Seasonal Effects on Leachate Quality from an Ozark Highlands Managed Grassland Using Automated, Equilibrium-Tension Lysimeters


In regions with concentrated broiler (Gallus gallus) production, land application is a useful means of managing broiler litter (BL). However, surface and subsurface water quality issues may arise when continued annual BL application to fields occurs for extended periods. The application of manure follows seasonal guidelines for surface water quality protection. The objective of this study was to evaluate the effects of BL rate (0, 5.6, and 11.2 Mg litter ha$^{-1}$) and season on drainage and leachate water quality over an 8-yr period (2003–2011) in the Ozark Highlands with karst geology using automated, equilibrium-tension lysimeters. During the 8-yr period, seasonal drainage was unaffected by season or BL rate, averaging 118 mm per season. Averaged across BL rates, seasonal leachate pH, electrical conductivity (EC), flow-weighted mean (FWM) NO$_3$–N, dissolved organic C, S, and Zn concentrations, and NH$_4$–N, Cu, Fe, and Se loads differed ($P < 0.05$) among seasons. Averaged across seasons, seasonal leachate EC, FWM PO$_4$–P, total P, and S concentrations, and Ni load differed ($P < 0.05$) among BL rates. With the exception of As and Se, seasonal FWM leachate Cd, Cr, Cu, and NO$_3$–N concentrations were at least five times smaller than their maximum contaminant level for drinking water during any of the four seasons. Since rainfall patterns seasonally change in many regions of concentrated poultry production, seasonal differences in the leachate water quality response to continuous annual application of BL are important to help tailor best management practices to protect soil and water resources in regions underlain by karst geology.

Abbreviations: BL, broiler litter; DOC, dissolved organic carbon; EC, electrical conductivity; FWM, flow-weighted mean.

Broiler litter is a byproduct, often considered a waste material, from raising broiler chickens. In many regions of concentrated broiler production, BL is commonly land applied as an organic soil amendment due to its fertilizer-nutrient value. Aside from N and P, BL contains appreciable amounts of numerous other essential plant nutrients (Patterson et al., 1998; Harmel et al., 2008) and trace metals (Gupta and Charles, 1999; Garbarino et al., 2003; Franzluebbers et al., 2004). In some regions of concentrated broiler production, such as the Ozark Highlands region of northwest Arkansas, where steep slopes are common, long-term land application of BL has increased soil-retention capacities and P retention levels to the point where maximum P retention capacities are being approached or exceeded (Edwards and Daniel, 1992; Sims and Wolf, 1994). These P-enriched soils may stimulate runoff P losses and potential eutrophication of nearby surface water bodies. In addition, subsurface leaching of soluble constituents contained in land-applied BL is also a potential water quality concern, particularly for areas underlain with karst geology, such as the Ozark Highlands (Brye et al., 2013). However, the evaluation of subsurface losses is much more difficult to quantify than runoff losses.
Lysimeters were developed in the late 1800s to initially track the fate of precipitation percolating through disturbed, soil-filled boxes (Joffe, 1932). From zero-tension to fixed-tension to weighing lysimeters, lysimetry offers a technique to quantify subsurface leaching losses of soluble constituents, in response to natural or simulated rainfall, from a variety of undisturbed natural or highly disturbed agricultural settings. Brye et al. (1999) described and tested (Brye et al., 2000, 2001, 2002a, 2002b) an equilibrium-tension lysimeter, an innovation of the fixed-tension lysimeter technique where applied suction was varied with time in accordance with matric potential fluctuations in the bulk soil surrounding the lysimeter. Initially conducted manually (Brye et al., 1999), varying the applied suction to the lysimeter was subsequently automated (Masarik et al., 2004), which allowed real-time adjustments, without manual intervention, to mimic the dynamic hydraulic gradient during times of soil wetting and drying.

Between the spring of 2002 and the spring of 2003, a research site in the Ozark Highlands region of northwest Arkansas was outfitted with automated, equilibrium-tension lysimeters to evaluate the long-term effects of BL application rate on drainage under pasture vegetation with a history of organic soil amendments. Soluble trace metal (Pirani et al., 2006) and plant nutrient (Pirani et al., 2007) leaching (FWM concentrations and loads) during the first 2 yr after initial BL application were measured, and the results were presented on a per-rainfall-event basis and summarized in 3-mo intervals (i.e., seasons). Pirani et al. (2006, 2007) reported similar quantities of drainage during most of the 3-mo seasons, inconsistent effects of BL rate on FWM trace metal and plant nutrient concentrations, and no effect of BL rate on trace metal or plant nutrient loads during the first year after litter application. However, their results also showed that simply ceasing land applications of BL did not substantially reduce FWM trace metal concentrations and loads from the unamended control relative to the litter treatments, indicating that subsurface water quality could still be impacted years after BL applications stopped (Pirani et al., 2006). Furthermore, leachate P loads were identified as a potential subsurface water quality concern if leachate subsequently discharged to surface waters in the karst landscape of the Ozark Highlands (Pirani et al., 2007).

After 8 yr of continuous measurements associated with the original field study, McMullen et al. (2014b) reported 8-yr trends (May 2003–May 2011) in drainage and leachate water quality, summarized as annual cumulative drainage and annual FWM concentrations and loads of soluble trace metals and plant nutrients. Their results showed that average annual drainage and leachate pH, electrical conductivity (EC), and FWM concentrations and loads of NO₃⁻–N, PO₄³⁻–P, Cd, Cr, K, total P, Zn, and dissolved organic C (DOC) did not vary with time and were unaffected by the BL application rate (McMullen et al., 2014b). However, average annual FWM concentrations and loads of NH₄⁺–N, As, Mn, and Ni decreased while Cu and Se increased during the continuous 8-yr period but were also unaffected by BL rate (McMullen et al., 2014b). Average annual FWM Na concentration also increased in the leachate of the BL treatments relative to the unamended control due to the continued annual additions of BL (McMullen et al., 2014b).

Since the results of McMullen et al. (2014b) were summarized on an annual basis, known seasonal variations in precipitation and lag times between precipitation infiltration and drainage at depth in the soil profile were ignored. Land application of animal manures is often not recommended during wet seasons or prior to approaching storm systems to minimize potential runoff losses. Thus, annual summaries of continuous leachate data could have easily overlooked important temporal variations that occur at short time intervals. Furthermore, few studies have used lysimeters to continuously measure long-term drainage and leachate water quality (>5 yr; Harsch et al., 2009). Therefore, the objective of this study was to evaluate the effects of BL rate and season on drainage and leachate water quality during an 8-yr period (May 2003–May 2011) in a Udult in the Ozark Highlands region of northwest Arkansas. It was hypothesized that FWM plant nutrient and trace metal leachate concentrations and loads differed more among broiler litter rates in the first 3-mo season (i.e., May, June, and July) immediately following annual litter application than in the other three 3-mo seasons.

Materials and Methods

Site Description

In 2002, six 6-m-long by 1.5-m-wide plots, which had previously been used in numerous runoff studies with various inorganic and organic soil amendments prior to 2002, were selected based on similar soil pH (6.2) and high Mehlich-3 extractable P (210 mg kg⁻¹) in the top 5 cm (Pirani et al., 2006) at the Agricultural Research and Extension Center in Fayetteville, AR (36°5’49.18” N, 94°10’44.65” W). The soil at the study site was mapped as a Captina silt loam (a fine-silty, siliceous, active, mesic Typic Fragiaqual), which is a relatively common residual soil in north-west Arkansas and southwestern Missouri and is part of Major Land Resource Area 116A (Ozark Highland; Brye et al., 2013). All plots had a 5% west-to-east slope and had steel edging installed around their perimeters to contain surface runoff within the plots and prevent run-on into the plots (Pirani et al., 2006). Throughout the duration of this study (2002–2011), vegetation within the plots was a mix of Bermuda grass [Cynodon dactylon (L.) Pers.], Johnsongrass [Sorghum halepense (L.) Pers.], and clover (Trifolium spp.). Additional site details were described by Pirani et al. (2006).

The 30-yr (1981–2010) mean annual precipitation, measured on the agricultural experiment station where this field study was conducted, is 115.6 cm (National Centers for Environmental Information, 2016). The 30-yr mean annual air temperature is 5...
Treatments and Experimental Design

Based on University of Arkansas Cooperative Extension Service BL application recommendations in 2002 when the field study began, three BL treatments, consisting of single annual applications of a low (5.6 Mg dry litter ha\(^{-1}\)) and high (11.2 Mg dry litter ha\(^{-1}\)) rate of BL and an unamended control, which received no BL or inorganic fertilizers, were replicated twice in a randomized complete block design to evaluate drainage and leachate water quality with time. Drainage and leachate water quality measurements with time were summarized into 3-mo seasons, starting when the one-time annual BL applications were made (summer [May–July], fall [August–October], winter [November–January], and spring [February–April]).

Lysimeter Operation

During late-summer 2002, stainless-steel equilibrium-tension lysimeters (Brye et al., 1999), 76.2 cm long by 25.4 cm wide with a 0.2-mm, porous stainless-steel collection plate, were installed at a depth of 0.9 m under an undisturbed soil column below the center of each plot. Heat dissipation sensors (Model 229-L, Campbell Scientific) were also installed above each lysimeter’s porous plate and in the bulk soil at the same depth outside each lysimeter and connected to a datalogger (Model CR10x, Campbell Scientific) to continuously monitor the soil matric potential every 10 min. The equilibrium-tension lysimeter setup for each plot was automated through datalogger programming and installation of a vacuum pump (TD-2N, Brailsford and Company) and a series of solenoids (Masarik et al., 2004) that maintained suction on the underside of the porous plate equivalent to 2 kPa less than the measured matric potential in the bulk soil to avoid ponding above the porous plate (Brye et al., 1999). This process allowed leachate collection from the soil column in close response to the natural fluctuations of the hydraulic gradient at the lysimeter depth (Brye et al., 1999). Additional lysimeter installation details were described by Brye et al. (1999) and Pirani et al. (2006).

Broiler Litter Characterization and Application

Broiler litter from a single chicken house of a local producer was obtained and used throughout the duration of this study. The BL consisted of a mixture of sawdust and rice (*Oryza sativa* L.) hulls as bedding material and was 12 to 18 mo old following production of six to eight flocks (Pirani et al., 2006). Prior to application to the field plots, the gravimetric moisture content was determined in triplicate by drying at 70°C for 48 h. Actual litter application amounts were on a dry-weight basis. Based on procedures for manure analyses (Peters, 2003), oven-dried litter subsamples were also chemically characterized in triplicate for pH and EC, KCl-extractable NO\(_3\)–N and NH\(_4\)–N concentrations, and total C, N, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Zn, Al, As, Cd, Cr, Ni, and Se concentrations after HNO\(_3\) digestion (Pirani et al., 2006; McMullen et al., 2014a, 2014b).

Between the last week of April and the first week of May each year, field plots were moved to a height of approximately 9 cm and the cut vegetation removed in preparation for BL application. Within 1 d of vegetation moving and removal, BL was subsequently applied once annually to the field plots by manual spreading.

Leachate Collection, Processing, and Analyses

Starting in May 2003, leachate solution was collected approximately every 2 wk during dry periods, or more frequently if necessary, from each lysimeter’s collection reservoir using a separate vacuum pump. In the field, the leachate volume was measured and up to 1 L of the leachate solution was retained for chemical analyses. Within 24 h typically, leachate pH and EC were measured potentiometrically on a small subsample and additional leachate subsamples were filtered through a 1.6-μm glass microfiber filter. Once filtered, three 20-mL aliquots were retained unacidified and three 20-mL aliquots were acidified with two drops of concentrated HCl and stored at 4°C for subsequent chemical analyses.

Using unacidified subsamples, the DOC concentration was measured using a total organic C analyzer (Model TOC-CSH, Shimadzu Scientific Instruments). Unacidified subsamples were also used the measure NO\(_3\)–N concentration, while acidified subsamples were used to measure NH\(_4\)–N and PO\(_4\)–P concentrations using an automated wet-chemistry analyzer (Skalar San Plus, Skalar Analytical). Total dissolved As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Se, and Zn concentrations were also measured, using acidified subsamples, by inductively coupled, argon-plasma mass spectrometry (CIROS CCD model, Spectro Analytical Instruments).

Elemental leachate concentrations (mg L\(^{-1}\)) measured from a given sample date were multiplied by the leachate volume (i.e., drainage, in L) collected at the same time to calculate leachate elemental masses (mg). Leachate elemental masses were then summed by 3-mo season (summer [May–July], fall [August–October], winter [November–January], and spring [February–April]) and divided by the total drainage volume for the same time period to calculate seasonal FWM leachate concentrations. Seasonal elemental masses were also divided by the 0.1935-m\(^2\) lysimeter surface area from which leachate solution was collected to calculate seasonal elemental loads (kg ha\(^{-1}\)). Drainage was summed, and the mean leachate pH and EC were calculated for each season. All seasonal data were summarized seasonally for the duration of the study.
summarizes were conducted on a plot-by-plot basis to retain replication for statistical analyses. Regardless of statistical differences, loads were calculated on a plot-by-plot basis using the actual measured drainage and FWM concentration from that particular plot.

Statistical Analyses
A two-factor analysis of variance (ANOVA) was conducted using PROC MIXED in SAS (Version 9.3, SAS Institute) to evaluate the effects of broiler litter rate (control, low, and high), season (summer, fall, winter, and spring), and their interaction on drainage and leachate water quality (i.e., pH, EC, FWM concentrations, and loads) during an 8-yr period (May 2003–May 2011). Year was treated as a random effect. When appropriate, treatment means were separated by least significant difference at the 0.05 level. Linear correlations were also conducted between seasonal precipitation and drainage and leachate water quality parameters using Minitab (Version 16, Minitab, Inc.). Significant differences were judged at the 0.05 level.

Results and Discussion
Initial, Pretreatment Site Characterization
Since the experimental field plots used in this study had received organic amendments prior to 2002, it was necessary to evaluate experimental field plot uniformity prior to making the initial BL application in May 2003. Based on numerous soil, plant, and runoff and leachate water quality parameters that did not differ among preassigned BL treatments during the 3 mo preceding the first BL application in this long-term study (Pirani et al., 2006, 2007; Menjoulet et al., 2009), which were further articulated in McMullen et al. (2014b), the experimental plots used in this field study were assumed to be as uniform as could reasonably be expected. Therefore, it was also assumed that any subsequent measured differences were due to actual imposed treatments rather than to inherent differences among experimental plots.

Broiler Litter Composition
Broiler litter from a local producer was applied annually as an organic nutrient source for forage production similar to regional management practices used for the disposal of excessive litter accumulations. During the course of this 8-yr study, the applied BL had an alkaline pH, contained a substantial amount of total C and N, and also contained numerous trace elements, such as, Cd, Cr, Cu, and Se (McMullen et al., 2014b). However, several BL constituents, such as NO$_3^-$, N, NH$_4^-$, and Na in particular, were highly variable from year to year. The BL used in this study had a similar composition to that used in previous studies in Arkansas (Adams et al., 1994), New York (Brock et al., 2007), Pennsylvania (Kleinman et al., 2002), and overseas in Nigeria (Agele et al., 2004). As reported by McMullen et al. (2014a), and as would be expected, annual aboveground dry matter production was consistently greater as a result of BL additions compared with the unamended control.

Precipitation and Drainage
During the 8-yr period from May 2003 to May 2011, mean seasonal precipitation ranged from 198 mm in winter to 360 mm in summer (Fig. 1). Mean seasonal precipitation represented a range of 79% in winter to 112% in spring of the 30-yr (1981–2010) precipitation normals (National Centers for Environmental Information, 2016). Overall, seasonal precipitation averaged 296 mm season$^{-1}$, which was only 2.4% greater than the 30-yr normal for seasonal precipitation (National Centers for Environmental Information, 2016). However, measured seasonal precipitation also differed ($P = 0.011$) among seasons (Fig. 1).

In contrast to seasonal precipitation, seasonal drainage, measured from the 0.9-m soil depth using automated, equilibrium-tension lysimeters, was unaffected ($P > 0.05$) by BL rate or season (Table 1). Seasonal drainage ranged from 89.1 mm in the low-litter treatment to 132.9 mm in the unamended control (Table 2), ranged from 83.3 mm during summer to 165.9 mm during spring (Fig. 1), and averaged 117.8 mm season$^{-1}$ across BL rates and seasons (Table 2). Large variations in measured drainage among treatment replicates probably contributed to the lack of ability to separate treatment means when large numeric differences existed. Kasteel et al. (2007) demonstrated that soil water may bypass a lysimeter’s porous plate, causing the resulting measured drainage flux to be underestimated relative to the actual drainage flux, which may have contributed added variability in this study.

Although there was an expected, natural time lag between any infiltrated precipitation and drainage, seasonal drainage represented a range of 23.1% in summer to 64.2% in winter of the measured seasonal precipitation during the same season. Precipitation and drainage during the same season were correlated ($P = 0.001$), as would be expected, but the correlation was weak ($r = 0.24$). Large drainage fluxes have also been reported to occur during spring months in south-central Wisconsin (Brye et al., 2000, 2001) and during winter months in Germany (Harsch et al., 2009), when
increased precipitation coincided with decreased transpiration. In northwest Arkansas, the greatest drainage fluxes have been reported in either spring (Pirani et al., 2006) or winter months (Pirani et al., 2006; Adams et al., 1994) depending on the year.

### Leachate Water Quality

#### Flow-Weighted Mean Concentrations

Averaged across seasons, seasonal leachate EC, flow-weighted mean PO₄–P, total P, and S concentrations (Table 1) differed \((P < 0.05)\) among BL rates during the 8-yr period. Seasonal leachate EC was 27% greater from the high-litter than from the low-litter and unamended control treatments, which did not differ (Fig. 2). The applied BL had large concentrations of salts, thus it was expected that leachate EC would be greater from the litter-treated than the non-litter-treated plots. Seasonal FWM leachate PO₄–P
concentration from the unamended control was 67% greater than from the high-litter treatment, while that from the low-litter treatment was intermediate (Fig. 2). Similarly, seasonal FWM leachate total P concentration from the unamended control was 76% greater than from the litter treatments, which did not differ (Fig. 2). It is likely that the BL-applied P remained concentrated near the soil surface in the litter treatments and consequently was more susceptible to runoff rather than leaching deeper into the soil profile. This contention is supported by the results of McMullen et al. (2014a), who reported 8-yr cumulative runoff losses of PO4–P and total P from the high-litter treatment, while that from the low-litter treatment exceeding the 10 mg L−1 drinking water standard and that from the high-BL treatment exceeding that from the unamended control. In addition, the added BL stimulated an aboveground biomass production difference among treatments (McMullen et al., 2014b), thus plant uptake of P probably further removed P from the soil profile to decrease the potential for P leaching. Although McMullen et al. (2014b) reported that the BL rate did not affect P leaching trends with time and that cumulative 8-yr leaching losses were unaffected by the BL rate, annual data summarization across seasons probably masked potential BL rate effects on P leaching across seasons. In contrast to leachate P concentrations, seasonal FWM leachate S concentrations from the littered treatments, which did not differ, were nearly twice that from the unamended control (Fig. 2), which was probably due to the large S concentration in the applied BL (McMullen et al., 2014b).

Seasonal leachate pH and FWM leachate concentrations of NO3–N, NH4–N, DOC, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Se, and Zn were unaffected (P > 0.05) by BL rate (Table 1). Seasonal leachate pH was slightly more acidic with time and averaged 6.2 across BL rates (Table 2). As would be expected from their rather large BL concentrations (McMullen et al., 2014b), seasonal FWM leachate Ca, K, Na, and Mg concentrations were numerically greatest among all other plant nutrients and trace metals measured in the study and averaged 15.3, 16.0, 12.0, and 5.3 mg L−1, respectively, across BL rates with time (Table 2). The C concentration of applied BL was largest among all elements measured; however, seasonal FWM leachate DOC concentrations averaged only 3.0 mg L−1 across BL rates with time (Table 2). Seasonal FWM leachate concentrations of all other elements and compounds measured in this study averaged <0.35 mg L−1 across BL rates with time (Table 2).

In contrast to the results of this study, although conducted on a similar soil in northwest Arkansas, the application of BL increased leachate NO3–N concentrations in the study by Adams et al. (1994). Adams et al. (1994) applied BL at three rates (0, 10, and 20 Mg ha−1) to a Captina silt loam in northwest Arkansas and used fixed-tension pan lysimeters and suction cup samplers to collect leachate using suctions of −8 to −12 kPa at the 60- and 120-cm depths, respectively. Leachate NO3–N concentrations at the 60-cm depth peaked at concentrations >10 mg L−1 from individual samplings about 30 d after BL application, then decreased to unamended-control levels during a dry period for all unamended treatments (Adams et al., 1994). The high-BL treatment had greater leachate NO3–N concentrations than the low-BL treatment (Adams et al., 1994). Adams et al. (1994) also reported that leachate NO3–N concentrations at the 120-cm depth for individual samplings peaked approximately 120 d after BL application for all treatments, with the leachate NO3–N concentration from the low-BL treatment being below the 10 mg L−1 drinking water standard and that from the high-BL treatment exceeding 10 mg L−1. The used of fixed-tension lysimeters probably contributed to the contrasting results of Adams et al. (1994) and those of this study that were based on automated equilibrium-tension lysimeters. The tensions used by Adams et al. (1994) could have underestimated the actual drainage flux by missing unsaturated flow that occurred at tensions lower than −8 to −12 kPa, which would have resulted in elevated NO3–N concentrations that were not representative of the actual soil leachate solution or the amount of drainage that might have occurred. In addition to BL application rate effects, numerous leachate water quality parameters differed temporally during the 8-yr study.

Averaged across BL rates, seasonal leachate pH, EC, and FWM NO3–N, DOC, S, and Zn concentrations (Table 1) differed (P < 0.05) among seasons during the 8-yr period from May 2003 to May 2011. Seasonal leachate pH was slightly acidic and 0.5 units greater during winter and spring, which did not differ, than during summer and fall, which did not differ and were more acidic (pH = 5.9; Fig. 3). Similar to leachate pH, seasonal leachate EC was also 64% greater during winter and spring, which did not
differ, than during summer and fall, which did not differ (Fig. 3). The natural, expected time lag for BL decomposition and soluble constituent transport through the soil profile to occur probably shifted the leaching pulse for the bulk of the soluble BL constituents ahead in time to explain the more alkaline seasonal leachate pH and greatest seasonal EC in the second half of the annual cycle compared with the first. This same seasonal pattern occurred for seasonal FWM leachate DOC and S concentrations. Seasonal FWM leachate DOC concentration was 32% greater in winter and spring, which did not differ, than in the summer and fall, which did not differ (Fig. 3). Seasonal FWM leachate S concentration was 51% greater during winter than during summer and fall, which did not differ, while that during spring was intermediate (Fig. 4). However, in contrast to the seasonal pattern for leachate pH, EC, DOC, and S, seasonal the FWM leachate NO$_3$–N concentration during fall was more than twice that during winter and spring, which did not differ (Fig. 4).

Unlike any other nutrient or compound measured in this study, only the seasonal leachate Ni load differed ($P < 0.05$; Table 4) among BL treatments (Fig. 5). Somewhat unexpectedly, the seasonal Ni load from the high-litter treatment was 154% greater than from the low-litter treatment, while that from the unamended control was intermediate (Fig. 5). The applied BL contained trace amounts of Ni (McMullen et al., 2014b) and the seasonal FWM leachate Ni concentration was identical among all three BL treatments (Table 2), which would suggest that seasonal Ni loads would be similar among BL treatments. However, although not significantly different (Table 1), seasonal drainage was nearly identical between the high-litter treatment and the unamended control and 48% numerically larger from the high-litter treatment and unamended control than from the low-litter treatment, which could explain the significantly lower seasonal Ni load from the low-litter treatment.

Similar to seasonal FWM mean concentrations, seasonal leachate Ca, K, Mg, Na, and S loads were numerically greatest among all other plant nutrients and trace metals measured in the study and averaged 19.7, 22.6, 6.8, 15.6, and 13.6 kg ha$^{-1}$, respectively, across BL rates with time (Table 2). Despite a large C concentration in the applied BL, DOC leaching was relatively...
low from the litter treatments because the C additions from the applied BL stimulated increased soil respiration (McMullen et al., 2015). Seasonal leachate loads of all other elements and compounds measured in this study averaged <0.3 kg ha\(^{-1}\) across BL rates with time (Table 2).

Unlike seasonal FWM leachate concentrations, averaged across BL rates, seasonal leachate NH\(_4\)–N, Cu, Fe, and Se loads differed (\(P < 0.02\)) among seasons (Table 4). The seasonal leachate NH\(_4\)–N load during spring was more than three times greater than during summer and winter, which did not differ, while that during fall was intermediate (Fig. 6). Similarly, the seasonal leachate Cu load during spring was more than four times greater than during winter, while that during summer and fall were intermediate, and the seasonal leachate Se load was more than three times greater during spring than during the other three seasons, which did not differ (Fig. 6). Although seasonal FWM leachate NH\(_4\)–N, Cu, and Se concentrations were unaffected by season (Tables 1 and 2), their seasonal leachate loads were numerically greatest during spring (Fig. 6), at least in part due to numerically greater drainage during spring than during the other three seasons (Fig. 1). In contrast to seasonal leachate NH\(_4\)–N, Cu, and Se loads, the seasonal leachate Fe load was 56% greater during winter than during the other three seasons, which did not differ (Fig. 6), probably due to the leaching of reduced Fe as seasonal drainage exceeded seasonal precipitation, on average, during winter (Fig. 1). Seasonal leachate NO\(_3\)–N, PO\(_4\)–P,
DOCs, As, Ca, Cd, Cr, K, Mg, Mn, Na, Ni, P, and Zn loads were unaffected \((P > 0.05)\) by season (Table 4).

Of the suite of leachate water quality parameters measured, only seasonal FWM leachate concentrations of Cr \((r = 0.18)\) and Se \((r = 0.37)\) were correlated \((P < 0.03)\) with seasonal precipitation. In contrast, seasonal leachate loads of NO\(_3^–\)N \((r = 0.17)\), DOC \((r = 0.25)\), Ca \((r = 0.22)\), Cr \((r = 0.26)\), K \((r = 0.23)\), Mg \((r = 0.22)\), Na \((r = 0.25)\), total P \((r = 0.16)\), S \((r = 0.25)\), and Zn \((r = 0.18)\) were all positively correlated \((P < 0.05)\) with seasonal precipitation. Considering the direct relationship between seasonal precipitation and drainage, this result was somewhat expected because greater precipitation presumably would result in greater infiltration, hence, a greater amount of soil water to leach soluble constituents deeper into the soil profile. Of the suite of leachate water quality parameters measured, seasonal leachate pH \((r = 0.20)\), EC \((r = 0.32)\), and FWM concentrations of Fe \((r = 0.31)\), K \((r = 0.29)\), and S \((r = 0.37)\) were positively correlated \((P < 0.05)\), while FWM concentrations of Cr \((r = 0.16)\), Ni \((r = 0.32)\), and Zn \((r = 0.27)\) were negatively correlated \((P < 0.05)\) with seasonal drainage. The variation in both positive and negative correlations with drainage indicates that there are more complex interactions at work than simple dilution occurring between some soluble constituents and the amount of soil solution draining past a particular soil depth. Dilution would be expected to result in a negative correlation between the FWM concentration of a soluble constituent and drainage.

**Leachate Water Quality Implications**

Although soil leachate solution measured from the vadose zone at a depth of 0.9 m would certainly not be considered drinking water, water quality standards for drinking water are probably the most relevant set of water quality standards for comparative purposes. Of the suite of leachate elemental concentrations measured in this study, only As, Cd, Cr (total), Cu, NO\(_3^–\)N, and Se have designated drinking water standards (USEPA, 2016b). The maximum contaminant level (MCL) concentrations are 0.01 mg L\(^{-1}\) for As, 0.005 mg L\(^{-1}\) for Cd, 0.1 mg L\(^{-1}\) for Cr, 1.3 mg L\(^{-1}\) for Cu, 10 mg L\(^{-1}\) for NO\(_3^–\)N, and 0.05 mg L\(^{-1}\) for Se (USEPA, 2016b). With the exception of As and Se, measured seasonal FWM leachate Cd, Cr, Cu, and NO\(_3^–\)N concentrations were at least five times smaller during every season and overall with time (Table 3) than their drinking water MCLs (USEPA, 2016b).

Measured seasonal FWM leachate As concentration exceeded the drinking water MCL during summer, fall, and winter and overall, and seasonal FWM leachate Se concentration exceeded the drinking water MCL during each season individually and overall across all four seasons with time (Table 3). Although seasonal FWM leachate As and Se exceeded their drinking water MCLs at 0.9 m below the soil surface and despite both As and Se typically existing in the soil environment as oxyanions, both As and Se would be reactive in the subsoil (Jackson and Miller, 1999; Álvarez-Benedí et al., 2005; McDonald et al., 2009), particularly in the absence of appreciable PO\(_4^3–\) as would be expected below depths of 1 m even under BL-amended soil. Phosphate-P is known to compete with As for soil adsorption sites (Manning and Goldberg, 1996; Rutherford et al., 2003). Consequently, both leachate As and Se would probably be further attenuated, primarily by sorption reactions with soil particles, as they continued to leach below the 0.9-m depth toward bedrock, which is at least 1.3 m deep and in many places much deeper in the Captina silt loam soil mapping unit, and/or the regional groundwater table, which is >3 m deep in most places but periodically fluctuates within 0.5 m of the soil surface due to perching. Furthermore, upon entering the regional groundwater, extensive dilution would probably occur to greatly reduce leachate As and Se concentrations if the leachate reached the groundwater at the concentrations measured at 0.9 m below
the soil surface. McLaren et al. (2004) reported increased leachate concentrations of Cd, Ni, and Zn with the application of metal-spiked sewage sludge. Although the amounts of Cd, Ni, and Zn leached were small relative to the amounts added, leachate concentrations of Ni and Zn exceeded New Zealand’s environmental drinking water standards (McLaren et al., 2004).

Considering that much of the Ozark Highlands is underlain by limestone and dolomitic bedrock (Brye et al., 2013), leaching through soils above karst topography is also a potential water quality concern because the soil leachate could become mixed, potentially rapidly, with surface waters via seeps and springs before being diluted upon entering the groundwater. Therefore, surface water quality standards could become relevant. Of the trace metals measured in this study, only Se has a surface water quality standard in Arkansas (0.02 mg L\(^{-1}\); USEPA, 2016c). Similar to the drinking water standard, the measured seasonal FWM leachate Se concentration exceeded the surface water quality standard during each season individually and overall across all four seasons with time (Table 3). Reporting on the results of the first 2 yr of BL application in this same long-term study, Pirani et al. (2006) demonstrated that leachate-As concentrations differed among BL rates in at least one 3-mo season and that As and Se leachate loads were at least numerically elevated in response to the increasing BL application rate. Similar results were also reported by McMullen et al. (2015) for the annual summary of the 8-yr data set. However, soil leachate solution would probably undergo many reactions and attenuations, even in areas of karst geology, before it was able to mix with nearby or regional surface waters.

Recommended water quality criteria also exist to protect aquatic life in surface freshwaters (USEPA, 2016a). Of the suite of leachate constituents measured in this study, criterion maximum concentrations (CMCs) for freshwater aquatic life protection exist for only As (0.34 mg L\(^{-1}\)), Cd (1.8 mg L\(^{-1}\)), Cr (0.57 and 0.016 mg L\(^{-1}\) for Cr(III) and Cr(VI), respectively), Ni (0.47 mg L\(^{-1}\)), and Zn (0.12 mg L\(^{-1}\)) (USEPA, 2016a). With the exception of leachate Zn, neither seasonal FWM leachate As, Cd, Cr (total), nor Ni concentrations exceeded their CMC for freshwater aquatic life protection (USEPA, 2016a) during any individual season or overall across all four seasons with time (Table 3). In contrast, seasonal FWM leachate Zn concentrations exceeded the Zn CMC for freshwater aquatic life protection (USEPA, 2016a) by more than 40% during each individual season (Fig. 4). However, similar to leachate Se, extensive attenuation and dilution of leachate Zn would be expected to occur before leachate from a depth of 0.9 m below BL-amended soil would enter any nearby surface water body to potentially negatively affect aquatic life.

**Conclusions**

With the use of automated, equilibrium-tension lysimeters, leachate below an undisturbed soil column was able to be collected and monitored from long-term experimental plots used in assessing land management practices on subsurface water quality associated with environmental and human health. Broiler litter application rates ranging from 0 to 11.2 Mg dry litter ha\(^{-1}\) to a managed grassland setting with a history of BL applications significantly affected few leachate quality parameters (i.e., EC, FWM PO\(_4\)-P, total P, and S concentrations, and total Ni loads) at a depth of 0.9 m. Despite a previous report of the effects of the BL application rate on annually summarized leachate water quality parameters (McMullen et al., 2014b), season also affected leachate quality parameters (i.e., pH, EC, FWM NO\(_3\)-N, DOC, total S and Zn concentrations, and NH\(_4\)-N, total Cu, Fe, and Se loads), with only leachate EC and FWM total S concentrations being affected by both BL rate and season. These results validated the need to evaluate leachate water quality data at a finer time scale than annual. Effects of BL application rates were consistent across seasons, as evidenced by a lack of significant interaction between BL application rate and season for any of the leachate quality parameters.

The leachate quality parameters affected by BL application rate or season did not exceed drinking water quality standards. However, although unaffected by BL rate, FWM As and Se concentrations exceeded drinking water standards throughout all seasons, on average, during the 8-yr measurement period. The accumulation of As and Se in the soil from a history of BL applications has possibly buffered any current effects of additional BL. Pastures overlying shallow, fractured karst formations, such as in the Ozark Highlands, may be vulnerable to preferential flow of leachate to surface waters. However, deeper soil profiles (i.e., >1.3 m to bedrock) will probably adsorb and further attenuate a portion of the leachate As and Se, thereby lowering their concentration in leachate that reaches the underlying karst network. In areas where BL-amended pastures and managed grasslands are concentrated, As and Se concentrations in perched or closed-water systems may be of concern. However, because leachate is transported to larger surface water bodies and potentially diluted by runoff water additions from neighboring landscapes, the risk of As and Se concentrations will probably diminish. Further research on the longitudinal and lateral distributions of As and Se concentrations in stream and lake sediments would be useful to determine if these metals are being transported farther within the watershed.

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**References**

