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Dairy Footbaths and Environmental Toxicity of Copper

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Copper sulfate is used in footbath solutions to prevent the spread of digital dermatitis—also known as foot rot or hairy heel warts—in dairy cows. However, spent footbath solutions are often disposed of in the milking center waste and significantly raise the concentration of copper in the slurry. When land-applied over long periods, this slurry raises the levels of copper in the soil, posing a threat to soil, crop, and livestock health.

Improper management and disposal of copper sulfate in footbath solutions pose four primary concerns to dairy producers:

1. The toxicity of excess soil copper to plants may reduce crop yields.
2. Forages grown on copper-enriched soil may become toxic to livestock (Fig. 1).
3. Recycling (such as the on-site reuse of copper-enriched feedstuffs, manure, and/or wastewater) causes copper to accumulate continuously on the dairy farm.
4. Improper management of footbath solution containing copper sulfate may result in a dairy farm being out of compliance with its environmental permit.

Dairy farmers can manage those four issues and protect herd, soil, and crop health by implementing the best management practices described in this publication.

Copper sulfate basics

Copper sulfate is commonly available in bags or pails of dry granules in the form of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). This chemical is highly poisonous and categorized in Toxicity Class I by the Environmental Protection Agency (EPA). Copper sulfate pentahydrate contains slightly more than 25 percent elemental copper.

Photo: DeLaval Inc., 2009

Figure 1. Copper sulfate is commonly used in footbath solutions to prevent the spread of hairy heel warts, but without proper management it poses a threat to soil, crop, and livestock health.

In nature, copper sulfate pentahydrate occurs as a bright blue mineral called chalcanthite. Like the natural mineral, the commercial granules are also bright blue. Other terms for copper sulfate are cupric sulfate,

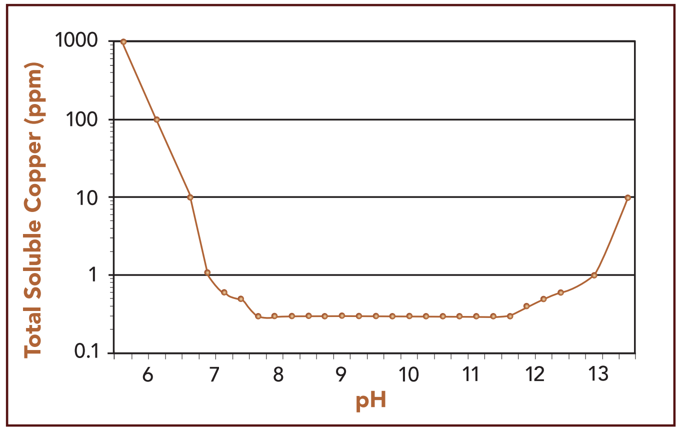
*Research Associate; Professor and Extension Agricultural Engineering Specialist, The Texas A&M University System bluestone, blue vitriol, chalcanthite, copper (II) salt, blue copperas, phyto-bordeaux, bonide copper, and Fehling's solution Part A.

Characteristics of copper in soil

Copper is naturally present in the soil. In the continental United States, the amount of elemental copper in soils ranges from less than 1 to 700 parts per million (ppm); the average is 15 ppm. In Texas, the elemental copper content in soils ranges from less than 1 to about 25 ppm.

Elemental copper is considered a plant micronutrient. Most plants take up less than 0.05 ounces of copper from an acre of soil (Table 1). Copper is not readily available to plants because the copper ion (Cu^{++}) is bound very tightly to organic matter and other soil minerals. The availability of copper to plants is further reduced in calcareous and/or clayey soils.

Because copper is tightly bound to soil particles, it does not readily leach through the soil profile or run off easily, except in acidic, sandy soils. Copper that has been applied to land tends to remain in the upper 6 inches of the soil profile. Copper accumulates in soil because (a) it is relatively immobile, and (b) only a negligible amount is removed by harvesting crops. When the amount of copper in soil rises to toxic levels, remediation is virtually impossible.



Source: Adapted from Pankow,1991.

Figure 2. Total copper solubility in water as a function of pH.

TABLE 1. Average copper uptake by crops

Crop	Plant part	Typical yield per acre	Mean Cu concentration (%)	Mean Cu removal (lb/acre)
Wheat	Straw	1.5 ton	0.0003	0.0000002
Barley	Straw	1.0 ton	0.0005	0.0000003
Corn	Stover	4.5 ton	0.0005	0.0000011
Timothy		2.5 ton	0.0006	0.0000008
Corn	Grain	120 bu	0.0007	0.0015000
Oats	Straw	2.0 ton	0.0008	0.0000008
Alfalfa		4.0 ton	0.0008	0.0000016
Soybeans	Stover	2.0 ton	0.0010	0.0000010
Oats	Grain	80 bu	0.0012	0.0030000
Wheat	Grain	40 bu	0.0013	0.0000260
Bermudagrass		8.0 ton	0.0013	0.0000052
Barley	Grain	50 bu	0.0016	0.0016667
Soybeans	Grain	35 bu	0.0017	0.0009917
Orchardgrass		6.0 ton	0.0017	0.0000051

Source: Adapted from NRCS NEH AWMFH Table 6-6.

Fate and transport of copper

Many toxic chemicals, especially organic chemicals, degrade naturally to relatively harmless forms. Copper is not one of them. Because it is generally present in soils in its elemental form as a positively charged ion, it cannot degrade further. As a result, once in the environment, it persists indefinitely unless it is leached into groundwater or carried away by soil erosion:

- In the case of leaching, copper is more prone to downward movement in low pH soils because the solubility of copper in water increases dramatically with acidity (Fig. 2).
- In the case of erosion, copper binds strongly to suspended solids and tends to accumulate in sediments. Therefore any water or wind erosion that transports particles from soil surfaces will also transport the copper bound to those particles.

Copper toxicity in water

Copper is acutely toxic to all aquatic organisms, especially in soft or acidic water. The negative effects of copper in ecosystems persist for long periods after exposure. The EPA drinking water standard is 1.33 milligrams per liter (mg/L), and levels that stress fish and kill algae are only slightly higher than the freshwater standard of 2.6 micrograms per liter (μg/L).

For example, changes in fish, insect, and invertebrate populations have been observed in streams with copper concentrations above 52 μg/L. Copper is toxic to rainbow trout at 0.1 mg/L and to catfish at 1.7 mg/L. Algae reproduction may be inhibited at 2.0 μg/L copper, and other species of beneficial macroalgae are adversely affected at 5.0 μg/L.

Copper toxicity in soil

The potential for soil toxicity is high where copper-rich manure or wastewater has been applied long-term. Although copper is an essential micronutrient, high concentrations in the soil can be toxic to plants. The degree of copper toxicity varies by plant species.

The toxicity of copper depends primarily on the amount that is available to plants. Plants can tolerate soil with copper levels as high as 125 ppm if most of the copper is not plant available. However, in acidic or mineral soils where copper availability is relatively high, it can become toxic to plants at levels as low as 25 ppm. Copper toxicity has occurred with repeated applications over many years in sandy soils.

Even low levels of copper can significantly damage crops. Copper toxicity reduces the vigor of young plant shoots, causes chlorosis of leaves, and inhibits root development.

Copper is also toxic to beneficial organisms in the soil even at concentrations below regulatory levels. For example, beneficial soil microbes have been harmed by copper at levels as low as 10 ppm in sandy soils with low organic matter content, and 30 ppm in humic soils with high organic matter content. Copper suppresses nitrogen fixation by legumes, harms or kills earthworms, and reduces the activity of soil enzymes.

Extensive use of copper has eliminated most of the living organisms, including microbes and earthworms, in orchard soils. Although microorganisms may develop some resistance to copper over time, its toxicity in soil may increase with time if its availability increases.

Testing soil copper

Different soil test methods may produce different results for the same soil sample, depending on the fraction of copper that is plant available. Tests based on total mineral digestion yield the total amount of copper in the soil. Tests based on the chemical extraction of available minerals generally provide a much lower estimate, depending on the soil conditions.

It is important to test both plant-available and total copper because the unavailable copper has the potential to become available and thereby increase toxicity. To assess the effectiveness of copper management practices, producers must know the amount of total copper that has accumulated in the soil.

Copper toxicity in livestock

Once ingested, copper is easily absorbed into the bloodstream, primarily in the acidic environment of the digestive tract. Although more than 99 percent of ingested copper is excreted in feces, the small amount that remains in the animal accumulates in the liver, brain, heart, kidney, and muscles.

The dietary requirements for copper are similar for most species of livestock, but the tolerance for copper varies widely across species. Table 2 presents estimates of the dietary requirements and tolerance for cattle, swine, sheep, goats, and poultry. Swine and poultry are often fed comparatively high levels of copper to promote growth. In contrast, sheep are particularly sensitive to copper and may die within

TABLE 2. Dietary requirements and tolerance for elemental copper in various livestock*

Copper (mg/kg diet)	Cattle	Swine	Sheep	Goats	Poultry
Requirement	10	5	8	no data	5
Tolerance	100	250	20	20–100**	300***

Conservative estimates derived from National Resource Council data, supported by Payne, 1988, Sutton, 1983, TOXNET Toxicology Data Network, 2001, National Organic Standards Board, 2001.

***Copper tolerance in goats has not been determined but is estimated to be higher than that of sheep and similar to that of cattle.*

****In contrast to NRC data, Fisher Scientific reports a TDLo (lowest published toxic dose) for chickens via parenteral administration of 10 mg/kg with tumorigenic effects (MSDS, 2002).*

hours of ingesting feed containing only 10 ppm. Several sheep deaths have been attributed to ingestion of copper from grazing on land where swine manure had been applied.

Of the primary crops used as livestock feed, forages and corn generally take up little copper. However, the continued application of manure containing copper may eventually increase the amount of copper in plants to levels that are toxic to sensitive species of livestock. We have not yet found evidence of copper toxicity to dairy cattle from high levels in forage, probably because copper is not very mobile in plants and tends to accumulate in the roots.

Copper cycling

A research farm in New York reported a tenfold increase in the concentration of copper in the dairy slurry after it began using copper sulfate in its footbath. Average copper levels rose from 80 ppm (dry basis) to 975 ppm in the slurry and 16,000 ppm in the milking center waste. The copper-laden manure was then land-applied, and after only 2 years the levels of copper in hay silage and corn silage had risen by nearly 40 percent. This forage, once fed back to the cattle, significantly increased the amount of copper in manure.

This cycling of copper on the facility is a self-reinforcing loop. One way of slowing this cycle is to balance livestock rations on the basis of actual copper values in the forage rather than on tabulated averages. Many nutritionists use values from standardized tables to determine the amount of copper in a particular feedstock. The value from laboratory tests should be used instead, especially if the feed was harvested from land fertilized with manure containing copper. If feedstocks meet or exceed NRC requirements or nutritionists' target formulations, avoid using supplements containing copper.

Copper toxicity in manure treatment processes

Anaerobic digestion of manure containing copper may be impaired because the strains of bacteria needed for the digestion process are highly sensitive to copper. The most toxic form of copper to thermophilic digestion processes is soluble copper; concentrations of only 0.5 ppm can inhibit anaerobic digestion. Maintaining a pH above 7.4 will provide some protection for the microbes that produce methane. Adding a chelating agent such as nitrilotriacetic acid may help reduce the amount of soluble copper during anaerobic digestion.

Copper also reduces the biological activity of beneficial microbes in anaerobic lagoons. Problems caused by low bacterial populations in some dairy lagoons have been attributed to copper sulfate footbaths.

Copper levels in manure

The best way to determine the concentration of copper in manure is to have it tested by a reputable laboratory. Standard tables for estimating manure characteristics do not report copper, including those published by the National Resource Conservation Service, American Society of Agricultural and Biological Engineers, and Midwest Plan Service. Other reports vary widely in their values for estimated average concentration of copper in manure.

TABLE 3. Copper concentrations in various as-collected manure sources

Copper (ppm,wb)	Dairy solid	Dairy liquid	Swine solid	Swine liquid	Poultry
Minimum	0	1	165	9	10
Average	5	14	250	74	330
Maximum	40	143	360	174	670

Source: Adapted from Combs, 1996.

In general, swine and poultry manure contain higher levels of copper than does dairy manure. Table 3 shows the average concentrations of copper found in manure from various sources in Wisconsin. The use of copper sulfate by the dairies in the study was not reported.

Copper sulfate accounting

Two easy methods to determine the amount of elemental copper being land-applied are shown in Tables 4 and 5.

TABLE 4. Quick reference for estimated annual copper application rate (lb/acre/yr)*

Weekly usage $CuSO_4$ (lb)	Number of acres							
	5	10	25	50	100	200	750	1000
5	13.2	6.6	2.6	1.3	0.7	0.3	0.1	0.1
10	26.5	13.2	5.3	2.6	1.3	0.7	0.2	0.1
25	66.2	33.1	13.2	6.6	3.3	1.7	0.4	0.3
50	132.3	66.2	26.5	13.2	6.6	3.3	0.9	0.7
100	264.7	132.3	52.9	26.5	13.2	6.6	1.8	1.3

Assumes spent footbath solution is disposed of in manure, and 100% of the manure produced annually is land-applied.

TABLE 5. Annual copper sulfate application rate calculation

Enter the amount of copper sulfate used per week in pounds:		
Multiply by 52 weeks:	x 52	
Multiply by 0.25 (25%); this is the amount of elemental copper in copper sulfate:	x 0.25	
Multiply by the fraction of manure that is land-applied. Unless some manure is diverted off-site or used as a biofuel, this will be 1.0 (100%) for most facilities:	x	
Divide by the total number of acres receiving manure:	÷	
The result is the number of pounds of elemental copper per acre being land-applied annually:	=	

TABLE 6. Estimated number of years to double the background levels of copper in soil

Background copper level in soil (ppm)	Annual copper application rate (lb/ac)							
	10	8	6	4	2	1.0	0.1	0.05
1	0.1	0.2	0.2	0.4	0.7	1.4	14	28
5	0.7	0.9	1.2	2	4	7	70	140
10	1.4	1.8	2	4	7	14	140	280
15	2	3	4	5	11	21	210	420
20	3	4	5	7	14	28	280	560

Based on the upper 6-inch soil profile with bulk density of 1.33 g/cm^3 and zero crop uptake/removal.

To obtain a quick, low-precision estimate, use Table 4. You will need to know how much copper sulfate is used per week in footbath solutions, and the number of acres being used for land application of manure and wastewater. This table assumes that the footbath solution is disposed of in the manure/wastewater system and that all of the manure is land-applied.

Table 6 shows the number of years needed to double the background copper level in soil at various application rates.

Regulation of copper

The EPA has established limits on copper loading to agricultural land when biosolids or sewage sludges are applied (40 CFR 503.13). Manure is a biosolid subject to regulatory limits despite the historical lack of monitoring by the EPA of its trace metals.

If the EPA begins monitoring copper, the annual loading rates of dairies, which typically range from 2 to 11 pounds per acre, are much lower than the regulatory level of 67 pounds per acre per year (Table 7).

The Texas Commission on Environmental Quality (TCEQ) has adopted the EPA levels (30 TAC §312.43). Note that if copper were applied at the maximum annual loading rate, it would take less than 20

TABLE 7. Regulatory limits for land application of copper in biosolids

Ceiling concentration*	Cumulative loading rate	Monthly average concentration*	Annual loading rate
mg/kg product	kg/ha	mg/kg product	kg/ha/yr
4,300	1,500	1,500	75
ppm	lb/ac	ppm	lb/ac/yr
4,300	1,338	1,500	67

Source: Adapted from 40 CFR 503.13.

Copper concentration in manure or biosolid product, not soil.

years to reach the cumulative loading maximum where no further copper could be applied to the soil.

Copper is further regulated by the National Pollutant Discharge Elimination System through its Concentrated Animal Feeding Operation (CAFO) general permit, which the TCEQ administers under 30 TAC 321 B §321.31-321.47. Recently the EPA cited a dairy producer in New Mexico for a permit violation because the dairy disposed of used footbath solution into its treatment lagoon. The citation stated in part that "discharges to containment structures must be composed entirely of wastewater." The CAFO rule in Texas contains similar language, designating retention control structures for the containment of "manure, litter, or wastewater." The charges laid in New Mexico may be an indication of increasing regulatory attention.

Photo: DeLaval Inc., 2009

Figure 3. A footbath such as this one allows the liquid to be drained and managed separately from the milking center waste.

An alternative management option is to dispose of spent footbath solutions containing copper sulfate separately (Fig. 3). However, this practice may trigger restrictive regulations, depending on how the regulator interprets the legislation.

If the footbath liquid cannot be drained or siphoned separately and dried, it can be absorbed with a material such as lime so that no liquid remains and the resulting mixture passes the Paint Filter Liquids Test (EPA Method 9095B). To prevent the waste from being designated as hazardous, adjust the pH of either form of waste to greater than 2.0 and less than 12.5.

Producers may opt to designate the waste as a Class 1 Industrial Waste. The regulations allow farmers to dispose of this waste on their own facility if they notify TCEQ in writing 90 days before the disposal and submit appropriate documentation and a full description of the waste. A permit is not required. Alternatively, the waste may be disposed of at an approved industrial waste disposal site with proper documentation. Although ecologically preferable, managing spent footbath solutions containing copper sulfate separately is not an economical option for most dairies.

Summary of management options

- Handle the footbath solution separately.
- Reduce the copper concentration and frequency of use in footbaths.
- Manage land-application of manure with elevated copper concentrations according to the following recommendations.

Recommendations

The current best management practice is to dilute spent footbath solutions into a large volume of manure and land-apply it according to nutrient management standards. In addition, follow these guidelines to reduce the risk of copper toxicity to crops, livestock, and the local ecosystem:

- Have the soil, crop, manure, and feed analyzed every year to monitor the accumulation and cycling of copper, and compare the results to those of previous years.

- Pay close attention to the strength of the copper sulfate solution in the footbath. Use only enough to maintain hoof health.
- Reduce the amount of copper sulfate used. Consider alternating, rotating, or replacing copper sulfate with alternative treatments such as tetracycline, formalin, or zinc.
- Maintain a regular foot-trimming schedule and provide good, clean flooring and bedding.
- Consider treating individually affected cows with other topical applications instead of treating the whole herd with a copper-based footbath.
- Walk cows through a clean water footbath ahead of the treatment bath to reduce contamination of the solution with manure and to reduce the interval between recharges.
- Dilute spent copper sulfate solution in as large a volume of slurry as possible.
- Prevent spent copper sulfate solution from entering any biological treatment unit such as lagoons, digesters, aerated ponds, or constructed wetlands.
- Avoid applying manure with high copper content continually to the same field.
- Increase the acreage receiving manure, or export manure off-site.
- Export copper-enriched feeds grown on site, and substitute low-copper alternatives from other sources.
- Provide your nutritionist with the actual values of copper in the forage being fed so that the rations are properly balanced.

Keeping spent footbath solution out of the manure is a more formal disposal method and eliminates any risk of toxicity from copper in the solution. However, doing so requires significantly more management, labor, and expense. Dairy producers in areas with naturally high background levels of copper, acidic mineral soils, or those who graze sheep or goats on pastures that receive manure containing copper may benefit from preventing footbath solution from contaminating the manure.

To keep the solution and manure separate, modify the construction of the footbath area so that it can be drained separately. The liquid may then be carefully absorbed with lime and transported in compliance with environmental regulations to an appropriate, approved industrial waste facility.

Summary

- Spent copper sulfate solution is regulated by the EPA whether it is managed separately or commingled with manure or wastewater.
- Separate management triggers restrictive waste regulations.
- The disposal of copper sulfate solution in anaerobic lagoons or runoff holding ponds may be a permit violation.
- Commingling spent copper sulfate solution with manure will eventually result in exceeding the EPA lifetime loading limit if the manure is continuously land-applied on soil.
- Elevated copper in manure will reduce the efficiency and biogas yield of anaerobic digesters and treatment lagoons.
- Herd, soil, and crop health may all be maintained through the judicious use of copper sulfate.

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