



Implication of Particulate Copper (Cu) in the Surface Runoff Transport of Cu From Land to Water Ways



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Introductory notes:

- Soil Cu contamination increases Cu-loading in surface runoff water which impacts water quality (He *et al.*, 2004).
- Copper can be transported to surface runoff water and groundwater in both dissolved and particulate forms (Rice *et al.*, 2002).
- Most Cu in sandy soils in South Florida was found to be in organic and oxide fractions and the organic fraction has a strong correlation with extractable Cu (Fan *et al.*, 2011).
- Soil solution contains organic and inorganic ligands which are capable of forming complexes with Cu, thus increasing total metal solubility (Kabata-Pendias, 2000).
- Water-soluble and exchangeable forms of Cu are especially prone to be released to the environment (Zhang *et al.*, 2003).

Objectives:

- Characterize particulate-Cu (PM) from both soils and surface runoff water with respect to its association with soil components and bio-accessibility.
- Determine chemical speciation of dissolved Cu in soil-water extracts and surface runoff water.
- Evaluate the effectiveness of liming in reducing Cu availability and potential for transport from land to water.

Sample collection procedure:

- 2 representative sandy soils (Alfisol and Spodosol) were collected at 0-20 cm depth randomly from commercial citrus groves.
- Surface runoff water samples were collected from the same field sites as soil samples using a pre-installed auto sampler.
- 3.5 L water samples from each site were collected, homogenized, and sieved (44 μm) to remove any entrained coarse materials.

Materials and methods:

- Soils were spiked with Cu as Cu (NO₃)₂ at levels of 0, 200, 600, and 1000 mg kg⁻¹.
- Treated with lime to raise soil pH to 6 and 7.
- Moisture content maintained constant (70% of WHC) during incubation period.
- Bulk soil PM was collected by particle size fractionation (Soukup *et al.*, 2008; Tang *et al.*, 2009) at soil:water ratio of 1:3.
- PM collected on 0.1 μm membrane and filtrate retained for chemical speciation.

Chemical and statistical analysis:

- Cu estimation by ICP-OES.
- Related soil properties - pH, EC, CEC, AEC, mineralogical composition.
- Available Cu by 0.01 M CaCl₂, 1 M NH₄OAc and Mehlich-III (M-3) extraction.
- Total recoverable Cu by acid digestion method (EPA method 3050B).
- Fractionation of Cu (sequential fractionation) (Amacher, 1996).
- XRD analysis of PM's in surface runoff water.
- Chemical speciation of the dissolved Cu by MINEQL+.
- Statistical analysis-R-program (R version 2.11.1, 2010), JMP 9.0.2 (SAS Institute, 2010); Statistical significance was accepted at α = 0.05 (P<0.05) level.

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Results and discussion section:

- Higher M-3 extraction rate suggests that PM contains larger amount of labile-Cu.
- M-3 extractable Cu increased with increase in total recoverable Cu when soils are grouped according to pH and external Cu load.
- Large portion of Cu in surface runoff PM are organic-and oxide bound; less Cu in readily available form.
- Cu sorbed to soil PM may be more difficult to release into water.

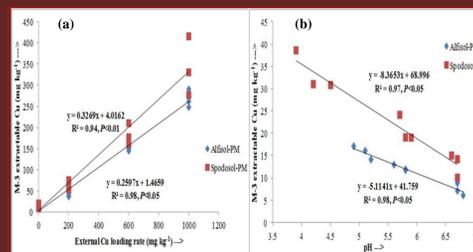


Fig. 1: Relationship between M-3 extractable Cu and (a) external Cu loading, or (b) pH of PM from Alfisol and Spodosol.

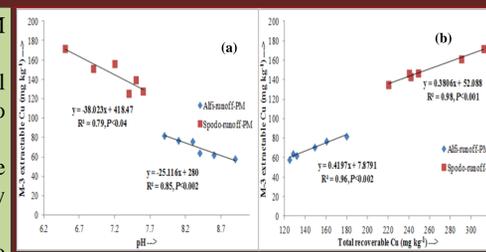


Fig. 2: Relationship between M-3 extractable Cu and (a) pH or (b) total recoverable Cu in PM obtained from surface runoff water.

- Dominance of organically bound Cu indicates control of mobility, fate and transport of Cu by organic matter (OM) from land to surface water via runoff (Fig. 3).
- Higher OM content for Spodosol accounted for greater increase in rate of organically-bound Cu with external Cu load (Fig. 3).
- Alfisol had a larger oxide-Cu rate with increasing external Cu load due to its higher oxide content (Fig. 4).
- Residual Cu increased with increasing pH indicating that addition of lime can restrict availability of Cu in contaminated soils (Fig. 4).
- Alfisol had a greater positive slope than Spodosol with external Cu loading rate, lower OM content, more Cu associated with PM at higher Cu loads. Also organically-bound Cu declined faster in PM than bulk soil at higher pH for Alfisol due to lower OM in the latter (Fig. 5).
- For surface runoff PM, no exchangeable and carbonate bound fractions were detected (data not shown), which may be related to its clay mineral composition: quartz and calcite (Fig. 6), lack of 2:1 clay. Calcite seemed not a good vector for Cu as acid-soluble Cu was minimal.

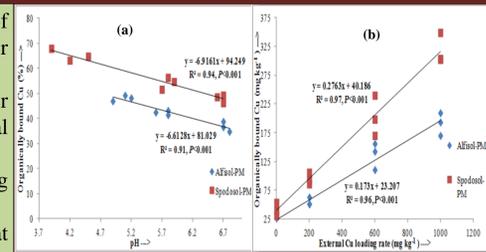


Fig. 3: Relationship between organically bound Cu with (a) pH and (b) external Cu loading rate of PM from both soils.

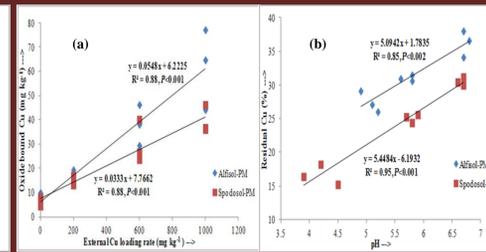


Fig. 4: Relationship between oxide bound Cu and external Cu loading rate (a), and residual Cu and pH of PM from both soils (b).

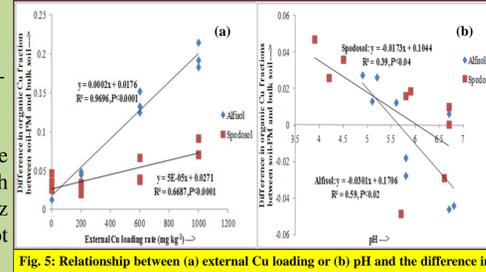


Fig. 5: Relationship between (a) external Cu loading or (b) pH and the difference in organic Cu fraction in soil-PM and bulk soil.

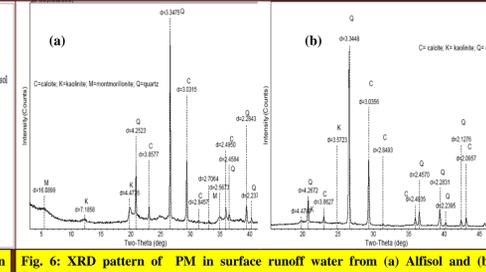


Fig. 6: XRD pattern of PM in surface runoff water from (a) Alfisol and (b) Spodosol.

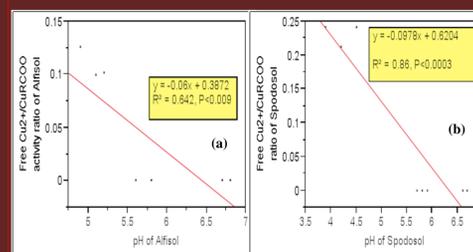


Fig. 7: Relationship between pH and free Cu²⁺/CuRCOO activity ratio in (a) Alfisol and (b) Spodosol.

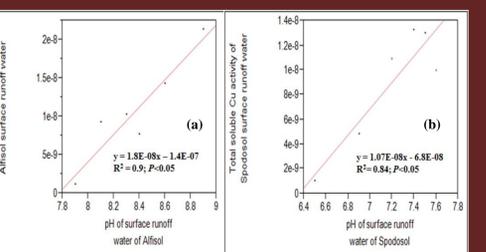


Fig. 8: Relationship between pH and total soluble Cu activity in (a) Alfisol and (b) Spodosol surface runoff water.

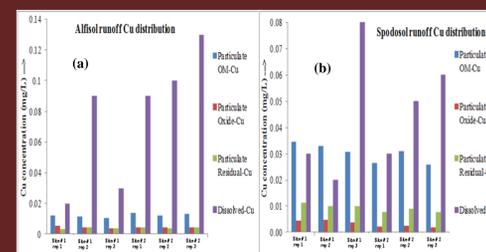


Fig. 9: Cu speciation in surface runoff water from (a) Alfisol and (b) Spodosol.

- From chemical speciation study, with increasing pH, activity of Cu²⁺ decreased, which may be due to a faster decrease in free Cu²⁺ than dissolved organic Cu complexes (Fig.7).
- An increase in total soluble Cu activity with increasing pH may be attributed to the fact that inorganic/organic ligands facilitate the release of metals into soil solution and such effect is greater at higher pH due to stronger complexation of organic ligands with Cu²⁺, which subsequently decreased free Cu²⁺ activity (Fig. 8). OR, may be due to the dominance of hydroxyl species at higher pH.
- In surface runoff water, dissolved Cu, including organic and inorganic Cu complexes, is the major constituent for Cu transport and mobility (Fig. 9).

Conclusions:

- Only a small portion of total recoverable Cu is available to plants, especially in rhizosphere where mobilization of OM and complexation and solubilization of Cu may occur in acidic environments.
- Mehlich-III extractable Cu has a good correlation with total recoverable Cu and can be used as an indicator of Cu availability.
- In PM, a large proportion of total recoverable Cu is associated organic fractions regardless of sources.
- Chemical speciation modeling indicates that activity of free Cu²⁺ can be reduced or converted to different organic and inorganic dissolved complexes at increased pH.
- Liming can be a potential management practice to increase Cu fixation in the soil, thus minimizing Cu mobility.

Take home messages:

- M-3 extraction is the best method for assessing Cu availability and bio-accessibility in sandy soils.
- Cu in PM is dominantly associated with organic fraction.
- Organically bound Cu in PM is highly correlated with total recoverable Cu and pH.
- Organically bound Cu increases with external Cu load and decreases with increasing pH.
- Liming affected Cu availability, as it converts Cu from mobile and available pools to more stable residual forms.
- Cu in surface runoff water is dominantly associated with dissolved organic forms.

Thank you section:

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