tomida et al., 2001) and/or in XPAM's case, by inhibiting drainage. The XPAA-related increase in K and P leaching losses is consistent with the nutrients' increased availability in the soils (Tables 3 and 6). On the other hand, it is not obvious why XPAA treatments

as a class boosted cumulative $NO_3$–N and $NH_4$–N leaching losses, since no increase in their availability was indicated by soil analysis (Tables 3 and 6). That XPAM decreased the overall average pH of leachate, while XPAA increased leachate pH, suggests that the XPAM-amended soils may have been slower to equilibrate with inflowing irrigation water than XPAA soils. Soil solution held in the interiors of intact XPAM gel masses would more slowly interact with irrigation water than solution held by the solubilized XPAA.

## 4.5 | Longevity of hydrogel effects

Relative to the control, most hydrogel-induced changes in soil nutrients persisted through 2017 but the difference between treatment and control values decreased over time (Figure 1). The exceptions to this were TC and TN; initial hydrogel changes to these properties persisted throughout the entire 8 yr (Supplemental Table S1). This suggests that the mineralization of the polymer C structure was very slow, confirming results of Kay-Shoemake et al. (1998). The change in leaching regime in 2014 had a notable impact on XPAM nutrient status. Presumably, the XPAM's effect on soil pH, EC, K, and Na would have been different in later years if the leaching regime had not been changed from I to II (Figure 1). It is likely that soil Na would have remained high in XPAM soils had not additional irrigation water been added to leach it from the soil. This could be a concern if XPAM were added to soils already high in Na and surplus irrigation water were not available to provide a leaching fraction. The effect on hydrogels on soil leaching mass losses over time generally followed the same temporal pattern as that of the nutrient properties (Supplemental Table S5).

## 5 | CONCLUSIONS

While XPAM and XPAA hydrogels are similar in terms of their initial physical structure, water-retentive nature, and source of anionic charge, their long-term effects on soil nutrient status differed substantially. The hydrogel characteristics primarily responsible for the differences were the quantity of the included counterions (K in our case) and the stability of the gel structure after placement in the soil. The hydrogels produced long-term changes in nutrient status of this soil but yields of crops grown under low-water-stress conditions of this study generally were unaffected by hydrogels. These biomass yield results contrast with hydrogel amendment research done under high-water-stress conditions, where hydrogel treatment yields often exceed those of the controls. Because of the persistent increase in water retention provided by XPAM, it may reduce leaching losses of nitrate-N and soluble salts. Thus, a potential for salt accumulation may occur, requiring additional irrigation water be applied to ensure an adequate leaching fraction. This was not a concern with XPAA because its gel structure rapidly degraded due to destruction of polymer crosslinkages. While the XPAA did not produce persistent water retention benefits like XPAM (Lentz, 2020), it provided greater soil nutrient benefits than XPAM, particularly with regard to Olsen P, extractable K, and extractable micronutrients.

## CONFLICT OF INTEREST
The authors declare no conflict of interest.

## ORCID
*Rodrick D. Lentz* https://orcid.org/0000-0003-2537-1628
*James A. Ippolito* https://orcid.org/0000-0001-8077-0088

## REFERENCES

Akinremi, O. O., & Cho, C. M. (1991). Phosphate and accompanying cation transport in a calcareous cation-exchange resin system. *Soil Science Society America Journal*, *55*, 959–964. https://doi.org/10.2136/sssaj1991.03615995005500040010x

Bowman, D. C., & Evans, R. Y. (1991). Calcium inhibition of polyacrylamide gel hydration is partially reversible by potassium. *HortScience*, *26*, 1063–1065. https://doi.org/10.21273/HORTSCI.26.8.1063

Chen, S., Zommorodi, M., Fritz, E., Wang, S., & Hüttermann, A. (2004). Hydrogel modified uptake of salt ions and calcium in *Populus euphratica* under saline conditions. *Trees*, *18*, 175–183.

Choudhary, M. I., Shalaby, A. A., & Al-Omran, A. M. (1995). Water holding capacity and evaporation of calcareous soils as affected by four synthetic polymers. *Communications in Soil Science and Plant Analysis*, *26*, 2205–2215. https://doi.org/10.1080/00103629509369440

Conyers, M. K., Uren, N. C., Helyar, K. R., Poile, G. J., & Cullis, B. R. (1997). Temporal variation in soil acidity. *Australian Journal of Soil Research*, *35*, 1115–1129. https://doi.org/10.1071/S97022

De Stefano, C., Gianguzza, A., Piazzese, D., & Sammartano, S. (2003). Quantitative parameters for the sequestering capacity of polyacrylates towards alkaline earth metal ions. *Talanta*, *61*, 181–194. https://doi.org/10.1016/S0039-9140(03)00249-2

De Varennes, A., & Torres, M. O. (1999). Remediation of a long-term copper-contaminated soil using a polyacrylate polymer. *Soil Use and Management*, *15*, 230–232. https://doi.org/10.1111/j.1475-2743.1999.tb00093.x

De Varennes, A., Torres, M. O., Conceição, E.A., & Vasconcelos, E. (1999). Effect of polyacrylate polymers with different counter ions on the growth and mineral composition of perennial ryegrass. *Journal of Plant Nutrition*, *22*, 33–43. https://doi.org/10.1080/01904169909365604

El-Hady, O. A., El-Kader, A. A. A., & Shafi, A. M. (2009). Physico-bio-chemical properties of sandy soil conditioned with acrylamide hydro-gels after cucumber plantation. *Australian Journal of Basic Applied Science*, *3*, 3145–3151.

El-Kady, A. F. Y., & Borham, T. I. (2014). Hydrogel amendment effects on the performance of buttonwood (*Conocarpus erectus* L.) seedlings growth under saline irrigation water. *Journal of Applied Science Research*, *9*, 6557–6566.

Falatah, A. M. (1998). Synergistic effects of elemental sulfur and synthetic organic conditioner amendments on selected chemical properties of calcareous soils. *Arid Soil Research and Rehabilitation*, *12*, 73–82. https://doi.org/10.1080/15324989809381499

Falatah, A. M., & Al-Omran, A. M. (1995). Impact of soil conditioner on some selected chemical properties of calcareous soil. *Arid Soil Research and Rehabilitation*, *9*, 91–96. https://doi.org/10.1080/15324989509385876

Gavlak, R., Hornect, D., Miller, R., & Kotuby-Amacher, J. (2003). *Soil, plant, and water reference methods for the western region* (2nd ed.). WREP-125, Western Region Extension Publication, Corvallis.

Hayat, R., & Ali, S. (2004). Water absorption by synthetic polymer (Aquasorb) and its effect on soil properties and tomato yield. *International Journal of Agriculture and Biology*, *6*, 998–1002.

Hüttermann, A. M., Orikiriza, L. J. B., & Agaba, H. (2009). Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands. *Clean-Soil Air and Water*, *37*, 515–526. https://doi.org/10.1002/clen.200900048

Hüttermann, A., Zommorodi, M., & Reise, K. (1999). Addition of hydrogels to soil for prolonging the survival of *Pinus halepensis* seedlings subjected to drought. *Soil and Tillage Research*, *50*, 295–304. https://doi.org/10.1016/S0167-1987(99)00023-9

Inskeep, W. P., & Silvertooth, J. C. (1988). Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic, and tannic acids. *Soil Science Society of America Journal*, *52*, 941–946. https://doi.org/10.2136/sssaj1988.03615995005200040007x

Ippolito, J. A., Bjorneberg, D. L., Blecker, S. W., & Massey, M. S. (2019). Mechanisms responsible for soil phosphorus availability differences between sprinkler and furrow irrigation. *Journal of Environmental Quality*, *48*, 1–10. https://doi.org/10.2134/jeq2019.01.0016

Islam, M. R., Mao, S., Xue, X., Eneji, A. E., Zhao, X., & Hu, Y. (2011). A lysimeter study of nitrate leaching, optimum fertilization rate and growth responses of corn (*Zea mays* L.) following soil amendment with water-saving super-absorbent polymer. *Journal of the Science of Food and Agriculture*, *91*, 1990–1997. https://doi.org/10.1002/jsfa.4407

Islam, M. R., Ren, C., Zeng, Z., Jia, P., Eneji, E., & Hu, Y. (2011). Fertilizer use efficiency of drought-stressed oat (*Avena sativa* L.) following soil amendment with a water-saving superabsorbent polymer. *Acta Agriculturae Scandinavica Section B-Soil and Plant Science*, *61*, 721–729.

Kay-Shoemake, J. L., Watwood, M. E., Lentz, R. D., & Sojka, R. E. (1998). Polyacrylamide as an organic nitrogen source for soil microorganisms with potential impact on inorganic soil nitrogen in agricultural soil. *Soil Biology and Biochemistry*, *30*, 1045–1052. https://doi.org/10.1016/S0038-0717(97)00250-2

Khaleel, R., Reddy, K. R., & Overcash, M. R. (1981). Changes in soil physical properties due to organic waste applications: A review. *Journal of Environmental Quality*, *10*, 133–141. https://doi.org/10.2134/jeq1981.00472425001000020002x

Lentz, R. D. (2006). Solute response to changing nutrient loads in soil and walled ceramic cup samplers under continuous extraction. *Journal of Environmental Quality*, *35*, 1863–1872. https://doi.org/10.2134/jeq2005.0458

Lentz, R. D. (2020). Long-term water retention increases in degraded soils amended with cross-linked polyacrylamide. *Agronomy Journal*, *112*, 2569–2580. https://doi.org/10.1002/agj2.20214

Leytem, A. B., & Westermann, D. T. (2003). Phosphate sorption by Pacific Northwest calcareous soils. *Soil Science*, *168*, 368–375. https://doi.org/10.1097/01.ss.0000070911.55992.0e

Li, W., Zhao, H., Teasdale, P. R., John, R., & Zhang, S. (2002). Synthesis and characterisation of a polyacrylamide-polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd. *Reactive and Functional Polymers*, *52*, 31–41. https://doi.org/10.1016/S1381-5148(02)00055-X

Liu, F., Ma, H., Xing, S., Du, Z., Ma, B., & Jing, D. (2013). Effects of super-absorbent polymer on dry matter accumulation and nutrient uptake of *Pinus pinaster* container seedlings. *Journal of Forest Research*, *18*, 220–227. https://doi.org/10.1007/s10310-012-0340-7

Mao, S., Islam, M. R., Xue, X., Yang, X., Zhao, X., & Hu, Y. (2011). Evaluation of water-saving superabsorbent polymer for corn (*Zea mays* L.) production in arid regions of northern China. *African Journal of Agricultural Research*, *6*, 4108–4115.

Martin, C. A., Ruter, J. M., Roberson, R. W., & Sharp, W. P. (1993). Element absorption and hydration potential of polyacrylamide gels. *Communications in Soil Science and Plant Analysis*, *24*, 539–548. https://doi.org/10.1080/00103629309368820

McDole, R. E., & Maxwell, H. B. (1966). Soil Survey: University of Idaho Research and Extension Center and USDA Snake River Conservation Research Center Kimberly *(Idaho Bulletin 656)*. Moscow, ID: University of Idaho Agricultural Experiment Station.

Mengel, K., & Kirkby, E. A. (1982). *Principles of plant nutrition* (3rd ed.). Bern, Switzerland: International Potash Institute.

Mikkelsen, R. L., Behel Jr., A. D., & Williams, H. M. (1993). Addition of gel-forming hydrophilic polymers to nitrogen fertilizer solutions. *Fertilizer Research*, *36*, 55–61. https://doi.org/10.1007/BF00749948

Mitchell, P. B., & Atkinson, K. (1992). The use of super-expanding polyacrylamide polymer in controlling the environmental impact of metalliferous mine waste. *Minerals Engineering*, *5*, 1439–1452. https://doi.org/10.1016/0892-6875(92)90178-C

Monger, C., Kraimer, R., Khresat, S., Cole, D., Wang, X., & Wang, J. (2015). Sequestration of inorganic carbon in soil and groundwater. *Geology*, *43*, 375–378. https://doi.org/10.1130/G36449.1

Olsen, S. R., Watanabe, F. S., & Cole, C. V. (1960). Effect of sodium bicarbonate on the solubility of phosphorus in calcareous soils. *Soil Science*, *89*, 288–291. https://doi.org/10.1097/00010694-196005000-00010

Pannkuk, T. R., Aitkenhead-Peterson, J. A., Steinke, K., Thomas, J., Chalmers, D. R., & White, R. H. (2011). Carbon, nitrogen, and orthophosphate leaching from soil under single- and mixed-species landscapes, *HortScience*, *46*(11), 1533–1539. https://doi.org/10.21273/HORTSCI.46.11.1533

Rivas, B. L., & Moreno-Villoslada, I. (1998). Chelation properties of polymer complexes of poly(acrylic acid) with poly(acrylamide), and poly(acrylic acid) with poly(N,N-dimethylacrylamide). *Macromolecular Chemistry and Physics*, *199*, 1153–1160. https://doi.org/10.1002/(SICI)1521-3935(19980601)199:6%3c1153::AID-MACP1153%3e3.0.CO;2-R

SAS Institute. (2012). SAS online documentation, version 9.4 *[CD]*. Cary, NC: SAS Institute, Inc.

Sherrod, L. A., Dunn, G., Peterson, G. A., & Kolberg, R. L. (2002). Inorganic carbon analysis by modified pressure-calcimeter method. *Soil Science Society of America Journal*, *66*, 299–305. https://doi.org/10.2136/sssaj2002.2990

Silverbush, M., Adar, E., & De Malach, Y. (1993). Use of an hydrophilic polymer to improve water storage and availability to crops grown in sand dunes II. Cabbage irrigated by sprinkling with different water salinities. *Agricultural Water Management*, *23*, 315–327. https://doi.org/10.1016/0378-3774(93)90043-A

Sojka, R. E., Bjorneberg, D. L., Entry, J. A., Lentz, R. D., & Orts, W. J. (2007). Polyacrylamide (PAM) in agriculture and environmental land management. *Advances in Agronomy*, *92*, 75–162. https://doi.org/10.1016/S0065-2113(04)92002-0

Tomida, T., Hamaguchi, K., Tunashima, S., Katoh, M., & Masuda, S. (2001). Binding properties of a water-soluble chelating polymer with divalent metal ions measured by ultrafiltration: Poly(acrylic acid). *Industrial and Engineering Chemistry Research*, *40*, 3557–3562. https://doi.org/10.1021/ie0009839

Trenberth, K. E. (2011). Changes in precipitation with climate change. *Climate Research*, *47*, 123–138. https://doi.org/10.3354/cr00953

Woodhouse, J., & Johnson, M. S. (1991). Effect of superabsorbent polymers on survival and growth of crop seedlings. *Agricultural Water Management*, *20*, 63–70. https://doi.org/10.1016/0378-3774(91)90035-H

## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

# SUPPLEMENTAL MATERIAL

**Cross-Linked Polymers Increase Nutrient Sorption in Degraded Soils**

R. D. Lentz[1*], and J. A. Ippolito[2]

[1] Northwest Irrigation and Soils Research Laboratory, USDA-ARS, 3793 N. 3600 E., Kimberly, ID 83341-5076, USA.

[2] Soil and Crop Science Dep., Colorado State Univ., 307 University Ave., Fort Collins, CO, 80523-1170, USA.

[*] Correspondence:
Rodrick D. Lentz, Northwest Irrigation and Soils Research Laboratory, USDA-ARS, 3793 N. 3600 E., Kimberly, ID 83341-5076, USA

**Supplemental Information (12 pages):**

**Tables S1 to S5**

**Figures S1 to S2**

Table S1.  Treatment and year effects on soil nutrient properties.  Values are the arithmetic means (std. dev.) of soil samples collected in spring each year from 2010 to 2017 ($n$=4).

| Treatment | 2010 | | 2011 | | 2012 | | 2013 | | 2014 | | 2015 | | 2016 | | 2017 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TC, %** | | | | | | | | | | | | | | | | |
| Control | 3.23 | (0.06) | 3.38 | (0.03) | 3.39 | (0.02) | 3.36 | (0.05) | 3.31 | (0.10) | 3.38 | (0.03) | 3.66 | (0.03) | 3.62 | (0.35) |
| Topsoil | 2.12 | (0.04) | 1.91 | (0.04) | 1.88 | (0.04) | 1.92 | (0.03) | 1.91 | (0.05) | 1.95 | (0.05) | 2.10 | (0.01) | 2.15 | (0.17) |
| XPAM1 | 3.42 | (0.19) | 3.50 | (0.03) | 3.51 | (0.07) | 3.53 | (0.10) | 3.48 | (0.03) | 3.49 | (0.02) | 3.82 | (0.08) | 3.51 | (0.07) |
| XPAM2 | 3.52 | (0.05) | 3.64 | (0.06) | 3.58 | (0.05) | 3.61 | (0.14) | 3.51 | (0.06) | 3.53 | (0.06) | 3.92 | (0.07) | 3.59 | (0.37) |
| XPAA1 | 3.36 | (0.31) | 3.19 | (0.08) | 3.25 | (0.07) | 3.25 | (0.07) | 3.24 | (0.17) | 3.29 | (0.12) | 3.51 | (0.08) | 3.37 | (0.11) |
| XPAA2 | 3.26 | (0.30) | 3.34 | (0.14) | 3.29 | (0.08) | 3.29 | (0.18) | 3.29 | (0.02) | 3.30 | (0.07) | 3.57 | (0.06) | 3.32 | (0.25) |
| **TIC, %** | | | | | | | | | | | | | | | | |
| Control | 2.76 | (0.13) | 2.91 | (0.14) | 2.83 | (0.03) | 2.90 | (0.05) | 2.81 | (0.02) | 2.85 | (0.04) | 2.82 | (0.10) | 2.92 | (0.03) |
| Topsoil | 1.21 | (0.05) | 1.12 | (0.02) | 1.11 | (0.16) | 1.14 | (0.02) | 1.12 | (0.03) | 1.22 | (0.02) | 1.17 | (0.05) | 1.11 | (0.03) |
| XPAM1 | 2.81 | (0.08) | 2.86 | (0.13) | 2.86 | (0.02) | 2.85 | (0.07) | 2.78 | (0.05) | 2.84 | (0.05) | 2.88 | (0.08) | 2.92 | (0.02) |
| XPAM2 | 2.71 | (0.16) | 2.86 | (0.13) | 2.84 | (0.05) | 2.91 | (0.03) | 2.83 | (0.05) | 2.80 | (0.06) | 2.89 | (0.05) | 2.95 | (0.05) |
| XPAA1 | 2.57 | (0.09) | 2.57 | (0.03) | 2.63 | (0.02) | 2.64 | (0.01) | 2.60 | (0.03) | 2.58 | (0.06) | 2.69 | (0.10) | 2.64 | (0.11) |
| XPAA2 | 2.71 | (0.02) | 2.58 | (0.02) | 2.64 | (0.04) | 2.67 | (0.04) | 2.59 | (0.05) | 2.60 | (0.06) | 2.73 | (0.07) | 2.69 | (0.05) |
| **TOC, %** | | | | | | | | | | | | | | | | |
| Control | 0.48 | (0.12) | 0.47 | (0.14) | 0.55 | (0.04) | 0.47 | (0.07) | 0.50 | (0.08) | 0.52 | (0.06) | 0.84 | (0.08) | 0.70 | (0.33) |
| Topsoil | 0.91 | (0.07) | 0.79 | (0.02) | 0.78 | (0.20) | 0.78 | (0.03) | 0.79 | (0.07) | 0.72 | (0.03) | 0.93 | (0.06) | 1.03 | (0.18) |
| XPAM1 | 0.62 | (0.20) | 0.65 | (0.13) | 0.64 | (0.08) | 0.68 | (0.11) | 0.70 | (0.05) | 0.65 | (0.05) | 0.95 | (0.05) | 0.58 | (0.06) |
| XPAM2 | 0.81 | (0.18) | 0.77 | (0.16) | 0.73 | (0.09) | 0.71 | (0.16) | 0.68 | (0.05) | 0.73 | (0.10) | 1.04 | (0.07) | 0.65 | (0.33) |
| XPAA1 | 0.79 | (0.34) | 0.62 | (0.05) | 0.61 | (0.05) | 0.60 | (0.07) | 0.64 | (0.17) | 0.71 | (0.16) | 0.82 | (0.16) | 0.73 | (0.14) |
| XPAA2 | 0.55 | (0.32) | 0.76 | (0.12) | 0.66 | (0.11) | 0.64 | (0.16) | 0.70 | (0.06) | 0.70 | (0.07) | 0.85 | (0.10) | 0.64 | (0.29) |
| **TN, %** | | | | | | | | | | | | | | | | |
| Control | 0.07 | (0.01) | 0.07 | (0.02) | 0.08 | (0.02) | 0.07 | (0.00) | 0.07 | (0.01) | 0.06 | (0.02) | 0.07 | (0.01) | 0.06 | (0.01) |
| Topsoil | 0.11 | (0.01) | 0.07 | (0.01) | 0.07 | (0.00) | 0.09 | (0.01) | 0.08 | (0.01) | 0.10 | (0.01) | 0.09 | (0.00) | 0.09 | (0.02) |
| XPAM1 | 0.09 | (0.01) | 0.08 | (0.01) | 0.07 | (0.01) | 0.18 | (0.15) | 0.10 | (0.01) | 0.10 | (0.01) | 0.11 | (0.01) | 0.10 | (0.02) |
| XPAM2 | 0.12 | (0.02) | 0.12 | (0.01) | 0.10 | (0.03) | 0.22 | (0.13) | 0.11 | (0.03) | 0.12 | (0.03) | 0.14 | (0.01) | 0.11 | (0.01) |
| XPAA1 | 0.06 | (0.01) | 0.06 | (0.01) | 0.05 | (0.01) | 0.09 | (0.01) | 0.07 | (0.01) | 0.08 | (0.01) | 0.08 | (0.01) | 0.06 | (0.01) |
| XPAA2 | 0.08 | (0.02) | 0.06 | (0.01) | 0.05 | (0.01) | 0.07 | (0.01) | 0.06 | (0.01) | 0.07 | (0.00) | 0.08 | (0.01) | 0.06 | (0.01) |
| **$NO_3$-N, mg $L^{-1}$** | | | | | | | | | | | | | | | | |
| Control | 3.91 | (0.59) | 13.51 | (0.09) | 5.15 | (0.75) | 5.15 | (1.03) | 22.6 | (1.31) | 1.89 | (1.29) | 8.29 | (1.52) | 4.40 | (0.69) |
| Topsoil | 34.8 | (9.05) | 7.64 | (0.15) | 6.84 | (1.22) | 5.51 | (0.63) | 14.9 | (2.92) | 3.63 | (3.44) | 22.7 | (11.1) | 5.93 | (1.17) |
| XPAM1 | 7.42 | (1.98) | 14.01 | (0.13) | 7.90 | (0.81) | 3.57 | (1.64) | 16.7 | (4.72) | 3.50 | (0.64) | 9.13 | (4.50) | 4.90 | (1.03) |
| XPAM2 | 12.2 | (6.68) | 14.55 | (0.25) | 21.6 | (2.28) | 9.05 | (0.69) | 24.9 | (2.92) | 6.35 | (2.31) | 8.87 | (2.96) | 6.69 | (1.24) |
| XPAA1 | 5.22 | (0.98) | 12.75 | (0.30) | 5.60 | (0.38) | 3.29 | (0.43) | 9.19 | (0.98) | 2.56 | (1.55) | 9.39 | (0.63) | 9.13 | (7.22) |
| XPAA2 | 7.30 | (1.80) | 13.35 | (0.55) | 6.14 | (0.38) | 5.88 | (1.29) | 12.6 | (3.41) | 2.78 | (0.93) | 11.7 | (2.58) | 5.33 | (0.65) |
| **$NH_4$-N, mg $L^{-1}$** | | | | | | | | | | | | | | | | |
| Control | 1.51 | (0.45) | 11.7 | (0.55) | 0.08 | (0.16) | 1.00 | (0.48) | 3.08 | (0.34) | 0.83 | (0.42) | 0.08 | (0.02) | 3.28 | (0.80) |
| Topsoil | 2.69 | (0.39) | 4.49 | (0.08) | 1.81 | (0.61) | 1.60 | (0.16) | 2.43 | (0.39) | 1.50 | (0.46) | 0.54 | (0.10) | 3.90 | (0.59) |
| XPAM1 | 1.87 | (0.72) | 11.4 | (0.51) | 0.96 | (1.33) | 1.02 | (0.72) | 1.56 | (0.71) | 0.64 | (0.38) | 0.02 | (0.04) | 3.56 | (0.73) |
| XPAM2 | 1.27 | (0.22) | 11.5 | (0.51) | 0.50 | (1.00) | 0.86 | (0.16) | 1.91 | (0.77) | 0.67 | (0.33) | 0.12 | (0.16) | 3.56 | (0.60) |
| XPAA1 | 1.53 | (0.70) | 10.3 | (0.11) | 1.85 | (0.38) | 1.22 | (0.32) | 1.21 | (0.48) | 0.68 | (0.22) | 0.21 | (0.24) | 3.73 | (0.16) |
| XPAA2 | 1.77 | (0.54) | 10.3 | (0.08) | 0.59 | (0.50) | 1.12 | (0.88) | 1.56 | (0.31) | 0.52 | (0.23) | 0.00 | (0.00) | 3.50 | (0.97) |
| **Olsen-P, mg $L^{-}$** | | | | | | | | | | | | | | | | |
| Control | 50.8 | (2.2) | 19.6 | (0.7) | 21.9 | (2.0) | 11.0 | (1.2) | 11.3 | (1.6) | 13.5 | (2.2) | 10.2 | (1.9) | 8.0 | (1.2) |
| Topsoil | 49.0 | (2.3) | 20.7 | (1.6) | 24.5 | (1.2) | 16.7 | (3.8) | 13.0 | (1.1) | 15.7 | (4.3) | 17.3 | (4.1) | 11.6 | (2.5) |
| XPAM1 | 46.6 | (3.7) | 19.2 | (1.5) | 22.1 | (1.4) | 12.5 | (1.5) | 11.7 | (0.9) | 13.6 | (3.8) | 11.9 | (2.1) | 8.2 | (1.7) |
| XPAM2 | 51.9 | (15.2) | 18.2 | (1.6) | 22.1 | (1.3) | 13.6 | (0.5) | 13.0 | (1.3) | 14.7 | (3.9) | 10.5 | (2.5) | 8.9 | (1.0) |
| XPAA1 | 58.1 | (0.3) | 22.0 | (0.9) | 24.5 | (0.4) | 17.0 | (1.8) | 11.2 | (1.1) | 16.5 | (1.4) | 14.9 | (1.0) | 10.8 | (1.2) |
| XPAA2 | 55.7 | (2.5) | 22.8 | (1.0) | 23.5 | (1.7) | 15.3 | (0.4) | 12.1 | (2.1) | 17.1 | (3.1) | 14.7 | (0.8) | 10.9 | (0.8) |
| **Na, mg $L^{-1}$** | | | | | | | | | | | | | | | | |
| Control | 196 | (19) | 188 | (22) | 240 | (11) | 121 | (14) | 260 | (72) | 108 | (21) | 110 | (32) | 88 | (13) |
| Topsoil | 152 | (13) | 196 | (18) | 229 | (10) | 210 | (14) | 307 | (45) | 173 | (24) | 243 | (84) | 118 | (23) |
| XPAM1 | 286 | (29) | 346 | (24) | 415 | (34) | 362 | (135) | 524 | (109) | 298 | (63) | 224 | (49) | 104 | (12) |
| XPAM2 | 351 | (37) | 500 | (73) | 577 | (44) | 492 | (42) | 445 | (188) | 291 | (109) | 294 | (168) | 111 | (42) |
| XPAA1 | 154 | (14) | 154 | (27) | 200 | (18) | 216 | (51) | 336 | (42) | 174 | (19) | 126 | (27) | 85 | (8) |
| XPAA2 | 185 | (9) | 181 | (11) | 221 | (17) | 263 | (41) | 352 | (19) | 177 | (18) | 126 | (20) | 82 | (9) |
| **K, mg $L^{-1}$** | | | | | | | | | | | | | | | | |
| Control | 16.0 | (6.9) | 44.5 | (1.9) | 56.5 | (1.5) | 49.0 | (1.1) | 41.2 | (1.8) | 23.0 | (7.5) | 28.6 | (2.3) | 35.7 | (2.1) |
| Topsoil | 70.9 | (6.1) | 94.6 | (3.8) | 135.0 | (18.8) | 94.9 | (9.3) | 76.1 | (10.9) | 43.1 | (9.8) | 61.1 | (12.8) | 58.0 | (8.7) |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XPAM1 | 153.0 | (7.4) | 181.5 | (8.5) | 226.5 | (20.7) | 152.1 | (7.5) | 134.5 | (11.3) | 75.3 | (5.8) | 88.1 | (17.6) | 74.4 | (9.0) |
| XPAM2 | 231.4 | (29.1) | 213.4 | (21.3) | 294.0 | (26.4) | 177.2 | (19.5) | 147.7 | (24.2) | 86.7 | (9.3) | 94.6 | (12.7) | 78.0 | (2.8) |
| XPAA1 | 494.4 | (16.7) | 435.4 | (14.1) | 560.5 | (35.7) | 335.0 | (33.5) | 295.7 | (45.1) | 166.1 | (23.4) | 149.1 | (23.7) | 112.5 | (4.4) |
| XPAA2 | 38.3 | (5.3) | 48.5 | (5.2) | 87.3 | (6.0) | 65.5 | (6.9) | 55.6 | (6.8) | 34.2 | (6.3) | 44.4 | (4.4) | 44.2 | (5.3) |

Mg, mg L$^{-1}$

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 450 | (9) | 391 | (12) | 584 | (33) | 414 | (5) | 503 | (11) | 381 | (13) | 483 | (17) | 450 | (17) |
| Topsoil | 369 | (5) | 300 | (5) | 385 | (5) | 380 | (12) | 407 | (10) | 370 | (11) | 448 | (17) | 418 | (24) |
| XPAM1 | 434 | (18) | 364 | (19) | 480 | (36) | 401 | (12) | 443 | (32) | 394 | (3) | 508 | (12) | 470 | (7) |
| XPAM2 | 439 | (27) | 373 | (25) | 509 | (28) | 367 | (2) | 446 | (30) | 371 | (20) | 475 | (16) | 449 | (10) |
| XPAA1 | 367 | (13) | 352 | (13) | 457 | (6) | 383 | (17) | 438 | (19) | 400 | (8) | 482 | (11) | 436 | (11) |
| XPAA2 | 338 | (12) | 299 | (14) | 403 | (16) | 356 | (15) | 389 | (21) | 379 | (14) | 460 | (8) | 433 | (4) |

Cu, mg L$^{-1}$

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 1.07 | (0.04) | 0.87 | (0.04) | 0.98 | (0.04) | 1.21 | (0.12) | 1.20 | (0.04) | 1.08 | (0.08) | 0.98 | (0.02) | 1.57 | (1.02) |
| Topsoil | 1.39 | (0.04) | 1.17 | (0.02) | 1.31 | (0.04) | 1.88 | (0.14) | 1.82 | (0.12) | 1.43 | (0.10) | 1.44 | (0.06) | 2.52 | (1.03) |
| XPAM1 | 1.08 | (0.05) | 0.90 | (0.05) | 0.97 | (0.02) | 1.31 | (0.31) | 1.28 | (0.04) | 1.06 | (0.04) | 0.98 | (0.04) | 1.79 | (0.70) |
| XPAM2 | 1.08 | (0.10) | 0.87 | (0.05) | 0.96 | (0.02) | 1.13 | (0.07) | 1.23 | (0.03) | 1.05 | (0.06) | 0.95 | (0.02) | 1.21 | (0.66) |
| XPAA1 | 1.58 | (0.06) | 1.34 | (0.05) | 1.41 | (0.03) | 1.88 | (0.33) | 1.82 | (0.07) | 1.54 | (0.05) | 1.42 | (0.05) | 1.20 | (0.47) |
| XPAA2 | 1.51 | (0.05) | 1.23 | (0.03) | 1.29 | (0.03) | 1.75 | (0.14) | 1.64 | (0.06) | 1.46 | (0.05) | 1.29 | (0.04) | 1.78 | (0.18) |

Fe, mg L$^{-1}$

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 3.04 | (0.09) | 3.26 | (0.09) | 2.80 | (0.31) | 2.97 | (0.13) | 4.26 | (1.18) | 2.57 | (0.23) | 2.28 | (0.07) | 3.11 | (0.32) |
| Topsoil | 6.46 | (0.15) | 5.86 | (0.15) | 4.96 | (0.16) | 5.00 | (3.28) | 5.59 | (3.66) | 4.58 | (0.19) | 4.60 | (0.65) | 5.63 | (0.59) |
| XPAM1 | 2.90 | (0.21) | 3.05 | (0.23) | 2.49 | (0.07) | 3.61 | (0.87) | 4.22 | (0.73) | 2.63 | (0.11) | 2.20 | (0.09) | 3.13 | (0.37) |
| XPAM2 | 2.91 | (0.48) | 2.74 | (0.37) | 2.38 | (0.40) | 2.72 | (0.26) | 3.86 | (0.65) | 2.12 | (0.44) | 2.35 | (0.19) | 3.31 | (0.55) |
| XPAA1 | 6.17 | (1.27) | 5.35 | (0.79) | 4.02 | (0.76) | 4.67 | (0.53) | 5.64 | (0.79) | 3.58 | (0.30) | 3.03 | (0.16) | 3.95 | (0.57) |
| XPAA2 | 5.35 | (0.44) | 4.31 | (0.18) | 3.09 | (0.21) | 4.00 | (0.21) | 4.64 | (0.18) | 3.12 | (0.24) | 2.51 | (0.07) | 3.56 | (0.17) |

Zn, mg L$^{-1}$

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 1.21 | (0.07) | 1.00 | (0.04) | 0.51 | (0.09) | 1.86 | (0.19) | 1.05 | (0.05) | 0.70 | (0.05) | 0.90 | (0.05) | 2.11 | (0.75) |
| Topsoil | 2.93 | (0.15) | 2.71 | (0.71) | 1.68 | (0.14) | 2.97 | (0.39) | 2.79 | (0.05) | 1.93 | (0.13) | 2.11 | (0.18) | 3.45 | (1.24) |
| XPAM1 | 1.13 | (0.02) | 0.82 | (0.12) | 0.44 | (0.07) | 1.69 | (0.30) | 1.01 | (0.02) | 0.68 | (0.10) | 0.77 | (0.02) | 2.49 | (0.59) |
| XPAM2 | 1.24 | (0.18) | 0.90 | (0.13) | 0.44 | (0.11) | 1.90 | (0.81) | 1.02 | (0.05) | 0.65 | (0.10) | 0.77 | (0.05) | 1.80 | (0.53) |
| XPAA1 | 5.71 | (0.28) | 4.71 | (0.11) | 2.79 | (0.22) | 5.14 | (0.60) | 4.12 | (0.44) | 2.91 | (0.35) | 3.53 | (1.21) | 2.44 | (0.22) |
| XPAA2 | 7.24 | (0.64) | 5.80 | (0.57) | 3.77 | (0.90) | 6.37 | (1.30) | 4.40 | (0.31) | 3.05 | (0.20) | 3.41 | (0.24) | 2.79 | (0.44) |

Mn, mg L$^{-1}$

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 5.91 | (1.30) | 4.17 | (0.24) | 4.56 | (0.17) | 5.56 | (0.22) | 4.94 | (0.28) | 4.02 | (0.88) | 5.74 | (0.40) | 6.91 | (0.68) |
| Topsoil | 6.10 | (0.72) | 3.95 | (0.08) | 6.90 | (0.40) | 8.21 | (0.42) | 7.49 | (0.15) | 5.00 | (0.19) | 8.15 | (0.52) | 8.66 | (2.09) |
| XPAM1 | 5.20 | (0.52) | 4.67 | (0.93) | 5.47 | (0.68) | 5.73 | (0.89) | 4.72 | (0.04) | 3.87 | (0.56) | 5.73 | (0.42) | 6.30 | (0.97) |
| XPAM2 | 4.87 | (1.01) | 3.77 | (0.61) | 4.59 | (0.86) | 5.57 | (0.42) | 4.68 | (0.60) | 3.49 | (0.40) | 5.54 | (0.40) | 6.18 | (0.64) |
| XPAA1 | 7.17 | (0.54) | 4.66 | (0.19) | 6.02 | (0.30) | 6.40 | (0.36) | 5.16 | (0.34) | 4.58 | (0.25) | 6.15 | (0.74) | 6.27 | (0.90) |
| XPAA2 | 7.08 | (0.61) | 4.12 | (0.31) | 5.42 | (0.76) | 6.35 | (0.75) | 4.93 | (0.17) | 4.32 | (0.17) | 5.91 | (0.63) | 6.55 | (0.73) |

pH

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 8.16 | (0.09) | 8.00 | (0.05) | 8.10 | (0.06) | 7.73 | (0.07) | 7.73 | (0.13) | 7.88 | (0.13) | 7.78 | (0.21) | 8.19 | (0.26) |
| Topsoil | 7.72 | (0.05) | 7.75 | (0.02) | 7.82 | (0.04) | 7.69 | (0.02) | 7.75 | (0.13) | 7.85 | (0.06) | 7.79 | (0.03) | 7.97 | (0.03) |
| XPAM1 | 8.01 | (0.20) | 8.05 | (0.04) | 8.24 | (0.08) | 7.89 | (0.07) | 7.98 | (0.19) | 8.13 | (0.17) | 7.96 | (0.07) | 8.30 | (0.07) |
| XPAM2 | 7.96 | (0.09) | 7.99 | (0.02) | 8.09 | (0.02) | 7.89 | (0.04) | 7.85 | (0.13) | 8.10 | (0.14) | 7.94 | (0.22) | 8.11 | (0.42) |
| XPAA1 | 8.16 | (0.02) | 8.02 | (0.04) | 8.04 | (0.04) | 7.87 | (0.07) | 7.98 | (0.10) | 7.85 | (0.06) | 7.89 | (0.05) | 8.24 | (0.24) |
| XPAA2 | 8.13 | (0.10) | 8.03 | (0.06) | 8.06 | (0.03) | 7.91 | (0.05) | 7.93 | (0.13) | 7.98 | (0.21) | 7.86 | (0.07) | 8.26 | (0.21) |

EC, dS m-1

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 0.43 | (0.07) | 0.45 | (0.02) | 0.52 | (0.01) | 0.39 | (0.01) | 0.77 | (0.07) | 0.40 | (0.02) | 0.28 | (0.06) | 0.39 | (0.03) |
| Topsoil | 0.94 | (0.14) | 0.64 | (0.06) | 0.46 | (0.04) | 0.51 | (0.03) | 0.69 | (0.04) | 0.36 | (0.04) | 0.59 | (0.28) | 0.49 | (0.05) |
| XPAM1 | 0.75 | (0.17) | 0.70 | (0.12) | 0.74 | (0.04) | 0.61 | (0.18) | 0.87 | (0.04) | 0.47 | (0.03) | 0.31 | (0.04) | 0.43 | (0.01) |
| XPAM2 | 0.81 | (0.08) | 1.06 | (0.16) | 1.53 | (0.31) | 0.78 | (0.04) | 1.03 | (0.13) | 0.49 | (0.07) | 0.25 | (0.08) | 0.48 | (0.04) |
| XPAA1 | 0.47 | (0.02) | 0.48 | (0.02) | 0.47 | (0.01) | 0.51 | (0.06) | 0.71 | (0.04) | 0.37 | (0.03) | 0.32 | (0.07) | 0.41 | (0.02) |
| XPAA2 | 0.67 | (0.07) | 0.63 | (0.06) | 0.51 | (0.01) | 0.71 | (0.15) | 0.77 | (0.04) | 0.42 | (0.03) | 0.35 | (0.04) | 0.41 | (0.01) |

Table S2.  Treatment and year effects on above-ground biomass. Values are arithmetic means (std. dev.) from biomass samples harvested from 2009 to 2013 ($n=4$).  Treatment label numbers 1 and 2 identify 0.25% and 0.5% application rates, respectively.

| Treatment | 2009 | | 2010 | | 2011 | | 2012 | | 2013 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Biomass, Mg ha$^{-1}$ | | | | | | | | | |
| Control | 1.06 | (0.64) | 10.59 | (1.86) | 2.25 | (0.78) | 3.80 | (1.77) | 17.33 | (1.87) |
| Topsoil | 0.65 | (0.39) | 6.71 | (0.69) | 1.48 | (0.21) | 5.05 | (0.51) | 21.21 | (3.40) |
| XPAM1 | 1.43 | (0.74) | 9.79 | (1.76) | 1.67 | (0.40) | 3.07 | (0.44) | 17.23 | (1.50) |
| XPAM2 | 2.45 | (0.67) | 10.07 | (0.93) | 1.17 | (0.24) | 3.46 | (1.56) | 20.69 | (2.84) |
| XPAA1 | 2.00 | (0.32) | 9.55 | (0.70) | 1.40 | (0.31) | 4.42 | (1.14) | 18.34 | (1.27) |
| XPAA2 | 1.52 | (0.36) | 7.94 | (077) | 1.25 | (0.22) | 3.93 | (0.65) | 18.69 | (1.29) |

Table S3.  Treatment and year effects on elemental uptake in above-ground biomass. Values are arithmetic means (std. dev.) from biomass samples harvested from 2009 to 2013 (n=4). Treatment label numbers 1 and 2 identify 0.25% and 0.5% application rates, respectively.

| Treatment | 2009 | | 2010 | | 2011 | | 2012 | | 2013 | |
|---|---|---|---|---|---|---|---|---|---|---|
| TC, Mg ha$^{-1}$ | | | | | | | | | | |
| Control | 0.44 | (0.27) | 4.43 | (0.70) | 0.89 | (0.31) | 1.56 | (0.77) | 6.32 | (0.81) |
| Topsoil | 0.27 | (0.17) | 2.83 | (0.27) | 0.51 | (0.08) | 1.97 | (0.19) | 8.26 | (1.33) |
| XPAM1 | 0.60 | (0.32) | 4.01 | (0.72) | 0.69 | (0.16) | 1.13 | (0.20) | 6.69 | (0.57) |
| XPAM2 | 1.03 | (0.29) | 4.37 | (0.44) | 0.45 | (0.10) | 1.30 | (0.68) | 7.73 | (1.20) |
| XPAA1 | 0.84 | (0.14) | 3.97 | (0.27) | 0.56 | (0.12) | 1.55 | (0.37) | 7.13 | (0.47) |
| XPAA2 | 0.64 | (0.16) | 3.28 | (0.34) | 0.50 | (0.09) | 1.50 | (0.30) | 7.14 | (0.63) |
| TN, Mg ha-1 | | | | | | | | | | |
| Control | 25.9 | (14.9) | 159 | (35.4) | 62.6 | (32.3) | 90.8 | (44.1) | 138 | (30.9) |
| Topsoil | 20.7 | (12.4) | 134 | (22.0) | 35.6 | (7.3) | 124 | (28.5) | 205 | (65.9) |
| XPAM1 | 37.9 | (15.8) | 158 | (21.7) | 36.8 | (10.5) | 64.6 | (8.6) | 181 | (19.1) |
| XPAM2 | 60.4 | (15.8) | 170 | (17.3) | 19.8 | (5.9) | 78.8 | (44.0) | 177 | (52.6) |
| XPAA1 | 56.9 | (13.6) | 169 | (11.5) | 28.3 | (8.3) | 102 | (30.8) | 192 | (11.7) |
| XPAA2 | 43.0 | (5.9) | 137 | (11.3) | 30.0 | (8.8) | 85.8 | (16.0) | 184 | (17.1) |
| Ca, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 21.8 | (10.5) | 22.4 | (4.7) | 29.5 | (7.9) | 53.2 | (23.0) | 23.2 | (5.6) |
| Topsoil | 19.6 | (11.9) | 22.2 | (4.0) | 26.4 | (2.2) | 77.0 | (6.0) | 35.0 | (8.9) |
| XPAM1 | 24.9 | (12.3) | 18.3 | (4.5) | 20.7 | (6.1) | 42.7 | (4.2) | 24.9 | (2.4) |
| XPAM2 | 35.4 | (7.0) | 18.7 | (2.1) | 21.5 | (5.1) | 46.7 | (17.2) | 24.4 | (5.0) |
| XPAA1 | 39.7 | (6.0) | 21.0 | (3.7) | 19.5 | (4.6) | 55.2 | (14.7) | 26.9 | (3.1) |
| XPAA2 | 30.6 | (2.6) | 15.0 | (3.2) | 16.8 | (3.4) | 43.9 | (8.8) | 25.0 | (2.0) |
| K, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 18.9 | (9.5) | 196 | (37.3) | 39.6 | (10.2) | 84.4 | (42.9) | 250 | (40.5) |
| Topsoil | 11.8 | (6.6) | 151 | (12.8) | 26.9 | (2.3) | 113 | (30.3) | 305 | (42.3) |
| XPAM1 | 30.0 | (14.1) | 179 | (42.0) | 33.8 | (10.4) | 86.1 | (16.7) | 261 | (14.3) |
| XPAM2 | 50.1 | (10.8) | 194 | (20.4) | 40.5 | (11.5) | 112 | (45.4) | 315 | (20.9) |
| XPAA1 | 44.4 | (8.3) | 216 | (22.1) | 37.5 | (8.6) | 132 | (27.0) | 298 | (14.4) |
| XPAA2 | 47.8 | (8.3) | 193 | (22.1) | 50.1 | (12.3) | 124 | (16.2) | 333 | (9.1) |
| Mg, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 7.6 | (4.4) | 23.8 | (4.2) | 11.3 | (3.4) | 22.5 | (10.1) | 44.2 | (12.6) |
| Topsoil | 5.0 | (2.9) | 13.9 | (1.8) | 7.0 | (0.3) | 22.7 | (1.1) | 45.0 | (10.6) |
| XPAM1 | 9.1 | (4.3) | 21.1 | (4.2) | 8.0 | (2.2) | 16.8 | (1.9) | 36.7 | (3.5) |
| XPAM2 | 12.2 | (2.4) | 22.2 | (2.9) | 7.5 | (1.9) | 18.1 | (6.8) | 38.4 | (9.4) |
| XPAA1 | 14.1 | (1.9) | 19.2 | (1.2) | 7.5 | (1.7) | 20.3 | (4.9) | 35.3 | (3.7) |
| XPAA2 | 10.2 | (1.5) | 14.8 | (1.3) | 6.7 | (1.2) | 15.1 | (2.2) | 33.4 | (3.2) |
| Na, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 0.6 | (0.5) | 36.2 | (8.0) | 7.9 | (5.3) | 5.1 | (3.9) | 3.4 | (1.5) |
| Topsoil | 0.4 | (0.3) | 24.7 | (1.8) | 2.9 | (0.5) | 5.0 | (2.0) | 2.0 | (1.3) |
| XPAM1 | 1.2 | (0.7) | 35.1 | (10.3) | 5.5 | (2.4) | 4.5 | (1.6) | 4.8 | (2.7) |
| XPAM2 | 1.4 | (0.8) | 29.6 | (7.0) | 8.9 | (1.0) | 6.7 | (1.6) | 8.2 | (5.7) |
| XPAA1 | 1.0 | (0.2) | 32.5 | (5.4) | 3.8 | (1.1) | 3.6 | (0.4) | 1.7 | (0.6) |
| XPAA2 | 0.8 | (0.2) | 27.7 | (7.9) | 7.4 | (1.2) | 4.1 | (1.8) | 2.3 | (0.9) |
| P, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 2.7 | (1.8) | 19.9 | (4.2) | 9.3 | (3.3) | 13.9 | (7.8) | 18.4 | (3.4) |
| Topsoil | 2.2 | (1.4) | 7.3 | (1.0) | 5.6 | (1.6) | 17.1 | (3.1) | 24.3 | (8.7) |
| XPAM1 | 4.7 | (2.2) | 16.8 | (3.4) | 7.0 | (1.4) | 11.8 | (2.3) | 18.4 | (2.2) |
| XPAM2 | 6.1 | (1.5) | 17.1 | (2.6) | 4.3 | (1.0) | 14.0 | (6.6) | 24.9 | (9.9) |
| XPAA1 | 7.4 | (1.1) | 16.4 | (2.0) | 5.8 | (1.2) | 15.4 | (2.8) | 15.7 | (0.8) |
| XPAA2 | 5.6 | (1.1) | 12.6 | (0.5) | 5.2 | (0.7) | 12.8 | (1.3) | 16.0 | (1.5) |
| S, kg ha$^{-1}$ | | | | | | | | | | |
| Control | 1.7 | (1.1) | 21.4 | (4.8) | 4.3 | (1.0) | 7.4 | (3.6) | 6.3 | (1.5) |
| Topsoil | 1.4 | (0.9) | 9.7 | (2.3) | 2.9 | (0.4) | 8.4 | (0.2) | 7.2 | (1.0) |
| XPAM1 | 2.3 | (1.0) | 19.7 | (4.9) | 3.4 | (0.9) | 6.2 | (0.7) | 6.9 | (0.7) |
| XPAM2 | 3.2 | (0.8) | 21.4 | (3.1) | 5.9 | (1.9) | 8.1 | (2.8) | 8.0 | (1.9) |
| XPAA1 | 3.9 | (0.4) | 17.9 | (1.6) | 3.0 | (0.6) | 7.4 | (1.5) | 7.5 | (0.4) |
| XPAA2 | 2.7 | (0.6) | 13.2 | (0.9) | 3.4 | (0.8) | 6.9 | (1.2) | 6.7 | (0.5) |

|  | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Cu, g ha⁻¹** | | | | | | | | | | |
| Control | 10.2 | (9.8) | 32.9 | (10.5) | 15.5 | (2.3) | 19.8 | (10.3) | †_ | - |
| Topsoil | 7.7 | (5.2) | 34.8 | (6.8) | 9.4 | (0.3) | 26.2 | (4.5) | - | - |
| XPAM1 | 12.7 | (5.8) | 27.6 | (3.6) | 13.3 | (3.3) | 19.6 | (6.7) | - | - |
| XPAM2 | 18.6 | (5.0) | 29.1 | (4.9) | 13.9 | (3.2) | 20.7 | (7.6) | - | - |
| XPAA1 | 21.6 | (2.4) | 35.9 | (4.8) | 10.8 | (1.6) | 23.4 | (5.7) | - | - |
| XPAA2 | 16.6 | (2.4) | 40.0 | (7.7) | 11.6 | (2.3) | 18.9 | (3.2) | - | - |
| **Fe, g ha⁻¹** | | | | | | | | | | |
| Control | 194 | (121) | 593 | (159) | 120 | (37) | 554 | (226) | 640 | (224) |
| Topsoil | 218 | (195) | 972 | (315) | 113 | (23) | 839 | (196) | 618 | (142) |
| XPAM1 | 373 | (237) | 608 | (122) | 115 | (30) | 484 | (102) | 604 | (203) |
| XPAM2 | 502 | (54) | 609 | (117) | 80 | (22) | 597 | (220) | 1042 | (639) |
| XPAA1 | 455 | (109) | 696 | (149) | 100 | (30) | 760 | (239) | 525 | (68) |
| XPAA2 | 300 | (92) | 685 | (342) | 103 | (23) | 600 | (242) | 596 | (38) |
| **Mn, g ha⁻¹** | | | | | | | | | | |
| Control | 38.2 | (15.8) | 377 | (73.2) | 58.6 | (24.3) | 173 | (87.1) | 687 | (186) |
| Topsoil | 35.1 | (20.1) | 250 | (36.7) | 50.0 | (5.9) | 232 | (90.1) | 834 | (178) |
| XPAM1 | 41.4 | (14.9) | 392 | (57.7) | 40.3 | (8.6) | 119 | (28.2) | 611 | (150) |
| XPAM2 | 56.9 | (10.6) | 445 | (82.7) | 40.1 | (10.5) | 157 | (51.2) | 701 | (182) |
| XPAA1 | 57.2 | (13.2) | 241 | (15.9) | 35.4 | (7.6) | 198 | (47.1) | 732 | (159) |
| XPAA2 | 42.9 | (4.4) | 209 | (14.5) | 37.9 | (8.6) | 166 | (34.9) | 770 | (130) |
| **Zn, g ha⁻¹** | | | | | | | | | | |
| Control | 18.9 | (12.5) | 328 | (62.3) | 82.4 | (15.5) | 110 | (57.0) | 318 | (96.3) |
| Topsoil | 23.9 | (14.1) | 288 | (41.7) | 69.2 | (9.3) | 149 | (29.8) | 503 | (105) |
| XPAM1 | 33.9 | (15.6) | 306 | (46.9) | 67.6 | (16.1) | 88.1 | (6.0) | 313 | (18.9) |
| XPAM2 | 49.4 | (14.8) | 346 | (30.0) | 64.1 | (14.6) | 108 | (37.7) | 302 | (68.3) |
| XPAA1 | 75.7 | (17.7) | 568 | (47.2) | 108 | (20.8) | 144 | (26.4) | 569 | (54.9) |
| XPAA2 | 65.3 | (10.3) | 627 | (46.9) | 110 | (19.5) | 122 | (24.0) | 562 | (73.4) |

† Cu concentrations were not available in 2013.

Table S4.  Treatment and year effect on leachate nutrient concentrations in spring.  Values are the arithmetic means (std. dev.) from leaching events performed each year from 2009 to 2017 (*n*=4).  Treatment labels 1 and 2 identify 0.25% and 0.5% application rates, respectively.

| Treatment | 2009 | | 2010 | | 2011 | | 2012 | | 2013 | | 2014† | | 2015 | | 2016 | | 2017 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Na, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 253 | (16) | 184 | (10) | 268 | (55) | 173 | (10) | 137 | (27) | 357 | (77) | 96 | (8) | 89 | (35) | 67 | (3) |
| Topsoil | 373 | (117) | 188 | (25) | 174 | (20) | 135 | (4) | 155 | (17) | 394 | (136) | 103 | (14) | 151 | (21) | 80 | (19) |
| XPAM1 | 245 | (29) | 257 | (25) | 290 | (40) | 199 | (40) | 336 | (141) | 597 | (112) | 196 | (35) | 120 | (37) | 77 | (5) |
| XPAM2 | 718 | (238) | -† | - | - | - | - | - | - | - | 653 | (189) | 210 | (78) | 138 | (72) | 113 | (68) |
| XPAA1 | 142 | (21) | 142 | (9) | 196 | (22) | 157 | (29) | 230 | (41) | 462 | (44) | 134 | (15) | 90 | (21) | 79 | (14) |
| XPAA2 | 152 | (32) | 196 | (16) | 213 | (8) | 167 | (23) | 274 | (32) | 543 | (87) | 132 | (12) | 91 | (6) | 73 | (11) |
| **Ca, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 377 | (29.1) | 71 | (12) | 58 | (19) | 31 | (5) | 50 | (8) | 91 | (17) | 32 | (1) | 44 | (2) | 39 | (1) |
| Topsoil | 409 | (25) | 284 | (66) | 101 | (12) | 48 | (4) | 68 | (8) | 157 | (23) | 35 | (3) | 108 | (35) | 56 | (12) |
| XPAM1 | 421 | (48) | 178 | (42) | 113 | (19) | 51 | (13) | 58 | (30) | 123 | (46) | 20 | (2) | 38 | (5) | 47 | (7) |
| XPAM2 | 819 | (83) | - | - | - | - | - | - | - | - | 110 | (40) | 33 | (5) | 41 | (5) | 49 | (6) |
| XPAA1 | 51 | (19) | 52 | (12) | 56 | (4) | 40 | (8) | 41 | (5) | 89 | (25) | 24 | (3) | 40 | (4) | 47 | (10) |
| XPAA2 | 84 | (53) | 76 | (16) | 54 | (18) | 35 | (7) | 56 | (10) | 70 | (16) | 17 | (1) | 38 | (2) | 44 | (6) |
| **K, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 37 | (3.5) | 15.2 | (2.7) | 18.4 | (4.0) | 11.5 | (3.5) | 9.6 | (2.5) | 10.1 | (4.4) | 4.7 | (0.3) | 7.9 | (6.9) | 2.5 | (0.5) |
| Topsoil | 18 | (2.7) | 18.1 | (2.0) | 16.5 | (5.4) | 24.2 | (7.2) | 21.6 | (6.0) | 17.8 | (11.9) | 4.4 | (1.4) | 39.7 | (39.2) | 2.9 | (1.0) |
| XPAM1 | 73 | (3.0) | 64.4 | (6.8) | 62.4 | (10.2) | 45.4 | (11.2) | 45.2 | (21.7) | 38.7 | (5.5) | 11.2 | (2.1) | 15.6 | (6.6) | 8.1 | (3.0) |
| XPAM2 | 170 | (33.3) | - | - | - | - | - | - | - | - | 43.9 | (29.0) | 22.7 | (4.3) | 26.0 | (16.8) | 13.2 | (5.7) |
| XPAA1 | 52 | (8.7) | 64.3 | (1.1) | 80.9 | (3.8) | 62.9 | (10.1) | 56.3 | (5.9) | 59.5 | (3.2) | 22.1 | (2.9) | 20.1 | (2.4) | 11.2 | (1.7) |
| XPAA2 | 170 | (60.3) | 181 | (14.6) | 154 | (19.7) | 116 | (5.5) | 144 | (10.8) | 133 | (12.4) | 47.2 | (3.7) | 50.9 | (36.7) | 18.6 | (3.1) |
| **Mg, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 109 | (11.8) | 23.7 | (6.1) | 25.8 | (9.4) | 12.1 | (1.9) | 24.8 | (4.3) | 50.4 | (6.0) | 18.7 | (2.4) | 28.8 | (2.9) | 24.7 | (1.1) |
| Topsoil | 99 | (17.9) | 78.4 | (9.4) | 28.8 | (3.6) | 12.4 | (1.0) | 19.8 | (2.3) | 43.9 | (7.2) | 10.8 | (0.3) | 36.7 | (9.6) | 20.9 | (2.3) |
| XPAM1 | 124 | (9.9) | 62.9 | (10.7) | 45.1 | (9.9) | 16.5 | (3.5) | 21.4 | (11.0) | 46.7 | (20.4) | 7.9 | (0.9) | 18.4 | (5.0) | 26.8 | (3.9) |
| XPAM2 | 298 | (82.3) | - | - | - | - | - | - | - | - | 47.0 | (19.2) | 13.8 | (1.8) | 18.9 | (7.4) | 28.3 | (4.5) |
| XPAA1 | 46 | (1.0) | 22.4 | (4.9) | 23.9 | (1.5) | 14.5 | (2.8) | 17.3 | (2.3) | 35.8 | (9.1) | 9.7 | (1.3) | 18.5 | (4.8) | 25.8 | (5.8) |
| XPAA2 | 45 | (25.2) | 31.2 | (7.6) | 21.4 | (7.5) | 12.2 | (2.2) | 22.0 | (4.6) | 25.6 | (4.9) | 6.4 | (0.7) | 15.9 | (1.8) | 23.8 | (4.0) |
| **P, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 0.13 | (0.04) | 0.27 | (0.05) | 0.47 | (0.08) | 0.60 | (0.12) | 0.46 | (0.07) | 0.22 | (0.06) | 0.77 | (0.78) | 0.26 | (0.19) | 0.08 | (0.04) |
| Topsoil | 0.21 | (0.01) | 0.18 | (0.05) | 0.54 | (0.04) | 0.62 | (0.18) | 0.72 | (0.12) | 0.41 | (0.19) | 0.36 | (0.07) | 0.33 | (0.16) | 0.18 | (0.09) |
| XPAM1 | 0.10 | (0.02) | 0.21 | (0.07) | 0.70 | (0.21) | 1.51 | (0.52) | 1.21 | (0.32) | 0.55 | (0.15) | 1.04 | (0.72) | 0.58 | (0.38) | 0.22 | (0.12) |
| XPAM2 | 0.17 | (0.04) | - | - | - | - | - | - | - | - | 0.50 | (0.17) | 0.61 | (0.09) | 0.44 | (0.12) | 0.20 | (0.03) |
| XPAA1 | 0.10 | (0.07) | 0.30 | (0.06) | 0.56 | (0.15) | 0.76 | (0.25) | 0.65 | (0.21) | 0.42 | (0.05) | 0.53 | (0.20) | 0.47 | (0.11) | 0.21 | (0.04) |
| XPAA2 | 0.15 | (0.02) | 0.31 | (0.05) | 0.56 | (0.09) | 0.74 | (0.11) | 0.69 | (0.15) | 0.45 | (0.11) | 0.49 | (0.07) | 0.45 | (0.20) | 0.24 | (0.05) |
| **S, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 331 | (27) | 86 | (11) | 92 | (25) | 47 | (6) | 30 | (2) | 152 | (54) | 19 | (1) | 30 | (9) | 21 | (1) |
| Topsoil | 448 | (116) | 174 | (33) | 78 | (5) | 35 | (3) | 62 | (7) | 181 | (61) | 17 | (3) | 80 | (32) | 25 | (14) |
| XPAM1 | 295 | (35) | 242 | (42) | 164 | (32) | 79 | (8) | 73 | (42) | 232 | (42) | 27 | (4) | 35 | (8) | 31 | (8) |
| XPAM2 | 481 | (120) | - | - | - | - | - | - | - | - | 233 | (102) | 49 | (21) | 46 | (15) | 44 | (27) |
| XPAA1 | 45 | (8) | 69 | (16) | 78 | (7) | 54 | (11) | 63 | (18) | 175 | (27) | 23 | (2) | 31 | (6) | 28 | (12) |
| XPAA2 | 55 | (5) | 126 | (23) | 91 | (18) | 59 | (11) | 131 | (23) | 195 | (28) | 23 | (2) | 30 | (2) | 29 | (9) |
| **NO₃-N, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 29.0 | (19.4) | 16.4 | (2.8) | 39.4 | (10.4) | 16.6 | (1.3) | 18.4 | (3.5) | 72.5 | (3.4) | 9.1 | (6.9) | 18.2 | (4.9) | 13.1 | (4.8) |
| Topsoil | 602 | (177) | 168 | (27.2) | 5.7 | (1.1) | 23.6 | (4.9) | 23.1 | (4.3) | 114 | (12.2) | 7.1 | (6.7) | 49.2 | (8.6) | 13.6 | (4.1) |
| XPAM1 | 58.5 | (7.6) | 32.6 | (15.5) | 57.6 | (6.6) | 22.0 | (2.0) | 19.3 | (9.8) | 93.1 | (25.7) | 11.6 | (3.0) | 10.4 | (3.1) | 12.1 | (8.8) |
| XPAM2 | 379 | (41.8) | - | - | - | - | - | - | - | - | 118 | (7.1) | 18.1 | (5.8) | 14.2 | (1.6) | 19.7 | (4.4) |
| XPAA1 | 18.3 | (7.8) | 17.3 | (4.3) | 44.7 | (3.8) | 25.5 | (5.4) | 25.2 | (4.2) | 95.5 | (14.5) | 10.9 | (4.9) | 12.2 | (1.8) | 15.5 | (6.7) |
| XPAA2 | 42.2 | (5.4) | 35.3 | (6.2) | 45.5 | (8.4) | 29.6 | (3.4) | 49.1 | (9.0) | 104 | (20.9) | 11.3 | (3.4) | 11.9 | (2.1) | 13.0 | (6.3) |
| **NH₄-N, mg L⁻¹** | | | | | | | | | | | | | | | | | | |
| Control | 0.12 | (0.08) | 0.07 | (0.02) | 0.05 | (0.03) | 0.01 | (0.00) | 0.08 | (0.02) | 0.09 | (0.01) | 0.34 | (0.11) | 0.42 | (0.23) | 0.11 | (0.03) |
| Topsoil | 1.39 | (0.57) | 0.18 | (0.11) | 0.02 | (0.04) | 0.16 | (0.03) | 0.23 | (0.06) | 0.12 | (0.03) | 0.17 | (0.15) | 0.54 | (0.02) | 0.11 | (0.05) |
| XPAM1 | 0.25 | (0.09) | 0.24 | (0.29) | 0.31 | (0.20) | 0.32 | (0.36) | 0.27 | (0.18) | 0.15 | (0.03) | 0.27 | (0.12) | 0.39 | (0.15) | 0.11 | (0.02) |
| XPAM2 | 0.64 | (0.13) | - | - | - | - | - | - | - | - | 0.25 | (0.15) | 0.27 | (0.05) | 0.59 | (0.19) | 0.10 | (0.04) |
| XPAA1 | 0.25 | (0.22) | 0.02 | (0.03) | 0.21 | (0.04) | 0.09 | (0.06) | 0.19 | (0.06) | 0.10 | (0.06) | 0.21 | (0.09) | 0.31 | (0.15) | 0.14 | (0.04) |

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| XPAA2 | 0.49 (0.19) | 0.14 (0.10) | 0.23 (0.16) | 0.08 (0.04) | 0.34 (0.08) | 0.13 (0.03) | 0.25 (0.02) | 0.27 (0.04) | 0.11 (0.03) |
| **Cl, mg L$^{-1}$** | | | | | | | | | |
| Control | 347 (149) | 51.0 (19.4) | 125 (21.9) | 35.4 (11.5) | 23.2 (3.1) | 109 (21.8) | 15.0 (0.9) | 33.5 (10.5) | 19.0 (2.4) |
| Topsoil | 799 (86.7) | 216.3 (28.9) | 37.7 (4.0) | 45.6 (5.3) | 96.9 (26.8) | 112 (49.0) | 12.6 (3.4) | 135 (23.7) | 21.9 (6.4) |
| XPAM1 | 508 (27.3) | 232 (41.4) | 218 (28.7) | 57.5 (5.7) | 112 (128) | 210 (59.4) | 15.3 (2.0) | 54.2 (14.4) | 28.7 (5.5) |
| XPAM2 | 937 (106) | - | - | - | - | 225 (84.9) | 24.1 (6.4) | 50.5 (12.7) | 45.3 (29.9) |
| XPAA1 | 49.2 (7.0) | 45.8 (14.9) | 114 (6.4) | 49.5 (15.8) | 66.0 (27.4) | 106 (10.1) | 14.6 (1.0) | 37.2 (5.4) | 30.1 (11.0) |
| XPAA2 | 176 (242) | 165 (98.8) | 145 (23.3) | 52.7 (12.1) | 211 (68.5) | 140 (20.5) | 13.3 (0.8) | 52.7 (26.5) | 25.6 (7.5) |
| **DOC, mg L$^{-1}$** | | | | | | | | | |
| Control | 36.2 (13.4) | 29.3 (3.2) | 36.1 (11.3) | 41.5 (3.4) | 30.4 (7.1) | 31.7 (10.4) | 54.0 (13.3) | 10.0 (3.3) | 7.1 (0.6) |
| Topsoil | 35.4 (4.3) | 25.5 (4.7) | 33.1 (4.8) | 39.9 (4.4) | 39.5 (8.9) | 37.8 (11.7) | 61.4 (5.4) | 21.2 (1.2) | 10.7 (4.0) |
| XPAM1 | 84.8 (15.5) | 42.8 (0.5) | 59.7 (13.4) | 91.3 (9.8) | 80.8 (13.0) | 42.0 (10.1) | 128 (63.5) | 27.1 (6.1) | 12.4 (3.2) |
| XPAM2 | 160 (64.3) | - | - | - | - | 58.2 (20.6) | 256 (181) | 57.2 (54.7) | 22.2 (4.2) |
| XPAA1 | 16.7 (2.8) | 25.1 (2.7) | 37.4 (5.1) | 39.3 (11.1) | 40.5 (11.6) | 31.8 (4.6) | 49.8 (9.0) | 18.4 (3.4) | 15.7 (3.0) |
| XPAA2 | 15.9 (2.4) | 33.1 (5.5) | 43.3 (3.3) | 59.5 (15.2) | 52.0 (11.5) | 43.7 (6.1) | 59.7 (10.6) | 29.6 (6.6) | 11.5 (3.3) |
| **pH** | | | | | | | | | |
| Control | 7.42 (0.16) | 7.49 (0.29) | 8.09 (0.15) | 8.39 (0.04) | 8.09 (0.05) | 7.87 (0.15) | 7.72 (0.09) | 8.31 (0.15) | 8.05 (0.09) |
| Topsoil | 7.19 (0.06) | 7.31 (0.10) | 7.80 (0.03) | 8.38 (0.05) | 7.82 (0.04) | 7.81 (0.04) | 7.59 (0.10) | 8.38 (0.04) | 7.98 (0.12) |
| XPAM1 | 7.17 (0.45) | 7.21 (0.13) | 8.00 (0.15) | 8.46 (0.04) | 8.09 (0.13) | 7.89 (0.11) | 8.05 (0.27) | 8.21 (0.34) | 8.09 (0.03) |
| XPAM2 | 7.32 (0.11) | - | - | - | - | 7.76 (0.28) | 7.64 (0.30) | 8.39 (0.06) | 8.00 (0.29) |
| XPAA1 | 7.61 (0.02) | 7.63 (0.27) | 7.87 (0.06) | 8.42 (0.04) | 8.02 (0.04) | 7.92 (0.06) | 7.85 (0.09) | 8.47 (0.05) | 8.03 (0.04) |
| XPAA2 | 7.32 (0.31) | 7.56 (0.11) | 7.94 (0.02) | 8.53 (0.03) | 8.01 (0.05) | 8.01 (0.06) | 7.95 (0.02) | 8.38 (0.06) | 8.09 (0.05) |
| **EC, dS m$^{-1}$** | | | | | | | | | |
| Control | 2.92 (0.57) | 1.43 (0.28) | 1.96 (0.89) | 1.00 (0.07) | 1.02 (0.05) | 2.14 (0.81) | 0.88 (0.03) | 1.10 (0.58) | 0.66 (0.07) |
| Topsoil | 3.56 (0.49) | 4.50 (2.50) | 1.34 (0.13) | 0.99 (0.09) | 1.32 (0.06) | 3.24 (1.19) | 0.83 (0.09) | 1.08 (0.18) | 0.75 (0.13) |
| XPAM1 | 2.54 (0.48) | 4.59 (1.06) | 3.06 (1.03) | 1.26 (0.26) | 1.98 (1.05) | 4.28 (0.53) | 1.19 (0.14) | 1.16 (0.48) | 0.73 (0.07) |
| XPAM2 | 4.97 (2.03) | - | - | - | - | 4.19 (1.32) | 1.44 (0.35) | 0.89 (0.08) | 0.92 (0.32) |
| XPAA1 | 0.94 (0.07) | 1.07 (0.17) | 1.37 (0.06) | 1.24 (0.17) | 1.46 (0.32) | 2.89 (0.20) | 1.00 (0.07) | 0.98 (0.26) | 0.74 (0.14) |
| XPAA2 | 1.99 (1.36) | 3.49 (1.85) | 1.70 (0.20) | 1.35 (0.19) | 2.86 (0.38) | 3.75 (0.50) | 1.01 (0.04) | 0.85 (0.19) | 0.72 (0.10) |

[†] Nutrient concentrations could not be measured due to limited sample volume (too little drainage occurred in pots that year).

Table S5.  Treatment and year effects on leachate nutrient mass losses in spring.  Pot soils were subjected to a controlled leaching event in spring each year.  Values are the arithmetic means (std. dev.) from leaching events performed from 2009 to 2017 ($n$=4).  Treatment label numbers 1 and 2 identify 0.25% and 0.5% application rates, respectively.

| Treatment | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 |
|---|---|---|---|---|---|---|---|---|---|
| **Na, mg** | | | | | | | | | |
| Control | 292 (20) | 130 (35) | 170 (73) | 133 (21) | 108 (22) | 289 (65) | 59 (6) | 60 (24) | 51 (3) |
| Topsoil | 141 (37) | 103 (19) | 149 (18) | 104 (5) | 114 (10) | 327 (95) | 65 (13) | 96 (10) | 61 (15) |
| XPAM1 | 171 (23) | 56 (26) | 60 (22) | 29 (39) | 50 (38) | 550 (125) | 141 (33) | 76 (22) | 57 (4) |
| XPAM2 | 74 (77) | - | - | - | - | 325 (63) | 137 (54) | 112 (83) | 84 (45) |
| XPAA1 | 163 (11) | 134 (15) | 179 (29) | 110 (19) | 178 (41) | 462 (63) | 86 (12) | 57 (4) | 59 (14) |
| XPAA2 | 172 (39) | 165 (26) | 189 (18) | 112 (29) | 213 (28) | 406 (72 | 84 (9) | 62 (8) | 51 (8) |
| **Ca, mg** | | | | | | | | | |
| Control | 439 (75.3) | 49.1 (10.1) | 35.1 (14.0) | 24.6 (7.8) | 39.3 (5.8) | 73.5 (10.1) | 19.7 (1.5) | 29.2 (1.2) | 29.6 (2.1) |
| Topsoil | 159 (30.6) | 155 (37.7) | 86.4 (8.1) | 37.2 (4.3) | 50.7 (9.1) | 133 (17.1) | 22.1 (2.9) | 68.8 (20.8) | 42.5 (8.4) |
| XPAM1 | 295 (43.4) | 36.4 (13.6) | 28.2 (12.5) | 5.7 (5.6) | 8.5 (7.7) | 110 (32.0) | 14.8 (2.7) | 24.1 (4.4) | 33.8 (3.6) |
| XPAM2 | 80.2 (68.1) | - | - | - | - | 57.8 (27.1) | 21.5 (3.5) | 29.5 (4.0) | 37.7 (4.4) |
| XPAA1 | 62.4 (32.4) | 49.1 (10.5) | 51.3 (4.2) | 27.9 (4.2) | 31.6 (6.2) | 87.8 (17.1) | 15.4 (1.5) | 26.2 (7.7) | 35.5 (10.0) |
| XPAA2 | 95.2 (62.2) | 64.4 (17.7) | 48.1 (18.7) | 23.1 (3.8) | 43.1 (7.1) | 54.0 (18.3) | 10.6 (0.9) | 26.0 (2.6) | 31.1 (3.9) |
| **K, mg** | | | | | | | | | |
| Control | 42.8 (7.1) | 10.4 (1.9) | 12.0 (6.3) | 9.2 (4.3) | 7.5 (1.7) | 8.1 (3.3) | 2.9 (0.3) | 5.2 (4.6) | 1.9 (0.3) |
| Topsoil | 6.9 (2.0) | 9.9 (1.8) | 14.1 (4.2) | 18.7 (5.8) | 15.8 (3.9) | 14.6 (9.2) | 2.8 (0.9) | 25.4 (24.6) | 2.2 (0.8) |
| XPAM1 | 52.3 (15.3) | 13.8 (5.9) | 15.8 (7.4) | 5.4 (5.6) | 6.8 (6.0) | 35.2 (3.8) | 8.1 (2.3) | 9.9 (4.3) | 6.0 (2.4) |
| XPAM2 | 17.1 (15.8) | - | - | - | - | 20.8 (12.2) | 14.7 (3.5) | 19.1 (10.7) | 9.9 (3.6) |
| XPAA1 | 61.4 (19.4) | 60.7 (4.8) | 73.9 (8.1) | 44.0 (2.7) | 43.8 (8.0) | 59.4 (5.8) | 14.2 (2.4) | 13.1 (3.7) | 8.3 (1.1) |
| XPAA2 | 192 (71.8) | 152 (24.7) | 137 (25.1) | 77.4 (15.3) | 112 (6.7) | 100 (13.6) | 30.3 (3.3) | 34.5 (23.2) | 13.0 (2.2) |
| **Mg, mg** | | | | | | | | | |
| Control | 125.7 (17.6) | 16.3 (4.2) | 15.4 (6.5) | 9.5 (2.9) | 19.5 (3.6) | 40.6 (3.3) | 11.5 (1.9) | 19.2 (1.9) | 18.8 (0.5) |
| Topsoil | 37.9 (5.7) | 42.6 (4.4) | 24.7 (1.9) | 9.6 (1.4) | 14.7 (2.6) | 37.5 (8.0) | 6.8 (0.5) | 23.3 (5.6) | 16.0 (1.3) |
| XPAM1 | 87.4 (16.1) | 13.3 (5.6) | 11.4 (5.4) | 1.8 (1.9) | 3.1 (2.5) | 41.5 (14.7) | 5.7 (1.3) | 11.8 (3.7) | 19.5 (1.7) |
| XPAM2 | 30.2 (29.9) | - | - | - | - | 25.5 (15.9) | 9.0 (1.8) | 13.1 (2.3) | 21.5 (2.6) |
| XPAA1 | 53.5 (8.5) | 21.0 (4.3) | 21.8 (2.5) | 10.1 (0.6) | 13.5 (2.9) | 35.3 (7.4) | 6.2 (0.7) | 12.4 (4.7) | 19.4 (5.6) |
| XPAA2 | 50.7 (29.4) | 26.4 (8.3) | 19.2 (7.8) | 8.0 (1.7) | 17.0 (3.3) | 19.7 (6.3) | 4.1 (0.4) | 10.9 (1.2) | 16.6 (2.8) |
| **P, mg** | | | | | | | | | |
| Control | 0.15 (0.05) | 0.18 (0.04) | 0.32 (0.17) | 0.48 (0.18) | 0.36 (0.05) | 0.18 (0.04) | 0.46 (0.45) | 0.17 (0.12) | 0.06 (0.03) |
| Topsoil | 0.08 (0.02) | 0.10 (0.04) | 0.47 (0.05) | 0.48 (0.13) | 0.53 (0.10) | 0.34 (0.14) | 0.23 (0.06) | 0.21 (0.11) | 0.14 (0.07) |
| XPAM1 | 0.07 (0.02) | 0.04 (0.02) | 0.17 (0.09) | 0.14 (0.13) | 0.23 (0.20) | 0.51 (0.16) | 0.80 (0.67) | 0.36 (0.22) | 0.17 (0.10) |
| XPAM2 | 0.02 (0.01) | - | - | - | - | 0.25 (0.06) | 0.39 (0.04) | 0.34 (0.15) | 0.15 (0.02) |
| XPAA1 | 0.12 (0.10) | 0.29 (0.06) | 0.51 (0.14) | 0.54 (0.18) | 0.49 (0.13) | 0.42 (0.01) | 0.33 (0.12) | 0.32 (0.14) | 0.15 (0.03) |
| XPAA2 | 0.17 (0.02) | 0.26 (0.03) | 0.49 (0.08) | 0.50 (0.13) | 0.53 (0.11) | 0.33 (0.04) | 0.31 (0.05) | 0.31 (0.12) | 0.17 (0.04) |
| **S, mg** | | | | | | | | | |
| Control | 384 (60.8) | 60.1 (14.8) | 56.9 (22.8) | 36.9 (9.9) | 23.6 (2.2) | 122 (42.8) | 11.5 (0.8) | 19.7 (6.1) | 15.9 (1.8) |
| Topsoil | 170 (32.5) | 94.3 (17.5) | 67.1 (6.3) | 26.9 (1.3) | 46.3 (8.5) | 151 (44.0) | 10.7 (2.1) | 50.4 (18.0) | 19.2 (10.3) |
| XPAM1 | 206 (27.2) | 51.2 (21.9) | 40.9 (21.0) | 11.6 (14.9) | 11.8 (8.7) | 211 (29.1) | 19.1 (1.8) | 22.2 (4.9) | 22.7 (4.6) |
| XPAM2 | 49.2 (47.5) | - | - | - | - | 118 (46.3) | 31.8 (13.6) | 36.5 (19.6) | 33.2 (18.1) |
| XPAA1 | 51.9 (7.9) | 65.2 (14.5) | 71.1 (9.6) | 37.5 (2.4) | 48.1 (12.0) | 173 (14.4) | 14.9 (1.5) | 19.4 (2.6) | 21.2 (10.1) |
| XPAA2 | 62.4 (7.1) | 107 (25.7) | 81.0 (20.5) | 39.5 (10.2) | 101 (16.1) | 147 (26.2) | 14.5 (1.4) | 20.3 (3.0) | 20.2 (6.1) |
| **$NO_3$-N, mg** | | | | | | | | | |
| Control | 32.3 (18.1) | 11.2 (1.7) | 24.4 (10.0) | 12.7 (1.6) | 14.5 (2.9) | 58.6 (2.4) | 5.5 (4.2) | 12.2 (3.3) | 10.1 (4.2) |
| Topsoil | 239 (111) | 91.4 (12.3) | 4.9 (1.1) | 18.4 (4.8) | 17.0 (3.4) | 96.8 (9.5) | 4.7 (4.9) | 31.5 (5.9) | 10.3 (2.7) |
| XPAM1 | 40.8 (5.3) | 6.0 (1.5) | 14.2 (6.4) | 2.9 (3.4) | 3.9 (3.7) | 84.8 (21.9) | 8.5 (3.0) | 6.7 (2.2) | 8.8 (6.1) |
| XPAM2 | 37.2 (31.8) | - | - | - | - | 60.5 (11.0) | 11.8 (4.1) | 10.5 (3.0) | 14.9 (2.2) |
| XPAA1 | 21.9 (12.0) | 16.3 (4.0) | 40.7 (4.3) | 17.7 (1.4) | 19.4 (3.1) | 95.0 (13.1) | 6.9 (3.2) | 7.8 (1.7) | 11.7 (5.6) |
| XPAA2 | 47.5 (5.5) | 29.4 (4.3) | 40.4 (8.4) | 19.5 (2.1) | 38.3 (8.6) | 78.3 (18.8) | 7.3 (2.4) | 8.3 (2.3) | 9.1 (4.4) |
| **$NH_4$-N, mg** | | | | | | | | | |
| Control | 0.14 (0.09) | 0.04 (0.02) | 0.03 (0.04) | 0.01 (0.00) | 0.06 (0.02) | 0.07 (0.01) | 0.21 (0.06) | 0.27 (0.15) | 0.08 (0.03) |
| Topsoil | 0.57 (0.36) | 0.09 (0.05) | 0.02 (0.03) | 0.12 (0.02) | 0.17 (0.03) | 0.10 (0.02) | 0.10 (0.09) | 0.35 (0.02) | 0.08 (0.03) |
| XPAM1 | 0.18 (0.10) | 0.05 (0.07) | 0.07 (0.06) | 0.01 (0.01) | 0.05 (0.03) | 0.14 (0.04) | 0.18 (0.05) | 0.25 (0.09) | 0.08 (0.02) |
| XPAM2 | 0.06 (0.05) | - | - | - | - | 0.12 (0.06) | 0.17 (0.03) | 0.47 (0.24) | 0.08 (0.03) |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XPAA1 | 0.30 | (0.30) | 0.02 | (0.03) | 0.19 | (0.03) | 0.07 | (0.05) | 0.14 | (0.03) | 0.10 | (0.07) | 0.13 | (0.06) | 0.19 | (0.05) | 0.10 | (0.03) |
| XPAA2 | 0.55 | (0.21) | 0.12 | (0.09) | 0.20 | (0.15) | 0.05 | (0.02) | 0.26 | (0.06) | 0.10 | (0.02) | 0.16 | (0.01) | 0.18 | (0.03) | 0.08 | (0.02) |

**Cl, mg**

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 395 | (139) | 34 | (9) | 84 | (43) | 28 | (13) | 18 | (3) | 88 | (18) | 9 | (1) | 22 | (7) | 14 | (2) |
| Topsoil | 308 | (53) | 117 | (10) | 32 | (2) | 35 | (5) | 71 | (16) | 93 | (36) | 8 | (2) | 86 | (14) | 17 | (5) |
| XPAM1 | 359 | (72) | 50 | (22) | 54 | (24) | 8 | (9) | 15 | (10) | 189 | (39) | 11 | (2) | 35 | (9) | 21 | (4) |
| XPAM2 | 91 | (77) | - | - | - | - | - | - | - | - | 113 | (35) | 16 | (5) | 39 | (19) | 34 | (20) |
| XPAA1 | 57 | (6) | 43 | (13) | 104 | (14) | 34 | (4) | 51 | (24) | 106 | (11) | 9 | (1) | 24 | (6) | 23 | (10) |
| XPAA2 | 201 | (279) | 142 | (96) | 129 | (27) | 35 | (10) | 163 | (52) | 105 | (17) | 8 | (0) | 36 | (16) | 18 | (5) |

**DOC, mg**

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 42.5 | (18.2) | 20.8 | (6.2) | 22.2 | (9.7) | 32.0 | (6.4) | 23.9 | (5.2) | 25.8 | (9.3) | 33.5 | (9.8) | 6.7 | (2.2) | 5.4 | (0.7) |
| Topsoil | 13.9 | (4.0) | 13.8 | (1.3) | 28.5 | (4.9) | 30.8 | (3.6) | 29.0 | (5.6) | 31.4 | (7.6) | 38.5 | (3.8) | 13.5 | (0.7) | 8.2 | (3.0) |
| XPAM1 | 58.7 | (6.8) | 9.5 | (4.5) | 14.9 | (8.0) | 11.5 | (13.4) | 16.0 | (17.8) | 39.0 | (11.9) | 92.2 | (49.4) | 17.2 | (2.9) | 9.0 | (2.1) |
| XPAM2 | 17.2 | (18.4) | - | - | - | - | - | - | - | - | 29.1 | (8.8) | 165 | (112) | 49.2 | (55.6) | 16.9 | (2.4) |
| XPAA1 | 19.4 | (3.9) | 23.8 | (4.0) | 34.0 | (4.4) | 27.8 | (8.4) | 31.0 | (8.5) | 31.6 | (4.0) | 31.8 | (6.2) | 12.4 | (4.9) | 11.6 | (1.5) |
| XPAA2 | 17.9 | (2.3) | 27.8 | (6.2) | 38.4 | (4.6) | 39.4 | (11.7) | 40.5 | (10.2) | 32.7 | (4.5) | 38.4 | (8.2) | 20.1 | (3.5) | 8.1 | (2.3) |

[†] Nutrient concentrations could not be measured due to limited sample volume (too little drainage occurred in pots that year).
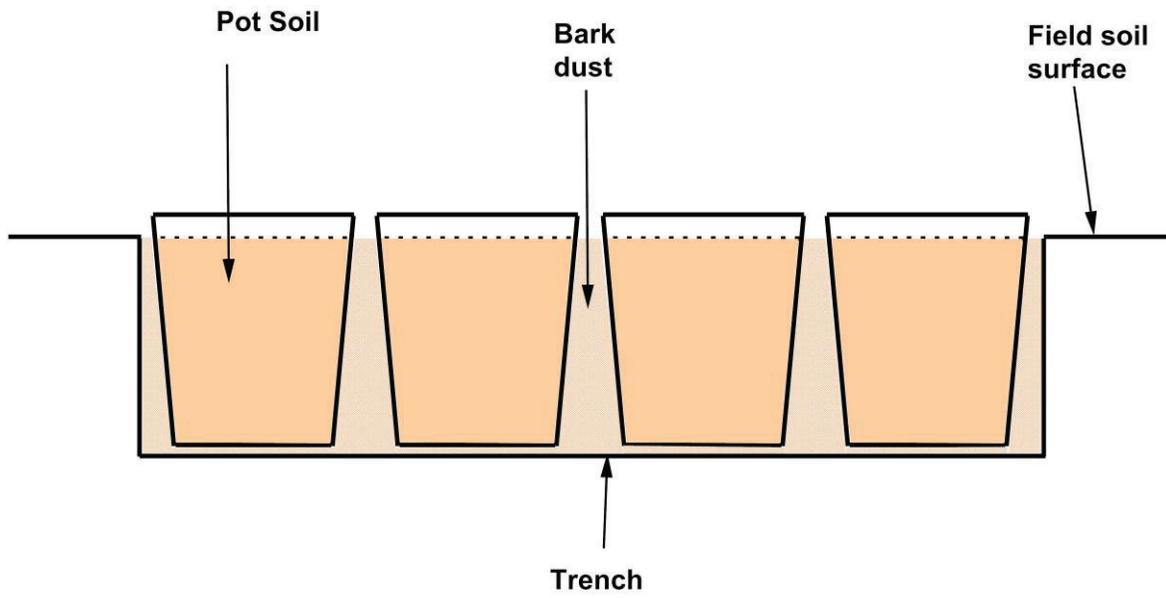
Figure. S1.  Diagram of pot arrangement in outdoor soil trench.
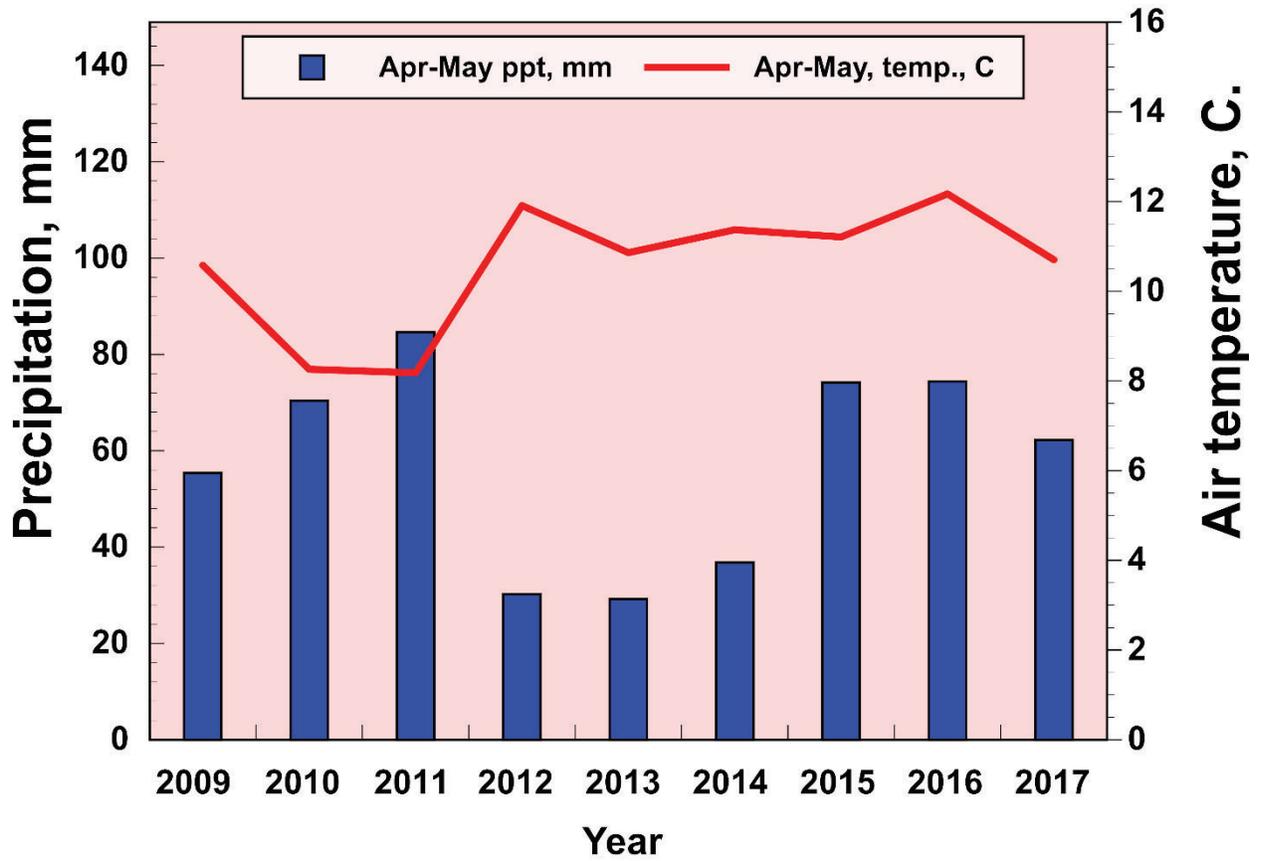
Figure S2. Cumulative precipitation amounts and mean air temperature during Spring (April-May) in each year of the study.