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AN ASSESSMENT OF THE RISKS ASSOCIATED WITH PESTICIDES VOLATILIZED AND DISLODGED FROM GOLF TURF

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ABSTRACT

Studies on risks associated with pesticide dislodged and volatilized from golf turf, golfer practices that lead to contact with applied pesticides, and the effect of MSMA application on arsenic (As) in a golf course green root zone, in percolate, in clippings, and on dislodged As were conducted from 1998 through 2002 at the University of Florida Ft. Lauderdale Research and Education Center and at the Everglades Research and Education Center.

Generally, the amount of pesticide dislodged decreased with time after application and was greatly reduced following irrigation. Of those pesticides studied, the lowest risks to golfers from dislodged pesticide were found for dicamba and chlorpyrifos. Even for fenamiphos, the pesticide from the group that posed the greatest risk from dislodgeable residues, little risk was calculated for a golfer who plays the day after pesticide application and irrigation everyday for 70 years.

The measured quantity of four pesticides that was lost by volatilization greatly exceeded that lost by leaching or clipping removal in previous USGA-sponsored studies we have conducted. A risk analysis for chlorpyrifos indicated that golfer exposure to airborne residues of this pesticide posed no health risk. A similar assessment indicated little health risk for inhalation of fenamiphos or fonofos applied to golf turf. An inhalation risk assessment for isazophos indicated values exceeding the USEPA chronic reference dose (Rfd) 18 - 19 hours after application. Of course, this assessment assumes inhalation of the residues during that time period by a golfer playing every day for 70 years. For a more realistic assessment, the risk can be reduced in proportion to the actual amount of exposure.

An assessment was made of the risks to golfers from exposure to chlorpyrifos and fenamiphos as a result of the combination of doses received from inhalation of volatilized pesticide and from pesticide applied to the turf that is dislodged and transferred to a golfer?s skin. Predicted exposure to the two pesticides differs significantly. For fenamiphos, by far the greatest predicted dose would be accumulated from the dislodged pesticide pathway, whereas for chlorpyrifos inhalation of volatilized pesticide would be an important pathway for exposure. Nevertheless, although it was estimated that some dosage of both pesticides would be received by golfers, even if a golfer played on 18 greens within 1 hour after application of chlorpyrifos every day for 70 years, the health risk would be negligible. For fenamiphos, however, the risk would be appreciable for the previously-stated unlikely playing scenario, but if the golfer played the day immediately following nematicide application every day for 70 years there would be negligible risk from the pesticide exposure.

A survey was conducted to quantify observable golfer habits that could lead to direct or indirect contact with pesticides applied to the turf. Ten practices that could lead to pesticide exposure were observed in the fairway and green collars, and twelve were observed on the greens. In the fairway/collar area, 22.3% of the players placed a club on the turf and later retrieved it. They could have contacted pesticide applied to the turfgrass indirectly if pesticide were transferred to the club grip, and then to the players? hand. Twelve percent of the players touched the club face, usually in returning the club to the bag after making a shot. On greens, players touched the golf ball an average of 1.25 times per player. A club was placed on the turf surface and retrieved 34.6% of the time. A ball marker was used by 23.3% of the players, and 19.3% retrieved the pin from the turf surface. Knowing the frequency of the practices that can lead to pesticide exposure can be useful for making risk assessments.

Following three applications of MSMA, As concentration increased in the root zone mixes. The greatest concentration of As was found in an artifically-coated sand root zone mix, which retained approximately 45% of the applied As in the upper 10 cm. Arsenic leaching ranged from 4 to 12% of that applied, with the greatest amount of As leaching occurring in a pure sand root zone. During the study period, less than 1% of the applied As was recovered in clippings. During the first month following the initial MSMA (MSM) application, most As leaching was either in the dimethylarsinic acid (DMA) or As(V) form. Observed As concentrations in all forms except As(III) rose to amounts considerably above the legal drinking water standard of 10 $\mu g\ L^{-1}$.

INTRODUCTION

Originally, the project was designed to be in collaboration with a project headed by Dr. John Clark, University of Massachusetts. However, Dr. Clark?s project was not funded by the USGA in the form originally envisioned, so our project was appropriately modified.

In 1998, studies on pesticide dislodgeability were conducted with assistance from Mr. Raymond Snyder, a University of Florida graduate student working on an M.S. degree in the Soil and Water Science Department. Drs. Cisar and Borgert, and Dr. Jerry Sartain of the Soil and Water Science Department in Gainesville, formed Mr. Snyder?s graduate committee and participated to varying degrees in that work.

In 1999 and 2000, pesticide volatilization studies were conducted. In 2001, a survey was conducted on golfer practices that can lead to pesticide exposure. In 2002, a study was conducted on arsenic (As) removal in clippings, retention in soil, dislodgeability, leaching, and speciation in leachate following MSMA (monosodium methanearsonate) application to four root zone mixes.

Since the dislodgeability studies, excluding those involving As, the volatilization work, and the survey results have been presented in Annual Reports (1998 - 2001), only a summary of these studies will be included herein. The As work will be reported to the extent that data are available. We intend

to continue this work, however, and will provide a full report on this subject to the USGA as a supplement to the Final Report.

PESTICIDE DISLODGEABILITY STUDIES

A series of pesticide dislodgeability studies were conducted to evaluate the risks associated with golfer exposure to pesticides. The work was performed by Mr. Raymond H. Snyder as part of a master of science degree program at the University of Florida. The pesticides 2,4-D and Dicamba were applied as liquids to a cv. Tifgreen bermudagrass USGA green with and without Poa trivialis overseeding, and to a cv. Tifdwarf USGA green. Isazofos, chlorpyrifos, and fenamiphos were spray-applied to the Tifdwarf green. Pesticides were dislodged with damp cheesecloth rubbed on the turf surface, damp cotton cloth pressed on the surface, damp leather pressed, by putting a golf ball over the surface, by rolling golf grips on the surface, and in a short rough off to the side of the green by swinging a golf club through the grass and wiping the club surface with damp cheesecloth.

Generally, the amount of pesticide dislodged decreased with time after application, and was greatly reduced following irrigation. By combining the data, risk assessment calculations could be made for various scenarios. The lowest risks were found for dicamba and chlorpyrifos. For example, exposure to chlorpyrifos on 18 greens one hour after application everyday for a lifetime was calculated to provide a Hazard Quotient of 0.31. Hazard quotients less than 1.00 are considered to pose little risk. A similar calculation for exposure after irrigation was 0.02. Chlorpyrifos has a rather high Reference Dose (Rfd), i.e., acceptable amount of exposure, which reduces the Hazard Quotient. However, even for fenamiphos, the pesticide from the group that posed the greatest risk from dislodgeable residues, little risk was calculated for a golfer who plays the day after pesticide application and irrigation everyday for 70 years.

PESTICIDE VOLATILIZATION STUDIES

In 1998, following laboratory studies to verify methodology, the concentration of ethoprop, fonofos, and isofenphos in air following application to a golf course fairway was determined. Although the weather was cloudy and rainy during the study, appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (20 $\mu g\ m^{-3}$ on day 2). Fonofos had a maximum concentration of 5.9 $\mu g\ m^{-3}$ on day 2, and isofenphos was 1.0 $\mu g\ m^{-3}$ on day 3. Although there was a general trend for increasing concentrations of ethoprop on the morning of the second day after application and a decline thereafter, trends were less evident for the other two pesticides. An inhalation risk assessment using isazophos volatilized residues data from two previous studies (USGA Final Report by Snyder and Cisar, December 1997) indicated values exceeding the USEPA chronic reference dose (Rfd) for 18 - 19 hours after application. Of course, this assessment assumes inhalation of the residues by a golfer playing every day for 70 years. For a more realistic

assessment, the risk can be reduced in proportion to the actual amount of exposure.

In 1999, the concentration of ethoprop, chlorpyrifos, and isofenphos in air following application to a golf course fairway was determined. Appreciable airborne pesticide residue was observed over a three-day measurement period. The highest concentration was found for ethoprop (33 $\mu g\ m^{-3}$). Chlorpyrifos had a maximum concentration of 4.0 $\mu g\ m^{-3}$, and the maximum for isofenphos was 1.7 $\mu g\ m^{-3}$, with all three maximum concentrations occurring on the day of application. There was a general trend for decreasing concentrations of all three pesticides over time, but mid-day increases in concentration generally were evident. A risk analysis for chlorpyrifos indicated that golfer exposure to airborne residues of this pesticide posed no health risk. A similar assessment using data from past-year experiments indicated little health risk for inhalation of fenamiphos or fonofos applied to golf turf. Nevertheless, the amount of each of the four pesticides that was lost by volatilization in the 1998 and 1999 trials greatly exceeded that lost by leaching or clipping removal in previous USGA-sponsored studies we have conducted.

RISK ASSESSMENT FOR THE COMBINATION OF DISLODGED AND VOLATILIZED PESTICIDES

Based on the experiments conducted on pesticide volatilization and dislodgeability, an assessment was made of the risks to golfers from exposure to an insecticide (chlorpyrifos) and a nematicide (fenamiphos) as a result of the combination of doses received from inhalation of volatilized pesticide and from pesticide applied to the turf that is dislodged and transferred to a golfer?s skin (Table 1). Predicted exposure to the two pesticides differs significantly. Chlorpyrifos has a much greater Rfd than fenamiphos, indicating greater toxicity for the latter. For fenamiphos, by far the greatest dose was accumulated from the dislodged pesticide pathway, with little being contributed by inhalation of volatilized pesticide. For chlorpyrifos, on the other hand, inhalation of volatilized pesticide was an important pathway for exposure, and generally exceeded that from dislodged pesticide. The dose of fenamiphos received by the golfer as dislodged pesticide far exceeded that of chlorpyrifos. This is most likely because fenamiphos was applied at almost 5 times the rate of chlorpyrifos (1.125 vs 0.229 g AI m^{-2}, respectively), although the calculated dose of fenamiphos generally exceeded that of chlorpyrifos by much more than a factor of 5.

Most of the estimated dose of the insecticide received by golfers came by way of inhalation, whereas most of the dose received from the nematicide came by way of dislodged pesticide. Although it was estimated that some dosage of both pesticides would be received by golfers, even if a golfer played on 18 greens within 1 hour after application of the insecticide every day for 70 years the health risk would be negligible, based on United States Environmental
Protection data used to assess such risks. For the nematicide exposure, however, the risk would be appreciable for the previously-stated unlikely playing scenario, but if the golfer played the day immediately following nematicide application every day for 70 years there would be negligible risk from the pesticide exposure (Table 1). Since the nematicide can be applied legally only twice per year, it is

extremely unlikely that a golfer would encounter the pesticide that frequently.

Table 1. Total hazard quotient from pesticide exposure due to dislodged and volatilized pesticides.

Pesticide	Scenario*	Dose of pesticide received by a golfer: Pesticide exposure pathway: Dislodged	Volatilized	Combination	Hazard quotient
		(μg/kg/day)			
Chlorpyrifos	1	0.92	0.913	1.833	0.61
	2	0.11	0.924	1.034	0.34
	3	0.06	0.864	0.924	0.31
	4	0.03	0.371	0.401	0.13
Fenamiphos	1	38.00	0.45	38.45	153.80
	2	4.26	0.03	17.16	68.64
	3	2.27	0.003	2.27	9.09
	4	0.21	0.001	0.21	0.84

* Scenario 1: Golfer plays on 18 greens within 1 hour after pesticide application every day
2: Golfer plays on one green immediately after pesticide application and on the remaining 17 greens after application and irrigation every day
3: Golfer plays on 18 greens after pesticide application and irrigation every day
4: Golfer plays on 18 greens the day after application and irrigation every day

A SURVEY OF PRACTICES THAT MAY BRING GOLFERS INTO DIRECT OR INDIRECT CONTACT WITH PESTICIDES APPLIED TO FAIRWAYS AND GREENS

In making risk assessments of golfer exposure to dislodged pesticides, assumptions have been made about the exposure pathways, i.e., how golfers come into contact with turf that has been sprayed with pesticides. Consequently, a survey was conducted to quantify observable golfer habits that could lead to direct or indirect contact with pesticides applied to the turf. Play by nearly 400 golfers spread over three golf courses was observed to determine the frequency of such habits. Ten practices that

could lead to pesticide exposure were observed in the fairway and green collars, and twelve were observed on the greens. However, only two of the practices on the fairway/collars and four on the greens were observed for over 10% of the players. In the fairway/collar area, 22.3% of the players placed a club on the turf and later retrieved it. They could have contacted pesticide applied to the turfgrass indirectly if pesticide were transferred to the club grip, and then to the players? hand. Twelve percent of the players touched the club face, usually in returning the club to the bag after making a shot. Again, this practice could result in indirect contact with pesticide.

On greens, players touched the golf ball an average of 1.25 times per player. A club was placed on the turf surface and retrieved 34.6% of the time. A ball marker was used by 23.3% of the players, and 19.3% retrieved the pin from the turf surface. Knowing the frequency of the practices that can lead to pesticide exposure will be useful for making risk assessments.

ARSENIC IN SOILS, BERMUDAGRASS CLIPPINGS, PERCOLATE WATER, AND DISLODGED FOLLOWING APPLICATION OF MSMA TO A GOLF GREEN

Herbicides containing monosodium methanearsonate (MSMA) often are used for weed control in bermudagrass (*Cynodon* sp.) golf greens and fairways. In a recent survey of Florida golf courses (Chen et al., 2000), 96% of the respondents had used MSMA within the past three years, and over 70% made multiple applications. MSMA contains arsenic (As), which is suspected to be responsible for various cancers (bladder, kidney, liver, lung, and skin). The USEPA has established a drinking water standard for As of 10 $\mu g\ L^{-1}$, and a variety of standards have been established as clean-up goals for various soils. The Dade County Department of Environmental Resources Management conducted a study of As in ground water and surface soils from golf courses in collaboration with the Florida Department of Agriculture and Consumer Services (Anon., 1999). Up to 815 μg As L^{-1} was found in groundwater, and 120.7 mg As kg^{-1} soil was found in the surrounding surface soil, which probably resulted from pesticide spillage, rather than from routine use. Using soils from golf courses in south Florida, Cai et al. (2001) concluded that As was correlated with soil iron, manganese, and aluminum, but not with organic matter. However, no direct measurements of volatilized As, or of As as dislodgeable residues, or in percolate, grass clippings, or soil following label-rate applications of MSMA to golf greens are available. Our study, conducted in cooperation with Dr. Ming Chen (University of Florida) and Dr. Yong Cai (Florida International University), is designed to obtain these data for MSMA, and to assess risks to golfers from MSMA use on golf courses.

A commercial grade MSMA was spray-applied on August 29, September 5, and September 12, 2002, at the maximum recommended rate of 0.224 g m^{-2} (2 lbs A.I. $acre^{-1}$) to established 'Tifdwarf' bermudagrass plots in a USGA green at the Ft. Lauderdale Research and Education Center. No As had been applied to these plots previously. The plots contained lysimeters for recovering percolate. There were four replications of four root zone media in the study, all having USGA-specification sand texture: 1) quartz sand, 2) quartz sand with 10% (volume) sphagnum peat, 3) naturally-coated (goethite,

gibbsite, kaolinite, hydroxy-interlayer vermiculite) sand with 10% peat, and 4) artifically clay-coated (Ca-montmorillonite) sand with 10% peat. At weekly intervals, percolate water was recovered and clippings were collected. On two occasions, an adjacent area on the green was sprayed with MSMA for measuring dislodgeable residues at several time intervals following MSMA application by rubbing a 25 cm square area three times in each of two right-angle opposed directions with moistened cheese cloth attached to a 10 cm square metal device weighing 2.93 kg. The cloth was separated from the metal surface with a layer of plastic film. The percolate water was analyzed for various As species, and the plant tissue and soil (0 - 10 cm depth) have been analyzed for total As. The cheese cloth will be analyzed for total As, and various species of As will be determined in fresh plant tissue, but these data are not available at this time. Studies of As volatilization following application to the green are planned.

Following three applications of MSMA, As concentration in the root zone mixes increased (Fig. 1). The greatest concentration of As was found in the artifically-coated sand root zone mix, which retained approximately 45% of the applied As in the 0 - 10 cm depth. After three applications of MSMA, As leaching ranged from 4 to 12% of that applied (Fig. 2). The greatest amount of As leaching was observed in the sand (without peat) root zone mix. Arsenic concentration in clippings taken after MSMA application averaged 12 to 23 $\mu g\ kg^{-1}$, but decreased substantially after MSMA useage ceased (Fig. 3). Nevertheless, during the study period less than 1% of the applied As was recovered in clippings regardless of the root zone mix.

During the first month following the initial MSMA (MSM) application, most As leaching was either in the dimethylarsinic acid (DMA) or As(V) form, and the latter increasingly predominated over time (Fig. 4). These results indicate that both methylation and decomposition occur after applying MSMA. Observed As concentrations in all forms except As(III) rose to amounts considerably above the legal drinking water standard of 10 $\mu g\ L^{-1}$.

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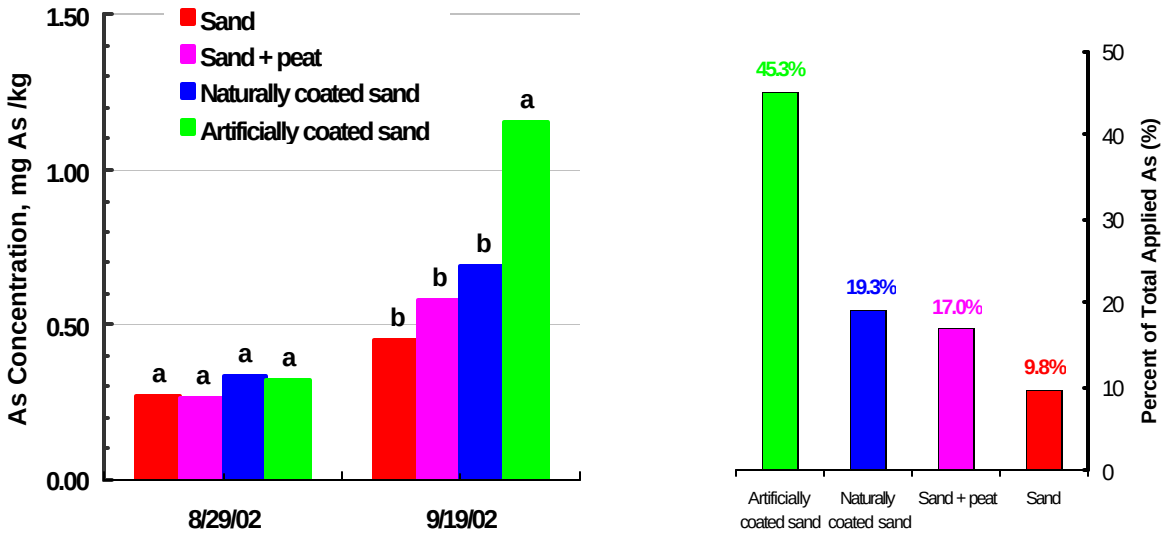

Fig. 1. Left: Concentration of As in 0 - 10 cm soil samples taken before and after three applications of MSMA at 0.224 g m^{-2} (2 lbs. A.I. $acre^{-1}$) to four root zone mixes on a bermudagrass green, and Right: Arsenic retained in the four root zone mixes, expressed as a percent of that applied.

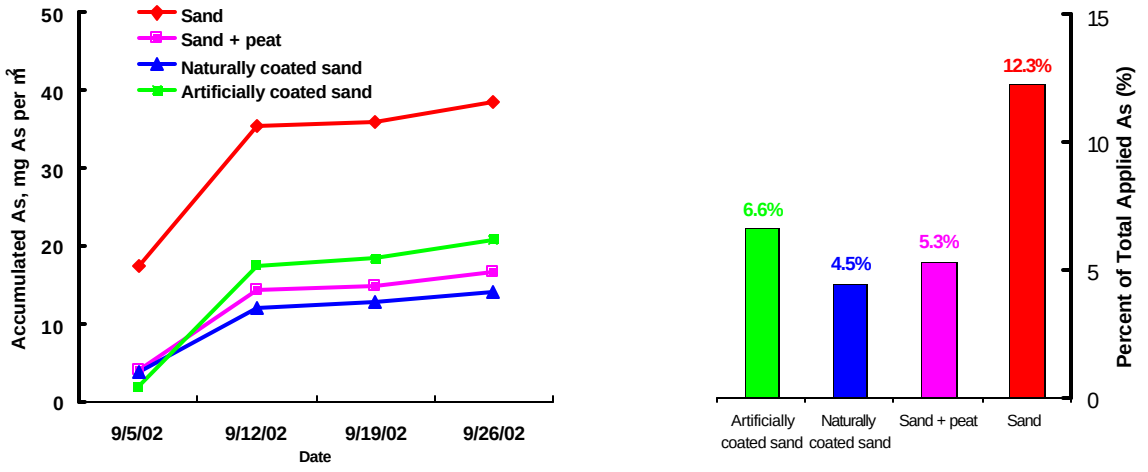

Fig. 2. Left: Accumulated As in percolate following three applications (8/29, 9/5, 9/12) of MSMA at 0.224 g m^{-2} (2 lbs. A.I. $acre^{-1}$) to four root zone mixes on a bermudagrass green, and Right: Total As in percolate water, expressed as a percent of that applied.

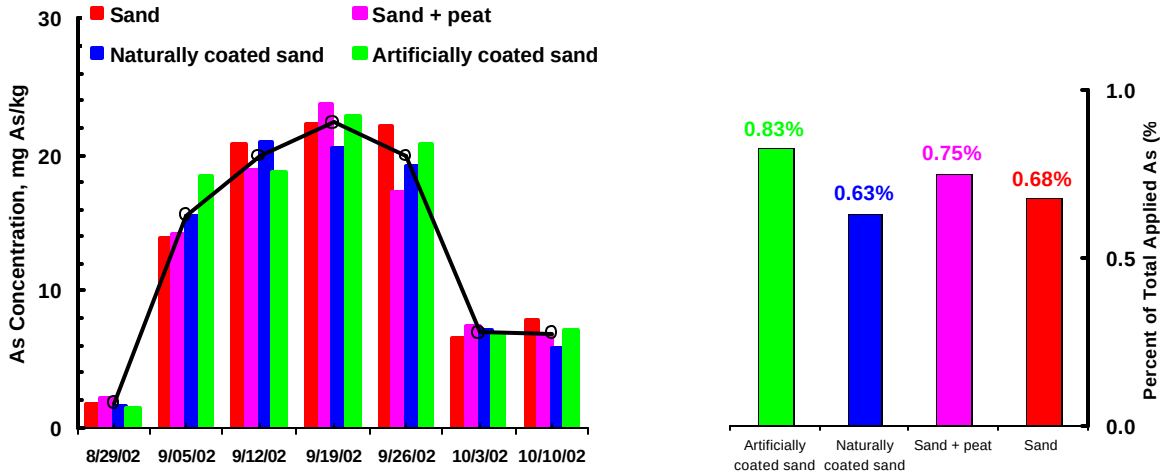

Fig. 3. Left: Arsenic in clippings following three applications (8/29, 9/5, 9/12) of MSMA at 0.224 g m^{-2} (2 lbs. A.I. $acre^{-1}$) to four root zone mixes on a bermudagrass green, and Right: Total As in clippings, expressed as a percent of that applied.

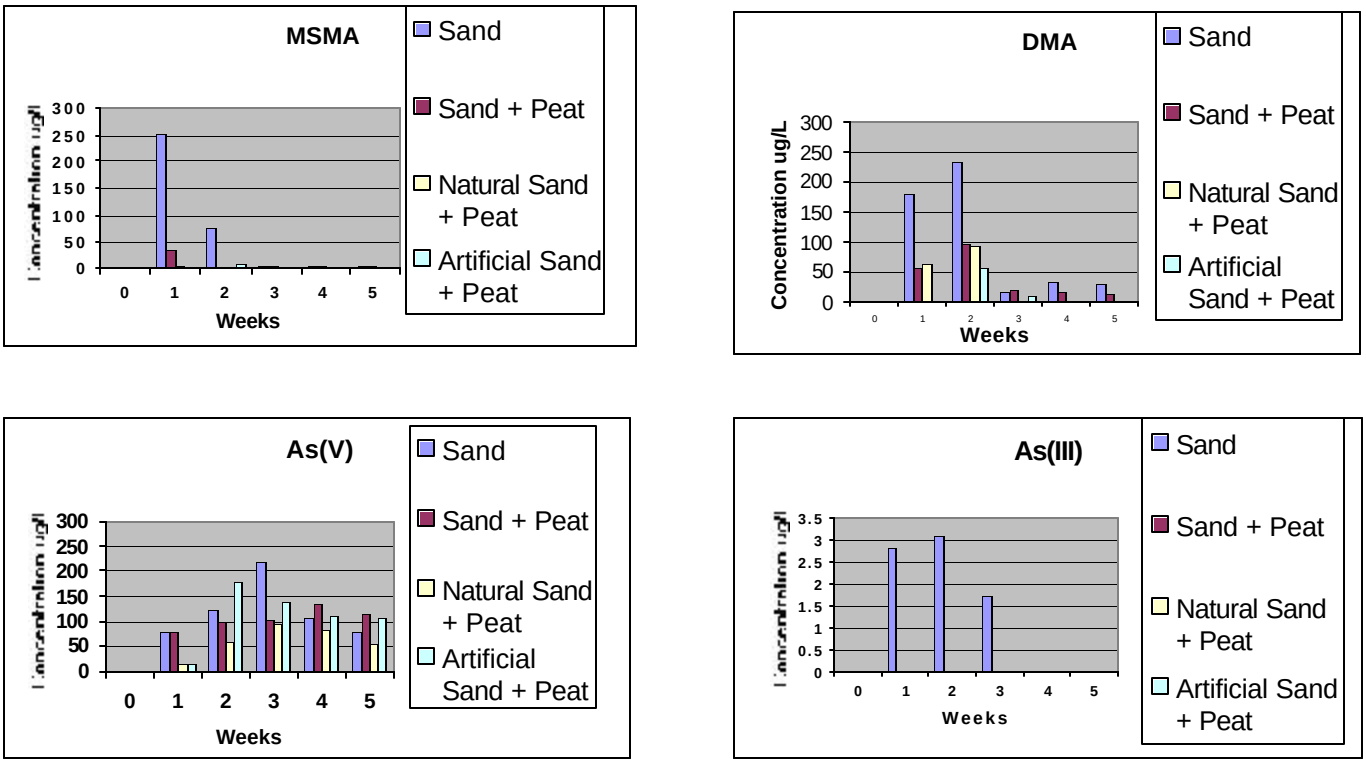

Figure 4. Concentration of As in percolate water by species and root zone mix following MSMA applications in weeks 0, 1, and 2.

USGA Turfgrass and Environmental Research Executive Summary

AN ASSESSMENT OF THE RISKS ASSOCIATED WITH PESTICIDES VOLATILIZED AND DISLODGED FROM GOLF TURF

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Are golfers exposed to dangerous risks from pesticides used to maintain golf courses? A series of studies was conducted by University of Florida researchers Dr. George H. Snyder and Dr. John L. Cisar, along with graduate student Mr. Raymond Snyder and toxicologist Dr. Christopher Borgert, to investigate that question. They observed golfers during play to see how they might come in contact with grass that had been sprayed with pesticides, or come in contact with items laid on the grass surface, such as golf clubs, ball markers, and towels, in order to determine ways that a golfer can be exposed to pesticides. The scientists also measured the amount of pesticide that can be dislodged from the grass in various ways and the quantity of pesticide that volatilizes into the air following pesticide application. Using these data in conjunction with US Environmental Protection Agency criteria for acceptable levels of chronic pesticide dosage, calculations were made of the risks incurred by golfers due to pesticide useage on the golf course. For the pesticides studied, which included some of the older widely-used organophosphate materials for which safety questions have been raised, exposure risks were determined to be insignificant for any likely playing scenario.