An assessment of nutrient dynamics in streambank soils of the Lower Little Bow River in southern Alberta using ion exchange membranes

J. J. Miller, E. Bremer, T. Curtis and D. S. Chanasyk

ABSTRACT

Nutrient dynamics in streambanks may impact nutrient movement to water, and may be influenced by cattle activity, river water level fluctuations, and time. Our objective was to determine the influence of these factors on nutrient (NO$_3$-N, P, S, Fe, Mn, Cu, Zn, Ca, Mg) dynamics in streambanks along the Lower Little Bow River in southern Alberta using Plant Root Simulator or PRS® probes. Three experiments were conducted from 2012 to 2015. In the first experiment, few significant ($P \leq 0.05$) effects were found among three reaches varying in cattle impact except for Fe and Mn, which generally increased with increasing cattle impact. In the second experiment (probe placement), adsorption of P, Fe, Mn, S, Ca, and Mg was significantly greater for submerged than exposed streambanks, and the opposite trend occurred for Cu and Zn. In the third experiment on the influence of probe burial periods from 0.2 to 14 days, maximum nutrient adsorption generally occurred within 1 to 7 days, and S adsorption showed an exponential increase with time. Overall, few cattle impact effects were found on nutrient dynamics, certain nutrients were greater in submerged than exposed banks, and 7-day burial of PRS probes was sufficient to assess nutrient dynamics.

INTRODUCTION

Streambanks are an important component of the riparian zone because they are the critical interface between water and land (Bohn 1986; Green & Kauffman 1989). Nutrient dynamics in streambanks may impact nutrient movement to adjacent surface water, and may be influenced by cattle activity, water level fluctuations, and time. Ion exchange membranes (IEMs) such as Plant Root Simulator or PRS® probes (Western Ag Innovations, Saskatoon, SK) may be useful for studying nutrient dynamics in streambank soils and sediments because they can be installed in situ with minimal disturbance, can be used to examine land use effects on multiple soil nutrients, can withstand submergence, and can be used to study nutrient dynamics over time (Qian & Schoenau 2002).

IEMs such as PRS probes have been used to study the influence of land use, depth, and burial period (time) on soil nutrient (e.g., N, P, S, Fe, Mn, Cu, Zn, K, Ca, Mg) dynamics (Drohan et al. 2005; Nelson et al. 2007; Obour et al. 2011; Kreiling et al. 2015; Wood et al. 2015; Miller et al. 2016). Studies on the effect of saturation on soil nutrients using IEMs have been conducted on submerged streambank soils using laboratory incubations (Miller et al. 2016), as well as field studies on soils in wetlands (Nelson et al. 2007), Spodosols (Obour et al. 2011), floodplains (Kreiling et al. 2015), and peatlands (Wood et al. 2015). Nutrient adsorption to IEMs in streambank soils may also indicate a potential for release to the stream water because there are significant positive correlations between certain nutrients adsorbed to IEMs or soil porewater in submerged soils and the overlying ponded water (Amarawansha et al. 2015; Miller et al. 2016).
The major factors influencing nutrient adsorption to IEMs are nutrient concentrations in soil solution, soil moisture, soil temperature, redox potential, depth of probe placement, and burial time (Qian & Schoenau 2002). Increases in nutrient adsorption with increasing soil moisture have been reported in many studies (e.g., Kusbach & Van Miegroet 2013; Kreiling et al. 2015), but not in others (Drohan et al. 2005; Wood et al. 2015). Increasing soil saturation and anaerobic conditions cause greater adsorption of certain redox-influenced nutrients (e.g., Fe, Mn) because of increased solubility under reducing conditions (Miller et al. 2016). In addition, lower adsorption of other nutrients such as NO₃ may occur due to denitrification (Nelson et al. 2007; Miller et al. 2016).

Little research has been conducted on nutrient dynamics in streambanks (McDowell & Sharpley 2001; Frey et al. 2015; Miller et al. 2016). In a laboratory incubation experiment, Miller et al. (2016) examined the effect of amendment type (cattle manure, roots, unamended), compaction (compacted, non-compacted), and time on nutrients adsorbed to IEMs (5, 7, 14 d burial periods) in a flooded saline-sodic soil (0–15 cm depth) taken from a streambank in southern Alberta. They found that amendment treatment had the greatest effect on nutrient dynamics, followed by burial time, while compaction had little impact.

Livestock mainly affects soil nutrient cycling by soil compaction, nutrient deposition in feces and urine, and loss of vegetation (Kauffman & Krueger 1984; Haynes & Williams 1993; Trimble & Mendel 1995; Fitch & Adams 1998). Few studies have been conducted on the influence of cattle on nutrients in riparian soils (Cooper et al. 1995; Zaimes et al. 2008a, 2008b; Walker et al. 2009; Miller et al. 2014), and in particular on streambanks. We hypothesize that nutrient adsorption to IEMs in exposed streambank soils should be greater with increased cattle activity.

Temporal changes in river discharge and water levels may cause streambanks to vary between exposed and submerged conditions. The greater soil moisture of submerged than exposed banks should favor greater adsorption of nutrients because of greater ion diffusion, and more anaerobic conditions may affect adsorption of nutrients (e.g., NO₃, Fe, Mn, Cu, Mn, S) that are influenced by redox potential. However, we are unaware of any field studies on the effect of exposed versus submerged streambanks on nutrient dynamics using IEMs. McDowell & Sharpley (2001) used soil sampling and chemical analysis and reported significant differences in certain P fractions in exposed bank sediments compared to submerged bed sediments, but did not compare exposed versus submerged streambanks.

Temporal trends in nutrient adsorption to IEMs or changes in concentrations in soil pore-water may also reveal important information about nutrient dynamics over time, and increases or decreases over time may reveal whether the soil is acting as a source or sink (Drohan et al. 2005; Nelson et al. 2007; Amarawansa et al. 2015; Kreiling et al. 2015). However, few researchers have studied nutrient dynamics in exposed streambanks over time using IEMs (Miller et al. 2016).

The overall objective of our study was to assess nutrient dynamics in streambanks of the riparian zone using IEMs. Nutrient adsorption by anion probes installed in exposed streambanks of three reaches varying in cattle impact was examined in Experiment 1. The influence of exposed versus submerged streambanks on nutrient adsorption by cation and anion probes was studied in Experiment 2, and nutrient dynamics over time in exposed streambanks was studied using anion probes in Experiment 3.

**MATERIALS AND METHODS**

**Study site**

The study site (latitude 50.08 N, longitude 112.68 W) is located within the Lower Little Bow (LLB) watershed and mixed grass natural subregion (Adams et al. 2005) in the southern portion of the province of Alberta, Canada. Detailed site descriptions have been reported (Miller et al. 2014). Dominant vegetation in this subregion is wheat grass (Agropyron spp.) and needle-and-thread grass (Stipa comata). The soils are mainly Dark Brown Chernozems. Long-term annual precipitation in the study area is 383 mm. The surface (0–15 cm) soils of the streambanks are calcareous (35% CaCO₃ equivalent) and alkaline with pH values of 7.5 to 8.0 (Miller et al. 2016).

The LLB River is a non-incised, regulated small river of Strahler stream order ≤3 (Miller et al. 2010). The river
bottom is coarse sediment consisting of mainly sand. The river is relatively narrow (8–9 m) and shallow (0.5–1.0 m). The LLB River flows through mainly native rangeland, with some reaches flowing through cultivated land. The river is intensively managed for irrigation, and flows are controlled by releases from a dam at the Travers Reservoir (Little 2001). However, flows in the river are most variable during the summer, as they are affected by inputs of rainfall and irrigation return flows and withdrawal of irrigation water. The dam is operated to maintain steady-state flows within the mainstem of the river, and releases 0.57 m³ s⁻¹ in the winter and 0.85 m³ s⁻¹ in the summer (Little 2001). However, flows of up to 13 m³ s⁻¹ have occurred in years with extreme rainfall (Miller et al. 2010). Irrigation return flows (runoff and drainage water) enter the LLB River between early May and early October. River water levels during the probe burial periods in the four study years were determined from historical data for the station at the mouth (Station 05AC023) of the LLB River (Environment Canada 2016).

Field experiments and probe installation

Three field experiments were conducted on exposed and submerged streambanks in the field using IEMs (Qian & Schoenau 2002) or PRS anion and cation probes (Western Ag Innovations, Saskatoon, SK). Anion probes were used in all experiments to monitor NO₃-N and P, while cation probes were also used in the final year of Experiment 2 to determine whether Ca and Mg could account for differences in P release (Miller et al. 2016).

Experiment 1 was a cattle-impact (reach) study of exposed streambanks on one fenced reach and two unfenced reaches using anion probes. Experiment 2 was a study on exposed versus submerged streambanks on a fenced reach using anion and cation probes. Experiment 3 was a burial time study on exposed streambanks of a fenced reach using anion probes. The PRS probes were installed perpendicularly into the soil of the riverbank so that the membranes were present at a depth of about 5 to 10 cm into the vertical face of the riverbank. For exposed streambanks, probes were installed into the wet capillary fringe within about 10 cm above the water level of the river to maximize soil moisture content and enhance diffusion of nutrients to the probes. For submerged streambanks, probes were installed about 10 cm below the water level of the river.

Cattle-impact (reach) study (Experiment 1)

For the cattle-impact study (Experiment 1), three reaches along the LLB River with varying cattle impacts were utilized. The details of these three treatments or reaches have been previously described (Miller et al. 2014). These were one fenced reach (fenced treatment, hereafter referred to as F treatment), one unfenced (UNF) and grazed reach with low (L) cattle-impact on the riparian zone (UNF-L treatment), and one unfenced and grazed reach with high (H) cattle-impact on the riparian zone (UNF-H treatment). The three reaches were all adjacent to each other, with the F treatment located at the upstream reach, UNF-H treatment on the middle reach, and UNF-L treatment on the downstream reach. The F, UNF-L, and UNF-H reaches have been previously referred to as unfenced, low-impact grazed, and high-impact grazed treatments, respectively (Miller et al. 2014).

The fenced (F) treatment had 1 km of streambank fencing (Reach 1) installed in 2001. Cattle were totally excluded from the riparian pasture of the fenced reach from 2001 to 2012. Thereafter (2013–2015), periodic grazing of the riparian pasture was conducted with about 50 head of cattle allowed to graze the riparian pasture (10 ha) for 2 weeks in July or August, for a stocking rate of 3.8 animal unit months (AUM) ha⁻¹. The change in management of the riparian pasture along the fenced reach from total cattle exclusion (2001–2012) to periodic grazing (2013–2015) was initiated to utilize the forage resource, reduce litter buildup and reduce fire risk, as well as control invasive and disturbance-caused plants. Since total cattle exclusion was dominant for 11 of 14 years for the F treatment, and our focus was on long-term effects of cattle on the riparian zone, we assumed that nutrient dynamics in the streambank of the F reach would reflect the historical effects of cattle exclusion in the ungrazed riparian pasture.

The two unfenced reaches have had the same grazing management for many decades (Miller et al. 2014). The stocking rates for pastures (grazed from June to August) adjacent to the UNF-H reach ranged from 0.3 AUM ha⁻¹.

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\[ \text{The river is relatively narrow (8–9 m) and shallow (0.5–1.0 m).} \]
\[ \text{The LLB River flows through mainly native rangeland, with some reaches flowing through cultivated land.} \]
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to 1.5 AUM ha\(^{-1}\) and it was 6.0 AUM ha\(^{-1}\) (grazed for 2 months in spring and fall) for the UNF-L reach. Although cattle stocking rates were lower for the UNF-H reach and higher for the UNF-L reach, there was more damage to the riparian zone and streambank along the UNF-H than UNF-L reach. This was because the riverbank was more accessible to cattle and there were more cattle-access sites for UNF-H (12 access sites) than UNF-L (six access sites) reach, the area of riparian pasture in the floodplain adjacent to the river was greater for the UNF-H (4.7 ha) than UNF-L (2.2 ha) reach, the upland pastures were closer to the river along the UNF-H than UNF-L reach, and cattle were in the riparian pastures for a much longer time for the UNF-H than UNF-L reach. A portable solar-watering system was installed adjacent (20 m) to the UNF-H reach from 2012 to 2015 which also kept cattle closer to the river. In contrast, a permanent water trough was installed in the pasture about 300 m from the river along the UNF-L reach, which kept cattle further away from the river along this reach.

The cattle-impact study was conducted over four years (2012–2015, inclusive). One PRS sample consisted of triplicate anion PRS probes, with each probe installed about 30 cm apart. The PRS probes were generally installed at an equal number of sites with high and minimal cattle activity that was based on visual observation. The PRS probes were installed into exposed streambanks on September 10 in 2012, August 27 in 2013, September 29 in 2014, and August 25 in 2015. The burial periods were 30 \(d\) in 2012 and 2013, and 7 \(d\) in 2014 and 2015. A shorter burial period was used in 2014 and 2015 to reduce the impact of changes in river flow, and because it was sometimes difficult to find the probes after one month due to sediment deposition. There were 122 PRS probe samples collected in 2012, 106 samples in 2013, and 54 samples each year in 2014 and 2015. There were 12 sites (replicates) for the fenced reach and 13 sites each for the two unfenced reaches in 2012 and 2013. In 2014 and 2015, there were six sites (replicates) for each of the three reaches. At each site, PRS probe samples were deployed at an average of six locations. The August or September installation dates for probes were chosen to assess nutrients in the streambanks later in the grazing season to maximize riparian impacts by cattle.

**Exposed versus submerged streambank study (Experiment 2)**

The exposed–submerged study (Experiment 2) was conducted along the fenced reach in 2014 and 2015 to determine the influence of river water level on nutrients in anion and cation PRS probes after a 7 day incubation period. In 2014, triplicate PRS anion probes (one PRS sample) were installed (September 29, 2014) in exposed and submerged soil of the streambank at three locations within six sites (replicates) along the fenced reach. A total of 36 PRS anion samples were collected in 2014. In 2015, triplicate PRS anion and cation probes (one PRS sample consisted of three anion or cation probes) were installed (August 25, 2015) in the exposed and submerged soils of the streambank at two locations within six sites along the fenced reach. There were a total of 36 anion probe samples and 12 cation probe samples collected in 2015.

**Burial time study (Experiment 3)**

For the burial time study (Experiment 3) in 2014, triplicate anion probes were installed in the exposed streambank on day 0 (July 23, 2014) at three locations within one site on the fenced reach and then the probes were removed after four burial periods (0.2, 1, 7, 14 days). A total of 12 anion probe samples were collected. Experiments 2 and 3 were conducted when river water levels were lower and stable.

**Probe extraction and nutrient analyses**

After incubation, the PRS probes from all three experiments were removed, cleaned, rinsed with distilled water, and then shipped to the Western Ag Innovations lab for analysis. Nitrate-N was analyzed by colorimetry using an automated flow injection analysis system, and P, S, Fe, Mn, Cu, Zn, Ca, and Mg were analyzed using inductively coupled plasma spectrometry (Perkin Elmer ICP-OES 8300\textsuperscript{®}) method (Soltanpour et al. 1996).

**Statistical analyses**

Statistical analyses were conducted on nutrients’ concentrations in PRS probes using a mixed model analysis (SAS
Institute 2005). If required, data were log-transformed to ensure a normal distribution and homogeneous variances. For the cattle-impact study (Experiment 1), reach was considered as a fixed effect and site (replicate) as a random effect in the model. For the exposed versus submerged streambank study (Experiment 2), probe position was considered as the fixed effect and site a random effect. No statistical analysis was conducted for the burial time study (Experiment 3) as the data are shown in graphs of adsorption versus burial time. Cattle-impact or reach effects were considered significant at the \( P \leq 0.05 \) level using a least-squares mean test, and use of the term ‘greater’ means ‘significantly greater’. Correlations were also conducted among the nutrients and Pearson correlation coefficients were considered significant at \( P \leq 0.05 \) level.

The cattle-impact hypothesis was that concentrations of nutrients should follow the order: UNF-H > UNF-L > F treatments. The exposed–submerged study hypothesis was that position of probes in exposed or submerged streambanks would have a significant effect on nutrient adsorption. The burial time hypothesis was that nutrient adsorption over time would reveal trends in nutrient dynamics, and that an increase of nutrient adsorption over time would be indicative of a nutrient ‘source’.

**RESULTS**

**Cattle-impact study on exposed streambanks of fenced and unfenced reaches using anion probes (Experiment 1)**

The water level in the LLB River varied during the period when PRS probes were installed in all years (Figure 1). During the 30-d burial time in 2012, the river water level declined after PRS probe installation and was generally lower than the initial water level. The water level during the 30-d incubation period in 2013 increased after probe installation to a maximum on Julian day 262 (September 19), and then decreased; and the water level during the incubation period was greater than the initial water level. The water levels in 2014 and 2015 generally decreased during the 7-d incubation periods and were lower than the initial level. Overall, most of the PRS probes were likely submerged during the latter half of the incubation period in 2013, but not in the other three years.

There were no significant cattle-impact effects on NO\(_3\)-N, P, and S adsorbed to PRS probes (Figure 2). The one exception was for S in 2015 where adsorption was significantly \( (P \leq 0.05) \) greater by two-fold for UNF-L than F and UNF-H reaches (Figure 2(c)).

There was a significant cattle-impact effect on Fe (Figure 3(a)) and Mn (Figure 3(b)) in PRS probes in three of four years (Figure 3(a)). Iron adsorption in 2012 and 2013 was 1.4- to 2.2-fold greater \( (P \leq 0.05) \) for UNF-H than UN-L and F reaches, and in 2015 it was 5.4-fold greater for UNF-L than F reach. Manganese adsorption in 2012 was 1.2-fold greater for UNF-H than UNF-L reach, 4.6-fold greater for UNF-H than F reach, and 3.9-fold greater for UNF-L than F reach. Manganese adsorption in 2013 was 1.5- to 1.8-fold greater for UNF-H than UNF-L reach, 4.6-fold greater for UNF-H than F reach, and 3.9-fold greater for UNF-L than F reach. Manganese adsorption in 2015 was 1.5- to 1.8-fold greater for UNF-H than UNF-L and F reaches, and in 2015 it was 7.1-fold greater for UNF-L than F reach.

There was a significant cattle-impact effect on Cu in PRS probes in one (2012) of four years (Figure 3(c)), where adsorption was 1.7-fold greater for UNF-H than UNF-L reach. There was a significant cattle-impact effect on Zn in PRS probes in two (2012, 2013) of four years (Figure 3(d)),...
where adsorption was 1.3- to 2.0-fold greater for UNF-H than UNF-L and F reaches.

**Exposed versus submerged streambank study on fenced reach using anion and cation probes (Experiment 2)**

Nitrate-N adsorbed to anion probes for 2014 and 2015 was similar in the exposed and submerged streambanks (Table 1). Phosphorus adsorption to anion probes in 2014 and 2015 was two- to three-fold greater for submerged than exposed streambanks. Iron and Mn adsorption to anion probes in 2014 was similar for both locations. However, Fe and Mn adsorption was 10- to 12-fold greater in submerged than exposed streambanks for anion probes in 2015, and it was 13- to 29-fold greater in submerged than exposed streambanks for cation probes in 2015. Copper and Zn adsorption was 3- to 15-fold greater in exposed than submerged streambanks for anion probes in 2014 and 2015, but was similar for both locations for the cation probes in 2015. Sulfur adsorption was similar in exposed and submerged streambanks for anion probes in 2014, and was three-fold greater in submerged than exposed streambanks for anion probes in 2015. Ammonium-N, Mg, and K adsorption to cation probes in 2015 was similar for both locations, but Ca and Mg adsorption was two-fold greater in submerged than exposed streambanks.

**Burial time study on exposed streambanks of fenced reach using anion probes (Experiment 3)**

Adsorption for certain nutrients to anion probes in 2014 showed temporal trends with increasing incubation time, but some nutrients exhibited considerable variability among locations or replicates (Figure 4). Nitrate adsorption during the 14-d incubation was low, and the maximum adsorption was 8.0 mg m$^{-2}$ at the shortest burial period (4 h). Phosphorus adsorption was also low, and it increased over time reaching a maximum of 2.4 mg m$^{-2}$ on day 14. Iron adsorption was relatively high with a maximum of 165 mg m$^{-2}$ on day 7. Manganese adsorption was considerably lower than Fe with a maximum of 8.3 mg m$^{-2}$ on day 0.2. Copper and Zn adsorption was also low reaching maximum values of 0.9 and 0.8 mg m$^{-2}$, respectively, on day 1.
Sulfur adsorption was highest among the seven nutrients, as it increased dramatically from day 0 to day 1, and then gradually levelled off to a maximum of 1,119 mg m\(^{-2}\) on day 14.

**DISCUSSION**

The hypothesis of lower adsorption with reduced or no cattle impact for Experiment 1 (exposed streambank) was supported for Fe and Mn in three of four study years, Zn in two years, S and Cu in one year, and not in any of the four years for NO\(_3\)-N and P. Therefore, the strongest evidence to support the hypothesis of greater adsorption to anion probes was for Fe and Mn. Greater Fe and Mn adsorption to PRS probes was likely caused by soil compaction by cattle, which would have enhanced anaerobic conditions and increased available Fe and Mn by reductive dissolution. Surface soil compaction at the 0.25 m distance from the riverbank was significantly greater for the unfenced than fenced reaches (Miller *et al.* 2014). Our field results were generally consistent with a laboratory incubation experiment conducted on a submerged, saline-sodic, surface (0–15 cm) soil from the streambank of the same fenced reach using anion PRS probes (Miller *et al.* 2016). They found significantly greater Fe (days 3 to 14) and Mn (day 3) adsorption for flooded soils amended with cattle manure compared to unamended control and root-amended soils. In addition, nutrients most sensitive to redox potential, Mn and Fe, also increased with compaction.
Amarawansha et al. (2015) also reported that Fe and Mn in soil porewater increased after flooding, and attributed this to reductive dissolution.

The lack of cattle-impact effect on NO$_3$-N adsorption was attributed to the masking effect of low NO$_3$-N in porewater due to high denitrification potential of the wet or saturated soil of the capillary fringe. The reduction in NO$_3$ in groundwater flowing through riparian soils of agricultural watersheds has been attributed to denitrification, plant uptake, and immobilization by microbes (Ranalli & Macalady 2010). Saturation of the soil may also inhibit nitrification (Nelson et al. 2007). Soil denitrification is enhanced by saturated and anaerobic conditions (Reddy & DeLaune 2008). Our NO$_3$-N findings were consistent with those of Miller et al. (2016). They reported no amendment or compaction effects on NO$_3$-N adsorption in PRS anion probes, and also attributed this to high denitrification potential.

The lowest NO$_3$-N adsorption rates in our study occurred in 2013 when the river water level increased after installation. Wetter soil conditions in 2013 may have enhanced denitrification and caused this low NO$_3$-N adsorption to anion probes. Our findings confirmed previous research that greater denitrification in the riparian zone protects water quality of rivers and streams by lowering soil NO$_3$ (Green & Kauffman 1989; Hill 1996; Ranalli & Macalady 2010; Vidon et al. 2010). In contrast, Miller et al. (2014) reported greater NO$_3$-N enrichment in surface (0–5 cm) soils of unfenced than fenced reaches, but the soil they sampled was aerobic and the exposed streambank where we installed the PRS probes was likely more anaerobic because of installation in the wet capillary fringe.

The absence of cattle-impact effect on P adsorption to anion probes in our study but significant amendment (manure) effects on P adsorption to ion probes in a laboratory incubation study (Miller et al. 2016) suggests that fecal deposition close to the riverbank in the field may not have been sufficient to elicit the influence of cattle-impacts. However, previous field studies that sampled the surface (0–5 cm) soil did detect cattle-impact effects on NH$_4$-N, NO$_3$-N, and soil test P (Miller et al. 2014). The PRS probes in the exposed streambank may not have been able to detect cattle-impact effects at the soil surface because of low mobility of P in calcareous soils (Havlin et al. 1999) which may have prevented P from reaching the probes that were installed in the capillary fringe of exposed streambank at a depth of 5 to 10 cm. In addition, P and other nutrients in the capillary fringe may be more dependent on river processes rather than land use on adjacent riparian soils.

Few cattle-impact or reach effects on nutrient adsorption in the exposed soil of the streambank may have been due to various factors. These may have been spatial and temporal variability, greater runoff than infiltration because of soil compaction, greater depth of probe installation,

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Exposed streambank mg m$^{-2}$ per burial length</th>
<th>Submerged streambank mg m$^{-2}$ per burial length</th>
<th>Treatment effect $P &gt; F$</th>
</tr>
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<tbody>
<tr>
<td>2014 (anion probes)</td>
<td></td>
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<tr>
<td>NO$_3$-N</td>
<td>1.8 ± 0.2</td>
<td>1.6 ± 0.2</td>
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<tr>
<td>Avail. P</td>
<td>1.7 ± 0.2</td>
<td>5.6 ± 1.3</td>
<td>0.0280*</td>
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<tr>
<td>Fe</td>
<td>215 ± 30.2</td>
<td>246 ± 31.1</td>
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<td>Mn</td>
<td>24.8 ± 6.9</td>
<td>21.5 ± 6.1</td>
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<tr>
<td>Cu</td>
<td>1.5 ± 0.5</td>
<td>0.1 ± 0.01</td>
<td>0.0292*</td>
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<tr>
<td>Zn</td>
<td>1.6 ± 1.5</td>
<td>0.3 ± 0.1</td>
<td>0.0009***</td>
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<td>S</td>
<td>649 ± 106</td>
<td>845 ± 97.3</td>
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<td>2015 (anion probes)</td>
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<tr>
<td>NO$_3$-N</td>
<td>6.3 ± 2.3</td>
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<td>Avail. P</td>
<td>2.4 ± 0.6</td>
<td>4.8 ± 1.0</td>
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</tr>
<tr>
<td>Fe</td>
<td>37.3 ± 15.8</td>
<td>450 ± 66.1</td>
<td>0.0006***</td>
</tr>
<tr>
<td>Mn</td>
<td>2.0 ± 0.5</td>
<td>20.7 ± 6.4</td>
<td>0.0334*</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9 ± 0.2</td>
<td>0.1 ± 0.03</td>
<td>0.0021**</td>
</tr>
<tr>
<td>Zn</td>
<td>0.8 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>0.0349*</td>
</tr>
<tr>
<td>S</td>
<td>242 ± 60.0</td>
<td>596 ± 116</td>
<td>0.0156*</td>
</tr>
<tr>
<td>2015 (cation probes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>3.0 ± 0.9</td>
<td>2.7 ± 0.5</td>
<td>0.8263</td>
</tr>
<tr>
<td>Ca</td>
<td>771 ± 166</td>
<td>1,707 ± 51.1</td>
<td>0.0030**</td>
</tr>
<tr>
<td>Mg</td>
<td>254 ± 31.0</td>
<td>495 ± 26.9</td>
<td>0.0014**</td>
</tr>
<tr>
<td>K</td>
<td>40.0 ± 9.7</td>
<td>15.3 ± 1.3</td>
<td>0.0524</td>
</tr>
<tr>
<td>Fe</td>
<td>2.5 ± 0.2</td>
<td>32.2 ± 8.0</td>
<td>0.0138**</td>
</tr>
<tr>
<td>Mn</td>
<td>0.6 ± 0.3</td>
<td>17.4 ± 3.1</td>
<td>0.0031**</td>
</tr>
</tbody>
</table>

Significance level (*P < 0.05, **P < 0.01, ***P < 0.001). N = 6 (number of sites). Adsorption values are mean ± standard error.
masking of grazing effects by anaerobic conditions, river processes and nutrient processes (e.g., denitrification), experimental design, and different sampling methods. No reach effects on major nutrients such as NO$_3$ were likely due to the masking effect of denitrification, and for P it was likely due to low mobility and depth of probe burial.

The wide range in adsorption, some isolated and extremely high maximum adsorption values, and high standard errors for NO$_3$, P, S, Fe, Mn, Cu, and Zn suggested that probe placement in relation to nutrient hot spots may have been an important factor contributing to lack of significant reach effects. Little research has simultaneously studied hot spots for multiple chemical constituents in riparian environments (Vidon et al. 2010), and IEMS are well suited for this. Nutrient hot spots are common in riparian zones (McClain et al. 2003), and have been documented for both N (McClain et al. 2003) and P (Vidon et al. 2010), but not for other minor nutrients. Nutrient hot spots in our study may have been caused by convergence of different hydrologic flow paths (e.g., hyporheic zone), episodic flow paths and precipitation-dissolution due to wet-dry cycles, non-uniform distribution of feces and urine by livestock, and sodic soil patches (McClain et al. 2003; Jacobs et al. 2007; Vidon et al. 2010). Sodic soil patches are common in the riparian zone of our study area (Miller et al. 2016). Our findings were consistent with previous studies that have reported nutrient hot spots in riparian zones, and suggested simultaneous hot zones for multiple nutrients.
Adsorption of P, Fe, Mn, S, Ca, and Mg to anion and cation probes were generally greater in submerged than exposed streambanks (Experiment 2), and the opposite trend generally occurred for Cu and Zn. Similar NO₃-N adsorption to anion probes in 2014 and 2015 was likely due to low NO₃-N supply caused by high denitrification potential in the capillary fringe of exposed streambank and to saturation in submerged soil. Nelson et al. (2007) also reported lower NO₃-N adsorption to PRS anion probes in flooded, saline-sodic soils from the upper streambank (0–15 cm) to high denitrification potential. In contrast, Wood et al. (2015) reported that NO₃-N adsorption did not vary along a moisture gradient in peatland soils.

For Experiment 2, significantly greater P adsorption occurred in submerged than exposed streambanks for anion probes in 2014 and 2015, and a similar trend was found for Fe and Mn adsorption for anion and cation probes in 2015, as well as for Ca and Mg on cation probes in 2015. These trends suggested possible reductive dissolution of Fe and Mn phosphates, as well as dissolution of Ca and Mg phosphates.

Significant positive correlations in the submerged streambank were generally found between P and Fe for anion probes in 2014 and 2015 (r = 0.56 to 0.58, P ≤ 0.05), and positive but not significant correlations occurred between P and Mn for anion probes and Fe in cation probes in 2015 (r = 0.54). Correlations between P and Mn for anion probes in 2014 and 2015 ranged from 0.28 to 0.39 (P > 0.05), and it was 0.46 (P > 0.05) between P (anion probes) and Mn (cation probes). Correlations between P (anion probes) and Ca or Mg (cation probes) were –0.37 (P > 0.05). These correlations suggested that reductive dissolution of Fe phosphates was likely a more dominant process in submerged streambanks than reductive dissolution of Mn phosphates or dissolution of Ca and Mg phosphates, and was consistent with previous findings (Amarawansha et al. 2015; Miller et al. 2016).

Greater reductive dissolution of Fe than Ca-Mg phosphates may have been related to their chemistry. Ortho-P in calcareous sediments is bound to Fe hydroxide rather than to CaCO₃ because the concentration of Fe hydroxide in a phase diagram has an effect on the equilibrium between ortho-P and Fe-phosphates, while CaCO₃ has no effect (Golterman 1988). In addition, the lower P adsorption in the exposed than submerged streambanks may have been due to more repeated cycles of wetting and drying, a decrease in sulfate-reducing bacteria, carbon limitations upon drying, aging of minerals, and transformation of P into more residual or occluded forms that were less available (Fabre 1992; De Groot & Fabre 1993; McDowell & Sharpley 2001).

Copper and Zn adsorption was significantly lower in the submerged than exposed soil for anion probes in 2014 and 2015. This suggested that sulfate reduction to sulfide under highly anaerobic conditions, and then formation of relatively insoluble Cu and Zn sulfides, may have caused lower concentrations under saturated and anaerobic conditions (Kadlec & Knight 1996; Reddy & DeLaune 2008). In addition, significantly greater adsorption of Cu and Zn in exposed than submerged soil may have implications for rainfall-induced runoff into the river. If the water level in the river dramatically lowers and exposes a gently sloping streambank to high-intensity rainfall, this may result in runoff of nutrients such as Cu and Zn from the exposed streambank into the river. Frey et al. (2015) reported that sloping and exposed sediments in rivers with low water levels could be a significant source of water pollution for reactive P and pathogenic bacteria.

Adsorption of Fe was much greater on anion than cation probes under both exposed and submerged conditions. Although both reduced and oxidized ionic Fe are cations, Fe is preferentially adsorbed by anion PRS probes due to the low mobility of the cation forms in soil and formation of ligands with ethylenediaminetetraacetic acid (EDTA) present on anion PRS probes (Liang & Schoenau 1995).

For the burial time study (Experiment 3), S was the only nutrient that showed a clear trend of increasing adsorption over time, and this resembled an exponential increase. In contrast, NO₃-N, P, Fe, Mn, Cu, and Zn did not show any consistent increase or decrease, and exhibited considerable variability among locations (replicates). Maximum adsorption was highest for S (1,199 mg m⁻²), followed by Fe (165 mg m⁻²), NO₃-N and Mn (8.0–8.3 mg m⁻²), and then Cu and Zn (0.8–0.9 mg m⁻²).
maximum adsorption of nutrients occurred most quickly for NO₃⁻N and Mn (0.2 d), followed by Cu and Zn (1 d), Fe (7 d), and was longest for S (14 d). Burial for 7 days was sufficient for impacts of streambank conditions on nutrient levels to be determined.

High S adsorption that increased with time indicated that the streambank was likely a significant source of S to the river. Assuming similar background S levels in PRS probes at day 0, Miller et al. (2016) also reported an exponential increase in S over 14 days in a laboratory incubation experiment on a saline-sodic, surface soil obtained from the fenced reach. Saline seeps or saline-sodic soils occur as patches along the streambank of our study (Miller et al. 2016). The dominance of sulfate salts in this region (Rodvang et al. 2002) likely contributed to high S adsorption in the streambanks. Our finding that the exposed soil of streambank was acting as a source of S was consistent with others (Nelson et al. 2007; Miller et al. 2016). In contrast, Kreiling et al. (2015) reported an increase followed by decrease in S supply with time along an increasing moisture gradient in the floodplain of the Mississippi River. The high S adsorption in our streambank soils suggests that saline or saline-sodic patches may have been a major influence of nutrient dynamics in these streambanks. The linkage between uplands and riparian zones is strongly dependent on saline or sodic patch characteristics, which enhance or diminish the flow of material such as nutrients (Jacobs et al. 2007).

CONCLUSIONS

Overall, few effects were found on nutrient dynamics using IEMs among reaches varying in cattle impact. Future research could install the PRS probes into the surface soil where cattle-impact effects might be more detectable, but they would have to be installed in such a way as to prevent damage by cattle (for example, at a 45° angle, or with a protective cover). The wide range and high spatial variability in nutrient adsorption for NO₃⁻, P, S, Fe, Mn, Cu, and Zn (Experiment 1) was consistent with previous studies that have reported nutrient hot spots in riparian zones. In addition, these findings suggested simultaneous hot spots for multiple nutrients, which has generally not been reported. Also, IEMs were well suited for detecting hot spots for multiple nutrients.

Certain nutrients such as P, Fe, Mn, S, Ca, and Mg were greater in submerged than exposed banks, and the reverse trend occurred for Cu and Zn. This suggested a potential for greater release of these nutrients to the river water if the streambank soil is submerged. In contrast, rainfall-induced runoff from exposed streambanks might enhance Cu and Zn transport into the river under low flow conditions. However, further research is required to study the possible relationship between nutrient adsorption in the soil and flux or release of nutrients into the water.

Maximum nutrient adsorption generally occurred within 1 to 7 days, and S adsorption showed an exponential increase with time. This suggested that the exposed streambank might be acting as a source of sulfate to the adjacent river, and was consistent with the prevalence of saline seeps along the streambank. Further research could examine the effect of burial time in submerged streambanks, as well as different burial times. In addition, future research could install PRS probes in streambank soils that are non-saline, non-sodic, saline, sodic, and saline-sodic to examine the influence of salinity and sodicity on nutrient dynamics in streambanks of riparian zones. Finally, PRS probes were found to be useful for in situ monitoring of nutrient dynamics of multiple chemicals within streambanks.

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