Nitrate leaching from Kentucky bluegrass soil columns predicted with anion exchange membranes

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Ideal nitrogen (N) management for turfgrass supplies sufficient N for high-quality turf without increasing N leaching losses. A greenhouse study was conducted during two 27-wk periods to determine if in situ anion exchange membranes (AEMs) could predict nitrate (NO$_3$–N) leaching from a Kentucky bluegrass (Poa pratensis L.) turf grown on intact soil columns. Treatments consisted of 16 rates of N fertilization, from 0 to 98 kg N ha$^{-1}$ mo$^{-1}$. Percolate water was collected weekly and analyzed for NO$_3$–N. Mean flow-weighted NO$_3$–N concentration and cumulative mass in percolate were exponentially related ($\text{pseudo-}R^2 = 0.995$ and 0.994, respectively) to AEM desorbed soil NO$_3$–N, with a percolate concentration below 10 mg NO$_3$–N L$^{-1}$ corresponding to an AEM soil NO$_3$–N value of 2.9 µg cm$^{-2}$ d$^{-1}$. Apparent N recovery by turf ranged from 28 to 40% of applied N, with a maximum corresponding to 4.7 µg cm$^{-2}$ d$^{-1}$ AEM soil NO$_3$–N. Turf color, growth, and chlorophyll index increased with increasing AEM soil NO$_3$–N, but these increases occurred at the expense of increases in NO$_3$–N leaching losses. These results suggest that AEMs might serve as a tool for predicting NO$_3$–N leaching losses from turf.

Abbreviations: AEM, anion exchange membrane; CIE, Commission Internationale de l’ Eclairage; MCL, maximum contaminant level

There is concern about the negative impacts on surface and groundwater quality of N losses from turf areas. These concerns are becoming more acute with the expansion of urban and suburban areas that may be dominated by managed turf areas. No soil test for N is commonly used in humid climates to guide N applications to turfgrass. Instead, turfgrass is often fertilized according to a predetermined schedule or according to expected quality response of the turf. However, scheduled N fertilizer applications do not take into account plant available N added to the soil by mineralization or residual mineral N from previous applications. Because scheduled applications are not adjusted for existing available N, applied N may be in excess of plant needs. Under common soil conditions, excess labile soil N may be converted to NO$_3$–N and become subject to leaching. The goal of turfgrass N fertilization is to apply sufficient N to achieve high-quality turf without the accumulation of excess soil N that could lead to higher N leaching losses.

A decrease in apparent N recovery at higher N fertilizer application rates has been noted in cool-season mixed species turfs (Kopp and Guillard, 2002a; Fitzpatrick and Guillard, 2004) and in sand-based creeping bentgrass (Agrostis stolonifera L.) turf (Huang and Petrovic, 1994). This effect has been noted also in orchardgrass (Dactylis glomerata L.), tall fescue (Festuca arundinacea Schreb.), and smooth bromegrass (Bromus inermis Leyss.) grass hay fields (Guillard et al., 1995a; Zemenchik and Albrecht, 2002; Hall et al., 2003; Singer and Moore, 2003). Furthermore, higher residual soil NO$_3$–N resulting from higher N application rates has been noted in grass hay fields (Guillard et al., 1995b; Hall et al., 2003; Singer and Moore, 2003). Higher rates of N application coupled with lower N recovery, which result in higher concentrations of residual soil NO$_3$–N, suggest that NO$_3$–N leaching is increased at high rates of N application. Increased NO$_3$–N leaching from turf with higher rates of N application has been noted (Morton et al., 1988; Mancino and Troll, 1990; Huang and Petrovic, 1994; Kopp and Guillard, 2005; Frank et al., 2006). However, soil NO$_3$–N available for leaching is decreased by microbial immobilization, plant uptake, and other losses and is augmented by mineralization of N-bearing organic matter. A measurement of available soil NO$_3$–N may serve as a better predictor of NO$_3$–N leaching than would N application rate.

Anion exchange membranes (AEMs) have been used in situ to estimate available soil N in a variety of crops and soils (Pare et al., 1995; Qian and Schoenau, 1995; Vander et al., 1995; Ziadi et al., 1999; Koehn et al., 2002). Soil NO$_3$–N desorbed from AEMs has been used as a predictor of perennial grassland yield (Collins and Allinson, 1999) and has been related to clipping yield, visual quality, and color in turfgrasses (Kopp and Guillard, 2002b; Mangiafico and Guillard, 2005; Mangiafico and Guillard, 2006b). In these studies, Cate–Nelson, linear plateau, and quadratic plateau models were used to indicate critical values of AEM-desorbed soil NO$_3$–N. There was a low probability of further turfgrass response to additional AEM-desorbed soil NO$_3$–N above these critical values. The implication of these studies was that soil NO$_3$–N added in excess of these critical AEM soil NO$_3$–N values, if not taken up by plants or immobilized by microbes, might be subject to leaching losses. No study has attempted to correlate AEM-measured soil NO$_3$–N with NO$_3$–N leaching losses from turfgrass.

Objective color measurements of turf can be made with hand held reflectance meters. Commission Internationale de l’ Eclairage (CIE) hue and lightness measurements from tristimulus chroma meters have been correlated with visual color assessments in bentgrass (Agrostis stolonifera L., A. capillaries L.) (Landschoot and Mancino, 2000), with foliar N concentration in creeping bentgrass (Landschoot and Mancino, 1997), and with chlorophyll concentration in clippings of Kentucky bluegrass and creeping red fescue.
Phosphorus as aqueous KH₂PO₄ and K as aqueous KH₂PO₄ and aqueous NH₄NO₃ was applied at seeding at a rate of 12.2 kg N ha⁻¹. Nitrogen was applied as aqueous NH₄NO₃.

The soil had a pH of 6.9, organic matter concentration of 29.1 g kg⁻¹, and 5.52 mg kg⁻¹ CaCl₂ extractable NO₃⁻N after initial fertilization at seeding. In April 2003 and April 2004, columns were seeded with Kentucky bluegrass blend (60% ‘Midnight’, 20% ‘Apollo’, 20% ‘Rambo’ by weight) (LESCO, Inc., Strongsville, OH). Treatments consisted of 16 rates of N fertilization: 0, 4.9, 9.8, 14.7, 19.6, 24.5, 29.3, 34.2, 39.1, 44.0, 48.9, 58.7, 68.5, 78.2, 88.0, and 97.8 kg N ha⁻¹ mo⁻¹ from May to October, 2003 and 2004, for a total of between 0 and 587 kg N ha⁻¹ yr⁻¹. After turf establishment, irrigation was applied at 2.5 cm wk⁻¹ from May to November. Turf was grown in a greenhouse under natural light. A whitewash shading compound (Continental Products Co., Euclid, OH) was applied to the greenhouse roof and walls each April and removed each October, resulting in a 38% reduction in light intensity during this period. Automated controls in the greenhouse were set for a temperature range of 16 to 24°C. Hydrogen dioxide (Biosafe Systems, Glastonbury, CT) was applied to the greenhouse roof and walls each April and removed each October.

The purpose of this study was to determine if soil NO₃⁻N desorbed from AEMs might serve as a predictor of NO₃⁻N leaching from turfgrass.

**MATERIALS AND METHODS**

**Experimental Design and Management**

A greenhouse study was conducted at the Plant Science Teaching and Research Farm at the University of Connecticut in Storrs, CT. Sixty-four intact soil columns were arranged in randomized complete block design and seeded to a Kentucky bluegrass blend (60% ‘Midnight’, 20% ‘Apollo’, 20% ‘Rambo’ by weight) (LESCO, Inc., Strongsville, OH). Treatments consisted of 16 rates of N fertilization: 0, 4.9, 9.8, 14.7, 19.6, 24.5, 29.3, 34.2, 39.1, 44.0, 48.9, 58.7, 68.5, 78.2, 88.0, and 97.8 kg N ha⁻¹ mo⁻¹ from May to October, 2003 and 2004, for a total of between 0 and 587 kg N ha⁻¹ yr⁻¹. Nitrogen was applied as aqueous NH₄NO₃.

Soil columns of an Agawam fine sandy loam (coarse-loamy over sandy or sandy-skeletal, mixed, active, mesic Typic Dystrudepts) were obtained following spring. This was done to limit mineralization and immobilization of N in the soil columns during the winter.

**Percolate Collection and Anion Exchange Membranes**

Percolate volumes in the collection vessels were measured gravimetrically weekly from April to November, 2003 and 2004. Subsamples were stored at 4°C and analyzed within 48 h for NO₃⁻N concentration on a Scientific Instruments continuous flow analyzer (WESTCO, Danbury, CT) using the Griess–Ilosvay method (Keeney and Nelson, 1982). When concentrations were below the nominal detection limit of 0.05 mg L⁻¹, a value of half the detection limit was recorded. This was appropriate because the frequency of samples with concentrations below the detection limit was 2.8% of total samples (USEPA, 2000). Mass loss was calculated as the product of percolate NO₃⁻N concentration and volume.

Sampling of available soil NO₃⁻N with AEM strips (Ironics, Inc. Watertown, MA) was conducted every 2 wk from May 2003 to October 2003 and from May 2004 to October 2004 for a total of 24 sampling dates. A large sheet of type-204 vinyl copolymer AEM fabric was cut into strips measuring 7.6 cm tall by 2.5 cm wide. Strips were prepared by shaking in 0.5 M HCl for 5 min, rinsing in deionized water, saturating with Cl⁻ ions by shaking for 2 h in 1 M NaCl, and rinsing again in deionized water. Strips were stored in deionized water until use.

Anion exchange membrane strips were inserted into the soil by making a slit at an angle of approximately 15° from vertical with a mason’s trowel. An AEM strip was inserted so that the top of the AEM was at the soil surface. Hand pressure was used to close the slit and ensure soil contact with the AEM. A monofilament line and flagging tape were attached to each AEM to facilitate removal. After 2 wk, the strips were removed, and new strips were inserted. A new slit was made in a different location in the soil column each time a new AEM was inserted. Upon removal from columns, the AEMs were rinsed lightly with deionized water and placed individually in 60 mL HDPE bottles containing 25 mL of 1 M NaCl. These bottles were transported immediately to the laboratory and shaken for 1 h to desorb NO₃⁻N from the AEMs. The resultant extracts were filtered through papers having a retention range of 8 to 12 µm (Schleicher and Schuell, Keene, NH). Extracts were stored at 4°C and analyzed within 48 h for NO₃⁻N. When concentrations were below the nominal detection limit of 0.05 mg L⁻¹, a value of half the detection limit was recorded. The frequency of samples with concentrations below the detection limit was 1.2% of total samples.

**Turf Chlorophyll Index, Color, Yield, and Tissue Nitrogen**

Chlorophyll index measurements were taken with the Spectrum CM1000 reflectance meter on 24 dates during the experiment corresponding to the AEM sampling dates. Ten chlorophyll index measurements per...
column of the turf canopy were taken and averaged per column. All measurements were taken between 1000 h and 1400 h with the meter facing away from the sun. Measurements were taken holding the meter approximately 30 cm from the turf canopy, yielding a circular area of evaluation of approximately 1.3 cm² per measurement. A Minolta CR-400 chroma meter (Konica Minolta Holding, Inc., Tokyo, Japan) was used to measure CIE hue and CIE lightness of the turf blades. For each measurement, fresh leaves were laid flat into an optically dense stack. A color measurement was taken in CIE L* a* b* coordinates at illuminant condition C. The leaf blades were then randomly rearranged in the stack, and another measurement was taken. This measurement was repeated for five measurements for each column. Values of L*, a*, and b* were averaged per column and converted to CIE hue and CIE lightness values (McGuire, 1992). Turf was clipped every 2 wk to a height of 3.8 cm. All clippings were collected, dried at 71°C for 48 h, and weighed. Turf tissue was ground in a UDY Cyclone mill (UDY Corp., Ft. Collins, CO) to pass through a 0.5-mm screen. Ground tissue samples were bulked for each column across all sample dates and analyzed for total N by persulfate digestion (Purell and King, 1996) and subsequent NO₃–N determination (Keeney and Nelson, 1982).

**Statistical Analysis**

Mean AEM soil NO₃–N value across dates was plotted against N application rate, and a linear regression was developed. Mean flow-weighted percolate NO₃–N concentration and cumulative mass across dates were calculated for each treatment. The fraction of applied N collected in percolate was calculated as the cumulative mass loss minus the cumulative mass loss for the 0 N treatment divided by the total amount of N applied. Mean flow-weighted percolate NO₃–N concentration, cumulative mass loss, and fraction mass loss were plotted against mean AEM desorbed soil NO₃–N, and exponential \( y = a + be^{cx} \) models were generated.

Cumulative N uptake was calculated for each treatment as the product of tissue N concentration and cumulative clipping yield across all sampling dates. Because tissue N concentration was determined on yield-weighted bulked samples, calculated N uptake was an unbiased estimate for actual N uptake. Apparent N recovery was calculated as the cumulative N uptake minus the cumulative uptake for the 0 N treatment divided by total amount of N applied. Cumulative N uptake and apparent N recovery were each plotted against mean AEM soil NO₃–N, and a Gaussian curve model \( y = a + b(e^{-0.5(x-b)^2}) \) was developed for each. In the absence of any theoretical models, this model was chosen because it fit the data well and indicated x-axis values at which y-axis values were maximized.

Mean chlorophyll index, hue, lightness, and yield values across dates were plotted against mean AEM NO₃–N values, and a curvilinear Mitscherlich–Bray model \( y = a - be^{-cx} \) was fit to each (Dahnke and Olson, 1990). Linear and curvilinear models were generated with the GLM or NLIN procedures in the Statistical Analysis Software package (SAS Institute, 1999) and were checked for homoscedasticity, normality of residuals, and independence of residuals (Tabachnick and Fidell, 2001).

**RESULTS AND DISCUSSION**

**Application Rate and Anion Exchange Membrane Soil Nitrate**

Mean AEM-desorbed soil NO₃–N was significantly \( p < 0.05 \) linearly related to N application rate (Fig. 1). This result corroborates results of previous studies that found significant relationships between AEM-desorbed soil NO₃–N and N application rate (Collins and Allinson, 1999; Kopp and Guillard, 2002b; Mangiafico and Guillard, 2006b). The reciprocal of the slope of this regression line gives some indication of the amount of additional N fertilizer required to realize a marginal increase in AEM-desorbed soil NO₃–N, about 11 kg N ha⁻¹ mo⁻¹ for each \( \mu g \) cm⁻² d⁻¹ for the conditions of this experiment. However, because the data for this relationship are averaged across sample dates from two growing seasons and because the response of AEM-desorbed NO₃–N to N application rate is affected by plant uptake, leaching losses, and microbial immobilization, this relationship may not hold on all sample dates or conditions.

**Percolate Nitrate Concentration and Mass**

Percolate was collected from at least some soil columns on 35 of 56 (63%) sample dates. Dates when no percolate was collected tended to be in summer months, presumably when evapotranspiration exceeded irrigation rate. In results from field studies that present NO₃–N leaching across time, periods in which no percolate was collected are evident (Guillard and Kopp, 2004; Mangiafico and Guillard, 2006a; Frank et al., 2006).

Significant exponential \( (p < 0.05) \) models were found relating percolate flow-weighted mean NO₃–N concentration, cumulative NO₃–N mass in percolate, and cumulative mass as fraction of N applied to AEM-desorbed soil NO₃–N (Fig. 2). A mean percolate NO₃–N concentration below the EPA maximum contaminant level (MCL) for drinking water of 10 mg NO₃–N L⁻¹ was found for a mean AEM soil NO₃–N value of 2.9 \( \mu g \) cm⁻² d⁻¹ (Fig. 2A). Similarly, based on the curvature of the model, Fig. 2B suggests moderate cumulative percolate NO₃–N mass when AEM soil NO₃–N values did not exceed about 3 \( \mu g \) cm⁻² d⁻¹. The fraction of applied N collected as NO₃–N in the percolate generally increased as AEM soil NO₃–N increased (Fig. 2C). As a percent of N applied, mass loss in percolate predicted by the exponential model ranged from about 7 to 28% across treatments (Fig. 2C). Because percolate NO₃–N concentrations of environmental concern may be much lower than the USEPA MCL for drinking water (Pierzynski et al., 2000), target soil NO₃–N values should probably be lower than those producing percolate concentrations close to the USEPA MCL.
Considering N application rates, our percolate NO$_3$–N concentrations are comparable to those presented by Frank et al. (2006) for a field study with an established Kentucky bluegrass turf. They reported flow-weighted concentrations of 4 and 21 mg NO$_3$–N L$^{-1}$ for 98 and 245 kg N ha$^{-1}$ yr$^{-1}$ applied, respectively. Our flow-weighted concentrations at similar rates were 6.7 and 11 mg NO$_3$–N L$^{-1}$, respectively. Also, our percolate concentration results are similar to those presented by Geron et al. (1993) for the first year after seeding of Kentucky bluegrass for a comparable N application rate. In general, though, our percolate NO$_3$–N concentrations are notably higher than other field studies, which reported mean concentrations up to 4.6 mg L$^{-1}$ for up to 244 kg N ha$^{-1}$ yr$^{-1}$ applied (Morton et al., 1988; Geron et al., 1993; Miltner et al., 1996; Guillard and Kopp, 2004; Mangiafico and Guillard, 2006a). Because our flow-weighted average for percolate NO$_3$–N concentration was greater than 3 mg NO$_3$–N L$^{-1}$ for our 0 N application treatment, our percolate NO$_3$–N concentration results may be elevated relative to some studies due to differences in N mineralization potential of the soil. If this is the case, it supports the argument that NO$_3$–N leaching losses may be better predicted by some measurement of excess soil NO$_3$–N than by N application rate alone. Fewer field studies reported mass losses for NO$_3$–N in percolate, but our value of 28 kg N ha$^{-1}$ yr$^{-1}$ loss at 147 kg N ha$^{-1}$ yr$^{-1}$ applied is similar to reported values for comparable rates by field studies in our area (Guillard and Kopp, 2004; Mangiafico and Guillard, 2006a).

**Nitrogen Uptake, Recovery, and Use Efficiency**

Significant ($p < 0.05$) Gaussian curve models were found relating cumulative N uptake in clippings and apparent N recovery to mean AEM-desorbed soil NO$_3$–N (Fig. 3). Cumulative N uptake increased with increasing AEM soil NO$_3$–N to a model-predicted maximum at 8.2 μg cm$^{-2}$ d$^{-1}$ of AEM soil NO$_3$–N (Fig. 3A). This trend is in agreement with studies that found increasing N uptake with increasing rates of N application (Kopp and Guillard, 2002a; Fitzpatrick and Guillard, 2004). Apparent N recovery ranged from 28 to 40% of applied N, with a maximum corresponding to 4.7 μg cm$^{-2}$ d$^{-1}$ AEM soil NO$_3$–N (Fig. 3B). This trend differs from studies that found monotonically decreasing apparent N recovery with increasing rates of N application (Kopp and Guillard, 2002a; Fitzpatrick and Guillard, 2004). These results suggest that increased leaching losses may be a result of less efficient recovery of N by turf when AEM soil...
NO₃–N was above 4.7 \( \mu g \) cm\(^{-2} \) d\(^{-1}\). Below this value, however, increased leaching losses occurred with increasing AEM soil NO₃–N leaching in spite of more efficient recovery. Values for cumulative N uptake and apparent N recovery included N collected only from clippings and do not include N in roots, rhizomes, or verdure.

**Turf Chlorophyll Index, Color, and Yield**

Significant \((p < 0.05)\) Mitscherlich–Bray models were found relating mean chlorophyll index, hue, lightness, and yield measurements to mean AEM-desorbed soil NO₃–N (Fig. 4). A higher CM1000 index implies a higher leaf chlorophyll concentration. A higher CIE hue in this range implies a greener leaf color. A lower CIE lightness implies a darker leaf color. Marginal changes in these variables with increases in AEM soil NO₃–N were greatest at low AEM soil NO₃–N values. However, these variables continued to change with increasing AEM soil NO₃–N at high AEM soil NO₃–N values. Color (Fig. 4C and 4D) and chlorophyll (Fig. 4A) development for our turf stand occurred at the expense of increases in NO₃–N leaching losses (Fig. 2).

This effect was especially pronounced at high AEM soil NO₃–N values when incremental additions of soil NO₃–N increased turf color and chlorophyll only slightly but increased NO₃–N leaching losses exponentially. Considering this, water quality concerns would dictate that turf N application should be managed to achieve acceptable quality for intended turf use and conditions but not to attempt to maximize turf color response.

**CONCLUSIONS**

Soil NO₃–N desorbed from in situ AEMs was found to be a predictor for cumulative NO₃–N mass and flow-weighted NO₃–N concentration in percolate water collected from intact soil columns. Because percolate NO₃–N flow-weighted concentration and cumulative mass were exponentially related to AEM soil NO₃–N, water quality concerns dictate minimizing excess soil NO₃–N when possible. Increases in NO₃–N leaching losses occurred with increases in AEM-desorbed soil NO₃–N despite increases N uptake by turf. Turfgrass color, chlorophyll index, and growth increased with increasing AEM soil NO₃–N. These increases, however, were achieved at the expense of increases in NO₃–N leaching. These results caution against managing nitrate N application to achieve color development beyond the requirements of the intended use of a specific turf stand. Our results suggest that AEMs might serve as a tool for predicting NO₃–N leaching losses from turfgrass.

Factors influencing NO₃–N leaching from turfgrass include soil type, irrigation, N source, N rates, and N application timing (Petrovic, 1990). Although AEMs may capture soil NO₃–N available for uptake or leaching, it is unclear how factors such as soil type or irrigation rate affect the relationship between NO₃–N leaching and measured AEM soil NO₃–N. Because soil NO₃–N is delivered to AEMs by mass flow and diffusion, low soil moisture contents may cause AEMs to underpredict the amount of soil NO₃–N subject to leaching. Likewise, a continual wetting front at the depth of the AEM may deliver soil NO₃–N to the AEM at a high rate, even if the nitrate leaching of that soil is relatively low.

Results of this study are limited by its greenhouse experimental conditions. For example, Geron et al. (1993) found seasonal effects on NO₃–N leaching from Kentucky bluegrass turf to be greater than effects of fertilizer program or N source; our greenhouse study could not accurately mimic seasonal changes. The ability of AEMs to predict soil NO₃–N leaching should be examined under field conditions to assess the robustness of the technique to variations in soil moisture and precipitation events and under a variety of climates, turf species, and soil types.

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