Acrylamide Monomer Leaching from Polyacrylamide-Treated Irrigation Furrows

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Water-soluble anionic polyacrylamide (WSPAM), which is used to reduce erosion in furrow irrigated fields and other agriculture applications, contains less than 0.05% acrylamide monomer (AMD). Acrylamide monomer, a potent neurotoxicant and suspected carcinogen, is readily dissolved and transported in flowing water. The study quantified AMD leaching losses from a WSPAM-treated corn (Zea mays L.) field using continuous extraction-walled percolation samplers buried at 1.2 m depth. The samplers were placed 30 and 150 m from the inflow source along a 180-m-long corn field. The field was furrow irrigated using WSPAM at the rate of 10 mg L\(^{-1}\) during furrow advance. Percolation water and furrow inflows were monitored for AMD during and after three furrow irrigations. The samples were analyzed for AMD using a gas chromatograph equipped with an electron-capture detector. Furrow inflows contained an average AMD concentration of 5.5 \(\mu\)g L\(^{-1}\). The AMD in percolation water samples never exceeded the minimum detection limit and the de facto potable water standard of 0.5 \(\mu\)g L\(^{-1}\). The risk that ground water beneath these WSPAM-treated furrow irrigated soils will be contaminated with AMD appears minimal.

A Natural Resource Conservation Service conservation practice standard (Sojka et al., 2007) for reducing soil erosion in furrow irrigation recommends applying 1 to 10 mg L\(^{-1}\) water-soluble anionic polyacrylamide (WSPAM) product to irrigation water inflows continually or only during the initial advance of water across the field, after which untreated water is used to finish the remainder of the irrigation (Lentz and Sojka, 1994). The practice substantially reduces sediment losses in furrow runoff relative to controls (80–99%) (Lentz and Sojka, 1994); decreases runoff losses of phosphorus, nitrogen, and pesticides, which are associated with eroded sediment; and reduces microbial biomass in furrow streams (Agassi et al., 1995; Sojka et al., 2007).

Water-soluble anionic polyacrylamide has low toxicity to aquatic and terrestrial organisms at concentrations used in this agricultural application (Barvenik, 1994). Because WSPAM is readily and irreversibly adsorbed to sediment and organic material (Nadler et al., 1992), it moves only 0 to 20 cm from its point of application in soil (Malik et al., 1991). Dissolved WSPAM concentrations in irrigation furrows and tail-water streams also decline rapidly as treated waters travel downstream (Lentz et al., 2002). The WSPAM polymer degrades relatively slowly in soil (approximately 10% yr\(^{-1}\)).

Concerns about the use of WSPAM in irrigated agriculture persist, however, because applied WSPAM products contain small amounts (<0.05% wt/wt) of acrylamide monomer (AMD), which is a residual of the WSPAM production process. The chemical and physical characteristics of AMD are very different from those of the WSPAM polymer, particularly with respect to toxicity, adsorption, and biodegradation. The acrylamide monomer is a 3-carbon molecule (Fig. 1) that has low toxicity to aquatic organisms but is an animal and human neurotoxin and a suspected human carcinogen (Rudén, 2004). Water-soluble polyacrylamide may be used to clarify drinking water supplies, but the U.S. Environmental Protection Agency (USEPA) regulates polymer applications so that drinking-water AMD concentrations do not exceed 0.5 \(\mu\)g L\(^{-1}\) (USEPA, 2003).

Acrylamide’s solubility in water and poor adsorption to minerals and organic matter make it susceptible to leaching in soil and a potential ground water contaminant (Brown et al.,...
Acrylamide is subject to biological degradation in soils. Under aerobic conditions at 22°C, 25 mg kg⁻¹ AMD in soil has a half-life of 18 to 45 h (Lande et al., 1979). Shanker et al. (1990) reported that 500 mg kg⁻¹ AMD applied to garden soil was completely degraded in 5 d. The degradation rate increases with decreasing AMD concentration and increasing temperature (Lande et al., 1979; Abdelmagid and Tabatabai, 1982). Soil bacteria are able to use acrylamide as both a C and N source (Shanker et al., 1990). Little or no AMD accumulates in plants grown in treated soils or water (Castle et al., 1991; Bologna et al., 1999), and given AMD’s low octanol-water partition coefficient (log Kow = −0.78; Lide, 1993), its potential for bioaccumulation in soil organisms is also very low. Thus, research has established that AMD introduced to soil is prone to leach because it is soluble and little influenced by processes such as volatilization, adsorption, and biological accumulation; however, it is subject to biological degradation in soil and water, which likely influences the amount of AMD available for leaching.

Given its susceptibility to biodegradation, AMD’s potential for leaching and subsequent ground water contamination would be greatest if it were transported rapidly through the soil via macropore (bypass) flow. Its transport through soil via matrix-pore flow would substantially reduce its potential for contamination because of its slower passage and thus more exposure for biodegradation. To our knowledge, little if any research has quantified AMD leaching through field soils. In this initial study, our objective was to determine if AMD was in leachate collected below the root zone in a silt loam soil shortly after WSPAM-treated furrow irrigations.

Materials and Methods

Experimental Approach and Site

To assess AMD leaching potential during the furrow irrigation season, percolation water produced during three of five irrigations was collected and analyzed for the contaminant. This selective sampling approach was used to limit the number of samples analyzed and to reduce the time and expense associated with AMD analysis. Percolation water from the first, third, and fifth (final) irrigations were selected for AMD analysis to represent early, mid, and late periods during the season.

We conducted the experiment in a long-term field plot experiment near Kimberly, ID. The plots were established in 1993 to evaluate the performance of three furrow irrigation treatments: WSPAM, emulsion-WSPAM, and an untreated control. For the two treatment plots, polymer was added to irrigation water at 10 mg L⁻¹ a.i. during the advance phase only, whereas the remaining irrigation water was untreated. These treatments have been in operation continuously since 1993. The complete randomized block design included the three irrigation treatments and three replicates. Each experimental unit consisted of a 3.8-m-wide by 180-m-long plot separated from adjacent plots by a 1.3-m-wide buffer strip (Fig. 2). Irrigation furrows spaced 1.52 m apart were marked out along the long axis of the plots (giving two furrows per plot and one furrow in each buffer strip). The plots had a 1.5% slope.

The WSPAM and control plots were instrumented in 1996 with continuous extraction soil water samplers placed at a depth of 1.2 m directly below one of the two treated furrows in each plot (Lentz and Kincaid, 2003). Three soil water samplers were installed at each of two positions per monitored furrow: one located 30 m downstream from the furrow inflow end and the second located 30 m upstream from the furrow outflow end (Fig. 2). For the AMD leaching study reported in this article, we monitored percolation water flux and leachate AMD concentrations only at the inflow-end positions in WSPAM-treated plots during the 1998 irrigation season. The AMD leaching potential was considered to be greater at inflow-end vs. outflow-end locations due to greater net infiltration at the inflow-end positions.

Soil and Polymer

Plots were established on Portneuf Silt Loam (coarse-silty, mixed, superactive, mesic, Durinodic Xeric Haplocalcids). These calcareous soils have deep, loess-derived profiles dominated by silt loam or very fine sandy loam textures, with silica and calcium carbonate cemented horizons (20–50% cementation) occurring at depths of 33 to 107 cm (Table 1). The pH ranges from 7.3 to 8.0, and organic carbon in the A horizon is 8.8 g kg⁻¹. Saturated hydraulic conductivity of soil horizons (volumetric water content, θ = 0.47) ranges from 9.8 to 17.8 mm h⁻¹. Unsaturated conductivity ranges from 0.7 to 0.91 mm h⁻¹ at θ = 0.4, 0.04 to 0.11 mm h⁻¹ at θ = 0.3, and 0.0001 to 0.005 mm h⁻¹ at θ = 0.2 (Robbins, 1977).

A commercially available granular anionic WSPAM with 18% charge density and molecular weight of 12 to
15 Mg mol$^{-1}$ (Superfloc A-836 Flocculant; Kemira Water Solutions, Stamford, CT) was mixed with water (electrical conductivity = 0.08 S m$^{-1}$; sodium adsorption ratio = 1.7) to produce aqueous 2400 mg L$^{-1}$ a.i. stock solutions. During the irrigation advance phase, a peristaltic pump injected the WSPAM stock solution into the manifold’s pre-stage section at a rate required to attain the target concentration of 10 mg L$^{-1}$ a.i. in the irrigation water. Analysis of the WSPAM product showed that it contained 0.018% AMD, which was less than the 0.05% AMD monomer concentration allowed by law for potable water treatment polymers. If the WSPAM product containing 0.05% AMD was applied to the irrigation water to attain the 10 mg L$^{-1}$ a.i. WSPAM treatment level, the AMD concentration in the treated water would be 5 $\mu$g L$^{-1}$.

To evaluate AMD leaching potential under the worst-case scenario, we adjusted the AMD concentration in WSPAM stock solutions upward for Irrigations 1, 3, and 5 using acrylamide (>$99\%$ pure) obtained from Sigma-Aldrich Co (St. Louis, MO). The goal was to produce a final AMD concentration in the WSPAM-treated furrow irrigation water of 5 $\mu$g L$^{-1}$.

Crop, Irrigation, and Monitoring

We tilled plots conventionally, applied alachlor [2-chloro-2′,6-diethyl-N-(methoxymethyl) acetanilide] for pre-emergence weed control, and planted to silage corn on 1 June 1998. Due to abundant late spring rainfall, the first of five irrigations was delayed until 8 July 1998, and its length was about two thirds as long as the subsequent four irrigations, which followed at 2-wk intervals. All irrigated furrows were wheel trafficked when formed in the field to reduce furrow infiltration variability (Yoder et al., 1996). Furrows were formed by a weighted v-shaped tool attached to the toolbar and aligned with the tractor wheels. The tractor wheel compresses the tilled soil layer and breaks up the larger soil clods ahead of the furrow tool, which cuts the furrow shape and smoothes its sides. The furrow forming process typically does not eliminate all macro pores but tends to reduce the range of pore sizes available for infiltration. The field was cultivated on 14 July 1998, and furrows were reformed at that time.

Irrigation water was supplied from the Snake River and had an electrical conductivity of 0.05 S m$^{-1}$ and a sodium adsorption ratio of 0.5. A manifold made from 0.15-m-diam. PVC pipe supplied irrigation water to the two furrows in each plot. A 0.05-m-diam. PVC pipe connected to the inflow end of the manifold acted as a pre-stage mixing chamber. For the polymer treatment, irrigation water entering the chamber was injected with WSPAM, and flow turbulence mixed the fluids before they entered the manifold. A gated pipe conveyed water to each manifold, and adjustable spigots controlled flow rates. Irrigation inflows in control furrows were set at 15 L min$^{-1}$. Because WSPAM increases infiltration and slows furrow advance (Lentz and Sojka, 1994), initial irrigation inflows for WSPAM furrows were set to 45 L min$^{-1}$. The use of WSPAM prevented erosion that would ordinarily occur at these high inflow rates. When water in treated furrows had traversed the field (advance), inflows were decreased to 15 L min$^{-1}$ to reduce runoff losses.
Irrigation sets were 20 to 30 h long. Irrigation sets for control furrows typically had to be lengthened to ensure that average net infiltration (over the entire furrow) for the control and WSPAM treatments was similar.

Furrow inflows, stream flow rate, and sediment concentrations were measured during each monitored irrigation at one third and two thirds furrow length downstream from the inflow end and at the outflow end (Fig. 2). Using the inflow rates measured at the top of the furrow and outflow rates measured at one third distance downstream, we computed the net infiltration and sediment loss occurring in the upper one third of the furrow (i.e., the location of monitored percolation). Inflow and outflow rate measurements and runoff water samples were taken at 0.5-h intervals early in the irrigation, every hour during the mid-irrigation period, and every 3 h later in the irrigation when outflows and sediment loads had stabilized (at >7 h into the set). Inflows were measured by timing the filling rate of a known volume, and outflows were measured with long-throated v-notch flumes. Details of the flow and sediment monitoring procedure were given by Lentz and Sojka (1994). The computer program WASHOUT (Lentz et al., 2002) calculated net infiltration and runoff sediment losses for furrows.

Meteorological conditions were monitored at a weather station located 5.6 km northeast of the experimental plot. A rain gauge located at the field plot obtained growing season precipitation values. Potential daily evapotranspiration (ET$_{ap}$) assumed to represent a maximum reference ET based on that of an actively growing alfalfa crop, was calculated from weather parameters using the Kimberly-Penman ET model (Wright et al., 1998). Corn crop evapotranspiration (ET$_{c}$) was estimated from ET$_{ap}$ = K$_{cc}$ × ET$_{ap}$, where K$_{cc}$ = the adjusted daily crop coefficient (Wright et al., 1998).

**Soil Water Percolation Sampling**

We used walled ceramic-cup samplers (Lentz and Kincaid, 2003) to collect downward flowing soil water at a 1.2-m depth. Samplers were installed such that an undisturbed column of soil extended from within the sampler, through its open top, and up to the soil surface. Thus, water flowing down macropores present in the undisturbed soil would be collected in the sampler, as would matrix-pore flow. The sampler’s collection surface was horizontally oriented and subject to a continuous vacuum. The vacuum was adjusted for in situ soil matric potential to maintain parallel water flow lines in the adjacent soil. This design, which produces valid measures of soil water flux rates and leachate solute concentrations, is described in previous reports (Lentz and Kincaid, 2003; Lentz, 2006), along with details of the vacuum extraction system and field installation. The use of ceramic cups for soil water collection and AMD monitoring is appropriate because AMD is not adsorbed to aluminosilicate (ceramic) materials (Brown et al., 1980; Arrowood, 2007); thus, AMD concentrations in water passed through the ceramic membrane are not susceptible to adsorption/desorption reactions.

At each monitoring site, three samplers with 0.2-m-diam., circular collecting surfaces were installed into the ceiling of individual cavities, which were excavated into the side of a backhoe pit. The installation ensured that an undisturbed soil column extended from the soil surface downward into the interior of each sampler. An electronic vacuum controller and data logger program set extraction vacuum independently for each site based on local soil water conditions (measured by soil tensiometers). A field-deployed vacuum pump and tank were connected via a gas dryer to a polyethylene tube main line and branch lines that supplied each sampling site. At each site, vacuum was supplied via a manifold to three 1-L vacuum flasks, which collected percolation water from individual samplers. These collection flasks were enclosed in an above-ground, insulated box.

**Sample Collection and Analysis**

Percolation water volumes were measured and collected daily during the irrigation season. Percolate water samples for AMD analysis were collected from the WSPAM plots at three different times (1–2, 5–8, and 9–13 d) after the first, third, and fifth irrigations. A 150-ml sample volume was required for AMD analysis. At most collection times, all three WSPAM plots produced enough percolation water for AMD analysis. In a few instances, only two out of the three plots produced the required volume. Samples for two collection times were not obtained due to insufficient volume (Irrigation 1, 1–2 d and Irrigation 3, 5–8 d). Water samples were frozen within 2 h after collection and stored at −4°C until analyzed.

We sampled furrow inflow streams during WSPAM application. Furrow stream samples were collected 15 m downstream from the manifold in Irrigation 1, directly from the manifold outlet in Irrigation 3, and 3 m downstream from the manifold in Irrigation 5. This collection method was used to assess potential variation in AMD concentration in the upper reaches of the furrow stream with a minimum number of samples. One sample was collected from a furrow stream in each WSPAM plot. These were centrifuged at 500 × g for 10 min to remove sediment, composited into one volume, and frozen for later AMD analysis. We also prepared 1 μg L$^{-1}$ and 10 μg L$^{-1}$ AMD standard solutions, divided each into three 150-ml volumes, froze, and analyzed them for AMD along with the field samples. All frozen volumes were submitted to the analytical lab in one group and as double-blind samples. The laboratory procedure derivatized the AMD with bromine to form 2,3-dibromopropionamide. The derivative was then extracted with ethyl acetate and converted to the more stable 2-bromopropenamide before gas chromatographic analysis, which used an electron-capture detector (Andrawes et al., 1987). The analysis provided an AMD minimum detection limit of 0.5 μg L$^{-1}$. The AMD recovery was 97% with a precision of ±0.21 μg L$^{-1}$ for 1 μg L$^{-1}$ AMD standards and ±0.75 μg L$^{-1}$ for 10 μg L$^{-1}$ AMD standards.

**Results and Discussion**

Of the 359 mm total precipitation received during 1998, 234 mm (65%) occurred before planting, and 67 mm (18%) fell during the growing season. The five irrigations supplied a total of 311 mm infiltrated water to the upper one third...
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(67 m) of the WSPAM irrigation furrows where the percolation and AMD monitoring sites were located. Net infiltration in this portion of the WSPAM-treated furrows was 27 mm in Irrigation 1, 66.1 mm in Irrigation 3, and 60.1 mm in Irrigation 5 (Table 2), with the remaining applied in Irrigations 2 and 4. The greater infiltration in Irrigations 3 and 5 was largely due to longer set times and warmer irrigation water temperatures, which increased infiltration during initial hours of the irrigations. However, the smaller net infiltration in Irrigation 1 was also attributed to the reduced soil water gradient present in Irrigation 1 soils caused by a 13 mm rainfall that occurred there 3 d before Irrigation 1.

Cumulative crop ET during post-irrigation intervals of Irrigations 1 and 3 exceeded precipitation amounts over the same intervals (Table 2), indicating that the corn crop was using soil water stored in the soil profile to supply a portion of its requirement. In this regard, the irrigation management approach used was relatively conservative. Conversely, our use of relatively large water applications spaced at 2-wk intervals may have caused greater percolation than if we had applied more frequent, shorter irrigations.

The AMD concentration in the furrow streams during Irrigations 1, 3, and 5 averaged 5.5 μg L⁻¹ (Table 3). This concentration is very close to the 5 μg L⁻¹ value expected when the residual AMD concentration in the applied WSPAM product is the maximum concentration allowed by the USEPA for potable water applications (0.05%). The AMD concentrations in percolation water samples collected during all post-irrigation periods and all irrigations were less than the minimum detection limit (Table 3). Because AMD adsorption by soil minerals, organic matter, and ceramic cup is minimal, this reduction in AMD concentration suggests that AMD in percolating water was diluted and/or degraded during transport. Wright et al. (1998) tracked the peak bromide concentrations in soil pore water as the bromide pulse moved in percolating water down through the Portneuf soil profile. They reported that the bromide concentration in the soil pore water showed a 2-fold reduction by the time the descending bromide pulse had progressed to the 0.92-m depth and a 10-fold reduction by the time it had reached the 3.8-m depth. Because bromide is a conservative tracer, its reduction in concentration is attributed to dilution as the bromide-bearing water pulse mixed with bromide-free soil pore water. In this study, if dilution was the only process influencing AMD concentration in the drainage water, we would expect only a 50% reduction in its concentration by the time it had leached to the 1.2-m soil sampler depth. The fact that AMD was not detected at the 1.2-m depth suggests that another process, most likely biological degradation, acted in addition to dilution to reduce the AMD load in percolating water. A subsequent study by Arrowood (2007) provided corroborating evidence that microbial degradation is a highly significant mechanism by which AMD is lost from soils.

The likelihood that an individual AMD molecule will be biodegraded during transport is a function of its residence time in the soil. Given a half-life (biodegradation) of 18 h (Lande et al., 1979), 3 d would be required to decrease the AMD concentration in percolating irrigation water from 5.5 to 0.3 mg L⁻¹. Under a piston flow regime, the residence time would likely exceed 30 d (Gamble et al., 1990), which is more than enough time for the AMD to degrade. However, these soils are subject to bypass flow even under relatively low-intensity water inputs (Wright et al., 1998). In structured, non-WSPAM–treated soils subject to bypass flow, soil residence times of the most rapidly percolating irrigation water fraction are less than 1 to 2 d (Jaynes et al., 1988). Under such conditions, biodegradation alone would not account for the low AMD concentrations observed in percolation water. There is evidence, however, that WSPAM treatment inhibits bypass flow in furrow irrigated soils. Lentz et al. (2001) showed that WSPAM treatment of irrigation furrow streams caused soil–water percolation rates to peak 5 to 7 d later than that of untreated furrow streams. They speculated that this may be related to WSPAM–induced increases in lateral wetting. The resulting increase in water residence time in WSPAM-treated soils would promote degradation of the introduced AMD.

### Table 2. Net infiltration and percolation for sampled irrigations in the upper third of water-soluble anionic polyacrylamide–treated furrows (mean of three replicates). Also included is the total rainfall and corn crop evapotranspiration occurring in the post-irrigation interval.†

<table>
<thead>
<tr>
<th>Irrigation no.</th>
<th>Date</th>
<th>Average irrigation net infiltration in the upper one third furrow</th>
<th>Rainfall</th>
<th>Crop evapotranspiration</th>
<th>Percolation at inflow-end site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28 June</td>
<td>27.0</td>
<td>3.3</td>
<td>96.2</td>
<td>15.6</td>
</tr>
<tr>
<td>3</td>
<td>5 Aug.</td>
<td>66.1</td>
<td>10.4</td>
<td>96.6</td>
<td>42.1</td>
</tr>
<tr>
<td>5</td>
<td>2 Sept.</td>
<td>60.1</td>
<td>19.1</td>
<td>63.1</td>
<td>24.4</td>
</tr>
</tbody>
</table>

† This period starts at noon on the day of irrigation and continues through noon of the following irrigation date. For Irrigation 5, this period ended on 22 Sept.

### Table 3. Acrylamide monomer (AMD) concentration in furrow stream and percolation water from early-, mid-, and late-season irrigations (Irrigations 1, 3, and 5).

<table>
<thead>
<tr>
<th>Irrigation†</th>
<th>Furrow stream</th>
<th>Percolation water collected days after start of irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1–2</td>
<td>5–8</td>
</tr>
<tr>
<td>Mean</td>
<td>5.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

† These irrigations were targeted a priori for AMD sampling. In these irrigations (Irrigations 1, 3, and 5), to evaluate AMD leaching potential under the worst-case scenario, we adjusted the AMD concentration in water-soluble anionic polyacrylamide (WSPAM) stock solutions upward by adding additional AMD. The goal was to produce a final AMD concentration in the WSPAM-treated furrow irrigation water of 5 μg L⁻¹.

‡ Samples were not collected due to insufficient volume.

§ The acrylamide monomer concentration was below minimum detection limit (0.5 μg L⁻¹).
Conclusions

Although WSPAM application to irrigation water provides substantial benefit to agriculture as an effective means of reducing irrigation-induced erosion and as a means of managing infiltration, there remains some concern that AMD, a residual contaminant and toxicant in the WSPAM product, may pollute ground waters below treated crop land. This study evaluated AMD leaching potential in WSPAM-treated furrow irrigations on calcareous silt loam soils having a history of WSPAM applications. Water-soluble polyacrylamide, containing 0.05% AMD, was applied during the irrigation advance phase at a concentration of 10 mg L$^{-1}$. No AMD was detected in percolation waters collected at 1.2-m depths from vacuum extraction soil water samplers (minimum detection limit $= 0.5 \mu g \cdot L^{-1}$) during the irrigation season. We conclude that, under the conditions of this study, AMD concentrations in WSPAM-treated percolating waters were reduced via dilution and biodegradation processes to concentrations below de facto levels recommended for drinking water by the EPA. This suggests that the risk of ground water contamination from WSPAM-treated irrigations in these soils is very small. The consideration that much of the potable-water–grade WSPAM products recommended for use in irrigation contain about half the allowable AMD (half the concentration used in this study) should further reduce risks of possible contamination.

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References
