An Evaluation of Analytical Methods to Determine Soil Copper Concentration Following High Copper Applications from Dairy Manure

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Introduction

- Use of copper sulfate ($CuSO_4$) in dairy footbaths to maintain foot health is a common practice on dairy farms.
- After the footbath is used, waste material from footbaths often ends up in manure storage and applied to fields.
- Annual application rates of Cu from dairy manure have been observed as high as 31.7 kg/ha at W. H. Miner Agricultural Research Institute (Chazy, NY) .
- Copper applied to fields is not mobile in soil and is bound as Cu^{2+} to clay minerals, Fe and Al oxides, or organic matter (**OM**).
- Determination of plant available Cu is important for determining potential of a negative impact from excess Cu application on crops.
- Extraction of trace minerals by $CaCl_2$ is recommended for determination of available minerals in soils that have received amendments high in trace minerals (McBride and Cherney, 2004).
- Extraction with ammonium acetate (pH 4.8, 1.25 mol L^{-1} acetate), also known as Modified Morgan's Extract (**MME**), is used in Vermont, Maine, and Massachusetts in routine soil testing for the determination of available minerals.

Objectives

The objectives of this experiment were to:

- Determine if soil type, crop, and Cu application rate affected Cu extracted by $CaCl_2$ or MME
- Determine the effect of extraction method on Cu concentration
- Examine the effects of season on the extraction of Cu by $CaCl_2$ or MME

Materials and Methods

- Soils were sampled from 3 different experiments where excess Cu was applied as $CuSO_4$ in dairy manure mixed with soil prior to planting
  - Experiment 1: Orchardgrass (**OG**) and Timothy (**T**) grown in a greenhouse in Trout River Gravelly Sandy Loam (**TRGSL**)
    - Cu application rates: 0, 5.6, and 11.2 kg/ha
  - Expermient 2: OG and T grown in a greenhouse in Roundabout Silt Loam (**RSL**)
    - Cu application rates: 0, 5.6, 11.2, and 18.5 kg/ha
  - Experiment 3: Corn (**C**) grown in field plots in Raynham Silt Loam (**RASL**)
    - Cu application rates: 0, 9.1, and 18.2 kg/ha
    - Plots were soil sampled in the fall following corn harvest and in the following spring prior to a second manure application
- All soils collected were analyzed for Cu concentration by 2 methods
  1. $CaCl_2$ at 90°C extraction (McBride and Cherney, 2004)
  2. Modified Morgan's Extraction (pH 4.8, 1.25 mol L^{-1} acetate)
- All sample extractans were analyzed on an ICP at the University of Vermont Agricultural and Environmental Testing Laboratory (Burlington, VT)

Statistical Analysis

- Cu (mg/kg) determined by $CaCl_2$ and MME was analyzed with Proc Mixed of SAS v. 9.1.3 (SAS Institute Inc., Cary, NC) to determine if Cu concentration differed based on soil type, crop, and Cu application rate.
- Difference ($CaCl_2$ – MME) and mean of 2 extraction methods for each sample was analyzed with Proc Mixed of SAS v. 9.1.3 using a Maximum Allowable Difference (**MAD**) of 0.05 to determine if Cu (mg/kg) extracted was the same based on soil type, crop, and Cu application rate.
- $CaCl_2$ and MME values for corn plots were analyzed with Proc Mixed of SAS v. 9.1.3 to determine if available Cu was different in the soil from fall and spring sampling.

Results and Discussion

Table 1. Means and standard deviations for soil pH, CEC*, and OM of soils used in the 3 experiments.

Soil	pH	CEC*	OM
Trout River Gravelly Sandy Loam (**TRGSL**)	6.6 (0.10)	14.7 (1.10)	7.3 (0.44)
Roundabout Silt Loam (**RSL**)	6.3 (0.20)	12.9 (0.50)	4.6 (0.27)
Raynham Silt Loam (**RASL**)	6.8 (0.36)	12.0 (0.84)	2.4 (0.17)

*CEC = Cation Exchange Capacity

Effect of Soil Type, Crop, and Cu Application Rate on Extraction of Cu by $CaCl_2$

- Extraction of Cu (mg/kg) was influenced by an interaction of the Cu application rate and soil type ($P < 0.001$, Figure 1)
- Lower OM and CEC in the RSL compared to the TRGSL may explain difference in these 2 soil types
- Differences in the growing conditions (outside plots vs. greenhouse) and greater uptake of available Cu by corn may have influenced difference between the RSL and RASL, despite lower CEC and OM in the RASL
- Crop grown did not influence concentration of Cu extracted

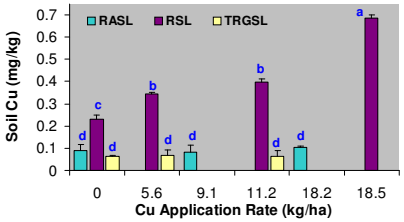

Figure 1. Interaction of Cu application rate and soil type on Cu concentration (mg/kg) extracted by $CaCl_2$. Bars with different letters are significantly different at $P < 0.05$.

Effect of Soil Type, Crop, and Cu Application Rate on Extraction of Cu by MME

- Interaction of Cu Application Rate and Soil Type
  - Extraction of Cu was influenced by an interaction of Cu application rate and soil type ($P < 0.001$, Figure 2)
  - Lower OM and CEC in RSL and RASL compared to TRGSL may explain the difference in soil types
  - Differences in the growing conditions (outside plots vs. greenhouse) may have influenced the difference between RSL and RASL despite lower CEC and OM in RASL
  - Corn grown in RASL experiment may have taken up available Cu as treatment increased
- Interaction of Cu Application Rate and Crop Type
  - At application rates of 11.2 and 18. 5 kg/ha more Cu was extracted from soils where T and OG were grown than C ($P < 0.001$, Figure 3).
  - Interaction likely due to differences in location of the experiments (outside plots vs. greenhouse)
  - Potential for leaching in C and greater uptake of Cu from plots

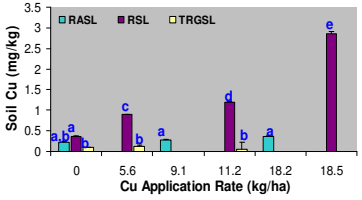

Figure 2. Interaction of Cu application rate and soil type for Cu (mg/kg) extracted by MME. Bars with different letters are significantly different at $P < 0.05$.

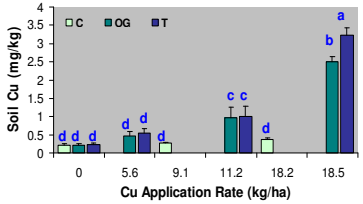

Figure 3. Interaction of Cu application rate and crop type for Cu (mg/kg) extracted by MME. Bars with different letters are significantly different at $P < 0.05$.

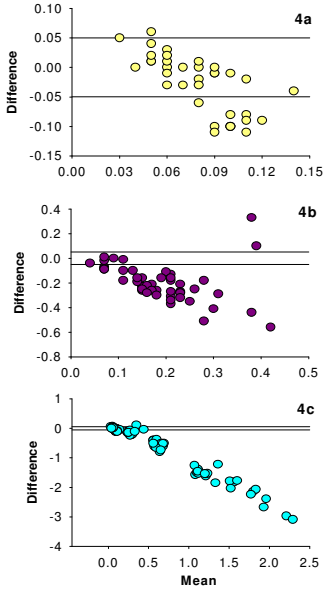

Figure 4abc. Comparison of the $CaCl_2$ and MME extractions for each soil type, mean of the 2 analysis vs. the difference ($CaCl_2$ – MME). (**a**) TRGSL (**b**) RSL (**c**) RASL.

Comparison of $CaCl_2$ and MME Extraction Values

- Due to soil type differences observed in earlier analysis, methods of extraction were first compared by soil type
- All three soil types showed a significant mean bias (Figure 4a, b, c)
- TRGSL was the only soil type where a majority of points fell in MAD
- When compared by crop or application rate values were outside MAD

Comparison of Cu Concentration Determined by $CaCl_2$ and MME for Fall and Spring Soil Samples from RASL

- Tendency for a season effect on the Cu (mg/kg) extracted by $CaCl_2$ ($P = 0.07$, Table 2)
  - Freeze-thaw cycle may be increasing most available Cu fraction
- MME extract showed a significant increase as treatment rate increased
- No effect of season on MME extraction

Table 2. LSMeans for the comparison of $CaCl_2$ and MME extractions from Fall and Spring samples from RASL soil that received excess application of Cu from dairy manure.

	Cu Application Rate (kg/ha)				Application Rate	Season	Season x Application Rate
$CaCl_2$	0	9.1	18.2	SE	*P*	*P*	*P*
Fall	0.09	0.06	0.05	0.02	0.82	0.07	0.26
Spring	0.09	0.11	0.16	0.02			
MME							
Fall	0.22	0.27	0.33	0.02	0.006	0.35	0.56
Spring	0.22	0.29	0.41	0.03			

Conclusions

1. When extracted with $CaCl_2$,Cu (mg/kg) will differ depending on soil type
2. When extracted with MME, Cu (mg/kg) will differ depending on soil type and crop
3. Extraction of Cu (mg/kg) with $CaCl_2$ and MME is similar only for TRGSL
4. Season and freeze-thaw cycles may effect most available fraction of Cu
5. Soil type should be considered when choosing a soil extract and evaluating results

Continued Research

- Further research with more soil types, crops, and soil analysis methods is need to establish recommendations for soil testing of Cu following excess application of Cu in dairy manures.

Acknowledgements
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References

McBride, M. and J. Cherney. 2004. Molybdenum, sulfur, and other trace elements in farm soils and forages after sewage sludge application. Commun. Soil Sci. Plant Anal. 35(3&4):517-535.