American Journal of Analytical Chemistry, 2014, 5, 604-612
Published Online June 2014 in SciRes. http://www.scirp.org/journal/ajac
http://dx.doi.org/10.4236/ajac.2014.59068

Chemical Forms and Phytoavailability of Copper in Soil as Affected by Crop Residues Incorporation

Shahrzad Kabirinejad[1*], Mahmoud Kalbasi[1], Amir Hossein Khoshgoftarmanesh[2], Mehran Hoodaji[1], Majid Afyuni[2]

[1]Department of Agriculture, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran
[2]College of Agriculture, Isfahan University of Technology, Isfahan, Iran
Email: [*]kabirinejad@khuisf.ac.ir

Received 20 April 2014; revised 2 June 2014; accepted 18 June 2014

Copyright © 2014 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/
Open Access

Abstract

Preceding crops as a source of organic matter are important sources of micronutrient and can play an important role in the soil fertility and soil cycling of micronutrients. In addition to the role of the organic matter in increasing the concentration of micronutrients in soil solution, attention should be also paid to the role of the kind and the quantity of the root's exudates released in response to the incorporation of different plant residues in the rhizosphere. Present research was conducted with the objective of studying the effect of the kind of preceding crops: Trifolium (*Trifolium pretense L*) and Sorghum (*Sorghum bicolor L*) on chemical forms of copper (Cu) in solid phases of a calcareous soil in a completely randomized block field experiment with split plot (3 m × 5 m) arrangement, consisting of 3 replications and 3 treatments. After incorporation of the residue, wheat (genotype back cross) was planted. After harvesting the wheat, soil samples were collected from root zone of wheat. Selected soil properties and chemical forms of Cu were determined in the solid phases of the soil samples. Incorporation of plant residues significantly increased the concentration of DTPA-extractable Cu, in the soil. The highest effect was obtained for Trifolium treatment. Incorporation of plant residues decreased the carbonate-bound Cu (Cu-Carb) fraction in the solid phase and increased oxide-bound Cu (Cu-Ox) as compared to the control (fallow treatment). Fraction of organic-bound Cu (Cu-Org) in the soil increased with incorporation of plant residues as compared with the fallow treatment. Trifolium was the most effective in increasing Cu-Org. Cu-Ox and Cu-Residual (Cu-Res) forms showed a significant negative correlation and Cu-Org showed a significant positive correlation with the concentration of DTPA-extractable Cu. Incorporation of *Trifolium* residues decreased the fraction (%) of Cu-Carb and Cu-Ox (less soluble forms) and consequently increased the fraction (%) of Cu-Org which in turn elevated the concentration of DTPA-extractable Cu. *Trifolium* was the most effective in increasing the phytoa-

[*]Corresponding author.

How to cite this paper: Kabirinejad, S., Kalbasi, M., Khoshgoftarmanesh, A.H., Hoodaji, M. and Afyuni, M. (2014) Chemical Forms and Phytoavailability of Copper in Soil as Affected by Crop Residues Incorporation. *American Journal of Analytical Chemistry*, **5**, 604-612. http://dx.doi.org/10.4236/ajac.2014.59068

vailability of Cu in soil.

Keywords

Crop Residues, Copper Fractionation, *Trifolium*, *Sorghum*, DTPA-Extractable Cu

1. Introduction

Copper is a vital micronutrient in organisms, particularly plants, most notably because Cu participates in protein synthesis, membrane activities, and photosynthesis [1] [2]. The chemical properties of Cu endow the metal with pivotal roles in cell physiology as a catalytic cofactor in many redox enzymes and as a structural contributor in protein conformation, making Cu an essential micronutrient for plants or even all organisms. Our knowledge of the mechanisms or processes in plants and soils influencing Cu oxidation state, speciation, solubility, mobility, uptake and transport in plants, is still scarce in most cases [3]. Copper is often applied to soil and crops as fertilizer to ameliorate micronutrient deficiencies caused by prolonged, intensive agriculture [4]. Therefore, with regard to the key role of Cu copper in plant, it is necessary that the Cu chemistry be evaluated in soil. There are several mechanisms for bounding Cu in soil solid phase such as carbonates, sulfates, Fe, Al and Mn oxides and organic matter. On the other hand, the distribution of Cu in different chemical forms influences its bioavailability. Cu Copper has also a strong tendency to bind to organic compounds, which in turn can affect its availability for plant uptake. Agbnyn (2010) showed that the characteristic chemical and physical soil organic matter played an important role in formation of Cu forms in the soil [5]. Incorporation of crop residues into the soil as a source of organic matter and micronutrients such as Cu can play an important role in the soil fertility and cycling of micronutrients. Because organic acids released from decomposition of crop residues can alter the mobility and bioavailability of metals such as Cu in the soil by modifying soil pH or by releasing soluble organic compounds to complex Cu. For example, about 50% to 80% of Zn, Cu and Mn taken up by rice and wheat crops can be recycled through residue incorporation [6]. Sequential fractionation can be used to determine the amounts and chemical forms of trace elements, as well as to infer the potential bioavailability and to predict the mobility affecting their movement within the soil profile and into groundwater. The number of studies concerning the effect of crop residues incorporation on the fractions of Cu in the soil solid phase and bioavailablility of Cu for plant are limited. Therefore, the objectives of this study were to investigate the effects of crop residues on: 1) the fractions of Cu in the soil solid-phase. 2) on the Cu bioavailability (DTPA-extractable Cu) in soil.

2. Methods and Materials

2.1. Field Experiment

The field selected for experiment was located in an area in the southeast city of Esfahan, in the central part of Iran. This area has a relatively flat topography with medium to heavy textured soils. The climate condition is dry with low annual rainfall (<100 mm) and high evapotranspiration (>1500 mm). The soil in the experimental site was classified as *Typic Haplocalcids* (Soil Classification Working Group, 1998).

Treatments consisted of control (fallow) plus incorporation of the residues of 2 crops: *Trifolium* (*Trifolium pretense* L.) and *Sorghum* (*Sorghum bicolor* L.) and subsequent planting of wheat (*Back Cross genotype*) in 3 replications. The experiment was conducted in a complete randomized block field experiment. This made a total of 9 plots (5 × 3). The air-dried crop residues were crashed into the 0.5 - 2 cm pieces and were completely incorporated into the top soil (0 - 30 cm) of each plot with 7 Mg/ha rate. Wheat was planted 30 days after crop residues incorporation and was harvested the following spring. Crop and soil samples were collected at the time of harvest. Soil samples were air-dried, ground and passed through 2 mm sieve and stored for chemical analysis. Available Cu in the soil samples was extracted by diethylenetetramine-penta-aceticacid (DTPA) and Cu concentration in the extract was determined using atomic absorption spectroscopy [7]. Selected properties of the top soil used in this study are shown in **Table 1**.

2.2. Sequential Extraction of Soil

Fractionation of soil Cu was carried out using the MSEP method [8]. All the five operationally defined binding fractions (exchangeable, bound to carbonates, bound to Mn-oxides and Fe-oxides, bound to OM and residual) could then be extracted using this method. The details of the MSEP are described in **Table 2**.

During the extractions, a centrifugation was performed at 3000 RPM to separate extracts from solid. The supernatants were transferred into 50 ml volumetric flask and diluted with DI-H_2O, then analyzed with flame atomic absorption spectrometer (AAS) for Cu.

2.3. Data Analyses

All statistical analyses were carried out using SAS program. Comparison of the mean values of treatments were tested using one-way analysis of variance (ANOVA). Significant differences between pairs of mean were identified using the LSD test at 5% level [9].

3. Results and Discussion

3.1. Properties of Plant Residues

Table 3 shows C/N ratio and Cu concentration of crop residues. The highest and lowest carbon to nitrogen ratios were related to *Sorghum* and *Trifolium* residues, respectively. The highest concentration of Cu was observed for *Trifolium* residues. Lower C/N ratio of *Trifolium* caused rapid decomposition of organic compounds and subsequent production of organic acids resulting in lower pH (**Table 3**).

3.2. Effect of Plant Residues Incorporation on Soil DTPA Extractable Cu

All the treatments significantly increased the concentration of DTPA-extractable Cu in soil. The highest effect was obtained for *Trifolium* and then *Sorghum* treatment (**Figure 1**).

Incorporation of crop residues decreased soil pH that could increase the solubility and availability of Cu compound. It also increased organic matter content and consequently increased the amount of Cu complexed with organic ligands. In addition, residues contains Cu which could be released upon decomposition of plant residues in soil. Stevenson (1991) reported that application of organic fertilizers increased the concentration and

Table 1. Selected soil properties.

Classification	Clay	Silt	Sand	pH	EC (dS/m)	OM (%)	$CaCO_3$ (%)	N (%)	Olsen-P (mg/kg)	NH_4-OACK (mg/kg)	Cu DTPA (mg/kg)	Cu Total (mg/kg)
Typic haplocalcids	42.5	46.3	21.2	7.5	6	0.4	33	0.05	11	289	1.4	35.8

Table 2. Summary of the Tessier *et al*. (1979) sequential extraction procedure.

Step	Fractions	Reagent	Shaking time and temperature
1	Exchangeable (EXC)	8 ml of 1 M $MgCl_2$ (pH 7) in 1 g soil	2 h at 25˚C
2	Bound to carbonates (CAR)	8 ml of NaOAc (pH 5.0 with HOAc)	5 h at 25˚C
3	Amorphous iron-manganese oxides (OXI)	20 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid (pH 2 with HNO_3)	6 h at 96˚C
4	Organic-bound (ORG)	5 ml of 30% H_2O_2 (pH 2), plus 3 ml of 0.02 M HNO_3 and 3 ml of 30% H_2O_2 (pH 2) Cool, add 20 ml of a mixture of 3.2 M NH_4Ac and 20% HNO_3	2 h at 85˚C
5	Residual (RES)	The residual fraction was digested by 8 ml of a mixture of HCl and HNO_3Volume ratio of 3 to 1, therefore they were reached by 0.5 M HNO_3	30 min at 25˚C

Table 3. C/N ratio and Cu concentration of crop residues.

Plant residues	C/N	Concentration of Cu (mg/kg)	Soil pH
Sorghum bicolor L.	54.2	4.9	7.3
Trifolium pretense L.	19.2	8.2	7.1

availability of micronutrients in the soil [10]. Eghball *et al.*, (2004) observed that application of organic fertilizers increased the availability of zinc for corn [11].

3.3. Effect of Plant Residues on Cu Fractions in Soil

3.3.1. Exchangeable Cu

Amount of exchangeable Cu in the soil samples was lower than AAS detection limit, therefore could not be measured with sufficient accuracy. Payne *et al.*, (1988) showed that the exchangeable Cu is available for plant. Exchangeable form of Cu is usually the lowest form of Cu in soil [12]. Gankl *et al.*, (2002) and (2003) and Yu and Zhou (2006) have also pointed out this [13]-[15].

3.3.2. Carbonate-Bound Cu (Cu-Carb)

Crop residues treatments significantly decreased ($p < 0.05$) Cu-Carb in soil in comparison with the control (**Table 4**). Largest amount of Cu-Carb was found in *Sorghum* treated plots while *Trifolium* treated plots had the lowest amount of Cu-Carb (**Figure 2**). Concentration of Cu-Carb in the *Trifolium* treated plots significantly decreased 12% in comparison with the control. In this study, Cu-Carb ranged from 0.87 mg/kg in *Trifolium* treated plots to1.4 mg/kg in the control plot. Ma and Uren (1995) reported that in calcareous soils, the average Cu-Carb is from 0.5 - 1.25 mg/kg of soil [16]. Ramos *et al.*, (1994) reported that average of Cu carb is about 0.92 mg per kg of soil [17]. Reduction of Cu-Carb concentration in soil as the results of crop residue incorporation probably was due to their impact on reducing soil pH, which in turn might have increased the solubility of carbonate compounds in soil. *Trifolium*-treated plots was more effective than *Sorghum*-treated plots in reducing soil pH that could be the reason for the higher effect in reducing the concentration of Cu-carb (**Table 3**). Mehra and Jackson (1960) reported that Cu in calcareous soils appeared to precipitate as carbonate or hydroxides [18]. Wei *et al.*, (2006) reported that available Cu was negatively correlated with soil available P and $CaCO_3$ content and a positively correlated with pH. In this study, Cu-Carb was from 0.87 mg/kg in *Trifolium* treatment and 1.4 mg/kg in control [19].

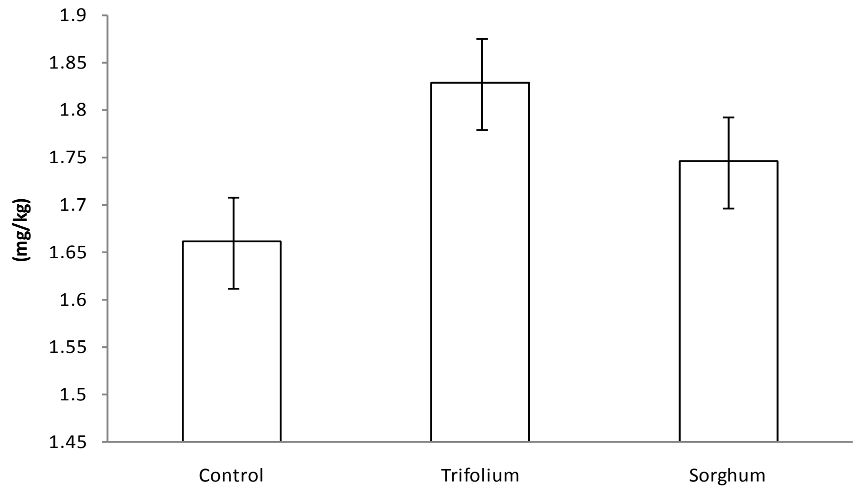

Figure 1. The effect of crop residues on the concentration of DTPA-extractable Cu.

Table 4. Analysis of variance of different fractions of Cu ($mg \cdot kg^{-1}$) in soil as affected by Incorporation of crop residues treatments.

		Mean Square			
Source of Variation	df	Cu-Carbonate	Cu-Oxide	Cu-Organic	Cu-Residual
Replication (RE)	2	0.018	0.12	0.019	3
Crop residues (P)	2	0.12*	1.17***	5.72***	3.77
Error	6	0.53	0.039	1.094	1.81

***, **, *Sighnificant at 0.001, 0.01 and 0.05 levels, respectively.

3.3.3. Fe and Mn-Oxides

Sorghum treatment significantly increased ($p < 0.001$) the concentration of soil Cu-Ox in comparison with the control treatment. *Trifolium* treatment, on the other hand, significantly decreased the concentration of soil Cu-Ox as compared with the control (**Figure 3**). Indeed the concentration of soil Cu-Oxide by *Trifolium* treatment decreased 14%, also increased 5.3% *by Sorghum* treatment in comparison with the control. Reduction of the concentration of soil Cu-Ox by *Trifolium* treatment may have been due to its effect on increasing the concentration of Cu-Org in soil. Indeed, when Cu is added to the soil, a series of interactions (e.g., adsorption, precipitation, complexation, etc.) would take place. The metal forms, associated with Fe, Al and Mn oxides, or bound with organic matter, could be considered potentially active or strongly bound, depending on the physical properties of soil [20]-[25]. Therefore, the form of Cu-Ox can act as a buffering capacity and potential for Cu in soil.

3.3.4. Organically Bound Cu (Cu-Org)

Concentration of Cu-Org significantly ($p < 0.001$) increased with the crop residues incorporation as compared with the control (**Table 4**). The largest amount of Cu-Org was found for the *Trifolium* treated plots (**Figure 4**). Indeed in the *Trifolium* and *Sorghum* treated plots Cu-Org significantly increased 72% and 50%, respectively in comparison with the control.

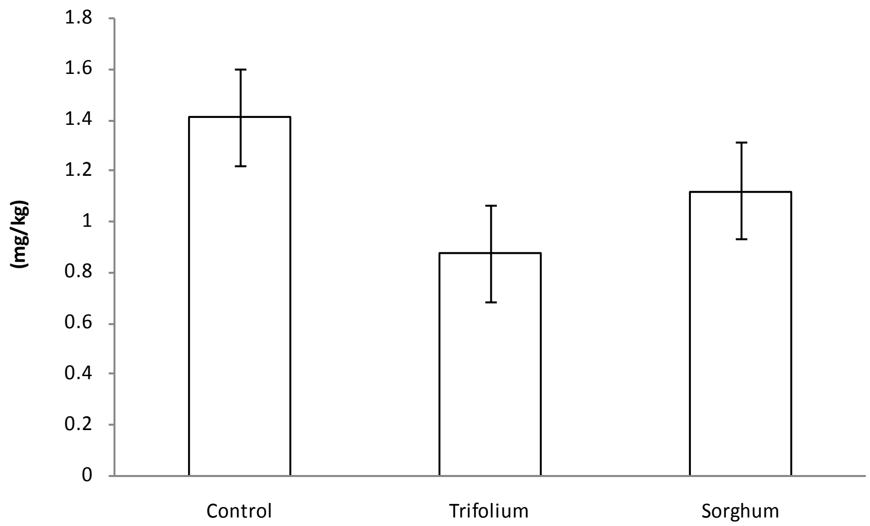

Figure 2. The effect of crop residues on Cu-Carbonate.

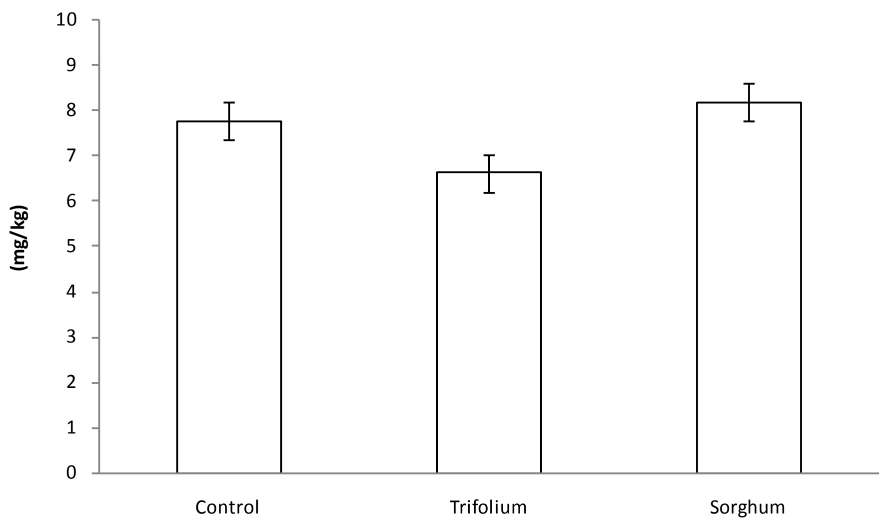

Figure 3. The effect of crop residues on Cu-Oxide.

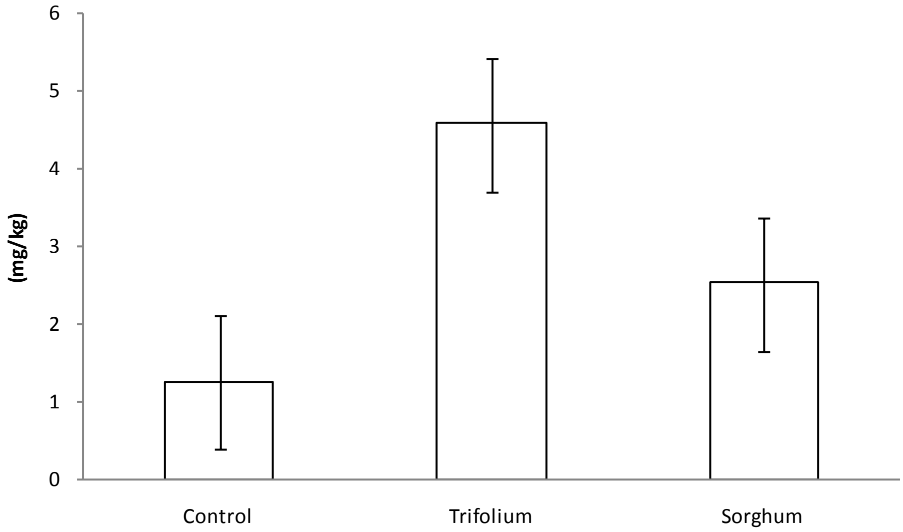

Figure 4. The effect of crop residues on Cu-Organic.

Higher increase of Cu-Org in Trifolium-treated plots was probably due to the lower C/N ratio of trifolium and consequent increase in decomposition of the added residues resulting in higher soluble organic matter and higher complexation of Cu by organic matter. Krishnamurti and Naidu (2002) showed that the partition coefficient of soil Cu was strongly influenced by the fraction complexed with soil organic matter [26].

Kawasaki *et al.* (2000) reported that most of the Cu in industrial effluents, are in organic form [27]. McGrath *et al.*, (1998) demonstrated that increase in soil organic matter resulted in the transfer of copper from other forms to organic form [28].

Part of this Cu (Cu bound to fulvic acids) can move to soil solution and exist as a part of dissolved Cu which is assumed to be an important factor in the phytoavailability of soil Cu. Tao *et al.*, (2003) in reported that the results of the five-step sequential extraction process followed the order: Organic (47.4%), Residual (30.8%), Oxide (15.9%), Carbonate (5.4%), and Exchangeable (0.5%) [29]. Other authors have already stated that the Cu-Org is the dominant fraction (mean 40.7%) in soils [30].

3.3.5.Residual Cu Form (Cu-Res)

Incorporation of *Trifolium* residues decreased Cu-Res in comparison with the control (**Table 4**) although the decrease was not significant (**Figure 5**). In this study around 90% and 66% of Cu fractions were in the form of Cu-Res in control and in *Trifolium* treatment, respectively.

Copper has a stronger affinity to associate with the crystalline structures of the minerals and the organic ligands. As Fuentes *et al.*, (2004) and Nemati *et al.*, (2009) have also pointed out [31] [32]. Burt *et al.* (2003) reported that around 93% of Cu and 41% of Zn was recovered as residual fraction and very low percentage of Cu was recovered as water soluble and exchangeable fractions [33]. Schramel *et al.* (2000) found that the copper bound in the residual phase in an uncontaminated soil was around 65% - 85% [34]. Review effect *Trifolium* on other forms of copper in soil identified that likely the effect of *Trifolium* on Cu-Organic with compared to *Sorghum* cause that decreased Cu-residual.

Overall distribution of Cu among different fractions followed the order below:

$$\text{Cu-Res} > \text{Cu-Ox} > \text{Cu-Org} > \text{Cu-Carb}$$

3.4. Relationships between Forms of Cu in Soil Solid Phase with DTPA-Extractable Cu

Cu-Carb showed no significant correlation with DTPA-extractable Cu in soil. Cu-Ox and Cu-Res forms showed a significantly negative correlation (0.05 and 0.01), respectively with DTPA-extractable Cu (**Table 5**). Amount of bioavailable Cu reduced by carbonates and oxides [35]. Cu-Org form showed a significant positive correlation (0.01) with DTPA-extractable Cu. This suggests that crop residues incorporation resulted in an increase in soil organic matter and consequent increase in the amount of Cu complexed with organic matter and bioavailable in

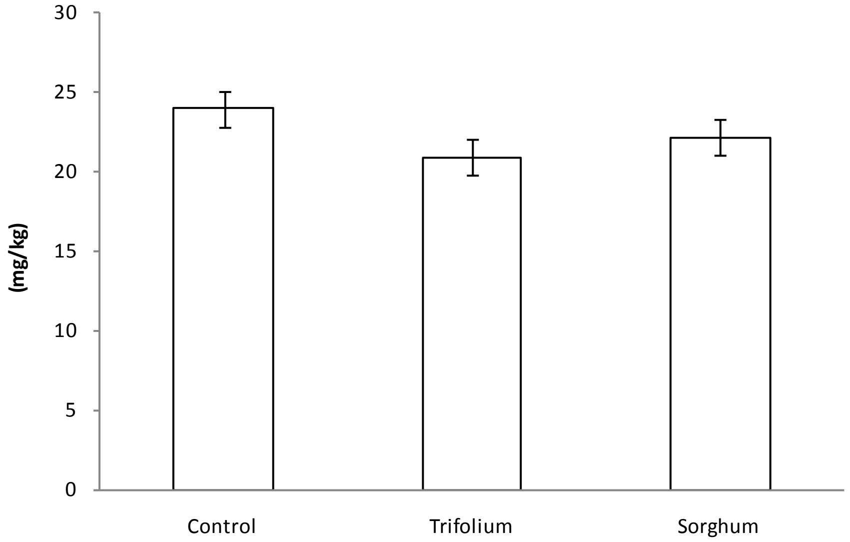

Figure 5. The effect of crop residues on Cu-Residual.

Table 5. Regression coefficient (r^2) between Cu fractions and the concentration of DTPA-extractable Cu in soil.

Cu-Carbonate	Cu-Oxide	Cu-Organic	Cu-Residual
0.56^{ns}	0.63^{*}	0.78^{**}	0.72^{**}

**Significant at $p < 0.01$; *Significant at $p < 0.05$; ^{ns}Non significant.

soil. Gunkel *et al.*, (2003) reported that organic forms of Cu are most correlated with available forms of Cu for plant uptake.

References

[1] Frausto da Silva, J.J.R. and Williams, R.J.P. (2001) The Biological Chemistry of the Elements. *The Inorganic Chemistry of Life*, University Press, Oxford, 584 p.

[2] Koch, K.A., Pena, M.M.O. and Thiele, D.J. (1997) Copper-Binding Motifs in Catalysis, Transport, Detoxification and Signaling. *Chemistry & Biology*, **4**, 549-560. http://dx.doi.org/10.1016/S1074-5521(97)90241-6

[3] Yruela, I. (2005) Copper in Plants. *Brazilian Journal of Plant Physiology*, **17**, 145-156. http://dx.doi.org/10.1590/S1677-04202005000100012

[4] Karamanos, K., Peratzakis, A., Kapiris, P., Nikolopoulos, S., Kopanas, J. and Eftaxias, K. (2005) Extracting Preseismic Electromagnetic Signatures in Terms of Symbolic Dynamics. *Nonlinear Processes in Geophysics*, **12**, 835-848. http://dx.doi.org/10.5194/npg-12-835-2005

[5] Agbenin, J.O. (2010) Extractability and Transformation of Copper and Zinc Added to Tropical Savanna Soil under Long-Term Pasture. *Communications in Soil Science and Plant Analysis*, **41**, 1016-1027. http://dx.doi.org/10.1080/00103621003648150

[6] Prasad, B. and Sinha, S.K. (1995) Nutrient Recycling through Crop Residues Management for Sustainable Rice and Wheat Production in Calcareous Soil. *Fertility News*, **40**, 15-23.

[7] Pyddtt, F.B. (1999) Comparison of Foliar and Stem Bioaccumulation of Heavy Metals by Corsican Pines in the Mount Olympus Area of Cyprus. *Ecotoxicology and Environmental Safety*, **42**, 57-61. http://dx.doi.org/10.1006/eesa.1998.1726

[8] Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, **51**, 844-851. http://dx.doi.org/10.1021/ac50043a017

[9] SAS Institute (1999) SAS System for Windows. Release 8.02. SAS Institute, Cary.

[10] Stevenson (1994) Human Chemistry: Genesis, Composition Reactions. John Wiley and Sons, New York.

[11] Eghball, B., Ginting, D. and Gilley, J.E. (2004) Residual Effects of Manure and Compost Applications on Corn Production and Soil Properties. *Agronomy Journal*, **96**, 442-447. http://dx.doi.org/10.2134/agronj2004.0442

[12] Payne, G.G., Martens, D.C., Kornegay, E.T. and Lindemann, M.D. (1988) Availability and Form of Copper in Three Soils Eight Annual Application of Copper-Enriched Swine Manure. *Journal of Environmental Quality*, **17**, 740-746. http://dx.doi.org/10.2134/jeq1988.00472425001700040038x

[13] Gunkel, P., Jezequel, K. and Faber, B. (2002) Temporal Evolution of Copper Distribution in Soil Fractions, Influence of Soil pH and Organic Carbon Level on Copper Distribution. *Environmental Technology*, **23**, 1001-1008.

[14] Gunkel, P., Roth, E. and Faber, B. (2003) Copper Distribution in Chemical Soil Fractions and Relationships with Maize Crop Yield. *Environmental Chemistry Letters*, **1**, 92-97. http://dx.doi.org/10.1007/s10311-002-0003-6

[15] Yu, Y. and Zhou, Q.X. (2006) Impacts of Soybean Growth on Cu Speciation and Distribution in Two Rhizospher Soils. *Biology and Fertility of Soils*, **42**, 450-456.

[16] Ma, Y.B. and Uren, N.C. (1995) Application of a New Fractionation Scheme for Heavy Metals in Soils. *Communications in Soil Science and Plant Analysis*, **26**, 3291-3303. http://dx.doi.org/10.1080/00103629509369527

[17] Ramos, L., Hernandez, L. and Gonzalez, M.J. (1994) Sequential Fractionation of Copper, Lead, Cadmium and Zinc in Soils from or Near Donana Natioinal Park. *Journal of Environmental Quality*, **23**, 50-57. http://dx.doi.org/10.2134/jeq1994.00472425002300010009x

[18] Mehra, O.P. and Jackson, M.L. (1960) Iron Oxide Removal from Soils and Clays by a Dithionate-Citrate System Buffered with Sodium Carbonate. *Proceedings of the National Conference on Clays and Clay Minerals*, Pergamon Press, New York, 317-327.

[19] Wei, X.R., Hao, M.D., Shao, M.G. and Gale, W.J. (2006) Changes in Soil Properties and Availability of Soil Micronutrients after 18 Years of Cropping and Fertilization. *Soil and Tillage Research*, **91**, 120-130. http://dx.doi.org/10.1016/j.still.2005.11.009

[20] Ahumada, I., Escudero, P., Castillo, G., Carrasco, A., Ascar, L. and Fuentes, E. (2004) Use of Sequential Extraction to Assess the Influence of Sewage Sludge Amendment on Metal Mobility in Chilean Soils. *Journal of Environmental Monitoring*, **6**, 327-334.

[21] Arain, M.B., Kazi, T.G., Jamali, M.K., Jalbani, N., Afridi, H.I. and Shah, A. (2008) Total Dissolved and Bioavailable Elements in Water and Sediment Samples and Their Accumulation in *Oreochromis mossambicus* of Polluted Manchar Lake. *Chemosphere*, **70**, 1845-1856. http://dx.doi.org/10.1016/j.chemosphere.2007.08.005

[22] Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Jalbani, N. and Adil, R.S. (2006) Correlation of Total and Extractable Heavy Metals from Soil and Domestic Sewage Sludge and Their Transfer to Maize (*Zea mays* L.) Plants. *Toxicological & Environmental Chemistry*, **88**, 619-632. http://dx.doi.org/10.1080/02772240600875052

[23] Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Jalbani, N. and Memon, A.R. (2007) Heavy Metal Contents of Vegetables Grown in Soil, Irrigated with Mixtures of Wastewater and Sewage Sludge in Pakistan, Using Ultrasonic-Assisted Pseudo-Digestion. *Journal of Agronomy and Crop Science*, **193**, 218-228. http://dx.doi.org/10.1111/j.1439-037X.2007.00261.x

[24] Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Jalbani, N., Memon, A.R. and Shah, A. (2007) Heavy Metal from Soil and Domestic Sewage Sludge and Their Transfer to Sorghum Plants. *Environmental Chemistry Letters*, **5**, 209-218. http://dx.doi.org/10.1007/s10311-007-0101-6

[25] Kabala, C. and Singh, B. (2001) Fractionation and Mobility of Copper, Lead and Zinc in Soil Profiles in the Vicinity of a Copper Smelter. *Journal of Environmental Quality*, **30**, 485-492. http://dx.doi.org/10.2134/jeq2001.302485x

[26] Krishnamurti, G.S.R. and Naidu, R. (2002) Solid-Solution Speciation and Phytoavailability of Copper and Zinc in Soil. *Environmental Science & Technology*, **36**, 2645-2651. http://dx.doi.org/10.1021/es001601t

[27] Kawasaki, A., Kimura, R. and Arai, S. (2000) Fractionation of Trace Elements in Wastewater Treatment Sludges. *Communications in Soil Science and Plant Analysis*, **31**, 2413-2423. http://dx.doi.org/10.1080/00103620009370595

[28] McGrath, S., Sanders, J.R. and Shalaby, M.H. (1998) The Effect of Soil Organic Matter Levels on Soil Solution Concentrations and Extractabilities of Manganese, Zinc and Cooper. *Geoderma*, **42**, 177-188. http://dx.doi.org/10.1016/0016-7061(88)90033-X

[29] Tao, S., Chen, Y.J., Xu, F.L., Cao, J. and Li, B.G. (2003) Changes of Copper Speciation in Maize Rhizosphere Soil. *Environmental Pollution*, **122**, 447-454. http://dx.doi.org/10.1016/S0269-7491(02)00313-5

[30] Arias, M., López, E., Fernández, D. and Soto, B. (2004) Copper Distribution and Dynamics in Acid Vineyard Soils Treated with Copper-Based Fungicides. *Soil Science*, **169**, 796-805. http://dx.doi.org/10.1097/01.ss.0000148739.82992.59

[31] Fuentes, A., Llorens, M., Saez, J., Soler, A., Aguilar, M.I., Ortuno, J.F. and Meseguer, V.F. (2004) Simple and Sequential Extractions of Heavy Metals from Different Sewage Sludges. *Chemosphere*, **54**, 1039-1047. http://dx.doi.org/10.1016/j.chemosphere.2003.10.029

[32] Nemati, K., Abu Bakar, N.K., Sobhanzadeh, E. and Abas, M.R. (2009) A Modification of the BCR Sequential Extraction Procedure to Investigate the Potential Mobility of Copper and Zinc in Shrimp Aquaculture Sludge. *Microchemical*

Journal, **92**, 165-169. http://dx.doi.org/10.1016/j.microc.2009.03.002

[33] Burt, R., Wilson, M.A., Keck, T.J., Dougherty, B.D., Strom, D.E. and Lindahl, J.A. (2003) Trace Element Speciation in Selected Smelter-Contaminated Soils in Anaconda and Deer Lodge Valley, Montana, USA. *Advances in Environmental Research*, **8**, 51-67. http://dx.doi.org/10.1016/S1093-0191(02)00140-5

[34] Schramel, O., Michalke, B. and Kettrup, A. (2000) Study of the Copper Distribution in Contaminated Soils of Hop Fields by Single and Sequential Extraction Procedures. *Science of the Total Environment*, **263**, 11-22. http://dx.doi.org/10.1016/S0048-9697(00)00606-9

[35] Lindsay, W.L. (1991) Iron Oxide Solubilization by Organic Matter and Its Effect on Iron Availability. *Plant and Soil*, **130**, 27-34. http://dx.doi.org/10.1007/BF00011852

Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

Other selected journals from SCIRP are listed as below. Submit your manuscript to us via either submit@scirp.org or Online Submission Portal.