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Response to Comment on Arsenic Transport and Transformation Associated with MSMA Application on a Golf Course Green

Sir: We are responding to the comments from Dr. Jennifer Saxe (*1*) of Gradient Corp. on our recently published paper (*2*). We would like to restate the objective of our work before addressing Dr. Saxe's concerns, that is, to understand the behavior of arsenic species in percolate water from MSMA applied to golf course greens, as well as to determine the influences of root zone media for United States Golf Association (USGA) putting green construction on arsenic retention and species conversion (*2*). We feel strongly that our results clearly demonstrated that substrate composition can significantly affect both arsenic retention in soil and arsenic speciation in percolate water. This study provides useful information on how to reduce the potential risk of arsenic contamination associated with MSMA application on golf courses.

We disagree with Dr. Saxe's suggestion that "the arsenic in the percolate could *all* have resulted from naturally occurring arsenic. The lack of a control plot precludes the ability to determine the source of the leached arsenic". Indeed, we did not have specific plots as controls because of the limitation of the number of the plots available and the types of soils needed to be tested. To overcome this limitation, we measured arsenic concentrations in the soil samples before and after MSMA application in each plot. The results indicated that the background concentration of arsenic in the soils was very low (<0.35 mg kg^{-1}) and therefore would not contribute significant amounts of arsenic to the leachate. We also measured arsenic concentration in the percolate before applying MSMA and found that it was very low compared to the amount measured in the following weeks. This was used as baseline information for comparison with arsenic measured following MSMA application. **Table 1** is an example showing total arsenic concentration (micrograms per liter) in percolate water averaged from four plots using uncoated sand (S) substrate. The results clearly indicate that arsenic in percolate sharply increased following MSMA application and that the arsenic leached in the percolate during the course of the experiment resulted *mainly* from the application of MSMA. We did not consider the contribution from naturally occurring arsenic (data in week 0) when estimating arsenic leaching rate (Table 4 in ref *2*) because the small value could be neglected (**Table 1**). Total arsenic concentration in percolate water was determined by several factors, including substrate composition and water amounts from rain and sprinkler systems. Large standard deviations in arsenic concentration in percolate were indeed observed among the four plots for each substrate. However, data from each plot showed a similar trend; that is, application of MSMA on the substrates *sharply increased* arsenic concentration in percolate water. Increase in arsenic concentration in groundwater caused by MSMA application has also been reported by others (*3*−*6*). Dr Saxe's statement "the data from Feng et al. (*1*) show that the arsenic in percolate totaled 12−40% of the natural arsenic present in test soils prior to MSMA application, but only 18.6%, at most, of the arsenic applied as MSMA" is incorrect because she used the arsenic concentration we reported for the top layer (0−10 cm) of soil to calculate the background arsenic concentration in the soil of the whole plot. This is wrong because it cannot be assumed that arsenic was evenly distributed in the plot.

Table 1. Total Arsenic Concentration in Percolate Water Averaged from Four Plots Using Uncoated Sand (S) Substrate

time (weeks)	sampling date	As concn (μg/L)
0	Aug 29, 2002	1.1
1	Sept 5, 2002	321.9
2	Sept 12, 2002	346.2
3	Sept 19, 2002	193.2
4	Sept 26, 2002	219.7
5	Oct 3, 2002	209.3
7	Oct 17, 2002	160.4
8	Oct 24, 2002	54.5
10	Nov 7, 2002	20.0
12	Nov 20, 2002	20.8
14	Dec 4, 2002	13.4

We understand Dr. Saxe's concern on the stability of arsenic in the environment. Arsenic species could be transformed from one species to another rapidly under environmental conditions (*7*−*10*). This is why we tested the stability of the field sample to ensure that arsenic speciation was not altered during sample storage time *after sampling*. Effort was made to conduct the field experiments under simulated real environmental conditions. We believe that collecting samples in sterile underground storage vessels as Dr. Saxe suggested is not appropriate and unrealistic. It should be pointed out that sampling intervals of 1−2 weeks would not change the total arsenic leached from the substrates. We disagree with Dr. Saxe's comments that "the apparent transformation rate of MSMA to other arsenic compounds described by Feng et al. is far more rapid and complete than in studies described in the literature (see, e.g., refs *3*−*5*) and may be due to experimental artifact". This is because the transformation rate of MSMA could be affected by a number of factors. We observed that monomethylarsonic acid (MMA) was leached from all three substrates, but mainly in the first few weeks when MSMA was applied. For substrate S (uncoated sand), which showed less arsenic sorption capacity, a large quantity of MMA leached out at 12.1 mg m^{-2} in 14 weeks, compared to only 1.1 and 0.3 mg m^{-2} for S + P (uncoated sand and peat) and NS + P (naturally coated sand and peat), respectively (Figure 4 in ref *2*). These results suggest that compared to substrate S, MMA underwent a much faster transformation and/or stronger adsorption in S + P and NS + P. In the literature cited by Dr. Saxe, various demethylation rates of MSMA were also reported (*11*, *12*). Von Endt et al. studied the degradation of MSMA in soil

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and found that 1.7−10% of MSMA was degraded in 60 days (*12*). From a study on microbial degradation of MSMA using a clay-type soil as the culture medium, Abdelghani et al. found that the degradation was dependent on MSMA concentration with peak rates of demethylation of 29%/month for all MSMA concentrations tested (*11*). It is apparently not appropriate to compare the degradation rates without considering the experimental conditions utilized.

We certainly have considered the involvement of microorganisms in the transformation of arsenic in our study and discussed in the paper the possible role of microorganisms in arsenic transformation and bioavailability of arsenic species. With regard to the possible presence of *Pseudomonas* in the soil, which could readily and tenaciously adhere to stainless steel and could be involved in demethylating MSMA (*13*, *14*), we did not have evidence of its presence in the soils used in our study and therefore we could not evaluate its exact role in MSMA demethylation. An investigation is currently being conducted in our laboratory about this issue and is beyond the scope of our paper.

Dr. Saxe questions the possible presence of arsenic sources besides MSMA, including wood used for box construction, fertilizers used during the experiments, and pond water used for irrigation. Indeed, we did not record whether the plywood used in the plots was CCA-treated. However, as indicated in our paper, the plots were encased with plywood along the perimeter to a depth of 30 cm in order to hydraulically isolate the added soil mixtures from the surrounding root-zone media. The boxes were sized 50 × 200 cm. The lysimeters had diameters of ∼36 cm. Thus, the nearest approach of the lysimeter to the box was 7 cm, and the distance rapidly increased from that to 82 cm. Because the soil is highly permeable, it can be assumed that water percolates almost vertically. Thus, little to none of the water that contacts the plywood surfaces likely enters the lysimeters. Most importantly, the soil arsenic concentrations before MSMA application (<0.35 mg kg^{-1}) were within the normal range of background concentration of Florida soils (*15*), indicating no arsenic contamination in the soils. It must be pointed out that the test plots were put in place 11 months before the arsenic study was initiated. The low arsenic concentration observed in percolate water before the application of MSMA (**Table 1**) clearly suggests that contribution of arsenic from the plot materials was insignificant. No fertilizers were applied during the course of this study. Again, week 0 sampling showed that there was little arsenic in the percolate at the time we started the study, and the spike in arsenic occurred in conjunction with the MSMA applications (**Table 1**). With regard to the irrigation water, we did analyze the pond water for arsenic during the course of the experiment and found that the irrigation water was of no concern (2.28 μg/L). In summary, we believe that other arsenic sources, if any, could not significantly contribute to the sharp increase in arsenic concentration in percolate water following the application of MSMA.

Dr. Saxe also questions that (1) the study was conducted on simulated golf course greens, "where drainage is engineered to be artificially rapid; however, MSMA is rarely, if ever, applied to golf course greens" and (2) only three low-clay, sandy soils were tested, which are not representative of most soils. We disagree with her first statement because, on the basis of a survey conducted by Chen et al. in 2000, 96.1% of the Florida golf courses were still using MSMA as a herbicide for weed control and 99% of Florida's golf courses were using bermudagrass as the greens (*15*). The 2004 University of Florida Pest Control Guide discusses the use of MSMA on Tifdwarf bermudagrass, which is almost exclusively used for golf course greens (*16*). Nothing is said about not using it on greens. In addition, the USGA specification greens are specifically designed to quickly drain water. The second statement is incorrect because, on the basis of the same study conducted by Chen et al. (*15*), 448 representative Florida soils from the Florida Cooperative Soil Survey Program are very sandy, with an average sand content of 89.3%. The 2000 golf course survey conducted by the same authors indicated that 73% of Florida golf courses were constructed on sands or sandy soils (*17*).

We agree with Dr. Saxe's comments that there was a high degree of variability among replicate plots as we also discussed in the paper. This is why four replicate plots were used in our experimental design and the average of the four was employed for the data analysis. The effects of soil variability and weather conditions in pesticide leaching in real field conditions have been well recognized (*18*). We strongly disagree with Dr. Saxe's conclusions that these results suggest problems with reproducibility and representativeness. We are all aware that arsenic leaching to groundwater associated with MSMA application is determined by a number of factors, particularly by the soil composition and rainfall. We discussed the reproducibility issue in our paper. Again, because most Florida golf course soils are very sandy, it is incorrect to simply compare the arsenic leaching rate from South Florida soil to those from other places without considering the experimental conditions used.

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