

## TRACE METAL TOXICITY FROM MANURE IN IDAHO: EMPHASIS ON COPPER

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### TRACE METALS: TOXIC OR ESSENTIAL

Plants have need for about 18 essential nutrients. Of these essential nutrients, several are classified as trace metals, namely: zinc, iron, manganese, copper, boron, molybdenum, cobalt, and nickel. In addition, other trace metals commonly exist in soil that can be taken up, such as arsenic, chromium, iodine, selenium, and others. Some of these elements are more or less inert in the plant and others can be utilized although they are not essential. Animals also have requirements for trace elements.

Although plants require certain trace elements, excessive quantities generally cause health problems. Plants typically show a variety of symptoms that depend on element and species, but there is generally a lack of vigor and root growth, shortened internodes, and chlorosis. Boron and copper are the two micronutrients most likely to induce toxicity. However, one time high rates of copper have been shown to be tolerated in some cases, but accumulations have been shown to be toxic in others. Copper has been used for centuries as a pesticide and, although bacteria and fungi are relatively more susceptible to it, excessively high exposure is detrimental to plants. Manganese toxicity is also common, but generally only in very acidic soils. Lime application raises pH and reduces the manganese solubility. Zinc and iron have a similar pH relationship, but are less frequently toxic in acid soils. Zinc, iron, manganese, and copper have a known relationship with phosphorus as well. High levels of these nutrients can interact with soil and plant phosphorus to induce a deficiency of this nutrient. Other cationic metals (such as cobalt and nickel) probably have a similar potential. Non essential trace elements have also been shown to be toxic to plants, but this is relatively less common due to their low background levels in most soils.

Animals also require trace elements for good health and many of these can become toxic if ingested in excess. The symptoms and toxicity level are widely varying, depending largely on species, breed, element, and interactions with other elements. Fortunately, these trace elements are commonly absorbed by the body in relation to need rather than amount ingested. Notable exceptions occur with arsenic and iron. Another example is that of chronic copper poisoning in (CCP) that will be focused on in this discussion.

Copper is an essential nutrient, being used for enzymes, immunity, blood, bone, brain cells, and hair/wool. Most animal species require somewhere between 3 and 10 ppm copper in the ration, with higher rates needed as molybdenum, sulfur, and other competitive elements increase. Swine are the notably exception, requiring from 125 to 250 ppm copper. Although the requirement is relatively low for most animals, many species will tolerate higher levels in the ration. Cattle can tolerate up to 100 ppm copper and horses have been shown to tolerate up to 800 ppm, with actual toxic level interacting with mineral balance, species, breed, environmental conditions, stage of growth, etc.

Although CCP is possible with many animals, it is particularly common in sheep. Feed ration levels over 10-20 ppm are likely to cause death within 1 to 2 days. Excess copper over time can result in accumulation in the liver, which can then be released into the bloodstream upon stress (weather, poor nutrition, transportation, etc.) as the liver cells rupture causing a drastic elevation in blood copper

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concentration. Chronic symptoms include anorexia, excessive thirst, and depression. Acute symptoms include anemia, pale mucous membranes, and lethargy followed by jaundice and death within a short time if treatments of excess molybdenum do not work. Given time to develop, post mortem tissues may be found to be pale and yellow with dark kidneys and urine. Dietary amounts of copper sufficient for some sheep breeds can be deficient or toxic to others. The most common incidents of CCP are with mature ewes of British breeds in the western states of the intermountain west.

Reports of CCP in sheep show the most common problems induced by feeding of the wrong ration mix (especially in operations with multiple species) or grazing on ground with applications of manure high in copper. Interactions with pH, other trace elements, etc. can impact the severity of most toxicities and this is certainly true in the case of CCP. A high level of molybdenum in the diet reduces the severity of CCP. A ratio of 10:1 or less of copper to molybdenum is required for sheep. Molybdenum is generally used as an anecdote for CCP and visa-versa for molybdenum toxicity. Sulfur in feed and water adds another dimension by forming complexes with molybdenum and making CCP more likely. Zinc, iron, and calcium are also antagonistic with copper nutrition. Removing trace mineral supplementation is often the first instinct when toxicities develop, but may actually worsen the situation due to the complex interactions among and between the many elements.

CCP is just one example of potential toxicities in animals. Toxicities of other trace elements are certainly possible. Acute problems generally get the most attention and focus, but the effects of long term exposure to high levels of trace elements are also of potential concern. Less is known regarding these effects, but caution is in order. Humans, for example, can tolerate high levels of most vitamins and trace elements. The body absorbs what it needs and most of the rest is secreted in the waste stream. This is not true for all elements, such as iron which can kill when ingested in excess. The cumulative effect of "trace element loading" is potentially a problem as well, but much less is known regarding this issue. The same is true for other animal species.

## TRACE ELEMENTS IN SOIL

Soil minerals naturally contain many chemical elements. Carbon, oxygen, and hydrogen are among the most common components of soils, but silica, iron, manganese, etc. are also present in large quantities. The definition of trace elements seems self explanatory, but it changes depending on whether the phrase is referring to plants or animals. Iron and manganese are certainly not trace elements when it comes to the soil, due to their prolific presence. However, these elements are generally thought of as trace elements from the perspective of animal nutrition. Most of the other metals are considered trace elements from the perspective of both plants and animals. Soils contain varying quantities of many elements (Table 1).

Soils sustain life by providing water and nutrients to microbes, plants, animals, and other organisms. Like most things in life, balance is the key to health. The presence of various organic and inorganic chemicals is essential for healthy soil. Deficiencies, excesses, or in some cases, improper ratios can result in poor soil conditions and may be toxic to the various organisms that live off of the soil. Table 1 shows the amount of nutrients removed in the seed portion of a corn crop. Additional concentrations are found in the crop residue, but the seed is the primary storage compartment and these values are used when calculating export/import balance. It is interesting to note that soil typically contains enough total nutrients to supply plant needs for thousands of years, but it is also important to realize that the soil can "fix" these nutrients in a form not typically available to organisms. This can cause deficiencies in plants and other organisms despite the total amounts available. However, this can be a benefit in reducing potential toxicities if the soil fixes or "neutralizes" these elements when present in excess.

**Table 1.** Essential plant nutrients and their average total amounts found in a six foot soil profile and the amount of removal estimated in terms of both pounds per bushel and pound per average US corn crop. Applying the total to the removal rate, the number of years taken to deplete the soil is estimated assuming no deposition and complete plant availability. Neither of these assumptions is true and the data is only shown to provide a relative indication of nutrients found in the soil compared to removal rates. (Estimates based on US soil database from Servi-Tech laboratories, Hastings, NE; Hopkins, 1998).

Nutrient	Total in Soil	----Corn Removal----		Depletion
	(lb./6 ft.)	(lb./bu.)	(lb./150 bu.)	(years)
chloride	74	0.10	15	5
nitrogen	5,280	1.10	165	32
phosphorus	4,294	0.46	69	62
sulfur	2,736	0.09	13	205
magnesium	8,832	0.22	33	268
zinc	259	0.0023	0.345	751
boron	271	0.0011	0.165	1,644
potassium	527,040	0.98	147	3,585
calcium	463,200	0.22	33	14,036
molybdenum	1,020	0.00005	0.008	136,000
copper	19,560	0.00069	0.104	188,986
iron	844,800	0.013	1.950	433,231
manganese	849,600	0.002	0.300	2,832,000

Elements found inside the mineral structure of the soil are biologically unavailable to plants and other organisms, barring weathering (breakdown) of the mineral structure. Further chemical transformation may also be necessary once the elements are released from the mineral structure. This process of converting mineral bound elements may take decades, centuries, and even millennia before they become biologically available. Organically bound elements can be similarly rendered biologically unavailable, but these compounds are typically cycled much more quickly in terms of months, years, and decades.

The challenge of soil testing for plant available nutrients is to extract a small portion of the total concentrations of soil nutrients that are mostly plant available. Three primary tests are used in the US to extract plant available micronutrients, namely: DTPA, Mehlich 3, and HCl. The later two are acid based and work best in neutral to acid pH soils. Mehlich 3 is emerging as the predominate method due to its high correlation with most of the plant essential nutrients. Mehlich 3 not only utilizes an acid extraction, but also includes a chelate that effectively solubilizes a higher percentage of trace elements. The DTPA test is also chelate based, but is not an acid extraction. It is designed for use on higher pH soils and has been found to be highly correlated with plant availability for some of the nutrient trace minerals such as zinc and manganese. Table 2 shows a comparison of one soil and the three methods commonly used to give an idea of the relative values commonly observed for these methods. The EPA utilizes a fourth extraction for evaluating trace element amounts in soils. This

method is based on a hot acid digestion that more completely dissolves minerals and gives a value more correlated with total nutrient content as compared to plant availability. It is noteworthy to compare the relative plant available values found in Table 2 with the totals found in Table 1.

Measuring toxicity with a soil test is a difficult proposition. Most agricultural soil tests only evaluate plant available zinc, iron, manganese, and copper are designed to examine deficiencies only. In Idaho, the common tests utilized for these nutrients are DTPA for all but boron, which is extracted with hot water. The range of values for each are 0.5 to 10 ppm-zinc, 4 to 400 ppm-iron, 1 to 50 ppm-manganese, 0.2 to 5 ppm-copper, and 0.4 to 2.0 boron. Toxic levels for iron or manganese are highly

**Table 2.** Determination of plant available nutrients for a soil using three different methods. Extraction of the various metal nutrients is dependent upon acidity and strength of chelation and, as a result, sufficiency values are subjective to test used. (Note: different soils will give different results.)

<b>Nutrient</b>	<b>Soil Test Method</b>		
	<b>HCl</b>	<b>Mehlich 3</b>	<b>DTPA</b>
zinc	11	20	1.0
copper	5	6	0.3
iron	66	111	4.2
manganese	45	77	5.7

unlikely in the alkaline conditions common to soils in Idaho. Toxic levels for zinc are also unlikely, but are more apt to occur if levels are excessively higher than the typical range. Boron is much more likely to become toxic at levels just above the average range. This toxicity is very species dependent, with plants such as alfalfa and potatoes having a very high requirement and tolerance and plants such as corn and barley having a much lower requirement and tolerance.

Copper is much more likely to become toxic, but it is unknown at what soil test level this occurs. A suggested rule of thumb is begin being concerned if levels are increasing over the average range listed above and extreme caution should be exercised if the levels are becoming five to ten times greater than the high end of this range (25 to 50 ppm), but this is merely a guess based on very few observations of copper toxicity. The toxicity value for Mehlich 3 is more documented at 50-100 ppm, but this is also largely based on an educated guess rather than significant correlation with toxic values.

The EPA requires testing for several trace elements when municipal or industrial waste is soil applied, such as chromium, cadmium, arsenic, cobalt, molybdenum, and selenium. These tests are again more designed to evaluate total levels in the soil rather than plant availability. Furthermore, the EPA approach to trace metal applications is based on lifetime loading limits designed to exercise extreme caution. For example, the lifetime loading limit for copper is 77 lb-copper per acre. This equates to approximately 35 ppm total copper in the plow layer (six inches) of soil. Most of this copper reverts to unavailable forms and, as such, this level is well below the level that would be considered toxic to plants. It should also be mentioned that copper has been used for centuries as a pesticide. Its toxicity to plants is much higher than most trace elements and its toxicity to microorganisms is relatively higher yet. Reports of high copper levels in manure reducing odor are common. The copper suppresses the activity of bacteria that breakdown the manure and release the gases that cause odor. This odor reduction benefit may be good, but the long-term effects of reducing soil microorganisms may be negative.

As mentioned with the boron, the toxicity of a trace element is dependent upon much more than just soil test. Like animals, plant species are variable in their susceptibility to trace element toxicity. Soil conditions will also make trace elements more or less likely to be toxic. Idaho agricultural soils are predominately alkaline in pH. These relatively high pH soils are more likely to suppress the biological activity of the various trace metals. The pH dependence is greater for some trace elements (iron, zinc, and manganese) and less so for others (copper). The mineralogy of the soil also interacts with biological availability. Idaho soils and irrigation waters are also dominated by the presence of free excess lime, which further reduce the solubility and, thus, the biological availability of most trace metals. Increase of clay percentage in the soil also reduces biological availability of copper.

The organic matter compounds in the soil will also interact with trace metals. In some cases, organic matter makes a metal more biologically available as it protects it from combining with soil minerals to become mostly insoluble. This is the case for zinc and manganese. However, copper is tightly bound by organic matter and, as a result, soils low in organic matter typically have a much lower tolerance for excessively applied copper. The higher the percentage of sand in the soil the more likely it is for the soil to have less water and, as a result, higher temperatures. High soil temperatures are conducive for degradation of organic matter and, as a result, sandy soils tend to have lower organic matter and a much higher susceptibility to copper toxicity from this perspective, as well as that of less clay interaction in sandy soils.

Fortunately, the soil has somewhat of a buffering effect on most of these trace elements. Soil minerals and organic matter effectively reduce the solubility of many trace elements, which allows for application of relatively more than what might be expected if accounting only for short-term plant removal balance.

## HOW DOES TOXICITY DEVELOP?

Naturally present soil minerals can result in toxicity in rare cases. The mining industry is based on the concept that some minerals are higher in metals than others. If the parent material from which the soil is derived is high in one or more of these trace minerals, then this soil is more likely to have toxic levels. However, this condition is rare, as Mother Nature has a remediation effect of topsoil over long periods of time. Soils from mine spoils, however, are more likely to result in toxic conditions. Deposition from eroded mine soils can also result in toxic levels of trace elements.

It is also possible to develop toxic levels of trace elements with fertilizer, although this is also extremely rare. Localized problems occur in the cases of large quantities of fertilizer spillage of micronutrients. From a field wide toxicity perspective, boron is the most likely to become toxic, due to the very narrow range between deficient and toxic for most plants. However, these incidents are very few and far between.

Application of industrial or municipal waste is also a potential problem, but stringent regulations over the last 30 years have essentially eliminated this source as a problem if federal rules are followed and accidents avoided.

Manure is the most likely source of developing toxicity in agricultural soils. Manure applications are largely unregulated (although regulations are increasing for this waste product). The concentration of trace elements in manure can be high, depending upon animal species, feed additives, and presence of other waste products in the effluent stream. Generally speaking, large Confined Animal Feeding Operations (CAFO) are becoming increasingly regulated based on phosphorus soil loading limits and it is unlikely that problems with trace metals will develop if these guidelines are genuinely followed. However, manures with unusually high concentrations of trace metals may induce toxicities if not

managed carefully. Swine and poultry tend to have higher concentrations of trace elements in their diet than most other types of livestock. Increases in selenium and arsenic in certain feed rations may also result in an increase in these elements in manure.

Swine and poultry operations are relatively rare in Idaho. The cattle industry is the predominate source of manure in this state. In Idaho, copper is the trace metal most commonly reported to be high in manure. Cattle manure can be high in copper concentration due to copper sulfate footbaths.

### COPPER SULFATE FOOTBATHS

Cow manure is the most common manure type in Idaho. Dairy cows are confined to small areas and, as a result, are more susceptible to various foot related health problems, such as digital dermatitis or hairy heel warts. Approximately half of the dairies nationally have problems with digital dermatitis, with larger dairies having a relatively greater problem. The common method of preventing foot maladies is a copper sulfate footbath. Disposal of these spent footbaths into the waste stream can result in very high copper concentrations in the manure.

This problem was brought to light by the famous W.H. Miner Agricultural Research Institute case in Chazy, New York. This relatively small herd of 160-190 cows started being treated with 254 lb of copper sulfate dissolved in frequent footbaths in 1998. As a result, the copper concentration in the manure increased from 0.04 lb to 0.81 lb-copper per 1000 gallons of liquid manure. Although this treatment effectively reduced the cases of hairy heel warts to zero, the copper load increased to 3300 lb of copper being applied over 470 acres each year. Calculations show that this is equates to seven lb of copper per acre per year, with normal removal rates well less than 1 lb of copper per acre. The increased copper loading resulted in a doubling of copper concentrations in both the soil tests and the forage material harvested from this land. It is apparent that the soil was “neutralizing” some of the copper, as evidenced by only a doubling of soil and forage values despite a more than ten times increase in the amount of copper being applied in excess of removal. Despite some “neutralizing”, the drastic build up of copper levels in the soil and forage was troubling.

**Table 3.** Average manure values from multi-state survey (Combs, 1998). Copper loading values calculated based on a manure application to provide a 160 lb-N rate.

<b>Type of Manure</b>	<b>min</b>	<b>max</b>	<b>average</b>	<b>Typcial copper loading</b>
	<b>-----ppm copper-----</b>			<b>lb-copper/acre/year</b>
Dairy solid	12	200	27	0.6
Dairy liquid	16	1320	191	2.4
Swine solid	270	515	381	11.1
Swine liquid	146	1923	673	4.9
Poultry solid	35	1350	438	3.7

A multi-state survey of manure found that it was common to have relatively high copper levels in manure (Table 3). This survey showed that the average level of copper in liquid dairy manure was 2.4 lb applied per acre with levels as high as 17 lb per acre (more than twice that found at the Miner Institute). A blind informal survey from Idaho dairies shows lower but similar values. Although this build up copper is concerning, it is important to keep the problem in perspective. Studies have shown that most crops can tolerate relatively high applications of copper and that the soil does “neutralize”

much of the copper in a relatively short amount of time (weeks) (Keith Kelling, University of Wisconsin, Madison WI, personal communication).

Estimations of copper from footbaths can be made by determining the pounds of copper sulfate used weekly and determining the rate based on acres available for disposal. For example, 500 lb-copper sulfate per week over 1000 acres is calculated as follows:

$$\begin{aligned} 500 \text{ lb/week} * 52 \text{ weeks/year} * 25\% &= 6500 \text{ lb annual application} \\ (\text{copper sulfate is generally } 25\% \text{ copper}) \\ 6500 \text{ lb copper} / 1000 \text{ acres} &= 6.5 \text{ lb copper per acre annually} \end{aligned}$$

## MANAGEMENT OF TRACE METALS IN MANURE

It is vital that animal operations comply with any regulations that currently exist and, furthermore, that they voluntarily provide good land stewardship. Continued abuse will lead to more regulations and the associated paperwork, permits, fines, and costs. Biosolids form municipalities and industries are an example of strict regulations and increased costs. The regulations for biosolid copper prevent application if levels exceed 4300 ppm, requiring exponentially higher toxic waste permitting and disposal. None of the manures tested in Table 3 exceeded this level, but it is possible that regulations (if written) could be lower than this for manure. The biosolid regulation for materials having concentrations between 1500 and 4300 ppm is 66 lb per acre of copper annually and a lifetime limit of 1349 lb per acre. No limit is given in the EPA regulations for biosolids with levels below 1500 ppm. These guidelines would lead one to believe that copper in manure isn't a problem based on average concentrations in manure. However, copper in manure (predominately the ionic form) is more biologically active than copper in biosolid waste (typically in the non-ionic form from industrial waste). If regulations are adopted for manure copper levels, they would likely be lower than those for biosolids and, from a practical standpoint, actual problems are more likely developed at a much lower level. Although copper is being used as the example because of it is the predominate concern for trace metal toxicity in Idaho, a similar situation potentially exists for the other trace metals.

From a management perspective, it is important to monitor soil, feed, plant, and manure trace metal concentrations. The greatest difficulty in doing so is obtaining a representative value. Multiple samples from well mixed materials should be sampled from throughout the area, pile, pond, bin, etc. The goal of sampling is to obtain both a range and an average of the materials tested. Unusual or problem spots need to be sampled separately. Records should be maintained over time to determine trends (Fig. 1 and 2). Sustained or dramatic increases in levels should be noted. In most cases, these increases aren't a problem in the short-term, but may become so depending on soil conditions and plant and animal species. The trace element balance is calculated by the following:

**Removal:**

$$\begin{aligned} (\text{Yield} = 5 \text{ tons per acre of alfalfa annually}) \\ (\text{Copper concentration from forage test} = 0.01\% \text{ or } 100 \text{ ppm}) \\ 5 \text{ tons} * 2000 \text{ lb/ton} * 0.01\% &= 1 \text{ lb-copper removed per year of alfalfa production} \end{aligned}$$

**Addition:**

$$\begin{aligned} (\text{Application rate} = 10 \text{ tons per acre annually}) \\ (\text{Copper concentration from manure analysis} = 0.04\% \text{ or } 400 \text{ ppm}) \\ 10 \text{ tons} * 2000 \text{ lb/ton} * 0.04\% &= 8 \text{ lb-copper applied per year of application} \end{aligned}$$

Following such a program as shown in the calculation above will result in 8 lb of copper application with only 1 lb of removal. The soil will "neutralize" some of this copper, but the long-term effects

will build up of copper in the soil and plants growing on it. Eventual toxicity may result with long term use.

There are many approaches to reducing the risk of trace element toxicity in soils. Manure should be spread over as many acres as possible. Excess of trace elements in feed rations should be avoided. Using the most soluble and biologically active form of trace element will often increase its adsorption in the body of animals and reduce the amount excreted into the waste stream. The rate of increase of soil test levels can be reduced by utilizing a crop that has a high removal rate. Multiple cuttings of alfalfa are generally the best method of maximizing trace element removal. In severe cases, unique genetically engineered plant species can be used for phytoremediation by companies that specialize in trace metal cleanup of soils. It is also a good practice to reduce the amount of trace metals in feed rations if the forages being used are correspondingly high (base on testing of the feeds being used rather than average values in the industry).

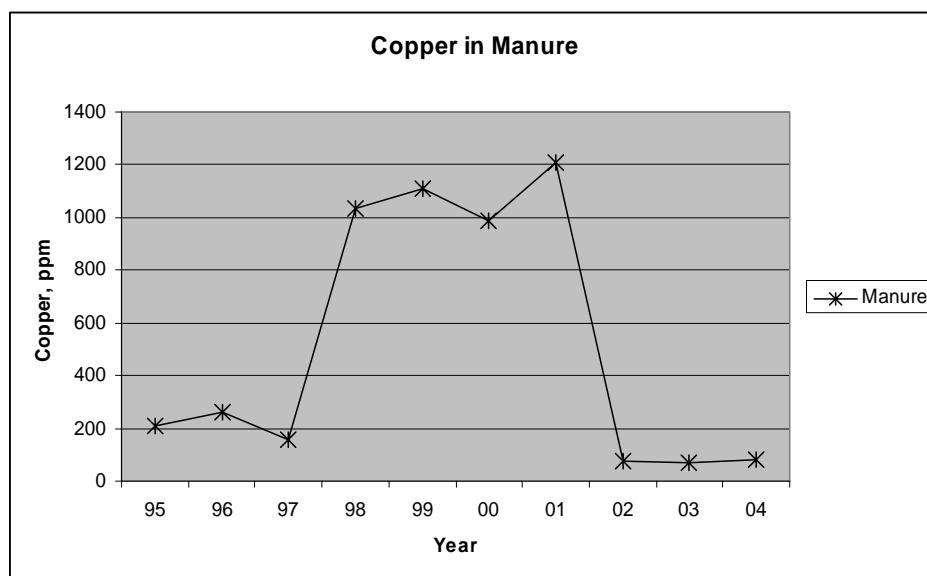


Fig. 1. Copper concentrations in manure over time. Spike in copper concentration in 1998 due to inclusion of spent copper sulfate footbaths into the waste stream. This practice was modified in 2002 due to concerns of copper toxicity in soil and plant tissue.

Soil test and forage copper levels rose quickly in response to increased copper in manure in 1998, but did not drop dramatically once copper was reduced in manure in 2002 (Fig. 1). The ration copper levels spiked significantly in 1998, but adjustments were made in the mineral concentrate added in order to reduce potential toxicity and further buildup of soil and forage copper levels from manure. In the case of footbaths, several approaches can be used to reduce risk of copper toxicity. It is a good practice to place a pre-wash basin (replaced prior to each milking) immediately prior to the copper sulfate footbath to extend the life of the footbath. This reduces the number of times the footbath has to be replaced and, thus, the total copper entering the waste stream. Utilizing a minimum size (8 feet by 2 or 3 feet with a depth of 5 inches) footbath will also reduce the amount of waste generated. (Footbath should placed at the exit to reduce risk of contaminating milk.) It is also important to utilize a nearly 100% water soluble copper sulfate source. Less soluble sources require a higher concentration and result in more copper use. The copper sulfate solution should be carefully calculated to be between 3 and 5%. Lower concentrations reduce foot health effectiveness and higher concentrations are unnecessary. It is also possible to alternate the copper sulfate in the footbaths with other products including zinc sulfate or tetracycline (20 ounces per 60 gallons). The Miller Institute

reduced their footbath treatments from five to three days per week every other week with tetracycline used in the alternating weeks. This approach reduced the copper in the waste stream by 70%, but increased the incidence of hairy heel warts from none to 15%. Formaldehyde was used commonly in the past, but concerns about the carcinogenic formalin have reduced its use. Increasing the feed levels of molybdenum, in particular, and also sulfur, calcium, zinc, and iron will also reduce the likelihood of CCP. It is important to exercise good hoof management techniques for an integrated control

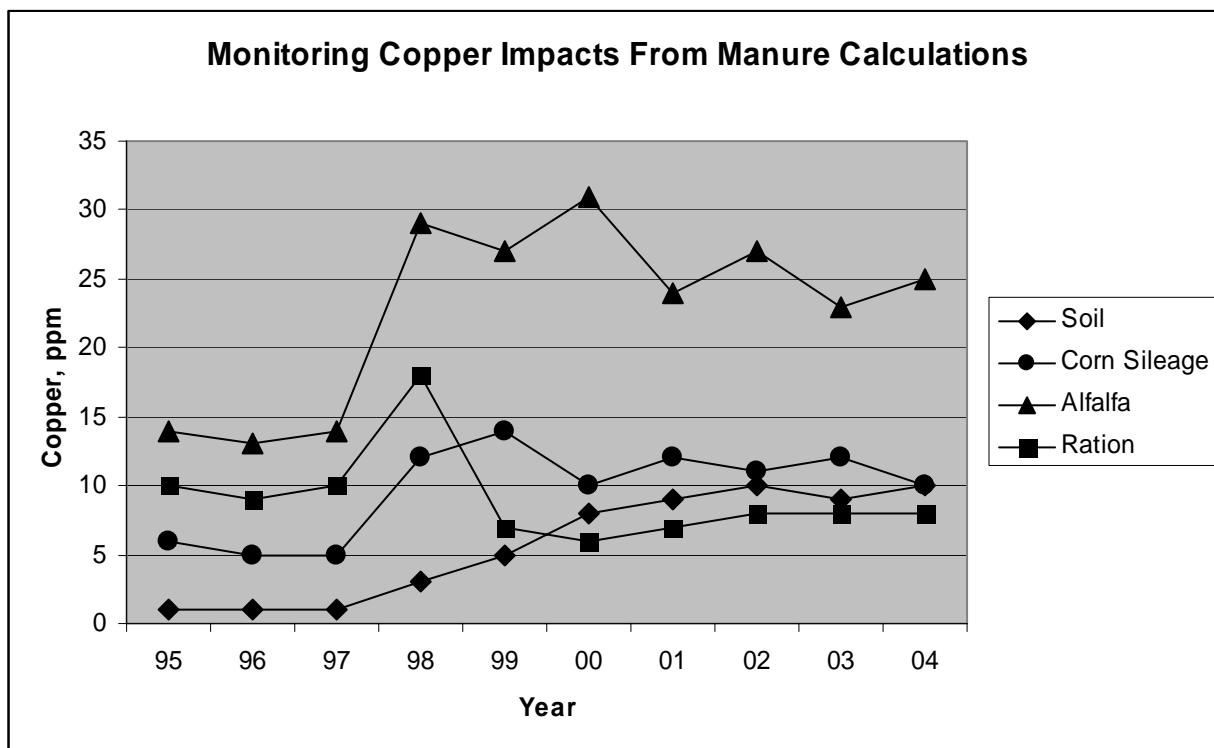


Fig. 2. Monitoring the impacts of copper from manure over time.

program. Avoid excessive slogging through manure/mud or excessive standing on concrete or stoney areas. Reduced stocking rates and clean, dry bedding and good ventilation also help. It is also important to dilute the footbaths well and/or mix the manure prior to application to prevent “hot spots” when the manure is applied.

## SUMMARY

Trace metal toxicity is cause for caution in Idaho, but not alarm in most cases. Many trace metals are required by plants and animals for normal health, but, as with most other things in life, excesses can be toxic. The soil has an ameliorating influence on many of the trace metals, but extremely high rates can overwhelm the equilibrium and result in high levels of biologically active trace elements. It is rare to have naturally high concentrations of trace elements in soils. It is also rare to develop toxicities based on fertilizer and biosolid materials if applied according to appropriate guidelines. Manures represent the greatest concern for trace element toxicity in Idaho soils, although the incidence of these problems is also rare and can be largely avoided by following NRCS guidelines for manure application. Swine and poultry manure generally have the highest concentrations of trace metals due to relatively high amounts of mineral concentrates added to the feed. Copper sulfate footbaths for dairy cattle also represent a concern in Idaho. The amount of copper in the footbaths should be minimized and levels in the soil, plant, feed, and manure should be monitored over time.

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