AGRICULTURAL AND FOOD CHEMISTRY

CORRESPONDENCE/REBUTTAL

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

Sir: Feng et al. (1) present a study in which the herbicide monosodium methanearsonate (MSMA) was applied to test plots simulating golf course greens and water percolated through the soil was analyzed for arsenic compounds. The authors concluded that (1) all of the arsenic detected in percolate resulted from MSMA leaching and (2) MSMA transformed *in soil* to dimethylarsinic acid (DMA) and inorganic arsenic, which were detected in the percolate. However, the study results do not support these conclusions due to two major weaknesses in the study design: (A) a lack of control plots and (B) disregard of the possible effect of long sampling intervals on the sample composition [percolate was collected in nonsterile underground stainless steel storage vessels for 1-2 weeks at warm ambient temperatures (22-29 °C) (2)].

(A) The study soils contained arsenic even before MSMA application. The data from Feng et al. (1) show that the arsenic in the percolate totaled 12–40% of the natural arsenic present in test soils prior to MSMA application [calculated by dividing the amount of arsenic leached (i.e., $20-55 \text{ mg m}^{-2}$ from Figure 1 of (1)) by the total amount present in the test plot prior to the experiment (i.e., the background arsenic concentration (0.27–0.34 mg kg⁻¹) multiplied by the specific plot volume (0.3 m³ m⁻²) multiplied by a typical value for sand density (1700 kg m⁻³))], but only 18.6%, at most, of the arsenic applied as MSMA. Thus, 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.

(B) The authors tested sample storage stability after sample collection from underground holding vessels, thus acknowledging the possibility that arsenic compounds were susceptible to transformation. In those tests, percolate was preserved cold and analyzed rapidly-conditions contrary to those in which percolate water had been held underground. 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 (e.g., refs 3-5) and may be due to experimental artifact. Shariatpanahi et al. (6) showed that some common soil microorganisms (e.g., Pseudomonas spp.) have the ability to demethylate MSMA. Pseudomonas are known also to readily and tenaciously adhere to stainless steel, forming an active biofilm capable of metabolizing chemicals, even when substrates are present in only trace amounts (7-9). Feng et al. allowed percolate samples to accumulate for 1-2 weeks in stainless steel lysimeters (10) before collection and analysis. These conditions favor the growth of microorganisms and raise

the likelihood of biotransformation of arsenic compounds in the lysimeter *after* leaching from soil.

These two major weaknesses in the study design prevent the data from explaining the leaching and transformation behavior of MSMA in soil. There are additional concerns that undermine the authors' conclusions and/or limit the scope of the data's applicability: (a) The presence of arsenic sources besides MSMA was not ruled out. For example, the authors could not rule out that the buried boxes holding test soils were constructed of wood treated with chromated copper arsenate (10); fertilizers added to the test plots were not tested for arsenic content, although numerous fertilizers contain substantial arsenic concentrations; and irrigation water was not regularly tested for arsenic, although it was drawn from ponds in areas where fertilizers were used (10). (b) The study was conducted on simulated golf course greens, the segments of golf courses where drainage (and thus leaching) is designed to be most rapid; however, MSMA is rarely, if ever, applied to golf course greens (11), and given this practice, the product label is being revised to disallow future use on greens (12), so the study's design is likely to overestimate arsenic leaching to groundwater beneath golf courses, which is noted as the question at which the study is aimed. (c) There was a high degree of variability among replicate plots, suggesting problems with reproducibility and representativeness. (d) The apparent depth of leaching is greater than in all other comparable published studies located (see, e.g., refs 13-15). The test plot construction (2 m \times 0.5 m, wood sidewalls) raises the possibility of short-circuit flow along soil packing inconsistencies or wooden walls during irrigation and rainfall events, which would exaggerate the appearance of leaching.

In summary, the authors' conclusions regarding MSMA transport and transformation, especially as conveyed in Figure 5, are seriously undermined because of the cumulative effect of these concerns.

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