Two Lysimeter experiments were conducted in Egypt to: explore possible effects of land-applying Al-WTRs and/or biosolids on the environment, and recommends ways to minimize human and animal impacts. The specific objectives were to (1) determine the co-application effects on Diethylene Triamine Penta Acetic acid (DTPA)-extractable heavy metals in relation to their accumulation in plant, (2) assess the effectiveness of WTRs in reducing bioavailability of heavy metals in the soils amended with different rates of biosolids, and (3) quantify the optimum application ratio of WTRs to biosolids in relation to the reduction of plant metal accumulation. Thus, in these lysimeter experiments, the WTRs and biosolids were obtained twice in 1999 and 2008. The used soil was classified as Typic torrifluvent. Treatments in both experiments consisted of the combination of WTRs (0, 20, 40, 80, and 160 Mg.ha\(^{-1}\)) and biosolids (0, 25, and 50 Mg.ha\(^{-1}\), DW) by fixing one rate of biosolids and with varying the rate of WTRs. The results showed that land application of biosolids increases the accumulation of toxic metals in corn tissues in slightly alkaline soils. However, WTRs-application of (20, 40, 80 and 160 Mg.ha\(^{-1}\)) to the soil amended with (0, 25 and 50 Mg.ha\(^{-1}\)) of biosolids decreases significantly the DTPA-extractable metal concentrations. The reduction in DTPA-extractable metals resulting from the application of WTRs to biosolid-amended soils can be explained by formation of metal-sulfate, low solubility product, and the floc-adsorption and the co-precipitation processes, in which the formation of a mixed solid phase by the incorporation of metal ions into the crystal lattice of another precipitating solid phase is expected. The combined studies clearly demonstrate that Al-WTRs should have no negative impacts on the environment when appropriate rates are land applied. Thus, Al-WTRs are safe soil amendments to control heavy metals contamination in soil and water bodies.

**Key words:** WTRs. heavy metals, bioavailability, biosolids.

**INTRODUCTION**

Biosolids are treated municipal sewage sludge, a byproduct of municipal wastewater treatments. Land application is becoming a preferred option for disposal of sewage sludge (biosolids) from wastewater treatment plants. However, it creates potential risks due to the heavy metal contents of these materials. The environmentally sound and sustainable land application of biosolids becomes increasingly popular because of their potential benefits for better soil fertility, structure and tilth (Hall and Coker, 1981; Oberle and Keeney, 1994; Peverly and Gates, 1994; Joshua et al., 1998; Johansson et al., 1999; Mosquera-Losada et al., 2001). However, such advantages are oftentimes diminished by the potential environmental risk of introducing toxic metals in the amended soils, which may lead to metal accumulation in food chains or other serious impacts on environmental and human health (Maclean et al., 1987; McGrath, 1987; Corey et al., 1987; King and Hajjar, 1990;
Berti and Jacobs, 1996; Sloan et al., 1998; Chaudri et al., 2000; Bhogal et al., 2003).

Drinking water treatment residuals (WTRs) or alumsludge are the byproduct from the pre-treatment of raw drinking water, and generally contain high contents of amorphous aluminum (Al) or iron (Fe) hydroxides that coagulate and flocculate dissolved and suspended cations and minerals in water (Elliott et al., 1990). Because of the formation of non-water soluble metal phosphate compounds or immobilized in Al-WTRs by mechanism of intraparticle diffusion, many earlier studies have been conducted to examine the effectiveness of the co-application of biosolids and WTRs in stabilizing P in the agricultural soil (Elliott et al., 2002; Makris et al., 2004; Wagner et al., 2008).

Usually remediation methods applicable to soils contaminated with metals are based on two approaches: removal/extraction of the heavy metals from the matrix by electrokinetic and/or “washing” processes which are characterised by high costs and laborious management (Virkutyte et al., 2002; Dong-Mei et al., 2004) or reduction of metal mobility with “in situ” techniques. In this case different additives (lime, zeolites, clay minerals, compost, peat, fly ashes, etc.) have been investigated (Badora et al., 1998; Garcia-Sanchez et al., 1999; Chen et al., 2000; Li et al., 2000; Schuman et al., 2002; Bilge and Mehmet, 2002; Alvarez-Ayuso and Garcia-Sanchez, 2003). In order to reduce the concentration of bioavailable forms of metals in contaminated soils we have begun a study based on the treatment of metal polluted soils with paper mill sludges.

The removal of negatively charged mineral particles from water through Al (or Fe)-induced coagulation suggests a promising process in which WTRs might be used to adsorb positively charged cations and, therefore, reduce the bioavailability of toxic metals in contaminated soils. Mahdy et al., (2012) found that addition of WTRs at 3% application rate to 3 % biosolids-treated soils (1:1 ratio) significantly reduced the bioavailability of some heavy metals in pot experiments. Given that the land application of WTRs in biosolid-amended agricultural soil has received considerable attention in recent years to stabilize P in the soil (Oladeji et al., 2007; Hovsepyan and Sommers, 1982), it is critically important to examine the potential impacts of WTRs on metal toxicity in biosolid-amended agricultural soil.

Thus, the main target of this study was: to explore possible effects of land-applying Al-WTRs on the environment, and recommends ways to minimize human impacts. The specific objectives were to:

(1) determine the co-application effects on Diethylene Triamine Penta Acetic acid (DTPA)-extractable heavy metals in relation to their accumulation in plant;
(2) assess the effectiveness of WTRs in reducing bioavailability of heavy metals in the soils amended with different rates of biosolids, and
(3) quantify the optimum application ratio of WTRs to biosolids in relation to the reduction of plant metal accumulation.

**MATERIALS AND METHODS**

**Material collection and preparation**

Soil in the lysimeter was classified as Typic torrifluvent. The experimental biosolids were obtained twice in 1999 and 2008 from the General Organisation Sanitary (GOS) (Station No 9) in the City of Alexandria, Egypt. The biosolids were air-dried and sieved (<2 mm) prior to their use (Makris and Harris, 2005). The WTRs was also obtained twice in 1999 and 2008 from the drinking water treatment plant in Kafr El-Dawar, El-Bohera Governorate, Egypt. The used WTRs in this study was the 2008 plant byproduct. The WTRs were air-dried and sieved (<2 mm) prior to their use (Makris and Harris, 2005).

**Chemical and physical analyses**

The following chemical and physical analyses were performed on background soil, WTRs and biosolids: the pH and electrical conductivity (EC) of soil were determined using the paste extract method (Richards, 1954), while pH and EC of WTRs and biosolids were measured in 1:2.5 suspension (Richards, 1954). Soil calcium carbonate content was determined by means of calciometer (Nelson, 1982). Particle size analysis was determined by the hydrometer method (Day, 1965). The soil organic matter content (OM) was determined by the dichromate oxidation method (Nelson and Sommers, 1982).

Cation exchange capacity (CEC) was determined by 1 M NaOAc (Rhoades, 1982). Available P was extracted by sodium bicarbonate (0.5 N) and determined by blue method (Olsen and Sommers, 1982). Extractable Al was determined using potassium chloride (1 M) extracting solution in the same treated plots and determined colorimetrically by Aluminon method (Barnhisel and Bertsch, 1982). Available nitrogen was determined by Kjeldahl method (Bremner and Mulvaney, 1982). Water holding capacity (WHC) was determined according to Skene et al. (1995). Concentrations of metals were determined according to the method described by Ure (1995). Selected chemical and physical properties of the soil, biosolids and WTRs are summarized in Table 1.

**Description of experimental site and lysimeter experiments**

The lysimeter experiments were conducted at the soil salinity and alkalinity laboratory at Alexandria, Egypt. This site lies between latitude 31° 2' N, and longitude 29° 6' E with an elevation of about 2.50 m below sea level. The annual rainfall averaged 200 mm and the relative humidity during daytime is about 67.30% at the experimental site. The mean maximum temperature during August and September ranged between 30.9°C and 29.6°C. The used plots have the dimensions of 0.6m by 0.6m by 0.4m deep. The bottom of each lysimeter plot was equipped with an outlet drain to facilitate leaching. Each plot was filled with 40 kg clay soil. Treatments in both experiments (2010 and 2011 years) consisted of the combination of WTRs (0, 20, 40, 80, and 160 Mg.ha⁻¹) and biosolids (0, 25, and 50 Mg.ha⁻¹, DW) by fixing one rate of biosolids and with varying the rate of WTRs. These rates were applied to the soil before twenty one days of planting and mixed well to a 15-cm depth. The experimental design was a split plot design with four replicates of each treatment. Control treatments represent soil with no source of fertilizer, biosolids and WTRs.

Corn seeds (Zea mays cv single hybide 30K8, white pioneer) were sown as a test plant in plots during the growing season (May...
to September) in two successive seasons, i.e., 2010 to 2011 (the day length was about 14 hrs., temperature range was 25 to 35°C). The seedlings were thinned to 6 seedlings per plot and irrigated according to water requirements of corn. Plants were harvested (above ground shoot with ears), after 13 weeks of sowing.

Heavy metals extractability

The DTPA (0.005M DTPA, 0.1 TEA, and 0.01 M CaCl$_2$, adjusted to pH 7.3) extracting solution was used to extract Cd, Pb, Cu, and Ni from the treated and control soils after harvest (Lindsay and Norvell, 1978). The soil extracts were analyzed for Cd, Cu, Ni, and Pb concentrations using atomic absorption spectrophotometry (AAS) (Baker and Amacher, 1982).

Plant biomass measurement

The plant grains and stover were harvested separately, and immediately washed with running tap water and rinsed three times with de-ionized water. The plant tissues were dried in a forced-air drying oven at 65°C for 48 h, ground in a stainless steel mill and dry matter yield was recorded. Sub-samples of ground plant material were ashed in a muffle furnace at 450 °C for 6 h (Jones, 2001). The ash was dissolved in nitric acid (1:1), diluted to a constant volume with de-ionized water and analyzed for Cd, Pb, Cu, and Ni (Jones, 2001).

Statistical analyses

The treatment effects on heavy metals extractability and metal uptake were evaluated by two-way analysis of variance (ANOVA). When significance was indicated by a Fisher's least significant difference procedure using a 0.05 significance level (SAS Institute, 1994).

RESULTS AND DISCUSSION

Physical and chemical properties of WTRs and biosolids

The chemical and physical characteristics of biosolids and WTRs are compiled in Table (1). The WTRs characteristics are changed from plant to other and from year to year. The WTRs of 2008 year is slightly alkaline (pH 7.65). The salinity of WTRs was < 4 dSm$^{-1}$ and the cation exchange capacity was 39.98 cmol (+) kg$^{-1}$, which indicates that WTRs can supply cationic nutrients for plant growth (Bohn et al., 1985). Surprisingly, the OM in the WTRs was 81.54 g kg$^{-1}$, which is greater than in the agricultural soils in Egypt. The Olsen-P in WTRs was greater than that of background soil. The WHC of the WTRs was 500.87 g kg$^{-1}$. The KCl-extracted Al was 24.87 mg kg$^{-1}$. Elliott and Dempsey (1991) stated that the WTRs have low contents of P. Elliott and Singer (1988) recommended that N-P-K fertilizers are necessary if WTRs were applied to agricultural lands. The main advantages of adding WTRs to agricultural soils include:

1. favorable water holding capacity,
2. drainage characteristics and (3) structural stability, rather than its inherent nutrient content (Skene et al., 1995).

Biosolids characteristics also are changed from year to other. The biosolids of 2008 year were slightly different from the biosolids of 1999 used previously in the pot experiment (Mahdy et al., 2009). So, the characteristics of biosolids produced in 2008 year were slightly acidic (pH 6.72) with high contents of O.M (475 gkg$^{-1}$) and essential nutrient contents (Table 1). The WHC of biosolids was much lower than the WTRs and relatively greater than the value of background soil because of high levels of clay in the WTRs that normally contains a high percentage of clay particles because the removal of clay particles from raw water is one of the primary objectives of water treatment. The KCl-extracted Al in biosolids was lower than in WTRs. Elliott and Dempsey (1991) indicated that land application of biosolids is feasible primarily because biosolids contain plant nutrients that are valuable in agricultural production. Total metal concentrations in WTRs were lower than the concentrations in the biosolids. However, the DTPA-extractable metal concentrations in WTRs were lower than those in the background soil. The total metal concentrations in biosolids were much higher than ones in WTRs. Concentrations of metals in both biosolids and WTRs are well below the maximum allowable values set by USEPA (1993) for land application.

Land co-application of aluminum-based WTRs and biosolids and agricultural production

Phytoavailability of heavy metals

Cadmium

Effects of WTRs on Cd accumulation in corn tissues in biosolids-amended soils are shown in Figure 1. Increasing the biosolids application ratio resulted in an increase in Cd accumulation in both grain and stover tissues with all plots. Cd accumulation (mg kg$^{-1}$, DW) in grains was smaller than in stover in all studied plots. The metal accumulation in the whole plant (i.e. including both grain and stover) was greater in plots treated with 50 Mg.ha$^{-1}$ biosolids than in plots treated with 25 Mg.ha$^{-1}$ (Figure 1).

These findings agreed with those reported by Singh and Agrawal (2007), indicating that the accumulation of metals (Ni, Zn, Cd, Cu, Cr, and Pb) was found more in shoots than in roots, except for Fe and Cr. At the 25 Mg.ha$^{-1}$ biosolids application rate, increasing the WTRs application rate significantly decreased the Cd concentration in grains and stover of corn in the studied soil. Furthermore, concentrations of Cd in grains and stover decreased by 83% and 81%, respectively, when
160 Mg ha\(^{-1}\) of WTRs was applied along with 25 Mg ha\(^{-1}\) of biosolids in the studied soil, whereas a decreases of 73% and 63% were found in plots treated with 50 Mg ha\(^{-1}\) . Increasing the WTRs application rate in the control soil (i.e. soil was not amended with biosolids) significantly decreased the Cd concentrations from 9.19 to 0.93 mg kg\(^{-1}\), giving a 90% decrease. These results were confirmed with the results of second season 2011. In summary, total Cd accumulation in corn was significantly affected by biosolids, WTRs as well as the interaction between biosolids and WTRs (Figure 1). These results are in agreement with previous findings by Chu (1999), showing that the use of recycled alum sludge increased heavy metals removal rates from 79 to 98% with 100 to 180 mg L\(^{-1}\) of recycled WTRs through the coagulation and precipitation mechanisms. Battaglia et al. (2007) reported that the addition of paper mill sludge and WTRs to the soil contaminated by Pb and Zn decreased concentrations of soluble Pb and Zn, which are the most readily bioavailable chemical forms to plants. Sarkar et al. (2007) also indicated the potential of WTRs in immobilizing arsenic (As) in contaminated soils, and thereby minimizing soil As bioavailability to plants. The study of Agyn-Birikorang et al. (2009) demonstrated that potential soil As availability to plants and humans decreased as Al-WTRs application rate increased. Al-WTRs added at 28 metric tons/ha (12.5 T/A) significantly decreased As phytoavailability compared with the control. However, greater WTRs application rates (>56 metric tons/ha (25 T/A)) were needed to decrease soil As bioaccessibility. Thus, application of WTRs at a minimum rate of 56 metric tons/ha could be a viable and effective field remediation method for As-contaminated soils that are low in Fe and Al oxyhydroxides. Thus, the perceived threat of As toxicity following land application of WTRs is not supported by the data. Mahdy et al. (2012) found that the increase in WTRs application from 1, 2, 3 to 4% (w/w)

### Table 1. Some physical and chemical analyses of background soil, biosolids, and Al-WTRs. All values are expressed on dry weight basis. #

<table>
<thead>
<tr>
<th>Property</th>
<th>Background soil</th>
<th>Units</th>
<th>1999</th>
<th>2008</th>
<th>1999</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>1.37±0.05</td>
<td>dSm(^{-1})</td>
<td>11.25±2.11</td>
<td>8.12±1.55</td>
<td>1.67±0.54</td>
<td>1.43±0.66</td>
</tr>
<tr>
<td>pH</td>
<td>7.90</td>
<td></td>
<td>6.69</td>
<td>6.72</td>
<td>7.45</td>
<td>7.65</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>70.04±3.55</td>
<td>g kg(^{-1})</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Sand</td>
<td>246.00±8.11</td>
<td>g kg(^{-1})</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Silt</td>
<td>322.33±4.56</td>
<td>g kg(^{-1})</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Clay</td>
<td>431.67±7.44</td>
<td>g kg(^{-1})</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Texture</td>
<td>Clay</td>
<td></td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>O.M</td>
<td>19.40±2.50</td>
<td>g kg(^{-1})</td>
<td>450.00±10.34</td>
<td>475.00±6.33</td>
<td>57.00±4.13</td>
<td>81.54±23.98</td>
</tr>
<tr>
<td>Available-N</td>
<td>13.24±1.45</td>
<td>mg kg(^{-1})</td>
<td>80.66±11.09</td>
<td>95.33±11.06</td>
<td>15.98±1.22</td>
<td>22.87±2.13</td>
</tr>
<tr>
<td>KCl-Al</td>
<td>122.85±12.98</td>
<td>mg kg(^{-1})</td>
<td>4.22±0.65</td>
<td>3.45±0.95</td>
<td>28.18±1.76</td>
<td>24.87±1.99</td>
</tr>
<tr>
<td>Olsen-P</td>
<td>8.55±2.11</td>
<td>mg kg(^{-1})</td>
<td>48.60±2.14</td>
<td>56.98±2.44</td>
<td>24.00±1.11</td>
<td>22.15±1.01</td>
</tr>
<tr>
<td>CEC</td>
<td>29.94±1.88</td>
<td>cmol(+) kg(^{-1})</td>
<td>73.57±3.88</td>
<td>86.34±4.33</td>
<td>34.78±2.34</td>
<td>39.98±2.07</td>
</tr>
<tr>
<td>W.H.C</td>
<td>231.15±5.98</td>
<td>g kg(^{-1})</td>
<td>250.00±6.87</td>
<td>286.00±12.32</td>
<td>470.00±10.23</td>
<td>500.87±23.14</td>
</tr>
<tr>
<td>Total Elements:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.32</td>
<td>g kg(^{-1})</td>
<td>32.00±1.56</td>
<td>28.00±1.66</td>
<td>4.20±0.13</td>
<td>3.76±0.90</td>
</tr>
<tr>
<td>P</td>
<td>1.45</td>
<td>g kg(^{-1})</td>
<td>4.60±0.12</td>
<td>4.33±0.87</td>
<td>1.90±0.15</td>
<td>2.08±0.11</td>
</tr>
<tr>
<td>K</td>
<td>1.85</td>
<td>g kg(^{-1})</td>
<td>1.90±0.08</td>
<td>2.10±0.66</td>
<td>2.20±0.21</td>
<td>1.94±0.08</td>
</tr>
<tr>
<td>Al</td>
<td>4.54</td>
<td>g kg(^{-1})</td>
<td>3.10±0.23</td>
<td>2.76±0.09</td>
<td>38.01±0.93</td>
<td>30.09±1.66</td>
</tr>
<tr>
<td>Ni</td>
<td>6.00</td>
<td>mg kg(^{-1})</td>
<td>108.00±1.01</td>
<td>120.43±7.09</td>
<td>9.40±0.07</td>
<td>8.00±1.06</td>
</tr>
<tr>
<td>Pb</td>
<td>75.00</td>
<td>mg kg(^{-1})</td>
<td>143.00±6.44</td>
<td>150.00±11.08</td>
<td>76.00±0.17</td>
<td>68.00±3.19</td>
</tr>
<tr>
<td>Cu</td>
<td>33.54</td>
<td>mg kg(^{-1})</td>
<td>128.00±0.44</td>
<td>125.98±8.08</td>
<td>49.00±0.02</td>
<td>38.07±1.99</td>
</tr>
<tr>
<td>Cd</td>
<td>1.22</td>
<td>mg kg(^{-1})</td>
<td>4.00±0.15</td>
<td>4.66±0.65</td>
<td>3.00±0.02</td>
<td>1.99±0.43</td>
</tr>
<tr>
<td>DTPA-Extractable Metals:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>6.92±0.04</td>
<td>mg kg(^{-1})</td>
<td>12.12±0.24</td>
<td>11.04±0.33</td>
<td>2.49±0.07</td>
<td>1.65±0.12</td>
</tr>
<tr>
<td>Pb</td>
<td>8.13±0.02</td>
<td>mg kg(^{-1})</td>
<td>62.13±0.22</td>
<td>56.98±0.66</td>
<td>1.58±0.04</td>
<td>1.33±0.09</td>
</tr>
<tr>
<td>Cu</td>
<td>7.19±0.03</td>
<td>mg kg(^{-1})</td>
<td>11.83±0.15</td>
<td>9.00±0.16</td>
<td>1.20±0.1</td>
<td>0.89±0.06</td>
</tr>
<tr>
<td>Cd</td>
<td>0.43±0.02</td>
<td>mg kg(^{-1})</td>
<td>0.72±0.04</td>
<td>0.45±0.05</td>
<td>0.09±0.02</td>
<td>0.08±0.01</td>
</tr>
</tbody>
</table>

# Means of three samples ± SD.
† Water holding capacity
‡ O.M: organic matter;
nd: not determined
Figure 1. Effects of WTRs on Cd concentrations in grain and stover of corn plants grown in biosolids-treated soil for two years of cultivation 2010 and 2011. Where no error bars are present, the standard error was too small to be represented as the scale of the diagram.

Figure 2. Effects of WTRs on Ni concentrations in grain and stover of corn plants grown in biosolids-treated soil for two years of cultivation 2010 and 2011. Where no error bars are present, the standard error was too small to be represented as the scale of the diagram.
Figure 3. Effects of WTRs on Cu concentrations in grain and stover of corn plants grown in biosolids-treated soil for two years of cultivation 2010 and 2011. Where no error bars are present, the standard error was too small to be represented as the scale of the diagram.

Figure 4. Effects of WTRs on Pb concentrations in grain and stover of corn plants grown in biosolids-treated soil for two years of cultivation 2010 and 2011. Where no error bars are present, the standard error was too small to be represented as the scale of the diagram.
significantly decreased concentrations of metals in tissues of plants grown in biosolids-amended soils with 1, 2, or 3% (w/w). Also, they found that the 1:1 application ratio of WTRs to biosolids at 3% application rate effectively reduced metal accumulation in plant tissues.

**Nickel**

In general, increasing the biosolid application rate from 0 to 50 Mg.ha\(^{-1}\) resulted in an increase in the accumulation of Ni in the grains and stover in the studied soil, and more Ni accumulated in stover than in grains (Figure 2). Similarly, Sinha et al. (2007), indicating that the accumulation of metals (Fe, Zn, Mn, Cu, Cr, and Pb) was found more in shoots than in roots, except for Fe and Cr. Increasing the WTRs application rate from 0 to 160 Mg.ha\(^{-1}\) in the plots amended with 25 Mg.ha\(^{-1}\) of biosolids significantly decreased the Ni concentration in corn grains by 83% and 73% in stover. However, a decrease of 68 and 62% was found in Ni concentrations of grains and stover, respectively in plots treated with 50 Mg.ha\(^{-1}\). These observations concur with those by Karthikeyan et al. (1996), indicating that the use of WTRs could reduce soil metal bioavailability by the floc-adsorption process. Lombi et al. (2004) concluded that WTRs were one of the most effective amendment materials in terms of decreasing metal mobility and diminishing bioavailability of metals.

The addition of WTRs to different alkaline soils significantly decreased concentrations of heavy metals in plant tissues (Mahdy et al., 2012). The total Ni concentrations was significantly affected by the biosolids, WTRs, and the interactions among these variables.

### Table 2. Effects of WTRs on DTPA-extractable cadmium (Cd), nickel (Ni), lead (Pb) and copper (Cu) in the studied soil treated with different rates of biosolids for two years of cultivations 2010 and 2011.

<table>
<thead>
<tr>
<th>Biosolids rate, Mg.ha(^{-1})</th>
<th>Extractable heavy metals, mg.kg(^{-1})</th>
<th>Cd</th>
<th>Ni</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.62 (0.05)</td>
<td>0.68 (0.04)</td>
<td>8.15 (0.03)</td>
<td>8.66 (0.05)</td>
<td>4.12 (0.07)</td>
</tr>
<tr>
<td>20</td>
<td>0.56 (0.04)</td>
<td>0.61 (0.06)</td>
<td>6.18 (0.04)</td>
<td>6.45 (0.06)</td>
<td>3.18 (0.05)</td>
</tr>
<tr>
<td>40</td>
<td>0.43 (0.06)</td>
<td>0.44 (0.07)</td>
<td>4.01 (0.05)</td>
<td>3.99 (0.04)</td>
<td>2.78 (0.07)</td>
</tr>
<tr>
<td>80</td>
<td>0.31 (0.05)</td>
<td>0.35 (0.06)</td>
<td>2.72 (0.08)</td>
<td>2.90 (0.06)</td>
<td>1.99 (0.08)</td>
</tr>
<tr>
<td>160</td>
<td>0.22 (0.03)</td>
<td>0.23 (0.04)</td>
<td>1.75 (0.03)</td>
<td>1.88 (0.02)</td>
<td>0.52 (0.03)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.43c</td>
<td>0.46c</td>
<td>5.14c</td>
<td>4.78c</td>
<td>2.52c</td>
</tr>
<tr>
<td>25</td>
<td>0.92 (0.06)</td>
<td>1.00 (0.07)</td>
<td>4.16 (0.13)</td>
<td>4.65 (0.08)</td>
<td>1.60 (0.06)</td>
</tr>
<tr>
<td>Mean</td>
<td>1.52b</td>
<td>1.62b</td>
<td>8.42b</td>
<td>11.37b</td>
<td>4.78b</td>
</tr>
<tr>
<td>50</td>
<td>0.53 (0.08)</td>
<td>0.59 (0.11)</td>
<td>26.16 (0.09)</td>
<td>27.10 (0.09)</td>
<td>17.13 (0.06)</td>
</tr>
<tr>
<td>Mean</td>
<td>3.20a</td>
<td>3.58a</td>
<td>15.05a</td>
<td>18.66a</td>
<td>9.89a</td>
</tr>
<tr>
<td>LSD, (WTRs)</td>
<td>0.06</td>
<td>0.08</td>
<td>0.91</td>
<td>0.88</td>
<td>0.46</td>
</tr>
<tr>
<td>LSD, (Biosolids)</td>
<td>0.15</td>
<td>0.13</td>
<td>0.97</td>
<td>0.85</td>
<td>0.45</td>
</tr>
</tbody>
</table>

ANOVA F-test

| WTRs | *** | *** | *** | *** | *** | *** | *** |
| Biosolids | *** | *** | *** | *** | *** | *** | *** |
| WTRs x Biosolids | *** | *** | *** | *** | *** | *** | *** |

Data are the average (n=3).
Numbers in parenthesis indicate the standard deviation.
*** are significant at 0.001 probability level.
† Values within columns followed by different letters are significant at the 0.05 probability level.
Copper

Increasing the WTRs application rate from 0 to 160 Mg.ha\(^{-1}\) dramatically decreased the total Cu accumulation in corn plants in the plots amended with biosolids (Figure 3). Overall, a significant reduction in total Cu accumulation in plant was observed in the soil amended with 80 or 160 Mg.ha\(^{-1}\) of WTRs along with 50 Mg.ha\(^{-1}\) of biosolids. The effect of the WTRs treatments varied significantly among biosolids, as well as the interaction between WTRs and biosolids.

In general, Cu accumulation in stover was higher than in grains in the biosolid-amended plots, and the plant Cu accumulation significantly decreased with increasing the WTR-application rate to the soil amended with biosolids (Figure 3). For example, concentrations of Cu in grains decreased from 16.16 to 3.12 mg kg\(^{-1}\) and from 29.28 to 6.07 mg kg\(^{-1}\) at 25 and 50 Mg.ha\(^{-1}\) of biosolids application rates, respectively. However, the concentrations of Cu in stover decreased from 17.17 to 4.45 and from 30.30 to 8.15 mg kg\(^{-1}\) in 25 and 50 Mg.ha\(^{-1}\) of biosolids, respectively. The same results were found in the second seasons of cultivation 2011 (Figure 3).

These observations are in agreement with the previous findings by Karthikeyan et al. (1996) and Lombi et al. (2004). Calace et al. (2005) stated that the use of different wastes or sludges could be an effective practice to reduce Cu toxicity in soil. Mahmoud and Elbaroudy, (2009) reported that the applications of WTRs, rice compost and their mixture(2:1 ratio) have significantly decreased the concentrations of Pb, Cd and Zn extracted from soils by DTPA-method.

Lead

Concentrations of Pb in corn stover were higher than in grains (Figure 4). Plant Pb concentrations were significantly affected by the biosolid and WTRs treatments. The Pb concentration in plant was reduced when increasing the application rate of WTRs from 20 to 160 Mg.ha\(^{-1}\) of WTRs. The application of WTRs at 80 and 160 Mg.ha\(^{-1}\) significantly decreased the total Pb accumulation in corn in all biosolid-amended plots. Co-application of 25 Mg.ha\(^{-1}\) of biosolids and 160 Mg.ha\(^{-1}\) of WTRs in soil resulted in a decrease of 76% in grain Pb concentrations, but 67% in stover Pb concentrations. However, Co-application of 50 Mg.ha\(^{-1}\) of biosolids and 160 Mg.ha\(^{-1}\) of WTRs in soil resulted in a decrease of 73% in grain Pb concentrations, but 69% in stover Pb concentrations. The greater reduction rate in total Pb concentrations in corn tissues could be resulted from flocculation and co-precipitation processes when a high rate of WTRs was supplied (Karthikeyan et al., 1996).

Land co-application of aluminum-based WTRs and biosolids effects on bioaccessibility

There is a concern that land application of Al-WTRs will
result in soil and water contamination with trace elements and that could be directly or indirectly ingested by humans and animals.

**WTRs as a novel sorbent for trace metals**

In the last few years, adsorption has been shown to be a cost effective technique for the removal of trace elements from wastewater and water supplies. There are a wide range of low-cost adsorbents has been studied worldwide for heavy metal removal. Among their current commercial prices, Al-WTRs are undoubtedly the most inexpensive alternative adsorbents compared to others. Although, the WTRs can dramatically reduce available P (Makris et al., 2005), a little is known about heavy metals such as Ni, Cd, Pb, and Cu sorption by WTRs and their potential effectiveness in reducing soluble metal concentrations in heavy metals-contaminated soils. Makris et al. (2009) reported that the Al-WTRs was highly effective in removing both As (v) and As(III).

The study of Hovsepyan et al. (2009) indicated that a strong affinity of Hg for Al-WTRs and can be used to remove Hg from aqueous solutions. This ability points to the potential of Al-WTRs as a sorbent in soil remediation techniques based on Hg-immobilization. Nagar et al. (2010) have been proposed the Al-WTRs as a low-cost alternative sorbent for arsenic (As)-contaminated aquatic soil system and they found that the Al-WTRs demonstrated 100% As(V) sorption in the entire pH range. Brown et al. (2005) found that both soil solution and ammonium nitrate extractable heavy metal(Cd, Pb, and Zn) were decreased by all treatments included lime, P, red mud, cyclonic ashes, biosolids, and water treatment residuals.

In a laboratory study, Agyin-Birikorang et al. (2009) that potential soil As availability to plants and humans decreased as Al-WTRs application rate increased. They concluded that application of WTRs at a minimum rate of 56 metric tons/ha could be a viable and effective field remediation method for heavy metals, especially As-contaminated soils that are low in Fe and Al oxyhydroxides. Thus, the perceived threat of As or other heavy metals toxicity following land application of WTRs is not supported by the data. Our current study demonstrated these results, where the effects of WTRs on DTPA-extractable Cd, Ni, Pb and Cu in the experimental soil amended with different rates of biosolids were studied (Table 2). The co-application of WTRs (20, 40, 80 and 160 Mg,ha⁻¹) and biosolids (0, 25 and 50 Mg,ha⁻¹) significantly altered the extractable heavy metals in the amended soil. For instance, in the 25 Mg,ha⁻¹ biosolids-amended soils, concentrations of DTPA-extractable Cd reduced from 2.19 to 1.28 mg kg⁻¹ at 160 Mg,ha⁻¹ application rates of WTRs. Also, in 50 Mg,ha⁻¹ biosolid-amended soils, the extractable Cd concentration reduced from 5.13 to 1.01 mg kg⁻¹ in the studied soil at 160 Mg,ha⁻¹ application rates of WTRs. The reduction in DTPA-extractable Cd was more pronounced at 50 Mg,ha⁻¹ biosolid-treated soils than that in 25 Mg,ha⁻¹ biosolid-treated soils (Table 2), which concurs with the previous findings by Chu (1999) who indicated that the use of WTRs increased heavy metals removal rates from 79 to 98% with 100 to 180 mg L⁻¹ of WTRs. Similarly, in all 50 Mg,ha⁻¹ of biosolids-treated plots, the highest reduction in Ni concentration was observed at a 160 Mg,ha⁻¹ application rate of WTRs.

Also, the DTPA-extractable Cu concentration was significantly reduced with increasing of WTRs application rates (Table 2). The greatest reduction in DTPA-extractable Cu concentration was found at 160 Mg,ha⁻¹ of WTRs (Table 2). There were significant (P < 0.05) differences in DTPA-extractable Cu between biosolids and WTRs treatments. However, the extractable Pb concentrations were significantly reduced with increasing of WTRs application rates (Table 2). The highest reduction in Pb concentration was observed at a 160 Mg,ha⁻¹ application rate of WTRs.

In summary, the extractable Cd concentration in all biosolid-treated plots was less than the DTPA-extractable Pb, Ni, and Cu concentrations, due to a low content of Cd in biosolids (Table 1). Finally, it can be concluded that the reduction in DTPA-extractable metals resulting from the application of WTRs to biosolid-amended soils can be explained by formation of metal-sulfate, low solubility product, and the flocc-adsorption and the co-precipitation processes, in which the formation of a mixed solid phase by the incorporation of metal ions into the crystal lattice of another precipitating solid phase is expected (Karthikyan et al., 1996).

**Regression between soil DTPA-extractable metals and plant metals accumulation**

DTPA has been widely used to estimate the bioavailability of metals in soil and sludge (Maiz et al., 1997; Halim et al., 2003), due to its capacity to chelate a wide range of metallic elements (Baker and Amacher, 1982). Its ability to form stable chelates with metallic elements in soil has been documented recently by Hong et al. (2002), suggesting that DTPA could be used to restore soils that have been contaminated by metals (Francis, 1999). Regression analysis showed that concentrations (mg.kg⁻¹) of Cd, and Ni in corn tissues from the soils treated with the WTRs and biosolids significantly (P < 0.05) correlated with the soil concentrations of DTPA-extractable metals (Table 3).

However, there are no significant relationships between Cu concentrations in corn tissues and DTPA-extractable Cu (Table 3). Also, there is no significant relationship between Pb concentrations in stover of corn and DTPA-extractable Pb (Table 3). Our results agreed with those of Brown et al. (2005), Agyin-Birikorang et al. (2009),
Mahdy et al. (2012) showing significant positive relationships between the DTPA-extractable metals and the metal accumulation in plant tissues in biosolids-amended soils.

Conclusion

Co-application of biosolids and WTRs in agricultural lands is a relatively new concept, with distinct advantages of a cost saving, agronomic benefits and potential reduction of available heavy metals. Our study demonstrated that land application of biosolids increases the accumulation of toxic metals in corn tissues in slightly alkaline soils. However, WTRs-application of (20, 40, 80 and 160 Mg ha\(^{-1}\)) to the soil amended with (0, 25 and 50 Mg ha\(^{-1}\)) of biosolids decreases significantly the DTPA-extractable metal concentrations. The reduction of plant metal accumulation and soil metal extractability demonstrated that WTRs be considered an ameliorating material for immobilizing metals in soils. This study suggests that the 160 application rate of WTRs to biosolids 50 Mg ha\(^{-1}\) application rate effectively reduce toxic metal accumulation in plant tissues. The combined studies clearly demonstrate that Al-WTRs should have no negative impacts on the environment and biological systems when appropriate rates (based on the chemical characteristics of WTRs) are land applied.

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