Heliyon 6 (2020) e03375

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Influence of soil characteristics and leaching rate on copper migration: column test

Fouad Amlal^a, Saad Drissi^{b,*}, Kacem Makroum^a, Khalid Dhassi^a, Hamid Er-rezza^c, Abdelhadi Aït Houssa^d

^a Faculty of Sciences Chouaib Doukkali University, El-Jadida, Morocco

^b National Agricultural School of Meknes, Department of Agronomy, Ecole Nationale d'Agriculture de Meknès, BP S/40, Meknès - Maroc, 50 000, Morocco

^c Hassan II Institute of Agronomy and Veterinary Sciences (IAV Hassan II), Rabat, Morocco

^d Agricultural Training and Research Center, Providence Verte Company, Morocco

ARTICLE INFO

Keywords: Agricultural science Agronomy Environmental science Soil science Copper Fertilization Leaching Soil contamination

ABSTRACT

Soil copper (Cu) supply is used to correct Cu deficiency in many crops grown in southern Mediterranean areas. Oversupply of this fertilizer may contaminate soil and groundwater. This study aims to assess Cu migration in different soils of Moroccan agricultural areas. Three soil samples were collected from different areas. For each soil, three annual leaching rates were tested: 35 mm, 237 mm, and 565 mm for a sandy soil; 35 mm, 70 mm, and 140 mm for a clay calcareous soil; and 35 mm, 103 mm, and 247 mm for silty clay soil. The leaching experiments were conducted in columns filled identically up to 30 cm with each soil sample. Then, 0.6 mg of Cu kg⁻¹ was added to the soil surface in the sulfate form (CuSO₄.5H₂O). The results showed that soil Cu loss increased mainly with leaching rate: $y = 0.004 \text{ x} - 0.10 \text{ (R}^2 = 0.97)$ where y: soil Cu loss $(10^{-4} \text{ meq } 100 \text{ g}^{-1})$ and x: leaching rate (mm). The regression analysis did not reveal a significant influence of the soil properties on Cu leaching. However, the Cu loss seems insignificant regarding the no recurrence of high annual leaching rate (over 500 mm), in south Mediterranean areas. Also, soil Cu accumulation risk occurred in all studied soils. For sandy soil, available Cu content was 78% higher in the top layer (0–10 cm) than its content in the middle (10–20 cm) and lower (20–30 cm) layers. Furthermore, a release of bioavailable Cu was recorded in silty clay and clay calcareous soils at a leaching rate of over 70 mm.

1. Introduction

Copper (Cu) deficiency is a worldwide nutrient constraint to many crops production (Graham, 2008). Several authors reported the efficacy of soil Cu supply to correct this deficiency (Marschner, 1995; Moore, 2001). However, an adequate nutrient supply requires a good knowledge of different guidelines including the rate of supply, the timing supply, the chemical forms, and the downward movement in the soil. Copper sulfate (CuSO₄.5H₂O) is commonly used by farmers regarding its solubility and its low cost (Goh and Karamanos, 2006; Souza et al., 2015). However, oversupply of this fertilizer may result in soil Cu accumulation (Gonzalez et al., 2015). In this regard, high Cu soil levels may induce long-term toxic effects on human health and the environment (Salam and El-Fadel, 2008). The Cu toxicity is related to its persistent, bio-accumulative, and toxic characters (EPA, 2002). The toxical Cu threshold

is around 0.2 mg l^{-1} in water (Pick, 2011) and around 20 mg kg⁻¹ in soil (Gonzalez et al., 2015).

Soil metals mobility is a concept frequently used to estimate the contamination risk (Acosta et al., 2011). Thecolumn test is carried out to evaluate the leaching and adsorption characteristics of soils and to explain nutrient migration (Arabzai and Honma, 2014). Copper in the soil is present in several forms that are associated with different soil components. The nature of such associations affects the mobility and availability of this trace element (Dong and Wang, 2012). Also, soil Cu availability is influenced by organic matter, iron (Fe), and manganese (Mn) sesquioxides contents, cation exchange capacity, soil pH, carbonate content and water infiltration rate (Moore, 2001; Shaheen et al., 2009; Gonzalez et al., 2015). Overall, several studies have reported the low mobility of Cu in different soils (Moore, 2001; Pietrzak and McPhail, 2004; Lal, 2016). On the other side, some authors noticed that a

* Corresponding author. E-mail address: sdrissi@enameknes.ac.ma (S. Drissi).

https://doi.org/10.1016/j.heliyon.2020.e03375

Received 25 May 2019; Received in revised form 24 November 2019; Accepted 3 February 2020

2405-8440/© 2020 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).





CellPress

long-term water logging in soil resulted in bioavailable Cu release due to reducing conditions (Phillips, 1999; He et al., 2006).

Concerning the south Mediterranean areas, including Morocco, many farmers applied Cu fertilizers in many crops such as citrus, corn, and wheat. However, few reports are discussing the availability and mobility of this trace element in this specific climate. Therefore, this study was conducted to determine relations between Cu loss by leaching and soil type of south Mediterranean climate. Also, the retention and release of Cu in different soils were investigated to understand Cu accumulation in different soil horizons. Such a study will help to establish good reasoning for Cu fertilization without threaten the environment.

2. Materials and methods

2.1. Characteristics of studied soils

Column leaching experiments were carried out to identify Cu migration in three soils located in three different Moroccan areas. The studied soils were collected from 0-30 cm in depth. The first soil (Arenosol) was taken from the Loukkos area (34.96° N, 6.21° W, Northwestern Morocco). It is sandy (86.2%) with a low cation exchange capacity (CEC) (3.7 meq 100 g⁻¹). Its DTPA Cu content was around 0.23 mg kg⁻¹. The second soil was collected from the Sais area (33.85° N, -4.69° W, Middle of Morocco). It has a clay calcareous texture (Calcisol) with a CEC of 29.3 meq 100 g⁻¹. Its DTPA Cu content was around 0.72 mg kg⁻¹. The third soil was taken from the Gharb area (33.53° N, 4.40° W, Northwestern Morocco). It has a silty clay texture (Vertisol) with a CEC of 21.6 meq 100 g⁻¹. Its DTPA Cu content was around 2.85 mg kg⁻¹. The other soil characteristics are shown in Table 1.

The average annual rainfall is around 692 mm, 429 mm, and 537 mm, respectively, for Loukkos, Sais and Gharb areas.

2.2. Leaching experiment

Table 1. Characteristics of the studied soils

Soil samples were air-dried, passed through a 2 mm sieve and homogenized. Each studied soil was subjected to a leaching experiment. Three annual leaching rates were tested for each soil: 35 mm, 237 mm, and 565 mm for sandy soil; 35 mm, 70 mm, and 140 mm for clay calcareous soil; and 35 mm, 103 mm, and 247 mm for silty clay soil. These leaching rates were determined from the annual leaching frequency analysis over 30 years (1980–2010) beyond 0.3 m soil horizon (MarocMeteo, 2019). For each soil, the leaching experiments were conducted in 12 polyvinyl chloride (PVC) cylinders (7.04 cm internal diameter and 35 cm in length). The experimental design was a randomized complete block with 4 replications. The columns were oriented vertically and placed on an iron stand. A gravel layer was placed on the bottom of each cylinder. Then, cylinders were filled identically up to 0.3 m with each soil (1.65 kg, 1.54 kg, and 1.45 kg, respectively, for sandy, clay calcareous and silty clay soils). The cylinders are uniformly taped in the sides to provide the original bulk densities of undisturbed soils. The bulk densities were 1.41, 1.32 and 1.24, respectively, for sandy, clay calcareous and silty clay soils. Thereafter, a leaching system was installed on the base of each column to collect the leachate.

Before setting up the leaching experiments, the soil columns were slowly saturated using distilled water. For each soil, 0.6 mg of Cu kg⁻¹ was applied to the soil surface as sulfate form (CuSO₄.5H₂O; 25% of Cu). This Cu rate is considered as adequate to correct Cu deficiency on wheat, which is reported as a high Cu sensitive crop (Flaten et al., 2004). The leaching rates were split in 6 days. Water was applied using a beaker at an effluent flow around 3 ml min⁻¹. The application rate allows a ponding on the top of the columns of 2 cm maximum. Columns were covered to minimize evaporation from the soil surface during the leaching period.

2.3. Leachate analysis

For each soil and leaching rate replication (n = 4), the leachate was collected from the bottom of each column and analyzed to determine cations and anions concentration. Leachate was filtered through Whatman No. 42 filter and acidified with HCl. The leachate content on extractable cooper (Cu²⁺), iron (Fe²⁺), zinc (Zn²⁺), manganese (Mn²⁺) and potassium (K⁺) was determined by an atomic absorption spectrophotometer (Varian 240 AA Fast Sequential, air + acetylene). The content on ammonium (NH⁴₄), nitrate (NO₃), chloride (Cl⁻), sulfate (SO²₄), phosphorus (H₂PO₄), calcium (Ca²⁺) and magnesium (Mg²⁺) was determined colorimetrically on a Skalar San ++ autoanalyzer according to Skalar standard methods. Boron (B) was determined colorimetrically using the Azomethine-H method (UV-Visible Varian). Appropriate dilutions were made from the original leachates for the final analyze determination. The results were reported using the average of four replicates columns.

The soil element loss through leaching was deduced from Eq. (1):

	0 1 1	ci 1 "1	0:1, 1 ::
Soli property	Sandy soll	Clay calcareous soli	Slity clay soli
World Reference Base	Arenosol	Calcisol	Vertisol
Clay (%)	8.4	47.5	58.2
Silt (%)	5.7	23.8	37.8
Sand (%)	86.2	29	4.2
pH (H ₂ O; 1/5)	7.3	8.6	8.1
Total carbonates (%)	0	14.6	10.4
Cation Exchange Capacity (meq 100g ⁻¹) (Cobaltihexamine Chloride)	3.7	29.3	21.6
Organic matter (%) (Walkley and Black method)	0.56	3.53	1.77
Extractable K (meq100g ⁻¹) (Ammonium Acetate extr.)	0.204	1.389	0.516
Extractable Mg (meq $100g^{-1}$) (Ammonium Acetate extr.)	0.555	2.645	9.171
Extractable Ca (meq $100g^{-1}$) (Sodium Acetate extr.)	4.105	39.695	37.159
Extractable Na (meq $100g^{-1}$) (Ammonium Acetate extr.)	0.123	0.242	2.1
DTPA extractable Zn (meq100g ⁻¹)	$7.65 \ 10^{-4}$	$12.54 \ 10^{-4}$	$38.54 \ 10^{-4}$
DTPA extractable Fe (meq100g ⁻¹)	0.129	0.037	0.110
DTPA extractable Mn (meq100g ⁻¹)	0.205	0.127	0.089
DTPA extractable Cu (meq100g ⁻¹)	$7.24 \ 10^{-4}$	$22.66 \ 10^{-4}$	$89.71 \ 10^{-4}$
Boron hot water extraction (mg kg ⁻¹)	0.49	0.44	0.63

2

Soil element loss (meq 100 g⁻¹) = $\frac{\text{Element content in the leachate (meq l⁻¹) x Leaching rate (l)}{\text{Column soil weight (g)}} *100$

2.4. Soil Cu content after leaching

At the end of each leaching experiment, the columns were sectioned into three superposed layers: top layer (0–10cm), middle layer (10–20 cm) and down layer (20–30 cm). Then, the soil was air-dried at 40 °C, during 48 h, to determine its content on bioavailable Cu. A subsample of 25g and 50ml of DTPA solution reagent (14.92g triethanolamine, 1.976g DTPA, 1.47g CaCl₂, and 1l distilled water) was placed in a plastic jar and closed. The jar was agitated for 2 h. Then, the extract was filtered using a filter paper. The extract was analyzed by the atomic absorption spectrophotometer (Varian 240 AA Fast Sequential, air + acetylene) at a wavelength of 324.8nm (Lindsay and Norvell, 1978).

2.5. Statistical analysis

Analysis of variance was used to test the effect of leaching amounts on nutrient soil loss and Cu distribution in each soil profile. The statistical differences were considered at P < 0.05. The comparison of means using the Student-Newman-Keuls test. Also, a regression analysis, using the step-wise method, was carried out to predict the Cu soil loss using leaching rate and different soil characteristics. Statistical analyses were carried out using the SPSS software (Version 20).

3. Results and discussion

3.1. Soil Cu loss after leaching

Soil Cu loss after leaching increased significantly with increasing leaching rates for all studied soils (Table 2). For sandy soil, located in a high rainfall area (Loukkos), the high recorded leaching rate (565mm) resulted in Cu loss of $2.31 \ 10^{-4}$ meq. 100 g⁻¹ of soil. Such Cu loss was around $0.33 \ 10^{-4}$ meq Cu 100 g⁻¹ for clay calcareous soil, located in a low rainfall area (Sais), at its high recorded leaching rate (140 mm). Concerning silty clay soil (Gharb), losses of Cu were around $0.73 \ 10^{-4}$ meq 100 g⁻¹ atthe high leaching of 247 mm. Besides, regression analysis revealed that soil Cu loss was mainly related to the leaching rate.

This Cu soil loss can be highly predicted ($R^2 = 0.97$) using the regression model Eq. (2):

```
Soil Cu loss (10^{-4} \text{meq } 100 \text{ g}^{-1}) = (0.004 \text{ x leaching rate (mm)}) - 0.10 (2)
```

From this regression model, the leaching rate explains around 97% of soil Cu loss. Thus, the high leaching rate of 500 mm resulted in Cu leaching around $1.9 \ 10^{-4}$ meq $100 \ g^{-1}$. This Cu loss represented around 10% of the initial Cu supply (18.9 10^{-4} meq 100 g^{-1}). Losses of this trace element were 100 times lower at the leaching rate of 30 mm. From these results, Cu application as sulfate seems not to be harmful to ground water due to no recurrence of high rainfall years in such studied Mediterranean areas. The same result was reported in the Hangzhou location of China (Chen et al., 2003). Nevertheless, caution must be taken towards Cu soil accumulation over the years as indicated by Yang et al. (2002). The reduced migration of Cu at a low leaching rate can be explained by Cu soil adsorption that reduces its downward movement (Chen et al., 2003).

On the other hand, the soil properties (texture, organic matter content, soil pH, CEC) did not enhance the prediction of the presented model (Eq. (2)). Also, soil Cu loss was not related to other soil cations (Native Cu^{2+} , Zn^{2+} , Mn^{2+} , Fe^{2+} , Mg^{2+} , Ca^{2+} , K^+ , and NH_4^+). This result is in contrast with the findings of He et al. (2006) who indicated that Cu leaching was related to native soil Cu and organic matter content for several sandy soils.

Indeed, in all soil types, the cations contents in the leachate were mainly related to the leaching rate. The most cations presented in the leachate were Na^+ and Ca^{2+} due to their high native levels in soils (Table 3).

3.2. Available soil Cu content after leaching

In contrast to soil Cu loss by leaching, migration of this metal through the soil profile was mainly influenced by soil characteristics. In sandy soil profile, bioavailable Cu content after leaching was not related to leaching rates. The content of this trace element in different layers was greater than the native soil level $(7.2 \ 10^{-4} \text{meq} \ 100 \ \text{g}^{-1})$. The high Cu concentration $(26.7 \ 10^{-4} \text{meq} \ 100 \ \text{g}^{-1})$ was recorded on the top horizon $(0-10 \ \text{cm})$. In this sandy soil, soil Cu content in the 0–10cm layer was 78% higher than the Cu level of the middle and lower layers (Table 4). Thus, the most supplied Cu amount remained in soil surface $(0-10 \ \text{cm})$ of sandy soil. Consequently, the percentage of the CEC occupied by Cu was significantly increased on the top layer $(0.072\% \ \text{of CEC})$ compared to other layers $(0.041\% \ \text{of CEC})$ (Figure 1). This result is in line with the earlier finding of Chen et al. (2003) who reported that DTPA extractable Cu in sandy soil decreased with increasing soil depth. Also, all studied

Table 2. Soils Cu loss $(10^{-4} \text{ meq } 100\text{g}^{-1})$ at different leaching rates.

Sandy soil (Loukkos area)			
Leaching rate (mm)	35	237	565
Cu leached $(10^{-4} \text{ meg } 100 \text{ g}^{-1})$	$0.07\pm0.01b$	$0.75\pm0.17b$	$2.31\pm0.73a$
Clay calcareous soil (Sais area)	'	, , , , , , , , , , , , , , , , , , ,	
Leaching rate (mm)	35	70	140
Cu leached $(10^{-4} \text{ meq } 100 \text{ g}^{-1})$	$0.17\pm0.01c$	$0.22\pm0.00b$	$0.33\pm0.00a$
Silty clay soil (Gharb area)	'		
Leaching rate (mm)	35	103	247
Cu leached $(10^{-4} \text{ meq } 100 \text{ g}^{-1})$	$0.10\pm0.02c$	$0.30\pm0.11b$	$0.73\pm0.12\text{a}$

Data are means \pm standard deviation (n = 4).

For each soil, means without common letter are significantly different (at $P \leq 0.05$, student-Newman-Keuls test).

Native Cu contents for sandy, calcareous, and clay soils are, respectively, 7.2, 22.7, and 89.7 10^{-4} meq 100 g⁻¹ soil. Before leaching, soils received 18.9 10^{-4} meq 100 g⁻¹ of Cu

(1)

Table 3. Cations loss $(10^{-4} \text{ meq } 100 \text{ g}^{-1})$ in the leachate at different leaching rates and studied soils.

Sandy soil			
Leaching rates (mm)	35	237	565
Ca ²⁺	$294\pm76c$	$1540\pm259\mathrm{b}$	$2399 \pm 310 a$
Na ⁺	$246\pm93b$	$451 \pm 135ab$	$654 \pm 173a$
Mg ²⁺	$133\pm52c$	$431\pm70b$	$664 \pm \mathbf{64a}$
K ⁺	$47.6 \pm 12.8 c$	$157.4\pm45.1b$	$254.3\pm58.3a$
NH ⁴⁺	$5.67\pm0.85a$	$6.14\pm0.64a$	$15.9 \pm 13.2 \mathrm{a}$
Fe ²⁺	$0.82\pm0.18c$	$13.5\pm3.81b$	$21.2\pm2.74a$
Mn ²⁺	$0.08\pm0.01c$	$0.56\pm0.19b$	$1.33\pm0.24a$
Zn ²⁺	<0.0001a	<0.0001a	<0.0001a
Silty-clay soil			
Leaching rates (mm)	35	103	247
Ca ²⁺	$1294\pm720a$	$2352\pm992a$	$1853 \pm 172 \mathrm{a}$
Na ⁺	$1764 \pm 741c$	$5957 \pm 1321 b$	$11042\pm1512a$
Mg ²⁺	$1023\pm681a$	$1771\pm727a$	$970\pm597a$
K ⁺	$22\pm 6.8c$	$102.5\pm3.8b$	$187.8\pm20.1a$
NH ⁴⁺	$0.43\pm0.22a$	$1.94\pm0.94a$	$4.04\pm3.46a$
Fe ²⁺	$0.32\pm0.45b$	$3.38 \pm 3.33 ab$	$6.49\pm2.02a$
Mn ²⁺	$0.04\pm0.025b$	$0.28\pm0.15a$	$0.37\pm0.14a$
Zn ²⁺	<0.0001a	<0.0001a	<0.0001a
Clay-calcareous soil			
Leaching rates (mm)	35	70	140
Ca ²⁺	$959 \pm 120 c$	$1787 \pm 105 \mathrm{b}$	$3766 \pm 222 a$
Na ⁺	123±4c	$212\pm10\mathrm{b}$	$400\pm23a$
Mg ²⁺	$212\pm15c$	$358\pm 30b$	$652\pm68a$
K ⁺	$14.3\pm0.8c$	$26.9\pm2.1b$	$54.7\pm2.5a$
NH ⁴⁺	<0.0001a	<0.0001a	<0.0001a
Fe ²⁺	$0.02\pm0.0b$	$0.24\pm0.032b$	$3.44\pm0.62a$
Mn ²⁺	$0.03\pm0.01\mathrm{b}$	$0.05\pm0.02 \mathrm{ab}$	$0.10\pm0.04a$
Zn ²⁺	$0.075\pm0.05c$	$0.14\pm0.0b$	$0.34\pm0.08a$

Data are means \pm standard deviation (n = 4).

For each soil and chemical element, means without common letter are significantly different (at P ≤ 0.05, Student-Newman-Keuls test).

Table 4. Extractable Cu content $(10^{-4} \text{ meg } 100 \text{ g}^{-1})$ of studied soils layers after leaching.

Soil texture	Leaching rate (mm)	Extractable Cu content $(10^{-4} \text{ meq } 100 \text{ g}^{-1})$		
		0–10 cm	10–20 cm	20–30 cm
Sandy soil	35	$29.8\pm0.9\text{Aa}$	$14.1\pm1.6\mathrm{Ab}$	$14.2\pm1.7\text{Ab}$
	237	$26.4\pm3.3\text{Aa}$	$16.5\pm1.9\text{Ab}$	$15.4 \pm 1.4 \text{Ab}$
	565	$23.9\pm2.0\text{Aa}$	$14.2\pm3.4\text{Ab}$	$15.7\pm2.2\text{Ab}$
Clay calcareous soil	35	$50.4\pm5.1Ba$	$38.9 \pm \mathbf{8.1Bb}$	$38.8 \pm \mathbf{4.2Cb}$
	70	65.6 ± 4.82Aa	$55.6 \pm 7.9 \text{Ab}$	$46.4\pm5.0Bc$
	140	$63.1\pm 6.8 \mathrm{Aa}$	$64.5\pm5.6\text{Aa}$	$63.1\pm5.5\text{Aa}$
Silty clay soil	35	$78.5 \pm 12.0 \text{Ba}$	$76.6\pm7.0\mathrm{Ba}$	$72.6\pm6.4Ba$
	103	$127.2\pm17.3\mathrm{Aa}$	$154.2\pm22.9\text{Aa}$	$148.2\pm25.4\text{Aa}$
	247	$134.4\pm35.2\text{Aa}$	164.2 ± 25.2 Aa	$156.9\pm26.3\text{Aa}$

Data are means \pm standard deviation (n = 4).

For each soil horizon, means without common capital letter are significantly different (at P < 0.05, Student-Newman-Keuls test).

For each leaching rate and studied soil, means without common small letter are significantly different (at $P \le 0.05$, Student-Newman-Keuls test). Native Cu contents for sandy, calcareous, and clay soils are, respectively, 7.2, 22.7, and 89.7 10^{-4} meq 100 g⁻¹ soil. Before leaching, soils received 18.9 10^{-4} meq 100 g^{-1} of Cu.

layers showed a low Cu level compared to the sum of soil Cu native content (22.7 10^{-4} meq 100 g⁻¹) and Cu supply before leaching (18.9 10^{-4} meq 100 g⁻¹). Therefore, it seems that significant Cu retention occurs in sandy soil. Immobility of Cu can be explained by its conversion to insoluble Cu compounds and reactions with the colloidal material of soil

(Moore, 2001). Thus, the supply of Cu under sulfate form must be placed near the root zone to be effective (Flaten et al., 2004).

Concerning clay calcareous soil, Cu migration was different from the sandy soil. All studied layers of this calcareous soil showed a high Cu level compared to the sum of soil Cu native content (22.7 10^{-4} meq 100



Figure 1. Percentages of the cation exchange capacity (CEC) occupied by copper (Cu) for sandy soil (a), calcareous soil (b), and silty clay soil (c) at different layers. Data are means \pm standard deviation (n = 4). For each leaching rate, means without common small letter are significantly different (at P \leq 0.05, Student-Newman-Keuls test). CEC for sandy, clay calcareous, and silty clay soils are, respectively, 3.7, 29.3, and 21.6 meq 100g-1 soil. For a given soil, the horizontal line indicates native Cu CEC occupation before leaching and Cu supply.

 g^{-1}) and Cu supply before leaching (18.9 10^{-4} meq 100 g^{-1}). Also, the bioavailable Cu concentration in different horizons increased significantly with leaching rates. Thus, at high leaching level (140 mm), the soil Cu content, increased around 25% and 63%, respectively, in the top and lower layers compared to the low leaching rate (35 mm). The percentage of CEC occupied by Cu was around 0.018% for all layers and at all leaching levels compared to the native occupation (0.008%) (Figure 1). Therefore, it seems that a significant Cu release occurs under soil

humidity due to reducing conditions. Similarly, He et al. (2006) stated that a long-term water logging in soil increased the bioavailable Cu release. The increased extractability of this trace element can be related to the dissolution of Fe and Mn oxides under reducing conditions. These oxides may induce a release of adsorbed Cu (Contin et al., 2007). Also, Cu release can be attributed to the dispersion of the organic matter-mineral complexes due to the high Na concentration in this soil (2.1meq $100g^{-1}$) compared to sandy soil (0.12 meq $100g^{-1}$). A similar hypothesis was reported by He et al. (2006) in different soils with high Na contents. From this described behavior of Cu in clay calcareous soil, we can suggest that the released Cu may be sufficient for plant nutrition. The same conclusion was reported by Hoang et al. (2008) for different soils.

However, for silty clay soil, the Cu release was noticed only at high leaching rates (103 and 247 mm). At these drainage levels, the soil Cu content (147.5 10^{-4} meq 100 g⁻¹) was 94% higher than Cu level (75.9 10^{-4} meq 100 g⁻¹) recorded at a low leaching rate (35 mm) for all soil layers. The absence of Cu release at a low leaching rate may be attributed to the absence of waterlogging conditions (Bigalke et al., 2010). Thus, we recorded that Cu occupation of CEC decreased at low leaching rate (0.035%) and it was enhanced at high drainage levels (0.060%) compared to the native CEC occupation (0.042%) (Figure 1).

From these soils analyses results, it seems that Cu retention was noticed only for sandy soil. In contrast, for clay calcareous and clay silty soils the Cu release was exhibited particularly at high leaching levels. Overall, Cu retention and release processes resulted in soil accumulation of this trace element. Therefore, caution must be taken concerning soil Cu enrichment over the years to preserve the soil environment against toxic levels of this trace element. Therefore, continuous soil analysis over the years is requested to control Cu soil content evolution in lands receiving Cu fertilization.

4. Conclusion

The results of this study have shown that Cu contamination risks of underground waters, due to leaching, are expected to be minimal in the studied south Mediterranean areas. However, Cu risk pollution can especially be related to its accumulation in soil. The behavior of Cu in soil was related to soil types. Indeed, in sandy soil, Cu remained in the soil surface (0–10 cm) due to its adsorption. However, Cu enrichment was recorded in different layers of clay calcareous and silty clay soils. Such enrichment seems to be mainly attributed to its release from the native soil Cu. The major limitation of the presented study is the distinction between the supplied and the native Cu after leaching that will help to clarify the behavior of added Cu in soils. Therefore, more research is needed to understand particularly mechanisms of adsorption/release of Cu in different soils. Overall, this study reveals that attention must be devoted to supplying the right rate of Cu fertilizer to prevent its accumulation in soil over the years.

Declarations

Author contribution statement

Fouad Amlal: Performed the experiments; Wrote the paper.

Saad Drissi: Analyzed and interpreted the data; Wrote the paper.

Kacem Makroum, Abdelhadi Aït Houssa: Conceived and designed the experiments.

Khalid Dhassi: Contributed reagents, materials, analysis tools or data. Hamid Er-rezza: Performed the experiments.

Funding statement

This work was supported by the Moroccan Laboratory of Agriculture "LABOMAG" and the Agricultural Training and Research Center/Providence Verte.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We wish to thank Mr. Coquant J M, Dr. Asfers A., Ms. El Youssefi N., and Mr. Labiad M. for their valuable help in conducting the experiments.

References

- Acosta, J.A., Jansen, B., Kalbitz, K., Faz, A., Martínez-Martínez, S., 2011. Salinity
- increases mobility of heavy metals in soils. Chemosphere 85 (8), 1318–1324.
 Arabzai, A., Honma, S., 2014. Adsorption and transport of heavy metal ions in saturated soils. Proc. Sch. Eng. Tokai Univ. 39, 27–32.
- Bigalke, M., Weyer, S., Wilcke, W., 2010. Stable copper isotopes: a novel tool to trace copper behavior in hydromorphic soils. Soil Sci. Soc. Am. J. 74 (1), 60–73.
- Chen, Y.X., Zhu, G.W., Tian, G.M., Chen, H.L., 2003. Phosphorus and copper leaching from dredged sediment applied on a sandy loam soil: column study. Chemosphere 53 (9), 1179–1187.
- Contin, M., Mondini, C., Leita, L., De Nobili, M., 2007. Enhanced soil toxic metal fixation in iron (hydr)oxides by redox cycles. Geoderma 140 (1-2), 164–175.
- Dong, W., Wang, Q., 2012. Experimental studies on the transport of copper down the soil profile and in runoff during rainfall. Aust. J. Crop. Sci. 6 (6), 1080–1087.
- EPA, 2002. Persistent, Bioaccumulative and Toxic Chemicals. Copper and Copper Compounds. Pollution Prevention Fact Sheet. Office of Pollution Prevention, Ohio, Columbus.
- Flaten, P.L., Karamanos, R.E., Walley, F.L., 2004. Mobility of copper from sulphate and chelate fertilizers in soils. Can. J. Soil Sci. 84 (3), 283–290.
- Goh, T.B., Karamanos, R.E., 2006. Copper fertilizer practices in Manitoba. Can. J. Plant Sci. 86 (4), 1139–1152.
- Gonzalez, D., Almendros, P., Alvarez, J.M., 2015. Mobility in soil and availability to triticale plants of copper fertilisers. Soil Res. 53 (4), 412–422.
- Graham, R.D., 2008. Micronutrient deficiencies in crops and their global significance. In: Alloway, J.B. (Ed.), Micronutrient Deficiencies in Global Crop Production. Springer Science., Dordrecht, pp. 41–61.
- He, Z.L., Zhang, M., Yang, X.E., Stoffella, P.J., 2006. Release behavior of copper and zinc from sandy soils. Soil Sci. Soc. Am. J. 70 (5), 1699–1707.
- Hoang, T.C., Rogevich, E.C., Rand, G.M., Gardinali, P.R., Frakes, R.A., Bargar, T.A., 2008. Copper desorption in flooded agricultural soils and toxicity to the Florida apple snail (*PomaceapaludosaL.*): implications in Everglades restoration. Environ. Pollut. 154 (2), 338–347.
- Lal, R., 2016. Encyclopedia of Soil Science. CRC Press, Boca Ratonhttps.
- Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42 (3), 421–428.
- MarocMeteo. http://www.marocmeteo.ma/, 2019-. (Accessed 21 November 2019). Marschner, H., 1995. Mineral Nutrition of Higher Plants, second ed. Academic Press,
- Harcourt Brace Jovanovich, Published, New York. Moore, G.A., 2001. Soilguide (Soil Guide): a Handbook for Understanding and Managing
- Agricultural Soils. Bulletin 4343. Department of Agriculture and Food, Western Australia, Perth.
- Pick, T., 2011. Assessing water quality for human consumption, agriculture, and aquatic life uses. https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs144p2_05130 2.pdf. (Accessed 21 November 2019).
- Pietrzak, U., McPhail, D.C., 2004. Copper accumulation, distribution, and fractionation in vineyard soils of Victoria, Australia. Geoderma 122 (2-4), 151–166.
- Phillips, I.R., 1999. Copper, lead, cadmium, and zinc sorption by waterlogged and air-dry soil. J. Soil Contam. 8 (3), 343–364.
- Salam, D., El-Fadel, M., 2008. Mobility and availability of copper in agricultural soils irrigated from water treated with copper sulfate algaecide. Water Air Soil Pollut. 195 (1-4), 3–13.
- Shaheen, S.M., Tsadilas, C.D., Mitsibonas, T., Tzouvalekas, M., 2009. Distribution coefficient of copper in different soils from Egypt and Greece. Commun. Soil Sci. Plan. 40 (1-6), 214–226.
- Souza, C.P.C.D., Abreu, C.A.D., Cunha, J.F.D., Costa, G.M.D., Andrade, C.A.D., 2015. Phytoavailability of copper in industrial by-products and mineral fertilizers. Rev. Bras. Ciênc. Solo. 39 (2), 553–562.
- Yang, X.E., Long, X.X., Ni, W.Z., Ye, Z.Q., He, Z.L., Stoffella, P.J., Calvert, D.V., 2002. Assessing copper thresholds for phytotoxicity and potential toxicity in selected crops. J. Environ. Sci. Heal. B. 37 (6), 625–635.