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4 **Management Considerations to Minimize Environmental Impacts of Arsenic Following**
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6 **Monosodium Methylarsenate (MSMA) Applications to Turfgrass**
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35 Monosodium methylarsenate (MSMA) is an organic arsenical herbicide currently utilized
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37 in turfgrass and cotton systems. In recent years, concerns over adverse impacts of arsenic (As)
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39 from MSMA applications have emerged; however, little research has been conducted in
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41 controlled field experiments using typical management practices. To address this knowledge gap,
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43 a field lysimeter experiment was conducted during 2012-2013 to determine the fate of As
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45 following MSMA applications to a bareground and an established turfgrass system. Arsenic
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47 concentrations in soil, porewater, and aboveground vegetation, were measured through one yr
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49 after treatment. Aboveground vegetation As concentration was increased compared to nontreated
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51 through 120 d after initial treatment (DAIT). In both systems, increased soil As concentrations
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53 were observed at 0-4 cm at 30 and 120 DAIT and 0-8 cm at 60 and 365 DAIT, suggesting that
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As was bound in shallow soil depths. Porewater As concentrations in MSMA-treated lysimeters from a 30-cm depth (22.0 to 83.8 $\mu\text{g L}^{-1}$) were greater than those at 76-cm depth (0.4 to 5.1 $\mu\text{g L}^{-1}$). These results were combined with previous research to devise management considerations in systems where MSMA is utilized. MSMA should not be applied if rainfall is forecasted within 7 DAIT and/or in areas with shallow water tables. Further, disposing of MSMA-treated turfgrass aboveground vegetation in a confined area – a common management practice for turfgrass clippings – may be of concern due to As release to surface water or groundwater as the vegetation decomposes. Finally, long-term MSMA use may cause soil As accumulation and thus downward migration of As over time; therefore, MSMA should be used in rotation with other herbicides.

Keywords: arsenic; environmental fate; MSMA; turfgrass; soil; porewater.

1. Introduction

Monosodium methylarsenate (MSMA) is an organic arsenical herbicide utilized in turfgrass sod farms, golf courses, roadways and cotton systems, and prior to 2006, 1.4 million kg of MSMA was applied annually in the United States (US) (USEPA 2009). MSMA provides substantial agronomic benefits such as excellent weed control and limited weed resistance (Camper et al. 2004; USEPA 2009), but MSMA-derived As additions to agronomic systems may be concerning from an environmental health perspective, as applied As could potentially contaminate groundwater and surface water (USEPA 2009). Accordingly, in 2006, the US Environmental Protection Agency (USEPA) enacted a phase-out of all organic arsenical herbicides, including MSMA. However, MSMA use is permitted until a National Academy of Sciences' review on carcinogenic effects of inorganic As is concluded in 2015 (USEPA 2013).

Effective regulation and management of MSMA require accurate assessment of the factors controlling the short- and long-term fate of As within plants, soil, and water following MSMA applications. MSMA is readily absorbed and translocated throughout plants (Sachs and Michael 1971; Sckerl and Frans 1969; Wauchope et al. 1992), and in turfgrass aboveground vegetation, applied As may persist through one yr after treatment (Matteson et al. 2014a). When MSMA is applied to agronomic crop or turfgrass systems, increased soil As concentrations have been detected to depths up to 15 cm (Akkari et al. 1986; Feng et al. 2005; Hiltbold et al. 1974; Matteson et al. 2014a; Robinson 1975), although most studies have not measured As distributions in a turfgrass system over time. Less work has been conducted examining As in soil aqueous phases following MSMA application, but Feng et al. (2005) detected up to 18% of As from MSMA in soil porewater (41-cm depth) over 14 wk within packed turfgrass-soil columns,

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4 whereas Matteson et al. (2014a) detected no increase in porewater As concentration (76-cm
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6 depth) in MSMA-treated field turfgrass and bareground lysimeters through one yr following
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8 applications. Differences between these studies may be attributed to MSMA application rates,
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10 soil texture, and sampling depths. Resolving these discrepancies and better understanding the
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12 factors controlling As mobility following MSMA application is critical for predicting potential
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14 environmental threats in different agronomic systems.
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19 The overarching goal of this research was to outline potential management practices for
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21 minimizing adverse environmental effects from real-case MSMA applications in turfgrass
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23 systems. Turfgrass systems possess unique contamination concerns, such as vegetation disposal
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25 following mowing. Additionally, little research has been conducted in this system to date, and
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27 previous studies often were not completed using realistic application rates and management
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29 scenarios. The specific objectives of this research were to 1) determine As distributions in
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31 turfgrass aboveground vegetation, soil, and porewater through one yr after MSMA treatment and
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33 2) identify potential environmental contamination risks following MSMA applications in
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35 bareground and turfgrass systems. To accomplish these objectives and determine MSMA
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37 management considerations, we built upon our prior work (Matteson et al., 2014a) and integrated
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39 results from new field lysimetry experiments with findings from previous studies. We conclude
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41 that although the majority of applied As remains in shallow soil, aboveground turfgrass
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43 vegetation represents a potential environmental contamination risk depending on how clippings
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45 are discarded. Further, environmental parameters such as rainfall may affect As distribution
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47 following MSMA applications, so care should be taken when selecting MSMA application times.
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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 with 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 eight wk before trial initiation to ensure that microbial populations were present 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 and was mown twice per wk (1.9 cm) with clippings returned. Irrigation was applied to bring the total applied water (rainfall plus irrigation) 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, porewater samplers (Prenart Equipment ApS, Frederiksberg, Denmark) were installed into unique turfgrass and bareground plots at 30 or 76 cm as described by Matteson et al. (2014b). Steel rods were inserted into the center of lysimeters using a mallet. A silica flour (900 g) (Prenart Equipment ApS, Frederiksberg, Denmark) and irrigation 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 to the specified depth, ensuring the tube extended above ground, and holes were backfilled with a slurry of native soil. Following backfilling, sampler tubing was connected to an airtight collection bottle. Collection bottles were wrapped with opaque black plastic to eliminate light exposure. Porewater samplers were placed at 30- and 76-cm depths in unique MSMA-treated bareground and turfgrass plots. Porewater samplers were also placed at 76-cm depth from nontreated plots totaling six unique porewater samplers.

2.2. Treatment

Following lysimeter and porewater sampler installation, two wk were allowed for acclimation before MSMA (Bueno 6; Drexel Chemical Co., Memphis, TN) was applied (2.25 kg ai ha⁻¹) to unique bareground and turfgrass plots on August 13 and August 20, 2012. This application rate represents a maximum single season application rate for turfgrass systems in the US. Applications were made using a CO₂-pressurized three-nozzle (XR 8002; TeeJet, Spraying

Systems Co. Wheaton, IL) sprayer calibrated to deliver 304 L ha⁻¹. 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. Nontreated lysimeters were also included in each system to serve as controls.

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 d 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 pH was measured in one subsample while the other subsample was acidified with trace metal grade nitric acid (1% v v⁻¹) to preserve the sample for subsequent analysis. 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 (pretreatment), 30, 60, 120, and 365 DAIT with nontreated lysimeters removed at each sampling date from each system. Lysimeters were 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 washed using ammonia:water (1:1) followed by water to avoid cross-contamination of lysimeters. Samples were stored in polyethylene bags at -18°C until analysis.

2.5. Soil Sample Analysis

Soil and vegetation sample analysis methods were previously described by Matteson et al. 2014. In short, three subsamples were dried and weights were recorded to determine moisture content. Solid-phase As concentrations were determined following digestion by a modified version of USEPA protocol SW846-Method 3050B (USEPA 1996), with resulting digests were analyzed on a Varian 820 ICP-MS (Bruker Daltonics, Billerica, MA).

2.6. X-ray Absorption Spectroscopy

A soil sample (turfgrass 0-2 cm, 30 DAIT) was analyzed via micro-synchrotron based X-ray fluorescence (μ -SXRF) and micro-X-ray absorption near edge structure (μ -XANES) spectroscopy at GeoSoilEnviroCARS beamline 13-ID-E of the Advanced Photon Source (Argonne National Laboratory, Argonne, IL). Micro-SXRF mapping was conducted with a micro-focused beam (≈ 5 -10 μ m) at 12,900 eV. Map size was 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 hotspots were further analyzed via μ -XANES for As speciation.

Arsenic (As) K α -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 11867 eV. Energy steps varied across the spectrum with steps of 5 eV (11767 to 11852 eV), 0.25 eV (11852 to 11895), 2 eV (11895 to 11970 eV). Spectra were normalized and background removed using SixPack (Webb 2005). X-ray absorption coefficients ($\mu(E)$) were then compared to spectra of known As standards (SigmaPlot 12.0, Systat Software Inc., San Jose, CA), including cacodylic acid, MSMA, schneiderhonite [for As(III)], and scorodite [for As(V)].

2.7. Data Analysis

Data were subjected to ANOVA using general linear models (SAS[®] for Windows, v 9.3, Statistical Analysis Systems Institute, Cary, NC). Significant main effects and interactions were presented with precedent given to interactions of increasing magnitude (Steele et al. 1997) and means were separated according to Fisher's Protected LSD ($P = 0.05$).

2.8. 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 of As added to each lysimeter from MSMA applications. Bulk densities used for calculations were previously reported from the field site (Cummings 2004). Total aboveground vegetation masses collected 30, 60, 120, and 365 DAIT were 26, 16, 9, and 10 g, respectively.

3. Results and Discussion

3.1. Arsenic in Soil Porewater following MSMA Application

The proposed phase-out of MSMA was due in part to As groundwater and drinking water contamination concerns, yet limited research is available that systematically evaluates As porewater concentration and downward migration in turfgrass systems. At our field site, As concentrations in 30-cm porewater at 0 DAIT (pre-treatment) were 27.1 and 30.1 $\mu\text{g As L}^{-1}$ in

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4 bareground and turfgrass systems, respectively (Figure 1A), which are above the USEPA As
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6 maximum contamination limit (MCL) for drinking water ($10 \mu\text{g L}^{-1}$). Following MSMA
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8 treatment, 30-cm-depth-porewater As concentrations increased immediately and then slowly
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10 decreased toward initial concentrations (above the USEPA MCL) through one yr. At 7 DAIT,
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12 porewater concentrations at 30 cm reached maxima of 83.8 and 55.7 $\mu\text{g L}^{-1}$ in the treated-
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14 bareground and -turfgrass systems, respectively, which were > 5.5 -fold above the USEPA As
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16 MCL for drinking water. Overall, the porewater As concentrations at 76-cm depth (0.4 to 5.1 μg
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18 L^{-1}) were lower than those measured at 30-cm depth (22.0 to 83.8 $\mu\text{g L}^{-1}$) (Figure 1B). The
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20 highest As concentration at 76-cm depth was detected 4 DAIT within the bareground system. At
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22 this date, As concentrations were 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,
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24 treated-turfgrass, and nontreated systems, respectively. Beyond this evaluation date, porewater
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26 As never exceeded 1.9 and 1.5 $\mu\text{g L}^{-1}$ in the bareground and turfgrass system, respectively, less
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28 than 20% of the USEPA As MCL.
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36 Downward leaching of applied As may have been influenced by the 8.4 cm of rainfall
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38 and irrigation 6 d prior to treatment (NC CRONOS 2014) and 12 cm of rainfall that occurred
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40 between MSMA application and the 7-d sampling (Figure 1C). Saturated soil and/or rainfall have
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42 been shown to increase nutrient or pesticide leaching soon after application (Kramers et al. 2012;
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44 Gish et al. 1991). The increased porewater As from 30 cm following MSMA application
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46 suggests that As from MSMA may be of concern in areas with shallow water tables or when
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48 MSMA is applied prior to rainfall events. However, even with multiple rainfall events > 2 cm
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50 within 7 DAIT, porewater As from a 76-cm depth never exceeded the USEPA As MCL (Figure
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52 1B). Similarly, Matteson et al. (2014a) reported MSMA did not increase porewater As at 76-cm
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depth from treated-bareground or -turfgrass systems. Collectively, these data suggest that with one season of typical MSMA treatment to turfgrass and bareground soils, As may reach shallow depths in soil porewater, but binding to soil solid phases may minimize extensive downward leaching through the soil profile. Other factors that may affect As leaching, such as As species transformation (Lafferty and Loeppert 2005) following MSMA application require elucidation for in-field turfgrass systems.

3.2. Arsenic in Turfgrass Aboveground Vegetation following MSMA Application

Arsenic concentration in turfgrass aboveground vegetation was greatest 30 DAIT with MSMA-treated aboveground vegetation having elevated As concentration compared to nontreated aboveground vegetation through 120 DAIT (Table 1). At 30 DAIT, As concentration in the turfgrass aboveground vegetation (17.5 mg kg^{-1}) was > 6-fold greater than in nontreated vegetation (2.8 mg kg^{-1}). At 60 and 120 DAIT, turfgrass aboveground vegetation As concentration was greater (by 7.3 and 5.3 mg kg^{-1} , respectively) than nontreated turfgrass aboveground vegetation. The percent of total applied As recovered in turfgrass aboveground vegetation at 30, 60, and 120 DAIT was 10, 3, and 1%, respectively.

Arsenic accumulation within turfgrass aboveground vegetation has been observed previously, and it represents an issue of potential environmental concern given the length of time elevated concentrations may persist. In a translocation study by Duble et al. (1969), 20% of disodium methanearsonate applied as a spot foliar treatment was detected in bermudagrass aboveground vegetation 30 d after treatment. At 30 DAIT within this research, only 10% of total applied As 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).

Figure 1. Porewater As concentrations and rainfall through 365 d after initial MSMA treatment (DAIT) to turfgrass and bareground lysimeters. Porewater samples from 0 DAIT were taken prior to MSMA treatment. A) Porewater As from 30-cm depth. B) Porewater As from 76-cm depth. C) Rainfall events.

This is further supported by a similar field lysimeter study on the fate of As from MSMA by Matteson et al. (2014a) where 10% of the total applied As was detected in turfgrass aboveground vegetation 36 DAIT. The turfgrass aboveground vegetation As pool may represent a source of off-target As contamination, depending on how and when clippings are dispersed following mowing events, as discussed below.

3.3. Arsenic in Soil following MSMA Application

Although As was detected in porewater and aboveground vegetation, the majority of MSMA-applied As ultimately resided in soil solid phases within our experiments. Arsenic concentrations in MSMA-treated soils were greater than those in nontreated soils at all sample dates (Table 1). Soil pH ranged from 5.7 to 6.1 (data not shown) and in agreement with previous studies (Matteson et al. 2014a), they did not correlate with As. There were no statistical differences in soil As concentrations between bareground and turfgrass systems; however, the results are presented separately because of system differences including turfgrass aboveground vegetation, soil bulk densities, and total As recoveries. In bareground and turfgrass systems, at 30 and 120 DAIT, elevated soil As concentrations were detected to a 4-cm depth in treated lysimeters, while soil As concentrations were elevated to an 8-cm depth at 60 and 365 DAIT (Table 1). Although increased As concentrations were detected in porewater from 30-cm depth (Figure 1A), soil As concentrations were only elevated to 8-cm depth, suggesting that As may in fact reach deeper depths, but solid-phase increases were masked by analytical detection limits.

Table 1. Arsenic concentrations in MSMA-treated and nontreated turfgrass and bareground soil and aboveground vegetation at various d after initial treatment.^{a-c}

System	Depth (cm)	As concentration (mg kg ⁻¹)							
		30 DAIT		60 DAIT		120 DAIT		365 DAIT	
		Treated	NT	Treated	NT	Treated	NT	Treated	NT
Turfgrass	Aboveground vegetation	17.5	2.8	9.4	2.1	6.5	1.2	2.9	1.6
	LSD ^d	10.5		4.3		1.4		NS	
	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	
Bareground	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	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, d 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.)

Recoveries in the turfgrass system were 70, 84, 50, and 73% at 30, 60, 120, and 365 DAIT, respectively. Figure 2 illustrates increased As in each bareground soil depth increment 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 120 to 365 DAIT, an increase was detected at 4-8 cm. In the turfgrass system, aboveground vegetation and 0–2 cm soil As content decreased over time (Figure 3). From 30 to 60 DAIT, an increase was detected at 2-4 and 4-8 cm, which may be attributed to root As exudation (Duble et al. 1969) or downward As migration. Arsenic content from 2-4 cm decreased from 60 to 120 DAIT but increased at 365 days after treatment. It is possible that As reached depths deeper than 8 cm but increases remained below detection, perhaps contributing to < 100% As recoveries.

Figure 2. Increased arsenic (As) mass in soil within the bareground system at various d after initial treatment (DAIT) of MSMA. A total of 3.8 mg As lysimeter⁻¹ was initially applied. Background (nontreated) As was subtracted from treated As to determine total As increases. Error bars represent standard deviation in As content between replications.

Figure 3. Increased arsenic (As) mass in soils within the turfgrass system at various d after initial treatment (DAIT) of MSMA. A total of 3.8 mg As lysimeter⁻¹ was initially applied. Background (nontreated) As was subtracted from treated As to determine total As increases. Error bars represent standard deviation in As content between replications.

In agreement with previous research, our soil data suggest As moved downward over time (Figures 2 and 3). 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 of Robinson (1975) were > 30 fold of the recommended and current presented research, the data suggest that As migrates downward and accumulates in soil over time. More recently, Matteson et al. (2014a) detected increased As concentrations 0-8 cm 119 DAIT from 4.5 kg MSMA ha⁻¹; however, at 364 DAIT, an increase was detected to 15 cm, also suggesting downward movement over time.

Arsenic mobility is dependent on its speciation (Huang et al. 2011; Shimizu et al. 2011). A soil sample from 0-2 cm depth, 30 DAIT revealed that As was predominantly present in the oxidized form (Figure 4), either as an organic or inorganic As species. Previous X-ray absorption spectroscopy analyses by Shimizu et al. (2011) showed As(V) as the predominant metabolite in an aerobic soil treated with monomethylarsonic acid (MMA). Within the current study, increased soil As concentration to an 8-cm depth may be due in part to the species present, as oxidized As species generally bind more strongly to soil than reduced species (Lafferty and Loeppert 2005; Shimizu et al. 2011). Further research is needed to elucidate As speciation within turfgrass systems over time following MSMA applications, as it has a profound effect on As mobility and toxicity.

Figure 4. A) A microscale (350x250 μm) X-ray fluorescence map of a soil sample from 0-2 cm depth, 30 DAIT shows an area of As accumulation (hot colors) within the soil of turfgrass system. Star indicates location of micro-X-ray absorption near edge structure (μ -XANES) spectroscopy analysis. B) A μ -XANES spectra of accumulated As from X-ray fluorescence map indicates that As was present in its oxidized form. Vertical lines indicate peak positions of inorganic As(III) and As(V) reference standards.

3.4. Management Considerations for MSMA Application

Arsenic contamination concerns have previously been derived from limited field research and laboratory studies following MSMA application. Moreover, previous studies have often used unrealistic MSMA loading rates when evaluating As fate. Results from the current research, which use labeled MSMA application rates and field conditions, suggest that As contamination or off-target injury may occur from various routes following application, but each may occur at different times and require different management considerations. Figure 5 illustrates and defines immediate (< 1 wk after MSMA application), intermediate (<30 d after application), and long-term (> 1 season) environmental concerns following MSMA applications to turfgrass.

Figure 5. Arsenic contamination potential over immediate (< 1 week), intermediate (< 30 d), and long-term (> 1 season) timescales following MSMA application to turfgrass.

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4 The most immediate concern with MSMA is movement of dissolved As away from the
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6 application site. Concerns of As contamination were highlighted by porewater analysis as As
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8 porewater concentration from a 30-cm depth was higher than the USEPA MCL at every
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10 evaluation date (Figure 1A). Although As concentrations above the USEPA MCL were detected
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12 in pre-treatment porewater samples, significant increases in As concentration suggest As was
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14 able to reach this depth. Arsenic movement is enhanced with saturated conditions, and these data
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16 suggest that MSMA should not be applied in areas with shallow water tables or immediately
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18 preceding expected rain events. Further, coarse-textured soils with minimal metal oxides (Fe, Al,
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20 or Mn) may have low As sorption capacities, and soil properties should be evaluated when
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22 considering As leaching potential (Jones 2007).
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28 Over intermediate timescales, accumulated As within turfgrass vegetation represents a
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30 potentially mobile source of As, depending on how clippings produced from a mowing event are
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32 managed. Arsenic from MSMA was the highest in the aboveground vegetation 30 DAIT, and As
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34 persisted in turfgrass aboveground vegetation at elevated concentrations through 120 DAIT
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36 (Table 1). Using the turfgrass dry mass collected ($26 \text{ g lysimeter}^{-1}$) and the total As foliar
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38 contents (14.7 mg kg^{-1} above background tissue concentrations, Table 1) at 30 DAIT, there was
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40 approximately 249 g As ha^{-1} in turfgrass aboveground vegetation. Disposing of the cut
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42 vegetation may lead to off-target contamination as significant amounts of As may be present and
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44 decomposition may lead to element release to the environment. For instance, Kopp and Guillard
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46 (2004) found > 88% of tissue N release within 16 wk of turfgrass clipping decomposition.
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48 Sanders and Osman (1985) detected 12% of sorbed As was weakly bound to the detrital *Spartina*
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50 leaves, with 81% deemed bioavailable. Therefore, disposing of MSMA-treated turfgrass
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52 aboveground vegetation in a confined area – a common management practice for turfgrass
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4 clippings – may be of concern due to As release to surface water or groundwater as the
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6 vegetation decomposes.
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9 Within the turfgrass system, the majority of MSMA-applied As was recovered in the soil
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11 (Table 1). Following repeated MSMA applications over time, soil-binding sites may become
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13 occupied (Girouard and Zagury 2008; Ljung et al. 2006), causing soil As to migrate downward.
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15 Long-term MSMA use, at labeled and above-labeled rates, has been previously examined, and
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17 elevated soil As concentrations < 15 cm depth have been observed after one (our data; Matteson
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19 et al., 2014a), five (Hiltbold et. al. 1974; Robinson 1975), and seven (Woolson and Isensee 1981)
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21 application seasons. Soil texture and rainfall may have influenced As mobility in these studies
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23 (Girouard and Zagury 2008; Ljung et al. 2006), and further research is needed to quantify the
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25 parameters effecting As accumulation and downward movement following repeated annual
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27 MSMA applications. Routine As additions may increase soil As to deeper depths and become
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29 hazardous to groundwater sources over time. Management practices could address this risk by
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31 using MSMA in rotation with other herbicides in order to reduce As additions into the
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33 environment.
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40 41 *3.5. Conclusions* 42

43 In recent years, concerns over the potentially adverse environmental impacts of As from
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45 MSMA applications have emerged. Our results indicated that various contamination routes may
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47 be present following MSMA application to managed turfgrass systems. Increased porewater As
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49 concentrations were above the USEPA MCL at a 30-cm depth; however, porewater from a 76-
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51 cm depth revealed As concentrations below the USEPA MCL at all sample timings.
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53 Additionally, rainfall within 7 DAIT may be associated with As pulses at the 30- and 76-cm
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55 depths. In turfgrass aboveground vegetation, increased As concentrations were detected through
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4 120 DAIT compared to nontreated turfgrass aboveground vegetation. Ultimately, the majority of
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6 applied As was recovered in the soil solid phases, suggesting that As from MSMA is partitioned
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8 here over time.
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11 In conclusion, caution should be taken when using MSMA for weed control. Turfgrass
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13 management considerations are needed as aboveground vegetation may be a significant As pool
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15 following application. Following MSMA applications, increased soil As concentrations were
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17 only detected at or near the soil surface; however, applications should be avoided in areas (or
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19 times) with saturated soil conditions (e.g. shallow water tables, prior to large rainfall events) or
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21 low soil metal oxide contents, as these conditions may enhance As downward leaching. Finally,
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23 MSMA should be used in rotation to minimize soil As accumulation and reduce As additions
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25 into the environment. Further research is needed to elucidate the effect of turfgrass management
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27 (e.g. collecting or returning clippings) on As distribution and species transformation over time
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29 following MSMA applications.
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