Pollution Study 2023, 4(1), 2113.
https://doi.org/10.54517/ps.v4i1.2113

Article

Effect of the application of composted manure on the mobility of Cu chemical fractions in a soil contaminated with mining waste

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CITATION

Mendoza-Jiménez MN, Quintero-Soriano RI, Zaragoza VMD, Carrasco-Hernández V. Effect of the application of composted manure on the mobility of Cu chemical fractions in a soil contaminated with mining waste. Pollution Study. 2023; 4(1): 2113. https://doi.org/10.54517/ps.v4i1.2113

ARTICLE INFO

Received: 13 March 2023
Accepted: 10 April 2023
Available online: 21 April 2023

Abstract: The weathering of mining wastes with a high content of metallic sulfides is involved in the release and mobility of heavy metals, being one of the main risk factors for the environment and public health. In this work, two types of manure were used to evaluate their effect on the mobile or bioavailable chemical fractions of Cu in a soil contaminated with mining waste. An experiment was conducted using a soil artificially contaminated with 25% mining waste from Zimapán, to which increasing doses of composted cow and pig manure (0, 3%, 6%, 12% and 24%) were added. The pseu-do-total Cu concentration was determined by atomic absorption spectrophotometry after acid digestion, while the Cu chemical fractions were determined from sequential extractions. The results obtained showed a high pseudo-total Cu concentration in the mining residues and low in the soil and in both types of manure. In the treatments with greater application of pig manure, there was a decrease in the concentration of soluble-interchangeable Cu and an increase in the concentration of Cu strongly bound to the organic fraction. While with cow manure there were higher concentrations of soluble-interchangeable Cu and an increase in the fraction of Cu weakly bound to the organic fraction.

Keywords: soil contamination; environmental analysis; sequential chemical fractionation; contaminated soils; tailings dams

1. Introduction

Mining is one of the most important economic sources in Mexico, generating wealth, but at the same time causing significant damage to the environment; its operation causes deforestation, habitat destruction, contamination of surface water bodies, and the generation of large quantities of waste [1]. The latter represent a source of contamination and a public health problem because they contain metallic sulfides, high concentrations of heavy metals, lack the physical, chemical and biological properties necessary for the development of vegetation, and because they are fine-particle, unstable materials that are dispersed into the environment by water and wind dragging, the latter causing erosion [2].

The degree of heavy metal contamination in soils is usually measured from the total concentration [3]. However, this parameter does not provide complete information on ecological risk, geochemical distribution, mobility or bioavailability [4]. To know the risk posed by heavy metal contamination, it is recommended to quantify the bioavailable concentration, defined as the amount of heavy metal dissolved in soil solution or present in exchange sites [5]. The soluble and exchangeable forms are considered the most mobile and bioavailable, while those that are incorporated into other components act as a reservoir, remaining retained with organic matter (OM), bound with carbonates and occluded with Fe and Mn oxides or inactive within the crystalline structures of clays [6].

The mobile concentration of heavy metals is determined from simple extractions with: neutral salts such as $CaCl_2$ 0.001–0.01 M, $NaNO_3$ 0.1 M or NH_4NO_3 1.0 M, and organic chelates such as EDTA and DTPA 0.05 M [7]; or sequential extractions are performed to quantify the labile fraction of contaminants and their distribution with soil components [8]. Sequential extractions are procedures applied to evaluate the mobility of heavy metals in sediments, soils and waste materials, and dissolve the different fractions of minerals that retain most of the trace elements, using a series of selective reagents [9].

Currently, the application of organic amendments is not only an alternative to improve the physical, chemical and nutritional conditions of the soil, but also an option to immobilize soluble heavy metals [10]. Among the organic materials used for that purpose are composts [11], biosolids [12] and animal manures [13], among others. The amount, composition and dynamics of soil organic matter (SOM) influence the mobility of heavy metals [14], as well as other abiotic factors such as pH, Eh, cation exchange capacity, clay content and type, salt content, Fe and Mn oxy-hydroxides, etc. [3]. Generally, it has been established that humified SOM forms more stable complexes with heavy metals, while fresh OM or light fraction of SOM, can increase the mobility and bioavailability of metals [15].

The objective of this study was to evaluate the effect of the application of composted cow and pig manure on the mobility of the chemical fractions of Cu in a soil contaminated with mining residues, considering as an analysis variable the proportion of manure applied in the retention and type of manure in the changes of the mobile or bioavailable fractions of Cu. As a working hypothesis, it was proposed that in the treatments with a higher proportion of manure applied, as well as in the manure with a higher cation exchange capacity, a lower concentration of Cu in the fraction with higher mobility (soluble-interchangeable) was recorded.

2. Materials and methods

2.1. Sampling and sample preparation

Sampling of mining waste was carried out on the slopes and upper part of the Santa María deposit in Zimapán, Hidalgo, located at geographical coordinates 0°44′17.6″ N 99°24′03.1″ W, and from which a sample representing the Cu concentration of the site was taken, composed in turn of 10 subsamples collected at 10 different points using an auger 30 cm long and 7 cm in diameter, with which 0.5 kg of waste was extracted per subsample. The soil was collected 10 km west of the sampled waste deposit at 20°42′10.764″ N 99°20′5.848″ W. The cow and pig manure were composted for four months in the backyard area of the Tecnológico de Estudios Superiores del Oriente del Estado de México and the samples were air dried and dried in the shade at room temperature.

2.2. Experimental design

The experiment was carried out in a greenhouse, based on the preparation of different treatments using cow and pig manure applied in different proportions to the soil artificially contaminated with mining residues (25% w/w). The manure proportions were 0, 3%, 6%, 12% and 24% (w/w). The experimental design was completely randomized with five treatments and three replicates for each type of manure. The experiment was maintained for two months at an average temperature of 30 °C, humidity was kept at 5% w/w and checked by gravimetry every third day. The total weight of each experimental unit was 1 kg in weight, made from PVC pipes of 35 cm in height and 2.5″ in diameter. Changes in the mobile fraction (F1, Soluble-Interchangeable) of Cu were determined from a sequential chemical procedure.

2.3. Analytical methods

The pH was determined by potentiometry [16] at a soil:water ratio of 1:4, then in the same solution after 20 h of equilibrium the electrical conductivity (EC) was measured with a conductivity bridge (Soil Survey Staff, 1975). The following analyses were determined by different methods: Organic matter (OM) and organic carbon (OC) by the Walkey and Black method modified by Nelson and Sommers [17]; total nitrogen (TN) by the micro Kjeldalh method and Texture analysis was performed by the Bouyoucos hydrometer technique [18]; cation exchange capacity (CEC) by the 1N ammonium acetate method pH 7 [19]; pseudo-total Cu content was determined in triplicate after acid digestion with the mixture of HNO_3:$HClO_4$:H_2O_2 (4:1:1:1) by Atomic Adsorption Spectrophotometry (AAS) with the Thermo Scientific ICE 3000 Series AA Spectrometer. Calibration was performed using a certified 1000 mg/L Cu standard (Perkin Elmer Pure: Part N9300183) with a calibration curve in the range of 0.2–1.6 mg/L.

2.4. Sequential procedure for the chemical fractions of Cu

The procedure for the determination of the Cu chemical fractions of each of the treatments consisted of using different chemical reagents sequentially and thus obtaining the fractions in the order described in **Table 1** [20].

Table 1. Sequential procedure for the determination of Cu chemical fractions.

Step	Fraction	Method and reagents used
F1	Cu-soluble interchangeable	Extraction with acetic acid 1 M at pH 5
F2	Cu-bonded to Fe and Mn oxides	Extraction with 0.1 M hydroxylamine hydrochloride and 25% acetic acid.
F3	Cu-bonded weakly with MO	Extraction with HCl 0.1 M.
F4	Strongly Cu-joined with MO	Extraction with 0.5 M NaOH and digestion with 65% HNO_3.
F5	Cu-bound to the sulfide phase	Digestion with 8 M HNO3.
F6	Cu-bonded in the residual solid	Digestion with HNO_3 + HCl, + H_2O_2

2.5. Statistical analysis

The following analyses were performed: a) analysis of variance (ANOVA) for a distribution of treatments, using the statistical software SAS v9.4 (Statistical Analysis System), and b) Pearson's correlation and Tukey's test for comparison of means.

3. Results and discussion

3.1. Physical and chemical characterization of materials and pseudo-total Cu content

The mining residues had a sandy texture, with 85% sand, 2.5% clay and 12.5% silt and low MO content, pH of 6.64, EC of 2100 dS/m, and low CEC. On the other hand, the soil presented a loam texture, with 14% clay, 48% silt and 38% sand, slightly alkaline pH, EC of 280 dS/m, CEC of 13 Cmol(+)/kg (**Table 2**). Pig manure had a neutral pH; while cow manure recorded a slightly alkaline pH, the latter with higher EC, lower MO content and lower CEC (**Table 2**). On the other hand, the pseudo-total Cu concentration in the mining residues was 2417 mg/kg, while in the soil it was only 46 mg/kg and 76 mg/kg in the cow manure and 39 mg/kg in the pig manure, the latter registering a higher MO and CO content than the other material.

Table 2. Physical and chemical characteristics of soil, mining waste and manure.

Variable	pH	Texture	CE (dS/m)	CIC (Cmol/kg)	MO (%)	CO (%)	C/N	Total *N* (%)
Soil	7.89	Franca	280	13	3.3	1.19	-	-
Mining waste	6.64	Arenosa	2100	5.8	1.5	0.87	-	-
Pig manure	6.8	-	789	30	26	17.4	3.6	4.85
Cow dung	7.8	-	1285	12	18	10.44	3.5	3

On the other hand, when both swine and cow manure were applied, changes in the chemical properties of the treatments were observed (**Table 3**): pH increased slightly as the proportion of cow manure increased, but not with swine manure where there was a slight decrease, remaining at a neutral pH. On the other hand, CEC changed from 12.6 to 23 Cmol(+)/kg with pig manure and only up to 14.30 Cmol(+)/kg with cow manure. EC increased from 810 in the 0% manure treatment to 960 dS/m with swine and 1240 dS/m with cow manure in the 24% treatments.

Table 3. Average chemical parameters measured in the different treatments.

Variable	Treatments									
	0%	3%	6%	12%	24%	0%	3%	6%	12%	24%
	Cow dung					Pig manure				
pH	7.1	7.2	7.4	7.7	7.8	7.1	7.1	7.0	7.0	6.9
EC (dS/m)	810	956	1089	1136	1240	810	816	837	924	960
CIC (Cmol(+)/kg)	12.6	12.9	13.4	14.26	14.30	12.6	13.7	18.1	21.3	23.0

Soil components are involved in controlling the mobility of heavy metals, under neutral and alkaline pH conditions there is less mobility and low bioavailability, while acid pH increases their mobility. Soluble salts have an important influence on the mobility of heavy metals in soil [21] and with the application of manures, these increased, which may influence their mobility. In the case of CEC, it is related to the capacity to exchange metal ions from the soil solution to the surface of clays, Fe and Mn oxides and to the MOS [22], although the CEC found in the applied manures was lower than in the results of other works with the same materials (up to 36 Cmol(+)/kg have been reported), this variable is related to the type and proportion of OM. According to Alloway and Trevors [23] and Caporale and Violante [24], other soil components that are also responsible for controlling mobility are the concentration and type of clays, SOM, Fe and Mn oxides, carbonates, microorganisms, and organo-mineral complexes. MO participates in controlling the mobility of heavy metals in soil, but it depends on its composition, salt content, C/N ratio, and degree of humification, so it becomes difficult to predict its behavior [25,26].

On the other hand, the mining residues presented a high Cu content, with a pseudo-total concentration similar to those reported by Tembo et al. [27], in the same residues. In addition, it was observed that both the soil and the manure used, being untreated materials, present Cu, although at very low levels of those considered for contaminated soils [28].

3.2. Chemical fractions of Cu in the treatments

Figure 1 shows the graphs of the chemical fractions of Cu with the application treatments of the two types of manure, where the error bars corresponding to their standard deviation and the Tukey test for the comparison of means are also shown.

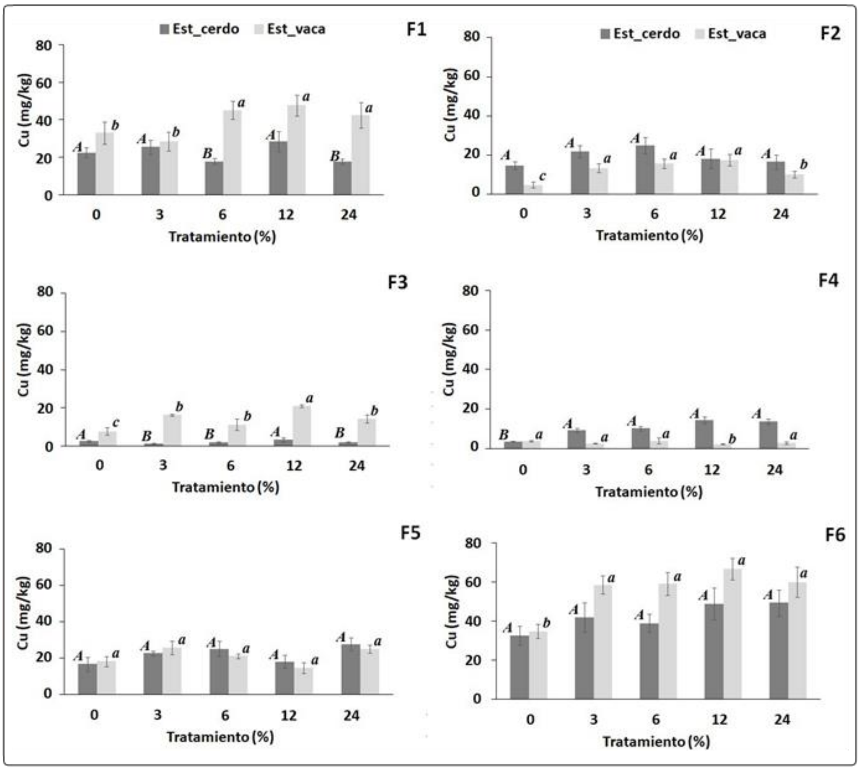

Figure 1. Chemical fractions of Cu in pig and cow manure treatments; F1 = Cu-soluble-exchangeable, F2 = Cu-bound to Fe and Mn oxides, F3 = Cu-bound weakly to OM, F4 = Cu-bound strongly to OM, F5 = Cu-bound to sulfide phase and F6 =

Cu-bound to residual solid. Treatments with the same letter in each graph are not significantly different (Tukey test: $\alpha = 0.05$). Personal elaboration.

In F1 (exchangeable Cu-soluble) a concentration of 22.5, 25.5, 17.8, 28.5 and 18.7 mg/kg Cu was recorded in the respective treatments of 0, 3%, 6%, 12% and 24% pig manure, with a mean of 22.4 mg/kg Cu. In the cow dung treatments, 33, 28.5, 45.1, 47.6 and 42 4 mg/kg Cu were recorded in the treatments at 0, 3%, 6%, 12% and 24%, respectively; with a mean of 39.3 mg/kg Cu. In both materials applied with significant difference between treatments (Pr < 0.0001).

In F2 (Cu-bound to Fe and Mn oxides), with pig manure 14.7, 21.7, 24.9, 18.2 and 16.6 mg/kg Cu were obtained in the 0, 3%, 6%, 12% and 24% treatments, respectively; with a mean of 19.3 mg/kg Cu, with significant difference among treatments (Pr = 0.0001). While with cow manure, 4.8, 13.3, 15.7, 17.5 and 10.2 mg/kg Cu were recorded with the application of 0, 3%, 6%, 12% and 24% manure, respectively; with a mean of 12.3 mg/kg Cu, no significant difference was observed among treatments (Pr < 0.4672).

In F3 (Cu-weakly bound to MO), treatments with pig manure application recorded 7.7, 16.4, 11.3, 21.1 and 14.4 mg/kg Cu at 0, 3%, 6%, 12% and 24% treatments, respectively; with a mean of 2.3 mg/kg Cu and a significant difference among treatments (Pr < 0.0001). While in the treatments with cow dung 5.3, 16, 11.2, 21.1 and 14.4 mg/kg Cu in the proportion of 0, 3%, 6%, 12% and 24%, respectively; with a mean 14.1 mg/kg Cu, and a significant difference between treatments (Pr < 0.0001).

In F4 (Cu-strongly bound to OM) pig manure treatments, 3.7, 9.4, 10.3, 14.6 and 13.8 mg/kg Cu were found in the 0, 3%, 6%, 12% and 24% treatments, respectively; with a mean of 14.59 mg/kg Cu. On the other hand, the treatments with cow manure, registered values of 4.1, 2.7, 4.2, 2.4 and 3.1 mg/kg Cu in the respective treatments of 0, 3%, 6%, 12% and 24%; with a mean of 3.3 mg/kg Cu. With both materials, a statistical difference between treatments was observed (Pr < 0.0001).

In F5 (Cu-bound to the sulfide phase), concentrations of 16.6, 22.6, 24.9, 17.9 and 27.6 mg/kg Cu were recorded in the respective treatments of 0, 3%, 6%, 12% and 24%; with a mean of 29.9 mg/kg Cu, with no significant difference among treatments (Pr = 0.5510). Very similar concentrations were recorded in the cow manure treatments, presenting 18.2, 25.6, 21.1, 14.6 and 24.9 mg/kg Cu in 0, 3%, 6%, 12% and 24% manure, respectively; with a mean of 20.9 mg/kg Cu, with no significant difference among treatments (Pr = 0.2310).

In F6 (Cu-bound to residual solid), with pig manure application, 32.7, 41.8, 38.9, 48.9 and 49.43 mg/kg Cu were found in the respective treatments of 0, 3%, 6%, 12% and 24%; a mean of 42.4 mg/kg Cu, with no significant difference between treatments (Pr = 0.2310). While in the cow dung treatments, concentrations of 34.8, 58.6, 59.1, 66.8 and 60.1 mg/kg Cu were recorded at 0, 3%, 6%, 12% and 24% dung, respectively; a mean of 50.9 mg/kg Cu, and significant difference between treatments (Pr = 0.0105).

With Pearson’s correlation analysis, the following results were obtained from: the concentration of Cu chemical fractions and soil chemical properties (pH, EC and

CEC) for each type of manure used. With swine manure, F1 recorded a low correlation coefficient (*r*), with pH $r = -0.1$, EC $r = -0.1$ and CIC $r = -0.21$; F2 with pH $r = -0.27$, EC $r = -0.32$ and CIC $r = -0.04$; F3 with pH $r = 0.48$, EC $r = 0.29$ and CIC $r = 0.22$; F4 with pH $r = 0.77$, EC $r = 0.84$ and CIC $r = 0.90$; F5 with pH $r = 0.22$, EC $r = 0.37$ and CIC $r = 0.49$; and F6 with pH $r = 0.75$, EC $r = 0.89$ and CIC $r = 0.86$.

With cow manure F1 recorded a high correlation coefficient (*r*), with pH $r = 0.71$, EC $r = 0.74$ and CIC $r = 0.80$; F2 with pH $r = 0.28$, EC $r = 0.55$ and CIC $r = 0.51$; F3 with pH $r = 0.54$, EC $r = 0.55$ and CIC $r = 0.64$; F4 with pH $r = -0.42$, EC $r = -0.35$ and CIC $r =-0.55$; F5 with pH $r = -0.11$, EC $r = 0.14$ and CIC $r = -0.15$; and F6 with pH $r = 0.59$, EC $r = 0.81$ and CIC $r = 0.76$. In summary, the highest correlations with soil chemical parameters were F4 and F6 in pig manure and F1, F3 and F6 in cow manure.

The different soil mixtures recorded an average pseudo-total concentration of 664 mg/kg of Cu, a level that, according to USEPA [26], should be considered as contaminated soil with environmental risk. However, it is relevant to mention that in the experiment the concentration of Cu in F1 (exchangeable soluble) represented the bioavailable fraction for plants and animals, due to its higher mobility. According to Usman et al. [29] and Abollino et al [30], the World Health Organization (WHO) sets a limit of total Cu concentration in soils of 30 mg/kg to consider it contaminated. In the study conducted by Hayes et al. [31] they evaluated the effect of cow dung on the immobilization of Pb, Cd, Cu and Zn directly in mining waste, where they reported a distribution of chemical fractions different from those found in this work, possibly because the waste belonged to a different mining waste deposit, although from the same area. In the soluble-interchangeable fraction of Cu, it was expected to register a lower concentration of Cu in the treatments with more manure applied; however, with cow manure F1 increased probably due to an increase in EC by the effect of soluble salts on the mobility of metals in the soil as has been reported by Concas et al. [32] and Jiang et al. [33]). Another possibility could be variation in temperature and humidity, already reported as an influence on the mobility of heavy metals in the soil.

Rodríguez, Ruiz, Alonso-Azcárate and Rincón established an environmental risk code, which is based on the strength of the bond between metals and the different geochemical fractions of the soil, the contaminants contained in the Soluble-Interchangeable Fraction indicate the risk they have on the environment, when F1 (soluble-interchangeable), is less than 1%, of the total concentration of the element, there is no risk; therefore, when F1 is in the following ranges the level of risk is valued for example: in a range of 1%–10% the risk is low; 11%–30% medium; 31%–50% high and greater than 50% the risk is very high. What this work indicates is that there is a low risk in the result with the treatments where pig manure was applied, since for F1 it was from 1.3% to 4.7%; and with cow manure it was from 7% to 11% with a low to medium risk.

SOM has a high influence on the retention of heavy metals, with their composition and dynamics in the soil being important factors in controlling their mobility. However, metals bound to the light fraction of OM (F3) are more susceptible to oxidation and release of contaminants; while metals bound to the heavy fraction of OM, due to the content of humic acids (F4), have a higher stability in the soil. Cow dung presented a higher concentration of Cu in F3, where the light fraction of the OM is extracted, which according to Bloomfield, metal complexes with fulvic acids, can be promoters of mobility in the soil. On the other hand, metals bound to the sulfide phase (S=) after sulfur oxidation (SO=) are released in their cationic phase M++ contaminating soils and surface water bodies [32]. The heavy metals recorded in the residual fraction (F6) are strongly stable, and bound to the crystal lattice of minerals.

4. Conclusions

The high pseudo-total concentration of Cu contained in the mining waste indicates an important risk for the environment and the health of the people and communities surrounding Zimapán; however, with the use of remediation strategies using organic materials, the bioavailable concentrations can be reduced and the specific risk represented by each of the waste deposits in the environment can be determined. A lower concentration of soluble-interchangeable Cu was not observed in the treatments with greater application of cow manure, probably due to the increase of soluble salts, or to the presence of a high proportion of soluble compounds; while with pig manure there was a decrease, but not statistically significant. The application of manure modified the chemical fractions of Cu, in cow manure there was a higher concentration in F3, and in swine manure in F4, Cu strongly bound with OM, it is related to the quality of the organic matter added, which is very important in the processes of Cu retention. The two types of manure seem to have a strong interaction with the soil and mining residues, probably due to the contribution of clay minerals, since a high correlation is observed between the proportion added and the concentration of copper retained in the residual fractions.

Author contributions: Conceptualization, RIQS and VMDZ; methodology, investigation, VCH; writing—original draft preparation, MNMJ; writing—review and editing, VMDZ. All authors have read and agreed to the published version of the manuscript.

Conflict of interest: The authors declare no conflict of interest.

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