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Dissipation of Monosodium Methane Arsonate (MSMA) on Peanuts

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Monosodium methane arsonate (MSMA), the salt of methylarsonic acid (MAA), is a herbicide commonly used to control weeds along roadsides, in cotton, in turf, and on noncrop sites. In recent years questions have arisen regarding the source and nature of arsenic residues in raw agricultural commodities relative to misuse, inadvertent exposure, or rotational crop residues. Field experiments were conducted to determine the fate of MSMA that is applied to peanut foliage. Persistence, dissipation, recovery, and detection of MAA from leaf rinsate were characterized as well as resulting total arsenic and MAA concentrations in peanut kernels. MSMA was applied to peanut foliage at 105, 210, 315, and 420 g of active ingredient (ai)/ha. Peanut leaves were sampled before and after irrigation events over the next 7 days. Peanuts were harvested at maturity and analyzed for MAA and total arsenic. A confined rotational crop experiment was conducted to determine the potential for MAA residues in soil to be taken up by peanuts in fields rotated from cotton that was treated with MSMA. MAA was not detected in any peanut samples from the rotational crop experiment, even when peanuts were planted only 30 days after MSMA application to the soil at 2.24 kg of ai/ha. Field experiments showed that MSMA recovery from leaves with an aqueous rinse declined quickly but was not greatly affected by irrigation. However, quantifiable amounts of MAA were present 1 week after application and after two irrigation events, and MAA and total arsenic were measured in mature peanut kernels from all plots that received MSMA. MAA was not detected in untreated checks. Total arsenic was below the limit of quantification in untreated controls.

KEYWORDS: Arsenic; MSMA; peanuts; analysis

INTRODUCTION

Monosodium methane arsonate (MSMA) is widely used for weed control in cotton, turf, and citrus, along roadside rights-of-way, and on noncrop sites. In recent years questions have arisen regarding the nature and source of arsenic residues in some food crops, especially related to possible illegal misuse of these pesticides inadvertent exposure, and possibly due to rotational crop exposure resulting from use in previous crops, such as cotton. Allegations of illegal misuse of MSMA for weed control in peanut, a crop for which MSMA is not labeled for use, have resulted in specific questions about the nature of arsenic in peanut.

Several arsenic species, some naturally occurring, may be detected in peanut or other food crops. These detections can arise from various routes of exposure. First, arsenic is a naturally occurring element, found at varying concentrations in most agricultural soils. Soil arsenic levels depend on soil minerology, historical contributions of arsenic from industrial and agricultural

chemicals, and current practices. The amount that accumulates and that can be detected in plants depends on soil factors, the species of arsenic present, and plant factors (*1*, *2*). Total arsenic concentration in agricultural plants is often determined by acid digestion and reduction and then followed by determination according to a variety of analytical methods, most often atomic absorption spectrophotometry. These quantitative methods reveal the total arsenic concentration, but they do not reveal the nature, or species, of arsenic that was present in the sample. Therefore, detection of arsenic in food crops via these methods is of limited value in determining the source of arsenic residues, nor are they of great value with respect to regulation.

Among the possible routes of exposure of peanut to arsenic is direct application. Several researchers have studied the fate of MSMA that is applied directly to peanut foliage. Total arsenic increased in peanut kernels as MSMA application rates increased (*3*, *4*). The amount of arsenic recovered from untreated peanuts varied greatly within and between these studies and was significant, illustrating the need for site-specific control samples. Despite background levels of total arsenic, application of MSMA resulted in increased amounts of total arsenic in each of these studies to the extent that arsenic concentrations in treated peanuts were distinguishable from untreated controls.

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It is possible that peanuts could acquire arsenical residues through inadvertent exposure routes. Peanuts could be exposed to arsenical pesticide drift, either MSMA or disodium methane arsonate (DSMA), from applications to roadsides, noncrop sites, or cotton fields juxtaposed to peanut fields. This phenomenon has not been studied in peanut. However, because MSMA is relatively nonvolatile, physical drift of the spray would be required. MSMA physically drifted onto soybeans during pod formation resulted in elevation of total arsenic in soybean seed (*5*). Poor sanitation practices can leave MSMA residues in spray equipment, which could lead to low-level contributions to peanuts sprayed with the same equipment.

Another potential route of exposure is where peanuts are grown in rotation with cotton that has been treated with MSMA or DSMA. Previous work has shown that even when exaggerated rates of MSMA or DSMA are applied to cotton, soil arsenic levels do not increase (*1*). However, MSMA has a reported half-life of ∼180 days, but the half-life has been measured as high as 2000 days (*6*). Also, it is known that both inorganic and organic arsenic species can be taken up by certain plants (*1*). Therefore, it may be possible to detect arsenic species in rotational crops. The potential for methylarsonic acid (MAA) to be absorbed by peanut has not been investigated.

There is a need to better understand the nature, quantity, and source of arsenic in peanut kernels. For food safety reasons it is imperative to quantitatively and qualitatively characterize arsenic in peanuts. Furthermore, there is a regulatory need to understand these issues. Determining total arsenic concentrations in peanut kernels after harvest is time-consuming and expensive and does not provide good support for regulation. It is of limited value with respect to enforcement of pesticide labels, nor does it provide a good deterrence to misuse. Peanuts quickly lose their identity once harvested. Peanuts from several fields that were grown quite differently may be mixed during processing, so that monitoring programs conducted on mingled lots of farmer stock peanuts are of little value in determining the source of arsenic residues.

A preferred monitoring method would allow for the determination of MAA, the free acid of MSMA, residues on crop leaves soon after exposure to MSMA is suspected. Due to the high water solubility of MSMA of 1.4×10^6 mg/L (*6*), it would also be necessary to know if MSMA or MAA residues on peanut leaves would be rainfast or if they would dissipate rapidly with rainfall or irrigation.

The objectives of these investigations were (1) to measure the persistence and recovery of MSMA residues (as MAA) on peanut leaves under irrigated and nonirrigated conditions, (2) to determine the relationship between MSMA application rate and resulting foliage concentrations on mature peanut kernel concentration of total arsenic and MAA, and (3) to determine the potential for peanut to absorb MAA from soil that was previously treated with MSMA.

MATERIALS AND METHODS

Confined Rotational Crop. A rotational crop experiment, similar to the confined rotational crop study required by the U.S. EPA for pesticide registration (*7*), was conducted to assess the potential for MAA to be taken up by peanuts from soil that had been previously treated with MSMA. The glasshouse experiments were conducted using a Spanish market-type peanut cv. Spanco. This variety was chosen as it has a faster maturity than cv. Sunrunner, the dominant variety grown in the southeastern United States, and it was felt that uptake would be greater as most growth of the peanut, and presumably uptake of MSMA, would be greatest at times closer to the time of application. The two soils used in the experiment were typical of soils of the peanut-growing

Table 1. Properties of Soils Used in Confined Crop Rotation Experiments

| soil	Griffin	Plains
soil type	Pacolet sandy loam	Faceville sandy clay loam
% sand	94	66
% silt	2	8
% clay	4	26
pH	5	6.6
% organic matter	1.3	2.9

region of the southeastern United States (**Table 1**). To our knowledge this soil had no prior history of pesticide use or crop use. The experiment was a $2 \times 2 \times 5$ factorial arrangement of treatments replicated three times within a completely randomized design. Factors were (1) soil type (two soil types), (2) MSMA treatment [treated (2.2 kg of active ingredient (ai)/ha) and untreated], and (3) plant-back interval (five levels: 30, 60, 90, 120, and 240 days). Each experimental unit consisted of a 38 L pot filled with screened soil of the appropriate type.

MSMA formulated as Bueno 6 was applied to the surface of treated pots with a CO_2-pressurized sprayer calibrated to deliver 187 L of water/ha. The MSMA rate was 2.2 kg of ai/ha, which is consistent with typical maximum single application rates for cotton in the southeastern United States. All pots (treated and untreated controls) were aged in a glasshouse under normal sunlight conditions prior to planting. During the aging period, soils were irrigated approximately once per week and just enough to maintain soil moisture. Average day/night temperatures were 30/20 °C. At the designated plant-back interval peanut seeds were hand planted ∼3 cm deep into the appropriate pots and allowed to grow to maturity. Peanuts were watered daily and fertilized periodically with soluble plant nutrients to obtain optimum growth. Mature kernels were hand-harvested, air-dried in the laboratory, shelled by hand, and then stored frozen in sealed plastic bags until analysis.

Field Residue Dissipation Experiments. Two field experiments, one irrigated and one not irrigated, were conducted simultaneously on the same site in Griffin, GA. Each experiment was a randomized complete block design with four replications. Each plot consisted of four 7-m-long rows of peanuts. Individual plots were separated by a 3.5-m-wide buffer. Treatments within each experiment included MSMA (Bueno 6) applied at 105, 210, 315, and 420 g of ai/ha. Treatments were applied with a CO_2-pressurized sprayer calibrated to deliver 187 L of water/ha. Untreated plots were sprayed with water first, and MSMA-treated plots were sprayed in ascending order of rate thereafter.

Leaf samples were collected immediately after application. To avoid cross-contamination, samples were collected in untreated plots first and transported to the laboratory on ice in an insulated chest. Personnel wore disposable plastic gloves, leg sleeves, and boots while collecting samples. Protective clothing was changed between treatments, and technicians were not allowed to pass from one plot to another during sample collection. After samples were collected from untreated plots, samples were collected from treated plots, in ascending rate order from lowest to highest rate. Immediately after collection, leaf samples were transported to the laboratory on ice and then frozen until analysis. After the initial sample collection was completed and within 6 h of herbicide application, irrigated plots received ∼3.8 cm of overhead sprinkler irrigation. All plots were resampled 24 h after irrigation using the procedure described above. Seven days after treatment, a third set of leaf samples was collected, another 3.8 cm of irrigation was applied, and a fourth set of samples was collected the following day. No rainfall occurred during this period. Peanuts were allowed to grow to maturity. They were hand-harvested 50 days after treatment with similar care taken to avoid cross-contamination as previously described.

Analysis of MAA on Peanut Leaves. Peanut leaves (10 g) were extracted with 50 mL of distilled−deionized (DI) water on a rotary shaker for 80 min. The water was decanted through a glass fiber filter and acidified to pH <2 with concentrated HCl. Residues of MAA in the extract were derivatized according to the method of Beckermann (*8*). Briefly, 0.5 mL of methylthioglycolate (MTG) (Aldrich Chemical

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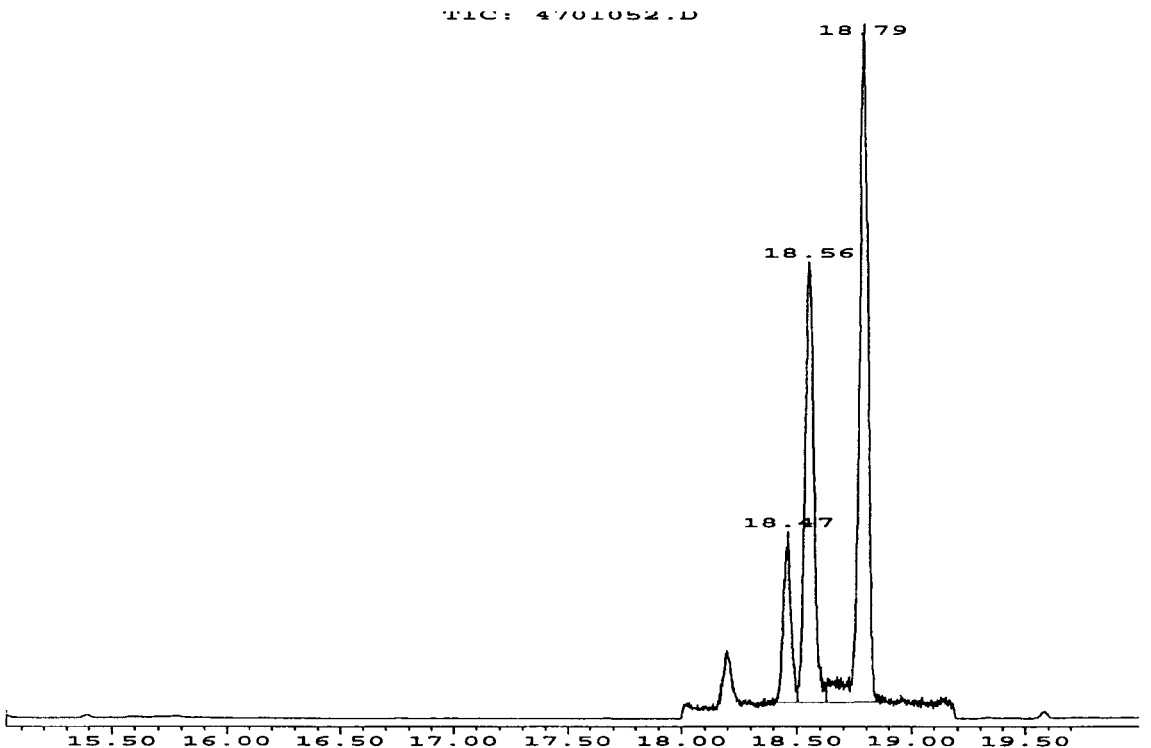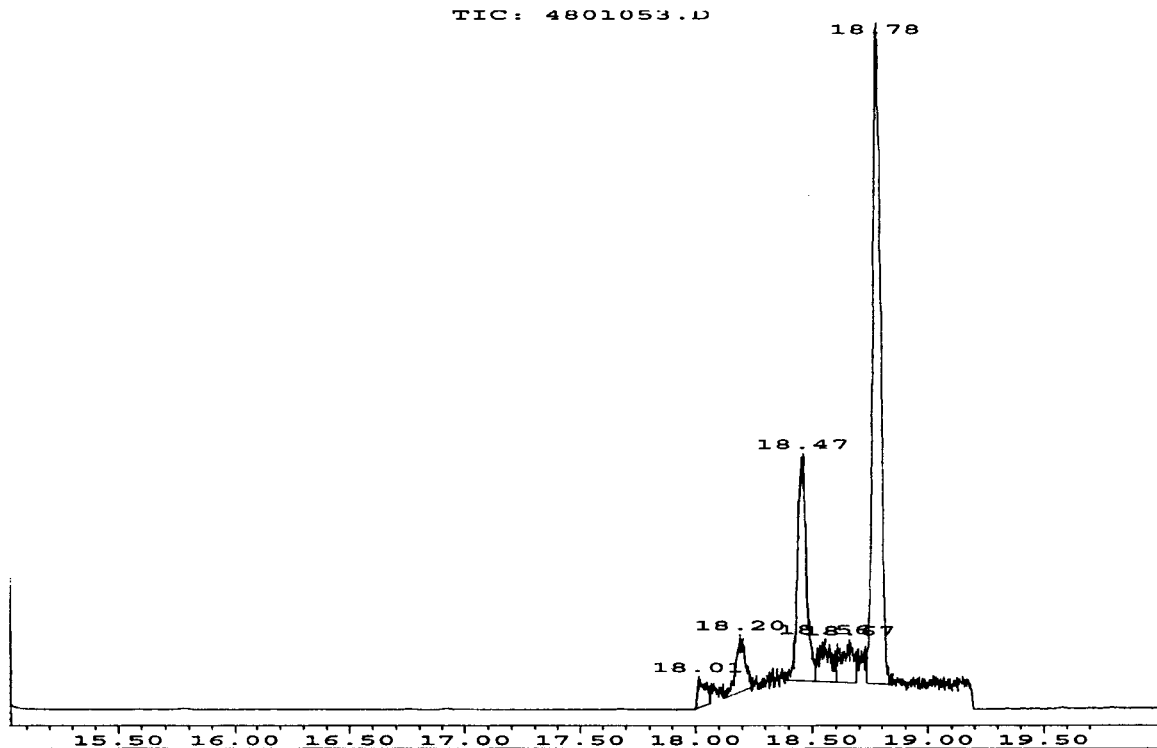
Figure 1. Example chromatograms of the methylthioglycolate derivative of MAA (t_R = 18.56 min) in extracts of peanut kernels collected from untreated control (top) and treated (bottom) plots.

Co., Milwaukee, WI) was added to the flask and allowed to react for 20 min. The derivative was extracted into 5 mL of hexane and analyzed by GC-MS.

GC-MS analysis was conducted using a Hewlett-Packard 5890 gas chromatograph with an HP 5971 mass selective detector using a 30 m DB-5 capillary column with 1.2-μm film thickness. After an initial hold time of 1 min at 60 °C, the column was raised to 220 °C at 10 °C/min and then to 300 °C at 50 °C/min and held at this temperature for 4

min. Ions m/z 253 and 285 were used for quantitation of the MAA thioglycolate derivative and followed in the selective ion mode.

Analysis of MAA in Peanut Kernels. The method for analyzing MAA in peanuts was provided by the Georgia Department of Agriculture and was based upon a method originally developed by PTRL East, Inc. (Richmond, KY) for the analysis of MAA and cacodylic acid in peanut commodities by GC-MS. Prior to extraction, peanuts were ground to a paste using a Waring laboratory blender

Table 2. Average Concentration of MAA on Peanut Leaves and MAA and Total As in Peanut Kernels

rate (g of ai/ha)	irrigation	peanut leaves, mg/kg (SD)				peanut kernels, mg/kg (SD)	
		Sept 16, 1999	Sept 17, 1999	Sept 23, 1999	Sept 24, 1999	total As	MAA
0	yes	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
0	no	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
105	yes	2.14 (0.45)	2.01 (0.91)	0.47 (0.40)	0.13 (0.05)	0.27 (0.31)	0.10 (0.04)
105	no	2.41 (0.71)	2.13 (1.34)	0.46 (0.26)	0.13 (0.08)	0.50 (0.70)	0.38 (0.30)
210	yes	3.88 (1.12)	1.53 (1.12)	0.42 (0.33)	0.44 (0.12)	0.74 (0.34)	0.50 (0.31)
210	no	3.79 (0.22)	1.60 (0.46)	0.46 (0.26)	0.51 (0.31)	1.33 (0.25)	0.20 (0.16)
315	yes	7.93 (4.13)	3.41 (2.52)	0.75 (0.38)	0.54 (0.43)	1.98 (1.01)	0.98 (0.88)
315	no	9.83 (1.81)	3.13 (2.06)	0.69 (0.35)	0.56 (0.44)	1.22 (0.95)	1.14 (1.13)
420	yes	12.59 (5.75)	4.47 (3.58)	0.71 (0.33)	2.52 (1.10)	1.44 (0.69)	1.77 (0.82)
420	no	16.86 (7.07)	5.26 (4.42)	0.86 (0.47)	2.00 (2.58)	1.01 (1.17)	0.44 (0.23)
LSD[a]		3.44	2.68	0.32	0.97	0.78	0.81[b]/0.84[c]

[a] Least significant difference across application rates based upon the average of irrigated and nonirrigated plots at a *p* level of 0.05. Except for MAA levels in peanut kernels, no significant difference was found between irrigated and nonirrigated plots. [b] Nonirrigated plots. [c] Irrigated plots.

(Winsted, CT). MAA was initially extracted from a 5.0-g sample of the paste by homogenizing the paste for 2 min using a second Waring blender and a 40-mL aliquot of distilled−deionized water. The homogenate was centrifuged for 10 min and the supernatant filtered into a 250-mL centrifuge bottle through Whatman No. 541 filter paper. The filter cake was re-extracted two additional times as above with 40-mL aliquots of DI water, and the filtered supernatants were combined into the centrifuge bottle.

Cleanup of the extract was performed by acidifying the extract to pH <2 with concentrated HCl and partitioning in a centrifuge bottle with 3 × 90 mL of hexane followed by 3 × 90 mL of diethyl ether. The resulting emulsified sample was then centrifuged at 12000 rpm for 5 min, the aqueous and organic layers were separated in a separatory funnel, and the organic layer was discarded. The solids in the centrifuged sample were collected on a Büchner funnel, and the last ether partition of the aqueous sample was transferred into a boiling flask. Meanwhile, the solids were transferred from the Büchner funnel into a centrifuge bottle that contained 5 g of 545 Celite and 40 mL of DI water. This sample was homogenized for 1 min and then centrifuged for 10 min. The supernatant was filtered through a glass fiber filter and added to the boiling flask.

The pH of the supernatant was adjusted to >12 by dropwise addition of a 17% NaOH solution and reduced in volume to ∼25 mL using a Zymark Turbovap (Hopkinton, MA). It was then acidified with ∼1.5 mL of concentrated HCl, and the boiling flask was fitted with a condenser and refluxed for 16−18 h. The hydrolysate was allowed to cool and then centrifuged for 5 min. Additional cleanup was performed by passing the hydrolysate through a C-18 solid-phase extraction cartridge (J. T. Baker, Phillipsburg, NJ) that had been preconditioned with methanol and pH 2 water. MAA residues in the hydrolysate were derivatized with MTG as described for the peanut leaves above.

Analysis of Total Arsenic in Peanut Kernels. Peanuts were analyzed by the Georgia Department of Agriculture for total arsenic residue using microwave digestion (CEM Corp., Matthews, NC) of the peanut meat and analysis of total arsenic residues in the digest by atomic absorption spectrophotometry with continuous flow hydride generation. Prior to digestion, peanuts were ground using a Waring blender to a paste and a 0.5-g sample was digested with 10.0 mL of concentrated HNO_3 (*9*). Following digestion, 10 mL of a 40% Mg-$(NO_3)_2$ solution was added, and the digest was boiled to dryness on a hotplate and then ashed for 3 h at 500 °C in an ash oven. The ashed sample was then redigested for 1 h with 30 mL of 6 N HCl on a hotplate. The volume of this digest was adjusted to 50 mL with additional HCl and analyzed for total arsenic with an atomic absorption spectrophotometer with continuous flow hydride generation.

Statistical Analysis. Analysis of variance was conducted using a two-way ANOVA analysis in a split-plot design with irrigation as the main plot and rate as the subplot. Mean separation was accomplished using Fisher's protected least significant difference (LSD) at a *p* value of 0.05. Where there was a significant interaction, the subplots were tested within each level of the main plot.

RESULTS AND DISCUSSION

Recoveries on Leaves and Peanut Kernels. Total As was consistently recovered at >85% from spiked samples with a limit of quantitation (LOQ) of 0.2 ppm. MAA residues were easily washed from leaves with DI water. Spiked recoveries showed that >95% of the residue was recovered from both peanut leaves and peanut kernels at concentrations ranging from 0.5 to 2.0 ppm. Based upon the standards used in the calibration the LOQ for MAA for this investigation was 0.05 ppm for peanut leaves and 0.1 ppm for peanut kernels. Untreated peanut samples spiked with MAA indicated that residues in the peanut meat could be fully recovered within 6 months, the longest period that samples were held prior to extraction. The thiogly-colate derivative (**Figure 1**) of MAA responded well by GC-MS. However, both the derivatives and the derivatizing agent have an obnoxious odor and require the availability of adequate ventilation both in their preparation and also around the gas chromatograph. Additionally, although relatively straightforward, the extraction and cleanup are labor intensive and time-consuming, with ∼40 h (5 work days) required to fully process, extract, and analyze a sample set.

Confined Crop Rotation. MAA was not detected in peanut kernels from any peanut sample produced in treated pots at either the 30-, 60-, or 90-day plant-back interval, indicating that even a 30-day plant-back interval would not result in detectable residue in peanut with either of the soils tested. Because no detections were present in the 30-, 60-, or 90-day plant backs, the 120- and 240-day intervals were not planted and natural background levels of inorganic arsenic were not measured. Burlo et al. (*10*) showed that tomatoes could accumulate various arsenicals, although in their study arsenic species were applied to pots containing tomatoes grown in sand. This does not represent the potential availability of "aged" residues of arsonate herbicides to crops that are planted into soils which received recent applications of herbicide. Additionally, with a reported K_{oc} of 7000 (*6*), MSMA would be strongly bound to soil collids and, as a result, the bioavailability of sorbed MSMA would not be expected to be high. Results from this study indicate that one would not expect MAA uptake and accumulation in peanut growth in rotation with cotton, even when planted with very short plant-back intervals.

Dissipation on Peanut Leaves. As expected, the highest concentrations of MAA were observed immediately after application. Statistical analysis of the data from each plot indicated that there was no significant difference between irrigated and nonirrigated plots. Rapid dissipation was observed

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immediately following application as shown in **Table 2**, probably due to sorption into the leaf cuticle because irrigated and nonirrigated treatments responded similarly. This was observed despite the fact that residues on peanut leaves were adequately recovered by water extraction in laboratory experiments with leaves spiked with MAA. It is possible that an ethanol wash that would remove a portion of the cuticle may have increased recoveries from leaves at subsequent sampling times, but the objective was to test a simple method that could be used to detect MSMA residues. The ethanol wash may prove to be useful if lower method detection limits are needed, especially at the later time points following application. With only a water wash, residues were detected up to 8 days postapplication at the lowest application rate and following two irrigation events, indicating that residues due to either illegal applications or spray drift could be measured. The irrigation events used in this investigation were each equivalent to a 3.8 cm rainfall event, which is common in the southeast during the summer growing season.

MAA and Total As Residues in Peanut Kernels. Total arsenic residues on average were generally higher than MAA residues in peanut kernels (**Table 2**), although not significantly higher. MAA was not detected and total arsenic was below the limit of quantification for all peanuts from untreated control plots. There was considerable variability in residues as indicated by the high standard deviation (SD) between samples collected from plots with replicated treatment regimes; thus, it is not possible to definitively correlate concentrations of total arsenic measured in peanuts to measured concentrations of MAA from these data. There was no significant difference between total arsenic residues in peanut kernels and irrigation. However, a significant difference was found for MAA; thus, LSDs were calculated separately for MAA in peanut kernels in irrigated and nonirrigated plots. Further statistical testing of the subplots within each level of the main plots did not follow a logical trend and was presumed to be an anomaly in the data. This can be observed in **Table 2** through careful observation of the concentration of MAA in peanut kernels at each treatment rate between irrigated and nonirrigated plots.

However, it is interesting and noteworthy that both MSMA and total arsenic were detected in peanuts even at the lowest application rate which would typically be used to control Florida beggarweed in peanuts and that no detection of either total arsenic or MAA was observed in samples collected from untreated plots. These data would indicate that even low-rate applications of MSMA on peanuts would result in detectable residues of MAA in peanut kernels at the time of harvest. Total arsenic was also quantifiable in peanuts at harvest, indicating an increase in total arsenic, because total arsenic levels were not quantifiable in the untreated plots. These results indicate

that a combination of leaf and peanut kernel samples with determination of both MAA and total arsenic can be diagnostic for contamination of peanut with MSMA.

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