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# RELATIONSHIPS BETWEEN SOIL NITRATE DESORBED FROM ANION-EXCHANGE MEMBRANES, CANOPY REFLECTANCE, AND NITRATE LEACHING LOSSES FROM COOL-SEASON LAWN TURF

Thomas J. Barry, Karl Guillard\*, and Salvatore S. Mangiafico

## ABSTRACT

Nutrient leaching studies are expensive and require expertise in water collection and analyses. Less expensive or easier methods that estimate leaching losses would be desirable. The objective of this study was to determine if anion-exchange membranes (AEMs) and reflectance meters could predict nitrate ( $NO_3$ –N) leaching losses from a cool-season lawn turf. A two-year field study used an established 90% Kentucky bluegrass (Poa pratensis L.)-10% creeping red fescue (Festuca rubra L.) turf that received 0 to 98 kg N ha<sup>-1</sup> month<sup>-1</sup>, from May through November. Soil monolith lysimeters collected leachate that was analyzed for NO<sub>3</sub>-N concentration. Soil NO<sub>3</sub>–N was estimated with AEMs. Spectral reflectance measurements of the turf were obtained with chlorophyll and chroma meters. No significant (p > 0.05) increase in percolate flow-weighted NO<sub>3</sub>-N concentration (FWC) or mass loss occurred when AEM desorbed soil NO<sub>3</sub>–N was below 0.84  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>. A linear increase in FWC and mass loss (p < 0.0001) occurred, however, when AEM soil NO<sub>3</sub>–N was above this value. The maximum contaminant level (MCL) for drinking water (10 mg L<sup>-1</sup> NO<sub>3</sub>-N) was reached with an AEM soil NO<sub>3</sub>-N value of 1.6  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>. Maximum meter readings were obtained when AEM soil NO<sub>3</sub>-N reached or exceeded 2.3  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>. As chlorophyll index and hue angle (greenness) increased, there was an increased probability of exceeding the NO<sub>3</sub>–N MCL. These data suggest that AEMs and reflectance meters can serve as tools to predict NO<sub>3</sub>–N leaching losses from coolseason lawn turf, and to provide objective guides for N fertilization.

**Abbreviations:** AEMs, anion exchange membranes; FWC, flow-weighted concentration; MCL, maximum contaminant level

**Keywords:** ion exchange technology, NO<sub>3</sub>–N leaching, soil NO<sub>3</sub>–N, turf color, spectral reflectance, nutrient management

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## **INTRODUCTION**

Quantifying nutrient leaching from turfgrass systems is expensive. There are costs for the installation and maintenance of lysimeters, sample collection parts and equipment, and labor required for sample collection and analyses. Some background in water science and the protocols regarding water sample collection, handling, and analyses is required for these types of experiments. These constraints and costs of water research conducting limit the practicality of extensive efforts in turfgrass leaching studies.

As an alternative to water collection, inferences about nutrient leaching potential in turf systems have been attempted by measuring soil extractable nutrients. particularly soil NO<sub>3</sub>-N (Rieke and Ellis, 1975; Exner et al., 1991; Higby and Bell, 1999; Miltner et al., 2001; Lee et al., 2003). The reasoning is that if soil NO<sub>3</sub>–N is high, then chances of NO<sub>3</sub>-N leaching are high when conditions limit plant uptake of NO<sub>3</sub>-N or when excess water induces percolation past the rootzone. However, there have been few turf studies that have directly correlated soil NO<sub>3</sub>–N concentrations to actual measurements of leachate NO<sub>3</sub>-N concentrations or losses. Of those studies that measured both soil NO<sub>3</sub>-N and leachate or soil pore water NO3-N concentrations, too few soil samplings were determine anv definitive taken to relationship (Gross et al, 1990; Bushoven et al., 2000), or no direct correlations were attempted (Hayes et al., 1990; Jiang et al., 2000). However, in these studies treatments with higher soil NO<sub>3</sub>-N concentrations tended to have overall higher NO<sub>3</sub>-N leaching losses, suggesting a functional relationship. positive Α correlation (r = 0.779, p = 0.0079) between soil NO<sub>3</sub>-N and log<sub>10</sub> pore water NO<sub>3</sub>–N concentrations

was observed for various landscape plants (including turf) in a climate and soil similar to ours (Amador et al., 2007). In agricultural cropping systems, elevated soil NO<sub>3</sub>–N concentrations or contents have been positively correlated with measured NO<sub>3</sub>–N leaching losses from collected percolate (Allaire-Leung et al., 2001; Williams et al., 2005).

A significant disadvantage in using extractable soil NO<sub>3</sub>-N concentration as a predictor of NO<sub>3</sub>–N leaching, however, is that soil sampling consists of point-in-time measurements; fluxes of NO<sub>3</sub>-N are not measured between samplings. These pointin-time measurements do not account for the dynamics of nutrient release and transport (Curtin et al., 1987; Abrams and Jarrel, 1992). Between samplings, soil NO<sub>3</sub>-N concentrations can vary due to leaching, denitrification, plant uptake, microbial transformations, atmospheric deposition, or additions from irrigation water. Consequently, the functional relationship between soil NO<sub>3</sub>–N and leaching may not be accurately estimated with infrequent point-in-time measurements.

Anion-exchange membranes function as a dynamic exchanger system that account for changes in ion can concentrations in the soil solution (Cooperband and Logan, 1994). They provide a more reliable measure of soil NO<sub>3</sub>–N fluxes than do traditional soil extraction methods due to their dynamic exchange properties and their ability to assess in situ NO<sub>3</sub>-N fluxes across a given period (Wander et al., 1995). Since they remain in contact with the soil between collection times, with new ones inserted when older ones are removed, AEMs are able to provide a continuous measure of plant-available soil NO<sub>3</sub>–N. They also have advantages over exchange-resin bags or

capsules. Unlike exchange-resin bags or capsules, very little soil disturbance occurs when AEMs are deployed, and there is less concern about internal and external diffusion differences that could be found within the resin beads or capsules (Cooperband and 1994). Also, following Logan, ion desorbtion, membranes can be reused after exchange sites are recharged. Soil NO<sub>3</sub>-N desorbed from AEMs has been related to turfgrass clipping yield, visual quality, color (Kopp and Guillard, 2002; Mangiafico and Guillard, 2005; Mangiafico and Guillard, 2006b), and N uptake in the clippings (Mangiafico and Guillard, 2007a).

Although anion-exchange resins contained in bags or capsules have been used in turf leaching studies (Petrovic, 2004; Sullivan and Jiang, 2004), few studies have evaluated AEMs as a predictor of NO<sub>3</sub>-N leaching losses. In a greenhouse soil column study, NO<sub>3</sub>-N leaching losses from a Kentucky bluegrass turf grown on a fine sandy loam soil were highly correlated to time-weighted AEM desorbed soil NO<sub>3</sub>-N values (Mangiafico and Guillard, 2007a). Field NO<sub>3</sub>-N leaching losses from Kentucky bluegrass and perennial ryegrass (Lolium perenne L.) plots were quantified using AEMs, and results indicated that most losses occurred during the first year of establishment (Easton and Petrovic, 2004). As far as we are aware, these are the only published studies where anion-exchange membranes were used as predictors of NO<sub>3</sub>-N leaching from turf. Inferences about nitrate leaching potential in field potato (Solanum tuberosum L.) have been made relative to а cumulative NO<sub>3</sub>-N availability index based on desorbed soil NO<sub>3</sub>-N AEMs (Whitley from and Davenport, 2003).

Objective assessment of turfgrass response to N has been reported using tristimulus chroma meters. Hue angle measured with this instrument was found to be correlated with foliar N concentrations of creeping bentgrass (Agrostis stolonifera L.) (Landschoot and Mancino, 1997) and bluegrass (Mangiafico Kentucky and Guillard, 2007b). Tristimulus chroma meter measurements have also been correlated with chlorophyll concentration and clipping yield in a Kentucky bluegrass-creeping red (Festuca rubra fescue L.) mixture (Mangiafico and Guillard, 2005), and with AEM desorbed soil NO<sub>3</sub>-N (Mangiafico and Guillard, 2006b).

Spectral reflectance readings of various cool- and warm-season turfgrass species, using different spectroradiometry instruments, have been used to quantify variables associated with N status in turfgrass: color, chlorophyll concentration, clipping yields, soil NO<sub>3</sub>-N, and leaf N concentrations (Rodriguez and Miller, 2000; Trenholm et al., 2001; Karcher and Richardson, 2003; Keskin et al., 2004; Bell et al., 2004; Mangiafico and Guillard, 2005; Volterrani et al., 2005; Stiegler et al., 2005; Mangiafico and Guillard, 2006a; Kruse et al., 2006; Mangiafico and Guillard, 2007b; Walker et al., 2007; Xiong et al., 2007).

Current technologies for AEMs and spectral reflectance have been shown to be reliable and relatively rapid for objective measurements associated with turfgrass N Therefore. they should status. have applicability in predicting NO<sub>3</sub>-N leaching losses from turf. The purpose of this study was to determine: (i) if in situ AEMs could serve as a predictor of NO<sub>3</sub>-N leaching from lawn turf, and (ii) the relationship between turf canopy reflectance and NO<sub>3</sub>-N leaching under lawn management.

# MATERIALS AND METHODS

# **Experimental Design and Management**

A field experiment was conducted at the University of Connecticut in Storrs, USA, across two Connecticut, years (2004-05 and 2005-06). The site was established in the summer of 2000 with a 90% Kentucky bluegrass and 10% creeping red fescue sod and contained soil monolith lysimeters (Mangiafico and Guillard, 2006a). The lysimeters included barrels made of high-density polyethylene, 56-cm in diameter and 86-cm deep. Attached to the barrels were polyvinyl chloride (PVC) fittings and 1.3-cm diameter polyethylene tube leading to a collection vessel made of PVC vented pipe. The barrels were pitched so that any water collected would run down the tube into the collection vessel. All of the barrels were lined with woven fiberglass fabric to prevent soil from moving into the collection vessel. There were fourteen lysimeters, with one lysimeter in each plot. The site was hand weeded and overseeded with Kentucky bluegrass at the beginning of 2004. Fourteen turf plots measuring 1.4 by 2.4 m each were arranged in a completely random design with 7 N-rate treatments (0, 9.8, 19.6, 29.3, 39.1, 48.9, and 97.8 kg N ha<sup>-1</sup> mo<sup>-1</sup>) and 2 replicates. Nitrogen treatments were applied monthly from May through November using a 30-1.7-3.2 (N-P-K)commercial lawn fertilizer (Greenview Green Power. Lebanon Seaboard Corp., Lebanon, Pennsylvania, USA), corresponding to total yearly amounts of 0, 68.6, 137.2, 205.1, 274, 342.3, and 684.6 kg N ha<sup>-1</sup>, respectively. This fertilizer had 74% of N as urea, 9% as  $NH_4^+$ , and 17% as water-insoluble N. Additional P as triple superphosphate and K as KCl were applied so that all plots received equal amounts of P and K, based on the P and K amounts that were applied with the highest N rate 73.0 kg  $ha^{-1}$ . treatment (38.8 and

respectively). Turf plots were maintained as a lawn and mowed weekly at a height of 4.5 cm. A hand-reel mower was used for mowing and clippings were returned. Plots were irrigated at a rate of  $2.5 \text{ cm wk}^{-1}$  from May to September in addition to natural precipitation. Weeds were removed as needed by hand.

# **Percolate Collection and Analysis**

Beginning in May of 2004, percolate water was collected and sampled on a weekly basis, or more if necessary, and analyzed for NO<sub>3</sub>–N concentration. The percolate sampling period for both years occurred from September through April of 2004–05 and 2005–06. Insufficient percolate precluded collection between May and September in each year. During sampling, percolate volume in the collection vessels was measured and a sub-sample was collected in a 120-ml HDPE bottle using a peristaltic pump. The remaining percolate in the collection vessel was emptied at each sampling. The samples were fixed with  $H_2SO_4$  and stored at 4°C for up to 28 days. The samples were analyzed for NO<sub>3</sub>–N with a Scientific Instruments continuous flow analyzer (WESTCO, Danbury, Connecticut, USA) using the Griess-Ilosvay method (Keeney and Nelson, 1982). When NO<sub>3</sub>-N 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 amount of samples with concentrations below the detection limit was less than 1% of the total samples (USEPA, 2000).

The mass of NO<sub>3</sub>–N lost by leaching was determined as the product between percolate volume and percolate NO<sub>3</sub>–N concentration for each lysimeter and sampling date. These were then converted to mass loss per hectare based on the surfacecollection area of the lysimeters. Cumulative mass loss of NO<sub>3</sub>–N was determined separately for each leaching year (May of one year through April of the following year) by summing the mass loss of the individual sampling dates for each year. Flow-weighted NO<sub>3</sub>–N concentration was determined for each leaching year (May through April) separately for each lysimeter by dividing the total mass of NO<sub>3</sub>–N leached for each year by the total percolate volume collected for each respective leaching year.

# Anion Exchange Membranes

Soil NO<sub>3</sub>-N was measured in situ using AEM strips obtained from a large sheet of vinyl copolymer AEM fabric (part #P5393102, type AR204SZRA, GE Water & Process Technologies, Watertown, Massachusetts, USA) that was cut into  $2.5 \times$ 6.35 cm segments. The AEM strips were prepared by shaking in 0.5 M HCl for five minutes, rinsing in deionized water, saturated with Cl<sup>-</sup> ions by shaking for two hours in 1 M NaCl, and then finally rinsed again with deionized water, and stored in deionized water until use. From 11 May to 22 November, 2004, and 12 May to 10 November, 2005, two AEM strips were inserted into the soil of each plot to a depth of 6 to 7 cm below the thatch layer approximately every two weeks, and previous strips were removed from the soil. A hand trowel was used to make a slit in the soil at an angle of approximately 15° from vertical for strip insertion, and foot pressure was applied to ensure good strip-soil contact and to prevent preferential flow through the slit to the strips. The strips were placed in different locations within the plots each time a new AEM was inserted. Flagging tape was connected to the strip by a monofilament line in order to locate the strips at the time of removal. After removal, the two AEM strips from each plot were lightly washed with deionized water to remove soil, and then both strips were placed in a single 120-ml HDPE bottles containing 50 ml of 1 M NaCl. The bottles were then transported to the lab where they were shaken for 1 hr to desorb NO<sub>3</sub>-N from the AEMs. The extracts were then filtered through soil analysis papers having the retention range of 8 to 12 µm (Schleicher and Schuell, Keene, New Hampshire, USA) and stored at 4°C. The extracts were analyzed for NO<sub>3</sub>–N on a Scientific Instruments flow continuous analyzer (WESTCO, Danbury, Connecticut, USA) using the Griess-Ilosvay method (Keeney and Nelson, 1982). When NO<sub>3</sub>–N concentrations were below the nominal detection limit of 0.05 mg  $L^{-1}$ , a value of half the detection limit was recorded. Samples with a concentration below the detection limit were less than 1% of the total. If extracts were not to be analyzed within 48 hours following being filtered, they were fixed with  $H_2SO_4$  and stored at 4°C.

# **Reflectance Measurements**

Approximately every two weeks corresponding to inserting and removing AEMs, reflectance measurements were taken using the Spectrum CM-1000 chlorophyll meter (Spectrum Technologies, Inc., Plainfield, Illinois, USA) and Minolta CR-400 chroma meter (Konica-Minolta Holding Inc., Tokyo, Japan). For the CM-1000 meter, ten measurements were taken for each plot and the average recorded. A11 measurements were taken in full sun from 1100 to 1300 h with the meter facing away from the sun. The meter was held at a constant height of 1.5 m above the turf canopy. This yielded a circular area being evaluated of approximately 180 cm<sup>2</sup> per measurement. For the Minolta CR-400 meter, leaf blade samples were clipped from the plots and arranged in an optically dense stack. Four readings were taken on the stack, then the stack rearranged and four more readings were taken. This was repeated three more times and the

individual values for  $L^*a^*b^*$  were averaged. Hue angle (°) was calculated as the arctangent (b\*/a\*) (McGuire, 1992). Hue angles of the four primary colors are: red-purple, 0°; yellow, 90°; bluish-green, 180°; and blue, 270°.

## **Statistical Analysis**

Yearly FWC and cumulative mass losses of NO<sub>3</sub>-N, and mean CM-1000 indices and CR-400 hue angles were against time-weighted AEM plotted desorbed soil NO<sub>3</sub>-N values for the growing season. Linear plateau models were applied to these data to determine a critical level of AEM desorbed soil NO<sub>3</sub>-N. These models suggest a critical AEM desorbed soil NO<sub>3</sub>–N value that partitions the response into a linear segment (linear response across the predictor variable) and plateau segment (static response across the predictor variable). Logistic curves for the probabilities of flow-weighted NO<sub>3</sub>-N concentration in leachate exceeding water quality benchmarks of 5 and 10 mg  $L^{-1}$  in relation to mean NO<sub>3</sub>-N desorbed from AEMs, mean CM-1000 index, and mean CR-400 hue were determined with linear logistic models  $(a + bx = \{\ln[p/(1-p)]\},$ where p is the probability of flowweighted NO<sub>3</sub>–N concentration of leachate exceeding the water benchmark). In the model for mean AEM NO<sub>3</sub>-N, a benchmark of 9.5 mg  $L^{-1}$  was used in place of 10 mg  $L^{-1}$  because the model using the 10 mg  $L^{-1}$  benchmark produced complete separation of the dataset and maximum likelihood estimates could not be determined. All models passed the Hosmer-Lemeshow Goodness-of-fit test  $(p \ge 0.1)$ . Linear plateau models were developed using the NLIN procedure, and logistic curves for the probabilities were developed using the LOGISTIC procedure of SAS (version 9.1.3, SAS Institute Inc., Cary, North Carolina, USA).

### RESULTS

# Percolate NO<sub>3</sub>–N Concentrations and Mass Losses

No significant (p > 0.05) increase in percolate flow-weighted NO<sub>3</sub>–N concentrations or mass loss occurred when time-weighted AEM desorbed soil NO<sub>3</sub>-N was below 0.85 and 0.84  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>, respectively. A linear response (p < 0.0001) was observed for both variables, however, when AEM desorbed soil NO<sub>3</sub>–N was above these values (Figs. 1, 2). Percolate concentrations for the unfertilized control plots were approximately 4 mg  $L^{-1}$ NO<sub>3</sub>–N, which could be considered the background concentration for this particular site. As available soil NO<sub>3</sub>-N increased, however, a steady, and incremental increase in percolate NO<sub>3</sub>-N concentration was observed, with a FWC increase of 8.1 mg NO<sub>3</sub>–N  $L^{-1}$  and a mass loss increase of 43.3 kg  $NO_3$ –N ha<sup>-1</sup> for every unit increase in AEM desorbed NO<sub>3</sub>-N.

Figure 1. Annual flow-weighted NO<sub>3</sub>-N concentrations in the percolate from Kentucky bluegrass–creeping red fescue lawn turf plotted against seasonal time-weighted AEM desorbed soil NO<sub>3</sub>-N across two years in Connecticut, USA. All replicate values were used in the plot. The fitted predicted response (solid horizontal and sloped lines) and critical concentration (solid vertical line to *x* axis) are based on a Linear-Plateau model. The gray box on the *x* axis represents the 95% confidence interval for the critical concentration. The dotted line represents the AEM desorbed soil NO<sub>3</sub>-N value and above that would result in a flow-weighted NO<sub>3</sub>-N concentration in the percolate at or above the maximum contaminant level (MCL) for drinking water (10 mg L<sup>-1</sup>NO<sub>3</sub>-N).\*\*\*, significant at p < 0.001.



Figure 2. Annual mass leaching loss of NO<sub>3</sub>–N in the percolate from Kentucky bluegrass–creeping red fescue lawn turf plotted against seasonal time-weighted AEM desorbed soil NO<sub>3</sub>–N across two years in Connecticut, USA. All replicate values were used in the plot. The fitted predicted response (solid horizontal and sloped lines) and critical concentration (solid vertical line to *x* axis) are based on a Linear-Plateau model. The gray box on the *x* axis represents the 95% confidence interval for the critical concentration. The dotted line represents the AEM desorbed soil NO<sub>3</sub>–N value and above that would result in NO<sub>3</sub>–N mass loss in the percolate at or above 50 kg ha<sup>-1</sup>. \*\*\*, significant at *p* < 0.001.



The USEPA maximum contaminant level (MCL) for drinking water of 10 mg NO<sub>3</sub>–N  $L^{-1}$ was reached with an AEM desorbed soil NO<sub>3</sub>-N value of 1.59  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup> (Fig. 1). At level of available soil NO<sub>3</sub>-N. this approximately 54 kg NO<sub>3</sub>–N  $ha^{-1}$  would be leached past the rootzone for this site (Fig. 2). This amount exceeds the standard recommended N fertilizer rate per application for lawn turf in the Northeast USA of  $49 \text{ kg N ha}^{-1}$ .

In our region, the state of Rhode Island's Department of Health sets an advisory level of 5 mg NO<sub>3</sub>–N L<sup>-1</sup> for public water suppliers that will trigger the requirement of more frequent monitoring and testing for NO<sub>3</sub>–N. This is done as a precaution and allows for remedial action before levels reach the 10 mg L<sup>-1</sup> MCL. Considering that our background percolate concentration was relatively high (4 mg NO<sub>3</sub>–N L<sup>-1</sup>), our site would exceed the

Figure 3. Logistic regression curves for the probability of flow-weighted concentration of leachate exceeding 5 mg L<sup>-1</sup> (dashed line) and 9.5 mg L<sup>-1</sup> (solid line) in relation to mean AEM desorbed soil NO<sub>3</sub>–N from Kentucky bluegrass–creeping red fescue lawn turf across two years in Connecticut, USA. Dotted vertical lines indicate values on the *x*-axis corresponding to a probability of 0.5 ( $P_{50}$ ) for each curve. *p* indicates least likelihood ratio *p*-value, and  $R^2$  indicates maximum adjusted *R-square*.



Rhode Island Department of Health advisory level with only nominal N fertilizer inputs. The probability of 0.5 ( $P_{50}$ ) for exceeding the water quality benchmarks of 5 and 9.5 mg L<sup>-1</sup> (substituted for 10 mg L<sup>-1</sup> since complete separation occurred with 10 mg L<sup>-1</sup>) NO<sub>3</sub>–N corresponded to 1.05 and 1.73 mg cm<sup>-2</sup> d<sup>-1</sup> AEM desorbed soil NO<sub>3</sub>–N, respectively (Fig. 3).

## **Turf Reflectance and Leaching**

Significant (least likelihood ratio p < 0.05) logistic models were found for determining the probability of flow-weighted NO<sub>3</sub>–N concentrations of leachate exceeding the water benchmarks of 5 and 10 mg L<sup>-1</sup> in relation to mean CM–1000 index (Fig. 4A), and mean CR–400 hue (Fig. 4B). The probability of 0.5 (P<sub>50</sub>) for exceeding water quality benchmarks 5 and 10 mg L<sup>-1</sup> NO<sub>3</sub>–N corresponded to CM–1000 indices of 349 and 401, respectively, and to CR–400 hue of 123.2 and 125.3 degrees.

Figure 4. Logistic regression curves for the probability of flow-weighted concentration of leachate exceeding 5 mg  $L^{-1}$  (dashed line) and 10 mg  $L^{-1}$  (solid line) in relation to mean CM–1000 index (A) and mean CR–400 hue (B) from Kentucky bluegrass–creeping red fescue lawn turf across two years in Connecticut, USA. Dotted vertical lines indicate values on the *x*-axis corresponding to a probability of 0.5 ( $P_{50}$ ). *p* indicates least likelihood ratio *p*-value, and  $R^2$  indicates maximum adjusted *R*-square.



## AEM Desorbed NO<sub>3</sub>-N and Turf Reflectance

Maximum color quality of the turf, as measured with reflectance meters, was reached at an AEM desorbed soil NO<sub>3</sub>–N value of 2.3  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup> (Figs. 5, 6). This value is considerably higher than the AEM level at which percolate FWC reached the MCL or when mass loss of NO<sub>3</sub>–N reached 50 kg ha<sup>-1</sup> (1.59 and 1.50  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>, respectively; Figs. 1, 2), and would correspond to a probability of 1.0 of exceeding water quality standards (Fig. 3). At maximum turf color, with an AEM desorbed soil NO<sub>3</sub>–N value of 2.3  $\mu$ g cm<sup>-2</sup> d<sup>-1</sup>, predicted NO<sub>3</sub>–N FWC would be 15.8 mg L<sup>-1</sup>, and mass loss 85 kg ha<sup>-1</sup> (Figs. 1, 2).

## DISCUSSION

Anion-exchange membranes proved to be a good predictor of NO<sub>3</sub>–N leaching losses from lawn turf. Previous studies (Petrovic, 2004; Easton and Petrovic, 2004; Sullivan and Jiang, 2004) indicated that ionexchange technology could measure NO<sub>3</sub>–N losses from turf without the expense and expertise needed with water collection, but the technology was used differently

compared with our study. These previous studies used exchange resins (bags, capsules, or membranes) to capture leached ions and thereby assess mass loss of NO<sub>3</sub>-N directly, rather than use the exchange resins as a measure of plant-available soil NO<sub>3</sub>-N in the rootzone that is subject to leaching. We used AEMs to measure the soil NO<sub>3</sub>-N fluxes in the shallow rootzone of turf, which was correlated to percolate concentrations and losses measured directly with lysimeters. Insertion and removal of the AEM strips in our approach is much simpler, and does not require placement of the AEMs below the turf rootzone. We were able to confirm the positive relationship between plant-available soil NO<sub>3</sub>-N in the rootzone of turf and NO<sub>3</sub>-N leaching losses by direct water measurements under field conditions (this study) and in controlled environments (Mangiafico and Guillard, 2007a). In each case, sufficient water was available from irrigation for turf growth and quality requirements.

Under drier conditions, however, measurement of soil  $NO_3$ –N with exchange resins may be underestimated since Figure 5. Mean CM–1000 Chlorophyll meter index of Kentucky bluegrass–creeping red fescue lawn turf plotted against seasonal time-weighted AEM desorbed soil NO<sub>3</sub>–N across two years in Connecticut, USA. All replicate values from treatment plots were used in the graph. The fitted predicted response (solid horizontal and sloped lines) and critical concentration (dotted vertical line to *x*-axis) are based on a Linear-Plateau model. The gray box on the *x*-axis represents the 95% confidence interval for the critical concentration. \*\*\*, significant at p < 0.001.



diffusion in the soil pores to the exchange resin sites is constrained due to lack of water in the large pores. The amount of NO<sub>3</sub>–N removed from soil by AEMs has been reported to decrease with decreasing soil moisture (Qian and Schoenau, 2002). Since plant uptake of soil NO<sub>3</sub>–N would be limited under these conditions as well, using critical soil NO<sub>3</sub>–N values derived from AEMs as a guide for fertilization must be considered in context with available water. Due to their dynamic exchanger properties, however, a continuous in situ monitoring of soil NO<sub>3</sub>-N fluxes with AEMs or other ion-exchange methods would more accurately determine when those pools of soil NO<sub>3</sub>-N become plant available under more favorable soilwater conditions than infrequent interval point-in-time soil sampling.

We see AEMs as serving a dual function: not only can they predict  $NO_3-N$  leaching losses, but can also provide a

Figure 6. Mean CR–400 chroma meter hue of Kentucky bluegrass–creeping red fescue lawn turf plotted against seasonal time-weighted AEM desorbed soil NO<sub>3</sub>–N across two years in Connecticut, USA. All replicate values from treatment plots were used in the graph. The fitted predicted response (solid horizontal and sloped lines) and critical concentration (dotted vertical line to *x*-axis) are based on a Linear-Plateau model. The gray box on the *x*-axis represents the 95% confidence interval for the critical concentration. \*\*\*, significant at p < 0.001.



measure of plant-available soil NO<sub>3</sub>-N, thus serving as an objective guide for turf N fertilizer recommendations (Kopp and Guillard, 2002; Mangiafico and Guillard, 2006b). Relationships between NO<sub>3</sub>–N desorbed from AEMs and plant-available soil NO<sub>3</sub>–N and/or NO<sub>3</sub>–N leaching losses, however, may vary among sites, especially where different soil properties, soil moisture relationships, and N uptake dynamics may in different NO<sub>3</sub>–N result leaching dynamics. This has been observed with common landscaping plants, including turf, in a temperate climate (Amador et al., 2007).

An objective guide for N fertilizer recommendations that measures plantavailable soil NO<sub>3</sub>–N would decrease the chance of applying N beyond turf needs, thus preventing the buildup of soil NO<sub>3</sub>–N in the turf rootzone that is subject to leaching. This is particularly important in a humid climate, especially during the overwinter dormancy period when most leaching from turf occurs (Roy et al., 2000; Guillard and Kopp, 2004; Frank et al., 2006; Mangiafico and Guillard, 2006a; Munster et al., 2006). Even with careful irrigation management during the growing season, excess NO<sub>3</sub>–N in the turf soil profile is still subject to leaching during episodic heavy rainfall or snowmelts due to preferential flow through macropores (Starrett et al., 1995) or with flushing of the soil profile that can occur during the non-growing season. These flushing events can be responsible for considerable NO<sub>3</sub>-N fluxes or loss from the soil (Sullivan and Jiang, 2004; Shuman, 2006; Mangiafico and Guillard, 2007a). Spring soil sampling in a cold humid environment (Michigan, USA) indicated that there was no appreciable residual soil NO<sub>3</sub>-N following Ν applications to Kentucky bluegrass the previous year (Rieke and Ellis, 1974), suggesting that some leaching occurred over the winter.

Based on monthly point-in-time soil sampling, previous studies indicated relatively low NO<sub>3</sub>–N leaching potential in golf courses based on low soil NO<sub>3</sub>-N concentrations (Higby and Bell, 1999; Lee et al., 2003), and greater NO<sub>3</sub>–N leaching potential with higher soil NO<sub>3</sub>-N concentrations (Miltner et al., 2001). Although the fate of NO<sub>3</sub>–N between samplings in these studies was not known, it can be presumed that monthly values were thought to be representative of soil NO<sub>3</sub>-N concentration between samplings. This may or may not be true. Continuous in situ measurement of NO<sub>3</sub>–N flux under golf greens grown on sandy soils with ion-exchange capsules estimated losses of 100 to 150 kg N  $ha^{-1} yr^{-1}$  (Sullivan and Jiang, 2004), suggesting that continuous monitoring of soil N and adjustment of fertilizer and water practices may be necessary to avoid water quality impairment for this type of turf system.

If soil NO<sub>3</sub>–N concentrations are an indication of NO<sub>3</sub>-N leaching potential, then lawns may pose a relatively higher threat of water quality impairment, especially when fertilized using infrequent larger N doses, than turf fertilized with "spoon-feeding" practices (Frank et al., 2006). A survey of 28 different lawns in Ohio, USA (6 fertilized with commercial service, 11 fertilized by homeowner, and 11 no-input) reported a range of soil NO<sub>3</sub>–N concentrations from 18 to 31 mg kg<sup>-1</sup> for lawns under commercial care, 17 to 26 mg kg<sup>1</sup> for homeownerfertilized lawns, and 16 to 22 mg kg<sup>-1</sup> for no-input lawns (Cheng et al., 2008a). Even for the no-input lawns, soil NO<sub>3</sub>-N concentrations were relatively high, considerable mineralization suggesting occurring at these sites.

Age of a turf stand can have considerable effect on N mineralization potential and N storage in the organic matter. It has been reported that an equilibrium in soil N storage and organic matter accumulation is reached in turf soils after 10 to 25 years (Porter et al., 1980). This suggests that older turfs may have an increased NO<sub>3</sub>-N leaching potential if N fertilization rates are not reduced in accordance to turf age, especially if clippings are returned (Qian et al., 2003). Even with organic and synthetic slow-release fertilizers, soil NO<sub>3</sub>-N concentrations from lawn turf can become relatively high following long-term applications, especially in the autumn. A 15-yr study in Ohio, USA with various N fertilizer formulations showed that by the last year of collection, October soil NO<sub>3</sub>–N data concentrations were about 11 mg  $kg^{-1}$  for organic sources at a rate of 216 kg N ha<sup>-1</sup> yr<sup>-1</sup> and 10 to 13 mg kg<sup>-1</sup> for mineral sources at 219 to 245 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Cheng et al., 2008b). This suggests that in the long-term, under equivalent total N loading rates, there may similar leaching potentials for both organic and mineral fertilizers. Therefore, an

accurate assessment of plant-available soil NO<sub>3</sub>–N is needed to guide N fertilizer recommendations for lawns and other turf areas that will include NO<sub>3</sub>–N derived from all sources including fertilizer, organic matter mineralization, irrigation water, biological fixation, atmospheric deposition, and residual soil NO<sub>3</sub>–N. This objective testing approach is lacking with current turf N fertilization practices. Ion-exchange resins can provide this capability for turf.

Our results suggest that measurements from reflectance meters also could serve as indicators for the probability of leachate NO<sub>3</sub>-N concentrations exceeding water quality benchmarks. As with AEM desorbed soil NO<sub>3</sub>–N, probability values for leaching as a function of reflectance readings may vary depending on turf species, variety, density, and health, as these factors may affect color and light reflectance of a turf stand relative to N status. A reasonable approach in using spectral reflectance to prevent excessive soil NO<sub>3</sub>-N buildup, assuming turf density is adequate and species composition is somewhat uniform, would be to include a small, well-fertilized strip for reference on any particular turf site, then adjust fertilization rates on the remaining area to 90% of CM-1000 index or 1.5 CR-400 hue degree less than the reference strip. This approach in our study would have resulted in a CM-1000 index of 379.8 and CR-400 hue of 124.9 degrees, which correspond to probabilities 0.2785 and 0.1985 in exceeding the MCL for NO<sub>3</sub>–N in drinking water, respectively. While not at maximum, turf color quality probably would be acceptable at these lower AEM desorbed soil NO<sub>3</sub>-N levels, but this would need to be verified with further research.

Although the USEPA MCL for drinking water is set at 10 mg NO<sub>3</sub>–N  $L^{-1}$ , concentrations as low as 0.05 to 0.1 mg NO<sub>3</sub>–N  $L^{-1}$  can cause significant

phytoplankton biomass increases in streams entering coastal waters (Mallin and Wheeler, 2000). Therefore, turf leachate NO<sub>3</sub>–N concentrations below the drinking water MCL, and above background, may be a concern when effects other than on drinking water are considered.

### CONCLUSIONS

Anion-exchange membranes and spectral reflectance meters were able to predict NO<sub>3</sub>-N leaching losses from a Kentucky bluegrass-red fescue lawn turf. Increasing the greenness of turf past the critical AEM soil NO<sub>3</sub>-N values with N fertilization increased the probability of exceeding drinking water standards for NO<sub>3</sub>-N set by U.S. federal and state agencies. This study suggests that critical AEM desorbed soil NO<sub>3</sub>-N values could be developed for any turf site to guide N fertilization rates. Likewise, maximum reflectance meter responses could be determined for any specific site and used to fertilization by maintaining guide N reflectance values below the maximum (for example, 90% of maximum for CM-1000 index and 1.5 degrees lower for CR-400 hue) that still maintain acceptable turf color and density. This would help to prevent excess NO<sub>3</sub>-N buildup in the soil, and in turn decrease the risk of NO<sub>3</sub>-N leaching losses. A key management practice to reduce threats to water quality from managed turf is to keep soil NO<sub>3</sub>-N concentrations low, especially prior to times of greatest leaching potential; this would be from autumn to the following spring in our climate. Infrequent soil sampling may not be able to detect fluxes in soil NO<sub>3</sub>-N as effectively as in situ AEMs. Maximizing turf color with current N fertilization recommendations on our site is not compatible with water quality goals. Since soil-water flux will affect diffusion rates of NO<sub>3</sub>–N, inclusion of soil-water measurements or hydrological models should increase the predicting power of AEMs to estimate plant-available soil NO<sub>3</sub>-N and leaching losses.

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