ASSESSMENT OF Cu, Fe AND Zn CONTAMINATION IN AGRICULTURAL SOILS AROUND THE MEFTAH CEMENT PLANT, ALGERIA

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ABSTRACT

An attempt was made to investigate the concentrations of Cu, Fe and Zn in agricultural soils around the Meftah cement plant, Algeria. Forty soil samples were collected at two soil depths, 0-10 cm and 10-20 cm. The soil samples were digested with the EPA method and the concentrations of heavy metals were determined by atomic absorption spectrometry. The concentrations ranged from 7.22 to 55.75 mg kg^{-1} for Cu, 16160.8 to 19742.2 mg $kg^{-1}$for Fe and 44.46 to 200.26 mg $kg^{-1}$for Zn. The magnitude of the mean concentration values indicated the following order: Fe >> Zn > Cu for both horizons. In accordance with the European guidelines, the mean concentrations of the analyzed metals did not exceed the threshold values for agricultural soils. Concentrations of Cu, Fe and Zn in surface soils were higher than in subsurface soil samples. The enrichment factor (EF) was applied to assess the soil contamination. The enrichment factor values of Cu and Zn in studied soils ranged from 0.75 to 5.03 and 1.79 to 6.68, respectively. Up to 75% and 5% of soil samples were moderately to highly contaminate with regard to Zn and Cu respectively, compared to the upper continental crust concentrations.

Keywords: *heavy metals, soil, enrichment factor, cement industry*

INTRODUCTION

Amongst soil degradation processes, soil contamination by heavy metals is one of the major problems of our time. The accumulation of such elements in the soil in concentrations which exceed the threshold values recommended by international standard scan result in a loss of its qualities, which will influence the productivity, the ecosystem and the refore the human health. Sources of these elements in soils mainly include natural occurrence derived from parent materials and anthropogenic activities

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such as mining, cement industry, the use of untreated wastewater, and agricultural practices (Elbana *et al*., 2013; Ogunkunle and Fatoba, 2012). Cement industry through the release of air pollutants such as heavy metals, generated in the process of crushing limestone, bagging, and transportation of cement are carried by wind and deposited on soil, plants and water bodies (Princewill and Adanma, 2011). Addo *et al*. (2013) reported that gases and chemical products emitted by the cement industry may contain soil heavy metals such as Pb, Cd, Cr, Fe and Zn, and soils close to the cement factory have the highest level. To our knowledge little information exists on the content of soil heavy metals around Meftahcement plant in Algeria. The main objective of this research is to assess soil contamination and determine the concentrations of Cu, Fe and Zn in agricultural soil around to this cement plant.

MATERIALS AND METHODS

Study area: The study area is located between latitude 36° 37′ 00″ N and longitude 3°14′00″ E with a total land area of 2.500 ha. It has a subhumid Mediterranean climate, a mean annual temperature of 18.1 °C and a mean annual rainfall of 600 mm. The main agriculture uses of the area are the production of vegetable crops, cereals and fruit trees. The geological setting of the area is mainly characterized by sedimentary formation. These formations consist of alluvial deposit. The soil types are mainly weakly developed soils, vertisols and calcimagnesic soils (CPCS, 1967).

Soil sampling and preparation: A total of forty soil samples were collected from 20 locations around Meftah cement plant (Figure 1). Soil samples were obtained at two depths, 0-10 cm and 10-20 cm, with hand auger and then were transferred into well labelled polyethylene bags for storage and laboratory analyses. The samples were air-dried at room temperature (approximately 20°C) and passed through a polyethylene sieve with 2 mm openings to remove stones, coarse materials and other debris.

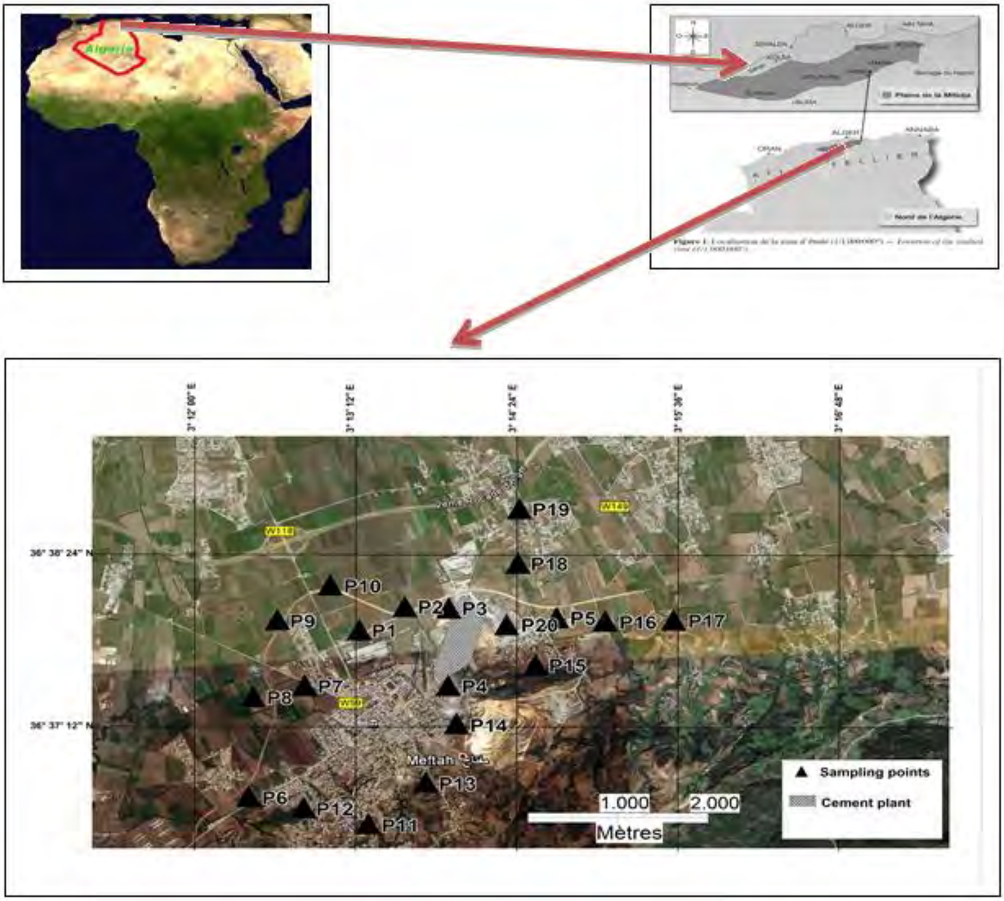

Figure 1. Distribution of sampling sites

Analytical procedures: The particle size distribution was determined by the pipette method. The pH was determined in water with a 1:2.5 soil to solution ratio, electrical conductivity in 1:5 extract, total carbonate by dissolution with HCl, and titration of the excess with NaOH using the Bernard calcimeter method. The percentage of organic matter in the soil samples was determined by the titration method, which is based on the oxidation of organic matter with $K_2Cr_2O_7$. Cation exchange capacity was obtained by extraction with 1M CH_3COONa (Jackson, 1958). Total concentration of metal was determined by a mixture of nitric acid and hydrogen peroxide method (USEPA, 1996). This process was carried out by direct digestion of 1 g of soil sample with repeated addition of HNO_3 and H_2O_2. The extract is then filtered and made to a volume with distilled water. The concentrations of Cu, Fe and

Zn in the extracts were determined by Atomic Absorption Spectroscopy (Perkin Elmer AAnalyst 100).

Assessment of soil contamination: The assessment of soil contamination by heavy metals was carried out by enrichment factor (EF) (Lu *et al*., 2009). The EF is expressed bellow as:

$$EF = \frac{\left[\frac{Cx}{CFe}\right] Sample}{\left[\frac{Cx}{CFe}\right] Background}$$

Where (Cx/CFe) sample is the metal to Fe ratio in the sample of interest; (Cx/CFe) reference soil is the natural background value of metal to Fe ratio. As we do not have metal background values for our study area, we used the values from the upper continental crust (UCC). According to Acevedo-Figueroa *et al*. (2006)seven contamination categories are generally recognized on the basis of the enrichment factor: EF<1, no contamination; 1<EF<3, deficiency to minimal enrichment; 3<EF<5, moderate enrichment; 5<EF<10, moderate to high enrichment; 10<EF<25, high enrichment; 25<EF<50, very high enrichment; EF> 50 extremely high enrichment.

All statistical analyses in this study were performed using Past 3 software. Data were subjected to descriptive statistic.

RESULTS AND DISCUSSION

Physico-chemical parameters

The main physico-chemical parameters determined for the studied soil samples are given in Table 1. The pH values ranged from 7.12 to 7.86, which suggests neutral to alkaline conditions. The soil total carbonate ranged from 0 to 14.94% and EC values ranged from 0.16-0.62 dS/m indicating non saline conditions. The total organic matter in the soil ranges from 0.48 to 3.23%, with a mean value < 2%. Cation exchange capacity of the soils ranged from 16.71 to 31.9 $Cmolkg^{-1}$. The clay contents of the soil were considerable from 9.29 to 78.55%.

Table 1. Range, standard deviation (SD) and mean for the selected soil properties

Parameters	0-10 cm			10-20 cm		
	Range	**SD**	**Mean**	**Range**	**SD**	**Mean**
pH	7.12-7.86	0.19	7.52	7.26-7.81	0.13	7.64
EC (dS/m)	0.16-0.38	0.06	0.23	0.16-0.62	0.14	0.34
OM %	0.48-3.23	0.66	1.55	0.55-2.92	0.58	1.35
$CaCO_3$%	0-14.94	5.16	4.66	0-14.94	5.25	4.81
CEC (Cmol.kg^{-}1)	16.71-31.9	4.43	23.54	17.21-29.76	4.03	23.11
Clay %	9.72-76.83	16.44	48.3	9.29-78.55	17.68	51.36
Silt %	1.55-77.38	17.90	32	6.95-72.76	17	33.46
Sand %	2.77-51.72	12	19.42	2.82-30.09	7.1	13.61

EC: electrical conductivity, OM: organic matter, CEC: cation exchange capacity.

Heavy metal concentrations

The concentrations of the heavy metals in both depths are listed in Table 2. Copper concentrations in upper soil (0-10 cm) were in the range of (7.22-55.75 mg kg^{-1}), with the mean concentrations of 31.5 mg kg^{-1}. The highest Cu value (55.75 mg kg^{-1}) in the upper horizon was recorded to the west of the cement plant. The concentrations in the lower soil (10-20 cm) were in the range of 7.23-53.6 mgkg^{-1}, with the mean concentration of 30.7 mg kg^{-1}. The highest concentration of Cu (53.6 mg kg^{-1}) in the lower horizon was observed to the east of the cement plant. Compared to the international guidelines, the mean concentrations of Cu were lower than the threshold value of 100 mg kg^{-1} (Gawlik and Bidoglio, 2006), but higher than the upper continental crust value of 25 mg kg^{-1} (Wedepohl, 1995). The concentration of Cu were correlated with pH ($r=-0.52$, $p<0.05$) and OM ($r=-0.46$, $p<0.05$) for surface horizon and only with OM ($r=-0.47p<0.05$) for subsurface horizon. Iron is reported, in studies focusing on soil heavy metal contamination, as reference element to establish the anthropogenic metal enrichment. In the study area the highest concentration of 19742.2 mg kg^{-1} (0-10 cm) was observed to the south of the cement plant. This value is in the range of normal values (19785-21794 mgkg^{-1}) found in agricultural soils (Ondo *et al.*, 2013). The mean and range values for Zn in surface (0-10 cm) and subsurface (10-20 cm) soils samples were 143.5, 46.35-200.26 and 132.9, 44.46-195.1 mgkg^{-1}respectively. The mean concentrations of Zn in the studied area exceeded the mean metal concentration of 65 mgkg^{-1}in the upper continental crust (Wedepohl, 1995) but remain below the threshold value of 200 mgkg^{-1} suggested by Gawlik and Bidoglio (2006) in European soils. The highest concentration of Zn was observed to the west of the cement plant. In respect to the influence of pedological parameters on Zn distribution, the statistical analysis showed a significant correlation with only clay ($r = 0.53$, $p<0.05$) for surface horizon.

Table 2. Range, standard deviation (SD) and mean for analyzed soil heavy metals (mg kg^{-1})

Para-meters	0-10 cm			10-20 cm		
	Range	SD	Mean	Range	SD	Mean
Cu	7.22-55.75	16.99	31.50	7.23-53.6	14.63	30.7
Fe	16361-19742.20	735.70	17675.38	16160.8-18799	618.30	17547.6
Zn	46.35-200.26	37.92	143.50	44.46-195.1	40,00	132.9

Moreover, a significant correlation was observed between Zn and Fe ($r=0.45$, $p<0.05$) for surface horizon and between Zn and Cu ($r=0.52$, $p<0.05$) for subsurface horizon. These results could be attributed to the similar dissolution-precipitation pattern. The magnitude of the mean concentration values for analyzed metals indicated the following order for both horizons.

$$\mathrm{Fe} \gg \mathrm{Zn} > \mathrm{Cu}$$

Based on mean concentrations, surface horizons showed higher concentrations of metals compared to subsurface horizons (Figure 2).

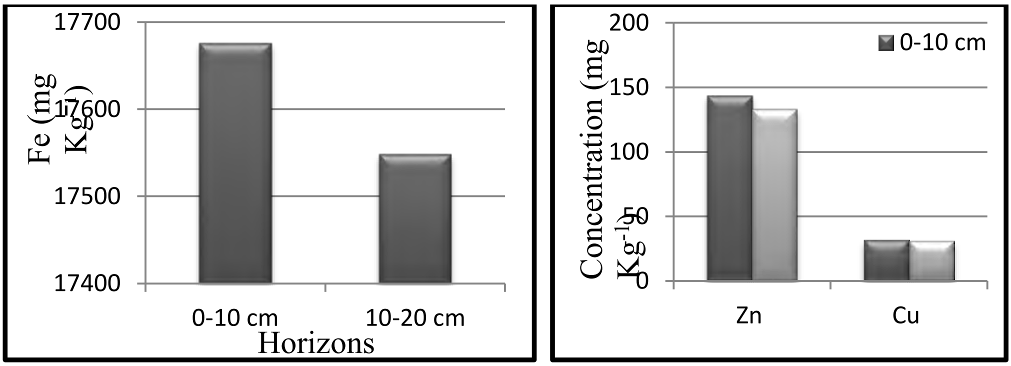

Figure 2. Concentrations of Cu, Fe and Zn in surface and subsurface soil samples

The results of EF corresponding to the two metals measured in the study area are given in Table 3. The lowest values of EF indicate that the occurrence of heavy metals in soils is due to natural process, while high values indicate enrichment by anthropogenic activities.

Table 3. Minimum, maximum and mean of EF in the studied area

Parameters	Min	Max	Mean
Zn	1.79	6.68	5.17
Cu	0.75	5.03	3,00

The EF of heavy metals in soils ranged from 0.75 (Cu) to 6.68 (Zn) (Figure 3). Mean value of EF was 3 for Cu, indicating moderate contamination. The mean EF value of Zn was 5.17, indicating moderate to highly enrichment in this element. The results revealed that up to75 and 5% of soil samples showed moderate to high enrichment for Zn and Cu respectively. In addition, 20 and 45% of soil samples showed a moderate enrichment for Zn and Cu.

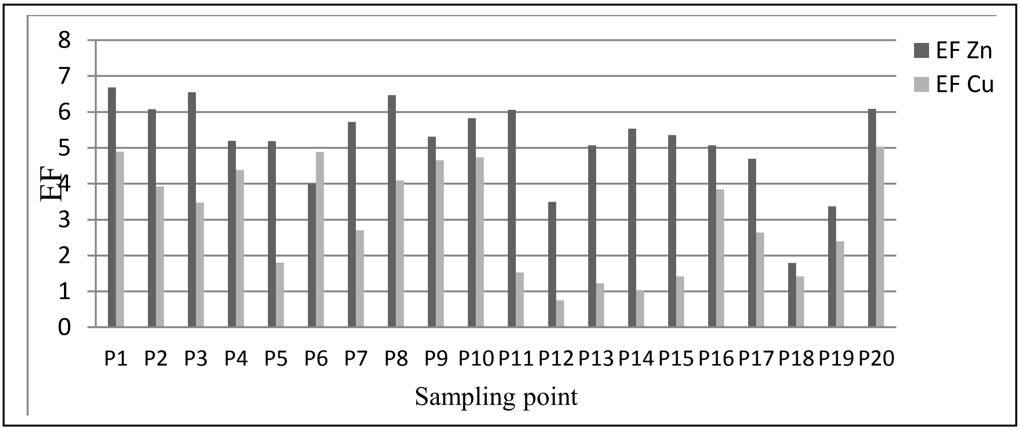

Figure 3. Spatial distribution of enrichment factor (EF) for Zn and Cu in the studied area

CONCLUSIONS

Although the results of this work showed an anthropogenic contribution compared to the upper continental crust, however the concentrations of Cu and Zn were below the European threshold values. Dust emissions from the cement plant activities are probably the cause of such enrichment with heavy metals in agricultural soils surrounding cement plant. Further studies with intensive sampling are needed to assess the distribution and contamination of other metals such us Cd, Ni and Pb in the studied area.

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