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## Organic Waste as Fertilizer in Semi-Arid Soils and Restoration in Mine Sites

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#### **Abstract**

The use of organic waste such as tannery sludge which has high organic matter, N and P content, as organic fertilizer is suitable for improving soil fertility in semi-arid soils and for remediation of abandoned mine sites. Retention of heavy metals on fractional processes of organic matter cannot be generalized, it depends on the chemical characterization of organic waste and soil. Addition of tannery sludge containing high concentrations of Cr and carbonates to semi-arid soils resulted in an increase in Cr loss in infiltration and runoff after 6 months of incubation followed by simulated rainfall. Under these characteristics, results suggest that tannery sludge represents a potential hals amended with organic compost. Chemical characteristics of organic waste such as nitrogen content, humified organic matter, pH, EC, CEC, ESP (interchangeable sodium percent), and SAR (sodium absorption ratio) are important properties to consider in organic matter amendment to semi-arid soils participating on the complexity and leaching of heavy metals and nutrients in the matrix of soil.

**Keywords:** tannery sludge, simulated rainfall, mobility of heavy metals, mine tailings, heavy metal fractionation

#### 1. Introduction

Soils of arid and semiarid regions need the amendment of organic compounds due to being low in organic C content and as consequence unable to improve their physicochemical and biological properties and thus their yield of crops and their natural fertility [1, 2].

Organic amendments, such as farmyard manures, have been used as common organic manure for supplying nutrients to plants. After the second world war, there was a great interest in



using other organic wastes as organic fertilizer, farmyard manure has been used as a reference when sewage sludge or other organic materials have to be judged [3]. The sewage sludge and sludge compost amendment were ceased when it was found that soluble heavy metals in the soil and the total heavy metals in the crops were increasing when these wastes were applied [4]. However, sewage sludge and compost are the most widely used organic amendments, mainly by their high organic matter, N and P content, which are important nutrients for plant growth, their contribution to soil structure, and resistance to soils erosion [5–8]. On the other hand, application of sewage sludge as agricultural fertilizer is associated to numerous environmental and health problems such as those implicated by toxic metals, organic compounds, and possible other health problems related to pathogens [9–12].

The gradual increase in industrialization and urbanization in the last decades has created an enormous increase in volumes of wastes produced all over the world. Usually, these wastes are discharged to the environment [13], especially in countries which regulatory control is not strict.

The objective of the case study described in this chapter, together with methodology and literature review is to provide different scenarios of the role of organic waste in semi-arid soils poor in organic carbon, the effect of heavy metals on soil biogeochemical processes, their dispersion and mobility in soils, and the availability of heavy metals to plants.

#### 1.1. Semi-arid soils and tannery sludge

Tannery sludge derives from a complex combination process where organic and inorganic materials become chemically bound to the protein of the hides and preserve it from deterioration. A significant number of operations within the tannery industry involve large amounts of water, chemicals, and energy leaving as waste large amounts of polluted water. These industrial effluents contain several types of chemicals such as dyes, levelling agents, acids, alkalis, phenols, carbonates, alcohols, cyanide, and heavy metals, among others [14].By-products generated during leather manufacturing are usually rich in proteic matter and organic substances, thus it is a potential resource that can be used as fertilizer in agriculture production. This leather processing waste is an attractive disposal for soil amendment as it has proven to improve the physical properties of soil and supply organic matter and plant nutrients [15–19].

The use of these waste in semi-arid soils as organic fertilizer of plants could be an alternative disposal method and simultaneously it will resolve the environmental risks presented when they are abandoned to open sky.

Under natural environmental conditions, chromium is present in either the trivalent Cr(III) or the hexavalent Cr(VI) [20, 21]. The effect of Cr on health have been widely studied [22]. Cr(VI) is about 300 times more toxic than Cr(III). Health effects of Cr have been reported in lung cancer, and birth defects [23, 24]. Cr(III) have relatively low toxicity and are easily precipitated and immobilized; however, Cr(VI) is toxic, water soluble, and highly mobile, and can then be transported into the surrounding surface soil and ground water [25, 26]. Tannery sludge contains both trivalent (CrIII) and hexavalent (CrVI) chromium. There is little information

about the biogeochemical conditions affecting solubility of heavy metals in arid and semi-arid soils including soil pH, Eh, and dissolved organic carbon contents [27]. The information generated in this study is critically important for assessing the benefits or potential risks of using tannery waste to treat semi-arid soils for re-forestation.

#### 1.2. Mine tailings amended with organic wastes

Mine tailing disposal sites from either inactive or abandoned mines are common in arid and semiarid regions throughout the mine region around the world. These tailings have been stored outside and have contaminated local ecosystems and harmed the nearby populations [28]. Today, areas containing mine tailings can be found in urban and agricultural zones and mine tailing storage after the closure of mining operations is becoming increasingly problematic in the arid and semiarid region because of wind erosion. These areas are a source of air pollution giving off particles [29]. Short-term exposure to mine tailing particles can lead to illness, while long-term exposure may lead to premature death in adults and children [30, 31].

#### 2. Research methods

#### 2.1. Sampling areas

The soil was sampled from three sites: Two around mesquite trees (*P. laevigata*), the dominant vegetation (Dolores Hidalgo, Guanajuato, Mexico), under the canopy and outside the canopy of mesquites (**Figure 1**), and the third one from a site cultivated with maize (*Zea mays*) for 20 years.



Figure 1. Under the canopy tree of mesquite (U), Outside the canopy of mesquite (O).

Soil was collected from a 0- to 5-cm layer, where the highest organic contents can be found. The first sampling was taken from under the canopy of four isolated mesquite trees, 1–2 m from the stem in four perpendicular directions randomly selected. The second one at a distance of 6–8 m from the stem, outside the canopy in the same perpendicular directions (**Figure 1**).

The soil was bulked; all the stones, visible roots, and fauna were removed, it was sieved to less than 2 mm and stored at 5°C to use latter.

#### 2.2. Tannery sludge

Tannery sludge, produced during leather manufacturing, when processing skin or hide to leather, was sampled from a tannery in Leon (Guanajuato, Mexico). It contained large quantities of hair, fatty fleshings, and soluble proteins, as well as sulphide, lime, chromium-sulphate, salts, dyes, acids, and leather trimmings.

#### 2.3. Incubation experiments

A pre-incubation process of soil samples was necessary to allow the soil microbial activity to stabilize after the sampling and sieve management. Soils were pre-incubated for 1 week prior to starting the experiment at conditions similar to the experiment, i.e. at  $20^{\circ}$ C in the dark, in a temperature and humidity controlled room. Three replicates were destructively harvested at days 0–90 or 120 and stored at  $-20^{\circ}$ C for N mineralization and soil microbial activities analysis.

#### 2.4. Soil microbial activities and nitrification

Maintaining soil fertility depends on biomass and activity of soil microorganisms vital in the biological cycles of most major plant nutrients [32]. Microorganisms are also involved in forming soil structure [33]. Several microbiological parameters have been suggested to measure soil environmental quality [34]. For instance, soil respiration and enzyme activities such as dehydrogenase activity and nitrification, can inform about the presence of viable microorganisms, and on the intensity, kind and time length of the effects of pollutants on the metabolic activity of soils.

Sub-samples of 40 g of soils were placed in 110-ml glass bottles, which were then put into 1-l jars containing 10 ml  $\rm H_2O$  and a vessel with 20 ml 1 M NaOH solution. The jars were air-tight sealed with plastic lids and incubated at 25 °C for 7 days. After incubation, vessels with 20 ml 1 M NaOH solution were removed, resealed, and stored for future  $\rm CO_2$  analysis. At the mentioned dates, soil was removed for analysis of  $\rm NO_3^-$ –N,  $\rm NO_2$ –N, and  $\rm NH_4^+$ –N, done by shaking for 30 min with 100 ml 0.5 M  $\rm K_2SO_4$  solution and filtered through Whatman No. 42 paper. Similarly, control fresh samples were extracted. Extractants were stored at  $\rm -20^\circ C$  until analysis. Concentration of  $\rm NO_3^-$ –N and  $\rm NO_2^-$ –N in the extracts was determined by colorimetric method [35] and  $\rm NH_4^+$ –N by Indophenol blue [36].

Dehydrogenase activity in soils has been used as measure for overall microbial activity [37]. The method is based on the estimation of triphenyltetrazolium chloride (TTC) reduction rate to triphenyl formazan (TPF) in soils after incubation at 30°C for 24 h. Soil dehydrogenase activity was measured using a modified form of the method used by Casida [37]. Five grams of fresh soil were incubated at 37°C for 24 h in test tubes containing 1 ml 3% 2,3,5- triphenyltetrazolium chloride (TPF), 67 mg CaCO<sub>3</sub>, and 2.5 ml distilled water. The accumulation of the end-product triphenyl formazan (TPF)was determined in acetone extracts (50 ml) using a PerkinElmer Lamda 3A Spectrophotometer at 520 nm.

#### 2.5. Measurement of CO<sub>2</sub>-evolved

Glass bottles of 110 ml containing the amended substrate and unamended control soils were placed in 1-l, wide-mouthed glass jars, with a glass flask of 30 ml containing 20 ml of 1 N NaOH solution to trap the evolved CO<sub>2</sub>. Jars were tightly closed and incubated at 20°C for up to 270 days at room temperature. The NaOH solution was exchanged every 7 days during the first 2 months, and monthly thereafter. Jars were aired each time for 2 min when they were opened to exchange the NaOH solution, to avoid anaerobic conditions in amended and unamended soils. Every time that the NaOH trapped were collected, a blank with non-soils in the jars were collected, too. The values of CO<sub>2</sub> in the blanks were used to correct the CO<sub>2</sub> trapped inside the jars. CO<sub>2</sub> trapped in 1 M NaOH solution was measured in a 5-ml aliquot by titrimetric methods with a standard 0.1 M HCl solution using the phenolphthalein indicator method [38].

#### 2.6. Chemical analysis

Total organic C in the soil and tannery sludge was measured using dichromate digestion [39], total N was measured using Kjeldahl digestion [40], and total hydrolysable and orthophosphate phosphorus were determined using the stannous chloride method [35]. The particle-size was analyzed using the hydrometer method [41]. To conclude, total Cr in tannery sludge, fleshing waste, and infiltration and runoff solutions was measured using absorption atomic spectrometry with a fitted graphite furnace spectrophotometer (Avanta M System 300, GF 3000 S/N 10288). Tannery sludge and fleshing waste were digested with 4:1 HCl: HNO<sub>3</sub> using a digiprep TM digestion system, prior to analysis.

#### 2.7. Fractionation of chromium

Tessier et al. scheme [42] is widely used, although application of sequential extraction is still subject controversy. The main problems of sequential extraction procedures are the non-selective use of extracts and the trace elements redistribution among phases during the extraction [43]. In spite of these restrictions, sequential extraction procedures have proved to be useful in the environmental analytical chemistry field [44].

Sequential extraction was utilized for partitioning Cr in soil and sludge amended soils into six operationally defined fractions described by Tessier et al. [42] and modified by Xiong et al. [45]. Six operationally defined fractions, exchangeable, bound to carbonates, bound to Mn oxides, bound to Fe oxides, bound to organic matter and residues according to procedure described by Tessier. Summarizing, 2 g of soil were placed in a 50-ml polycarbonate centrifuge tube and subjected to the following extraction program: Exchangeable fraction (I): soil extracted with 25 ml of 1 M ammonium acetate was shaken for 2 h, then centrifuged. Carbonate bound fraction (II): Fraction I residue extracted with 25 ml of 1 M sodium acetate, adjusted to pH 5 with acetic acid then shaken for 5 h and centrifuged. Mn-oxide-bound fraction (III): Fraction II residue extracted with 25 ml 0.1 M hydroxylamine hydrochloride adjusted to pH 2 with nitric acid then shaken for 12 h and centrifuged. Fe-oxide bound fraction (IV): Fraction III residue extracted with 25 ml of 0.2 M ammonium oxalate, adjusted to pH 3 with oxalic acid, and shaken for 24 h, then centrifuged. Organic and sulphide-bound fraction (V): Fraction IV residue

extracted with 5 ml of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2 with HNO<sub>3</sub> then heated in a water bath at 85°C. After cooling, 20 ml of I M ammonium acetate were added, shaken for 2 h, then centrifuged. Residual fraction (VI): Fraction V residue digested with 3:1 HCl: HNO<sub>3</sub> in digestion glass tubes. After digestion was completed, 25 ml water were added and then filtered. The levels of Cr in the six fractions (I to VI), plus a fresh sample, were analyzed with atomic absorption spectrometry as described above, at 1, 3, and 6 months of incubation.

Mobility factor percentage was calculated according to the equation:

%mobility factor = 
$$\frac{(I + II + III)}{(I + II + III + IV + V + VI)} \times 100$$

Hexavalent Cr (CrVI) was quantified employing diphenylcarbazide procedure described by Bartlett [46]. One gram of soil was extracted with 3 ml of 10 mM K<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub>, pH 7.2. One milliliterazide reagent was added to 8 ml of extract, mixed and stand for 20 min and read the color at 540 nm. Azide reagent was prepared with 120 ml of 85% phosphoric acid, diluted with 280 ml distilled water, to 0.4 g of S-diphenylcarbizide dissolve in 100 ml of 95% ethanol.

#### 2.8. Rainfall system experiment

For the experiment of simulated rainstorm, the rainfall system type Morin [47] was used (**Figure 2**).

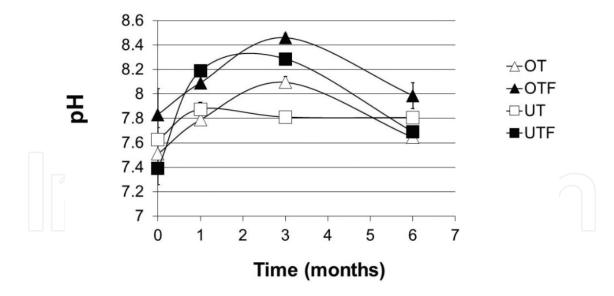


Figure 2. Rainfall system type Morin.

#### 2.9. Soil treatments

After adjusted to 50% WHC, sub-samples of 10 kg of soil were placed in 15 kg rough use plastic bags. Two different treatments were applied to the soils: tannery sludge (T) to outside (O) and under the canopy (U) of mesquite tree soils, and tannery sludge plus fleshing waste in outside and under the canopy soils (OTF and UTF, respectively). The amount of tannery sludge was chosen to give less than 300 mg Cr kg<sup>-1</sup>; the critical level of Cr for acceptable use of waste and bio-products in agriculture, as established by the US Environmental Protection Agency [48].

A cotton plug was adjusted to the plastic bags to allow ventilation. After moistening, the treated soils were incubated at 25°C for 1, 3, and 6 months in order to allow mineralization to occur and before they were submitted to a simulated rainfall system. A fresh control was included in order to compare the experimental results with it. The treated soils were air-dried and passed through a 4-mm sieve. They were sampled and then each one was packed to a depth of 4 cm in a 30 × 50-cm box over a 12-cm layer of gravel and 4-cm layer of coarse sand for moisture tension control. Soils were then wetted by capillarity while maintaining the water in a levelled position. Following saturation, the boxes were set at a 3% slope and then allowed to drain for 30 min (**Figure 3**). A total of four runs for each treated group were conducted, each one after an incubation period (0, 1, 3, and 6 months). For each run, the soil treatments were placed on assoil box carrousel and subjected to a simulated rainstorm using the rainfall system type Morin [47] (**Figure 2**). The full description of a simulated rain experiment is in Barajas-Aceves et al. [49].



**Figure 3.** pH after a simulated rainfall in semi-arid soils amended with fleshing waste and or tannery sludge. Bars indicate standard deviation. Source: Ref. [49].

Simulated rainfall at intensity of 50 mm h<sup>-1</sup> and a drop diameter of 3 mm was applied for 60 min. With these specifications, the process simulated the 6 months of a raining period in Dolores Hidalgo, Guanajuato, Mexico. During each run, water percolation through the soil and sediment samples were collected in separated plastic bottles every 5 min for 1 h. Weight

of sediment samples and infiltrated water was registered. Double aluminium potassium sulphate (20 ml at 10%) was added to the sediment samples to precipitate suspended solids and separate the water by decantation. The solids in the bottle were dried for 24 h at 105°C and the soil loss was measured by gravimetry, expressed in grams. Once the rainfall was stopped, the soil boxes were left for 24 h to allow the drainage ceased from them, the soil was randomly sampled, allow to dry slowly until it had a moisture equivalent to 40% WHC. Before the rainfall system started, the same soils with the same treatments were sampled and were adjusted to 40% WHC before the soil microbial activities determinations.

The decanted water was transferred to a plastic bottle and weighed. The volume was expressed in cm<sup>3</sup> (considering the water density of 1 g cm<sup>-3</sup>). The runoff was calculated by the equation:

$$Runoff(mm) = \frac{V \times 10}{A}$$

where V is the volume of runoff (cm<sup>3</sup>), A is the area exposed to rainfall (1500 cm<sup>2</sup>), and 10 is the factor to convert cm to mm.

The infiltration was calculated with a similar equation and expressed in mm [50–52].

$$Infiltration(mm) = \frac{V \times 10}{A}$$

The results of all these measurements were the sum of the 12 samples per treatment collected in one run.

#### 3. Case study

#### 3.1. Introduction

#### 3.1.1. Semi-arid soils and tannery sludge

Applications of tannery sludge are restricted due to high Cr content, even when Cr(III) content in the sludge is considered to be unavailable. Nevertheless, the use of tannery sludge for reforesting the north of Guanajuato (a natural reserve in Dolores Hidalgo, Guanajuato) is appealing because, it can avoid soil degradation due to the increasing erosion in the region, and at the same time, it can reduce contamination by tannery sludge dumping to open air in Leon, Guanajuato.

The influence of Cr on nitrogen transformation in soils has been studied and reports show somewhat mixed results. James and Bartlett [53] found no inhibition in treatments containing Cr(III) in sewage sludge or tannery effluent but that nitrification was inhibited by Cr(VI) at a concentration of  $10 \, \mu g \, g^{-1}$  in soil suspensions. Chang and Broadbent [54] observed that nitrogen

immobilization, mineralization, and nitrification were inhibited to a great extent by Cr(III) added to a neutral soil, but Cr(VI) was not measured in the extracting solutions used to characterize soil Cr in this study.

Previous studies in semi-arid soils collected in the same natural ecosystem with mesquite amended with tannery sludge to evaluate the biological functioning of soil, show that C and N mineralization increased. Similarly, there was not inhibition in the biological functioning of soil [2].

The aims of this research project were 1) to evaluate the environmental impact of heavy metals from tannery sludge by determining not only the total content in a matrix, but also their bioavailability and their capacity for mobilization and toxicity by chemical fractionation. 2) To indicate the effect of tannery waste type on soil aggregate stability, infiltration, runoff, sediments, nutrients, and Cr loss from semi-arid soils using a simulated rainfall system. This information will be useful for evaluating the ecological risk associated with the use of tannery sludge in semi-arid soils during reforestation projects.

Reducing exposure to contaminants from mining activities is important, especially in the old mining towns like Vetagrande, where large areas have been affected by the presence of mine tailings.

Mine tailings have chemical and physical properties limiting plant growth, like lack of organic matter or macronutrients. Usually, they are acidic, severely toxic, do not have soil structure, have low water retention and slow rates of water infiltration [31]. Organic supplements, such as compost, farmyard manure or biosolids, may be added to overcome these limitations. Moreover, the use of organic compost mixed with tailings could alter several qualities of soil such as potential mineralization of C and N from added organic waste and the mobility and availability of heavy metals in the soil.

The aims of the use of organic amendments on mine tailings were 1) to determine the mobility factor of heavy metals; 2) to evaluate the effect of different organic wastes amended in mine tailings on N and C mineralization potential; 3) to evaluate the availability of Pb and Zn in *Brasica juncea* as indicators of heavy metal availability for pollutants and two shrubs grown in mine tailings and mixed with compost

#### 3.2. Methods

#### 3.2.1. Sampling area

The soils were sampled from the natural reserve "El Cortijo", in which the dominant vegetation is mesquite (*Prosopis laeviginata*), located in Dolores Hidalgo, Guanajuato, Mexico. The soils were collected from two sites: under the canopy and outside the canopy of mesquite tree. The average altitude of sites is between 1750 and 2000 m above sea level and the average annual rainfall is between 400 and 600 mm (mainly from June to September).

#### 3.2.2. Tannery sludge

Tannery sludge produced during leather manufacturing was sampled from a tannery in Leon (Guanajuato, Mexico). The sludge contained large quantities of hair, soluble proteins, and fatty fleshings from processing the skin to hide, and sulphide, lime, chromium-sulphate, salts, dyes, acid, and leather trimmings from processing the hide to leather. Two tannery sludge samples were collected in two different tannery industries with different Cr concentrations. A third tannery sludge was sampled from a tannery in Leon where the fleshing sludge was separated from the leather at the beginning of the process and then followed by chemical treatments. The fleshing waste contained small quantities of hair, soluble proteins and fatty fleshing from the processing of skin to hide. The three different sludge samples and fleshing waste were used in different studies with the same semi-arid soils. Chemical characterization is shown in **Table 1**. Tannery sludge was air-dried before used for the experimental aerobic incubation.

	Tannery sludge 1	Tannery sludge 2	Tannery sludge 3	Fleshing waste (F)
Total C (g kg <sup>-1</sup> )	281	257.8	7.65	5.68
Total N (g kg <sup>-1</sup> )	53.4	18.7	0.77	1.5
рН	8.34	8.09	8.65	7.66
Cr (mg kg <sup>-1</sup> )	6690	1663	6516	136
Na (mg kg <sup>-1</sup> )	_	_	1174.6	119.95
Ca (mg kg <sup>-1</sup> )	_	_	10.94	188.7

— = no determined. Data from: Refs. [2, 49, 55].

Table 1. Characteristics of tannery waste from Leon Guanajuato, México.

Amounts of tannery sludge 1 and 2 added to soils were in accord with the criteria of the amount of N covering the recommended dose of N for maize crop growth in the region. The amount of tannery sludge 1 which amended soils from outside and under the canopy of mesquite trees was 1.5 g of wettannery sludge to 50 g of soil. The total amount added to under and outside the canopy soils was approximately 1308 mg C kg $^{-1}$ , 320 mg total N kg $^{-1}$ , 45 mg total P kg $^{-1}$ , and 414 mg Cr kg $^{-1}$  soils.

The amount of tannery sludge 2 added was  $0.0125 \text{ g g}^{-1}$  soils, an amount which covered three times the requirement for the region recommended dose of N for maize crop (i.e. 260 kg N ha  $^{-1}$ ). The following treatments with three replications were applied at a rate of 250 g g $^{-1}$  soil: control (without any amendment),Cr(III), Cr(VI), tannery sludge, Cr(III)+ tannery sludge, Cr(VI) + tannery sludge, Cr(III) (Cr $_2$ O $_3$ ), and Cr(VI) (K $_2$ Cr $_2$ O $_7$ ). The criteria for dose selected was near to the value of the maximum upper limits of 300 mg kg $^{-1}$  for acceptable utilization of waste and by-products in agriculture as established by the US Environmental Protection Agency, Part 503 [56].The jars were sealed with air-tight plastic lids and incubated at 25 °C for 180 days. After 0, 30, 60, 120, and 180 days' incubation the CO $_2$  and inorganic N (NH $_4$ <sup>+</sup>, NO $_2$ <sup>-</sup>, and NO $_3$ <sup>-</sup>) were analyzed as described above.

The amount of tannery sludge 3 (**Table 1**) was  $0.046 \text{ g g}^{-1}$  soils which was equivalent to  $22.08 \text{ Ton ha}^{-1}$  and fleshing waste was  $0.092 \text{ g g}^{-1}$  soil and was equivalent to  $3.7 \text{ Ton ha}^{-1}$ . The amount of tannery sludge was applied to give less than  $300 \text{ mg Cr kg}^{-1}$  that is the critical level of Cr for acceptable utilization of waste and bio-product in agriculture [48]. These amounts of tannery sludge and fleshing waste contained approximately 13.0 and 2.4% less than  $170 \text{ kg N ha}^{-1}$ , which is the maximum dose recommended by the European nitrate directive [57] to reduce water pollution by  $NO_3^--N$  from agricultural sources.

#### 3.3. Results and discussion

Addition of tannery sludge 1 to outside and under the canopy of mesquite soils had no inhibitory effect on N mineralization and increased CO<sub>2</sub> production and inorganic N concentrations, but did not increase available P concentrations. These results suggest that tannery sludge could provide valuable nutrients to mesquite tree, the dominant vegetation in Dolores Hidalgo [2].

#### 3.3.1. N and C mineralization

The amount of tannery sludge 2 used in another experiment [58]shows that inhibition of nitrification in outside the canopy soils increased when adding tannery sludge plus  $Cr_6^+$  from 30 to 180 days. Soils under the canopy, amended with the same treatment, did not show a constant effect on nitrification throughout the incubation time (**Table 2**).

Results from this study showed that nitrification is sensitive to Cr(VI) added alone in outside the canopy soils from 30 to 120 days' incubation (**Table 2**) and to Cr(VI)plus tannery sludge from 30 to 180 days in soils outside the canopy (data not shown).Cr(III) added alone or Cr(III) plus tannery sludge added to the two soils had no specific effect on the microbial activities (CO<sub>2</sub> production or dehydrogenase activity) or N-mineralization [58].

CO2 production rate	CO2 production rate						
Treatment	% inhibition (30 days)	% inhibition (120 days)					
UVI U	21.49	25,12					
UTVI	7.57	14.71					
OVI	98.48	_					
OTVI	22.11	_					
Dehydrogenase activity							
UVI	15.39	15.06					
UTVI	29.93	31.48					
OVI	61.26	83.63					

CO2 production rate		
OTVI	49.61	_
NO3-concentration		
UVI	52.82	_
OVI	69.64	83.81
OTVI	62.40	95.36
OTIII	43.38	27.73

All the values are significant at  $p \le 0.05$ , — not significant. U = under the canopy, and O = outside the canopy soils, VI = Cr(VI), III = Cr(III), T = tannery sludge 2. Source [55].

**Table 2.** Inhibition of CO<sub>2</sub> production rate, dehydrogenase activity, and NO<sub>3</sub><sup>-</sup> concentration in under- and outside-the-canopy soils from Dolores Hidalgo, Mexico, incubated at 25°C for 30 and 120 days.

There is a conflicting effect on using mineralization of organic C in metal contaminated soils because of the stimulation and inhibition on respiration [59, 60]. Results of under the canopy soils show that Cr(VI)could have effects on complex soil organic matter and render it less available by reducing Cr(VI) to Cr(III) [61, 62]. Thus, under the canopy soil which had more organic C, there was less inhibition of CO<sub>2</sub> production rate than outside canopy soils.

In soils outside the canopy with low organic matter, Cr(VI) may have effects on soil organic matter available which increases with the dying of cells. Thus, the sum of CO<sub>2</sub> produced by death and surviving microorganisms will reflect a small or not inhibition of CO<sub>2</sub> production by Cr(VI) (**Table 2**). Adding tannery sludge plus Cr(VI)may reduce inhibition of CO<sub>2</sub> production rate by complexing the Cr(VI) with organic matter from tannery sludge [62].

#### 3.3.2. Cr fractionation

Results from Cr fractionation in under and outside the canopy soils amended with Cr(VI), Cr(III), Cr(VI) plus tannery sludge 2, Cr(III)plus tannery sludge 2, or tannery sludge 2 alone was that the level of total Cr increased in the more resistant fraction (fraction VI which is the least soluble form) and increased further over time. The opposite trend occurred with non-residual fraction (sum of fraction I, II, III, IV, and V) which tended to decrease with time in the two soils (**Table 3**).

Time incubation	30 days		30 days	
Treatments	Residual	Non-residual	Residual	Non-residual
		Uno	der the canopy	
Cr(III)	5.4f	4.1g	41.4c	0.90 h
Cr(VI)	12.7e	31.2f	27.7g	16.8 f
Tannery sludge	26.0d	53.6c	50.1b	25.7 d
Tannery sludge + Cr(III)	31.2c	49.1d	66.4a	33.0 с

Time incubation	30 days		30 days	
Tannery sludge + Cr(VI)	38.4b	74.4b	42.2c	38.0d b
		Outside	e the canopy	
Cr(III)	22.0d	7.0g	39.7c	12.0 g
Cr(VI)	25.0d	44.2e	26.5h	24.1 e
Tannery sludge	23.4d	52.2c	33.0 d	32.4 c
Tannery sludge + Cr(III)	45.1a	39.1e	29.7f	26.1 d
Tannery sludge + Cr(VI)	22.0d	77.6a	27.6 g	65.5a

Residual = fraction VI; Non-residual = sum of fraction I, II, III, IV, and V. Values followed by the same letter in the same column are not significantly different at  $p \le 0.05$ , according to the Duncan's test.

**Table 3.** Fractionation of chromium (mg kg<sup>-1</sup>) in semi-arid soils from Dolores Hidalgo, México, amended with Cr(III), Cr(VI) and/or tannery sludge 2, incubated at 25°C for 30 and 120 days.

The greater percentage of Cr in the residual fraction at 120 days of incubation (**Table 3**) (40–65%) probably reflects the greater tendency of Cr to become unavailable once it is in the soil [63]. The residual and non-residual Cr suggest that the metal bioavailability does not only depend on its concentration but is also affected by the characteristics of the tannery sludge and soil components (such as Fe, Mn, oxides, or the quality of organic matter) into which it is sorbed [61]. This will have an impact in the interaction between Cr and the biota [64].

Tannery sludge 3 and fleshing waste were added to the same semi-arid soils incubated for 6 months and subsequently subject to simulated rainfall. In this study we evaluated the Cr loss that occurs due to runoff and infiltration, as well as Cr fractionation, Cr speciation, soil pH, and soil microbial activities before and after the simulated rainfall event.

#### 3.3.3. pH

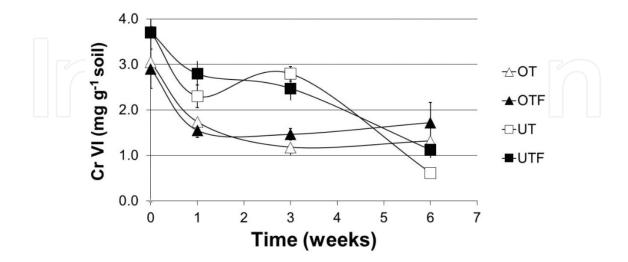
The highest pH was in soils amended with fleshing waste (OTF > UTF) (average 8.49, 8.12, respectively), followed by OT and UT at 3 months' incubation after rainfall (**Figure 3**). Similar results were observed in soil before simulated system [49].

The increment in soil pH also increased the solubility of organic molecules, which is especially important in semi-arid soils(Wolf, 1994). The pH decreases from 3 to 6 months agree with those found in a study conducted by Apple [65] who demonstrated that cycles of drying and rewetting might cause disruption of soil aggregation, resulting in a rapid mineralization by soil micro-organisms due to the release of accessible substrate.

#### 3.3.4. Hexavalent chromium

The concentration of Cr(VI) in soils after application of the simulated rainfall was significantly higher in the soils under the canopy treated with tannery sludge and fleshing waste, or tannery sludge only than in soils outside the canopy with the same treatments (**Figure 4**), even though there were no significant differences between soils treated with tannery sludge or tannery

sludge mixed with fleshing waste (data not shown). Values of Cr(VI) remained constant for 1–3 months (1.18–1.74 for outside soils and 2.30–2.80 mg Cr  $g^{-1}$  soil for under the canopy soils) under alkaline conditions (pH > 8.0).



**Figure 4.** Chromium hexavalent after a simulated rainfall in semi-arid soils amended with fleshing waste and or tannery sludge. Bars indicate standard deviation. Source: Ref. [49].

#### 3.3.5. Total Cr loss by runoff and infiltration

Total Cr loss in mg was observed in runoff compared to infiltration. The highest values of total Cr released was observed in runoff for UTF treatment, mainly at 1 and 3 months' incubation. The lowest value of total Cr was in infiltration in OTF treatment followed by OT (**Table 4**) [66].

The high concentration of total Cr observed in runoff from 1 to 3 months corresponds with the highest increase in pH (8.01–8.46). Cr measured between these pH values must be all Cr(VI) where anionic Cr(VI) formations are favoured [67]. Thus, the high concentration of Cr loss in runoff from 1 to 3 months suggests that it might be Cr(VI) which was available to the soil solution. Cr values at 1 and 3 months of incubation for under the canopy soils treated with tannery sludge alone or mixed with fleshing waste were higher than the upper limits of Cr (VI) established by the Mexican Norm [68].

Time (months)	OTF	UTF	UT	OT
Infiltration				
0	0.42 (0.161)	0.87 (0.074)	1.29 (0.123)	0.50 (0.074)
1	0.09 (0.042)	1.68 (0.134)	0.97 (0.141)	0.29 (0.233)
3	0.40 (0.124)	1.02 (0.128)	2.53 (0.133)	0.30 (0.132)
6	0.34 (0.127)	1.16 (0.187)	0.79 (0.147)	0.50 (0.169)
Total	1.25	4.73	5.58	1.59

Time (months)	OTF	UTF	UT	ОТ
Runoff				
0	0.71 (0.156)	1.24 (0.264)	1.33 (0.846)	1.55 (0.285)
1	4.84 (0.150)	11.50 (0.387)	2.64 (0.548)	3.84 (0.402)
3	1.10 (0.380)	13.42 (0.402)	7.89 (0.978)	6.50 (0.151)
6	1.03 (0.191)	1.10 (0.625)	1.01 (0.711)	1.11 (0.205)
Total	7.68	27.26	12.86	13.00

U: soil sampled under the canopy of mesquite tree; O: soil sampled outside the canopy of mesquite tree; T: tannery sludge; F: fleshing waste. Values in parentheses indicate standard deviation. Source [49].

Table 4. Total Cr (mg) releases in runoff and infiltrations in semiarid soils.

#### 3.3.5.1. Chromium fractionation

Dominant Cr fractionation in semi-arid soils was bound to carbonates (Fraction II) at 0, 3, and 6 months' incubation after rainfall (Table 5). Dominant Cr fractionation at 1 month incubation was bound to reducible (Fraction III bound to manganese oxide) followed by Fraction IV (bound to Fe oxides). These results demonstrate that Cr binding was influenced by pH and might also have been influenced by ammonium.

0 Months			Cr in f	raction (%)		
	I	II	III	IV	V	VI
OT	0.91	95.30	0	2.98	0.81	0.00
OTF	0.38	95.80	0	2.95	0.83	0.03
UT	0.98	91.79	0	4.64	2.48	0.11
UTF	0.46	92.31	0	4.64	2.47	0.12
1 Month						
OT T	1.44	4.33	23.51	27.95	42.76	0.02
OTF	2.47	2.07	65.30	17.64	12.51	0.01
UT	3.76	2.20	72.89	12.08	8.82	0.25
UTF	1.64	2.43	78.43	12.22	5.26	0.02
3 Months						
OT	2.35	86.77	2.23	2.25	5.99	0.40
OTF	1.90	89.69	2.12	1.57	4.69	0.02
UT	0.47	81.25	3.69	4.01	10.54	0.05
UTF	4.47	29.58	14.20	12.73	38.81	0.22
6 Months						

0 Months			Cr	in fraction (%)		
OT	2.91	84.20	5.23	4.11	3.30	0.25
OTF	2.64	84.38	5.57	4.37	2.88	0.16
UT	3.36	83.45	4.90	4.20	4.09	0.01
UTF	2.61	86.41	3.96	3.24	3.78	0.00

Source: Ref.[49].

Fractions: I = exchangeable, II = bound to carbonates, III = bound to Mn oxides, IV = bound to Fe oxides, V = bound to organic matter and VI = residues.

**Table 5.** Cr Fractionation (%) in semi-arid soils after rainfall amended with fleshing waste (F) and or tannery sludge 3 (T).

In addition, it has been shown that Cr associated with carbonate becomes susceptible to changes in pH, which results in its becoming soluble [42, 69].

#### 3.3.6. Runoff, soil loss, and infiltration

Water infiltration into soil is one of the most important processes in the hydrological cycle and is crucial in agriculture. Amount of cumulative soil loss and runoff was significantly higher (P<0.01) in soils from outside the canopy than those from under the canopy tree. The opposite occurred in infiltration, being higher under the canopy than outside the canopy tree [66]. Amendment of tannery sludge alone to outside the canopy soils reduced the cumulative soil loss and runoff followed by the tannery sludge plus fleshing waste. However, addition of tannery sludge reduced also cumulative soil loss and runoff under the canopy, but the mixture of tannery sludge plus fleshing waste was higher than those with tannery sludge alone. There were no significant differences in soil infiltration outside the canopy soils with or without amendments. However, infiltration under the canopy soils amended with tannery sludge or tannery sludge plus fleshing waste were higher than without amendment. Thus, the addition of tannery sludge plus fleshing waste to under the canopy soil increased the cumulative runoff [66].

Results reported by Barajas-Aceves et al. [66] suggest that high sodium and salt concentrations of tannery sludge plus fleshing waste (1174.68 mg Na kg<sup>-1</sup> tannery sludge and 119.95 mg Na kg<sup>-1</sup> fleshing waste and 188.70 mg Ca kg<sup>-1</sup> fleshing waste) and soil organic C (0.46 g kg<sup>-1</sup> under the canopy soil) affected soil aggregates of under and outside the canopy soils [70] in different ways, thereby allowing reduction of runoff and loss of solids [66, 71]. While elevated electrolyte concentration may enhance flocculation, sodium has the opposite effect in soils, causing dispersion. The contrary behavior occurred with the application of organic C, thus enhancing water infiltration, delaying runoff, and reducing erosion [72]. Thus, organic matter is known to stabilize soil aggregates. Stronger dispersive conditions (such as higher solidicity, lower salinity, and higher energy or impact of water irrigation) should be needed to disperse a stable aggregate [73].

Results of this study could indicate that the degree of dispersion and flocculation and in the treated soils is not only due to salts and sodium concentrations added in the treatments through tannery sludge and fleshing waste, but also to the clay mineralogy of soil [70, 74]. Thus, differences in CEC values for soils under and outside the canopy (51.3 and 22 meq 100 g<sup>-1</sup> soil) might reflect the nature of the predominant clay minerals of the soils [75]. Oster et al. [76] studied the flocculation values of montmorillonite and illite suspensions saturated with mixtures of Na and Ca ions in the exchange phase. They suggest that soils with illitic clays are more sensitive to dispersion and clay movement than soils with montmorillonitic clays.

Taken together, these findings suggest that fleshing waste contains sodium at concentrations (data cited above) that adversely impact the infiltration rate of soil collected under the canopy. Previous studies [74, 77] indicate that sodium may cause dispersion and plug soil pores. In this study, repeated wetting and drying of soil could have caused sodium dispersion from sodium coming in the treatments applied to the soil. This, in turn, could have negatively affected the soil structure, reducing infiltration and surface crusting [66, 71, 77].

This would also explain the higher runoff observed in soil collected from under the canopy amended with tannery sludge plus fleshing waste when compared to soil collected from under the canopy and amended with tannery sludge alone. These results suggest that great care must be taken when using waste as an organic fertilizer in semi-arid soil if the wastes contain salts and sodium, to avoid damaging the soil, especially if the goal is to preserve or improve fertile lands. Agassi et al. [74] postulated that the combination of these ESP values and rainwater low salinity caused crust formation and thus high runoff.

#### 3.3.7. Nitrogen loss

The highest values of  $NO_3^--N$  and  $NH_4^+-N$  concentration losses after simulated rainfall were found in the solution infiltration [66].

Outside the canopy of mesquite soils treated with tannery sludge only or tannery sludge plus fleshing waste showed the highest concentrations of NO<sub>3</sub><sup>-</sup>–N (341 and 560 mg l<sup>-1</sup> respectively) and a lower concentration of NH<sub>4</sub><sup>+</sup>-N (283 and 158 mg l<sup>-1</sup> respectively) in the infiltration solution together with the highest reduction of soil loss and infiltration [71] (71 and 55%, respectively) [66] suggesting that no changes regarding nitrification took place in those soils. However, the opposite occurred with soils under the canopy treated with tannery sludge plus fleshing waste, a higher concentration of NH<sub>4</sub><sup>+</sup>–N (452 and 582 mg l<sup>-1</sup>, respectively) and a lower concentration of NO<sub>3</sub>-N (445 and 316 mg l<sup>-1</sup> respectively) in the infiltration solution were observed. These results, together with no reduction of runoff and low reduction on soil loss (-7 and 43%, respectively) [66], suggest that in areas where treated soil drains poorly, the held water impedes O<sub>2</sub> diffusion, creating anoxic areas in the soil at a redox potential appropriate for denitrification. This suggestion is supported by results of high pH (more than 8) in treatments of OTF and UTF at 1 and 3 months of incubation after the simulated rainfall event (Figure 3) [49]. Furthermore, the high values of runoff and low infiltration in UTF amendment [66] suggest that clay mineralogy of under-the-canopy soils and Na concentration, plus the tannery waste added disrupted soil aggregates, leaching the NH<sub>4</sub><sup>+</sup>–N accumulated during the dry intervals prior to the rainfall event [78, 79].

Taken all this information together, it seems that the increasing pH values might have caused competition between chromium oxyanions and OH–, thus decreasing Cr(VI) sorption [80, 81].

Results of the tree different tannery sludge study suggest that tannery sludge characteristics are so important that they define the Cr fractionation in the soil [82]. Thus, the retaining metal in the solid phase depends on metal concentration and abundance of solid phase [83]. Solubility of the metal is mainly controlled by pH, concentration, state of mineral compounds, and type of ligands. Furthermore, these findings indicate that the incubation system used may influence microbial processes in the soil and that the presence of organic compounds plays an important role in determining which fraction of Cr dominates, enhancing metal adsorption to soil phases.

The relative importance of any solid phase for retaining a metal depends on the identity, concentration of metal, and abundance of the solid phase [83, 84]. Solubility of metal is mainly controlled by pH, concentration, type of ligands, chelating agent, oxidation state of mineral component, and the redox potential of the system [85], with TOC enhancing metal adsorption to sediment phases.

The use of tannery sludge with high concentration of carbonates and Cr as organic fertilizer in semi-arid soils could be potentially harmful due to chemical forms related to solubility and carbonate forms favouring heavy metal uptake by plants, and leaching.

#### 3.4. Mine tailings amended with organic wastes

There was a reduction in the mobility of Pb when bokashi and compost of vermicompost were added to agricultural and rangeland soils mixed with mine tailings at 0 or 169 days of incubation. However, mobility of Zn was reduced only in both soils mixed with vermicompost and mine tailings. Differences in Pb and Zn mobility between bokashi and compost treatments might have occurred because the effects of organic materials added to soils on soil properties depend on degradation of such materials, which could have affected heavy metals solubility [86, 87]. The high levels of humified organic matter in vermicompost probably influenced the mobility of Pb and Zn [86]. Some published results suggest that availability of Pb and Zn to soil microflora is also influenced by the high humus content in organic matter [62, 88].

Treatments in agricultural and rangeland soils containing mine tailings plus compost showed the greatest inhibition of cumulative C mineralization followed by bokashi [88]. The highest inhibition of N mineralization in agricultural soils was in treatment amended with vermicompost and in rangeland soils in treatments with compost and bokashi plus mine tailings (20.30 and 18.74% inhibition, respectively). The highest inhibition of dehydrogenase activity was observed in both soil amendments with tannery sludge (48–80% respectively) and the lowest in agricultural soil plus bokashi plus mine tailings and rangeland soils plus vermicompost plus tannery sludge (27 and 39% respectively [88]. These results suggest that the quality of the organic material together with the chemical characteristics of the soils could be important factors influencing decomposition of organic materials. Indeed, contents of nitrogen, cellulose, hemicellulose and lignin, the C/N ratio and the lignin/nitrogen ratio [89] have been reported to be some of the most important factors controlling decomposition processes of organic substrates.

Experimental values of N and C mineralization for the two soils in each treatment [88] were used by fitting to four commonly used kinetic models: Zero order, linearized power function, first order, and first order E [90–95].

Nitrogen mineralization in all treatments was best fitted to the linearized power function [88].

$$N_t = K_t^{\ m} a$$

The different values of *K* and *m* among treatments and soils did not follow a defined trend. K values in agricultural soils treated with mine tailing alone or with bokashi and vermicompost plus mine tailings increased to 32.1, 26.5, and 31.8% respectively. Similarly, the value of rate constant *K* in rangeland soils plus mine tailing alone increased to 76.7% compared to the value of K in soil alone. However, in rangeland soils treated with vermicompost plus mine tailing K decreased to 39%. These results suggest that bokashi and vermicompost in agricultural soils provide a similar pool of mineralizable N and the addition of mine tailings modified the decrease of these pools. Behavior of N mineralization in rangeland soils was different as well as the decrease of N mineralization with the three organic wastes [90–92].

The best-fit model for C mineralization was first-order E model for both soils in all treatments [88].

$$C_t = C_0 \left( 1 - \exp^{-kt} \right) + C_1 b$$

Potential C mineralization (C0) showed the highest values for treatments with low k values [88]. Murwira et al [93] reported that Co\*k parameter can be better estimated than only one parameter. Both single parameters are interdependent.

The combination of those two parameters showed high values of Co\*k in treatments with compost, bokashi, or vermicompost alone in agricultural soils, followed by rangeland soils(11.5–18.2 and 8.1–7.6 respectively). These values are in the range of those reported in the literature for different organic materials (40.6–1.3) [95]. Differences in the values of Co\*k in all treatments in both soils might suggest that the amount of lignin-humus present in the organic compost, the amount of nitrogen content, and the organic waste quality and the type of soil might be important in the process and rate of decomposition [96, 97]. The lowest values of Co\*k were in the treatments with mine tailings alone (3.96 in both soils plus mine tailings) compared with soils alone (56 and 65% less in agricultural and rangeland soils, respectively) or the amendment of organic waste alone. These results suggest that the chemical composition of organic waste (nitrogen content, lignin, and polysaccharides) together with the chemical characteristics of the soils could be important factors influencing decomposition of organic materials and even in the presence of heavy metals [98, 99].

*Brassica juncea* accumulates more Pb and Zn in roots than in shoots [100] growth in soil plus mine tailings. Concentration of Na and Mg measured in mine tailings was 5207 and 102,917

 $\mu$ g g<sup>-1</sup> soil respectively [100]. These results demonstrated that *Brassica juncea* had the ability to survive and tolerate several metals simultaneously, in the presence of high levels of Na and Mg (SAR between 2.5 and 3.7% and ESP between 18.3 to 20.7%) [100]. All metals measured from mine tailings were accumulated in the root and there was very low translocation to the shoots.

According to the literature, the typical behavior of an accumulator species such as *Brassica* is that there is higher accumulation of heavy metals in the leaves [101], which is opposite to the results of these study.

Results suggest that high levels of Na and salt in mine tailings and the physicochemical characteristic of mine tailings might influence translocation of heavy metals from roots to shoots; metals such as Pb and Zn which are the main metals extracted by *Brassica juncea*. This suggestion is according to reports showing that salt acts antagonistically, thus when plants grow in media with a high Pb concentration and high salt concentration, the amount of Pb accumulated by *Brassica juncea* decreases [102].

The mine tailings amended with 10% compost to growth two shrubs *Acacia retinodes* and *Nicotiana glauca* were able to survive at high concentrations of heavy metals in mine tailings (**Table 1**) when 10% compost was added. The dry biomass of both shrubs increase from 62 to 79% growth in mine tailings plus compost compared to mine tailing alone. *Echinochloa polystachya* was not able to grow on mine tailings, even when it was amended with compost, as was shown by the percentage inhibition data for its root and leaf biomasses. Pb and Zn concentrations in the three plants were higher in roots compared to leaves for all treatments (Pb from 514 to 861 in roots and from 14.6 to 90 ( $\mu$ g g<sup>-1</sup>) in leaves and Zn from 682 to 766 in roots and 541.4 to 254 ( $\mu$ g g<sup>-1</sup>) in leaves) [70]. The elevated contents of Pb and Zn in roots along with the low translocation factors [70] indicate that the two shrub species used in this study are appropriate for Pb and Zn phytostabilization.

#### 4. Conclusions

The drastic decrease in soil organic matter in semi-arid soils due to deforestation or in some areas used as deposits for mine tailings are attractive sites for soil restoration. These areas need application of organic residues to avoid subsequent soil erosion by losing soil structure and minimize high risk of pollution in adjacent areas. Application of organic wastes may provide nutrients to pioneering vegetation increasing organic content and improving soil physicochemical and biological properties and thus their natural fertility.

This work provides a clear demonstration of the role of organic waste to increase or release heavy metals according to the quality of organic matter amendment. Recycling valuable components such as C and N available in semi-arid soils was supported by the potential C and N mineralization, dehydrogenase activity, and plant growth. Retention of heavy metals on the fractionation of organic matter cannot be generalized, it will depend on the chemical characterizations of organic waste and soil. Chemical characteristics of the organic waste such as the

nitrogen and humified organic matter content, pH, EC, CEC, ESP (exchangeable sodium percent), and SAR (sodium absorption ratio) are important properties to consider in organic matter amendment to semi-arid soils participating on the complexity and leaching of heavy metals and nutrients in the matrix of soil. Measurements such as heavy metal fractionation, percent of heavy metal mobility, soil biochemical processes, and heavy metals accumulation in roots or translocation to plants give a global picture of the complexity of semi-arid soils amendment with organic waste, either in mine soils with heavy metal content, or when used for organic fertilization to semi-arid soils. Behavior of organic composts or organic waste as organic fertilizer in semi-arid soils will find two directions, one: as the organic matter increases heavy metal immobilization in soil and provides nutrients to plants; two: heavy metals present in organic waste or in semi-arid soils from mine sites will interact with soil microbial activities, plant growth, and heavy metal fractionation. Measurement of infiltration factor in both ecosystems containing high heavy metals and salts concentration under simulated rainfall deserve close attention. Monitoring constantly these types of ecosystems to look for the risk of heavy metal mobility after the season changes, and the potential C and N mineralization and heavy metal stabilization in plants should be a priority in semi-arid soils in process of remediation or reforestation.

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