HEAVY METAL FUNGICIDES - SOIL MOVEMENT

Stan Frederiksen, Manager Turf Products Mallinckrodt Chemical Works St. Louis, Missouri

A heavy metal made up the very first fungicide used on turf. In the late 19th century, long before organic non-heavy metal fungicides - indeed long before disease - causing fungi were even partially understood - turf managers knew that something they called "disease" was damaging their grass. On a strictly "I've got to try something" basis, those superintendents, through trial-and-error methods, and using all sorts of concoctions, found that bordeaux mixture, containing <u>copper</u> (a "heavy metal") would control and prevent the "disease". Thus, bordeaux mixture became the turf fungicide, particularly for putting greens on golf courses.

Likely, this chemical would still be a top contender for excellent disease control honors, except that the copper accumulated in the soil, and over a few years, began to damage turf more seriously than did "disease". As a result, bordeaux mixture fell into disfavor, and alternate fungicides were sought, on what amounted to a "crash" basis.

In the early 20's, Dr. John Montieth, then a young plant pathologist at Beltsville, discovered that mercury (a heavy metal), compounded as a 2 to 1 mixture of mercurous and mercuric chlorides, when used at rates as low as 1/2 ounce to 2 ounces per 1,000 square feet, and applied several times a month, was an excellent control for brown patch, dollar spot and other summer turf diseases, and an outstanding preventer of both typhula blight and fusarium patch snow molds through an entire winter when a single 3 ounce per 1,000 square feet treatment was applied in late fall.

In 1926 Mallinckrodt introduced the first turf fungicide, as such, based on Montieth's work. It was a 2 to 1 mix of finely divided mercurous and mercuric chlorides, with special additives, and was called "CALO-CLOR".

Competition jumped up immediately, with Woodridge Chemical Company introducing "Woodridge Mixture", Dogget and Pfeil launching their "Dap-Cal", Merck their "Bi-Cal" and Velsical their "2-1".

During the same period, heavy metal mercury, "<u>inorganic</u>" as the mercurous and mercuric chlorides, was also introduced by Cleary and duPont in <u>organic</u> form -Cleary with Phenyl Mercuric Acetate solution (PMAS) and duPont with their hydroxymercurichlorophenol. (Semesan).

Also appearing, beginning in the early 50's were variations of another heavy metal - Cadmium. Cleary introduced Caddy, a 20% solution of inorganic cadmium chloride, shortly after Mallinckrodt had launched CADMINATE, based on <u>organic</u> cadmium succinate. Later fungicides, such as broad-spectrum KROMAD, also contain cadmium as an active ingredient.

During all the years the heavy metals fungicides have been on the market they've been intended <u>only</u> for <u>professional</u> use - never, so far as I know, for homeowner use. Because of inherent user caution, over the entire period since 1926

37

we've never seen documented a single case of injury or death attributable to the use of either mercury or cadmium fungicides on professionally maintained fine turf.

Now there's agitation to ban the heavy metals from agriculture (which includes turf use) on several bases:

- 1. It is said there's danger of heavy metals adversely affecting the environment, just as a general principle.
- 2. It's contended that alternate <u>organic non-heavy metal</u> turf fungicides now available make the heavy metals no longer essential in turf management.
- 3. It's alledged that lateral movement through soils will bring them into nearby streams and ponds, where methylation will occur, getting the heavy metals into fish and other edible water inhabitants, and thus into the "food chain".

Let's tackle these contentions briefly, one by one.

First, as regards heavy metals adversely affecting the environment, this is, of course, a possibility. However, such a problem would have to be created almost purposefully or by sheer gross negligence, because the heavy metals are, in themselves, integral parts of the physical earth. For example, there are millions of tons in the oceans of the world and in the many fossil fuels routinely used as energy sources. No one has yet discovered a way to remove them, because the laws of the Universe assure that, aside from an occasional "space probe" that may carry a small capsule of something out beyond our solar system, or the remote possibility that a stray asteroid from outer space may strike the earth, <u>nothing</u> can ever be added to, or subtracted from, the physical earth. This means that essentially all mercury and cadmium now present in the earth was here when the earth was born - and no matter what <u>man</u> may do, these elements will remain here on into the dim and indefinite future.

Oh, there have been instances of stream and lake pollution with mercury and cadmium effluents from industrial plants, but this is essentially a problem of complete disregard for the local environment - and is more of a "housekeeping" problem than an "ecology" problem. It has now been largely eliminated by the industrial plants themselves, through their own control measure and re-cycling techniques.

Secondly, concerning new <u>non-heavy</u> metals turf fungicides now being available to fully replace the mercurials and cadmiums, this turns out to be "wishful thinking". No non-metallic fungicide has yet been found adequate to control all major snow mold diseases, including typhula blight, fusarium patch, sclerotinia and other unidentified basidiomycetes. Several promoted to control one or the other have provided a degree of control. However, there are indications that in continued use they may not provide control, because of developed resistances or a shift in pathogen dominance. It was precisely these facts which persuaded Minnesota and Wisconsin (both of which had banned heavy metals fungicides for <u>all</u> purposes) to re-instate the mercurials specifically for fine turf use.

The situation is quite similar in connection with control of summer diseases. Well documented is the case of the midwestern superintendent whose turf disease control program included periodic sprays of <u>all greens</u>, tees and fairways with the familiar combination of thiram and mercury, the latter in either organic or inorganic form. His entire bentgrass course had been free from all summer diseases, including deadly pythium. This meshed precisely with a USGA Green Section representative's statement several years back, when he said "I've seldom seen pythium on turf areas routinely sprayed with <u>mercurials</u>". When this superintendent was persuaded by two chemical companies to try their new "systemics", one on each of two fairways, (instead of his standard thiram/mercury combination) pythium promptly broke out on his course. Significantly, the <u>only</u> pythium on the course clobbered the two fairways treated with the two new "systemics". There was <u>no pythium</u> on any of the sixteen fairways treated with the standard thiram-mercury mix.

More recently, limitations have been discovered with some of the <u>non-heavy</u> metal "systemic" fungicides, in that disease resistances have built up to some of them, and most plant pathologists now recommend alternating the systemics with the tried-and-true <u>contact</u> fungicides, which, of course include mercury and cadmium fungicides.

Thirdly, (and finally), as to the <u>lateral</u> movement of the heavy metals in soils: This facet of the overall concern involves the contention (for example) that a mercury or cadmium fungicide periodically applied to a putting green or tee close to a pond or stream, will "migrate" through the soil <u>laterally</u>, and eventually enter the nearby water, to cause water pollution and potential fish pick-up of the heavy metal.

In early 1971, when the EPA had begun to study mercurial fungicides with a view towards a potential national ban, we determined to approach this problem with reason and objectivity. For help we called upon such authorities in the field as Drs. Howard, Jackson and Fenstermacher at Rhode Island, Dr. Virgil Freed at Oregon State, Dr. Ward Stienstra of Minnesota and Dr. Harry Young, at Oklahoma State, Dr. Martin Harrison of Cornell, and a host of others. Through their unstinting assistance we came up with a highly technical and significant submission to the EPA in January, 1971 and followed it with important amendments in April, 1972. These contained some very important findings, of which the following will be of special interest to you.

- On a Canadian golf green, treated annually with an average of 6 ounces of mercuric chloride per 1,000 square feet, Dr. Jack LeBeau found that substantially all the mercury remained precisely at the application site, and in the top 12 inches of soil. At a depth of 12 to 36 inches, only trace amounts were found. The same trace amounts likely would be found at that depth in distant turf areas which had never been treated with mercurial fungicides.
- 2. At Mohawk Park Country Club in Tulsa in December, 1970 soil samples from a 14-year old green, treated regularly with mercurials, over all its history, disclosed <u>no difference</u> in the mercury content of the water, mud and fish upstream, at the treatment site, and downstream, in a brook adjoining the green.
- 3. At Twin Oaks Country Club, at Springfield, Missouri, a 14-year old green treated summer and winter annually with mercurials was found not to produce lateral movement of the mercury into a stream only 125 feet away.
- 4. Dr. Virgil Freed, on July 1, 1970, wrote to Dr. Frank Howard, "I know of no instance where mercury salts used on turf for disease control in the prescribed manner has caused losses of birds or animals. This can be

attributed to the ready binding of mercury by organic matter and soil colloids. Not only will mercury salts react with the sulfhydral groups of enzymes in plants and microorganismal tissue, but it also reacts with the colloids of soil. The binding, in either case, is very strong, <u>rendering the mercury all but unavailable.</u>" This, among other things, means <u>no lateral</u> movement of the mercury.

5. In the 1970 Rhode Island report on "EVALUATION OF SOME TURFGRASS FUNGICIDES", by Drs. Noel Jackson and Jim Fenstermacher the statement is made "Against fungal diseases of turfgrasses, the mercurials, both inorganic and organic formulations, have held an admirable record for over thirty years as being effective and reliable fungicides with <u>no documented</u> instances of human toxicity or harm to the environment."

All this adds up to (a) the heavy metals turf fungicides remaining at the site where they are applied, and (b) in the top 12 inches of soil where they are tightly bound chemically with the enzymes in plants and microorganism tissues, and (c) there's <u>NO</u> <u>LATERAL MOVEMENT</u> through the soil into even nearby waters, where they could cause problems or pollution to water, mud or fish.

The University of Illinois research group has found, further, that the microflora in soils treated routinely with mercurials, does not differ from that in soils never treated with heavy metals at all.

As regards cadmium, another "heavy metal", a putting green in Wisconsin was found to contain cadmium in significantly larger percentage than the surrounding area <u>ALTHOUGH THAT GREEN HAD NEVER BEEN TREATED WITH ANY CADMIUM</u> <u>FUNGICIDE!</u> Where did the cadmium come from? From routine treatments of <u>sewage</u> <u>sludge fertilizer</u> - which, according to the Sewage Commission Handbook on Milorganite contains cadmium as one of its numerous beneficial trace elements. Here, again, the much lower cadmium content (only a tiny trace) away from the green supports the conclusion of <u>no lateral movement</u> of the cadmium applied as part of the Milorganite. As pointed out earlier, both Minnesota and Wisconsin have re-instated mercurials for turf use. This leaves only New York, Vermont and Connecticut with bans at this time, and we believe they may soon permit variances for turf use.

The most constructive approach to the "be-careful-with-heavy-metals" question may be that voiced by the Dean of the College of Agriculture and Dr. Phil Halisky, Plant Pathologist at Rutgers, during the recent state hearings in New Jersey. They proposed that NO PESTICIDE EVER BE "BANNED" - rather that all pesticides about which there are questions should be placed in "unrestricted" and "restricted" categories, with turf disease control being one of the uses of heavy metals fungicides to be permitted under the "restricted" category.

All pesticides should be used with caution and according to label directions. Responsible actions by the manufacturer and the user are essential requirements in a modern society.

In conclusion, let's <u>not</u> "ban" heavy metals fungicides - let's <u>not</u> "throw out the baby with the bath water". Otherwise, you, as superintendents, might find yourselves in the fix described by Dr. Ward Stienstra, of Minnesota, when, in his December 23, 1970 letter to Bill Small, he wrote "The Turtle River Golf Club was opened for playing August, 1969. That fall no snow mold treatments were applied the following spring no greens remained."