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Accumulation and Potential Remediation of Copper in Golf Course Putting Greens

Adam W. Gore [a*], Lambert B. McCarty [b], Philip J. Brown [c], Virgil Quisenberry [b] and William C. Bridges [d]

[a] Clemson University Cooperate Extension Service, Clemson University, 123 East Liberty St, Sumter, SC 29150, USA.
[b] Department of Plant and Environmental Sciences, Clemson University, 50 Cherry Rd, Clemson, SC 29632, USA.
[c] School of Plant and Environmental Sciences, Virginia Tech, 416 Smyth Hall, Blacksburg, VA 24061, USA.
[d] Department of Mathematical and Statisical Sciences, Clemson University, O-110 Martin, USA.

Authors' contributions

This work was carried out in collaboration among all authors. Authors AWG, LBM, PJB, VQ, and WCB designed the study and wrote the protocol. Author AWG conducted the research, data collection, performed the statistical analysis and managed the literature searches. Author AWG wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The objective of this study was to determine the potential accumulation of copper (Cu) within a USGA golf green profile and analyze potential remediation techniques of soils containing toxic Cu concentrations. Accumulation study utilized: copper phthalocyanine pigment (Par), copper hydroxide (Junction DF), varying concentrations of copper sulfate ($CuSO_4$) within irrigation, and combinations of each. Products were applied over 13 weeks at Clemson University horticulture

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**Corresponding author: E-mail: awgore@clemson.edu;*

greenhouses with samples taken at thatch depth, 0-5.1 cm below thatch, and 5.1-10.2 cm below thatch at conclusion of study. Average Cu concentrations in thatch layer was 634.7 kg Cu ha^{-1}, with 0 - 5.1 cm and 5.1 - 10.2 cm depth concentrations of 11.26 and 6.84 kg Cu ha^{-1}, respectively. Remediation studies exposed 5 mg Cecil sandy loam to 15 ml 1000 ppm of $CuSo_4$-Cu followed by 4 sequential 20 ml filtration cycles of 1 N ammonium sulfate, 1 N calcium nitrate, 1 N gypsum, or water. Single filtration of ammonium sulfate removed similar or greater amount of Cu than cumulative impact of 4 filtrations of any other products with 2064 mg Cu kg^{-1}. Studies suggest that the management or removal of thatch may alleviate toxic accumulation of copper, however the use of ammonium sulfate in irrigation water may provide additional remediation options to turfgrass managers.

Keywords: turfgrass; thatch; copper toxicity; remediation; accumulation; adsorption.

1. INTRODUCTION

Hybrid bermudagrass [*Cynodon dactylon* (L.) *Pers.* x *C. transvaalensis* Burtt-Davy] is the most commonly used warm-season turfgrass in the southeastern United States in both sports turf and golf course turf areas due to its ability to withstand high temperature and humidity associated with the climate as well as its aggressive rhizomatous and stoloniferous growth habits allowing for very low mowing heights (3.2 – 4 mm) and relatively quick turf recovery, if damaged [1]. As a C_4 plant, bermudagrass experiences a state of dormancy normally associated with consistent temperatures below 10ºC in which the plant ceases active growth and exhibits an aesthetically undesirable yellow to brown appearance [2]. Applications of pigmented products, of which copper (Cu) is often a component, is common in high visibility locations in place of traditional overseeding practices [3]. Copper is also used in fungicides and algaecides, often as copper sulfate ($CuSO_4$) or copper hydroxide ($Cu(OH)_2$), due its ability to denature proteins and enzymes in fungi. The use of Cu in agriculture can be traced back to 1885 in Bordeaux, France in vineyards to prevent downy mildew development. The continued use of Cu-based fungicides is the largest contributor of soil Cu in the agriculture industry [4].

Healthy turfgrass leaves typically contain Cu between 5 to 38 ppm depending on grass species. Toxicity symptoms can develop at 20 to 30 ppm Cu [5-6]. Due, in large part, to its oxidation-reduction potential, Cu is required for specific enzymatic conversions of amino acids to proteins, cell wall metabolism, electron transport, along with other processes. Excessive Cu cycling can lead to creation of free radicals via Fenton reactions, damaging plant structures [7-8]. Weekly foliar applications of 250 ppm Cu have been reported to reduce turf quality in as few as 28 days [9].

In soils, Cu is adsorbed to charged surfaces of clay, and iron (Fe), aluminum (Al), and manganese (Mn) oxides using oxygen as an intermediary in these surface bonds [10]. Cupric copper (Cu^{2+}) is absorbed by roots either individually in solution or as a component in natural or synthetic complexes. Absorption is greatly affected by Cu immobility associated with increases in soil pH, cation exchange capacity (CEC), and percentage of organic content [11]. When exposed to the equivalent of 50 kg Cu ha^{-1} followed by eight soil pore volume replacements of water, some Florida soils yielded less than 3% of total Cu in leachate. Further research indicated up to 98% of total Cu remained in the upper 5 cm of soil columns for those containing a greater percentage of organic matter [12]. Decreases in bentgrass (*Agrostis palustris* L.) dry clipping weight and root mass were reported when Cu levels in soil were increased from 0 to 600 mg kg^{-1} [13].

Accumulation of various ions to toxic levels and buildup of organic and inorganic substrates are longstanding issues faced by turfgrass managers, with concerns of excessive soil salinity, pH, and thatch management being commonplace [2]. When tackling issues of salinity, whether caused by poor irrigation water quality, natural soil occurrence, or product applications, organic substrates including humic acid and calcium-containing products such as gypsum ($CaSO_4•2H_2O$) have been evaluated for ability to improve turfgrass quality. These materials also have been examined for their role in flushing and/or binding metallic salts such as sodium chloride which otherwise may cause soil dispersion [14-16].

The removal of thatch by the processes of verticutting, fraze mowing, or hollow tine aerification is a common practice by turfgrass managers striving to maintain a thin layer of living and dead stems, leaves, and roots of grass between the actively growing shoots of grasses and the soil surface [17]. Danneberger and Turgeon [18] reported core cultivation and vertical mowing could reduce the overall content of a thatch layer while causing an increase in the overall cation exchange capacity (CEC) on a per volume basis.

Studies were conducted at Clemson University, Clemson SC, to assess zones of Cu accumulation in a bermudagrass USGA specification putting green, and to evaluate various products ability to remove Cu from the rootzone.

2. MATERIALS AND METHODS

2.1 Copper Profile Accumulation

TifEagle bermudagrass plugs (10 cm diameter x 10 cm deep) were removed from a two-year-old USGA-standard constructed green at the Clemson University Turfgrass Research Facility in Clemson, South Carolina (34.670682, -82.834950) and placed into a 100% sand rootzone meeting USGA particle size specifications contained within 15.24 cm diameter x 15.24 cm deep greenhouse pots. Turf was established for 3 weeks in the Clemson University greenhouse facility at a temperature of 23.9ºC (75ºF) until reaching 15 cm diameter and maintained at 1.3 cm height. Pots were then treated over the span of 13 weeks with varying species, compounds, and concentrations of Cu. Treatments consisted of an untreated control and various Cu-containing products, rates, and combinations (Table 1) with four pots per treatment being the replications. Due to the presence of mancozeb, a zinc, manganese, and nitrogen containing fungicide, in Junction DF, mancozeb (Fore 80WP) (Dow Agrosciences LLC., Indianapolis, IN) was applied at 2.29 kg ha^{-1} (0.75 oz 1,000 ft^{-2}) to all plots not containing Junction DF as a treatment. Treatments of the commercial pigment Cu phthalocyanine (Par) (Harrell's LLC, Lakeland, FL) and copper hydroxide (Junction DF) (SePro Corporation, Carmel, IN) were applied at respective rates and timings via foliar application delivered at 187.3 L ha^{-1}. Treatments of $CuSO_4$ (copper sulfate pentahydrate, LabChem, Zelienople, PA) were applied via 1-inch (2.54 cm) equivalents of irrigation water weekly.

Table 1. Treatments and rates applied to 'TifEagle' hybrid bermudagrass

Treatment†	**Rate**
Phthalocyanine pigment (Par)	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A}
Par (2X)	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{B}
Copper hydroxide + mancozeb (Junction DF)	12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C}
0.25 ppm $CuSO_4$	0.25 mg $CuSO_4$ L$^{-1\ B*}$
2.0 ppm $CuSO_4$	2.0 mg $CuSO_4$ L$^{-1\ B*}$
50 ppm $CuSO_4$	0.05 g $CuSO_4$ L$^{-1\ B*}$
100 ppm $CuSO_4$	0.1 g $CuSO_4$ L$^{-1\ B*}$
200 ppm $CuSO_4$	0.2 g $CuSO_4$ L$^{-1\ B*}$
Par + 0.25 ppm $CuSO_4$	01.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A} + 0.25 mg $CuSO_4$ L$^{-1\ B*}$
Par + 2.0 ppm $CuSO_4$	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A} + 2.0 mg $CuSO_4$ L$^{-1\ B*}$
Junction DF + 0.25 ppm $CuSO_4$	12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C} + 0.25 mg $CuSO_4$ L$^{-1\ B*}$
Junction DF + 2.0 ppm $CuSO_4$	12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C} + 2.0 mg $CuSO_4$ L$^{-1\ B*}$
PAR + Junction DF	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A} + 12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C}
PAR + Junction DF + 0.25 ppm $CuSO_4$	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A} + 12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C} + 0.25 mg $CuSO_4$ L$^{-1\ B*}$
PAR + Junction DF + 2.0 ppm $CuSO_4$	1.17 L ha^{-1} (0.37 oz 1,000 ft^{-2}) ^{A} + 12.21 kg ha^{-1} (4.0 oz 1,000 ft^{-2}) ^{C} + 2.0 mg $CuSO_4$ L$^{-1\ B*}$

†All treatments not including Junction DF received mancozeb (Fore 80 WP) (Dow Agrosciences LLC., Indianapolis, IN) at a rate of 2.29 kg ha^{-1}(0.75 oz 1,000 ft^{-2}).

^{A} *Applied bi-weekly*

^{B} *Applied weekly*

^{C} *Three applications applied bi-weekly*

**Applied as 1-inch irrigation equivalent*

At the conclusion of 13 weeks, 5 cores (2 cm diameter x 15 cm deep) were extracted from each pot and divided by depths: thatch (approximately 1.27 cm), 0 - 5.08 cm below thatch layer, and 5.09 – 10.16 cm below thatch layer. Cores were submitted to Clemson University Ag Services Laboratory for Cu concentration analysis using Mehlich I extractant.

2.2 Copper Remediation

Five g (approximately 4 ml) of a Cecil sandy loam were mixed with 15 ml of solution containing 1,000 ppm $CuSO_4$-Cu within 50 ml test tubes at a constant rate of 180 oscillations per minute with 3-inch stroke for 24 hours. Contents were centrifuged at 1500 revolutions per minute for 1 hour. Supernatant was extracted and analyzed for Cu concentrations by Clemson University Agricultural Services Lab to develop an average concentration of adsorbed copper.

Soil in test tubes was then exposed to treatments consisting of 20 ml of tap water, 20 ml 1 N gypsum ($CaSO_4 \cdot 2H_2O$) (SoftCal Pellets, Austinville Limestone Co., Austinville, VA), 20 ml 1 N calcium nitrate ($CaNO_3$) (15.5-0-0) (Hi-Yield, Voluntary Purchasing Groups, Bonham, TX), and 20 ml 1 N ammonium sulfate ($(NH_4)_2SO_4$) (21-0-0) (Hi-Yield, Voluntary Purchasing Groups, Bonham, TX) (AMS). Soil and solutions were shaken for 5 minutes at a rate of 180 oscillations per minute with a 3-inch stroke and placed in a Damon/IEC HN-SII centrifuge (Thermo Scientific, Waltham, MA) at a rate of 1500 revolutions per minute for 1 hour. Supernatant was extracted for analysis. Soil samples were retreated with 20 ml of the same solution they were initially treated with, shaken, centrifuged, and supernatant extracted 3 more times. Supernatants were analyzed for Cu concentration by Clemson University Agricultural Services Lab. All treatments had 4 soil sample replications.

2.3 Statistical Analysis

Studies were designed as two factor treatments and completely randomized. Greenhouse pot locations were rotated weekly to remove potential for localized microclimate impact. Due to high variability probability of soil chemical and physical characteristics within a given area as well the potential impact of Type II errors in environmental studies, analysis of soil samples was performed using 2-way Analysis of Variance and Fisher's Protected LSD (P=.10) [19-20].

3. RESULTS AND DISCUSSION

3.1 Results

Copper Profile Accumulation: Statistical differences were present between thatch and underlying soil depths with average Cu concentrations of 634.7, 11.26, and 6.842 kg ha-1 for thatch, 0 – 5.08 cm, and 5.08 – 10.16 cm sampling intervals, respectively (Fig. 1). This corresponds to a 58-100X increase in Cu between the predominantly organic thatch and the mineral component of the soil. Within each sampling interval, irrigation treatments containing 200 and 100 ppm $CuSO_4$ resulted in greater Cu accumulation than all other treatments. Within the thatch layer 200, 100, and 50 ppm $CuSO_4$ treatments were an order of magnitude greater than all other treatments, averaging 3763.9, 3274.6, and 1321.4 kg Cu ha^{-1}, respectively. Samples from the 200 and 100 ppm treatments were statistically higher than 50 ppm. In 0 – 5.08 cm and 5.08 – 10.16 cm depth intervals below thatch layer, 200 ppm treatments were statistically higher than 100 ppm (Fig. 2). While 50 ppm was higher than all treatments except 200 and 100 ppm, it was not statistically greater than other treatments in intervals below thatch layer.

3.1 Copper Remediation

Replacement treatments were analyzed by individual treatment filtration and cumulative impact of sequential filtrations. Individually, first filtration AMS resulted in the greatest concentration of Cu removed from soil, extracting an average 2064 mg kg^{-1} (Fig. 3). First filtration $CaNO_3$ was similar to first filtration $CaSO_4$ removing 958 and 715 mg kg^{-1}, respectively. With the exception of water treatment, first filtrations resulted in the greatest amount of displaced Cu.

Ammonium sulfate resulted in the greatest cumulative impact removing 2628, 2744, and 2804 mg Cu kg^{-1} after 2, 3 and 4 filtration cycles, respectively. These cumulative averages were statistically greater than all other treatments and their respective cumulative impact (Fig.4). A single filtration of AMS was statistically similar to all cumulative AMS amounts, and also to four filtrations of $CaSO_4$, and cumulative effect of three and four filtrations of $CaNO_3$. Water by itself resulted in the lowest Cu displacement with one filtration yielding 496 mg kg^{-1} of Cu, and four filtrations yielding a combined 831 mg kg^{-1}, approximately 43% of the predicted quantity of Cu added to the soil.

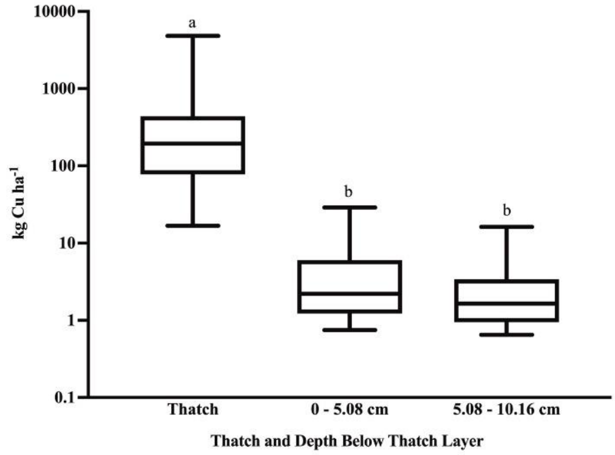

Fig. 1. Concentration of copper within subsurface layers following 13 weeks of treatments with various copper-containing products. Verticals lines represent 10 and 90 percentiles. Different letters indicate significant differences between treatments using Fishers Protected LSD (*P*=.10)

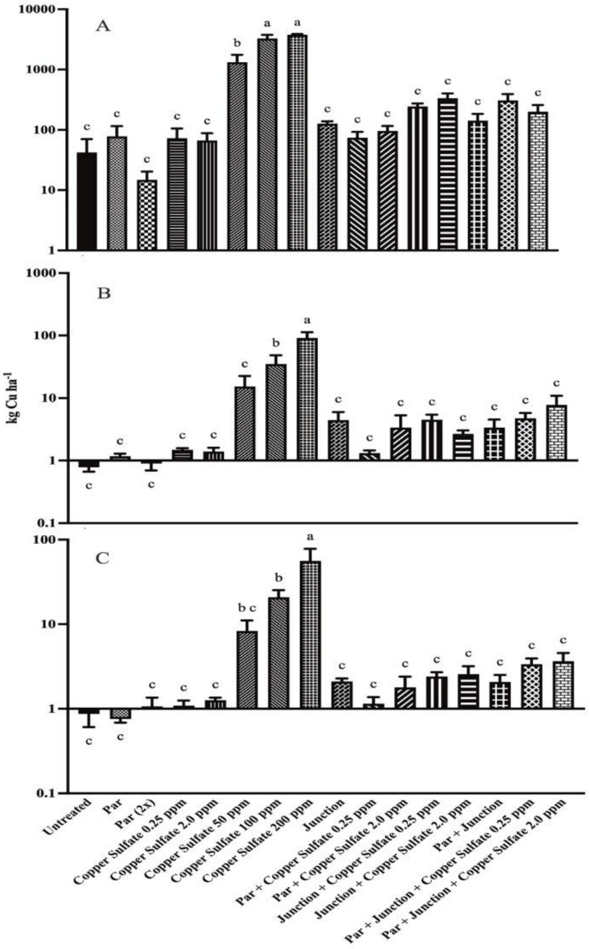

Fig. 2. Copper concentration of hybrid bermudagrass rootzone within (A) thatch layer (B) 0 – 5.08 cm below thatch layer (C) 5.08 – 10.16 cm below thatch layer after being exposed to copper-containing products. Vertical bars represent standard errors. Different letters indicate significant differences between treatments within depths using Fishers Protected LSD (*P*=.10)

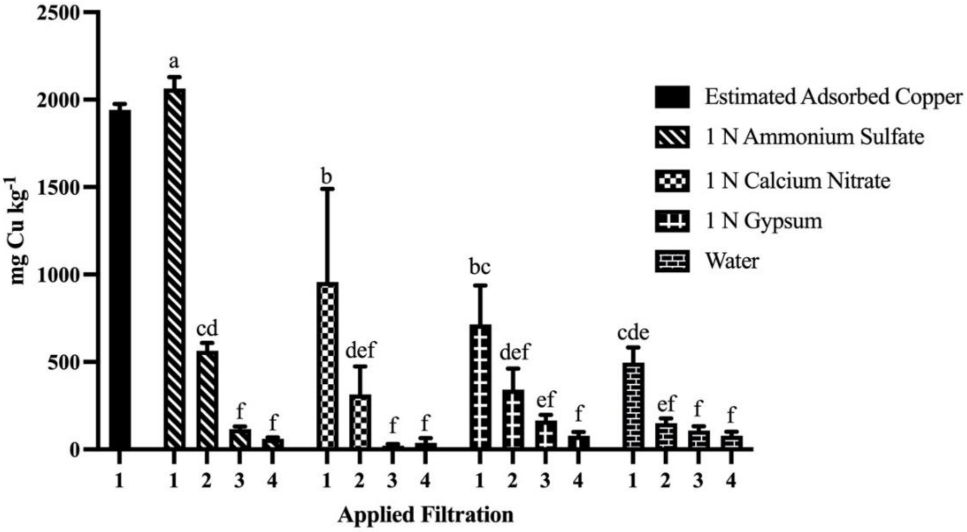

Fig. 3. Copper concentration of sequential filtration treatments to Cecil sandy loam previously exposed to 1000 ppm $CuSO_4$-Cu. Vertical bars represent standard errors. Different letters indicate significant differences between treatments using Fishers LSD (*P*=.10)

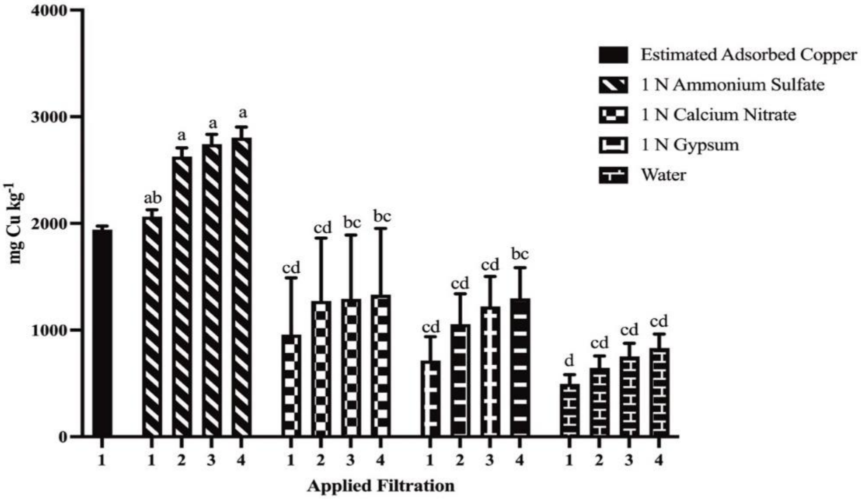

Fig. 4. Cumulative extracted copper concentration of sequential filtration treatments to Cecil sandy loam previously exposed to 1000 ppm $CuSO_4$-Cu. Vertical bars represent standard errors. Different letters indicate significant differences between treatments using Fishers LSD (*P*=.10)

3.2 Discussion

Elevated levels of Cu within the thatch layer are consistent with similar findings in vineyards where Cu concentrations were highest in soil profiles with high organic matter content [21-22]. Thatch is a collection of dead and decaying organic material, which provides many potential preferred negative binding sites for Cu. Below the thatch layer within a golf green built to USGA specifications, there is potential for other binding sites depending on use of organic substrates such as peat moss during construction process; however, pure sand greens lack this organic material, thus, Cu adsorption in these situations is reliant on various organic compound complexes [22]. Results from this study indicate the thatch layer should be the part of the rootzone turfgrass managers should focus on when trying to remediate effects of excess Cu.

Of particular interest is the efficacy of AMS compared to that of products containing calcium in removing Cu. Lyotropic series suggest that divalent calcium should be more apt in removal of Cu^{2+}, however the acidification of solution corresponding with AMS compared to that of $CaNO_3$ or $CaSO_4$ likely encourages increased solubility and disassociation of Cu from soil, similar to observed desorption of lead (Pb^{2+}) in low pH solutions resulting from AMS incorporation [23]. With AMS providing potential Cu displacement from soil profiles, turf managers may have a viable option for removal of Cu. More evaluation is needed to determine minimum necessary amount of AMS required for efficient removal of Cu to avoid unwanted fertility or phytotoxic effects associated with excess soluble nitrogen fertilizer. There is a potential for turfgrass managers to incorporate AMS into their fertility program to remediate high levels of Cu plus provide a nitrogen source. Gypsum is not a source of nitrogen providing an alternative with minimum impact to turfgrass fertility programs; however, it is not as affective at removing Cu as AMS. Additionally, water carrier volume must be evaluated to assess the necessary volume of water for displacement.

4. CONCLUSION

As a result of its potential adsorption of excessive levels of Cu, management practices aimed at reduction of the thatch layer such as hollow tine aerification, fraze mowing, and vertical mowing, may also result in reduction of Cu in soil profile. Aggressive aerification has been reported to reduce thatch content by approximately 10% [17]. These practices can be impractical for golf course superintendents and other turf managers at times due to the potential temporary damage to a facility's aesthetics and playability. In situations where mechanical removal is impractical or rootzones contain higher percentages of clay particles, the use of AMS may serve as an alternative to aid in flushing heavy metals from turfgrass rootzones in practice similar to salinity flushing.

Continued research is needed to evaluate Cu absorption dynamics in dormant grasses to determine critical thresholds prior to plant death. Further research should build upon the potential use of AMS to aid in removal of Cu ions from soil profiles by investigating the minimum required AMS to avoid turfgrass damage in addition to irrigation water volume necessity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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