Copper in farm effluents

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ABSTRACT

Effluent water and sludge samples from a number of dairy and piggery units were collected. These samples were analysed for the free-ionic and the organic-complexed copper (Cu). A glass house experiment was conducted to examine the transformation of Cu in soils and the uptake of Cu by pasture. Three Cu sources were used which included fast-release copper sulphate ($CuSO_4$), slow-release copper oxide (CuO), and sludge Cu. The pasture samples were analysed for Cu concentration. The transformation of Cu in soils was monitored by analysing the soil samples for various fractions of Cu.

The concentration of Cu was higher in the sludge than in the effluent water. Higher concentration of Cu was observed in effluents collected from farms which regularly use Cu to treat lameness and as a growth promoter. The total Cu concentration ranged from < 0.1 to 1.55 mg/litre and from 0.5 to 10.5 mg/litre in the piggery and diary effluent water, respectively. The corresponding values for the sludge samples are 3 - 526 and 25 - 105 mg/kg. Most of the Cu in both the effluent water and the solid sludge material was organically complexed.

The results from the glass house experiment indicated that increasing levels of Cu applied through fertilizers and sludge increased the Cu concentration in plants. At the same rate of application, plants tended to take up less Cu from sludge and CuO fertilizer than from $CuSO_4$ fertilizer. There was however a greater translocation of Cu from root to shoot when Cu was added through sludge application. The Cu fractionation study indicated that there was greater accumulation of organic bound Cu in the sludge treated soils than the fertilizer-treated soils.

KEYWORDS: Copper, dairy cows, farm effluents, growth promoter, lameness, piggery units, plant availability

INTRODUCTION

Copper sulphate is increasingly being used as a footbath in milking yards to treat lameness in dairy cattle and as a growth promoter in piggery units. In some areas with severe lameness problems, as high as 6 kg of copper sulphate is used daily for a herd size of 400 cows during the spring season. In milking yards, the residual copper sulphate solution is often flushed to the effluent pond. The average Cu content in piggery feed in New Zealand is about 125mg Cu per kg of feed.

Copper (Cu) is very strongly bound to organic matter in the effluent and the land application of Cu-rich farm effluents is likely to result in the accumulation of Cu in soils. Copper levels

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are low in some New Zealand soils (Wells, 1957; Haynes and Swift, 1983; McLaren *el al.*, 1984) and in these soils application of Cu-enriched farm effluents can overcome the Cu deficiency in pasture and grazing animals.

Copper is essential for both plants and animals. Copper is involved in the functioning of a wide range of enzymes and is required in very small amounts by both plants and animals. Korte *el al.* (1996) reported wide spread Cu deficiency in grazing animals in New Zealand costing the farming industry several million dollars in animal remediation each year. Excessive accumulation of Cu in soils, however, is toxic to both plants and soil microorganisms. There have been increasing concerns about the safe disposal of Cu-enriched effluents, and the probable effects of Cu-enriched effluents upon soil and pasture qualities need to be examined. The aim of the project is to monitor Cu concentration in the pond effluents of dairy and piggery units and to investigate the transformation of effluent-derived Cu in soils and its subsequent uptake by plants.

MATERIALS AND METHODS

Effluent sampling

Effluent and sludge samples were collected from a number of piggery and dairy units. The amount of Cu used to treatment lameness in the dairy units and as a growth promoter in the piggery units was recorded. The effluent and the sludge samples were analysed for nutrients such as nitrogen, phosphorus and potassium, and a number of heavy metals including Cu.

Plant growth experiment

A completely randomised block design was used in the glass house trial. The treatments included three Cu sources and four Cu levels. The treatments were replicated four times. The sources of Cu used in the plant growth experiment are given in Table 1. The solubility data indicate that $CuSO_4$ is more readily soluble than the other two sources. The fertiliser rates included (0, 25, 50 and 100 mg Cu kg^{-1} soil (0, 2.5, 5 and 10 kg Cu ha^{-1}). After two weeks of Cu application, fifty seeds of rye grass (*Lolium perenne* cv. Super Nui) were sown in each pot. The first Cu-free nutrient solution was given 21 days after sowing and the nutrient solution was added twice a week.

Table 1. Sources of Cu used in plant growth experiment.

Copper source	Copper content	Solubility in water	Supplied by
Copper sulphate	251	100	Ravensdown Fertilisers
Copper oxide	255	0.10	BOP Fertilisers Ltd.
Sludge	5.25	0.01	Cu enriched sludge from Massey University No4 Dairy Unit

The grass was harvested 96 days after sowing. The plants were cut to a height of approximately 1.0 cm from the surface of the soil. The roots were separated from the soil and washed with deionised water. The samples were dried at 70°*C* and their dry weights recorded. The samples were then ground using a coffee grinder and kept in air tight polyethylene bags for chemical analysis. The soil samples were air dried, ground and passed through 2.0 mm sieve. The soil samples were analysed for different Cu fractions (McLaren and Swift, 1976). The plant and the sludge samples were digested using Aristar grade HNO_3 (69%). Copper in the digests and the soil extracts was analysed using a flame atomic absorption Spectrophotometry (F-AAS).

RESULTS AND DISCUSSION

Copper in farm effluents

The range in the concentration of Cu in the piggery and the dairy farms effluent water and sludge samples is given in Table 2. The data indicate that the concentration of total Cu in the effluent water was much less than that of the sludge samples. This indicates that most of the Cu in the treatment ponds is associated with the organic matter in the sludge. In general, the Cu concentration in the sludge was higher in farms which regularly use $CuSO_4$ for lameness treatment and as a growth promoter. In both sludge and effluent water samples, the majority of Cu remains as organic Cu.

Table 2. Cu levels in sludge and pond effluent of dairy and piggery units.

Farms	Cu use	Cu concentration			
		Effluent water (mg/litre)		Sludge (mg/kg)	
		Total	Free	Total	Free
Dairy	Cu used for lameness	2.5-10.5	0.15-0.80	52-105	0.1-0.5
	Cu is not used	0.5-1.5	<0.1	25-42	<0.1
Piggery	Cu used as growth promoter	<0.1-1.55	<0.1	12.5-526	<0.1-0.3
	Cu is not used	<0.1	<0.1	3-105	<0.1

It is interesting to note that very high Cu concentration (526 mg/kg) was observed in the sludge sample collected from one of the piggery units. This farm produces a fish fertilizer which uses high concentration of Cu. The waste from this operation is flushed into the effluent pond which is the main reason for the high concentration of Cu in the sludge. In many piggery units, the solids are screened from the liquid effluent, composted and used as a soil conditioner and nutrient source. These composts arc likely to be enriched with Cu.

Calculations indicated that land application of these effluents, based on N loading of 150kg N/ha, is likely to add < 1 - 31.5 kg and < 1 - 73.7 kg Cu per hectare through effluent water and sludge applications, respectively. Most New Zealand soils require an annual application rate of 2 - 5kg Cu per hectare. Thus, land application of most effluents meets the Cu requirements of pasture; application of effluents from some farms, which regularly use copper sulphate, is likely to result in the build-up of excessive amounts of Cu in soils.

Since effluent application is based on N loading, the rate of Cu loading through effluent water and sludge application is a function of their N contents. With increasing N concentration in the effluent the Cu loading through effluent application is decreased. It has often been found that the N content of farm effluent varies greatly throughout the season. The peak N content of effluent is observed during spring which coincides with the highest incidence of lameness and therefore Cu use. Longhurst *et al.* (2000) stated that the disposal area should be calculated using peak N concentrations. This will ensure Cu loading rates to land are minimised.

Copper is toxic to plants and soil microorganisms only when it is present as free Cu ions. Most of the Cu in both the effluent water and the solid sludge material is present as organically complexed form. Thus only a small amount of free Cu (< 1.0 kg/ha) is added to soils. Thus, majority of the Cu added through effluent application is in organic complexed form which is not toxic to plants and microorganisms.

Plant growth experiment

The dry matter yields of ryegrass for the three Cu sources are given in Figure 1. The data indicate that there was only a small increase in dry matter yields of both shoot and root with the application of $CuSO_4$ and CuO fertilizers. There was, however a significant increase in dry matter yield with increasing levels of Cu addition through sludge application. This may be attributed to addition of other nutrients, especially N through sludge application. At the highest level of sludge application, 228mg N is added per kg of soil which is equivalent to about 25kg N per ha.

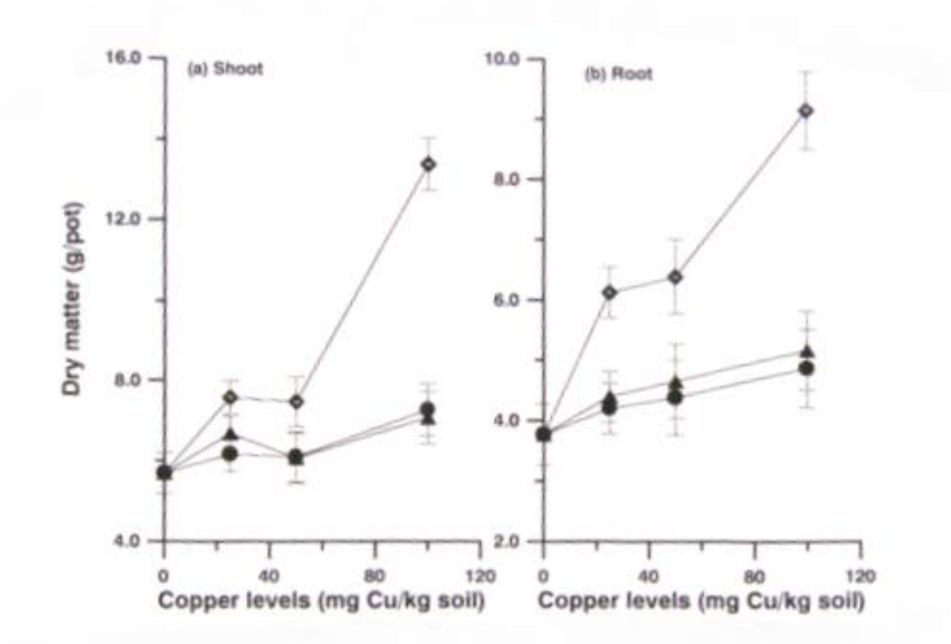

Figure 1. Dry mailer yields of (a) shoot and (b) root with increasing levels of Cu through $CuSO_4$ (•), CuO (Δ) and sludge (♦).

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Khan *et al.* (1996) in an earlier field trial showed that ryegrass yields did not respond to Cu application. It has often been observed that dry matter yield responses to Cu occur only where the Cu concentration in plants is below 4 mg kg ^{1} (Sherrell and Rawnsley, 1982). Forbes (1978), in a survey on the Yellow Brown Pumice soils, found very few pasture stands with <4 mg kg^{-1} Cu, indicating widespread dry matter yield response to Cu is unlikely to occur in these soils.

The Cu concentration in rye grass increased with increasing levels of Cu application, and in general, the Cu concentration was higher in root than in shoot (Fig. 2). It has often observed that Cu is held strongly in roots and there is less movement of Cu from root to shoot (Lidon and Henriqucs, 1993). Application of $CuSO_4$ resulted in the highest Cu concentration both in shoot and root. The difference in Cu concentration in rye grass between the Cu sources is attributed to the difference in the solubility of Cu sources. Copper sulphate is a readily soluble fertiliser, resulting in higher concentration of Cu in plants. There was a large increase in Cu concentration in shoot, with a corresponding decrease in the root, at the highest level of Cu through sludge application. At this level of sludge application the N concentration in the grass was high (5.58% N). High levels of N in roots increase the concentration of amino acids which are involved in the transport of Cu from root to shoot.

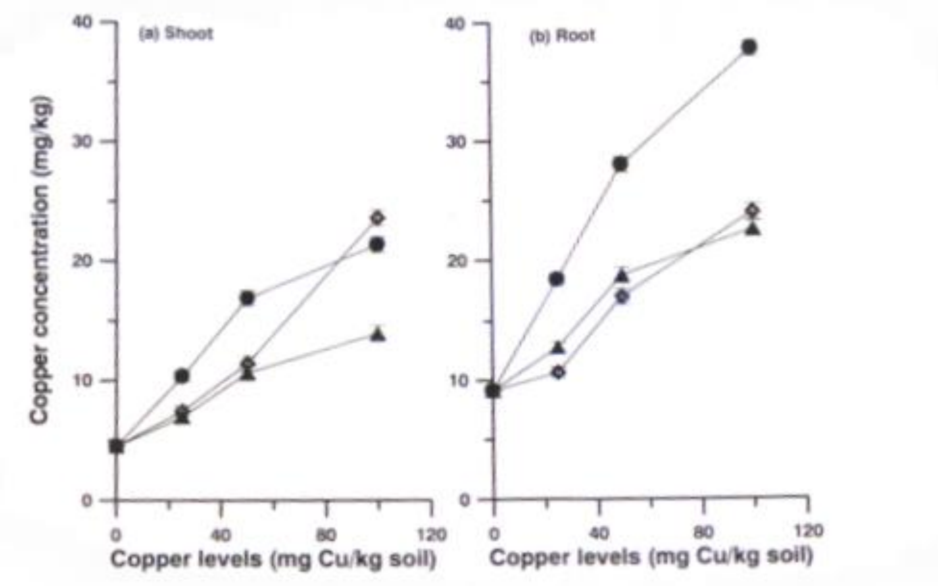

Figure 2. Copper concentration in (a) shool and (b) root with increasing levels of Cu through $CuSO_4$ (•), CuO (Δ) and sludge (♦).

A number of authors observed that increasing levels of Cu through fertilizer application increased the Cu concentration in plants. For example, Sherrell and Rawnsley (1982) found that application of 2 to 4 kg Cu ha^{-1} as $CuSO_4$ increased herbage Cu concentration from 5 to 12 mg kg^{-1} within 28 days after fertilizer application. Similarly. Khan *el al.* (1996) observed that application of 2 to 10 kg Cu ha^{-1} as $CuSO_4$ increased the pasture Cu concentration from 4.8 to 15.89 mg kg^{-1} within 73 days after fertiliser application. Only few studies have examined the effect of farm effluent application on Cu concentration in pasture. In a 12 months field trial, Lowe (1992) observed no increase in pasture Cu concentration with the application of piggery waste at the rates of 165 and 330kg N/ha/yr (equivalent to 2 - 4 kg Cu/ha). Similarly, Baker (1990) observed that applications of Cu-enriched pig manure at the rate of 12.3kg Cu/ha/yr resulted in only a slight increase in herbage Cu concentration.

Soil Copper Fractions

Figure 3 shows the fractions of Cu for the 0 and 100 mg Cu/kg soil treatments. The data show that there was an increase in the concentration of Cu in all fractions with Cu application. More than 80% of soil Cu was present in the organic and oxide bound Cu forms. There was only a small increase in the concentration of exchangeable Cu and the effect was more pronounced in the case of $CuSO_4$ fertilizer. Highest concentration of Cu in the organic fraction was obtained with the application of sludge, which is attributed to high level of organically complexed Cu in the original sludge sample. Highest concentration of oxide bound Cu was obtained with the application of CuO, which may be attributed to the low solubility of this source. There was only a small increase in the residual Cu and the effect was more pronounced in the case of CuO fertilizer.

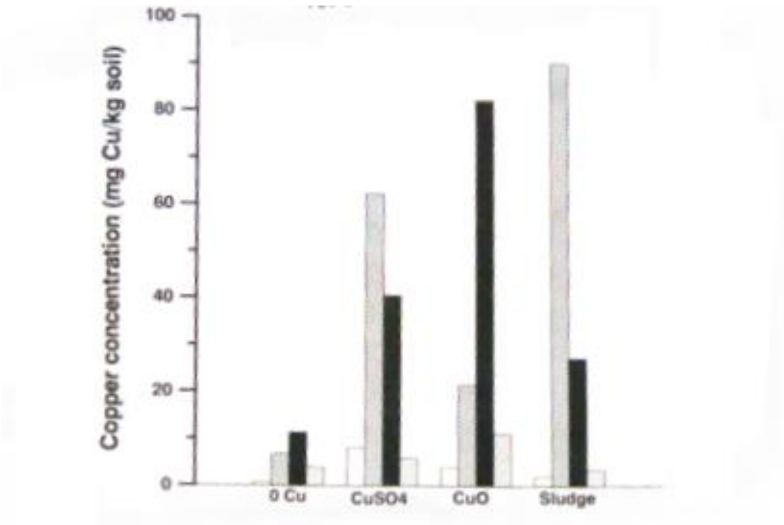

Figure 3. Copper concentration in exchangeable (clear), organic (crossed). oMtk* hound (black) and residual (striped) fractions in soil.

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