Mobility and Availability of Copper in Agricultural Soils Irrigated from Water Treated with Copper Sulfate Algaecide

D. Salam · M. El-Fadel

Abstract In this paper, downward movement and availability of copper in soils irrigated with $CuSO_4$ algaecide treated water were examined using column leaching experiments. Two simulations considering 1 and 10 years irrigation period were conducted at copper application rate of about 18.7 kg $CuSO_4$/ha/year. Effluent copper concentrations and vertical distribution of acid and DTPA-extractable copper in the soil columns were determined. Nearly 99% of the applied copper was retained in the soil with a C_e/C_0 values on the order of 10^{-3}. Retention profiles showed that copper was retained in the upper 2 to 3 cm of the soil. However, a significant fraction of the retained copper was detected in available form (DTPA-Cu) suggesting that plants toxicity could be a major limitation for the use of $CuSO_4$ treatment in irrigation water.

D. Salam · M. El-Fadel (✉)
School of Civil Engineering and the Environment,
University of Southampton,
Highfield,
Southampton SO17 1BJ, UK
e-mail: m.el-fadel@soton.ac.uk

D. Salam · M. El-Fadel
Department of Civil and Environmental Engineering,
American University of Beirut,
Beirut, Lebanon

M. El-Fadel
Faculty of Engineering and Architecture,
American University of Beirut,
Bliss street, P.O. Box 11-0236, Beirut, Lebanon

Nomenclature/Abbreviations

C_e	leachate concentration
C_0	influent concentration
C_e/C_0	relative effluent Cu concentration to influent concentration
DTPA	diethylene triamine pentaacetic acid
TEA	triethylamine
DTPA-Cu	Cu fraction extractable with DTPA and constituting the available Cu for plants
48-h EC_{50}	effective Cu concentration which will adversely affect 50% of the population after 48 h of exposure
DOC	dissolved organic carbon
OM	organic matter
SOM	soluble organic matter
CEC	cation exchange capacity
AAS	atomic absorption spectrophotometry
GF-AAS	graphite furnace-atomic absorption spectrophotometry

1 Introduction

Due to its biological inhibitory activity on algae, copper sulfate ($CuSO_4$) has been used since the early 1900s for algae control in surface waters (Haughey et al. 2000; Hullebusch et al. 2002). Its application is still widely

practiced to control algae and higher aquatic plants (Karan et al. 1998; Sytsma and Parker 1999; WSDE 2002). As such, integrated aquatic vegetation management in irrigation canals is currently being planned in a way that decreases reliance on chemical techniques to eliminate potential non-target and off-site impacts (Sytsma and Parker 1999). Doses of CuSO$_4$ required to inhibit algae growth are ten to 100 times those known to be lethal to beneficial zooplankton algae grazers (Cooke et al. 1993; Nature 2004). In their comparative study on the susceptibility of freshwater species to copper-based pesticides, Oliveira-Filho et al. (2004) concluded that the use of copper pesticides is likely to adversely affect a variety of non-target aquatic species. They reported a 48-h EC$_{50}$ of 0.013 mg Cu/L for the cladoceran Daphnia similis which has proved to be the most susceptible organism to copper induced toxicity among the tested species. In an attempt to evaluate the effects of non lethal CuSO$_4$ concentrations up to 4 mg/L on carp fish, Karan et al. (1998) demonstrated an increase in the activity of some functional enzymes in the carp gills and serum, pointing out that the recommended CuSO$_4$ application rate for algae control (0.3–2 mg/L) could affect fish health. The maximum acceptable toxicant concentration for bluegills was cited between 0.021 and 0.040 mg Cu/L (Cooke et al. 1993). While copper toxicity to non-target aquatic organisms at recommended rates of application as algaecide is well documented in the literature, little attention is paid to copper impacts beyond the treated water body. Irrigation and natural systems are often interconnected, and the risk of off-site impacts of management activities can be high (Sytsma and Parker 1999). Copper in treated irrigation water may contribute to copper accumulation in the field soil with potential negative impacts on the groundwater and crops. Indeed, copper concentrations in water supplies can be seriously elevated as a result of copper-based algaecide treatment (ANZECC 2000; Haughey et al. 2000). Lakes and reservoirs recently treated with copper compounds to control algae may have equally high concentrations of dissolved copper (EPA 2002). While the majority of copper applied to an aquatic system will eventually sorb to sediments (Sytsma and Parker 1999; OMRI 2001), high residence time of copper in the water column has been reported in water bodies with important organic matter and colloids content. Copper content in Lake Courtille (France) returned to its background level only 2 months

after copper sulfate application which was attributed to colloids stabilization with high levels of humic substances (DOC of 7.3 mg/L) decreasing copper settlement towards bottom sediments (Hullebusch et al. 2002). Also, solubilization and remobilization of sediment-sorbed copper increases copper levels in the water column although a significant release would only be possible under extreme changes in water chemistry. Haughey et al. (2000) found that approximately 20% of the Cu applied to Lake Mathews, a source of drinking water supply for southern California, was exported from the reservoir over a 70-day period following an 8.85 metric ton CuSO$_4$·5H$_2$O treatment, suggesting a slow release of Cu from the sediments. In addition, copper may be transported to the field within silt carried in the irrigation water (OMRI 2001). Hence, the compatibility of CuSO$_4$ with sustainable agriculture should be carefully examined prior to its application as an algaecide.

While copper in soil is known to be an essential element for plant growth with copper sulfate pentahydrate (CuSO$_4$·5H$_2$O) being the usual copper fertilizer source (Alloway 1995), copper accumulation in soils constitutes a great concern as Cu is a persistent, bioaccumulative, and toxic (PBT) chemical which once released into the environment, may present increasing long-term toxic effects to human health and the environment, even if released in small amounts. Copper does not appear to leach significantly from soil due to its high binding capacity. Yong et al. (2001) reported significant copper retention in the top 2 cm of the soil columns leached with Cu solution of concentration as high as 509.2 mg/L and very acidic pH (1.45). However, levels of copper as high as 2.8 mg/L have been found in groundwater (Irwin et al. 1997). The high water solubility of copper sulfate makes it one of the most mobile metals in soils (OMRI 2001). Vertical movement may occur due to soil particle transport facilitated by funnel action and gravity or water transport through cracks and root channels (Kabata-Pendias and Pendias 2001). Changes in soil environmental conditions over time due to various remediation schemes and natural weathering processes could equally enhance the metal mobility (Mclean and Bledsoe 1992). Another concern of Cu accumulation in soils is the increased risk of phytotoxicity. High levels of Cu cause plants toxicity and occur in areas with high Cu availability (Tisdal et al. 1993). Toxicity relates to the ability of copper to displace other metal ions, particu-

larly iron, from physiologically important centers (Sytsma and Parker 1999). Also, copper can change the soil biota profile, and is toxic at fairly low levels to such organisms as earthworms (OMRI 2001).

The objectives of this study are to evaluate the effects of the addition of copper to soils through copper-treated irrigation water envisaged for algae control and its potential transport in soils. For this purpose, column leaching experiments were conducted to simulate short term (1 year) and long term (10 years) irrigation events.

2 Materials and Methods

2.1 Context

$CuSO_4$ is proposed to control intensive weed and algae proliferation in a major irrigation Canal. A treatment program is anticipated with $CuSO_4$ levels up to 2 mg/L being suggested in instances of significant algae presence in the Canal. Since the Canal is concrete lined, sediment sorption is limited and hence the use of copper may adversely impact water quality. Further, if sustained over the whole irrigation season, the highest suggested $CuSO_4$ treatment dosage can contribute to a loading rate of 18.7 kg $CuSO_4$/ha/year (7.4 kg Cu/ha/year) corresponding to the European Community recommended maximum annual rate of Cu addition in soils (7.5 kg Cu/ha/year) (Kabata-Pendias and Pendias 2001). Thus, with time, undesirable levels could be reached in the top soil.

2.2 Sample Collection, Preparation and Characterization

Thirteen representative soil samples were collected from the top layer (0–30 cm) of the agricultural lands irrigated from the Canal. The samples were characterized and the most vulnerable area with soil parameters suggesting a relatively lower metal retention capacity was selected for the column sorption studies. Additional samples from the selected area were collected from the upper 30 cm, air-dried, crushed, mixed thoroughly and passed through a 2 mm sieve. Two 0.5 g aliquots of the sieved soil were digested in a microwave system (Milestone Ethos Plus microwave with MPR-300/125 medium pressure

rotor) using the aqua regia method (1:3 HNO_3/HCl). The samples were then filtered and made up to 50 mL using distilled water and analyzed for total P, K, Ca, Na, Mg, Zn, Fe, Mn, and Cu. Exchangeable P (Olsen P) was extracted with a 0.5 M $NaHCO_3$ solution (pH=8.5). Exchangeable K, Ca, Na, and Mg were extracted with 1 N NH_4OAc solution (pH=7), and exchangeable Zn, Fe, Mn, and Cu were extracted with a DTPA–TEA solution (pH=7.3). Phosphorus (P) was measured by colorimetric analysis using a spectrophotometer whereas K, Ca, Na, and Mg were measured by flame photometry, and Zn, Fe, Mn, and Cu were measured by flame atomic absorption spectrophotometry (AAS) with an air/acetylene flame and background correction with a deuterium lamp. Copper standard solutions were prepared by dilution of a stock solution of 1,000 ppm±1% (prepared in 2% HNO_3) with a 0.5% HNO_3 solution free of metals. The analysis of samples and standard solutions was based on the mean of triplicate readings.

The soil pH was measured using a calibrated pH meter with glass electrode (Orion research microprocessor, pH/millivolt meter 811) in a 1:2.5 (weight/volume) suspension of soil in distilled water. The soil density was determined using the core method applied on site. The soil organic matter (OM) content was determined by ignition at 350°C. Total calcium carbonate content was determined by acid neutralization. Soil particle size distribution was determined in accordance to the ASTM standard test method for particle size analysis of soils. Cation exchange capacity was determined using ammonium acetate at pH 7.0. Basic properties and chemical characteristics of the soil are presented in Table 1.

2.3 Columns Preparation and Leaching Experiments

Transparent Plexiglas columns (52 cm length and 11.4 cm internal diameter) with perforated Plexiglas discs fitted to their bottoms, were used in the experiments. Homogeneous soil columns were prepared through a uniform packing of ground soil (<2 mm) to a height of 30 cm at a bulk density of 1.25 g/cm³. The bottom of the soil column was padded with a cloth to hold small size particles. The top end of the soil column was also covered with a cloth to prevent disturbance of the column by the input liquid. Two column leaching experiments were carried out simulating one and 10 years irrigation with $CuSO_4$

Table 1 Basic properties and chemical characteristics of the soil sample used in the leaching experiments

	Property								Element (mg/kg, dry)								
	Moisture content[a]	Density (g/cm³)	pH	Conductivity (µS)	CaCO₃ (%)	Organic matter (%)	CEC (meq/100g)	Texture	P	K	Ca[b]	Na	Mg	Zn	Fe	Cu	Mn
	4.85	1.25	6.8	102.9	3.77	3.4	23.22	Clay									
Total ions (acid-extractable)									1,261.5	1,140	–	88	1,947.75	93.91	23,113.5	22.93	666.84
Exchangeable ions									93.09	332.5	2,445	62	281.21	0.78	12.39	1.627	61.39
Cu guideline Acid-Cu																135[c]/7.5[d]	
DTPA-Cu																0.3–1[e]	

[a] Moisture content percent in air dried soil sample

[b] Total Ca was not determined due to interference with hydrogen

[c] The European Community recommended upper limit of Cu in soil to plow depth after sludge addition (milligram per kilogram) (cited in Kabata-Pendias and Pendias 2001)

[d] The European Community recommended maximum annual rate of copper addition to soil (kilogram per hectare per year) (cited in Kabata-Pendias and Pendias 2001)

[e] Medium DTPA-Cu concentration in soils (milligram per kilogram) (Bashour and Sayegh 2007)

application corresponding to 18.7 kg/ha/year. Two columns, A and B (1A and 1B in the case of the one year simulations, and 10A and 10B in the case of the 10 year simulations), were leached in each simulation with three consequent stages of leaching. The first two stages consisted of leaching both columns A and B in each experiment with tap water and CuSO₄ solution. In the third leaching stage, distilled water was added only to column A of each simulation. Details about the different leaching phases are given below.

1. Saturation with tap water at a pH adjusted to 7.2 to eliminate entrapped air, homogenize the soil, and prevent potential preferential movement in macro-pores.
2. Leaching with CuSO₄ solution at Cu concentration equal to 2 mg Cu/L. The solution's pH was periodically adjusted to 6.8. Leached volumes were 3.8 and 38 L for the short and long term simulations respectively, corresponding to a loading rate in the irrigated soils of 7.4 kg Cu/ha/year.
3. Leaching with distilled water for rainfall simulation based on the average annual rainfall in the irrigated area of 715 mm (only column A of each simulation). Total leached volume was equal to 7.3 L. The pH of distilled water was about 5 and no further adjustment was introduced.

The solutions were added by means of a peristaltic pump adjusted to maintain a constant head of 10 cm on the soil column, while the overflow was drained back to the feeding solution container. Solutions were supplied from different reservoirs enabling a reliable water balance to be calculated for each soil column. At the onset, the outlet solutions were collected at definite times, and the volume and pH of the collected leachate were measured. Leachate samples were centrifuged, filtered, acidified to pH<2 with concentrated HNO₃ and stored at 4°C in polyethylene centrifuge tubes until the determination of Cu by GF-AAS. The glassware were soaked in 1% HNO₃ for at least 48 h before use, and then rinsed with distilled water. Fig. 1a and b show a schematic layout and pictures of the columns leaching experiments.

2.4 Columns Dissection and Soil Analysis

After leaching, the columns were extruded and the soil samples were sliced into ten layers, the thickness of which were 1, 1, 1, 2, 2.5, 2.5, 5, 5, 5, and 5 cm
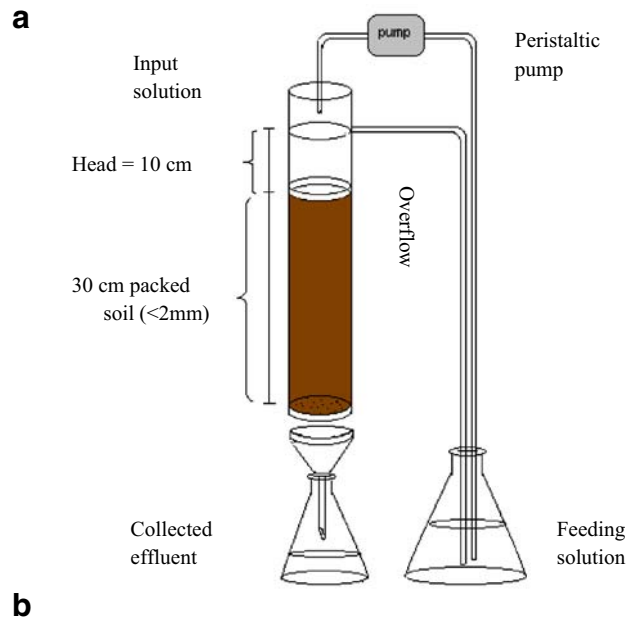
Fig. 1 **a** Layout of the column leaching experiments; **b** Illustrative photographs of laboratory sorption column experiments

from top to bottom. Total (acid extractable) and available (DTPA-Cu) copper were extracted from each layer and the Cu level in the extracts was determined by flame AAS.

3 Results and Discussion

3.1 Leaching with Copper Sulfate Solution

The results indicate no breakthrough of copper in the effluents in all experiments. Breakthrough curves (Fig. 2) show that the relative Cu concentrations recorded (C_e/C_0) are in the order of 10^{-3} with more than 99% of Cu being retained in the columns.

Evidently, low C_e/C_0 values are attributed to the extremely low C_e values measured in the effluents (Fig. 3).

Variation of copper concentration in the leachate (C_e) from columns A and B of the two simulations are presented in Fig. 3. The C_e levels were low and gradually decreasing with continuous leaching. This was more remarkable in the long term (10 years) simulation where larger volumes of copper solution were leached with copper concentrations as low as 1.39 μg/L being detected. Observed peaks of Cu concentrations in this simulation could be related to potential preferential flow through macropores, or to contamination of the glassware used during sample handling and analysis. The pH values depicted in the

Fig. 2 Breakthrough profiles of copper and effluent pH (1 and 10 year simulations, second leaching stage with CuSO$_4$ solution at 2 mg Cu/L and pH=6.8)
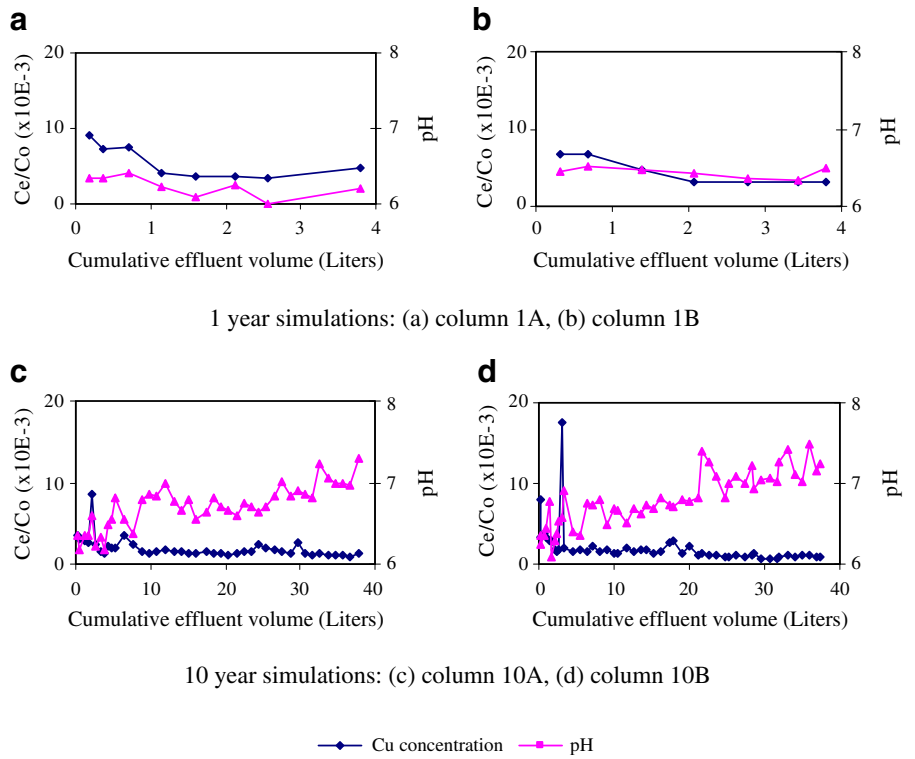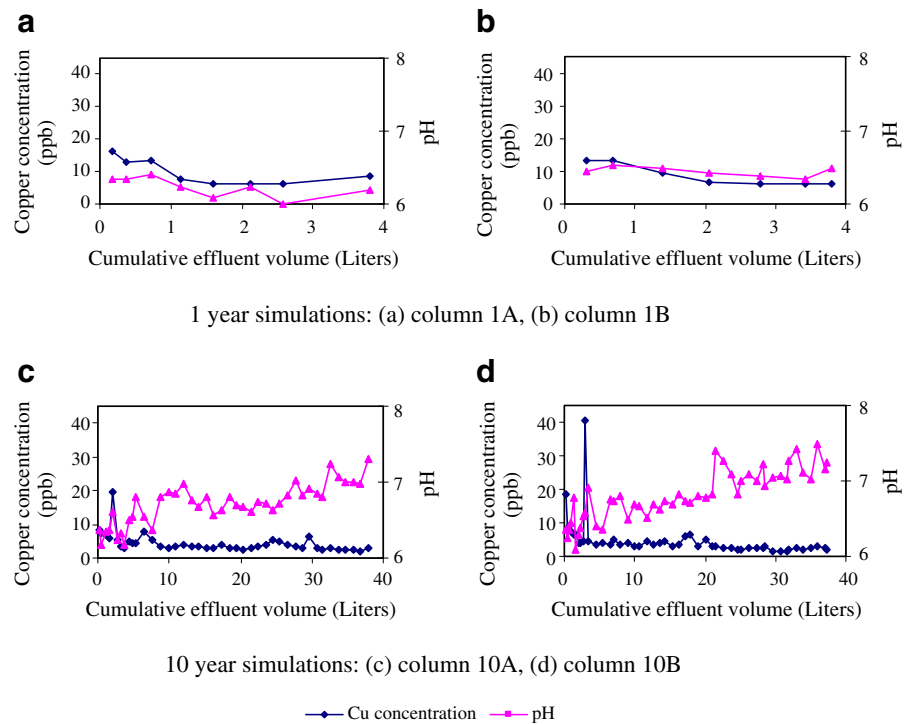

1 year simulations: (a) column 1A, (b) column 1B

10 year simulations: (c) column 10A, (d) column 10B

Cu concentration   pH

Fig. 3 Effluent copper concentration and pH (1 and 10 year simulations, second leaching stage with CuSO$_4$ solution at 2 mg Cu/L and pH=6.8)

1 year simulations: (a) column 1A, (b) column 1B

10 year simulations: (c) column 10A, (d) column 10B

Cu concentration   pH

same figures ranged from 6.01 to 6.40 with an average of 6.23±0.13 for column 1A, and from 6.34 to 6.52 with an average of 6.44±0.06 for column 1B. A broader pH range varying from 6.17 to 7.30 for column 10A, and from 6.08 to 7.50 for column 10B, was recorded in the 10 year simulations. The average pH in this case was 6.70±0.26 and 6.8±0.33 for columns 10A and 10B respectively, being equal to the pH of the soil and to the pH of the introduced copper solution. The initially low effluent pH relative to the copper solution pH (6.8) is most likely due to Cu hydrolysis in the soil system with pH>6, generating H^+ ions which contribute to the effluent acidification: $Cu^{2+} + H_2O \rightarrow Cu(OH)^+ + H^+$. Copper hydroxide has more affinity to the soil adsorptive sites than its free Cu^{2+} form and is strongly adsorbed to the soil (McLean and Bledsoe 1992; Tisdal et al. 1993).

It is worth noting that collected leachate were of yellow color due to soluble organic matter (SOM) leaching from the soil columns. This was demonstrated by the color disappearance following the addition of H_2O_2 oxidizing agent. Copper has a high affinity to soluble organic ligands, and the formation of these complexes may greatly increase Cu mobility in soils (McLean and Bledsoe 1992). Citing field lysimeter experiments, Ni and Cu were reported to completely combine in organic–metal complex compounds in colored soil solutions (Barcan 2002). On the other hand, Madrid and Diaz-Barrientos (1998) reported a significant mobilizing effect of olive mill wastewater (OMW) on copper retained by a sandy soil, and attributed this to the formation of Cu soluble complexes with organic polymers present in the OMW. Accordingly, the presence of copper in the effluents is attributed to its complexation to soluble organics present in the soil, increasing its mobility. However, measured copper concentrations are still

considered low. As leached volume increases, the yellow color gradually disappeared with very clear solutions being collected from columns of the 10 year simulation due to the relatively larger leached volume. This explains the continuous decrease in effluents Cu as SOM leakage decreased with continuous leaching.

3.2 Leaching with Distilled Water

Copper concentrations in effluents from distilled water leaching were expectedly low but increased in comparison to Cu levels measured in effluents associated with leaching using copper sulfate solutions (Fig. 4). The increased Cu levels were accompanied by the reappearance of the yellow color in the effluent indicating SOM leaching. A continuous leaching with distilled water favored SOM leaching from the soil columns carrying with them complexed copper. Increased copper concentrations is also due to the fact that the solubility of metals increases with reduced pH values, with some of the copper ions previously retained by the soil being re-dissolved upon addition of distilled water at pH 5 and appearing in the effluent. Increased Cu levels may also be due to competition for available adsorption sites with H^+ introduced with the slightly acidic water (McLean and Bledsoe 1992). This also explains the increase of effluents pH as compared to the influent distilled water whereby H^+ ions are being retained by the soil and possibly exchanged versus other major cations (besides copper) of basic nature (Ca, Mg, Na, and K).

Although the concentration of copper in leachate increased following distilled water application, the peak value (11.6 μg/L) was below Cu guidelines for drinking water quality of 2,000 μg/L set by the World Health Organization (WHO 2006). This implies that

Fig. 4 Effluent copper concentration and pH (1 and 10 year simulations, third leaching stage with distilled water of pH=5)

Column A (1 year simulation)　　　　Column A (10 year simulation)

◆ Cu concentration　■ pH
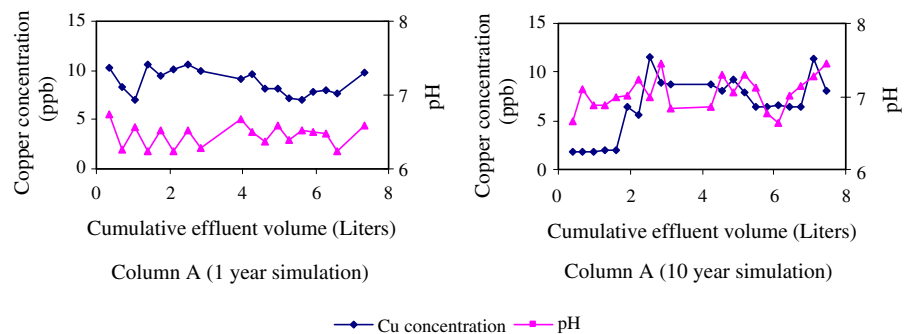
copper sulfate addition to the irrigated soils over 10 years at an application rate as high as 18.7 kg $CuSO_4$/ha/year is not likely to cause significant Cu groundwater pollution.

3.3 Vertical Distribution of Cu in the Soil Column

For short and long term simulations, total copper (acid extractable) migration profiles (Figs. 5 and 6) show the highest copper concentrations in the first 1 cm layer of the soil columns (49.1 and 62.3 mg/kg in columns 1A and 1B, and 535.5 and 447.2 mg/kg in columns 10A and 10B, respectively). These concentrations decreased significantly in the second 1 cm layers (27.0 and 28.4 mg/kg in columns 1A and 1B, and 34.7 and 34.5 mg/kg in columns 10A and 10B, respectively), and return to background levels in underlying sections indicating high Cu retention and immobilization by the soil with no significant movement occurring downwards.

Measured copper concentrations below the top 2 cm layer ranged from 21.3 to 26.4 mg/kg and from 22.8 to 27.2 mg/kg in columns 1A and 1B, respectively. This range varied between 22.6 and 25.4 mg/kg in column 10A, and between 22.9 and 25.3 mg/kg in column 10B.

The average background Cu in the study soil was found to be 22.9 mg/kg with values as high as 25.1 mg/kg being measured. Background Cu in soils in the vicinity of the Canal varied between 19.6 and 32.4 mg/kg and averaged 24.5 mg/kg. Hence, measured Cu concentrations in the soil columns which are slightly higher than the mean value, could be attributed to newly added or to a background Cu.

Assuming that background values of Cu in the soil columns are constant throughout the soil profile and equal to the lowest measured concentration in each column, mass balance calculations indicate that 93.0% and 77.6% of added Cu were retained in columns 10A and 10B respectively, of which 88.1% and 73.2% being found in the first 2 cm layers. Mass balance calculations in the short term simulation exhibited an exaggerated amount of Cu retained in the columns as compared to the total added metal. This can be attributed to the relatively small quantity of Cu applied in this simulation, of which 56.3% and 75.8% were found in the upper 2 cm layers of columns 1A and 1B respectively.

Similarities between Cu profiles in columns A and B of each simulation indicate that rainfall events extending over one year as simulated in the current

Fig. 5 Vertical distribution of acid and DTPA-extractable copper concentrations in soil layers (1 year simulations)
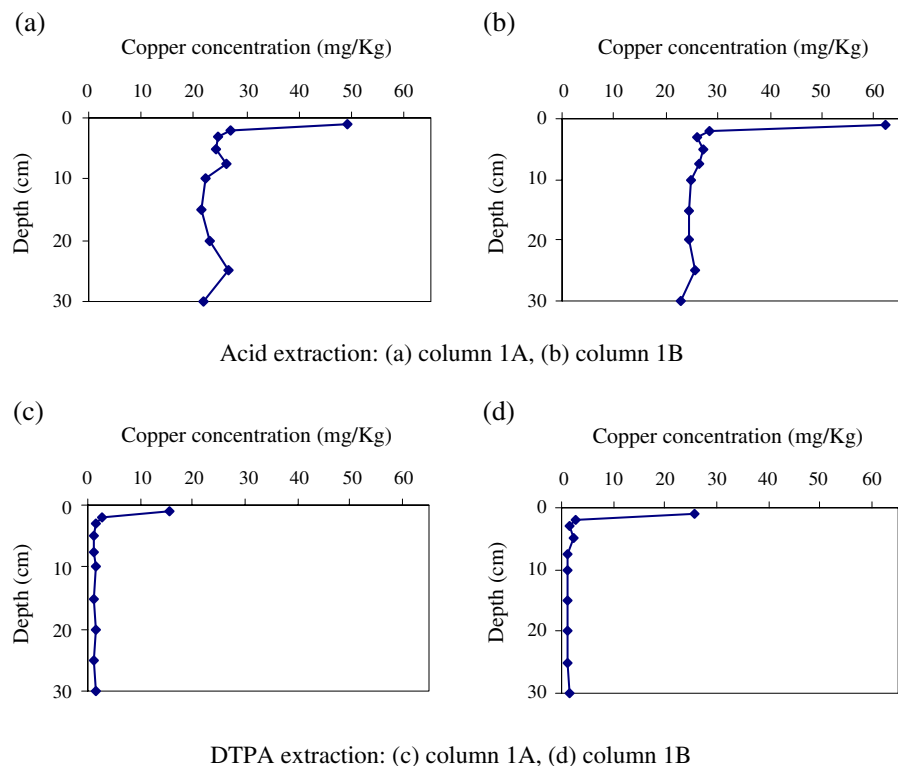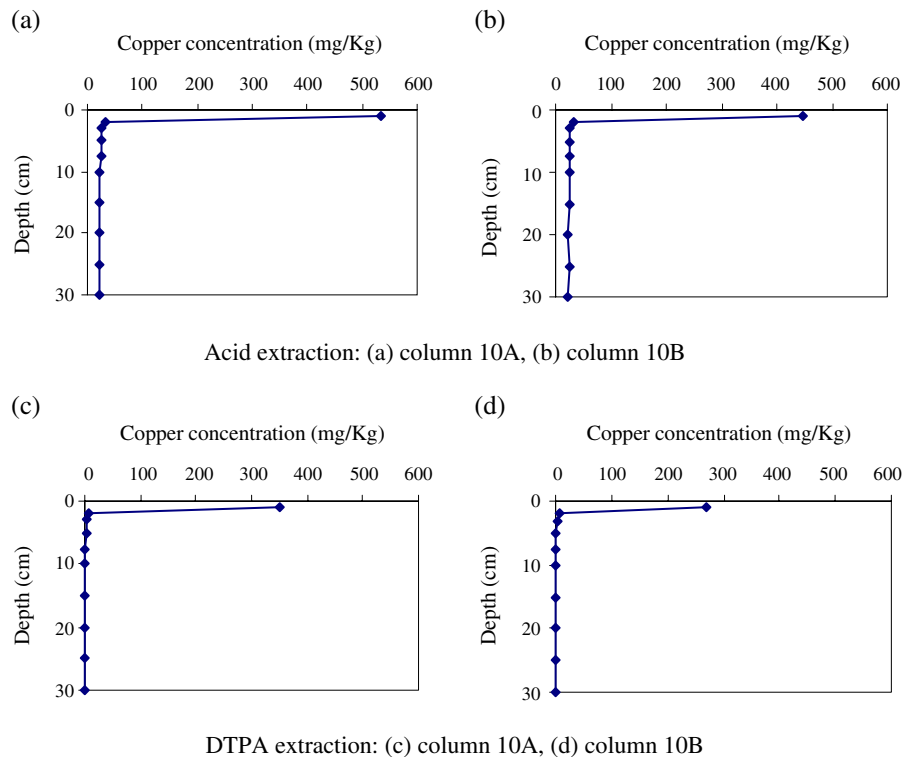

Acid extraction: (a) column 1A, (b) column 1B

DTPA extraction: (c) column 1A, (d) column 1B

Fig. 6 Vertical distribution of acid and DTPA-extractable copper concentrations in soil layers (10 year simulations)

Acid extraction: (a) column 10A, (b) column 10B

DTPA extraction: (c) column 10A, (d) column 10B

experiments (simulations carried out on column A in each experiment), are not expected to cause the downward movement of retained copper in the soil in spite of the acidic nature of the applied water (pH= 5). Differences in Cu concentrations in the upper 1 cm layers of columns A and B in both simulations can be attributed to imprecise columns dissection and possible soil losses during its handling throughout drying and grinding activities. These losses could also explain the difference between the amounts of Cu expected to be retained in the soil columns as anticipated from the leachate Cu analysis, and the actual measured levels.

DTPA-Cu vertical distribution profiles (Figs. 5 and 6) exhibited similar variations as those of the total Cu in both short and long term simulations. Remarkably, DTPA extractable Cu in the first 1 cm layers constitutes a significant part of the total extractable Cu and increased with increasing the amount of added Cu (32.1% and 41.2% in columns 1A and 1B respectively, and 65.4% and 60.2% in columns 10A and 10B respectively). Therefore, an important part of the added Cu is being retained in an available form increasing the labile solid phase fraction of Cu in the soil. This labile fraction would be readily available for

plants through roots extraction and can be easily exchanged against other solutes increasing the risk for Cu mobility in the soil. Excessive bioavailability levels of Cu may alter plant growth and cause various changes in plant metabolism. Also, tolerant plants, by virtue of their ability to grow in polluted soils, may pose a greater risk on the food chain by accumulation of the metal without exhibiting phytotoxicity (Kabata-Pendias and Pendias 2001). Note that, background DTPA-Cu in the soil (1.627 mg/kg) already exceeds the recommended range of DTPA-Cu levels necessary for plant growth proposed by Bashour and Sayegh (2007) for soils in arid and semi-arid regions including the study area (DTPA-Cu: 0.3–1 mg/kg).

Assuming a complete mix and a uniform distribution of retained Cu up to 30 cm soil depth through tillage (equivalent to the plowing depth in the study area), experimental results suggest that available Cu concentrations (DTPA-Cu) in the field at 30 cm depth would be 2.5 and 13.5 mg/kg after 1 and 10 years, respectively, of irrigation from the Canal water. While concentrations following one irrigation year could be tolerated by plants, those available after 10 years are 13 times higher than the expected plants' needs based on the highest critical Cu concentration of 1 mg/kg,

posing concerns of phytotoxicity. Although available forms of soluble Cu to plants may be decreased through complexation to clay–humus particles or through the formation of insoluble humic complexes reducing the concentration of Cu^{++} to a non toxic level when excess Cu^{++} is present (SSSA 1991), the increasing available Cu from year to year is expected to accumulate in the plants, deteriorating the quality of the food chain and possibly reaching toxic levels.

Hence, while irrigation with $CuSO_4$ treated water could be adopted with minimal groundwater pollution risk, the high increase in soil available copper poses a limitation for its adoption for algae treatment. Field monitoring and correlation studies between DTPA-Cu concentrations in the irrigated soils and plants tissues remain however necessary to ascertain the risk of plants toxicity.

4 Conclusion

The leaching behavior of Cu in a clay soil irrigated with copper treated water for algae control showed that the retention of the heavy metal was very high in the upper 2 to 3 cm of the soil. DTPA-Cu constituted an important part of the retained copper in the soil increasing the risk of Cu phytotoxicity. The study demonstrated that the complete reliance on chemical treatment to control algae may not be compatible with sustainable agricultural principles. Field monitoring and correlation studies between DTPA-Cu concentrations in the irrigated field and plants tissues remain necessary for a more accurate risk assessment of plants toxicity. Alternative algae control methods should be considered depending on the ultimate water usage.

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