

ABSTRACT

MAHONEY, DENIS JOSEPH. Environmental Fate of Arsenic Following Monosodium Methylarsenate (MSMA) Applications to a Turfgrass System. (Under the direction of Dr. Travis Gannon and Dr. Matthew Polizzotto).

Arsenic (As) has been an active ingredient in numerous pesticides since the late 1800's. Monosodium methyl arsenate (MSMA) is an organic arsenical postemergence herbicide that has commonly been used in cotton production and turfgrass since the 1960's. In 2006, the Environmental Protection Agency proposed a phase-out of all organic arsenical herbicides, including MSMA. The phase-out was enacted because of groundwater contamination concerns due to As addition from applications. A field lysimeter experiment was conducted from 2012-2013 to determine the fate of As following MSMA and As-containing fertilizer applications to bareground and established turfgrass systems. MSMA-treated lysimeters received two sequential MSMA applications ($2.25 \text{ kg a.i. ha}^{-1}$) on a 7 d interval. Fertilizer treatments were based on nitrogen loading rates and treated lysimeters received either three applications at 54 kg N ha^{-1} , one application at 294 kg N ha^{-1} , or two applications at 294 kg N ha^{-1} with sequential applications on 30 d intervals. Fertilizer rates provided 0.08, 0.16, and 0.32 mg As per lysimeter, respectively. Aboveground vegetation, soil, and porewater As concentrations were measured through 1 yr following MSMA and fertilizer applications. Increased As concentrations in aboveground vegetation, soil, or porewater were not detected at any time following fertilizer treatments in either system, compared to nontreated lysimeters. MSMA-treated aboveground vegetation As concentration was increased through 120 d after initial treatment (DAIT) compared to nontreated. Increased

soil As was observed at 0-4 cm at 30 and 120 DAIT and 0-8 cm at 60 and 365 DAIT, suggesting that As was bound in shallow soil depths. Porewater revealed lower As concentrations at 76 cm depth (0.4 to $5.1 \mu\text{g L}^{-1}$) compared to 30 cm depth (22 to $83.8 \mu\text{g L}^{-1}$). Within porewater samples, As concentration maximums in bareground samples from 30 and 76 cm depth (83.8 and $5.1 \mu\text{g L}^{-1}$, respectively) were greater than turfgrass samples at these depths (56 and $0.9 \mu\text{g L}^{-1}$, respectively). Results indicate that vegetation management needs to be considered, as it may be a potential source for off-target As movement. Additionally, turfgrass coverage may help prevent As leaching through soil due to plant and soil conditions, but contamination may occur in areas with shallow water tables.

Based on results from field lysimeter experiments, further research was warranted to determine As distribution and speciation following a MSMA application to managed turfgrass. Therefore, greenhouse lysimeters were utilized to determine As distribution, mass balance, and porewater speciation over time following a MSMA application ($4.5 \text{ kg a.i. ha}^{-1}$). Samples collected included turfgrass clippings, remaining vegetation, roots, soil (0-5, 5-15, and 15-30 cm depth), porewater (5 and 15 cm depth), and leachate (30 cm depth). At 1 week after treatment (WAT), up to 10% of As from MSMA was removed in clippings. Soil As was only increased at 0- to 5-cm depth at 8 WAT, with elevated porewater concentration detected at 5 cm. Porewater revealed As species transformed from 1 to 2 WAT with inorganic arsenate becoming predominant. Substantial amounts of monomethylarsonic acid ($\geq 28\%$ of As detected) and dimethylarsonic acid ($\geq 13\%$ of As detected) were detected through 2 WAT. Arsenic concentrations did not increase in any sample below 5 cm throughout the entire study; however, mass balance calculations revealed that As was predominately in the

soil, which indicates that soil As may accumulate over time. Data from this research suggest turfgrass clippings should be returned for at least 2 WAT following a MSMA application.

Further, MSMA should not be applied in conditions favoring downward movement in soils to groundwater (shallow water table depth, soil that favors leaching, and heavy rainfall forecasted).

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Environmental Fate of Arsenic Following Monosodium Methylarsenate (MSMA)
Applications to a Turfgrass System

by
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DEDICATION

This thesis is dedicated to my wife, Amanda Mahoney, with all my love and gratitude, for without her I could not have accomplished what I have. It is also in honor of my parents, Kevin and Tina Mahoney, whose support and encouragement was, and is, always unwavering.

BIOGRAPHY

Denis Joseph (DJ) Mahoney was born and raised in Darlington, SC to Kevin and Tina Mahoney. After graduating from The Byrnes Schools, he attended Clemson University, earning numerous awards along the way, and graduated Magna Cum Laude in spring of 2012 with a Bachelor of Science degree in Turfgrass Management Science. Following graduation, he married Amanda Martin Mahoney and spent his summer working at Clemson Extension with Dr. Bruce Martin, conducting fungicide and nematode research, before making his trek to North Carolina State University. He accepted a Research Assistant position under the guidance of Drs. Travis Gannon and Matthew Polizzotto where he has conducted research on then environmental fate of arsenic from MSMA and various fertilizers. Further, his work has included a novel approach in studying the effect of turfgrass management practices on arsenic distribution and species transformation following MSMA applications.

While at NC State, DJ received the Weed Science Society of North Carolina Outstanding MS Student Award. He was also recognized for his work by placing 1st in the oral poster presentation for the Weed Science Society of North Carolina and 2nd in the oral poster presentation for the Southern Weed Science Society. DJ and his wife are currently living in Cary, NC and are excitedly waiting for the birth of their first child.

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INTRODUCTION AND LITERATURE REVIEW

Versatility of Arsenic over Time: A Brief History

Arsenic (As) is a naturally occurring element and has been used throughout history in a variety of ways, ranging from medicinal purposes to an assassin's tool. It is a metalloid, present in organic and inorganic forms, which shares the properties of a metal; however, elemental As is nonductile (Hughes et al. 2011). Although As is best known for its toxicity, it has also been utilized for many beneficial purposes. Various As compounds were used to fill in cavities, reduce hypertension, treat skin and breast cancer, preserve food and wood, and control weeds and pests (Adams 2008; Hughes et al. 2011; Dumlu et al. 2007; Sepkowitz 2011).

Arsenic use in medicine can be seen as far back as 2700 B.C. in a Chinese medical journal, Nuci-King (Hyson 2007). The journal describes the use of arsenous acids or arsenates of sodium, potassium, or copper, to fill in tooth cavities and kill tooth worms. Arsenic is still used today in medicine; a product known as Trisonex, As trioxide, was approved by the Food and Drug Administration in 2000 for the treatment of relapsed Acute Promyelocytic Leukemia (Adams 2008).

Arsenic has also found a home in agriculture for hundreds of years. Paris Green (copper acetoarsenite), formally used as a pigment in wallpaper, was utilized as an insecticide to control the Colorado potato beetle and mosquitos in the latter half of the 19th century (Hughes et al. 2011; Sheindlin 2005). Lead arsenate was developed in the late 1800s to control gypsy moths in Massachusetts and was found to be less phytotoxic to crops than Paris Green because of its lower solubility. It was widely used in orchards in the early 1900s

(Peryea 1998). Organic arsenicals were used beginning in the 1950s and are present today in such compounds as disodium methylarsonate (DSMA) and monosodium methylarsenate (MSMA) (Hughes et al. 2011).

Despite the utility of many As-bearing compounds, the use of these products has raised concern due to the threat of groundwater As contamination following application. Recently, MSMA use on golf courses has been held responsible for significant environmental and human health threats. Feng et al. (2005) reported As species transformation and substantial leaching following MSMA applications in a constructed lysimeter experiment representing a golf course green. In other research, it was suggested that MSMA use in turfgrass was responsible for increased As concentrations of a nearby lake and research wells (Whitmore et al. 2008). In contrast, previous research has shown low mobility of As from MSMA in agricultural soils (Akkari et al. 1986; Hiltbold et al. 1974; Robinson 1975). Further, it may be hypothesized that turfgrass may help prevent losses due to MSMA foliar interception and absorption and/or root uptake following application (Duble et al. 1969). These results warrant further investigation.

Turf has many ecological benefits including soil erosion control, evapotranspirational-cooling, air cleansing qualities, and noise abatement properties (NTRI 2003; Sherrat 2011). Additionally, turfgrass systems have been reported to minimize pesticide leaching when compared to bareground systems. Cummings et al. (2009) reported that actively growing turfgrass minimized ^{14}C -simazine when compared to a bareground system. Matteson et al. (2014) determined As from MSMA increased soil As concentration to similar depths in turfgrass and bareground systems. However, total As recoveries in the

turfgrass system were increased compared to bareground, suggesting turfgrass was able to prevent downward movement of As from MSMA. Similar results were also reported by Gannon (2011) in regards to atrazine, mesotrione, MSMA, pendimethalin, and sulfentrazone applications to a bareground and turfgrass system. Pesticide leaching was increased in the bareground system compared to turfgrass. Each of the previous authors also detected increased pesticide concentration in treated turfgrass foliage compared to nontreated, which may have helped minimize downward movement. Previous research suggests that turfgrass may minimize downward mobility of pesticides, including MSMA, which may be due to foliar interception and/or root uptake. Further research is needed to quantify other potential concerns following MSMA applications to turfgrass (*e.g.* turfgrass clipping As concentration), to ensure proper management practices are in place to minimize As contamination potential from MSMA.

MSMA Use and Properties

MSMA falls under the organic arsenical class of herbicides, which have monomethylarsonic acid (MAA or MMA) as a shared structure (Figure 1). This class also includes dimethylarsonic acid (DMA) and calcium methylarsonic acid (CMA) (Massey et al. 2006). MSMA was first introduced to the public in December of 1963 with use sites including roadsides, cotton, turfgrass, and other crop and non-crop areas. It was estimated that ≈ 1.4 million kg of MSMA was applied annually prior to 2006, with the majority applied in cotton or turf systems (EPA 2009a).

MSMA is used as a post emergent herbicide to control many weeds including, but not limited to, goosegrass, crabgrass, dallisgrass, nutsedge, johnsongrass, foxtails, pigweeds,

and cocklebur (Hughes et al. 2011; Orme and Kegley 2006; Senseman 2007). MSMA has a very high water solubility ($1,040,000 \text{ mg L}^{-1}$ at 25°C), high organic carbon sorption (K_{oc} ; 250 to $2,850 \text{ mL g}^{-1}$), high soil adsorption coefficient (K_d ; 0.5 to 34.8 mL g^{-1}), low vapor pressure ($1.33 \times 10^{-3} \text{ Pa}$ at 20°C), and long soil half-life (180 days under field conditions) (Senseman 2007). Though the water solubility is very high, suggesting it may leach through soil, high K_{oc} and K_d values suggest it may bind to soil particles.

MSMA is readily absorbed by plant foliage and roots (Wauchope et al. 1992). Once it enters the plant, it may be translocated in the symplast or apoplast. Certain plant species metabolize MSMA to cacodylic acid (CA) or conjoin it with sugars, amino acids, organic acids, and/or other molecules. To date, evidence of demethylation into inorganic arsenicals or reduction to trivalent arsenic compounds has not been detected within plants (Senseman 2007). Although MSMA is readily absorbed by roots from solution, generally, translocation to shoots is limited (Duble et al. 1969; Wauchope et al. 1992).

There is little known resistance to MSMA (Camper et al. 2004), but the exact herbicidal site of action eludes researchers to date. Sckerl and Frans (1969) suggested that the MAA metabolite blocks a protein synthesis pathway or some other unknown biosynthetic pathway. Later, Knowles and Benson (1983) proposed that MAA interferes with photosystem I electron transport and enzymes of CO_2 fixation. Wauchope (1983) also suggested that MSMA affects photosynthetic electron transport, chlorophyll synthesis, and respiration in susceptible species. Senseman (2007) concluded that rapid desiccation in affected plants suggests cell membrane destruction. Further research is needed to determine

MSMA's site of action as it may lead to a better understanding of the herbicide and potentially aid in the discovery of new herbicide chemistries.

Regulation of As-based Herbicides

In 1988, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) was amended to accelerate the re-registration of active ingredients which were registered before November 1, 1984 (EPA 2009a). Just as with inorganic arsenical pesticides, regulations were enacted on organic arsenical use, including MSMA. In 2006, the United States Environmental Protection Agency (USEPA) enacted a phase-out in which products containing MSMA were ineligible for reregistration because of human health and environmental contamination risks. By March of 2009, herbicide labels were amended to adopt new mitigation techniques, and their use was to stop completely after December 31, 2013 (EPA 2009a). In cotton production, one postemergent application of 2.25 kg ai ha⁻¹ was allowed, with a second for salvage purposes only (*e.g.* for pigweed eluding the first application). A 50-foot buffer must be maintained around bodies of water. In golf courses, spot treatments (100 ft² per spot) were allowed; however, total spot treatments cannot exceed 25% of total acreage. One full application was allowed for newly constructed courses. In sod farms, one to two applications were allowed while maintaining a 25-foot buffer around bodies of water. Highway right-of-ways were restricted to two applications with a 100-foot buffer maintained around bodies of water. MSMA use for residential turf, forestry, non-bearing fruits and nuts, citrus, and bluegrass, fescue, and ryegrass grown for seed was to be deleted from product labels (EPA 2009b).

Changes were later made to the reregistration availability of MSMA in select use sites. In February 2009, the USEPA granted MSMA reregistration eligibility for use in cotton only, with the phase-out remaining intact for all other use sites. A 2012 Congressional directive has since halted the phase-out for sod farms, golf courses, and highway rights-of-ways set forth by the USEPA, therefore allowing these sites to continue MSMA use while maintaining the mitigation measures previously stated. The 2009 agreement was amended to include a National Academy of Sciences review of the mode of action for carcinogenic effects by inorganic As, scheduled to be completed in late 2015 (EPA 2013).

Arsenic Speciation: Toxicity, Mobility, and Transformation

Although As is generally thought of as a poison or serious toxin, its speciation is a significant factor in these characteristics. Arsenic may be present in various valence states, such as As(-III), As(0), As(+III), or As(+V) and either organic or inorganic forms (Smith et al. 2002; Jones 2007). Many unknowns persist on how As may react in complex, real-world environments. Research to date has not evaluated soil As speciation in a turfgrass system, with very limited research on porewater As species following MSMA applications.

Arsenic speciation and toxicity

Inorganic As species are listed as carcinogens (Hughes et al. 2011), but it has been suggested that they may play an essential role for metabolism of methionine, an essential amino acid (Uthus 1992). Nonetheless, increased incidence in cancer of the lungs, bladder, skin, kidney, liver, and potentially prostate have been linked to As ingestion (ATSDR 2007). Exposure to As in drinking water may also cause other non-cancerous problems, including skin lesions, cardiovascular disease, neurological effects, and diabetes (ATSDR 2007). In

general, arsenite [As(III)] is more toxic than arsenate [As(V)], with both forms being highly more toxic than organoarsenicals (Table 1), with the exception being monomethylarsonous acid [MMA(III)] (Caussy 2003; Hughes et al. 2011; Mass et al. 2001; Peryea 1998; Schneindlin 2005). Organic As exposure may cause diarrhea, decreased body weight, respiratory arrest, or in serious cases, death ($> 2500 \text{ mg kg}^{-1} \text{ day}^{-1}$) (ATSDR 2007). While these effects are concerning, the paramount concern is not organic As species directly, but their metabolites, which may consist of inorganic species (EPA 2009; Voice et al. 2011).

Arsenic speciation and mobility within soils

In addition to toxicity, As speciation also effects binding capacities within soil. Arsenic species are fixed by iron and aluminum hydrous oxides in soil, with sorption generally increasing as particle size decreases (Caussy 2003; Jones 2007; Porter et al. 2010; Senseman 2007; Smith et al. 2002). Pigna et al. (2006) reported As(V) sorption capacities of metal oxides in the following order: ferrihydrite $>$ goethite $>$ noncrystalline $\text{Al}(\text{OH})_x$ $>$ gibbsite. Generally, As(V) maximum soil sorption occurs in pH ranges below neutral (pH 3.5-6) while the As(III) sorption maxima is above neutral (pH 8-10) (Lafferty and Loeppert 2005). Additionally, Lafferty and Loeppert (2005) suggested that as methylation proceeds from inorganic to organic As species, the adsorption potential decreases. Yet, Shimizu et al. (2011) detected binuclear bidentate complexes between MMA and As(V) with goethite, suggesting MMA may form strong bonds in soil that are difficult to break, minimizing desorption.

However, despite the strong affinity of As species for soil, desorption of As(V) and MMA has been shown to occur. Lafferty and Loeppert (2005) detected desorption of MMA

and As(V) with pH changes of + 3 units or more. In contrast, DMA desorption occurred readily as pH increased from 3.5 to 9. Pigna et al. (2006) detected desorption of As(V) from gibbsite (56%) and Al(OH_x) (48%) when phosphate, a competing ligand with similar structure to arsenate, was added to the system. The authors further reported that as As residence time in the system increased, the amount desorbed by phosphate decreased.

In general, it may be concluded that As is readily bound to soil, but many factors affect its bond formation and strength. The majority of studies on As speciation have been completed in a laboratory setting with very time- and model limited studies. Accordingly, field research is needed to investigate As mobility in the environment following MSMA application in order to better establish complexities such as herbicide application, rainfall, and vegetation that may impact the fate of As in real-world settings.

Arsenic species transformation

The As species present can have impacts on its binding potential, water solubility, and toxicity. Consequently, previous research has examined As species transformations after organic arsenical treatment. Shimizu et al. (2011) evaluated methylarsenic reactivity and speciation transformation over time in aerobic soil suspensions. Following incubation with MMA, the water samples suggested that initial MMA sorption was 100% as concentrations in the solution were consistently low and did not change significantly over the year. In contrast, DMA was detected in higher concentrations at one-week after incubation, but was eventually sorbed by soil throughout a year. The lower initial affinity of DMA may be attributed to the extra methyl group, which affects size, charge, and geometry. Shimizu et al. (2011) attributed the higher sorption over time to demethylation and formation of As(V),

which was then sorbed to soil. The authors also reported bidentate binuclear complexes between MMA and goethite and were also detected with As(V) and goethite following demethylation of MMA and DMA. The binding trends suggest, once introduced into the environment, species transformation may occur and As(V) will be bound to soil. Further investigation is needed to determine how As from MSMA will react under real-world environmental conditions (*e.g.* application to a turfgrass system) and its effect on mobility through the system.

Bednar et al. (2002) measured the presence of As in water and soil samples in areas where organoarsenicals were commonly used. In rice field overflow, the authors reported low As concentrations ($\approx 2 \mu\text{g L}^{-1}$) consisting of primarily As(III) with trace amounts of DMA, which was attributed to the highly reducing environment. Arsenic concentrations $> 10 \mu\text{g L}^{-1}$ from surface water samples at crop duster airstrips showed significant concentrations of MMA, DMA, As(III), and As(V). Arsenic(III) was present in lowest concentration in each sample. Within soil samples, using sequential extractions, the authors reported As(V) as the predominant species ($> 58\%$). Irrigation well samples were also taken from 10 wells at various distances (0.4 to 16 km) from a crop duster airstrip. Arsenic concentrations decreased as distance from the airstrip increased and never exceeded $5.9 \mu\text{g L}^{-1}$. Within the samples, methylated As species were not detected. Irrigation and domestic well samples adjacent to cotton fields with long-standing organic arsenical use showed background As concentrations of 0.1 to $0.5 \mu\text{g L}^{-1}$. The authors concluded that As species transformation occurs within the soil, causing As cycling in surface water and/or groundwater that interacts with the soil.

Determining the cycling mechanisms and/or management practices that impact As species transformation, is critical as they may impact contamination potential following MSMA applications to turfgrass.

Feng et al. (2005) determined the effect of soil substrate on As species mobility following MSMA applications using constructed lysimeters. Evaluated soil substrates included uncoated sand (pure washed quartz), uncoated sand plus peat (90:10), and naturally coated sand plus peat (90:10). Porewater samples were collected from 40.6 cm depth weekly for 14 weeks. Overall, the total As leached (as a percent of total applied) was as follows: uncoated sand substrate (18.6%) > uncoated sand plus peat (10.8%) > naturally coated sand plus peat (7%). The authors attributed lower detected As amounts in the natural substrate to the mineral-clay coating, which provided binding sites for As. Within porewater from each substrate, DMA was the predominant species detected through 2 weeks after final MSMA treatment, and As(V) was the predominant species thereafter. These results may be attributed to the lower binding affinity of DMA (Lafferty and Loeppert 2005; Shimizu et al. 2011), causing increased leaching initially but eventual demethylation to As(V) and retention of As.

Although As speciation was determined by Feng et al. (2005) in a more real-world scenario, discrepancies within the research warrant further investigation. For instance, the authors investigated MSMA applications to bermudagrass putting greens, which is not commonplace because of injury to turfgrass following application (Johnson 1980). Additionally, putting greens built to U.S. Golf Association specifications are engineered to percolate water rapidly and are not representative of other golf course areas. Soil and its constituents have been shown to significantly impact As retention (Feng et al. 2005; Lafferty

and Loeppert 2005; Pigna et al. 2006; Shimizu et al. 2011), suggesting that further investigation is needed as the soil used by Feng et al. (2005) consisted of 0.2% silt + clay. MSMA applications evaluated are also unrealistic, as three applications of MSMA at 2.25 kg ha⁻¹ is over the current labeled limit. The authors state that percolate was collected following “leachable events”; yet, the “events” were never defined or cited, which limits the ability to draw conclusions on potential contamination concerns following rainfall events.

Sierra-Alvarez et al. (2006) measured biotransformation of organic arsenical pesticides under anaerobic conditions. MMA(V) was added to heat-killed sludge and nontreated sludge under methanogenic conditions. After 112 d, a reduction in MMA(V) (49.3%) was detected with concentrations remaining constant to 236 d in nontreated sludge. MMA(III) was the byproduct and was equivalent to the 28.9% of the MMA(V) that was removed. Under sulfate-reducing conditions, near-total reduction of MMA(V) (95.8%) was detected 57 d after incubation, with MMA(III) concentrations (19.4%) significantly increasing over time. Under denitrifying conditions, no MMA(III) was detected; however, DMA(V) was detected as a metabolite consisting of only 2.5% of reduced MMA(V). Arsenic species remained unchanged in the heat-killed sludge, suggesting that species transformation is biologically mediated. Additionally, it was concluded that dangerous amounts of MMA(III) may occur under very reducing conditions. In a managed turfgrass system, anaerobic conditions are avoided by various management practices (*e.g.* aerification, verticutting, etc.) to ensure proper turfgrass health (Zhang et al. 2013), suggesting that these species transformations may not be a significant factor in managed turfgrass.

Arsenic Fate Following MSMA and Other Organic Arsenical Applications to Soil and Vegetated Systems

Arsenic fate in plants

MSMA and other organic arsenicals have been studied to determine the potential risk of As accumulation in plants. Wauchope and Street (1987a) measured the absorption of MSMA into rice foliage (*Oryza sativa* L. cv. Labelle) over time following a broadcast application at two different rates and plant growth stages. Approximately 50% of the product had been absorbed within two hours and was unable to be recovered by vigorous washing. The authors reported complete absorption occurred one week after treatment and concluded that unless rainfall occurs within hours following application, minimal loss will occur via foliar dislodgement (Wauchope and Street 1987b). Turfgrass may reduce groundwater contamination risks as MSMA may absorb readily into turfgrass and minimize movement into the soil or porewater.

Sachs and Michael (1971) determined As speciation following MSMA sorption. The authors reported rapid absorption of MSMA into bean foliage (*Phaseolus vulgaris* L. 'Black Valentine'). MSMA demethylation to inorganic As or trivalent As compounds was not detected within the plant. It has been suggested that MSMA coalesces with sugars, amino acids, and other organic acids (Senseman 2007; Duble et al. 1969) as opposed to being broken down. Sachs and Michael (1971) determined that MSMA forms a ninhydrin-positive complex in bean plants, which was hypothesized to be the herbicidal activity.

In regards to another organic arsenical, Duble et al. (1969) detected rapid absorption of ^{14}C -DSMA into Coastal Bermudagrass (*Cynodon dactylon* L. Pers.). Within five d after

treatment (DAT), 76% of DSMA remained at the site of application and 24% was found in the roots. Translocation of ^{14}C -DSMA through the vascular system of the plant was detected. The bermudagrass was clipped to ground level at seven DAT, and As concentrations were measured in the roots and regrowth. The regrowth contained low As concentration, while root concentration decreased from 45 to 13 mg kg⁻¹, suggesting exudation into the soil. Arsenic continued to be mobile within the bermudagrass, with 80% of initial applied As being found in the roots 30 DAT. Dubble et al. (1969) also detected uptake of DSMA from a nutrient solution. This may have implications on As cycling in a turfgrass system, depending on clipping management.

Matteson et al. (2014) reported elevated turfgrass aboveground vegetation As concentrations one year after MSMA applications, when compared to nontreated turfgrass. These results suggest that there may be potential As contamination risks through grass clipping displacement following MSMA applications. Clipping As concentration may be elevated and when returned to the surface following mowing, may re-introduce As to the surface. Following tissue degradation, As may be released, enter soil solution, and be taken back up into the plant (Dubble et al. 1969). Further investigation is needed to determine the effects of clipping management on As cycling following MSMA applications to managed turfgrass.

Arsenic fate in soil

Previous research has also been completed to determine the effects of MSMA applications on total As concentration within soil. Robinson (1975) detected As residues in soil annually over a five-year period following MSMA applications. Soil samples (10 cm

depth) were taken throughout the experiment through 90 cm (15 cm increments) sampled two and five years after treatment. Soil analysis showed rates $< 36 \text{ kg MSMA ha}^{-1}$ did not increase soil As concentration over the evaluation period. In contrast, two high rates (144 and 288 kg ha^{-1}) resulted in increased soil As concentration each year. Following five applications, 288 kg ha^{-1} increased As concentrations through a 30-cm depth. Current maximum application rates (4.5 kg ha^{-1}) fall below these tested rates (EPA 2009), suggesting that MSMA may not impact soil As concentration.

Hiltbold et al. (1974) measured the soil As distribution following six annual MSMA applications. From 1966 to 1971, three different soil types (Hartsells fine sandy loam, Decatur silt loam, and Dothan loamy sand soils) received 10, 20, or $40 \text{ kg MSMA ha}^{-1}$ (2.5, 5, or 10X normal use rate). Increased soil As was detected in the upper 15 cm from the Decatur silt loam and Dothan loamy sand, with an increase to 30 cm detected from the Hartsells fine sandy loam. The increase below 15 cm was attributed to management as the field was tilled at a 23 cm depth. Within the soils, 67, 57, and 39% of applied As was recovered in Hartsells fine sandy loam, Decatur silt loam, and Dothan loamy sand soils, respectively. Hiltbold et al. (1974) attributed the low recoveries to gaseous loss due to As methylation leading to volatilization. Quantifying these losses from the system is critical in understanding the fate of As from MSMA. Arsenic mass balance following a MSMA application has not been completed to date, but is needed to understand As distribution over time within a system. Determining As distribution over time may highlight potential contamination risks.

A four-year study by Akkari et al. (1986) was conducted to determine MSMA degradation over time in soil. MSMA was applied at 4.4 kg ha^{-1} annually with samples to a 15 cm depth taken each year prior to and at intervals following application. An average As increase of 0.85 mg kg^{-1} was detected in the first two months, but was later reduced to background concentrations. The sample dates were not expressed by the authors, but they suggested that at normal use rates, MSMA might not cause As accumulation in soil due to losses by crop removal and leaching. These conclusions warrant investigation to ensure the integrity of human and environmental health.

Johnson and Hiltbold (1969) evaluated soil and crop As content following four annual organic arsenical applications. The study was completed on an established bermudagrass site with four annual MSMA and DSMA applications of 2.23, 4.47, or $8.95 \text{ kg a.i. ha}^{-1}$. Following the final year, soil samples were taken at 0-5, 5-15, or 15-30 cm depth. The authors detected the greatest As concentration in the top 5 cm of soil. At the lowest rate, all of the applied As was found in the top 30 cm of soil, with 75% and 50% being recovered at 4.47 and 8.95 kg ha^{-1} rates, respectively. Incomplete recoveries at the higher application rates were attributed to crop removal or leaching below 30 cm. Clippings were removed at each mowing event following application and leachate samples were not collected. These As pools need to be quantified over time to determine potential threats presented by each.

Matteson et al. (2014) monitored As concentrations in bermudagrass, soil, and porewater samples (76 cm depth), through one year, following two MSMA applications (2.25 kg ha^{-1} per application) in a turfgrass and bareground system. The authors detected elevated As concentration in bermudagrass aboveground vegetation through one-year after treatment

compared to nontreated bermudagrass. Through 120 days after initial treatment (DAIT), increased soil As concentrations were detected to a 8 cm depth. By 365 DAIT, increased soil As concentrations were detected to a 15 cm depth. Porewater As concentrations ($< 2 \mu\text{g L}^{-1}$) from MSMA-treated areas remained similar to nontreated areas.

Quantification of As in turfgrass clippings requires investigation as it has not been previously determined, and elevated As concentration in turfgrass aboveground vegetation was reported one year after treatment (Matteson et al. 2014). Further, the data suggest downward As movement over time as soil As concentrations were elevated to deeper depths at 365 DAIT when compared to previous sample dates. In contrast to Feng et al. (2005), Matteson et al. (2014) reported no increased porewater (76 cm depth) As concentration. This may be attributed to soil texture differences, as soil evaluated by Feng et al. (2005) consisted of 0.2% silt + clay, while Matteson et al. (2014) evaluated soil consisting of 8% silt + clay. Sample depth differences also likely affect porewater differences, suggesting that dissolved As may be able to reach shallow water tables instead of being bound to soil. Further investigation is required to determine potential threats following MSMA application from a turfgrass system.

Objectives

Currently, numerous knowledge gaps exist concerning the fate of As from MSMA applications to established turfgrass systems. Previous research has determined elevated As concentrations in bermudagrass aboveground vegetation one-year after treatment, which warrants further investigation as clipping As content was not determined and they may pose environmental contamination concerns following disposal. Additionally, As speciation in

soil, porewater, and leachate over time following MSMA application require identification, as they impact binding and mobility potential within the system and significantly impact As toxicity. A comprehensive As mass balance over time following a MSMA application to turfgrass has not been completed to date. Understanding As pools and fate over time is critical in identifying contamination concerns and/or proper management practices for end users in order to mitigate environmental and human health risks.

Based on the importance of turfgrass systems, the wide reliance on MSMA, and current unknowns about the fate of As following MSMA applications to turfgrass, the specific objectives of the current research were to:

1. Identify potential environmental threats over time following MSMA applications in a bareground and turfgrass system.
2. Determine a comprehensive mass balance of As in a turfgrass system following a MSMA application.
3. Quantify As species transformations over time at different depths following a MSMA application to a turfgrass system.

To accomplish these objectives, this research employed field and greenhouse lysimeter experiments to establish the impacts of MSMA applied to bermudagrass. Results from this work will help determine the potential for As groundwater contamination, best management practices to prevent off-target damage/contamination, and the cycling of As following MSMA application to a turfgrass system.

Literature Cited

- Adams, S.L. 2008. Arsenic: medicinal double-edged sword. *Hem/Onc Today*. 9:32.
- Akkari, K.H., R.E. Frans, & T.L. Lavy. 1986. Factors affecting degradation of MSMA in soil. *Weed Sci.* 34:781-787.
- ATSDR. 2007. Toxicological profile for arsenic. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Atlanta,GA. Available at: <http://www.atsdr.cdc.gov/ToxProfiles/tp2.pdf>.
- Bednar, A.J., J.R. Garbarino, J.F. Ranville, and T.R. Wildeman. 2002. Presence of organarsenicals used in cotton production in agricultural water and soil of the southern United States. *J. Agr. Food Chem.* 50:7340-7344.
- Camper, N.D., R.J. Keese and P.S. Coker. 2004. MSMA resistance studies. *J. Environ. Sci. and Heal. B.* 39:665-673.
- Caussy, D. 2003. Case studies of the impact of understanding bioavailability: arsenic. *Ecotox. Environ. Safe.* 56:164-173.
- Cummings, H.D., J.B. Weber, F.H. Yelverton, R.B. Leidy. 2009. Downward mobility of ¹⁴C-labeled simazine in a bermudagrass system vs. a fallow soil system. *Crop Sci.* 49:704-713.
- Duble, R.L., E.C. Holt, and G.G. McBee. 1969. Translocation and break-down of disodium methanearsonate (DSMA) in coastal bermudagrass. *J. Agr. Food Chem.* 17:1247-1250.
- Dumlu, A., M. Guvercin, V. Olgac, and S. Yalcinkaya. 2007. Osteomyelitis due to arsenic trioxide Use for tooth devitalization. *Int. Endod. J.* 40:317-22.

- EPA. 2009a. Revised reregistration eligibility decision for MSMA, DSMA, CAMA, and cacodylic acid. Retrieved from EPA.gov website:
<http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockkey=P10013JM.PDF>
- EPA. 2009b. Guidance for products containing the organic arsenicals. EPA Office of Pesticide Programs. Available at:
http://www.epa.gov/pesticides/reregistration/arsenic_guid_label_table.pdf
- EPA. 2013. FR Doc. 2013–07089. EPA Office of Pesticide Programs. Available at:
<http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2009-0191-0026>.
- Feng, M., J.E. Schlau, R. Snyder, G.H. Snyder, M. Chen, J.L. Cisar, and Y. Cai. 2005. Arsenic transport and transformation associated with MSMA. *J. Agr. Food Chem.* 53:3556-3562.
- Gannon, T.W. 2011. Leaching Potential and Efficacy of Select Herbicides in Turfgrass Environments. Ph.D. dissertation. Raleigh, NC: North Carolina State University. 151 p.
- Hiltbold, A.E., B.F. Hajek, and G.A. Buchanan. 1974. Distribution of arsenic in soil profiles after repeated applications of MSMA. *Weed Sci.* 22:272-275.
- Hughes, M.F., B.D. Beck, Y. Chen, A.S. Lewis, and D.J. Thomas. 2011. Arsenic exposure and toxicology: a historical perspective. *Toxicol. Sci.* 123:305-332.
- Hyson, J.M., Jr. 2007. A history of arsenic in dentistry. *J. Calif. Dent. Assoc.* 35:135-39.
- Johnson, L.R. and A.E. Hiltbold. 1969. Arsenic content of soil and crops following use of methanearsonate herbicides. *Soil Sci. Soc. Amer. Proc.* 33:279-282.

- Johnson, B.J. 1980. Goosegrass (*Eleusine indica*) control in bermudagrass (*Cynodon dactylon*) turf. Weed Sci. 28:378-381.
- Jones, F.T. 2007. A broad view of arsenic. Poultry Sci. 86:2-14.
- Knowles, F.C. and A.A. Benson. 1983. Mode of action of a herbicide: johnsongrass and methanearsonic acid. Plant Physiol. 71:235-240.
- Lafferty, B.J. and R.H. Loeppert. 2005. Methyl arsenic adsorption and desorption behavior on iron oxides. Environ. Sci. Technol. 39:2120-2127.
- Mass, M.J., A. Tennant, B.C. Roop, W.R. Cullen, M. Styblo, D.J. Thomas, and A.D. Kligerman. 2001. Methylated trivalent arsenic species are genotoxic. Chem. Res. Toxicol. 14:355-361.
- Massey, J.H., J.M. Taylor, N. Binbuga, K. Chambers, G.E. Coats, and W.P. Henry. 2006. Iron antagonism of MSMA herbicide applied to bermudagrass: characterization of the Fe^{2+} -MAA complexation reaction. Weed Sci. 54:23-30.
- Matteson, A.R., T.W. Gannon, M.D. Jeffries, S. Haines, D.F. Lewis, and M.L. Polizzotto. 2014. Arsenic retention in foliage and soil after monosodium methyl arsenate (MSMA) applications to turfgrass. J. Environ. Qual. 43:379-388.
- NTF. 2011. National turfgrass research initiative. National Turfgrass Federation. Available at: <http://www.ntep.org/pdf/turfinitiative.pdf>.
- Orme, S. and S. Kegley. 2006. PAN pesticides database. <http://www.pesticideinfo.org>
- Peryea, F.J. 1998. Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation. In: Proceedings of the 16th World Congress of Soil Science. 20–26 August 1998, Montpellier, France, pp. 7.

- Pigna, M., G. Krishnamurti, and A. Violante. 2006. Kinetics of arsenate sorption-desorption from metal oxides: effect of residence time. *Soil Sci. Soc. Am. J.* 70:2017-2027.
- Porter, S.K., K.G. Scheckel, C.A. Imperlitteri, and J.A. Ryan. 2010. Arsenic. In: *Toxic Metals in the Environment: Thermodynamic Considerations for Possible Immobilization Strategies for Pb, Cd, As, and Hg* (pp. 546-562). London: Taylor and Francis.
- Robinson, E.L. 1975. Arsenic in soil with five annual applications of msma. *Weed Sci.* 23:341-343.
- Sachs, R.M. and J.L. Michael. 1971. Comparative phytotoxicity among four arsenical herbicides. *Weed Sci.* 19:558-564.
- Sckerl, M.M. and R.E. Frans. 1969. Translocation and metabolism of MAA-¹⁴C in johnsongrass and cotton. *Weed Sci.* 17:421-427
- Senseman, S.A. 2007. *Herbicide handbook*. Lawrence, KS: Weed Science Society of America.
- Sepkowitz, K.A. 2011. One hundred years of salvarsan. *N. Engl. J. Med.* 365:291-293.
- Sherratt, P. 2011. The benefits of turf. Sports Turf Managers Association. Available at: http://www.stma.org/sites/stma/files/Technical_Resources/OSU_Benefits_of_turf.pdf.
- Shimizu, M., Y. Arai, and D.L. Sparks. 2011. Multi-scale assessment of methylarsenic reactivity in soil: 2. distribution and speciation in soil. *Environ. Sci. Technol.* 45:4300-4306.

- Sierra-Alvarez, R., U. Yenai, J.A. Field, M. Kopplin, A.J. Gandolfi, and J.R. Garbarino. 2006. Anaerobic biotransformation of organoarsenical pesticides monomethylarsonic acid and dimethylarsinic acid. *J. Agr. Food Chem.* 54:3959-3966.
- Smith, E., R. Naidu, and A.M. Alston. 2002. Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. *J. Environ. Qual.* 31:557-563
- Uthus, E.O. 1992. Arsenic essentiality: a role affecting methionine metabolism. *J. Trace Elem. Exp. Med.* 16:345–355.
- Voice, T.C., L.V. Flores del Pino, I. Havezov, and D.T. Long. 2011. Field deployable method for arsenic speciation in water. *Phys. Chem. Earth.* 36:436-441.
- Wauchope, R.D. 1983. Uptake, translocation and phytotoxicity of arsenic in plants. In: *Arsenic: Industrial, Biochemical, Environmental Perspectives*; Lederer, W.H., Fensterhein, R.J., Eds.; Van Nostrand Reinhold Company Inc.: NY, 348–375.
- Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W. Augustijn-Beckers, and J.P. Burt. 1992. The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.* 123:1-155.
- Wauchope, R.D. and J.E. Street. 1987a. Fate of a water-soluble herbicide spray on foliage. part 1. Absorption and dissipation of foliar msma deposits: Mathematical modelling. *Pestic. Sci.* 19:253-263
- Wauchope, R.D. and J.E. Street. 1987b. Fate of a water-soluble herbicide spray on foliage. part 2. Absorption and dissipation of foliar msma deposits: Mathematical modelling. *Pestic. Sci.* 19:253-263.

- Whitmore, T.J., M.A. Riedinger-Whitmore, J.M. Smoak, K.V. Kolasa, E.A. Goddard, and R. Bindler. 2008. Arsenic contamination of lake sediments in Florida: evidence of herbicide mobility from watershed soils. *J. Paleolimnol.* 40:869-884.
- Zhang, Q., A.J. Zuk, and K. Rue. 2013. Turfgrass responded differently to salinity, waterlogging, and combined salinity-waterlogging conditions. *Crop Sci.* 53:2686-2692.

Table 1. Arsenic species toxicity in rats over various exposure durations.^a

Species	Exposure duration	mg kg ⁻¹ d ⁻¹	As species	Symptoms
Rat	Once	44	As(III)	Death
Rat	Once	112	Calcium arsenate [As(V)]	Death
Rat	Once	175	Lead arsenate [As(V)]	Death
Rat	Once	3184	MSMA	Death
Rat	52 wk	106.9	MMA	Increased mortality
Rat	6 wk	10.9	As(V)	Decreased body weight gain
Rat	16 wk	0.92	As(III)	Decreased erythrocyte and leukocyte numbers
Rat	2.25 yrs	30	As(V)	Increased mortality
Rat	2 yrs	1	As(III)	Increased mortality and decrease life span
Rat	2 yrs	72.4	MMA	Increased mortality

^aTable adapted from ATSDR 2007

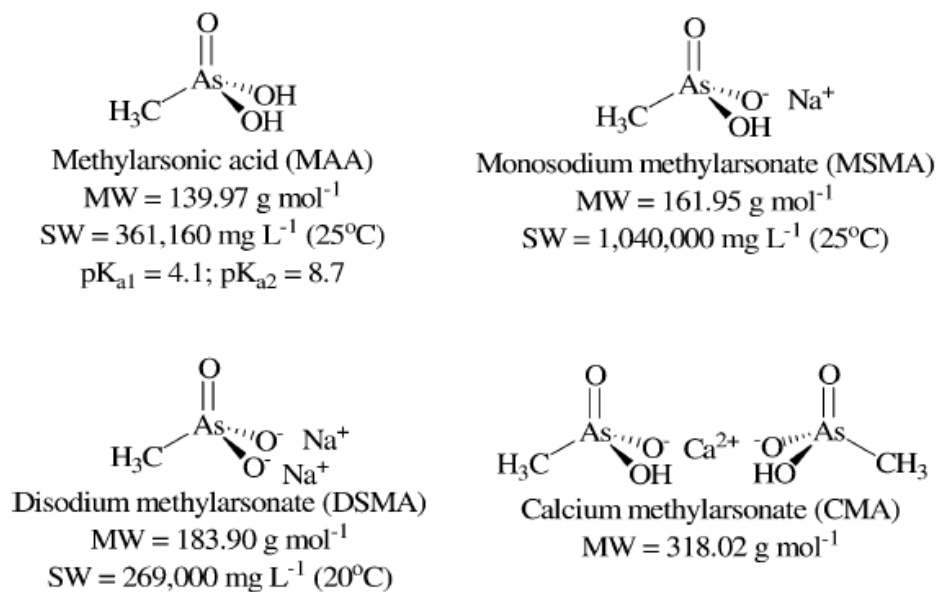


Figure 1. Organic arsenical herbicides, MSMA, DSMA, and CMA, share the common MAA (or MMA) structure (Massey, 2006).

ARSENIC FATE FOLLOWING HERBICIDE AND FERTILIZER APPLICATIONS IN A MANAGED TURFGRASS SYSTEM

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A field lysimeter experiment was conducted from 2012-2013 to determine the fate of arsenic (As) following monosodium methylarsenate (MSMA) and As-containing fertilizer applications to bareground and established turfgrass systems. MSMA-treated lysimeters received two sequential MSMA applications ($2.25 \text{ kg a.i. ha}^{-1}$) on a 7 d interval. Fertilizer treatments were based on nitrogen loading rates and treated lysimeters received either three applications at 54 kg N ha^{-1} , one application at 294 kg N ha^{-1} , or two applications at 294 kg N ha^{-1} with sequential applications on 30 d intervals. Fertilizer rates provided 0.08, 0.16, and 0.32 mg As per lysimeter, respectively. Aboveground vegetation, soil, and porewater As concentrations were measured through one year following MSMA and fertilizer applications. Increased As concentrations in aboveground vegetation, soil, or porewater were not detected at any time following fertilizer treatments in either system, compared to nontreated lysimeters. MSMA-treated aboveground vegetation As concentration was increased through 120 d after initial treatment (DAIT) compared to nontreated. Increased soil As was observed at 0-4 cm at 30 and 120 DAIT and 0-8 cm at 60 and 365 DAIT, suggesting that As was bound in shallow soil depths. Porewater revealed lower As concentrations at 76 cm depth (0.4 to $5.1 \text{ } \mu\text{g L}^{-1}$) compared to 30 cm depth (22 to $83.8 \text{ } \mu\text{g L}^{-1}$). Within porewater samples, As concentration maximums in bareground samples from 30 and 76 cm depth (83.8 and 5.1

$\mu\text{g L}^{-1}$, respectively) were greater than turfgrass samples at these depths (56 and $0.9 \mu\text{g L}^{-1}$, respectively). Results indicate that vegetation management needs to be considered, as it may be a potential source for off-target As movement. Additionally, turfgrass coverage may help prevent As leaching through soil due to plant and soil conditions, but contamination may occur in areas with shallow water tables.

1. Introduction

Monosodium methylarsenate (MSMA) and fertilizers are commonly used in turfgrass systems to control weeds and promote plant health. This is concerning due to potential off-target arsenic (As) contamination following application. MSMA is an organic arsenical herbicide common to agronomic systems and is labeled for use in cotton (5 million ha), turfgrass sod farms (165,700 ha), golf courses (608,700 ha), and roadways (6.6 million km) (USDA 2007; USGA 2012; USDOT 2013). In the United States (US), 1.4 million kg of MSMA was applied annually prior to 2006 (EPA 2009). However, in 2006, the US Environmental Protection Agency (USEPA) enacted a phase-out of all organic arsenical herbicides, including MSMA, due to groundwater As contamination concerns. MSMA use has since been extended pending a National Academy of Sciences' review, which will conclude in 2015 (EPA 2013).

Fertilizers, which are commonly used in agronomic systems, home lawns, and many other systems, may also contain As (Cheraghi et al. 2012). Fertilizer use sites may be expansive, as it was estimated that there is 132 million ha of cropland and 16.4 million ha of turfgrass in the US (USDA 2013; Milesi et al. 2005). Approximately 19 billion kg of fertilizer was applied to various use sites in the US during 2011 (USDA 2013). Regulations have been placed on fertilizer heavy metal content, including As, to reduce adverse environmental and human health impacts. By 1947, fertilizer regulations were in place in all but one state (AAPFCO 2008). Further regulations have been enacted to reduce As content in fertilizers, allowing 13 mg kg⁻¹ per 1% P₂O₅ or 112 mg kg⁻¹ per 1% micronutrient (AAPFCO 2008). However, concerning amounts of As may be continually applied, as Jiao et al. (2012)

reported 7% of sampled fertilizers ($n = 203$) had As concentrations $> 20 \text{ mg As kg}^{-1}$ with 2 samples reporting at 85 and 155 mg As kg^{-1} .

Although fertilizer- and MSMA-derived As additions to cropland and turfgrass systems are concerning from an environmental perspective, these As-bearing products provide substantial agronomic and aesthetic benefits (EPA 2009; Turner and Hummel 1992); accordingly, these additions have spurred research on As fate following application. Previous research has been completed to determine As fate within plants and soil following MSMA applications. It has been reported that MSMA is readily absorbed by and translocated throughout plants (Armbrust and Bridges 2002; Sachs and Michael 1971; Sckerl and Frans 1969; Wauchope et al. 1992) and may persist, as Matteson et al. (2014) detected increased As concentration in MSMA-treated-turfgrass-aboveground-vegetation compared to nontreated, one year after MSMA treatment. Within soil, previous research has detected increased As from 0-15 cm depth in agronomic crop or turfgrass systems following repeated MSMA applications (Akkari et al. 1986; Feng et al. 2005; Hiltbold et al. 1974; Matteson et al. 2014; Robinson 1975). While previous research suggested As from MSMA is bound near the soil surface, further research is needed to determine potential contamination risks following application. The fate of As in turfgrass systems requires particular attention because little research has been conducted in these systems, where MSMA is commonly applied. Further, unique contamination concerns such as vegetation disposal following mowing events may be present and need to be evaluated.

Although the phase-out of MSMA was due in part to groundwater contamination concerns, research is limited in this area. Feng et al. (2005) detected up to 18% of As from

MSMA in porewater (40.6 cm depth) over 14 weeks following three applications. In contrast, Matteson et al. (2014) detected no increase in porewater (76 cm depth) As concentration within MSMA-treated lysimeters compared to nontreated lysimeters through one year following applications. Differences may be attributed to experimental setup, as Feng et al. (2005) used constructed lysimeters with shallower porewater sampling depth while Matteson et al. (2014) utilized field lysimetry and a deeper sampling depth. Further, Feng et al. (2005) evaluated a pure quartz sand soil, whereas Matteson et al. utilized a sand soil consisting of 4% each silt and clay. New research is needed to address multiple issues such as, the effect of rainfall following application, potential management practices to prevent off-target and/or groundwater contamination, and the ability of As to reach shallow depths before being bound to soil.

Although limited, previous research has examined the effects of fertilizer applications on soil As concentrations. Fertilizer applications from 1888-1947 were reported to have increased soil As (0-23 cm depth) in a hay field; however, in the same field, from 1959-2011 increased soil As was not detected, which was attributed to the reduced As content in fertilizer (Hartley et al. 2013). Chen et al. (2007) detected no increase in soil As concentration over a 100 yr simulation of high-As (13 mg kg^{-1}) fertilizer applications to cropland, which included a sandy loam and clay loam soil. Cheraghi et al. (2012) detected increased As (0-20 cm depth) in cucumber, potato, and sugar beet fields following long-term fertilizer applications that contained high As concentrations ($19\text{-}273 \text{ mg kg}^{-1}$), but attributed the increase to other variables, which were not made clear. Research to date has not determined potential groundwater contamination concerns following high-As fertilizer

applications in any system. Further, previous research studying fertilizer As inputs has focused on soil As concentrations in cropland areas. Determining fertilizer As inputs is critical as it may affect turfgrass health (Turner and Hummel 1992) and use sites (*e.g.* golf courses) may be adjacent to sensitive areas such as lakes, ponds, and wetlands.

Currently, numerous knowledge gaps exist regarding the fate of As from MSMA and fertilizer applications to turfgrass. Whereas research has been conducted on crop As residues following MSMA and fertilizer application, research is limited in regards to turfgrass aboveground vegetation. Further investigation is warranted to determine As concentrations within turfgrass vegetation following application because potential contamination may exist following disposal. Additionally, groundwater contamination risks need to be further elucidated within the system, to ensure proper application and management practices to mitigate environmental and human health risks. To date, contamination assessment following MSMA and fertilizer applications to turfgrass are limited. The objectives of this research were to determine 1) As distribution in aboveground vegetation, soil, and porewater and 2) contamination risks following As containing fertilizer and MSMA applications in a bareground and turfgrass system. Results indicate that As following fertilizer and MSMA applications is largely allocated within shallow soil depths, but other contamination risks were determined.

2. Materials and Methods

2.1. Field Lysimetry

The experiment was conducted from August 2012-August 2013 at the Sandhills Research Station in Jackson Springs, NC (35°11'12.0"N 79°40'12.7"W) on a Candor sand soil (sandy, kaolinitic, thermic Grossarenic Kandiudults) consisting of 92% sand, 4% silt, and 4% clay (3% organic matter w w⁻¹). The soil represents a “favorable scenario” for leaching, with respect to soil texture, due to the high sand and low organic matter content. Preceding the trial, glyphosate was applied and sod was removed from half of the bermudagrass (*Cynodon dactylon* (L.) Pers. × *Cynodon transvaalensis* Burt-Davey, cv. ‘Tifway 419’) area. Following sod removal, the area was tilled and fumigated with methyl bromide (90%) (bromomethane, MeBr) and chloropicrin (10%) (trichloronitromethane) (448 kg ha⁻¹) (MBC Soil Fumigant, Hendrix and Dail Inc., Greenville, NC). Fumigation occurred at least eight wk before trial initiation to ensure that microbial populations were present in natural populations during the experiment. Stromberger et al. (2005) observed no change in microbial biomass and recovery of enzymatic activity 4 wk after MeBr treatment.

Lysimeters (18 gauge steel; 15.2 cm diameter by 91.4 cm length) were installed in the center of unique bermudagrass and bareground plots (1.5 m by 1.5 m) with an inverted post driver. The trial area contained < 0.5% slope and 1.4 cm of each lysimeter was left above the soil surface to prevent lateral aboveground contamination. The bermudagrass area was maintained as a golf course fairway, mowed twice per wk (1.9 cm) with clippings returned. Irrigation was applied to bring the total precipitation to 6.4 cm weekly during the summer months while irrigation was not applied in the winter (October – May). Irrigation and

fertilization practices were identical in the bareground and bermudagrass areas. The bareground plots were kept vegetation-free with glyphosate (Roundup WeatherMax, Monsanto Co., St. Louis, MO). Weather data were collected onsite by the North Carolina Agriculture Research Service.

Following lysimeter installation, soil porewater samplers (Prenart Equipment ApS, Frederiksberg, Denmark) were installed into unique turfgrass and bareground plots as described by Matteson et al. (2014) at 30 or 76 cm depths. Briefly, steel rods were inserted into the center of lysimeters using a mallet. Tubing was attached to porewater samplers, which allowed for collection above the soil surface. A silica flour (900 g) (Prenart Equipment ApS, Frederiksberg, Denmark) and water (700 mL) slurry was prepared and the samplers were soaked for 10 min. Prior to installing samplers, the slurry was poured into the prepared hole. Porewater samplers were then placed into unique holes, ensuring the tube extended above ground, and backfilled with a slurry of native soil. Following backfilling, tubing from the porewater sampler was connected to an airtight collection bottle. Collection bottles were wrapped using opaque black plastic to eliminate light exposure. A total of twelve unique porewater samplers were installed. Porewater samplers at a 30 cm depth were placed in bareground and turfgrass plots to collect from MSMA-treated areas. Porewater samplers at a 76 cm depth were placed in bareground and turfgrass plots, each representing a unique fertilizer treatment (x 6) or MSMA-treated (x 2) plot, including nontreated (x 2) plots.

2.2. Treatments

Following lysimeter and porewater sampler installation, two wk were allowed for acclimation. MSMA (Bueno 6; Drexel Chemical Co., Memphis, TN) was applied ($2.25 \text{ kg ai ha}^{-1}$) to unique bareground and turfgrass plots on August 13 and August 20, 2012.

Applications were made using a CO_2 -pressurized three-nozzle (XR 8002; TeeJet, Spraying Systems Co. Wheaton, IL) sprayer calibrated to deliver 304 L ha^{-1} . Immediately after application, treatments were irrigated with 2 cm of water to simulate a favorable scenario for downward leaching. Air temperature, relative humidity, and wind speed at the initial and subsequent application were 28 C , 59% , 7.9 km h^{-1} and 22 C , 83% , and 3.5 km h^{-1} , respectively.

Based on analysis of 20 commercially available fertilizers, Lebanon fertilizer was selected ($6\text{-}1\text{-}11 \text{ N-P}_2\text{O}_5\text{-K}_2\text{O}$) (Lebanon Proscape with iron (4.2%), LebanonTurf, Lebanon, PA) as it had the highest As concentration ($18.1 \text{ mg As kg}^{-1}$) (Table 1). Fertilizer was applied using shaker jars to unique bareground and turfgrass plots. Initial applications occurred on August 13, 2012 with sequential applications on 30 d intervals. Application rates were based on nitrogen loading and included: three applications at 54 kg N ha^{-1} ($0.08 \text{ mg As ha}^{-1}$), one application at 294 kg N ha^{-1} ($0.16 \text{ mg As ha}^{-1}$), and two applications at 294 kg N ha^{-1} ($0.32 \text{ mg As ha}^{-1}$). Two replicates were included in each experiment and nontreated lysimeters were exhumed at each evaluation date.

2.3. Porewater Sampling and Analysis

Sampling dates included: 0 (pretreatment), 1, 2, 4, 7, 9, 11, 14, 17, 22, 28, 37, 42, 56, 70, 85, 98, 127, 158, 178, and 365 days after initial treatment (DAIT). Porewater samples

were collected by applying vacuum (-50 to -70 kPa) to collection bottles 24 h prior to sampling. Following collection, porewater volume was recorded and the total sample was split into two separate containers. One sample was used to measure pH while the other sample was acidified with trace metal grade nitric acid (1% v v⁻¹) to preserve the sample. Arsenic concentration in collected samples was measured by inductively coupled plasma-mass spectrometry (ICP-MS) as described below.

2.4. Lysimeter Exhumation

Lysimeters were exhumed 0, 30, 60, 120, and 365 DAIT for MSMA-treated plots and at 0, 60, and 120 days after last treatment (DAIT) for fertilizer-treated plots. Two treated and one nontreated lysimeter were exhumed at each sampling date. Lysimeters were then capped with sheet insulation cut to inner diameter, secured with a polyethylene bag, and transported back to the Lake Wheeler Turfgrass Field Laboratory (Raleigh, NC). Lysimeters were then cut lengthwise from bottom to top and sectioned into 0-2, 2-4, 4-8, 8-15, 15-30, 30-45, 45-60, or 60-90 cm depths. Aboveground vegetation was also retained from the turfgrass plots. Metal plates were used to divide depths and sampling occurred from deeper to shallower depths. Sampling utensils were thoroughly washed in-between lysimeters using ammonia:water (1:1) followed by water to avoid contamination. Samples were stored in polyethylene bags at -18°C until analysis.

Table 1. Arsenic concentration of various commercially available fertilizers.^a

Product Name	Product analysis	
	— N-P ₂ O ₅ -K ₂ O —	— mg As kg ⁻¹ —
Anderson's Golf Products	13-2-13	0.8
Camp	5-0-10	1.4
Camp	10-10-10	1.0
Camp	10-20-20	ND ^b
Contec DG	24-0-10	ND
Country Club	10-18-18	3.1
Country Club	16-4-8	1.0
Green Eagle	18-24-12	0.5
Green Eagle Pro-Turf	16-4-8	3.0
Harrells	25-6-12	1.8
Harrells Plant Food	14-12-14	1.2
Harrells Professional	7-23-19	3.2
High Yield Ammonium Sulfate	21-0-0	ND
Ironite	1-0-1	1.1
Lebanon ProScape w/ Fe^c	6-1-11	18.1
Milorganite	6-2-0	4.2
Nature Safe Fine-grade	5-6-6	ND
Scott's Turf Builder Starter	24-24-4	4.5
Souther Ag w/ minor elements	20-20-20	ND
Woodace	14-14-14	2.1

^a Detection limit was 0.018 mg As kg⁻¹ fertilizer.

^b ND: non-detectable.

^c Fertilizer used in this study.

2.5. Soil Sample Analysis

All samples through 45 cm depth were analyzed as previous research has shown increases in soil As concentrations following MSMA application through 15 cm (Akkari et

al. 1986; Feng et al. 2005; Hiltbold et al. 1974; Matteson et al. 2014; Robinson 1975).

Preceding analysis, three subsamples (2.5 g soil or 1.5 g aboveground vegetation) were dried at 105°C for 24 hr and weights were recorded to determine moisture content. Total As was extracted from duplicate samples of each depth by a modified USEPA protocol: SW846-Method 3050B (EPA 1996). Trace metal grade acids were used throughout the extraction. Briefly, 2.5 g soil or 1.5 g aboveground vegetation fresh weight was placed into 75 mL hot block digestion tubes. Nitric acid (7 M; 15 mL) was added to each tube, fitted with glass caps and vortexed. After 16 hr, tubes were heated on a digestion block to 95°C (15 min). Tubes were then removed from the block and allowed to cool (10 min). Nitric acid (14 M; 5 mL) was then added to each tube, vortexed, and heated to 95°C (45 min). The tubes were removed, allowed to cool, and the previous step was repeated. Following heating, loose fitting caps were removed and the tubes were refluxed at 95°C (2 hr). The tubes were then removed, capped, and allowed to cool. After cooling, deionized water (3 mL) was added to each tube followed by hydrogen peroxide (30%; 2 mL) (1 mL per addition). The tubes were then placed back on the block, brought to reflux until no effervescence from hydrogen peroxide was observed. Subsequent hydrogen peroxide additions (1 mL per addition) were added to each tube, returned to the block, and allowed to effervesce. In total, 6 mL of hydrogen peroxide was added. Following the final addition of hydrogen peroxide, the tubes were vortexed, caps removed, and placed back on the block at 95°C for 2 hr. The heating block and tubes were allowed to cool, and then concentrated hydrochloric acid (12.1 M; 5 mL) was added to each tube and vortexed. The tubes were placed on the heating block and slowly heated to 95°C (30-45 min). The tubes were then cooled and the digest liquid was

decanted and filtered (#41 filter paper, Whatman Inc. Piscataway, NJ) into volumetric flasks (50 mL). Samples were brought to final volume (50 mL) with deionized water.

Digests were diluted 1:5 with deionized water and analyzed on a Varian 820 ICP-MS (Bruker Daltonics, Billerica, MA). Limit of quantification and limit of detection was $3.50 \mu\text{g L}^{-1}$ and $0.35 \mu\text{g L}^{-1}$, respectively. All samples were analyzed with a Collision Reaction Interface with hydrogen gas at 75 mL min^{-1} to correct argon chloride (75 g mol^{-1}) interference on As (75 g mol^{-1}). Rhodium was used as an internal standard to correct for small differences in sample uptake and solution viscosity, matching acid backgrounds in standards to samples. Standards were prepared by dilution of 10 mg L^{-1} stock multicalibration solutions and were injected every 12 samples. Two blank and two soil standard samples (SRM271a Montana soil II, National Institute of Standards and Technology, Gaithersburg, MD) were processed with every 36 samples to ensure materials were not contaminated and verify digestion efficiency. Mean As concentration from the soil standard was 101% ($\pm 1\%$) of expected values throughout the experiments. All concentrations are reported on a dry weight basis.

2.6. Data Analysis

Data were subject to ANOVA using general linear models (SAS[®] for Windows, v 9.3, Statistical Analysis Systems Institute, Cary, NC, USA) to determine the effect of MSMA and fertilizer applications on As distribution in bareground and turfgrass systems. Significant main effects and interactions are presented accordingly with precedent given to interactions of increasing magnitude (Steele et al. 1997). Means were separated according to Fisher's Protected LSD at $P = 0.05$.

2.7. Arsenic Recovery Calculations

Sample depths with As concentrations greater than background levels were utilized to determine As recovery as a percentage of the total As from MSMA applications using the following equation:

$$\% \text{ recovery} = \{([T] - [NT]) * m_s\} / 3.8 \text{ mg As per lysimeter}$$

where $[T]$ is the treated plot As concentration, $[NT]$ is the nontreated plot As concentration, m_s is the soil mass (kg) of the respective depth increment, and 3.8 mg As is the amount added from MSMA applications. Bulk densities used for calculations were previously reported from the field site (Cummings 2004). Because turfgrass growth varies over time, the total aboveground vegetation mass collected 30, 60, 120, and 365 DAIT, were 26, 16, 9, and 10 g, respectively.

3. Results and Discussion

3.1. Arsenic from MSMA Applications

3.1.1. Aboveground vegetation and soil arsenic

In general, soil As concentrations were increased above background concentrations at all sample dates following MSMA applications (Table 2). There were no statistical differences in soil As distributions between bareground and turfgrass systems, but the results are presented separately to discuss turfgrass aboveground vegetation and porewater differences.

At 30 DAIT, MSMA-treated lysimeters had increased aboveground vegetation and soil As, ≤ 8 cm, compared to nontreated lysimeters at their respective systems (Table 2). In the turfgrass system, the As concentration in the aboveground vegetation increased $>$ six-fold

(14.7 mg kg⁻¹) compared to nontreated vegetation. Soil concentrations were increased at 0-2 cm and 2-4 cm depth in both bareground (3.0 and 1.7 mg kg⁻¹, respectively) and turfgrass (4.9 and 1.2 mg kg⁻¹, respectively) systems. Although not significantly different, at 4-8 cm depth As concentrations in the treated bareground (0.8 mg kg⁻¹) and turfgrass system (0.4 mg kg⁻¹) were greater than the nontreated. The data suggest turfgrass may mitigate downward movement of As from MSMA, as the As concentration increase at 2-4 cm was greater in bareground compared to the turfgrass system, which may be in part to foliar interception, absorption, and retention of applied MSMA.

Increased aboveground vegetation and soil As concentrations following organic arsenical application have previously been observed. In a translocation study by Duble et al. (1969), 20% of disodium methanearsonate (DSMA) applied as a spot foliar treatment was detected in bermudagrass aboveground vegetation 30 d after treatment (DAT). At 30 DAIT within this research, less was detected in the aboveground vegetation; however, it cannot be assumed that 100% of the application was intercepted by turfgrass (Carroll et al. 1999; Sears et al. 1987). Further, in a similar study by Matteson et al. (2014), 10% of the total applied As was recovered in turfgrass aboveground vegetation 36 DAIT. The authors also reported increased soil As concentrations through 8 cm at this evaluation date.

At 60 DAIT, MSMA-treated turfgrass and bareground As concentration were generally increased above nontreated lysimeters, as also seen at 30 DAIT (Table 2). In aboveground vegetation, As concentrations were 7.3 mg kg⁻¹ greater than nontreated aboveground vegetation. An increase in soil As concentration was detected at 0-2, 2-4, and 4-8 cm depths in turfgrass (4.6, 2.1, and 0.6 mg kg⁻¹, respectively) and bareground (2.7, 0.8,

and 0.8 mg kg^{-1} , respectively) systems. Similarly, Matteson et al. (2014) reported increased As concentration in aboveground vegetation and similar soil depths 64 DAIT.

Trends similar to 30 DAIT were detected 120 DAIT, with increased aboveground vegetation and soil As, through 0-4 cm depth, detected in MSMA-treated turfgrass and bareground compared to nontreated lysimeters (Table 2). In the turfgrass system, MSMA increased aboveground vegetation As concentration by 5.3 mg kg^{-1} with increased soil As in 0-2 and 2-4 cm depth (3.7 and 1.2 mg kg^{-1} , respectively) compared to the nontreated. Increased soil As concentration was also detected in the bareground system at these depths (2.1 and 1.2 mg kg^{-1} , respectively).

At 365 DAIT, increased soil As concentrations though 0-8 cm depth were detected in turfgrass and bareground systems, but aboveground vegetation As concentration was similar between treated and nontreated turfgrass lysimeters (Table 2). Specifically, soil As concentrations were increased at 0-2, 2-4, and 4-8 cm in the turfgrass (3.1 , 1.6 , and 1.1 mg kg^{-1} , respectively) and bareground (1.8 , 0.8 , and 1.4 mg kg^{-1} , respectively) system. The increased As concentrations over background samples, at deeper depths, over time suggest As fluctuation and downward movement in the systems, which is discussed below.

3.1.2. Arsenic distribution and recoveries

Although mean percent As recovery was greater in the turfgrass system compared to bareground, differences were not statistically significant. At 30, 60, 120, and 365 DAIT As recoveries in the bareground system were 66, 63, 44, and 67% of the total As applied, respectively. Recoveries in the turfgrass system were 70, 84, 50, and 73% at 30, 60, 120, and

365 DAIT, respectively. Turfgrass aboveground vegetation represented 10, 3, 1, and 0% of recovered As at the aforementioned dates, respectively.

Increased As recovery from the turfgrass system at 60 DAIT compared to bareground system may be due to root exudation. While not significantly different, As recovery in the turfgrass system (84%) was greater compared to bareground (67%). In the Mid-Atlantic States, bermudagrass is physiologically acclimating for winter dormancy around 60 DAIT sampling (Bruneau et al. 2009). In preparation for dormancy, bermudagrass translocates compounds to the roots and other organs or alters various compounds (carbohydrates, nitrogen, lipids, etc.) (Dunn and Nelson 1974; Samala et al. 1998). Although roots were not specifically sampled within the current discussed research, the authors hypothesize As may complex with organic acids or sugars, translocate to roots or rhizomes, and be exuded into the rhizosphere. Further research is needed to define the timing and mechanisms of specific As-transfer processes and/or mechanisms.

Arsenic recoveries in both bareground and turfgrass systems were < 100%, which may be attributed to management and sampling practices and/or analytical detection limits. Turfgrass was mowed with a rotary mower and clippings may have been displaced from each unique lysimeter. This may contribute to reduced recoveries, as a 0.38 mg As increase (10% of total applied) was detected in the aboveground vegetation 30 DAIT. Additionally, turfgrass roots may have also impacted As concentrations within the system, as they have been reported to exude and sorb As (Li et al. 2009; Xu et al. 2007). Elevated root As content was also detected in parallel greenhouse research (Thesis chapter 2).

Table 2. Arsenic concentrations in MSMA-treated and nontreated turfgrass and bareground soil and aboveground at various d after initial treatment.^{a-c}

System	Depth (cm)	DAIT							
		30		60		120		365	
		Treated	NT	Treated	NT	Treated	NT	Treated	NT
mg As kg ⁻¹									
<u>Turfgrass</u>									
	Aboveground vegetation	17.5	2.8	9.4	2.1	6.5	1.2	2.9	1.6
	0-2	7.8	2.9	7.3	2.7	6.3	2.6	5.5	2.4
	2-4	4.2	3.0	4.5	2.4	3.8	2.6	4.2	2.6
	4-8	2.9	2.5	3.3	2.7	2.8	2.6	3.4	2.3
	8-15	2.4	2.6	2.5	2.2	2.0	2.2	2.4	2.0
	15-30	1.4	1.6	1.3	1.7	1.3	1.8	1.3	1.4
	30-45	0.8	0.8	0.9	0.9	0.8	0.6	0.9	0.8
	LSD ^d	0.9		0.6		0.8		1.1	
<u>Bareground</u>									
	0-2	5.5	2.5	4.7	2.0	4.4	2.3	3.5	1.7
	2-4	4.1	2.4	3.4	2.6	3.5	2.3	3.4	2.6
	4-8	3.3	2.5	3.0	2.2	2.9	2.6	3.8	2.4
	8-15	2.2	2.3	2.2	1.6	1.9	2.2	2.3	2.1
	15-30	1.8	1.4	1.3	1.2	1.3	1.4	1.6	2.4
	30-45	0.9	0.9	0.8	0.9	0.7	0.9	1.0	1.3
	LSD ^d	1.2		0.8		1.0		0.5	

^a Standard deviation in soil As measurements was < 1.5 mg kg⁻¹ at 0-2 cm depth with remaining depths being < 0.5 mg kg⁻¹.

^b Treated and nontreated concentrations from quadruplicate and duplicate samples, respectively.

^c Abbreviations: DAIT, days after initial treatment; NT, nontreated.

^d LSD values for comparison within DAIT. (Aboveground vegetation cannot be compared using the LSD values due to differences in density compared to soil. Its LSD values are 10.5, 4.3, 1.4, and NS for 30, 60, 120, and 365 DAIT, respectively.)

Errors may also be associated with not directly measuring soil bulk densities and/or variation within background As concentration of our sample site, as these values were subtracted to obtain recovery amounts.

Figure 1 illustrates recovered As in bareground soil over time following MSMA applications. From 30 to 60 DAIT, a decrease in As mass was detected at 2-4 cm with an increase at 4-8 cm. From 60 to 120 DAIT, while not statistically significant, a decrease was detected at 0-2 cm with an increase at 2-4 cm. Finally, from 120 to 365 DAIT, at 0-2 and 2-4 cm As decreased; however, an increase was detected at 4-8 cm. In the turfgrass system, aboveground vegetation As content decreased over time as did, soil As content at 0-2 cm by 365 DAIT (Figure 2). From 30 to 60 DAIT, an increase was detected at 2-4 and 4-8 cm, which may be attributed to root As exudation, as previously discussed. From 60 to 120 DAIT, soil As contents from 2-4 cm decreased, but increased at 365 DAT, as did the 4-8 cm depth. In general, As content fluctuated at shallow depths and decreased over time with an increase detected at deeper depths.

The fluctuations in recovered As suggest a downward movement of As within both systems over time (Figures 1 and 2). In general, below the depth increment where increased As concentration was detected, MSMA-treated soil As concentration was increased compared to nontreated soil, although not statistically significant (*e.g.* see bareground > 4 cm depth 30 DAIT, Table 2). Arsenic likely reached deeper depths but was below detection limits; consequently, resulting in < 100% recovery may be attributed to this distribution.

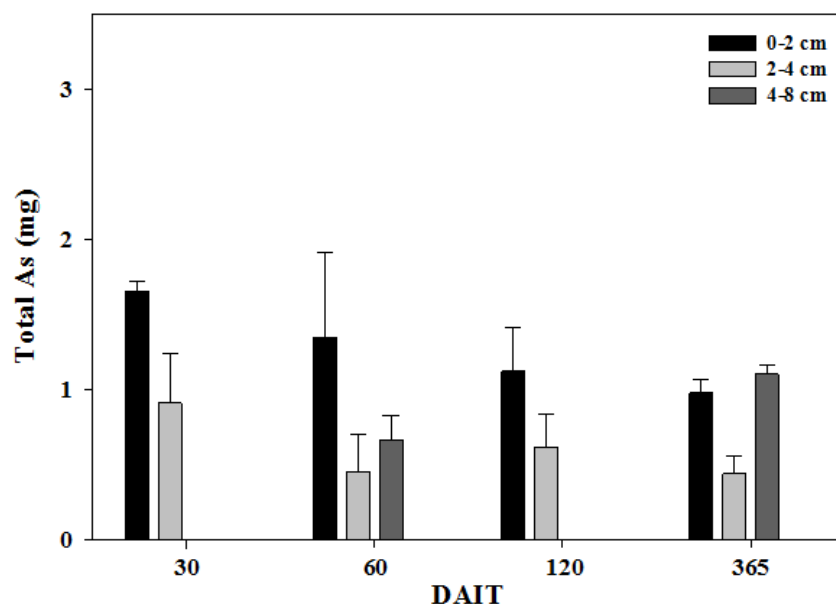


Figure 1. Increased arsenic (As) mass in soils within the bareground system at various days after initial treatment (DAIT) of MSMA. A total of 3.8 mg As was initially applied to each lysimeter. Background As mass was removed from plotted values. Error bars represent standard deviation in As content between replications.

Downward migration of As over time has previously been observed. Robinson (1975) reported increased As concentrations at 0-15 cm depth following two and five annual MSMA applications at 144 kg a.i. ha⁻¹. Additionally, increased soil As concentrations were detected at 0-15 and 15-30 cm depth following two and five annual applications at 288 kg a.i. ha⁻¹. While the tested rates were > 30 fold of the current presented research, the collective data suggest that applied As migrates downward and accumulates in soil over time. At a similar tested rate (4.5 kg MSMA ha⁻¹), Matteson et al. (2014) detected increased As concentrations

0-8 cm 120 DAIT; however, at 365 DAIT, an increase was detected to 15 cm, also suggesting downward movement over time.

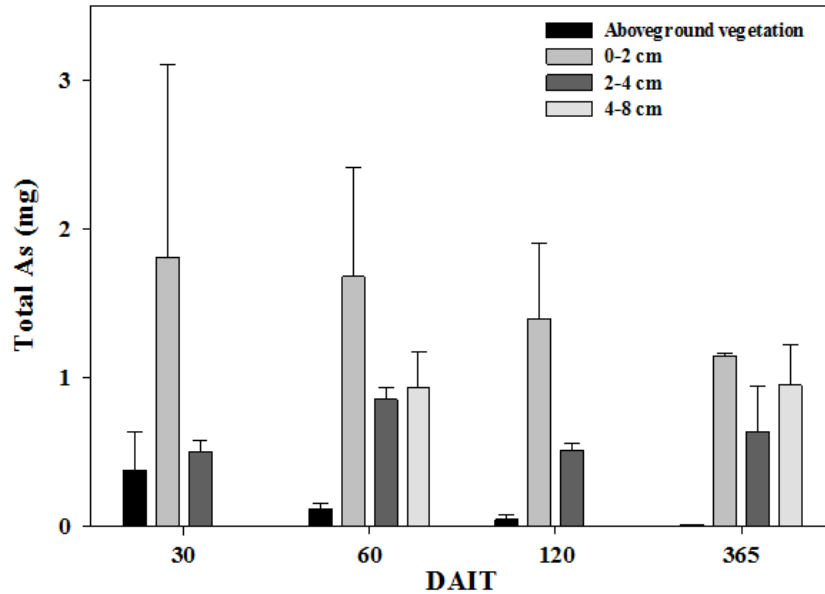


Figure 2. Increased arsenic (As) mass in soils within the turfgrass system at various days after initial treatment (DAIT) of MSMA. A total of 3.8 mg As was initially applied to each lysimeter. Background As mass was removed from plotted values. Error bars represent standard deviation in As content between replications.

3.1.3. Porewater arsenic

In general, 30-cm-depth-porewater As concentration increased immediately following MSMA applications, and then slowly returned to initial concentrations over a year after treatment. Arsenic concentration in 30-cm porewater at 0 DAIT (before application) were

27.1 and 30.1 $\mu\text{g As L}^{-1}$ in bareground and turfgrass systems, respectively (Figure 3). At 7 DAIT, the porewater concentrations at 30 cm depth were 83.8 and 55.7 $\mu\text{g L}^{-1}$ in the treated-bareground and -turfgrass systems, respectively, which are above the USEPA As maximum contamination limit (MCL) (10 $\mu\text{g L}^{-1}$). Downward leaching of applied As may have been influenced by the 6.3 cm of rainfall 6 d prior to treatment and 12 cm that occurred in the 6 d between MSMA application and the 7-day sampling (NC CRONOS 2014). Arsenic concentration decreased over time following the 7-day maximum, but concentrations remained above the USEPA MCL through 365 DAIT.

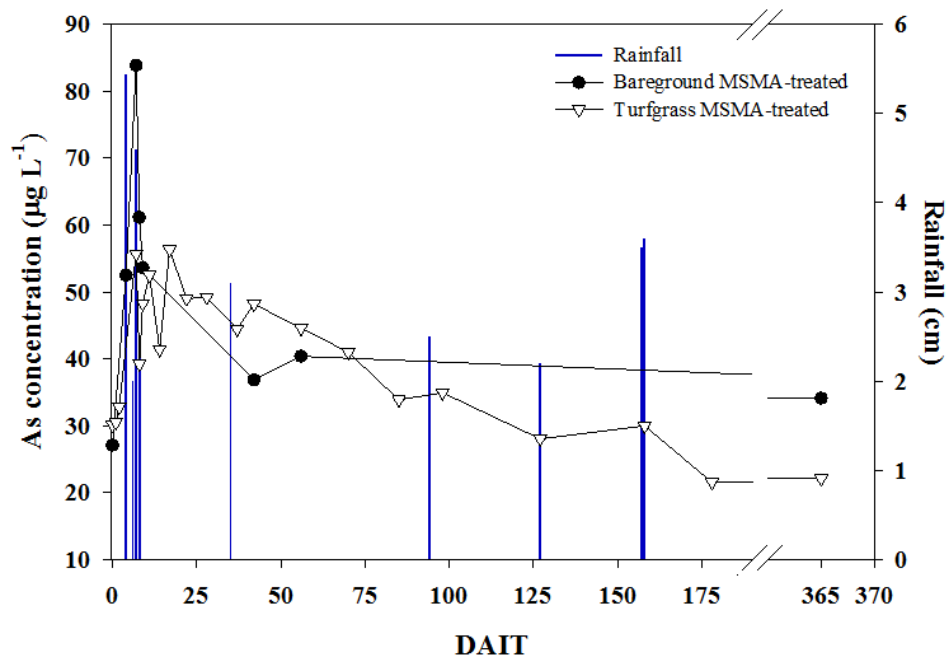


Figure 3. Porewater arsenic (As) concentrations from 30-cm depth and rainfall at various days after initial treatment (DAIT) of MSMA.

Much lower porewater As concentrations were detected at 76 cm depth (0.4 to 5.1 $\mu\text{g L}^{-1}$) compared to 30 cm depth (22 to 83.8 $\mu\text{g L}^{-1}$). The highest As concentration at 76-cm depth was detected 4 DAIT within the bareground system (Figure 4). At this date, As concentration was 5.1 $\mu\text{g L}^{-1}$, 0.9 $\mu\text{g L}^{-1}$, and 0.7 $\mu\text{g L}^{-1}$ in the treated-bareground, -turfgrass and nontreated system, respectively. Beyond this evaluation date, porewater As concentrations never exceeded 1.9 and 1.5 $\mu\text{g L}^{-1}$ in the bareground and turfgrass system, respectively. In general, treated lysimeters ($\leq 1.9 \mu\text{g L}^{-1}$) had elevated As compared to nontreated lysimeters ($\leq 1 \mu\text{g L}^{-1}$); however, porewater As concentration at 76-cm depth remained below the USEPA MCL through the experimental period for all samples.

Water-saturated soil and rainfall soon after application have been shown to increase nutrient or pesticide leaching (Kramers et al. 2012; Gish et al. 1991), which may have caused the increased porewater As concentrations within a week after MSMA application. In similar research by Matteson et al. (2014), increased porewater As was not detected at a 76-cm depth for any treatment or time point. Rainfall patterns were different in the Matteson et al. study, as a 7.5 cm rainfall event occurred 4 d prior to treatment with only 0.05 cm of rainfall prior to 4 DAIT sampling (NC CRONOS 2014), which is 12.0 cm less than the presented research. Additionally, in parallel greenhouse research, As speciation conversion from predominantly organic (monomethylarsonic acid or MMA) to predominantly inorganic forms [As(V)] occurred between 7 and 14 DAT (Thesis chapter 2). Rainfall events within 7 d of application may have increased leaching as MMA generally has lower soil sorption compared to As(V) (Huang et al. 2011). Therefore, it may be hypothesized that rainfall, coupled with As species present, may have increased As leaching from MSMA soon after application. This may also

explain why another As pulse was not detected following 14 DAIT. Although multiple rainfall events > 2 cm occurred (NC CRONOS 2014), they may not have effectively leached As due to an increased presence of As(V) which was readily bound to soil.

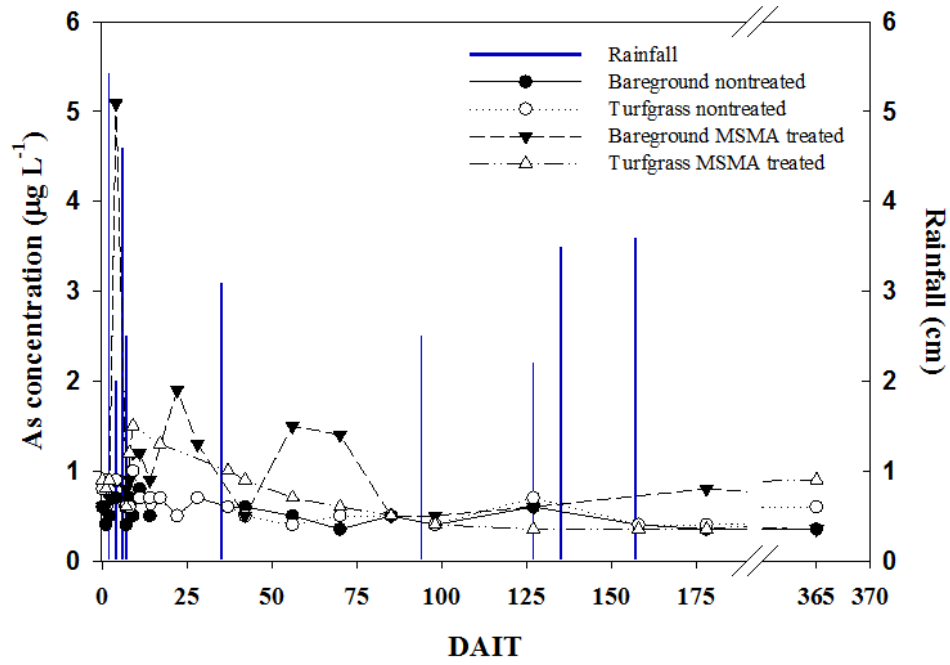


Figure 4. Porewater arsenic (As) concentrations from 76-cm depth and rainfall at various days after initial treatment (DAIT) of MSMA.

3.2. Arsenic from Fertilizer Applications

3.2.1 Aboveground vegetation and soil arsenic

Soil As concentrations did not significantly increase following fertilizer applications at any sample depth within bareground or turfgrass systems (Table 3). Although the selected fertilizer had a relatively high As concentration (Table 1), a small amount of As was added to the system. Three applications at 54 kg N ha⁻¹, one application at 294 kg N ha⁻¹, and two applications at 294 kg N ha⁻¹ provided 0.08, 0.16, and 0.32 mg As lysimeter⁻¹. Theoretically, assuming all As remained in the 0-2 cm depth, soil As concentrations in the bareground system would have increased by 0.15, 0.3, and 0.6 mg kg⁻¹, respectively and 0.3, 0.6, and 1.2 mg kg⁻¹, respectively, in the turfgrass system. Because of natural As variation at our field site and analytical detection limits, such increases may not be detected. Additionally, 100% of the As may not have been released by the fertilizer application and/or the As was not confined to 0-2 cm depth, further complicating detectable increases in soil As concentrations.

Previous research has been conducted on As inputs from fertilizers in various systems. Chen et al. (2007) detected no increase in soil As concentration over a 100 yr simulation period in California cropland soil that received 31.5 g As ha⁻¹ yr⁻¹. Further, a long-term study conducted in a hay field by Hartley et al. (2013) revealed a two-fold increase in soil As from 1888-1947; however, fertilizers applied during this period contained 401-1575 mg As kg⁻¹. In contrast, no As increase was detected in soil samples from 1959-2011, presumably because of lower As concentrations of the fertilizers (0-13 mg kg⁻¹). One and two applications of 294 kg N ha⁻¹ represent over-applications for N in a turfgrass setting (Turner and Hummel 1992), and the low observed increases in soil As concentrations indicate that As

additions from fertilizers common to turfgrass do not pose a significant environmental threat, even with repeat applications.

3.2.2 Porewater arsenic

Excluding one isolated sample, 76-cm-depth porewater As concentration never exceeded $1.3 \mu\text{g L}^{-1}$, and concentrations within fertilizer-treated plots were similar to nontreated (Figure 5). The 56 DAIT porewater sample from the 294 kg N ha^{-1} treatment revealed elevated As ($3.6 \mu\text{g L}^{-1}$) in the bareground system compared to turfgrass ($0.4 \mu\text{g L}^{-1}$) and nontreated ($0.5 \mu\text{g L}^{-1}$). The cause for this spike is unknown, but the observed ‘elevated’ concentration was below the USEPA As MCL ($10 \mu\text{g L}^{-1}$).

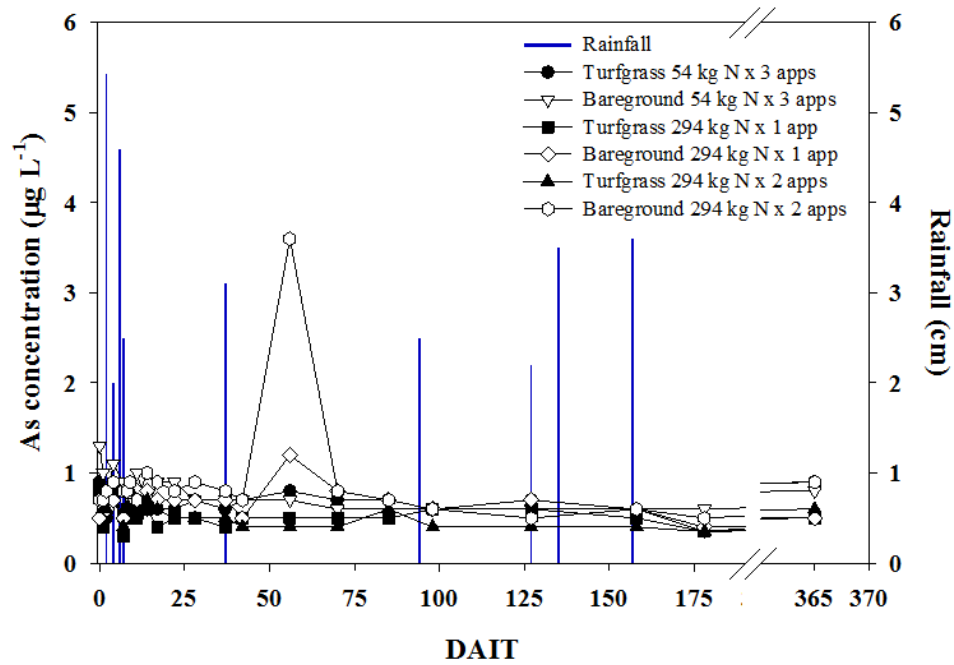


Figure 5. Porewater arsenic (As) concentrations at 76-cm depth and rainfall at various days after initial treatment (DAIT) of high-As fertilizer.

Table 3. Arsenic concentrations in fertilizer treated- and nontreated- turfgrass and bareground soil and aboveground at various d after last treatment.^{a-c}

		DALT							
		60				120			
System	Depth (cm)	54 kg N 3 apps	294 kg N 1 app	294 kg N 2 apps	NT	54 kg N 3 apps	294 kg N 1 app	294 kg N 2 apps	NT
		mg kg ⁻¹							
<u>Turfgrass</u>									
	Aboveground vegetation	2.5	2.4	2.4	2.1	2.1	2.2	1.9	2.2
	0-2	2.1	2.5	2.3	2.7	3.0	2.6	3.0	2.5
	2-4	2.5	2.3	2.1	2.4	3.1	2.6	3.0	2.5
	4-8	2.5	2.2	2.2	2.7	3.1	2.4	3.0	2.4
	8-15	2.4	2.2	2.4	2.2	2.5	2.0	2.7	2.0
	15-30	1.4	1.4	1.4	1.6	1.1	1.2	1.6	1.2
	30-45	1.0	0.8	0.8	0.8	1.0	0.8	1.0	0.8
	LSD	NS				NS			
<u>Bareground</u>									
	0-2	2.6	2.5	2.3	2.2	2.6	2.3	2.7	2.3
	2-4	2.4	2.2	2.3	2.1	2.6	2.1	2.6	2.2
	4-8	2.4	2.7	2.8	2.3	3.0	2.4	2.7	2.4
	8-15	2.2	2.3	2.6	1.9	2.7	2.3	2.2	1.6
	15-30	1.5	1.4	1.4	1.6	1.6	1.2	1.6	1.3
	30-45	0.9	0.7	0.8	0.8	0.9	0.7	0.9	0.8
	LSD	NS				NS			

^a Fertilizer rates are on a per ha basis.

^b Treated and nontreated concentrations are from quadruplicate and duplicate samples, respectively.

^c Abbreviations: DALT, days after last treatment; NT, nontreated.

3.3. Arsenic Contamination Potential Following MSMA Applications

Arsenic contamination concerns have focused on speciation, transformation, and leaching towards groundwater following MSMA application. Results from the current research suggest that As contamination or off-target injury may occur from various routes following application, but each may occur at different times after treatment. Immediate concerns have been denoted as < 1 wk, intermediate concerns are < 30 d, and long-term concerns are > 1 season. Figure 6 illustrates and defines these concerns following MSMA applications to turfgrass. Due to the insignificant As increases to background levels from fertilizer applications, As contamination potential from fertilizers is not considered here.

Elevated solid-phase As concentration was detected at depths ≤ 8 cm within soils following MSMA applications (Table 2), suggesting that As is strongly retained near the soil surface. However, As concentration in porewater from a 30-cm depth was higher than the USEPA MCL at every evaluation date (Figure 4). The data suggest that MSMA should not be applied in areas with shallow water tables or immediately preceding expected large rain events. As seen in Figures 4 and 5, large rainfall events may cause a pulse of As to migrate downward. Further, coarse-textured soils with minimal metal oxides (Fe, Al, or Mn) may have low As sorption capacities perhaps enabling As leaching (Jones 2007).

Increased porewater As following application may also be due in part to rainfall coupled with the As species present. In prior studies, MMA (65%) was the most abundant As species 7 DAT (Thesis chapter 2), which generally has lower sorption in soils compared to As(V), its main metabolite (Huang et al. 2011). In contrast, by 14 DAT As(V) was the predominate species, limiting porewater As concentrations beyond 7 DAIT, even following

large rainfall events. Additionally, data suggest turfgrass systems may prevent As leaching compared to bareground systems. This may be attributed to foliar interception and absorption following application causing a reduced As in soil solution. Furthermore, root As sorption from soil solution may have reduced leaching from the turfgrass system (Li et al. 2009).

Although precaution was taken to prevent runoff in this experiment, conclusions concerning As contamination potential from surface runoff may be drawn from previous research. Direct runoff - via foliar dislodgment - from MSMA may be minimal because unless rainfall occurs within a few hours after application, as the majority of MSMA may be absorbed by the plant tissue (Wauchope and Strett 1987a, 1987b; Sachs and Michael 1971; Sckerl and Frans 1969; Armbrust and Bridges 2002). Runoff may be of more concern in bareground systems, as vegetation coverage has been shown to increase water infiltration and reduce runoff (Milesi et al. 2005; Steinke et al. 2007; Thompson et al. 2010).

MSMA absorption into plant foliage occurs readily (Wauchope and Street 1987a, 1987b; Sachs and Michael 1971; Armbrust and Bridges 2002) and may persist long after treatment, as elevated turfgrass As concentration has been reported up to one year after MSMA application (Matteson et al. 2014). Within the current research, increased As concentration in aboveground vegetation was detected through 120 DAIT (Table 2). Consequently, precautions must be taken when disposing of plant material following mowing events. Best management practices dictate mowing should occur when only one-third of the tissue will be removed to achieve the desired height (Turner and Hummel 1992). In some instances (maintenance schedule, weather delays, etc.), this guideline is not always achievable and more tissue is removed (Hull 2000).

Removing extensive turfgrass aboveground vegetation within 30 DAIT of MSMA may lead to off-target As risks. Turfgrass tissue As concentrations were 14.7 mg kg^{-1} above background tissue concentrations 30 DAIT (Table 2). Using the turfgrass dry mass collected and the total foliar contents at 30 DAIT, there was approximately 249 g As ha^{-1} in turfgrass aboveground vegetation. Precautions should be taken when disposing of turfgrass clippings following MSMA applications, as large amounts of As may be present. Kopp and Guillard (2004) detected N release from turfgrass clippings as they decomposed and found $> 88\%$ of tissue N release within 16 wk of collection. Sanders and Osman (1985) detected 12% of sorbed As was weakly bound to the detrital *Spartina* leaves, with 81% deemed bioavailable. Therefore, it may be hypothesized that disposing of clippings in a confined area may be of concern if As is released to surface water or groundwater when the clippings degrade.

Within the turfgrass system, the majority of As from MSMA was recovered in the soil (Table 2). Following repeated applications over time, soil-binding sites may become occupied or resist binding due to ion competition (Girouard and Zagury 2008; Ljung et al. 2006), causing soil As to build-up and migrate downward. Long-term MSMA use, at labeled and above-labeled rates, has been previously examined with As concentrations increasing $< 15 \text{ cm}$ depth after five (Hiltbold et. al. 1974; Robinson 1975) and seven application seasons (Woolson and Isensee 1981). Soil type may have affected As reaching deeper depths, as each of the previous studies evaluated finer textured soils than the current presented research, which have been shown to increase As sorption capacity (Girouard and Zagury 2008; Ljung et al. 2006). Woolson and Isensee (1981) reported that soil equilibrium would occur after 17 yr of repeated MSMA applications at $5.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$, suggesting annual applications of

MSMA may cause potential environmental concerns over time. However, their equilibrium calculation was based on a higher application rate and As loss from volatilization as alkylarsines each year, which warrants further investigation as arsine volatilization rates reported is variable (Atkins and Lewis 1976; Gao and Burau 1997; Woolson and Isensee 1981). Long-term research is needed to evaluate repeated annual MSMA use effects on soil As build-up over time.

In conclusion, with proper management practices, MSMA and the evaluated fertilizer applications may be used without posing adverse environmental effects; however, many precautions should be taken. Further research is needed to elucidate turfgrass management (collecting or returning clippings) effects on As distribution and species transformation over time following MSMA applications.

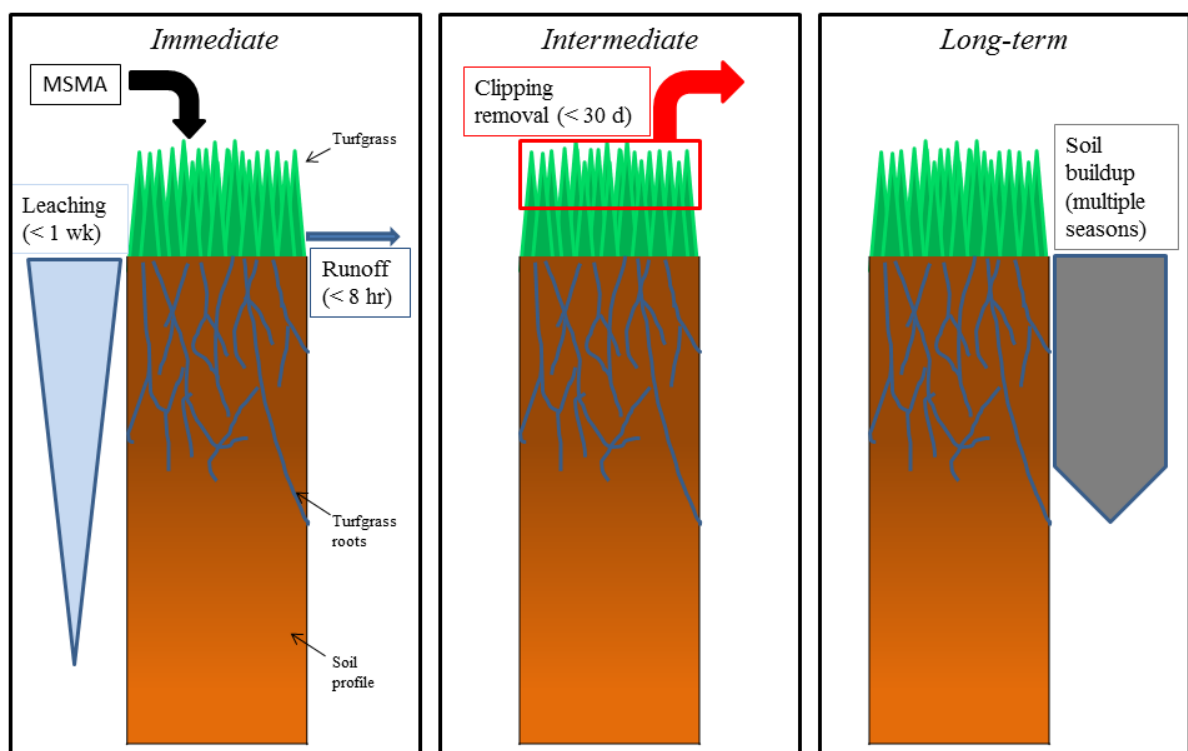


Figure 6. Arsenic off-target injury or contamination potential over immediate (< 1 week), intermediate (<30 d), and long-term (> 1 season) timescales following MSMA applications to turfgrass.

Literature Cited

- [AAPFCO] Association of American Plant Food Control Officials. 2008. AAPFCO's statement of uniform interpretation and policy (suip) #25 "the heavy metal rule". Retrieved from AAPFCO.org website: <http://www.aapfco.org/rules.html>
- Akkari, K.H., R.E. Frans, & T.L. Lavy. 1986. Factors affecting degradation of MSMA in soil. *Weed Sci.* 34:781-787.
- Armbrust, K.L. and D.C. Bridges. 2002. Dissipation of monosodium methane arsonate (MSMA) on peanuts. *J. Agr. Food Chem.* 50:1959-1963.
- Atkins, M.B., and R.J. Lewis. 1976. Chemical distribution and gaseous evolution of arsenic-74 added to soils as DSMA-⁷⁴ As. *Soil Sci. Soc. Am. J.* 40:655-658.
- Bruneau, A.H., G.L. Miller, and C.H. Peacock. 2009. Carolina lawns. North Carolina Cooperative Extension Service. 24 p.
- Carroll, M.J., R.L. Hill, S. Raturi, A.E. Herner, and E. Pfeil. 1999. Dicamba transport in turfgrass thatch and foliage. p. 228-242 *In* J. Clark et al. (ed.) *Fate and Management of Turfgrass Chemicals*. ACS Symposium Series; American Chemical Society: Washington, DC, 1999.
- Chen, W., A.C. Chang, and L. Wu. 2007. Assessing long-term environmental risks of trace elements in phosphate fertilizers. *Ecotox. Environ. Safe.* 67:48-58.
- Cheraghi, M., B. Lorestani, H. Merrikhpour. 2012. Investigation of the effects of phosphate fertilizer application on heavy metal content in agricultural soils with different cultivation patterns. *Biol. Trace Elem. Res.* 145:87-92.

- Cummings, H.D. 2004. Pesticide downward movement in a bermudagrass system compared with movement in a fallow system. Ph.D. dissertation. Raleigh, NC: North Carolina State University. 224 p.
- Duble, R.L., E.C. Holt, and G.G. McBee. 1969. Translocation and break-down of disodium methanearsonate (DSMA) in coastal bermudagrass. *J. Agr. Food Chem.* 17:1247-1250.
- Dunn J.H. and C.J. Nelson. 1974. Chemical changes in three bermudagrass turf cultivars in relation to cold hardiness. *Agron. J.* 66:28-31
- [EPA] United States Environmental Protection Agency. 1996. Method 3050B (SW-846): Acid digestion of sediments, sludges, and soils. Revision 2.
- [EPA] United States Environmental Protection Agency. 2009. Guidance for products containing the organic arsenicals. Washing, DC: EPA Office of Pesticide Programs.
- [EPA] United States Environmental Protection Agency. 2013. FR Doc. 2013–07089. Washington, DC: EPA Office of Pesticide Programs.
- Feng, M., J.E. Schrlau, R. Snyder, G.H. Snyder, M. Chen, J.L. Cisar, and Y. Cai. 2005. Arsenic transport and transformation associated with MSMA. *J. Agr. Food Chem.* 53:3556-3562.
- Gao, S., and R.G. Burau. 1997. Environmental factors effecting rates of arsine evolution from and mineralization of arsenicals in soils. *J. Environ. Qual.* 26:753-763.
- Girouard, E. and G.J. Zagury. 2008. Arsenic bioaccessibility in CCA-contaminated soils: influence of soil properties, arsenic fractionation, and particle-size fraction. *Sci. Total. Environ.* 407:2576-2585.

- Gish, T.J., A.R. Isensee, R.G. Nash, C.S. Helling. 1991. Impact of pesticides on shallow groundwater quality. *Trans. ASAE*. 34:1745-1753.
- Hartley T.N., A.J. Macdonald, S.P. McGrath, and F.J. Zhao. 2013. Historical arsenic contamination of soil due to long-term phosphate fertilizer applications. *Environ. Pollut.* 180:259-264.
- Hiltbold, A.E., B.F. Hajek, and G.A. Buchanan. 1974. Distribution of arsenic in soil profiles after repeated applications of MSMA. *Weed Sci.* 22:272-275.
- Huang, J.H., K.N. Hu, and B. Decker. 2011. Organic arsenic in the soil environment: speciation, occurrence, transformation, and adsorption behavior. *Water Air Soil Poll.* 219:401-415.
- Hughes, M.F. 2002. Arsenic toxicity and potential mechanisms of action. *Toxicol. Lett.* 133:1-16.
- Hull, R.J. 2000. Mowing: its impact on turfgrasses. *Turfgrass Trends*. 9:1-16.
- Jiao, W., W. Chen, A.C. Chang, and A.L. Paige. 2012. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: a review. *Environ. Pollut.* 168:44-53.
- Jones, F.T. 2007. A broad view of arsenic. *Poultry Sci.* 86:2-14.
- Kopp, K.L., and K. Guillard. Decomposition rates and nitrogen release of turf grass clippings. *In* New directions for a diverse planet: Proceedings of the 4th International Crop Science Congress Brisbane, Australia, 26 Sep - 1 Oct 2004.

- Kramers, G., N.M. Holden, F. Brennan, S. Green, and K.G. Richards. 2012. Water content and soil type effects on accelerated leaching after slurry application. *Vadose Zone J.* doi:10.2136/vzj2011.0059
- Li R.Y., Y. Ago, W.J. Liu, N. Mitani, J. Feldmann, S.P. McGrath, J.F. Ma, and F.J. Zhao. 2009. The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. *Plant Physiol.* 150:2071-2080.
- Ljung, K., O. Selinus, E. Otabbang, and M. Berglund. 2006. Metal and arsenic distribution in soil particles relevant to soil ingestion by children. *Appl. Geochem.* 21:1613-1624.
- Matteson, A.R., T.W. Gannon, M.D. Jeffries, S. Haines, D.F. Lewis, and M.L. Polizzotto. 2014. Arsenic retention in foliage and soil after monosodium methyl arsenate (MSMA) applications to turfgrass. *J. Environ. Qual.* 43:379-388.
- Milesi, C., S.W. Running, C.D. Elvidge, J.B. Dietz, B.T. Tuttle, and R.R. Nemani. 2005. Mapping and modeling the biochemical cycling of turf grasses in the United States. *Environ. Manag.* 36:426-438.
- [NC CRONOS] North Carolina Climate Retrieval and Observations Network of the Southeast Database. 2014. State Climate Office of North Carolina. <https://www.nc-climate.ncsu.edu/cronos>. Accessed: September 20, 2014.
- Robinson, E.L. 1975. Arsenic in soil with five annual applications of msma. *Weed Sci.* 23:341-343.
- Sachs, R.M. and J.L. Michael. 1971. Comparative phytotoxicity among four arsenical herbicides. *Weed Sci.* 19:558-564.

- Samala, S., J. Yan, and W.V. Baird. 1998. Changes in polar lipid fatty acid composition during cold acclimation in 'Midiron' and 'U3' bermudagrass. *Crop Sci.* 38:188-195.
- Sanders, J.G. and R.W. Osman. 1985. Arsenic incorporation in a salt marsh ecosystem. *Estuar. Coast Shelf S.* 20:387-392.
- Sckerl, M.M. and R.E. Frans. 1969. Translocation and metabolism of MAA-¹⁴C in johnsongrass and cotton. *Weed Sci.* 17:421-427.
- Sears, M.K., C. Bowhey, H. Braun, and G.R. Stephenson. 1987. Dislodgeable residues and persistence of diazinon, chlorpyrifos and isofenphos following their application to turfgrass. *Pestic. Sci.* 20:223-231.
- Steele, R.D., J.H. Torrie, and D.A. Dickey. 1997. *Principles and Procedures of Statistics: A Biometrical Approach*. 3rd ed. New York: WCB McGraw-Hill. Pp. 352-384.
- Steinke, K., J.C. Stier, W.R. Kussow, and A. Thompson. 2007. Prairie and turf buffer strips for controlling runoff from paved surfaces. *J. Environ. Qual.* 36:426-439.
- Stromberger, M.E., S. Klose, H. Ajwa, T. Trout, and S. Fennimore. 2005. Microbial populations and enzyme activities in soils fumigated with methyl bromide alternatives. *Soil Sci. Soc. Am. J.* 69:1987-1999.
- Thompson, S.E., C.J. Harman, P. Heine, and G.G. Katul. 2010. Vegetation-infiltration relationships across climatic and soil type gradients. *J. Geophys. Res.* doi:10.1029/2009JG001134.
- Turner, T.R. and N.W. Hummel. 1992. Nutritional requirements and fertilization. p. 385-441 *In* D.V. Waddington et al. (ed.) *Turfgrass*. Madison, WI: ASA, CSSA, SSSA.

- [USDA] United States Department of Agriculture. 2007. Census of agriculture. Washington, DC. http://www.agcensus.usda.gov/Publications/2007/Full_Report/usv1.pdf
- [USDA] United States Department of Agriculture. 2013. Crop production: 2012 summary. Washington, DC. <http://usda01.library.cornell.edu/usda/nass/CropProdSu//2010s/2012/CropProdSu-01-12-2012.pdf>
- [USDOT] United States Department of Transportation. 2013. Public road length-2012. Washington, DC: Federal Highway Association. <http://www.fhwa.dot.gov/policyinformation/statistics/2012/hm16.cfm#foot1>
- [USGA] United States Golf Association. 2012. Golf's use of water: solutions for a more sustainable game. Far Hills, NJ. TGIF Record Number 214418.
- Uthus, E.O. 1992. Arsenic essentiality: a role affecting methionine metabolism. J. Trace Elem. Exp. Med. 16:345–355.
- Wauchope, R.D. and J.E. Street. 1987a. Fate of a water-soluble herbicide spray on foliage. part 1. Absorption and dissipation of foliar msma deposits: Mathematical modelling. Pestic. Sci. 19:253-263
- Wauchope, R.D. and J.E. Street. 1987b. Fate of a water-soluble herbicide spray on foliage. part 2. Absorption and dissipation of foliar msma deposits: Mathematical modelling. Pestic. Sci. 19:253-263.
- Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W. Augustijn-Beckers, and J.P. Burt. 1992. The scs/ars/ces pesticide properties database for environmental decision-making. Rev. Environ. Contam. Toxicol. 123:1-155.

Woolson, E.A. and A.R. Isensee. 1981. Soil residue accumulation from three applied arsenic sources. *Weed Sci.* 29:17-21.

Xu, X.Y., S. P. McGrath, and F.J. Zhao. 2007. Rapid reduction of arsenate in the medium mediated by plant roots. *New Phytol.* 176:590-599.

**ARSENIC DISTRIBUTION AND SPECIATION IN A MANAGED TURFGRASS
SYSTEM FOLLOWING A MONOSODIUM METHYLARSENATE (MSMA)
APPLICATION**

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Greenhouse lysimeter experiments were conducted to determine arsenic (As) distribution, mass balance, and porewater speciation over time following a monosodium methylarsenate (MSMA) application ($4.5 \text{ kg a.i. ha}^{-1}$) to established bermudagrass. Samples collected included turfgrass clippings, remaining vegetation, roots, soil (0-5, 5-15, and 15-30 cm depth), porewater (5 and 15 cm depth), and leachate (30 cm depth). At 1 week after treatment (WAT), up to 10% of As from MSMA was detected in clippings. Soil As only increased at 0- to 5-cm depth 8 WAT, with elevated porewater concentration detected at 5 cm. Arsenic concentration did not increase in soil or water samples below 5 cm throughout the study; however, mass balance calculations revealed As was predominantly located in the soil. Porewater As species transformed between 1 and 2 WAT from monomethylarsonic acid (MMA) to mostly arsenate. Although, substantial amounts of MMA ($\geq 28\%$) and dimethylarsonic acid ($\geq 13\%$) were also detected through 2 WAT. Data from this research suggest that turfgrass clippings should be returned for 2 WAT following a MSMA application. Further, MSMA should not be applied in conditions favoring downward movement in soils to groundwater (i.e. shallow water table depth, sandy soil, or rainfall events < 1 WAT).

INTRODUCTION

Arsenic (As) has been an active ingredient in numerous pesticides since the late 1800s, including organic arsenical herbicides, which were introduced in the 1950s.¹ The organic arsenical monosodium methylarsenate (MSMA) was introduced in the 1960s and is still used in agronomic systems today¹. Arsenic from MSMA may be concerning for human and environmental health reasons (carcinogenic effects, groundwater contamination, etc.), but it is commonly used to control weeds in various settings.² Prior to 2006, An estimated 1.4 million kg MSMA was applied annually to various use sites in the United States, with the majority applied to cotton, turfgrass, sod farms, and roadsides.² However, due to groundwater As contamination concerns, the United States Environmental Protection Agency (USEPA) enacted a phase-out of all organic arsenical herbicides, including MSMA, in 2006. Subsequently, MSMA use has been extended pending a National Academy of Sciences' review set to conclude in 2015.³

Although MSMA is commonly used in turfgrass settings, limited research has been conducted with respect to As fate following application. Previous research on As fate from MSMA has been completed in other use sites, such as forage and food crops, because of its known toxicity. Research has examined absorption, translocation, and residues in various crops following MSMA application to address human safety concerns.⁴⁻⁶ Previous research evaluated the fate of As following disodium methanearsonate (DSMA) applications in coastal bermudagrass [*Cynodon dactylon* (L.) Pers.] forage crops to address livestock safety concerns.⁷ In these studies, rapid uptake and basipetal translocation were reported, but the focus was plant As residues and forage and food crop safety. Research is needed to determine

turfgrass As content over time, especially with respect to turfgrass clippings as they may present environmental contamination concerns following disposal.

Concerns of As groundwater contamination and soil residue accumulation has spurred soil and porewater studies aimed at assessing the fate of As following MSMA applications in agronomic settings.⁸⁻¹² Increased soil As concentrations down to 15 cm following MSMA applications have previously been reported in agronomic crop settings⁸⁻¹⁰ with similar results reported in a turfgrass system.¹¹ Furthermore, in a field lysimeter experiment, Matteson et al.¹¹ reported that porewater As concentrations at 76 cm depth following MSMA applications to a bareground and turfgrass were similar to nontreated samples. In contrast, Feng et al.¹² reported elevated porewater As in a constructed turfgrass lysimeter experiment at 40.6 cm depth. Previous studies suggest low mobility of As from MSMA in soil, with elevated porewater As being a concern at shallow depths. Further investigation is needed to determine how turfgrass cover and management may effect As distribution over time. Additionally, determining As mass balance following MSMA applications has largely been ignored due to the many system components, including aboveground vegetation, roots, soil, and porewater. Elucidating mass balance over time in a turfgrass system is critical as it may help quantify known and previously unrecognized areas of potential contamination.

Research on porewater As speciation following organic arsenical treatment has shown transformations over time. Feng et al.¹² reported that arsenate [As(V)] was the main metabolite with dimethylarsonic acid (DMA) also detected in porewater (40.6 cm depth) following MSMA treatment to turfgrass in a constructed lysimeter experiment. Gao and Burau¹³ and Shimizu et al.¹⁴ also reported As(V) as the main metabolite detected in soil

incubation studies, but DMA was present in negligible fractions. Arsenic speciation significantly affects mobility and toxicity;^{1,15} therefore, further investigation is needed to elucidate porewater and leachate As speciation following MSMA application in turfgrass settings.

MSMA is an important herbicide in turfgrass for control of crabgrass, goosegrass, dallisgrass, sedge species, and other common and troublesome weeds.¹⁶⁻¹⁸ Although previous research on the environmental fate of As following MSMA applications has been conducted, knowledge gaps remain. Comprehensive As mass balance and porewater speciation analysis are needed to quantify known and undetermined contamination risks following a MSMA application. Additionally, As concentrations in MSMA-treated bermudagrass vegetation may be elevated over background for up to one year after treatment,¹¹ suggesting that turfgrass clipping management may effect As cycling and environmental contamination in a turfgrass system. The objectives of this research were to quantify 1) As mass balance over time in a managed turfgrass system, 2) the effect of turfgrass clipping management on As cycling, and 3) porewater As species transformation over time following a MSMA application. Results from this work are useful for determining the allocation of As from MSMA between aboveground and belowground turfgrass biomass and soil.

MATERIALS AND METHODS

Greenhouse Lysimetry. Greenhouse lysimetry experiments were conducted at North Carolina State University's Method Road Greenhouse Complex in Raleigh, North Carolina. Lysimeters (schedule 40 PVC; 10 cm diam. x 30 cm length) were suspended from racks (0.5

m height) and constructed with a drain to allow for leachate collection (Figure 1). Select lysimeters were split in half (prior to drain addition) which allowed for destructive soil sampling at 2, 4, and 8 weeks after treatment (WAT). Very-coarse sand (> 2 mm) was used to coat the inner lysimeter walls to mitigate preferential flow and was held in place by a waterproof epoxy (DAP[®] Weldwood[®] Original Contact Cement; DAP Products Inc., Baltimore, MD). Previous laboratory testing determined the epoxy did not sorb As from solution. After curing for 24 h, lysimeters were packed with a Candor sand soil (sandy, kaolinitic, thermic Grossarenic Kandiodults) (1.5 g cm^{-3}), planted with a bermudagrass plug ('Tifway 419'; 5 cm depth x 10 cm diam.) and allowed to acclimate for six weeks. Funnels (Westward Utility Funnel; W. W. Grainger Inc., Lake Forest, IL) and collection bottles (Nalgene Amber HDPE; Thermo Fisher Scientific Inc., Rochester, NY) were attached to the bottom of select lysimeters for leachate collection. Holes were bored (1.25 cm diam.) into bottle caps and were inserted over the funnel mouth and held in place with waterproof epoxy.

Eight additional lysimeters were constructed with modifications to collect porewater and leachate samples for As speciation analysis. Funnel exteriors were painted black to eliminate the effect of light on As speciation¹⁹ and needles (12 gauge stainless steel; 5.08 cm) (Blunt-Tip Reusable Dispensing Needle; McMaster-Carr, Atlanta, GA) were installed through the lysimeter walls at 5 and 15 cm depth, allowing for porewater collection via syringe (Figure 1).

Overhead irrigation was applied to ensure proper soil moisture ($\approx 25\% \text{ v v}^{-1}$) for plant growth; irrigation was controlled by soil moisture readings (Field Scout TDR-200; Spectrum Technologies, Pittsburgh, PA) from 7 cm depth, taken throughout the experiment. Three

fertilizer applications (21-0-0 N-P₂O₅-K₂O; 0.56 kg N ha⁻¹) (Hi-Yield Ammonium Sulfate; VPG Inc., Bonham, TX) were made at 4, 3, and 2 weeks before experiment initiation and 2 and 5 WAT; this fertilizer was previously determined to have non-detectable As concentrations (< 0.02 mg kg⁻¹). Bermudagrass was mown (5 cm) with scissors (Razor Edge™ fabric shears; Fiskars Brands, Inc., Madison, WI) twice per week throughout the entire experiment.

Treatment. One day prior to MSMA application, lysimeters were saturated and allowed to drain, as irrigation is not recommended within 24 h after application.²⁰ MSMA (4.5 kg ai ha⁻¹) (MSMA 6 Plus; Drexel Chemical Co., Memphis, TN) was applied using a CO₂-pressurized single-nozzle (XR 8002E; TeeJet, Spraying Systems Co., Wheaton, IL) sprayer calibrated to deliver 304 L ha⁻¹.

Experimental Design. Unique lysimeters represented a clipping management practice (clippings collected or returned) and sample time (8 weeks total) equaling 16 treated lysimeters per replicate. Clippings were collected at each mowing event for those lysimeters designated as clipping collected (CC) while they were returned to those designated as clippings returned (CR) until sampled. Twelve nontreated lysimeters (six per management practice) were included and all lysimeters were re-randomized weekly to compensate for irrigation or light variation. The experiment was arranged in a randomized complete block design with four replications, and the entire experiment was repeated in time.

Sample Collection for Total As Analysis of Plant, Soil, and Water. Samples for total As analysis included turfgrass clippings, remaining aboveground vegetation, various soil depths (0-5, 5-15, and 15-30 cm), roots, porewater and lysimeter leachate. Turfgrass clippings and

remaining vegetation were sampled weekly from lysimeters designated for the respective WAT. All samples were stored in polyethylene bags at -18 °C until analysis.

Soil sampling occurred at 2, 4, and 8 WAT; one-half of the lysimeter was used for soil collection, with soil depths sampled accordingly from deep to shallow depths to minimize contamination potential. The remaining half was sieved (1.4 mm) and washed clean with water, and then roots were collected. Sampling utensils were washed with a 1:1 (v v⁻¹) ammonia:water solution, rinsed with water, and dried prior to subsequent lysimeter processing. All samples were stored in polyethylene bags at -18 °C until analysis.

Leachate was collected weekly for 8 weeks with porewater collection occurring 0.5, 1, 2, 4, and 8 WAT. Volumes were recorded and samples were stored in vacuette vials (Vacuette[®] EDTA Tubes; Greiner Bio-One, Kremsmünster, Germany) at 4°C until analysis. Following sampling, clean collection-bottles were reinstalled to prevent contamination.

Sample Collection for Porewater As Speciation. Porewater and leachate samples were collected 0 (before treatment), 0.5, 1, and 2 WAT. Immediately before collection, irrigation water (100 mL) was added to the lysimeter to allow porewater or leachate to be collected. After collection, precautions were taken to mitigate light exposure, and samples were filtered (0.2 µm nylon syringe filter; VWR International L.L.C., Radnor, PA) into a vacuette vial containing EDTA to prevent As species transformation.¹⁹ All samples were stored in opaque-brown bags at 4 °C until analysis.

Tissue As Analysis. Tissue digestions were completed via wet digestion²¹ using a DigiPREP MS digestion block (SCP Science, D'Urfé, Quebec, Canada). Trace-metal-grade acids were used throughout all analyses. Prior to digestion, plant tissue was dried at 37 °C

until mass was constant. To ensure a representative subsample from the remaining vegetation and roots, samples were blended (Cuisinart® SmartPower®; Cuisinart, Stamford, CT) thoroughly. Plant tissue (0.10 g) was placed into a unique digestion tube with concentrated nitric acid (10 mL). Tubes were swirled and placed onto the block (110 °C) for one h with additional swirling (3 times) during heating. Following heating, samples were removed from the block and allowed to cool for 10 min. Hydrogen peroxide (1 mL) was added to each sample, swirled, and returned to the block (110 °C). After 20 min, samples were removed and cooled, and digestion liquid was filtered (#41 filter paper; Whatman Inc. Piscataway, NJ) into unique DigiTubes (SCP Scientific, D'Urfé, Quebec, Canada). Samples were brought to final volume (25 mL) with deionized water.

Digests were diluted to 1:31 (v v⁻¹) with ultra-filtered deionized water (18 megohm) and analyzed for As concentrations on an Agilent 7500 inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent Technologies Inc., Englewood, Co). The limit of quantification and limit of detection was 35 ng As L⁻¹ and 7 ng As L⁻¹, respectively. All samples were analyzed in a Reaction Cell with helium gas at 4 mL min⁻¹ to correct argon chloride (75 g mol⁻¹) interference on As. Indium, terbium, and yttrium were used as internal standards to correct for small differences in sample uptake and solution viscosity, matching acid backgrounds in standards to samples. Standards were prepared by dilution of a 10 mg As L⁻¹ multicalibration stock solution (IV-Stock-27; Inorganic Ventures, Christiansburg, VA), and a check standard (Claritas PPT Grade Multi-Element Solution 2A; SPEX CertiPrep Group L.L.C., Metuchen, NJ) was repeated every 20 samples. Two blank and two soil standard samples (SRM1573a tomato leaves; National Institute of Standards and

Technology, Gaithersburg, MD) were processed with every 44 samples to ensure materials were not contaminated and to verify the digestion technique. The overall percent As recovery was 99% throughout the analyses.

Soil As Analysis. Total soil As was extracted utilizing a modified version of USEPA protocol SW846-Method 3050B.²² Preceding analysis, three subsamples (2.5 g) were dried at 105 °C for 24 h and weights were recorded to allow for moisture correction. Once moisture contents were determined, 2.5 g of fresh soil was placed into 75 mL hot block digestion tubes. Fifteen mL of nitric acid (7 M) was added to each tube, fitted with glass caps and vortexed. After 16 h, tubes were heated on a digestion block to 95 °C (15 min) and allowed to cool (10 min). Concentrated nitric acid (5 mL) was added to each tube, vortexed, and heated to 95 °C (45 min). The tubes were removed and allowed to cool, and the previous acid addition and heating procedure were repeated. Following heating, loose fitting caps were removed and the tubes were refluxed at 95 °C (2 h). The tubes were then removed, capped, and allowed to cool. After cooling, deionized water (3 mL) was added to each tube followed by hydrogen peroxide (30%) (2 mL, 1 mL per addition). The tubes were then placed on the block and brought to reflux until no effervescence from hydrogen peroxide was observed. Six subsequent hydrogen peroxide additions (1 mL per addition) were added to each tube, returned to the block, and allowed to effervesce. Following the final hydrogen peroxide addition, the tubes were vortexed, caps removed, and placed back on the block at 95 °C for 2 h. The heating block and tubes were allowed to cool, and then concentrated hydrochloric acid (5 mL) was added to each tube and tubes were vortexed. The tubes were placed on the heating block and slowly heated to 95 °C (30-45 min). The tubes were then cooled and digest

liquid was decanted and filtered (#41 filter paper, Whatman Inc. Piscataway, NJ) into volumetric flasks. Samples were brought to final volume (50 mL) with deionized water.

Digestion solutions were analyzed by ICP-MS as described above to determine total As concentrations. Two blank and two soil standard samples (SRM271a Montana soil II; National Institute of Standards and Technology, Gaithersburg, MD) were processed with every 36 samples to ensure materials were not contaminated and to verify the digestion technique. The overall percent As recovery was 101% ($\pm 2\%$) throughout the analyses.

Leachate and Porewater As Analysis. Leachate and porewater samples were acidified (2% nitric acid v v⁻¹) and analyzed via ICP-MS, as previously described, to determine total As concentrations.

Porewater As Speciation Analysis. For speciation analysis, liquid chromatography–inductively coupled plasma–mass spectrometry (LC-ICP-MS) was performed on a Varian 820 ICP-MS (Bruker Daltonics, Billerica, MA). Data were collected in Collision Reaction Interface mode, with hydrogen gas (70 mL min⁻¹), to eliminate argon chloride interferences. An anion exchange chromatographic column (PRP-X100, 250 x 4.1 mm; Hamilton Co., Reno, NV) was used for As species separation. The concentration, pH and flow rate of the mobile phase solution were 30 mmol L⁻¹, 6.0, and 1.0 mL min⁻¹, respectively, using isocratic elution. Arsenic standards were made for the following species: inorganic arsenite [As(III)] (CGAS(3)1-1; Inorganic Ventures Inc. Christiansburg, VA), DMA (sodium cacodylate trihydrate; Thermo Fisher Scientific Inc., Rochester, NY), monomethylarsonic acid (MMA) (MSMA sesquihydrate; Chem Service Inc., West Chester, PA), and inorganic arsenate [As(V)] (CGAS(5)1-1; Inorganic Ventures Inc. Christiansburg, VA) with retention times of

2.5, 3.4, 4.2, and 8.2 min, respectively. Chromatographic data were collected and processed using Galaxie software (Varian Ltd, Oxford, UK).

X-ray Absorption Spectroscopy. Select soil samples were analyzed via synchrotron-based micro-X-ray fluorescence (μ -XRF) and micro-X-ray absorption near edge structure (μ -XANES) spectroscopy at GSECARS beamline 13-ID-E of the Advanced Photon Source (Argonne National Laboratory, Argonne, IL). Samples included those from 0-5 cm depth taken 2, 4, and 8 WAT (treated and nontreated). Homogenized subsamples were thinly smeared on double-sided tape fixed to a polycarbonate slide. Micro-XRF mapping was conducted with a micro-focused beam (≈ 5 -10 μ m) at 12,900 eV. Map sizes were generally 1 mm x 1 mm with a scan step size of 2 μ m at 0.03 s counting time per pixel. Mapping allowed for multiple As hotspots to be detected, and these spots were further analyzed via μ -XANES for As speciation.

Arsenic K-edge spectra were internally calibrated with sodium arsenate (11,874 eV). At least three μ -XANES scans were performed on each hotspot. Micro-XANES scans were performed at -100 to 100 eV about the As K α edge of 11,867 eV. Energy steps varied across the spectrum with steps of 5 eV (11,767 to 11,852 eV), 0.25 eV (11,852 to 11,895), and 2 eV (11,895 to 11,970 eV). Spectra were normalized and background-removed using SixPack.²³ X-ray absorption coefficients were then compared to spectra of known As standards, including DMA, MSMA, shneiderhonite [As(III)], and scorodite [As(V)].

Arsenic Recovery Calculations. Soil sample depths with increased As concentration were converted to a total As basis by the following equation:

$$\text{Total As} = ([T] - [NT]) * m_s$$

where $[T]$ (mg kg^{-1}) is the treated As concentration, $[NT]$ (mg kg^{-1}) is the nontreated As concentration, m_s is the mass of soil (kg) in the respective depth increment. Bulk densities values were previously reported for our field site.²⁴ Sample As contents were then utilized to determine As recovery as a percentage of the total As applied from MSMA (1.7 mg per lysimeter):

$$\% \text{ recovery} = (C_{As} + RV_{As} + S_{As} + R_{As} + P_{As}) / 1.7 \text{ mg}$$

where C_{As} , RV_{As} , S_{As} , R_{As} , and P_{As} represent the total As content within clippings, remaining vegetation, soil, roots, and porewater, respectively.

Data Analysis. Data were subject to ANOVA using general linear models (SAS[®] for Windows, v 9.4; Statistical Analysis Systems Institute, Cary, NC). Significant main effects and interactions are presented with precedent given to interactions of increasing magnitude.²⁵ Means were separated according to Fisher's Protected LSD at $P = 0.05$.

RESULTS AND DISCUSSION

Arsenic Distributions Over Time.

Clippings. For both clipping management regimes (clippings collected and returned), clippings from nontreated lysimeters did not show detectable As; therefore, it can be stated that increased clipping As concentration is directly from MSMA. Clipping As concentration and content increased following MSMA application under both respective clipping

management practices, with each greatest at 1 WAT (Table 1). Clipping management affected bermudagrass clipping As concentration and content through 3 and 2 WAT, respectively, as increased As was detected in the clippings under the clippings collected (CC) regime when compared to the clippings returned (CR) regime. From 1 to 8 WAT, As content decreased from 160.2 to 1.0 $\mu\text{g lysimeter}^{-1}$ and 16.7 to 0.6 $\mu\text{g lysimeter}^{-1}$ within the CC and CR regimes, respectively. It should be noted that the increased clipping As content from the CC regime compared to CR may be exaggerated because mean clipping mass was approximately three fold more, since two clipping events were combined per week for analysis. Nonetheless, increased clipping As concentration and content under the CC regime compared to the CR suggest that substantial amounts As may be removed from the system within 1 WAT if clippings are not returned.

Remaining vegetation. Clipping management affected remaining vegetation As concentration and content when pooled over time (Table 2). Remaining vegetation As concentration and content under CR regime (97 $\mu\text{g As g}^{-1}$ and 348 $\mu\text{g lysimeter}^{-1}$, respectively) were greater than CC (80 $\mu\text{g As g}^{-1}$ and 262 $\mu\text{g lysimeter}^{-1}$, respectively). These differences may be due to sample collection and will be discussed later. The main effect of time was also a significant factor on both concentration and content when pooled over clipping management practice (Table 2). Similar to clipping samples, increased remaining vegetation As concentration and content were detected though 2 and 3 WAT, respectively. From 1 to 8 WAT, As concentration and content decreased from 236 to 24 $\mu\text{g As g}^{-1}$ and 936 to 94 $\mu\text{g lysimeter}^{-1}$, respectively. Additionally, as with clipping samples, very little As (max

0.51 mg kg⁻¹) was detected in nontreated remaining vegetation suggesting increased As was directly due to MSMA.

Soil. Increased soil As concentration was only detected in MSMA-treated lysimeters at 0- to 5-cm depth, at all evaluation dates, compared to nontreated lysimeters (Table 3); therefore, only this increment will be discussed. Within treated lysimeters, soil As concentration at 8 WAT was increased compared to 2 WAT ($p = 0.0413$). Additionally, soil under the CR regime was increased compared to CC regime, although it was not statistically significant (Table 4). The slight increase may be attributed to returned clippings As to the system over the evaluation period. However, because only a maximum of 205.5 µg As (12% of applied) (Table 1, sum of CC 1 to 8 WAT) could have theoretically been returned to the system, the increase detected was not significant due to the large As content within the soil solid phase. In general, the data show increasing soil As concentration over time, indicating that As cycling within the plant-soil-water system ultimately retains As within the top 5 cm, as discussed below.

Roots. Increased root As concentration and content from MSMA-treated bermudagrass was detected at each evaluation date compared to roots from nontreated lysimeters (Table 5). Additionally, although not significant, root As concentration at 2 WAT (27 µg As g⁻¹) was less than 4 (33 µg As g⁻¹) or 8 WAT (31 µg As g⁻¹), suggesting root As accumulation occurs following MSMA application. This increase may be attributed to As basipetal movement following turfgrass absorption or uptake from soil solution following MSMA application.^{7,26}

Porewater and leachate. Collection of porewater from the 5-cm depth was only possible in two treated lysimeters, under the CR regime (Figure 2), and as such, the effect of clipping

management on porewater As concentration could not be determined. Inconsistent sample collection may be in part to the limited suction created by the syringes. Samples taken prior to MSMA application revealed As concentrations of 5.1 and 3.2 $\mu\text{g L}^{-1}$. Maximum porewater As concentration in each lysimeter was detected 1 WAT (110 and 30.6 $\mu\text{g L}^{-1}$ for the two lysimeters). Although porewater As concentration varied between lysimeters, they exhibited similar temporal trends, as As concentration increased through 1 WAT and decreased thereafter. This trend suggests that As from MSMA, which was initially in solution, was later bound by soil and/or bermudagrass roots, in agreement with previous studies.^{7,27}

Porewater sample collection from the 15-cm depth was only possible for one treated CR lysimeter through 2 WAT. The data suggest that As did not reach this depth as porewater As concentration fluctuated from 3 to 4.2 $\mu\text{g L}^{-1}$, the approximate background concentration of As in porewater. Additionally, leachate As concentration from MSMA-treated lysimeters were not elevated over those from nontreated lysimeters ($p = 0.4475$). Over the evaluation period, leachate As concentration was 2.8 $\mu\text{g L}^{-1}$ ($\pm 1.7 \mu\text{g L}^{-1}$) and 4.1 $\mu\text{g L}^{-1}$ ($\pm 2.2 \mu\text{g L}^{-1}$) for MSMA-treated ($n = 8$) and nontreated ($n = 4$) lysimeters, respectively, and no systematic trends in concentrations were observed over time. Through the experimental period, leachate As concentrations never exceeded 7 $\mu\text{g L}^{-1}$ in any treated lysimeter, suggesting that MSMA-derived As was readily bound in the upper portion of the lysimeter profile.

Arsenic Mass Balance Following MSMA Application. Arsenic from MSMA was confined in bermudagrass tissue and at the soil surface (0-5 cm) over the duration of the experiments, with 107, 114, and 113% of total applied As recovered at 2, 4, and 8 WAT, respectively (Table 6). Remaining vegetation, root, and soil samples were pooled over

clipping management, as its effect was not significant on As concentration or content over time (Tables 2, 3, and 5).

The majority of As from MSMA was initially present in turfgrass aboveground vegetation (Tables 1 and 2), due to foliar interception following application, but ultimately was recovered in soil (Table 6). At 1 WAT, the majority of As from MSMA was present in the clippings (1 and 10% for CR and CC, respectively) and remaining vegetation (55%), but by 2 WAT, the As content of clippings (0.6 and 1.4% for CR and CC, respectively) and remaining vegetation (29%) had declined (Tables 1 and 2). At this time, the majority of applied As was partitioned below the vegetation and was present in soil (64%) and plant roots (13%). This trend continued through 4 WAT, as aboveground vegetation As content decreased through 3 (20%) and 4 WAT (13%) (Tables 1 and 2), while soil and root As content at 4 WAT were 86 and 15% of the total As applied, respectively (Table 6). Ultimately, by 8 WAT, 91 and 16% of applied As was recovered in 0- to 5-cm soil depth and roots, respectively, with just 6% of the applied As in the aboveground vegetation.

Arsenic Speciation in Soil and Porewater following MSMA Application. Porewater collection was only possible from two treated lysimeters from the 5-cm depth under the CR regime. Although total As concentration varied between lysimeters at each sample date, As species concentration between lysimeters was consistent (standard deviation < 9.5%).

Porewater As species concentration varied over time following MSMA application (Figure 2), suggesting that species transformation occurred. Porewater samples taken prior to MSMA application revealed As concentration of 5.1 and 3.2 $\mu\text{g L}^{-1}$ and consisted only of inorganic As species. At 0.5 WAT, MMA (58%) was the predominant As species compared to As(III),

DMA, and As(V) (9.8, 23, and 9.2%, respectively). Similarly, at 1 WAT, MMA (65%) was the predominant species and was more than 4-fold greater than concentrations of As(III), DMA, and As(V) (13, 13, and 10%, respectively). From 1 to 2 WAT, As species transformed to predominantly As(V) (43.5%) compared to As(III) (12%), DMA (16.5%), and MMA (28%). Because As(V) was dominant 2 WAT, concern for As leaching is greatest within two weeks of treatment, when MMA is the main species, as it is generally more mobile than As(V).²⁷ Additionally, DMA is present in substantial quantities at earlier time points, and it has been shown to be more mobile than MMA and As(V).^{15,27}

X-ray absorption spectroscopy indicated that multiple As species were present in soil samples at the 0- to 5-cm depth (Figure 3). Micro-XRF mapping revealed As “hotspots” (circled) of high As content, and these spots were chosen for μ -XANES analysis. Three As hotspots detected in soil from 2 WAT (Figure 3A) showed As(V) as the predominant species. There is also evidence of As(III) in spot 1, as indicated by the spectra “shoulder” at 11,871.3 eV. Similar results were detected in soil from 4 WAT (Figure 3B). The six spots revealed a predominant presence of As(V) with As(III) detected at only 1 analyzed hotspot. At 8 WAT, As(V) dominated all hotspots (Figure 3C). In agreement with the porewater speciation data, the collective μ -XANES spectra indicate that As species conversion is occurring within the lysimeters, with potential demethylation of MMA to form As(V) – a relatively immobile As species.

Factors Influencing Arsenic Cycling Following MSMA Application to Turfgrass.

Clipping management. The discussed As distribution and speciation trends following a MSMA application are supported by previous research, which may help determine potential

environmental impacts associated with MSMA application to turfgrass. Clipping As content was greater in the CC regime than the CR regime at 1 WAT (Table 1), which can be attributed to the 0.5 WAT clippings collected with CC 1 WAT sample. A decline in clipping As content was detected from 1 to 2 WAT. Cisar and Snyder²⁸ reported a similar decline in turfgrass clippings with organophosphate pesticides by 1 WAT.

When comparing remaining vegetation under CR to CC regime pooled over time, As concentration and content from CR was greater ($97 \mu\text{g As g}^{-1}$ and $348 \mu\text{g lysimeter}^{-1}$, respectively) than CC ($80 \mu\text{g As g}^{-1}$ and $262 \mu\text{g lysimeter}^{-1}$, respectively). At the mid-week mowing events, under CR regime, clippings were cut, placed onto the remaining vegetation, and lightly brushed in. When sampling the remaining vegetation portion at the week's end, all remaining vegetation from the soil surface and up was collected. Therefore, increased remaining vegetation As concentration and content under CR regime compared to CC may be due to returned turfgrass clippings that were inadvertently sampled with the remaining vegetation portion. These returned clippings likely elevated the remaining vegetation As concentration and content within the CR regime.

Clipping content may have affected soil As concentration at the 0- to 5-cm depth. Under the CR regime, soil As concentration was greater than that of the CC regime, although differences were not significant (Table 4). If total clipping As content from CC regime ($205.5 \mu\text{g}$) (Table 1) was added to the 0- to 5-cm depth, soil As concentration would have increased by 0.48 mg kg^{-1} . Soil As concentration under CR regime was $0.7 \text{ mg As kg}^{-1}$ greater than CC, suggesting that As from returned clippings were released into the soil (Table 4). However,

because of inherent natural As variation and analytical limits, such differences would not be detectable.

Previous studies have identified element leaching potential from decomposing grasses. Sanders and Osman deemed 81% of As within detrital *Spartina alterniflora* Loisel. to be “bioavailable” based on 1 N HCl extractions. Additionally, Drifmeyer et al.²⁹ detected desorption (50%) of other metals such as manganese, iron, copper, and zinc, in *Spartina* detritus and suggested that a substantial portion of the metals are held in readily exchangeable surface reaction sites which may be released into the environment. Kopp and Guillard³⁰ detected that > 80% of tissue nitrogen was released from turfgrass clippings within 8 weeks after mowing. Based on the current data and previous research, it can be hypothesized that As was released from turfgrass clippings through 8 WAT in this study causing increased soil As concentration in the CR regime compared to the CC regime.

Plant cycling and root exudation of arsenic. Soil As concentration increases at 0- to 5-cm depth over time (Table 3) may be due, in part, to root As exudation, which has previously been hypothesized from bermudagrass following a DSMA application⁷. This trend may be seen when examining bermudagrass vegetation and root As content as a whole. Over time, aboveground vegetation content decreased (Tables 1 and 2) while root As content increased (Table 5). This translocation pattern has been previously reported in black bean (*Phaseolus vulgaris* L. 'Black Valentine'),⁴ cocklebur (*Xanthium trumarium* L.),²⁶ and bermudagrass⁷ following MSMA and DSMA applications. Inside the plant, MSMA may have been complexed with organic acids⁵ to enable exudation into the rhizosphere,³¹ thereby increasing total soil As concentrations over time.

Arsenic retention by soil. At 2, 4, and 8 WAT, soil As concentrations in MSMA-treated lysimeters were greater than comparable As concentrations from nontreated lysimeters at only the 0- to 5-cm depth (Table 3). Previous research has reported MSMA-applied As reached deeper depths than observed in this research, but differences may be explained by experimental conditions and evaluation parameters. In a constructed-lysimeter research experiment, Feng et al.¹² detected elevated soil As concentrations to a 10 cm depth 3 weeks after MSMA treatment. Within their research, soil As distribution was determined following higher application rates than in our study and on a soil consisting of 0.2% silt + clay. In our current study, a Candor sand soil consisting of 8% silt + clay was used, which may have more As binding sites available, increasing sorption before As reached deeper depths. In other field research, Matteson et al.¹¹ detected elevated soil As concentrations to 8 cm depth 60 days after MSMA treatment in a Candor sand soil. Increased As mobility may be attributed to rainfall during the field experiment, as five rainfall events > 3 cm occurred prior to the 60-d evaluation date.³²

Soil and porewater arsenic speciation. Soil and porewater As speciation may also contribute to the confinement of applied As near the soil surface. Soil and porewater speciation indicated As(V) was the predominant metabolite from MSMA over time (Figures 2 and 3), and similar results have been observed in lab and field studies. Using synchrotron-based μ -XRF, Shimizu et al.¹⁴ detected MMA as the predominant species one week and one month after soil was incubated with MMA. However, after 6 months, substantial species transformation occurred, with As(V) being the predominant As species. Gao and Burau¹³ detected As(V) as the predominant metabolite following a 70-day incubation period of

MMA in soil, but ultimately, more MMA (57%) was detected compared to As(V) (43%). In a constructed lysimeter experiment, Feng et al.¹² detected small amounts of MMA (1.4% of total As) in leachate (40.6 cm depth) through 14 weeks after three MSMA applications to turfgrass. Through 2 weeks after the last treatment, DMA was the predominant species detected in leachate, and As(V) was the predominant species thereafter. Within soils, DMA is generally more mobile than MMA, and both are more mobile than As(V)^{14,27}, suggesting that the extent and rate of species conversion will influence the leaching potential of As following MSMA application.

Oxide mineral content and soil texture may also be an important factor governing As speciation transformation rates following MSMA treatment. Coarse-textured soil, such as the evaluated soil used by Feng et al.¹² or Candor sand used in this study, will have fewer As sorption sites which may allow MMA to be more available in solution for species transformation.¹⁴ In contrast, fine-textured soils with high clay content, such as those used by Shimizu et al.¹⁴ and Gao and Burau¹³, are able to sorb more MMA from solution than the coarse-textured soils^{11,34} meaning less As is available in solution for species transformation. Thus, although As(V) is generally the ultimate metabolite formed following MSMA application, the soil type, specifically oxide content, may impact the time over which demethylation occurs.

Environmental and Management Implications. This study is the first published research that quantifies As mass balance following a MSMA application to turfgrass, thereby providing insight to potential environmental impacts associated with MSMA. Because clipping As content, under the CC regime, was elevated through 2 WAT compared to CR

(Table 1), precautions must be taken when disposing of collected clippings following MSMA application to turfgrass. For example, the average irrigated golf course tee and fairway area is 13.8 ha,³³ and if the 1 WAT As content ($160.2 \mu\text{g lysimeter}^{-1}$) is extrapolated to this area, 2.7 kg As may be removed from the system following mowing events with collected clippings. If clippings are deposited within a confined area offsite, clipping degradation and subsequent As release may result in potential As contamination concerns. Therefore, it may be concluded that clippings should be returned to their location when mowing for no less than 2 WAT in order to minimize off-target injury or localized As contamination of surface water and groundwater.

Another As pool which may be of concern, if not managed properly, is remaining vegetation. Substantial As from MSMA ($> 10\%$ of applied) was detected in the remaining vegetation through 4 WAT (Table 2), reaffirming the need of the “one-third” mowing rule, which states that only one-third of the vegetation should be removed at any mowing event.³⁴ Aside from plant health benefits, following the “one-third” rule may help minimize As removal from this As pool and should be practiced following MSMA applications to turfgrass.

Although As did not leach beyond 5-cm depth in this study, As mobility concerns may be drawn from the porewater As species that were detected over time (Figure 2). Substantial amounts of DMA ($\geq 13\%$) and MMA ($\geq 28\%$) were detected through 2 WAT. Accordingly, large rainfall events within 2 WAT may enhance As leaching due to the presence of these more mobile organic As species. Because As species with greater mobility were detected through 2 WAT, MSMA should not be applied in areas with shallow water tables and/or very

coarse soil with little to no oxide minerals. In conclusion, MSMA may be used for weed control if precautions are taken; however, to minimize long term As contamination concerns, MSMA should be used in rotation in lieu of being consistently applied.

LITERATURE CITED

1. Hughes, M. F. Arsenic toxicity and potential mechanisms of action. *Toxicol. Lett.* **2002**, *123*, 1-16.
2. United States Environmental Protection Agency *Guidance for Products Containing the Organic Arsenicals*; Revised Reregistration Eligibility Decision for MSMA, DSMA, CAMA, and Cacodylic Acid; United States EPA; Washington, DC, 2009; http://www.epa.gov/oppsrrd1/REDs/organic_arsenicals_red.pdf. *RED 2009, EPA-HQ-OPP-2006-0201*, 1-46.
3. United States Environmental Protection Agency Organic Arsenicals; Amendments to Terminate Uses; Amendment to Existing Stocks Provisions. *Federal Register* **2013**, *FRL-9380-4*, 18590-18590.
4. Sachs, R. M.; Michael, J. L. Comparative phytotoxicity among four arsenical herbicides. *Weed Sci.* **1971**, *19*, 558-564.
5. Sckerl, M. M.; Frans, R. E. Translocation and metabolism of MAA-¹⁴C in johnsongrass and cotton. *Weed Sci.* **1969**, *17*, 421-427.
6. Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W.; Burt, J. P. The SCS/ARS/CES pesticide properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1-155.
7. Duble, R. L.; Holt, E. C.; McBee, G. G. Translocation and break-down of disodium methanearsonate (DSMA) in coastal bermudagrass. *J. Agr. Food Chem.* **1969**, *17*, 1247-1250.
8. Akkari, K. H.; Frans, R. E.; Lavy, T. L. Factors affecting degradation of MSMA in soil. *Weed Sci.* **1986**, *34*, 781-787.
9. Hiltbold, A. E.; Hajek, B. F.; Buchanan, G. A. Distribution of arsenic in soil profiles after repeated applications of MSMA. *Weed Sci.* **1974**, *22*, 272-275.
10. Robinson, E. L. Arsenic in soil with five annual applications of MSMA. *Weed Sci.* **1975**, *23*, 341-343.
11. Matteson, A. R.; Gannon, T. W.; Jeffries, M. D.; Haines, S.; Lewis, D. F.; Polizzotto, M. L. Arsenic retention in foliage and soil after monosodium methyl arsenate (MSMA) applications to turfgrass. *J. Environ. Qual.* **2014**, *43*, 379-388.

12. Feng, M.; Schrlau, J. E.; Snyder, R.; Snyder, G. H.; Chen, M.; Cisar, J. L.; Cai, Y. Arsenic transport and transformation associated with MSMA. *J. Agr. Food Chem.* **2005**, *53*, 3556-3562.
13. Gao, S.; Burau, R. G. Environmental factors effecting rates of arsine evolution from and mineralization of arsenicals in soils. *J. Environ. Qual.* **1997**, *26*, 753-763.
14. Shimizu, M.; Arai, Y.; Sparks, D. L. Multi-scale assessment of methyarsenic reactivity in soil: 2. distribution and speciation in soil. *Environ. Sci. Technol.* **2011b**, *45*, 4300-4306.
15. Huang, J. H.; Hu, K. N.; Decker, B. Oragnic arsenic in the soil environment: speciation, occurrence, transformation, and adsorption behavior. *Water Air Soil Poll.* **2011**, *219*, 401-415.
16. Blum, R. R.; Isgrigg, J. I.; Yelverton, F. H. Purple (*Cyperus rotundus*) and yellow nutsedge (*C. esculentus*) control in bermudagrass (*Cynodon dactylon*) turf. *Weed Technol.* **2000**, *14*, 357-365.
17. Henry, G. M.; Yelverton, F. H.; Burton, M. G. Dallisgrass (*Paspalum dilatatum*) control with foramsulfuron in bermudagrass turf. *Weed Technol.* **2007**, *21*, 759-762.
18. Johnson, B. J. Tank-mixed postemergence herbicides for large crabgrass (*Digitaria sanguinalis*) and goosegrass (*Eleusine indica*) control in bermudagrass (*Cynodon dactylon*) turf. *Weed Technol.* **1996**, *10*, 716-721.
19. Garbarino, J. R.; Bednar, A. J.; Burkhardt, M. R. Methods of Analysis by the U. S. Geological Survey National Water Quality Laboratory's Arsenic Speciation in Natural-Water Samples using Laboratory and Field Methods. *U. S. Geological Survey Water-Resources Investigations* **2002**, *02-4144*, 1-40.
20. *MSMA 6 Plus Label*; 41SP-0113; Drexel Chemical Co.: Memphis, TN, May 5, 2014.
21. Cai, Y.; Georgiadis, M.; Fourqurean, J. W. Determination of arsenic in seagrass using inductively coupled plasma mass spectrometry. *Spectrochim. Acta B.* **2000**, *55*, 1411-1422.
22. United States Environmental Agency Method 3050B (SW-846): Acid Digestion of Sediments, Sludges, and Soils. Revision 2. *SW-846* **1996**, 1-12.
23. Webb, S. M. Sixpack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scripta.* **2005**, *T115*, 1011-1014.

24. Cummings, H. D. Pesticide downward movement in a bermudagrass system compared with movement in a fallow system. North Carolina State University, Raleigh, NC, 2004.
25. Steele, R. D.; Torrie, J. H.; Dickey, D. A., Eds.; In *Principles and Procedures of Statistics: A Biometrical Approach*; Steele, R. D., Ed.; Principles and Procedures of Statistics: A Biometrical Approach; WCB McGraw-Hill: New York, New York, 1997; Vol. 3rd, pp 672.
26. Nimbal, C. I.; Wills, G. D.; Duke, S. O.; Shaw, D. R. Uptake, translocation, and metabolism of ^{14}C -MSMA in organic arsenical-resistant and -susceptible Mississippi biotypes of common cocklebur (*Xanthium strumarium* L.). *Weed Sci.* **1995**, *43*, 549-554.
27. Lafferty, B. J.; Loeppert, R. H. Methyl arsenic adsorption and desorption behavior on iron oxide. *Environ. Sci. Technol.* **2005**, *39*, 2120-2127.
28. Cisar, J. L.; Snyder, G. H. Mobility and persistence of pesticides applied to a USGA green. III: organophosphate recovery in clippings, thatch, soil, and percolate. *Crop Sci.* **1996**, *36*, 1433-1438.
29. Drifmeyer, J. E.; Cross, F. A.; Zieman, J. C. Sorption and desorption of trace elements by *Spartina alterniflora* detritus. *Plant Soil* **1982**, *66*, 69-80.
30. Kopp, K. L.; Guillard, K. In *Decomposition rates and nitrogen release of turf grass clippings*; Fischer, T., Turner, N., Angus, J., McIntyre, L., Robertson, M., Borrell, A. and Lloyd, D., Eds.; New directions for a diverse planet: Proceedings of the 4th International Crop Science Congress; International Crop Science Society: Brisbane, Australia, 2004; Vol. 4, pp 3.
31. Walker, T. S.; Bais, H. P.; Grotewold, E.; Vivanco, J. M. Root exudation and rhizosphere biology. *Plant Physiol.* **2003**, *132*, 44-51.
32. State Climate Office of North Carolina. North Carolina Climate Retrieval and Observations Network of the Southeast Database. **2014**. <https://www.nc-climate.ncsu.edu/cronos>.
33. Lyman, G. T. In *How Much Water Does Golf Use and Where Does It Come From?* Harivandi, A., Brown, P. and Kenna, M., Eds.; Golf's Use of Water: Solutions for a More Sustainable Game; United States Golf Association: Far Hills, NJ, 2012; Vol. 4, pp 14-15.
34. Watschke, T. L.; Schmidt, R. E. In *Ecological aspects of turf communities*; Waddington, D. V., Carrow, R. N. and Shearman, R. C., Eds.; Turfgrass; American Society of

Agronomy, Crop Science Society of America, Soil Science Society of America:
Madison, WI, 1998; pp 129-175.

Table 1. Effect of clipping management and time on clipping arsenic concentration, content and recovery within MSMA-treated lysimeters.^{a-c}

WAT	— CC —	— CR —	— CC —	— CR —	— CC —	— CR —	— CC —	— CR —
	concentration ($\mu\text{g As g}^{-1}$)		— mass of clippings (g) —		content ($\mu\text{g As lysimeter}^{-1}$)		— As recovery (%) ^d —	
1	383	109	0.42	0.15	160.2	16.7	9.4	1.0
2	121	52	0.20	0.18	23.7	9.6	1.4	0.6
3	54	14	0.21	0.12	11.1	1.7	0.7	0.1
4	19	7	0.23	0.19	4.3	1.3	0.3	< 0.1
5	13	6	0.21	0.17	2.7	1.0	0.2	< 0.1
6	7	3	0.23	0.13	1.6	0.4	< 0.1	< 0.1
7	5	2	0.18	0.20	0.9	0.4	< 0.1	< 0.1
8	4	3	0.25	0.20	1.0	0.6	< 0.1	< 0.1
LSD ^e	36		NS		11.2		-	-

^a Abbreviations: WAT, week after treatment; CC, clippings collected; CR, clippings returned; As, arsenic; NS, not significant.

^b MSMA provided 1.7 mg As per lysimeter.

^c Arsenic was not detected in nontreated clipping samples; therefore, it can be stated that As detected was the result of the MSMA application.

^d Arsenic recoveries are a percent of total As applied.

^e LSD values for comparison within measurement. LSD values were not calculated for As recoveries.

Table 2. Effect of time on remaining vegetation arsenic concentration, content and recovery within MSMA-treated lysimeters.^{a-c}

WAT	Pooled over clipping management		
	conc. ($\mu\text{g As g}^{-1}$)	content ($\mu\text{g As lysimeter}^{-1}$)	As recovery (%) ^d
1	283	936	55
2	145	488	29
3	87	323	19
4	66	216	13
5	41	152	9
6	36	134	8
7	24	98	6
8	24	94	6
LSD ^e	25	108	-

^a Abbreviations: WAT, week after treatment; conc., concentration.

^b MSMA provided 1.7 mg As per lysimeter.

^c Remaining vegetation As concentration and content were $\leq 0.51 \text{ mg As kg}^{-1}$ and $1.77 \mu\text{g lysimeter}^{-1}$, respectively.

^d Arsenic recoveries are a percent of total As applied.

^e LSD values for comparison within measurement. A LSD value was not calculated for percent As recovery.

Table 3. MSMA-treated and nontreated arsenic concentrations in soil at various weeks after treatment.^{a, b}

Depth (cm)	2 WAT		4 WAT		8 WAT	
	Treated ^c	Nontreated	Treated	Nontreated	Treated	Nontreated
	mg As kg ⁻¹					
0-5	5.1	2.5	6.1	2.6	6.8	3.1
5-15	1.8	1.5	1.7	1.5	1.8	1.8
15-30	1.7	1.5	1.6	1.5	1.8	2.0
LSD ^d	1.2		0.8		0.8	

^a Treated and nontreated from quadruple and duplicate samples, respectively.

^b Abbreviations: WAT, week after treatment; As, arsenic.

^c Treated concentrations are pooled over clipping management practice as it was not statistically significant.

^d LSD values for comparison within WAT.

Table 4. Effect of clipping management and time on soil arsenic concentration from 0- to 5-cm depth.^a

	2 WAT		4 WAT		8 WAT	
	CC	CR	CC	CR	CC	CR
	mg As kg ⁻¹					
MSMA-treated	5.0	5.3	5.8	6.3	6.4	7.2
Nontreated	2.5	2.7	2.5	2.7	3.1	3.2
LSD	2.0		1.9		2.0	

^a Abbreviations: WAT, week after treatment; CC, clippings collected; CR, clippings returned.

Table 5. Root arsenic concentration and content of treated and nontreated turfgrass over time.

	Treated	Nontreated	Treated	Nontreated	Treated	Nontreated
	— $\mu\text{g As g}^{-1}$ —		— Root mass (g) —		— $\mu\text{g As lysimeter}^{-1}$ —	
2 WAT ^a	27	1	8.4	9.6	234	10
4 WAT	33	1	7.7	7.6	252	8
8 WAT	31	2	8.6	10.3	267	21
LSD ^b	— 9 —		— 2 —		— 50 —	

^a WAT: week after treatment

^b LSD values for comparison within measurement.

Table 6. Total and percent recovery of total MSMA-applied arsenic to turfgrass lysimeters.^a

Sample	2 WAT		4 WAT		8 WAT	
	— mg As (SD) —	— % —	— mg As (SD) —	— % —	— mg As (SD) —	— % —
Clippings	0.017 (± 0.01)	1%	0.003 (± 0.001)	0%	0.008 (± 0.0)	0%
Remaining vegetation	0.488 (± 0.14)	29%	0.22 (± 0.08)	13%	0.10 (± 0.04)	6%
Soil	1.08 (± 0.54)	64%	1.46 (± 0.51)	86%	1.54 (± 0.59)	91%
Roots	0.23 (± 0.06)	13%	0.25 (± 0.04)	15%	0.27 (± 0.08)	16%
Porewater ^b	0.0001	0%	0.0008	0%	0.0006	0%
Total ^c	1.82	107%	1.93	114%	1.92	113%

^a Abbreviations: WAT, week after treatment; SD, standard deviation.

^b Porewater from 5 cm depth.

^c Total arsenic applied from MSMA was 1.7 mg per lysimeter.

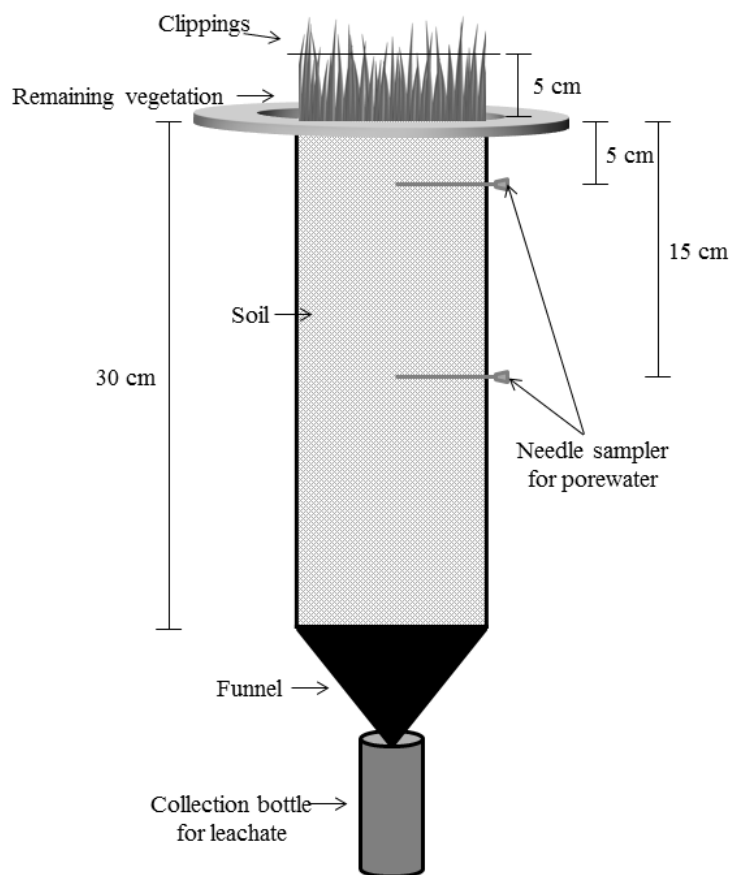


Figure 1. Schematic of a greenhouse lysimeter.

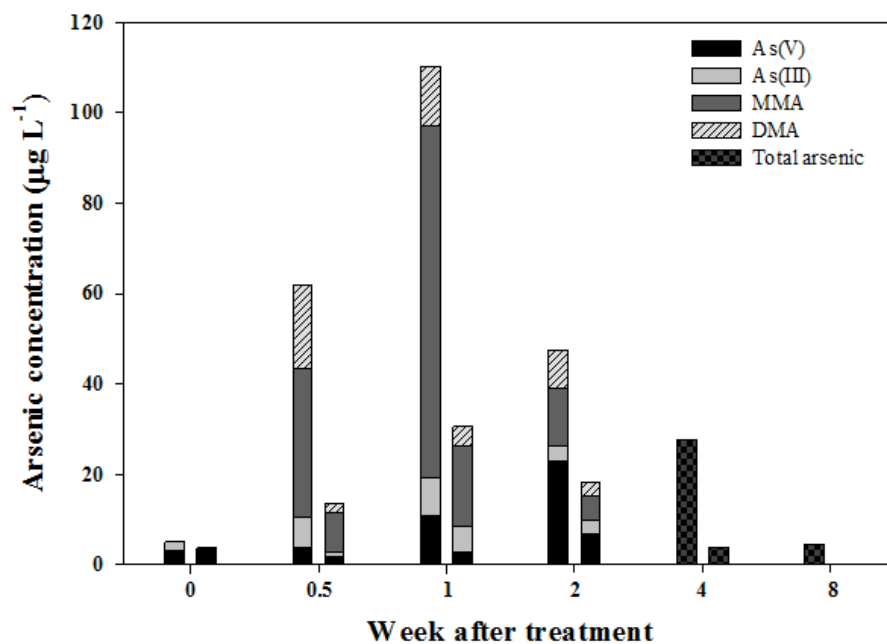


Figure 2. Arsenic species and total concentration in 5-cm-depth porewater over time following a MSMA application. The two bars for each time point represent data from two unique CR lysimeters. Porewater was unable to be collected from one lysimeter 8 WAT. Speciation data were not obtained for 4 and 8 WAT.

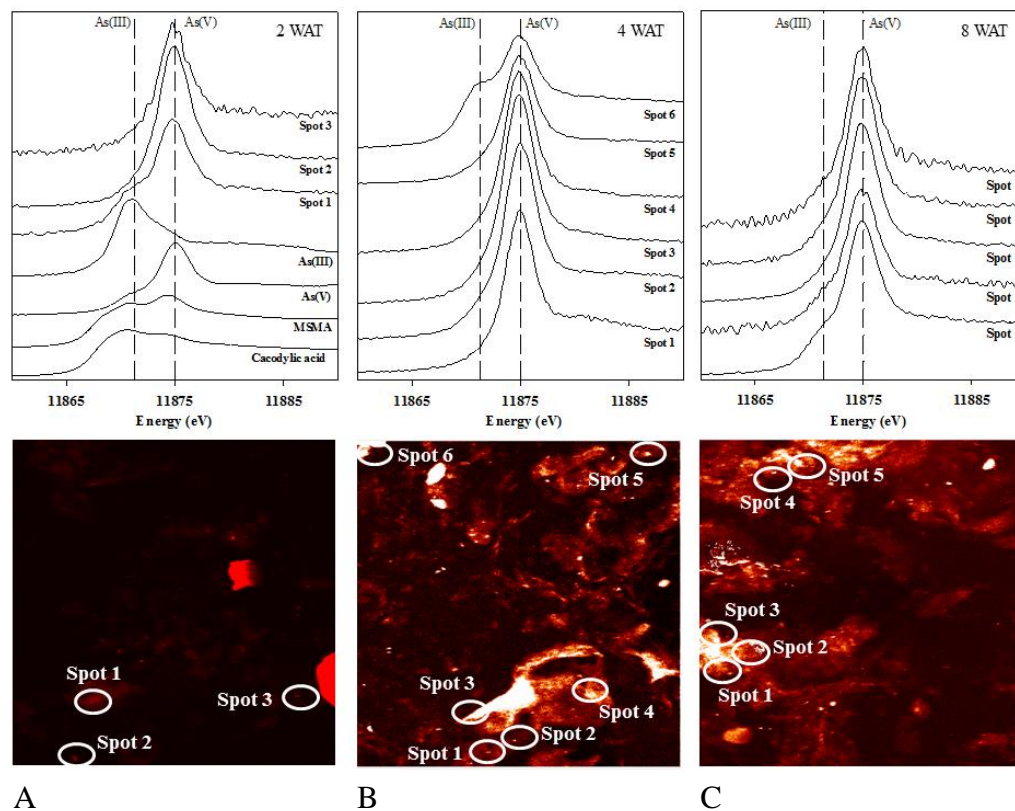


Figure 3. Micro-XANES spectra of MSMA-treated soil samples, with dashed lines to denote peak energies of As(V) and As(III) reference standards. (A) As standards (bottom 4 spectra) and 2-WAT soil samples (upper 3 spectra), (B) 4-WAT soil samples, and (C) 8-WAT soil samples. In the bottom panels, microscale (1 x 1 mm) X-ray fluorescence maps show areas of As accumulation (hot colors) within the soil samples (0-5 cm depth) corresponding to the spectra above.