MSMA

A loaded gun to your head?

By Dr. Phil Busey

That's harsh language, but it metaphorically describes the situation of those of us who use MSMA. Monosodium methanearsonate (MSMA) is the most effective broad-spectrum postemergence grass herbicide for use in bermudagrass golf and sports turf. It's also a heavy element and Class A human carcinogen.

Each typical application of MSMA adds to the environment 1.0 kg/ha (nearly one pound per acre) of elemental arsenic. Two to four applications may be required for a single series of treatments to control grass weeds such as goosegrass.

Arsenic has only slight volatility, that is, tendency to evaporate; therefore additional applications will, for the most part, either accumulate at increasingly higher concentrations in soil, or move in water. The Florida Department of Environmental Protection's Leslie Smith said that, south of Orlando, one should be concerned about both a groundwater and soil problem. Her remarks (including the loaded-gun expression) were made at the United States Golf Association Green Section Regional Conference in Palm Beach Gardens, Nov. 14.

One attendee asked Leslie, "What's its half-life?" She correctly pointed out that as an element, arsenic never breaks down. To emphasize that in my own way, I say, "its half-life is infinity."

So you can study to no end the complex models for the transformation of arsenic compounds, some of which are more toxic than others, but the bottom line is, the majority of the arsenic stays around. (Unless the owner pays someone to excavate the golf course or sports field and move the arsenic to someone else's property.) What little leaches into the groundwater may be a serious health problem in some cases, but will not diminish greatly what is accumulated in the soil.

If a single application of MSMA were mixed thoroughly in the top 15 cm (about 6 inches) of soil, based on a bulk density of 1.5, there would be a concentration of 474 ppb elemental arsenic in the soil throughout the root zone. This exceeds the existing 400 ppb soil screening level of the US Environmental Protection Administration. In one application. If even a small percentage of the arsenic reached the drinking water, it would also exceed the EPA limit of 10 ppb arsenic in drinking water, depending on the level of dilution.

Houston, we have a problem.

Or do we? Ironically, MSMA has a very low acute toxicity, based on a high LD50. It takes a relatively large lethal dose to kill 50 percent of laboratory animals. The acute oral LD50 is 2833 mg/kg for rats. For an 80-kilogram rat, about the weight of an adult human male, that would be equal to about 9 shot glasses, a pretty distasteful and unrealistic way to die. The chronic effects of small doses are not easily predicted, but arsenic is not good to be in contact with. If I were an 80-kilogram rat, I'd be more concerned about chronic exposure to MSMA, than the unlikely shot glass. And that's why I always wear protective clothing, whatever I am spraying.

When was MSMA first used in turf in Florida?

MSMA was first used publicly in 1963, and by 1967 Dr. Evert O. Burt of the University of Florida, Fort Lauderdale, reported that it was equal or slightly more effective than disodium methanearsonate (DSMA) for grassy weed control in bermudagrass. Although that was a long time ago, both DSMA and MSMA were already late arrivals. The arsenicals as a group were the first chemicals widely tested for chemical weed control. Long before the 1942 discovery of the phenoxyacetic acid herbicides (e.g., 2,4-D), the US Army Corps of Engineers was using sodium arsenite for control of water hyacinth in Louisiana, in 1902.

Some of the early arsenical products used in Florida turfgrass include the Florida East Coast Fertilizer Company's S.A.M.A. 70, a monosodium arsenical, possibly MSMA, and Dal-E Rad 70, a DSMA powder by Vineland Chemical Company. These products usually required four applications to give a serious chance to eliminate goosegrass, especially the more mature goosegrass. Very mature goosegrass could not be controlled.

Aware of the hazards of arsenic, scientists attempted for years to find replacements. In describing metribuzin as such a prospect in 1979, the University of Georgia's Dr. B. J. Johnson said as an afterthought, "If EPA takes MSMA off the market, we may be left with Sencor as our base material."

Rather than seeing MSMA disappear, however, Dr. Johnson made it better by developing (with others) the synergistic combination of tank mixtures with the triazine herbicide metribuzin.

Sencor was Mobay Chemical Company's formulation of metribuzin, and Dupont had attempted to develop another formulation called Lexon. Another chemical, methazole, formulated as Probe, was being looked at along with metribuzin, but by 1993 its herbicide registration was voluntarily canceled by Sandoz Agro, Inc.

It was the MSMA + metribuzin tank mixture that proved to be very effective at selective control of goosegrass, even mature goosegrass, in bermudagrass turf. The number of sequential applications of MSMA could be reduced from four to two, and with a little bit of metribuzin as Sencor, there would be better goosegrass control than with MSMA alone.

I was present at a 1976 meeting in Arkansas when Dr. Johnson described the promise of metribuzin for goosegrass control in fairways. By 1978, Dr. Max Brown described in the South Florida Green (Volume 5 No. 3) that Sencor could be used for grass weed control. But tank mixtures with MSMA were not mentioned.

History in the Making

The big breakthrough for Florida golf course superintendents and sports turf managers came around 1979, when Dr. B. J. Johnson described metribuzin as the "best product researched and now on the market" for grass weed control in bermudagrass, and he described a 1/8-pound-per-acre active ingredient metribuzin tank-mixed with 2 pounds active ingredient MSMA. At that time he had done some three years of research on MSMA + metribuzin tank mixtures. The interview was conducted by Dave Bailey, at that time superintendent of Atlantis Country Club, and staff writer for *The South Florida Green* which was edited by Dan Jones.

There was also a flurry of abstracts (not full scientific reports), also in 1979, by Dr. Johnson, as well as by the University of Arkansas's Dr. John King, and the University of Florida's J. A. Tucker and Dr. Wayne L. Currey. There followed a full scientific article on the subject by Dr. Johnson, in 1980. I first became aware of the MSMA+metribuzin tank mix in the summer of 1980, when my bermudagrass breeding plots were overrun with crowfootgrass. But I opted not to include the metribuzin because it was still too new, and I didn't want to take a chance of messing up my experiment.

The Lost Discovery?

One of the interesting mysteries about the MSMA + metribuzin tank mixture is that the first scientific report goes back to 1974. This synergistic mixture was reported in *Agronomy Journal*, a widely disseminated journal, by the University of Hawaii's Dr. Chuck L. Murdoch and David Ikeda. Dr. Johnson was aware of that paper in 1975, because he cited Murdoch and Ikeda's work when he published a study involving MSMA and metribuzin. But the most novel aspect of the Hawaii paper was the tank mixture, which was not a part of Johnson's studies until later.

In conclusion, MSMA appears to have been used in Florida since the mid-1960s for postemergence goosegrass and other grassy weed control in bermudagrass turf. DSMA had formerly been used for the same purpose, but did become established. MSMA was not very effective against mature goosegrass until 1979 or 1980, when the MSMA + metribuzin tank mixture swept the industry based largely on the research of Dr. B. J. Johnson. The same mixture was reported, and appears to have been ignored, from work in Hawaii in the early 1970s.

These dates are approximate, but based on written documentation. If anyone has a better memory of the history of MSMA use, I would appreciate hearing from you.

Peter Harrison responds on Organic Arsenicals (MSMA question)

I have no issue with the question mark over using, and the soil accumulation data regarding the organic arsenicals. However, the arsenic while it *remains* in the soil is an unlikely problem for workers and users, and I also support your comments regarding sprayer user and protection, where chronic problems *may* occur, although I am not aware of reported problems. Movement from soil is a medium-term problem and of increasing interest.

Arsenic in soil and water, esp. mobile forms is an ongoing issue in a number of areas including widespread problems in at least one country (Bangladesh, where well water can be serious health problem if drunk), old precious-metal mining areas, older tanneries (where arsenic compounds were used at times) even soil in old animal yards and quite a lot of work is being done and some has been published about converting this to nonmobile forms in the soil/water. Some soil microbial solutions are being touted, among various options.

It will not "go away" as you point out, but it may be made a minor issue for those areas where transfer to groundwater, etc. is a problem. Solutions to the issue may arise from left field in areas of bioremediation and phytoremediation sciences... but there is no doubt that these products do an excellent job with weeds... including many sedges, notwithstanding newer products that have become available. Often their use can be moderated by practicing some rotational use among products, a sound ecological practice anyway, although immediate costs are sure to rise.

Similar issues and concepts over the arsenicals are receiving thoughts in Australia, so Florida is not alone. I am looking forward to the balance of the articles.

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MSMA vs. other sources of Arsenic: Phil Busey replies to Peter Harrison

Peter correctly points out the global aspects of arsenic pollution arising from many sources. In Florida and other warm U.S. states, we have leftover CDVs (Cattle Dipping Vats) used by government mandate from 1917 to 1944 to dunk cattle in an arsenic solution (probably arsenic trioxide) to successfully eradicate Cattle Fever Ticks that were causing 50 percent mortality. This nice brew was augmented later with DDT, toxaphene, and chlordane, and the arsenic was later dropped. Cattle could only be moved short distances; therefore Florida has a legacy of 3200 CDVs with a high concentration of arsenic in the soil.

Since then, many "safer" acaricides and insecticides and anthelminthics have been developed for veterinary use in the tropics, subtropics, and warm areas where animal husbandry people have so many difficulties with worms, bots, ticks, etc. Unfortunately, the narrow-spectrum "safer" pesticides are often prone to break down due to evolution of resistance in the target pest, whereas the legacy products of arsenic are dependable poisons.

Today most of the concern and press coverage on arsenic in the U.S. is about CCA (chromated copper arsenate) used to treat lumber for outdoor use, such as playgrounds. I had trouble understanding this, considering the seemingly small areas affected, and the fact that I didn't eat playground equipment when I was a kid. However, as I point out below, CCA-treated wood accounts for about 60 percent of the import of arsenic to Florida. But the story is never simple.

In one instance in Broward County, after a playground was remediated by replacing soil and play equipment, the sampling extended into adjacent areas of bermudagrass turf maintained with MSMA, and, no surprise, there was arsenic there also.

Natural background levels of arsenic vary tremendously around the world. While the geometric mean of 441 near-pristine Florida soils was reported by the University of Florida's Dr. Lena Q. Ma and coworkers as 0.42 mg/kg (420 parts per billion), marl soils such as in Everglades National Park average around 5 mg/kg (around 500 ppb) which exceeds the Florida Department of Environmental Protection (FDEP) industrial soil cleanup goal of 370 ppb, and far exceeds the residential soil cleanup goal of 80 ppb.

No one is talking about excavating the Everglades to remediate a natural background arsenic level exceeding the environmental guidelines. Much of the arsenic there is tied up pretty well by calcite, organic matter, and with oxides of iron and aluminum, depending on pH, and the labyrinth of transformations that arsenic can undergo. The point is to use different background levels appropriate to different soils. And it is extremely difficult to predict what will cause arsenic to show up in drinking water.

Worldwide the major problem with arsenic involves entirely natural origins in well water used by people. The longest-term unintended experiments involving human consumption of arsenic in water have involved skin cancers in Taiwan, and internal cancers in Taiwan, Chile, and Argentina. Many of the natural sources exceeded 500 micrograms per liter (parts per billion), which is associated with approximately a 1-in-10 lifetime chance of internal cancer. The U.S. Environmental Protection Agency threshold is now 10 ppb.

The arsenic crisis in West Bengal and Bangladesh was due to the well-intentioned efforts to provide a safe drinking water supply, free from the problem of gastrointestinal microbes. For example, UNICEF and the Bangladesh Department of Public

Health Engineering, and later private partners, installed some 3 million tube-wells, mostly since the 1980s, and unknowingly at the time the majority of wells were contaminated with horrendous levels of arsenic which was released from natural arsenic-bearing aquifer sediments.

Since the "safe" drinking water was not tested, the problem was discovered only in 1983 after people, eventually thousands, were diagnosed with arsenic poisoning symptoms, such as gross skin lesions in children. The confirmation of the problem as arsenic contamination of well water was confirmed in 1993, but by 1997, UNICEF was still patting itself on the back for surpassing its 2000 goal of "safe" drinking water.

Bangladesh is now grappling with the largest mass poisoning of a population in history, and if the estimated 200,000 victims of arsenicosis in West Bengal is any indication, the number affected in Bangladesh is far greater, based on 20 million people estimated to have been exposed. The British Geological Survey reported that among 9037 wells tested, 22 percent have arsenic concentrations above 100 micrograms per Liter (ppb).

Arsenic bioaccumulation by lowland plants and aquatic organisms contributes to elevated arsenic in some lowland soils, and bioaccumulation may also be a remedy. The University of Florida's Lena Q. Ma and coworkers showed in *Nature* magazine in 2002 that the brake fern Pteris vittata can accumulate up to 126-fold enrichment of arsenic, and the highest concentration was 22,630 ppm arsenic in the plant. The fern naturally grows better in alkaline environments where arsenic is more available, and grows better in arsenic-contaminated soil than in uncontaminated soil.

As the FDEP's Leslie Smith pointed out on Nov. 14, turf fertilizer cannot be ignored as a possible source of elevated levels of arsenic in golf courses. But the most complete report that would shed light on arsenic in Florida is an extensive draft report, "Quantities of arsenic within the state of Florida, by University of Miami's Dr. Helena Solo-Gabriele and others such as UF's Dr. Timothy Townsend. The bottom line is that about 2500 metric tons of arsenic moved into Florida in the year 2000, 60 percent associated with CCA-treated wood, 20 percent from herbicides, 15 percent from geologic sources such as phosphate mining, and 4 percent from coal.

Although Florida has about 50,000 tons of "accessible" natural arsenic reservoirs, including geological reserves, roughly 50 percent is associated with CCA-treated wood, and between 7 and 20 percent is associated with arsenical pesticides. MSMA (and DSMA) were described as a "difficult dilemma since these chemicals are applied in liquid form directly on crops and golf courses. Contamination from these arsenical herbicides is immediate, quick to disperse, and thus difficult to control. Given these observations, efforts in Florida should focus on reducing the use of arsenical herbicides for controlling weed growth on crops and golf courses," and properly dealing with CCA-treated wood and wood waste.

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Editor's Note: While not disputing the obvious import of arsenic into Florida soils through chemical use, I do question some of the figures in the report by Dr. Helena Solo-Gabriele referenced above. In the report they used the generally accepted figure of 150 acres per golf course times 1400 golf courses in Florida to estimate the amount of arsenic applied annually. When you break down the actual acreage per golf course that might logically receive MSMA treatments combined with the fact that many of the 1400 courses don't treat wall to wall or even use MSMA other than some spot treatments, their figures need to be adjusted downward significantly. However, that factor does not relieve superintendents of the responsibility of reducing the use of a product whose final impact to the environment is under scrutiny.

ADA Guidelines Target Golf and Recreational Facilities

If your club is planning to expand or renovate its course or other facilities, you should be aware that the federal government has issued new ADA guidelines that specifically deal with golf courses and