Compost and Vermicompost as Soil Amendments to Immobilize Cu and Cd Under Wheat Growth Conditions
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ABSTRACT
Field experiment was conducted during wheat cropping season on a calcareous soil to assess the efficacy of vermicompost and compost to immobilize copper (Cu) and cadmium (Cd) in soil. The soil amendments applied alone and in combinations with mineral fertilizers to compare their efficacy for metals immobilization. Both of amendments significantly reduced extractable Cu and Cd in soil at wheat harvest. Copper and cadmium fractionation showed significant decreases in the extractable fractions by the vermicompost 47.06% and 98.81% in untreated with heavy metals soil whereas 46.46% and 80.06% in treated soil with heavy metals respectively or compost 22.35% and 79.17% in untreated with heavy metals soil whereas 20.56% and 73.05% in treated soil with heavy metals respectively. Vermicompost and compost amendments enhanced metals immobilization which reduces their expected uptake by plant and subsequent accumulation in the grains of wheat, particularly with vermicompost. In conclusion, the results indicated that compost and vermicompost have great potential to remediate Cu and Cd contaminated soils.

Keywords: Copper, cadmium, fractionation, mobility, vermicompost, soil, compost

INTRODUCTION
Environmental pollution may cause soil, air and water quality deterioration. The agricultural wastes including agro-industrial wastes in Egypt estimated to be about 30 million tons per year (El-Haggar et al., 2004; Hussien and Sawan, 2010 and Gomaa et al., 2011). The agricultural wastes and food processing factories wastes disposal caused environmental pollution and health problem. Improper disposal of these residues consequences in environmental degradation of landfills (Danthurebandara et al., 2015). So, it is necessary to reduce this pollution sources during industrial processing (Pleissner and Carol, 2013). Food wastes may be recycled into organic fertilizer to reduce the amount of food waste in landfill and greenhouse gas emission to surrounding (Scholwin et al., 2016). Human technological advancements, have led to the introduction of huge amount of heavy metals (HMs) into the soil. Heavy metals are attracting human concern due to their non-biodegradable nature in the environment as well as their ability to effect on human health and metabolic activities of living organisms. Soil is the major sink for HMs. Heavy metals reaching the soil through various sources reactions with different soil components, which affect their solubility, mobility and availability in the environment (Scokart et al., 1983).

Heavy metals do not degrade by biochemical processes because its resistance to microbial degradation and it may be accumulate along the food chain (Mokhtar et al., 2009; liao et al., 2005 and Ali & Sajad, 2013). The effects associated with heavy metals dependent critically on their chemical species (Yobouet et al., 2010). Addition of organic matter to soil plays a considerable role to sequester metal by chelation process and form the metal-organic complex. Due to metal complexation by organic ligands, mobility and availability of heavy metals may be decreased (Rieuwerts et al., 1998). These reduction levels of heavy metals in soil may be caused by several factors such as nature itself and degradability of natural count number, salts contents, soil pH, redox ability and type of soil (Rieuwerts et al., 1998; Rashad et al., 2010; Sheoran et al., 2011 and Rashad et al., 2013). Thus, the chemistry of these metals in soils is often very complex (Twiss et al., 2001 and Sandrin and Hoffman, 2007). The mineral fertilizers may also supply metallic elements to the soil and the organic materials may act as an immobilizer of these metals, lowering their availability (Wuana and Okieimen., 2011) . This study aimed to evaluate the application of vermicompost and compost produced from agro-industrial wastes on the availability and stability of Cu and Cd under wheat growth conditions in polluted and unpolluted calcareous soil.

MATERIALS AND METHODS
Field experiment was carried out at City of Scientific Research and Technological Applications (SRTA-City), experimental farm located at 30° 53’ 33.17” N, 29° 22’ 46.43” E, Alexandria, Egypt. Wheat seeds (Triticum aestivum L.) Sakha 93 was cultivated on November 15th, 2015. The experiment conducted in sandy clay loam soil using surface irrigation system. Soil samples collected
from the experimental site, air-dried, ground and passed through 2 mm sieve for physicochemical and heavy metal analysis. The soil pH in 1:2.5 soil: water suspension and Electrical conductivity in 1:1 soil: water extract were determined (Jackson, 1967). Soil texture determined by Hydrometer method (Jacob and Clark, 2002). Organic carbon content determined by Walkley Black wet oxidation method (Nelson and Sommers, 1982). Soil organic matter (SOM) was calculated by multiplied organic carbon content with a factor of 1.72. Na2EDTA titration method used for measuring calcium and magnesium (Bhatti et al., 2016). Potassium and sodium measured by flame photometer (Jackson, 1967). Available phosphorus extracted with 0.5N NaHCO3, pH 8.5 according to Olsen and Sommers (1982). Heavy metals (HM) were extracted by diethylene triamine pentaacetic acid (DTPA) according to Norvell and Lindsay., 1972 and measured with Atomic Absorption Spectrophotometer (AAS-PE2380). The chemical and physical properties of the soil are shown in Table 1.

The experimental soil area (486m²) divided into two sections. One section was heavily treated with Cu and Cd (Bello et al., 2016) to toxic level (as 100mg Cu /kg soil and 3mg Cd /kg soil). The mineral fertilizers were applied according to Ministry of Agriculture and Land Reclamation as follow: 118kg N/fed.as ammonium nitrate (33.5% N), 29kg P2O5/fed.as superphosphate (15.5%P2O5) and 59kg K2O/fed.as potassium sulphate (48% K2O). Nitrogen fertilizers split in two doses, half of the quantity applied at the time of sowing and remaining another half quantity at first irrigation. Full dose of superphosphate and potassium fertilizers was at the time of sowing (FAO, 2009). The vermicompost and compost (Food industrial wastes i.e., mixture of vegetables, fruits peel and pulp collected separately at the farag-allah, Saker and Tamajet factories) added before plant cultivation to rich the level of organic matter in soil to 2% (37.7gm/plot) and their chemical properties are shown in Table 2. The treatments were arranged in a factorial design with 3 factors in complete randomized design (RCBD) and the experiment lasted for 20 weeks. The experimental treatments were:

**Non-Treated Soil with Heavy Metals**
- Control without mineral fertilizers (UT0)
- Control with 50% of recommended NPK of mineral fertilizers (MF) as a (UT50)
- Control with 100% of recommended NPK of mineral fertilizers (MF) as a (UT100)
- Compost (UC0)

**Treated Soil with Heavy Metals**
- Control without mineral fertilizers (CT0)
- Control with 50% of recommended NPK of mineral fertilizers (MF) as a (CT50)
- Control with 100% of recommended NPK of mineral fertilizers (MF) as a (CT100)
- Compost (CC0)
- Compost + 50% MF as a (CC50)
- Compost + 100% MF as a (CC100)
- Vermicompost (CV0)
- Vermicompost + 50% MF as a (CV50)
- Vermicompost + 100% MF as a (CV100)

After harvest (155 days from sowing), plant samples were separated into roots, shoots and grains, washed with tap water followed by distilled water, oven dried at 70 °C for 48 hrs., digested by H2SO4/H2O2 mixture according to the method described by Chapman et al., 1961 and kept for the elements determination (N, P, K, Cu, and Cd).

Soil samples collected from each plot at the end of the field experiment were air-dried, ground and passed through a 2-mm sieve and stored for chemical analyses. Soil samples were subjected to sequential extraction and Cu and Cd were partitioned into five components according to Tessier et al., (1979) as shown in Table 3. In order to evaluate the potential risk of heavy metals in the soils, the mobility assessment was adopted through the mobility factor (MF) weakly bound to soil components by all fractions as follows (Kabala and Singh, 2001):

\[
MF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100
\]

In agricultural soils suggested the tendency for entering easily to the food chain, thus have high risk. MF calculation method is corresponding to Singh’s risk assessment code (RAC) (Singh et al., 2005) Table 4. The recorded data, previously standardized, were statistically analyzed using STATISTICA 10 of Stat Soft, Inc. (Tulsa, Oklahoma, USA).
Table 1. Analyses of the experimental soil

| Soil Properties | Levels       |
|-----------------|--------------|
| **Particular size distribution** |                |
| Sand %          | 60.59        |
| Silt %          | 12.82        |
| Clay %          | 26.59        |
| Soil texture    | Sandy Clay Loam |
| pH (1:2.5 Soil: water) | 8.39        |
| EC dS/m (1:1 soil: water) | 2.69        |

| Soluble cations, meq/L (1:1 soil: water) |
|------------------------------------------|
| Ca$^{2+}$                                | 7.15 |
| Mg$^{2+}$                                | 0.82 |
| Na$^+$                                   | 7.97 |
| K$^+$                                    | 0.80 |

| Soluble anions, meq/L (1:1 soil: water) |
|-----------------------------------------|
| HCO$_3^-$                                | 4.52 |
| Cl$^-$                                   | 6.07 |
| SO$_4^{2-}$                               | 7.12 |

| Total N, % | Available Phosphorus, mg/Kg | Available potassium, mg/Kg | Total carbonate, % | Organic matter, % |
|------------|-----------------------------|---------------------------|-------------------|------------------|
| 0.09       | 5.00                        | 105.22                    | 36.02             | 0.98             |

| Heavy metals (DTPA-extractable), mg/kg |
|----------------------------------------|
| Cu                                     | 0.848 |
| Fe                                     | 4.180 |
| Mn                                     | 7.740 |
| Zn                                     | 0.648 |
| Cr                                     | 0.024 |
| Cd                                     | n.d   |
| Pb                                     | 0.4   |

Table 2. Some characteristics of the studied amendments

| Character        | compost | Vermi-compost |
|------------------|---------|---------------|
| pH(1:5)          | 7.50    | 7.98          |
| EC, dS m$^{-1}$ (1:5) | 2.16    | 3.01          |
| OC, %            | 25.93   | 36.41         |
| OM, %            | 44.59   | 62.63         |
| C/N ratio        | 16.51   | 19.26         |

| Total content of macronutrients, % |
|-----------------------------------|
| N                                 | 1.57   | 1.89          |
| P                                 | 0.52   | 0.23          |
| K                                 | 1.02   | 0.41          |

| Dry Ash of heavy metals, mg kg$^{-1}$ |
|---------------------------------------|
| Fe                                   | 4870   | 2081          |
| Mn                                   | 315    | 127           |
| Zn                                   | 35.4   | 28.11         |
| Cu                                   | 11.3   | 7.22          |
| Pb                                   | 5.93   | 2.25          |
| Cd                                   | 0.23   | 0.10          |
| Cr                                   | 0.54   | 0.32          |
Table 3. Determination of the studied heavy metals fractions in soil according to (Tessier et al, 1979)

| Metal fractions                  | Extraction procedure                                      |
|----------------------------------|-----------------------------------------------------------|
| Water soluble& Exchangeable (F1) | 1 M MgCl₂ (pH 7, 1 h, 25 °C)                             |
| Carbonate associated fraction (F2)| 1 M CH₃COONa (pH 5, 5 h, 25 °C)                          |
| Fe-Mn oxides bound fraction (F3) | 0.04 M NH₃OH.HCl in 25% acetic acid (5 h, 96 °C)         |
| Organically bound fraction (F4)  | 30% H₂O₂ + 0.02 M HNO₃ (pH 2, 5 h, 85 °C), and after cooling 3.2 M NH₄OAc in 20% HNO₃ |
| Residual fraction (F5)           | HNO₃ conc. (2 h, 100 °C)                                 |

Table 4. Classification of stability and risk of heavy metals in soil (Singh et al., 2005)

| MF(%)  | Stability     | Risk     |
|--------|---------------|----------|
| MF≤ 1  | Very high     | No risk  |
| 1 < MF ≤ 10 | High Stability | Low risk |
| 10 < MF ≤ 30 | Medium Stability | Medium risk |
| 30 < MF ≤ 50 | Low Stability | High risk |
| 50 < MF ≤ 75 | No Stability  | Very high risk |

MF: Mobility factor.

RESULTS AND DISCUSSION

Distribution of Cu and Cd in soil fractions

Data in Figure 1a showed the effect of different amendments on copper distribution. The untreated soil contained Cu forms in the following descending order: F5 > F4 > F3 > F2 > F1, but in treated soils with organic amendments, they were F4 > F5 > F3 > F2 > F1. Similar results were obtained by Adriano et al., (2001) who reported that Cu was bound strongly to clay minerals and organic matter in soil by two mechanisms; complexation and adsorption. The un-contaminated soil treated by vermicompost showed significant decreases in Cu in the F1 fraction (47.06%), F2 fraction (67.96%) and F5 fraction (26.05%) as compared to the control treatment. Compost treatment decreased F1 fraction by (20.35%), F2 fraction by (54.22%) and F5 fraction by (8.31%) as compared to control. In contaminated soil treated by vermicompost treatment showed significant decreases in Cu in the F1 fraction (46.46%), F2 fraction (26.81%) and F5 fraction (29.76%) as compared to the control treatment. Compost treatment decreased F1 fraction by (20.56%), F2 fraction by (20.99%) and F5 fraction by (29.31%) as compared to control.

Mahler et al. (2006) stated that extractable levels of heavy metals in soil were known to be affected by soil organic matter content and other many factors. It is clear that the organic treatments increased Cu in form of Fe and Mn oxides bound and organically bound rather than the control treatment, as a type of metal complexation. Metal complexation may additionally be in the form of chelation, where the complex forming ligands from two or more co-ordination bonds with the metal ion (Lindsay, 1995), such as humic acid. Furthermore, humic substances in soils can serve as strong reducing agent and can influence the processes controlling mobilization of many toxic metals (Adriano, 2001). Copper ions however, form very stable complexes with organic substances over a wide range of pH (Barančíková and Makovníková, 2003). Due to the strong affinity of Cu to organic matter in soil by two mechanisms; complexation and adsorption so that the organic-fraction Cu is high compared to that for other metals (McGrath et al., 1998 and Adriano, 2001).

Data in Figure 2 showed the distribution of cadmium in soil as affected by different amendments. The uncontaminated soil contained Cd forms in the following descending order: F5 > F3 > F2 > F4 > F1, but in treated soils with organic amendments, they were F4 > F5 > F3 > F2 > F1. Similar results were obtained by Adriano, (2001) who reported that Cd was decreased by increasing in CEC by the addition of organic matter also resulted in the increased growth of the oat shoots. This probably was due to inhibition of Cd availability, which in turn diminished the harmful effects of Cd on the growth. Others (Deswal and Laura., 2019) also showed that negative correlation between leaf Cd values and CEC. In contrast, Mahler et al. (1978), found that positive effect on Cd lettuce leaf content by used multiple regression analysis on lettuce, soil EC, in addition to Cd in the saturation extract, they used eight soil types with CEC ranging from 6.5 to 37.9 meq/100 g.

The un-contaminated soil treated by vermicompost showed significant decreases in Cd in the F1 fraction (98.81%), F2 fraction (55.05%), F5 fraction (53.86%) as compared to the control treatment. Compost treatment decreased F1 fraction by (79.17%), F2 fraction by (35.66%) and F5 fraction by (33.66%) as compared to control. The contaminated soil treated by vermicompost treatment showed significant decreases in Cd in the F1 fraction (80.06%), F2 fraction (59.96%) and F5 fraction (58.54%) as compared to the control treatment. Compost treatment decreased F1 fraction by (73.05%), F2 fraction by (30.01%) and F5 fraction by (25.56%) as
compared to the control. Application of vermicompost reduced the amount of exchangeable Cd from the soil, while compost can even increase Cd to 18.8 -19.2 mg/kg. The increased in organic-matter application increased adsorption of Cd by soil components because of the existence of ligands or functional groups that can chelate metal ions and also alter the adsorption characteristics of soil inorganic phase (Adriano et al. 2004 and Ahmad 2010). However, Cd immobilization by precipitation as sulfate and carbonates component appears to be the dominate process in an alkaline calcareous soil in forms especially when sulfate and carbonates concentration is high (Adriano 2001).

Fig. 1a. Copper concentration in the different fractions in un-contaminated soils as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)

Fig. 1b. Copper concentration in the different fractions in contaminated soils as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)
Assessment of the mobile fraction of Cu and Cd

Mobility of the two metals were assessed by calculating MF. The results of MF are represented graphically in Fig. 3(a&b). It can be seen that there is obvious difference for the mobility of each metal and spatial difference among the organic treatments and NPK fertilizers.

The average decreased of Cu potential mobile fraction ($Cu_{MF}$) in Un-contaminated soil treated with vermicompost was 61% as compared with control treatments. Compost treatments decreased Cu mobility ($Cu_{MF}$) by 51% as compared with control treatments. In contaminated soil treated with vermicompost was decreased by 22% as compared with control treatments. Compost treatments decreased Cu mobility ($Cu_{MF}$) by 12% as compared with control treatments. The average decreased of Cd mobility ($Cd_{MF}$) in Un-contaminated soil treated with vermicompost was 44% as compared with control treatments. Compost treatments decreased Cd mobility ($Cd_{MF}$) by 35% as compared with control treatments. In contaminated soil treated with vermicompost was 59% as compared with control treatments. Compost treatments decreased Cd mobility ($Cd_{MF}$) by 45% as compared with control treatments. In contaminated soils was quite high implying that under favorable conditions they can be released to pollute the environment. They pose a potential major environmental hazard due to the increase of free metallic ions in the medium. The mobilization of pollutants depends on
several factors: their mobility, their concentration in the soil and their solubility. Metal associations with oxides and organic fractions are not dangerous for the environment because this fraction is less extractable. But when the environment becomes increasingly reducing or oxidizing, metals can be mobilized (Yin et al., 2002 and Yobouet et al., 2010).

![Fig. 3.a. Scale of Cu mobility factor (MF) values in Soil](image1)

![Fig. 3.b. Scale of Cd mobility factor (MF) values in Soil](image2)
Weight of Grains and Elements Concentration of Wheat Plants:

Data in figures (4, 5, 6 and 7) showed the grain yield, N, P and K concentrations in wheat plants cultivated as affected by different organic amendments. It is clear that yield of wheat plant, N, P and K concentrations were significantly higher due to application of organic amendments (compost and vermicompost) to the studied soil. Probably due to the relatively improvement of soil physical and chemical properties, beside of decreasing bioavailability of heavy metals in soil, which encouraged plant yields. The highest effect on increasing yield obtained from the treatment of vermicompost followed by compost. These results agree with those obtained by (Najar and Khan, 2013), they confirmed that the vermicompost is a potential source of plant nutrients for sustainable tomato production. The concentrations of Cu and Cd in wheat plants as affected by the different organic amendments showed in figures (8 and 9). The obtained results showed that the concentrations of these metals in wheat plants, in general, significantly decreased due to application of such amendments, with the highest effect due to vermicompost treatment. These results went hand by hand with the effect of vermicompost on decreasing solubility and leach-ability of Cu and Cd in soil. In this concern, the decrease in heavy metals concentrations may be due to growth dilution, which occurred with an increase in biomass production and partially decreased these metals concentration in soil solution with amendments through formation of less soluble compounds (Abd-Elrahman et al., 2012 and Bolan et al., 2003). Also, it can be noticed that organic substances significantly decreased heavy metals concentrations and their translocations in roots, shoots and grains of wheat plant compared to the control treatment. Similar results were obtained by Karapanagiotis et al., (1991) who stated that metal-organic matter associations in both solution and solid phases by way of complexation and specific adsorption are the important mechanisms responsible for rendering the indigenous and applied metals less available for absorption by the plants.

Fig. 4. Grain yield of wheat plants as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)

Fig. 5. TN% concentrations in grains as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)
Fig. 6. P (mg.kg-1) concentrations in grains as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)

Fig. 7. K (mg.kg-1) concentrations in grains as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)

Fig. 8. Cu (mg.kg-1) concentrations in grains as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)
Fig. 9. Cd (mg.kg-1) concentrations in grains as affected by all treatments; T: Control (0 NPK, 50 NPK, 100 NPK); C: Compost (0 NPK, 50 NPK, 100 NPK); V: Vermicompost (0 NPK, 50 NPK, 100 NPK)

CONCLUSION

The organic amendments (compost and vermicompost) decreased the concentration of Cu and Cd ions (soluble, exchangeable and carbonate fractions) in soil and the expected uptake of these elements by wheat plants. However, decreased in Cu and Cd concentration was greater in vermicompost treated soil more than compost treated soil. It's clear from results that application of these organic amendments could mitigate the risk of food chain contamination by decreasing the tested metals concentrations in soil. The mobility fractions of the tested metals in the soil was quite low especially with vermicompost. Keeping in view the importance of organic amendments application in decreasing metal entry into the food chain.

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الملخص العربي

استخدام الكمبوست والفيرمكمبوست كمحسنات للترية لثبت النحاس والكادميوم في ظل ظروف نمو القمح

أجريت دراسة حقلية خلال موسم زراعة محصول القمح في الأراضي الجزءية بهدف دراسة تأثير استخدام الكمبوست والفيرمكمبوست كمحسنات للترية وتأثيرها على عدم حركية عنصر النحاس والكادميوم في التربة. وقد تم تطبيق المحسنات بمرورها ومع استخدام الأسمدة المعدنية ومقارنة تأثيرها على عدم حركة النحاس والكادميوم. وقد أوضحت النتائج أن استخدام الكمبوست والفيرمكمبوست كمحسنات للترية أدى إلى خفض صور الذائبة للنحاس والكادميوم القابل للاستخلاص من التربة بعد حصاد محصول القمح. وقد أظهر الاستخلاص المتعاقب للنحاس والكادميوم اختلاط معنوي في الجزء القابل للاستخلاص نتيجة تطبيق الفيرمكمبوست بنسبة 47,06% و (F1).