Journal of King Saud University – Science 32 (2020) 307–311

Contents lists available at ScienceDirect

Journal of King Saud University – Science

journal homepage: www.sciencedirect.com

Original article

Physico-chemical characterizations and impact of organic matter on the dynamics of heavy metals (Cu, and Zn) in some soils of Biskra (Algeria)

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ARTICLE INFO

Article history:
Received 31 March 2018
Accepted 15 May 2018
Available online 18 May 2018

Keywords:
Copper
Zinc
Mobility
Biskra region
Organic matter
Algeria
Soil

ABSTRACT

In this study, our work aims to study the effects of some organic matter on the mobility of zinc and copper in the soil of the region of Biskra. This study is twofold concept and showed that: according to heavy metal toxicity thresholds (Cu^{++} and Zn^{++}) our samples are very distant to toxicity thresholds for both sites. For contents of heavy metals reached after the leaching experiment for soil, samples of M'ziraa are greater than those soil samples El-Ghrous treated in the same way. Organic matter EFV (Extract from chicken droppings) to a significant effect in contributing to the accumulation of heavy metals (Cu^{++} and Zn^{++}) compared with EDTA (ethylene diamine tetra acetic acid) and the treatment control. In the end we can say that the microelements (Cu^{++} and Zn^{++}) were little affected by leaching. This is indicated by the low initial levels of the ground by these metals.

1. Introduction

In Algeria, arid zones account for 95% of the national territory, 80% of which is in the hyperarid region, where rainfall does not exceed 100 mm. In these areas, more than 95% of the soils are either limestone, gypsum or salsodic (Halitim, 1988). Each year, large quantities of fertilizers and mineral or organic amendments are applied to soils to increase their productivity (Charbonneau et al. in Giroux et al., 2005). On the other hand, consumption continues to grow in the Third World. Between 1970 and 2000, fertilizer use increased by 450% in Asia, 200% in Latin America and 100% in Africa (Ramade, 1982).

In areas with arid and semi-arid climates, many development programs have been initiated to meet the needs of the population and to revitalize agriculture in these areas, which contribute to a rapid expansion of areas devoted to various crops. Agricultural activity requires farmers to apply all factors of intensification of modern agriculture, including the use of plant protection products, fertilizers and organic matter to increase yields (ANAT, 2003). The organic matter has an important effect on the mobility of heavy metals (Zn^{++} and Cu^{++}) in soil. and this means by the leaching experiment of Mahrous (2007) which shows that there is a leaching of heavy metals (Cu^{++} and Zn^{++}) in the soils studied, namely that the initial values of heavy metals (Cu^{++} and Zn^{++}) in the soil are above the toxicity thresholds.

In this context, our work aims to study the effects of some organic matter on the mobility of zinc and copper in the soil of the Biskra wilaya region.

2. Experimental details

2.1. Study area

The studied soils are located at M'ziraa 60 km, east of the city of Biskra, and El-Ghrous 40 km, west of the town of Biskra (Fig. 1) representing some differences in terms of ground water quality

Abbreviations: EFV, Extract from poultry droppings (as natural organic matter); EDTA, Ethylene diamine tetraacetic acid (as synthetic organic material); S1, Site of the M'ziraa; S2, Site of El-ghrous; T, Control soil is not affected (not treated) by pesticides and fertilizers; Tr, Soil affected (treated) by phytosanitary products and fertilizers; Cu, Copper; Zn, Zinc.

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jksus.2018.05.016
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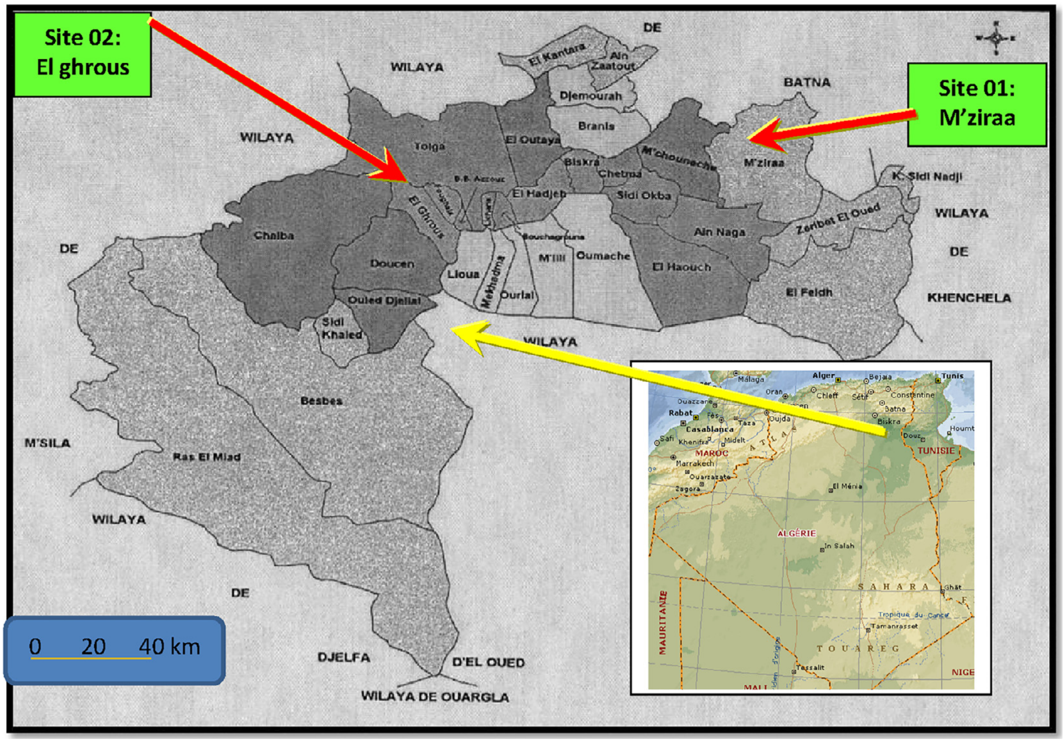

Fig. 1. Location map of the study area.

And soil characteristics. Both sites represent a very important agricultural potential, especially in plasticulture.

2.2. Soil sampling

Sampling of soils affected by plant protection products and fertilizers at each site is taken either from greenhouses or from a soil historically occupied by greenhouses, and plots must be representative for each site (homogeneity). On the other hand, samples of the control soils are taken from bare plots without agricultural activities. We did a single sampling for each site at a depth of 0–30 cm.

The total number of samples: 12 soil samples.

2.3. Laboratory study

The soil samples were dried in the open air. After drying comes the grinding and finally sieving with a 2 mm sieve.

2.3.1. Routine analysis

Table 1 shows the analyzes and methods used for soil.

Table 1
Analytical results of soil.

Types of analysis	Determination elements	Methods used
Soil Reaction (pH)		pH meter with a ratio Soil/water of 2/5
Electrical conductivity (EC) (mS/cm).		Conductivity meter, with a soil/water ratio of 1/5
Total limestone		Calcimeter of Bernard
Organic material		Anne method using potassium dichromate in the presence of sulfuric acid
Granulometry		Sieving
Determination of anions Dilute extract (soil/ water ratio of 1/5)	Cl^- SO_4^{-2} HCO_3^- and CO_3^{-2}	Titration (silverometry) Turbidimetry Titration
Determination of soluble cations Dilute extract (soil/water ratio of 1/5)	Na^+ and K^+ Ca^{++} and Mg^{++}	Flame spectrophotometry Complexometry with EDTA
Determination of exchangeable cations	Na^+ and K^+ Ca^{++} and Mg^{++}	Flame spectrophotometry Complexometry with EDTA

2.3.2. Determination of heavy metals (Cu, Zn) by ammonium acetate in the presence of EDTA

All soil samples are subjected to heavy metals (Cu, Zn) analysis.

Principle

The extraction of the soluble forms of copper and zinc is carried out by a mixed solution of ammonium acetate and EDTA at pH = 7. The elements present in the extraction solution are assayed by atomic absorption spectrophotometry.

This method leads to estimate the quantity of copper and zinc that can be assimilated by plants. It applies mainly to agricultural soils (Clément and Françoise, 1998).

2.3.3. Description of leaching columns

The experiment was carried out in PVC columns 5 cm in diameter and 35 cm in height to study the effects of the doses of added organic matter on the mobility of heavy metals (Cu, Zn) in studied soils. The soils studied were placed in the same way in the PVC columns with a height of 30 cm. Place a paper filter in the base of the columns that allows only water and salts to pass through.

The experimental design adopted comprises 07 columns for each type of soil studied.

2.3.4. Preparation of treatments for organic matter

2.3.4.1. EDTA. Ethylene diamine tetra acetic acid (EDTA) is a synthetic organic material that is used and applied every week at levels of 2, 4 and 6 mmol/kg soil. The available amount of EDTA powder for each level was dissolved in the necessary amount of distilled water for a saturation capacity of the soil. Each solution of each level was added every week to the soil columns at the end of the experiment (8 weeks).

2.3.4.2. EFV (Extract from poultry droppings). The collected poultry droppings were air dried, screened by a 2 mm sieve and stored in a plastic bag. For the preparation of poultry manure extract (EFV); the levels using 25, 50 and 75 g of poultry droppings suspended in 1 liter of distilled water for 2 h, filtered by filter paper, and Stored in the refrigerator at +6 °C. Each solution of each level of organic matter was added every week to the soil columns until end of the experiment (8 weeks).

Each soil treated with the organic materials and compared by a control with distilled water

3. Results and discussion

3.1. Physical and chemical characterization of soils before treatment

The physical and chemical characterizations of the soils before treatment for both sites M'ziraa (S1) and El-ghrous (S2) are shown in Table 2.

Based on the analytical results shown in Table 2 we can see that:

According to the detailed classification chart textures (US, 1976 and taxonomy keys to soil taxonomy, 1986 in Clement and Frances, 1998). Soil samples can be distinguished that are classified into three classes:

1- Class sandy clay loam soil: for sample S1 Soil T and S2: Tr
2- Class of Clay Soil for sample S1 Soil Tr
3- Class sandy loam soil: for sample S2 Soil: T

For $CaCO_3$: For total limestone, content is always observed there a small change between the control soils and treated soils at both sites. The decrease and increase of rates limestone soils treated compared to control soil may be due to the dissolution of limestone as a result of irrigation, the contribution of organic matter and fertilizer (O.R.S.T.O.M, 1972). It is also observed that the levels of calcium in the site 02 are significantly lower than those of the site 01. This is probably due to the presence of gypsum in the site 02, which dominates the solid fraction of the soil.

Site soils 02 are classified as moderately limestone soils of Site 01 are classified as highly calcareous (Baize, 2000).

For the CE: we notice that there a slight deference in the levels of CE treated soil compared with control soils at both sites.

The decrease in EC treated soils compared to controls is possibly due to irrigation, which causes leaching of salts. As against the increase in EC is possibly due to fertilizer inputs and evapotranspiration (Koull, 2007).

According to (Sarkar and Haldar, 2005) are studying the pH of the samples is usually very alkaline, the minimum value is recorded to the ground Site 2 treated with a pH of 8.15 and the maximum value is recorded for the control soil site 2 with a pH of 8.58.

Based on the results of the organic matter is noted that the treated soils have low organic matter rates higher compared to control soil this is due to manure inputs by farmers.

According to (ITA, 1977) treated soils are poor in organic matter against witnesses soils are very poor.

For anions: For contents anions we note that there is a dominance of primary sulfates for site 1, with rates ranging from 88.77% and a content of 18.97 meq/l S1: T and 87.69% for the S1: Tr with a grade of 19.23 meq/l and secondarily chlorides with rates ranging from 9.83% and a content of 2.1 meq/l S1:T and 10.94% for S1: Tr with a grade of 2.4 meq/l. As against a dominance of chloride to the site 2 with rates ranging from 71.17% and a content of 7.9 meq/l S2: T and 79.65% for S2: Tr with a grade of 11 meq/l, and sulfates are second with rates ranging from 26.58% and a content of 2.95 meq/l S2: T and 18.54% for S2: Tr with a grade of 2.56 meq/l. The values of HCO_3^- is still at very low concentrations, and CO_3^{-2} with concentrations zero for both sites.

For soluble cations: For contents of soluble cations we note that there is a dominance of Ca^{++} in the control soils for both sites with rates ranging from 65% and a content of 11.94 meq/l S1: T and 59.05% for S2: T with a grade of 28.46 meq/l, but with a significant difference in the levels of the site by reporting 02 to 01 levels of $CaCO_3$ website although the rate of 01 site is clearly superior to the site 02. Thus the high values of soluble calcium site 02 are probably due to the presence of gypsum which is more soluble than the CaCO3. By against a shared dominance between Na^+ and

Table 2
Physico-chemical analysis of soils before treatment with solutions of organic matter.

Dosed element		Site	S1 T	S1 Tr	S2 T	S2 Tr
Granulometry		Particle diameter size	%	%	%	%
		<50 μm	18.1	12.2	9.4	7.7
		50–250 μm	40	28.2	57.2	44
		250–500 μm	14.9	15.4	17.9	24.5
		500 μm-2 mm	27	44.2	15.5	23.8
$CaCO_3$ (%)			41.12	42.80	15.94	14.27
EC (mS/cm)			2.95	2.9	4.73	5.55
pH			8.35	8.4	8.58	8.15
MO (%)			0.67	1.07	0.67	1.47
Anions		CO_3^{-2} (meq/l)	0	0	0	0
		HCO_3^- (meq/l)	0.3	0.3	0.25	0.25
		Cl^- (meq/l)	2.1	2.4	7.9	11
		$SO_4^{=}$ (meq/l)	18.97	19.23	2.95	2.56
Cations	Soluble	Na^+ (meq/l)	3.78	12.53	14.04	2.48
		K^+ (meq/l)	0.68	0.73	1.64	2.03
		Ca^{++} (meq/l)	11.94	12.02	28.46	28.46
		Mg^{++} (meq/l)	1.7	2.83	4.05	87.48
	Exchangeable	Na^+ (meq/100 g)	0.77	1.11	1.16	0.29
		K^+ (meq/100 g)	0.2	0.21	0.16	0.19
		Ca^{++} (meq/100 g)	11.82	9.22	26.85	28.06
		Mg^{++} (meq/100 g)	0.20	0.81	5.06	6.08
Heavy metals		Zn^{++} (μg/g)	0.10	0.11	0.01	0.05
		Cu^{++} (μg/g)	0.02	0.28	0.34	0.36

Table 3
Leaching effect of organic matter on heavy metals (Zn^{++} and Cu^{++}) in the M'ziraa region.

Material used		EFV			EDTA			Distilled water
Element analysed	Level	25 g	50 g	75 g	2 mmole	4 mmole	6 mmole	
Zn (μg/g)	00–10 cm	0.26	0.19	0.41	0.33	0.19	0.17	0.31
	10–20 cm	0.31	0.41	0.27	0.11	0.14	0.13	0.18
	20–30 cm	0.20	0.25	0.35	0.13	0.20	0.15	0.15
	Average	0.26	0.28	0.34	0.19	0.18	0.15	0.21
Cu (μg/g)	00–10 cm	1.15	1.43	1.00	0.67	1.10	0.62	1.85
	10–20 cm	1.44	1.21	0.80	1.32	0.74	1.00	0.43
	20–30 cm	1.30	3.03	1.38	1.28	0.86	0.80	0.45
	Average	1.30	1.89	1.06	1.09	0.90	0.80	0.91

Table 4
Effect of leaching of organic materials on heavy metals (Zn^{++} and Cu^{++}) in the El-ghrous region.

Material used		EFV			EDTA			Distilled water
Element analysed	Level	25 g	50 g	75 g	2 mmole	4 mmole	6 mmole	
Zn (μg/g)	00–10 cm	0.35	0.16	0.17	0.20	0.10	0.09	0.07
	10–20 cm	0.16	0.34	0.40	0.17	0.09	0.08	0.23
	20–30 cm	0.23	0.23	0.18	0.08	0.06	0.07	0.23
	Average	0.24	0.24	0.25	0.15	0.08	0.08	0.18
Cu (μg/g)	00–10 cm	1.00	0.98	1.11	1.29	0.62	0.32	1.42
	10–20 cm	0.41	1.46	1.03	0.73	0.77	0.93	0.69
	20–30 cm	0.33	0.76	1.03	0.96	1.00	0.41	1.05
	Average	0.58	1.07	1.06	0.99	0.80	0.55	1.05

Ca^{++} to the treated soil site 1 with rate 44.57% and a content of 12.53 meq/l and 42.76%, which corresponds to 12.02 meq/l successively and a Mg^{++} dominance for soils treated site 2 with a rate of 72.62% which can be influenced by the presence of residues of fertilizer. K^{+} of the contents are significantly lower compared to other cations.

For exchangeable cations: Note that the most learned exchangeable bases on the clay-humic complex are divalent cations (Ca^{++} and Mg^{++}) compared to monovalent cations (Na^{+} and K^{+}) for the site 2 with rates ranging from 80.80% and 15.23% for S2: T and 81.05% and 17.56% for S2: Tr for Ca^{++} and Mg^{++} in succession, but with a significant difference in the levels of Ca^{++} Mg^{++} by reporting to content. And Ca^{++} for site 1 because of the rich soil $CaCO_3$ for 01 $CaSo_4 2H_2O$ site and for the site 02 with rates of 90.99% and a content of 11.82 meq/l for S1: T and 81.23%, which corresponds to 9.22 meq/l for S1: Tr.

For heavy metals: For heavy metals results show that there are high concentrations in the levels of zinc and copper soil treated compared to the control soils grades. Cu^{++} save the contents in the 01 site that matches 0.02 μg/g for the control soils and 0.28 μg/g for the treated soil is less than that of Site 02, which corresponds to 0.34 μg/g for soil witnesses and 0.36 μg/g for the treated soils. As against the contents of Zn^{++} register in the 01 site that matches 0.10 μg/g for control soils and 0.11 μg/g for the treated soil is greater than that of Site 02, which corresponds to 0.01 μg/g for soil and witnesses 0.05 μg/g for the treated soils.

According soil toxicity thresholds proposed by (Coïc and Coppenet in Baize, 2000) our samples are very distant thresholds toxicities that are 100 mg/kg for Zn^{++} and 120 mg/kg for Cu^{++}.

3.2. Effect of leaching organic matter on the mobility of heavy metals (Zn^{++} and Cu^{++})

3.2.1. Site 01

Effect of leaching organic matter on heavy metals (Zn^{++} and Cu^{++}) from the M'ziaa region are shown in Table 3.

According to the consultation of Table 3 we seem that the microelements were very little affected by the leaching. This is indicated by the low concentration (<1 μg/g for Zn^{++} and <1.5 for Cu^{++}) of the initial Zn^{++} and Cu^{++} soil contents. Our results are in agreement with those of several authors (Bugbee et al., 1991; Cabrera et al., 1989; Emerich et al., 1982; Giusquiani et al., 1992 in Soumaré et al., 2000).

3.2.2. Site 02

The leaching effect of organic matter on heavy metals (Zn^{++} and Cu^{++}) in the El-ghrous region is shown in Table 4.

According to Table 4, it seems that the microelements were very little affected by leaching. This is indicated by the low concentration (<1 μg/g for Zn^{++} and <1.5 for Cu^{++}) of the initial Zn^{++} and Cu^{++} soil contents.

The increase in Zn^{++} and Cu^{++} levels after the leaching experiment, compared to the initial values, is probably due to:

- The increase of the water-soluble fraction of soils and organic matter (Soumaré et al., 2000a and b in Soumaré et al., 2002) and the adsorption process on colloids or Complexity with organic matter (Boyle and Fuller, 1987; Kabata-Pendias, 1995 in Soumaré et al., 2002).
- Contribution of the organic matter by their contents of these elements (the repeated contributions of the organic matter).

4. Conclusions

At the end of this study, we try to study the effects of some organic matter on the mobility of zinc and copper in the soil of some region of Biskra with abusive use of pesticides and fertilizers.

This region is characterized by an arid to temperate winter climate, a dry period spreading along the year with low and irregular rainfall, high average temperatures and very prolonged periods of drought, intense evapotranspiration, low humidity and brightness Important.

This two-part concept and study showed that:

- The first part consists of identifying and quantifying the initial levels of zinc and copper in the soil as a function of the essential parameters of the soils before treatment by solutions of the organic materials where the results obtained are:

According to the toxicity thresholds of the heavy metals (Cu^{++} and Zn^{++}) of the soil proposed by Coïc and Coppenet (1989) in Baize (2000), our samples are very far from the toxicity thresholds for the two sites where these thresholds are 100 mg/kg for Zn^{++} and 120 mg/kg for Cu^{++}. On the other hand, the norms of (AFNOR U 44 041 in Baise D., 1997) set at 300 mg/kg for Zn^{++} and 100 mg/kg for Cu^{++} are set too high to indicate most abnormalities, whether natural or Where our samples are still very far from the threshold of toxicity.

- The second part consists of characterizing the changes induced after the application of the solutions of the organic materials where the results obtained are:

The leaching of heavy metals (Cu^{++} and Zn^{++}) to the deep layers in the leaching columns for soils studies varies according to the type of material used, its level of application and the type of soil that has been leached.

For the heavy metal levels achieved after the leaching experiment for soil samples of M'ziraa are superior to those of soil samples of El-grous treated in the same way. This can be relatively due to the physico-chemical characteristics of the soil such as: high clay content for M'ziraa soils.

The organic matter EFV has an important effect in the contribution of the accumulation of heavy metals (Cu^{++} and Zn^{++}) in comparison with EDTA and that of control treatment.

In general

The microelements (Cu^{++} and Zn^{++}) were very little affected by leaching. This is indicated by the low initial soil levels of these metals (<0.5 μg/g). Our results are in agreement with those of several authors (Bugbee et al., 1991; Cabrera et al., 1989; Emerich et al., 1982; Giusquiani et al., 1992 in Soumaré et al.

Finally

The microelements (Cu^{++} and Zn^{++}) were very little affected by leaching. This is indicated by the low initial soil levels of these metals.

Acknowledgments

The authors appreciate with thanks to the Department of Agronomy, Mohammed Kheider University, for equipment and technical support during the research work.

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