Dynamics of Copper and Lead Originating from Biosolids in Arid Calcareous Soils: Effect of Nanomaterials Produced from Byproducts of Water Treatment Industry

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ABSTRACT

This study investigates the dynamics of copper (Cu) and lead (Pb) in biosolids-amended calcareous soils under arid conditions and evaluates the potential of nano-sized water treatment residuals (nWTRs), derived from drinking water treatment byproducts, as a sustainable remediation agent. A field lysimetric experiment was conducted using calcareous soil amended with 3% biosolids and varying rates of nWTRs (0.1%, 0.2%, 0.3%). The effects on Cu and Pb uptake by maize (Zea mays L.), their speciation in soil solution, and geochemical fractionation were assessed over two growing seasons. Characterization of nWTRs revealed high specific surface area (129 m²/g), amorphous morphology, and reactive Al/Fe-oxide surfaces conducive to heavy metal sorption. Application of biosolids alone significantly increased both Cu and Pb bioavailability, plant uptake, and soluble concentrations in soil solution. In contrast, the incorporation of nWTRs reduced soluble and plant-available Cu and Pb, particularly at the 0.3% rate. Sequential extraction results confirmed a shift in Cu and Pb from labile (exchangeable, carbonate-bound, and oxide-bound) fractions toward the residual, stable form, rising from 22% to 81% for Cu and from 51% to 79% for Pb. Chemical speciation modeling using MINEQL+ showed a dramatic reduction in free Cu^{2+} and Pb^{2+} ions, with increased formation of less mobile hydroxide and carbonate species in nWTR-amended soils. These findings demonstrate that nWTRs effectively immobilize Cu and Pb in biosolids-amended soils by altering their speciation and distribution, thus reducing environmental risk and enhancing the sustainability of biosolid reuse in agriculture.

Keywords: heavy metals, immobilization, speciation, bioavailability, sustainability

INTRODUCTION

Soil degradation in arid regions is a major environmental issue, involving declines in soil fertility, productivity, contamination, and the loss of vegetation cover (Cerda et al., 2010). As a response, recent strategies have explored the potential of reusing municipal waste for soil restoration (Fernandez-Calvino et al., 2016, 2017). One approach involves applying biosolids to agricultural land, which can provide vital nutrients to plants and enhance soil characteristics like infiltration, drainage, and water retention (Mousavi et al., 2017a). However, the high concentrations of heavy metals such as copper and lead in biosolid-amended soils raise significant public health concerns, limiting their responsible use worldwide. Therefore, reducing the bioavailability of these metals is crucial for maintaining soil productivity and ensuring the safety of agricultural products (Mousavi et al., 2017b). Water treatment residuals (WTRs), byproducts from purifying raw water, often contain aluminum or iron salts and sediments that can help immobilize metals in soils when applied with biosolids (Elkhatib and Moharem, 2015).

Recent advances in nanotechnology have introduced new agricultural tools that improve the effectiveness of soil amendments, contributing to more sustainable farming. These benefits are due to the unique size, surface properties, and internal structures of nanoparticles compared to bulk materials (Elkhatib et al., 2015; Elkhatib et al., 2018). Although nanoscale WTRs have shown promise in land application and wastewater treatment (Moharem et al., 2019; Elkhatib et al., 2019), few studies have focused on stabilizing heavy metals in biosolid-amended soils. The application of chemically reactive coagulants, such as nanoscale $Al_2(SO_4)_3$ in water treatment residues (WTRs), presents opportunities for enhancing agricultural productivity and environmental quality through the stabilization of heavy metals (Elkhatib et al., 2017). This research seeks to (1) evaluate the capacity of nanoscale WTRs (nWTRs) to stabilize and diminish the availability of copper (Cu) and lead (Pb) in soils amended with biosolids, and (2) investigate their impact on corn growth and yield, along with the distribution and bioaccumulation of Cu and Pb within plant tissues.

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MATERIALS AND METHODS

Collecting soils, biosolids, and water treatment residuals (WTRs)

A specific type of calcareous soil (Typic haplocalcids) was selected for this study, obtained from Borg Al-Arab in the Alexandria Governorate of Egypt. Soil samples were collected from a depth of 0–30 cm at the specified location. Subsequently, the air-dried samples were crushed and sifted to achieve a particle size of less than 2 mm.

The experimental biosolids were procured from the General Organization Sanitary (GOS) located in Alexandria City (Station 9), Egypt. These biosolids were air-dried, ground, and subsequently sieved to a size of less than 2 mm before application, as referenced by Makris and Harris (2005).

The original water treatment residuals (WTRs) were obtained from a local drinking water treatment facility in Alexandria, Egypt, which employs aluminum sulfate for the flocculation process. Samples of WTRs were collected, transported to the laboratory, and air-dried. Sub-samples were then ground and passed through two sieves with pore diameters of 2 mm and 51 µm. The chemical properties of the WTRs were analyzed, with pH measured in a 1:2.5 suspension (WTRs to distilled water ratio of 1:2.5) using a pH meter. The surface morphology, composition, and elemental content of the WTRs were examined using scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (INCAx-Sight model 6587, Oxford Instruments, UK).

Chemical and physical characteristics of soils, WTRs and biosolids

The overall physicochemical characteristics of the soil, biosolids, and WTR were evaluated following the standard procedures outlined by Tan (1996), with the results presented in Table1.This assessment included measuring soil pH and electrical conductivity (EC) in the saturated soil paste extract, as well as the pH and EC of WTRs in a 1:2.5 suspension (Richards 1954). The calcium carbonate content was evaluated using a calcimeter (Nelson 1982), while particle size distribution was analyzed through the hydrometer method (Day 1965). The organic matter (OM) content of the soil was quantified via the dichromate oxidation method (Nelson and Sommers 1982). Cation exchange capacity (CEC) was measured using 1 M NaOAC (Rhoades 1982), and water holding capacity was determined following the protocol established by Skene et al. (1995). Metal concentrations were analyzed according to the procedure outlined by Ure (1995). The total aluminum content of dried WTRs (DWTRs) was assessed using the acid ammonium oxalate method (Ross and Wang 1993). Available copper (Cu), and lead (Pb) were extracted using DTPA (Lindsay and Norvell 1978) and quantified through inductively coupled plasma spectrometry (Perkin Elmer Optima 2000 DV).

Synthesis and characterization of nWTRs

Subsamples with a diameter of less than 51µm and a weight of 6 g were processed using the Fritsch planetary mono mill Pulverisette 6 classic line. This equipment was equipped with an 80 ml stainless steel grinding bowl and 150 g of 1 mm steel grinding balls. The milling procedure was performed at a disk speed of 650 rpm for a total duration of 75 minutes. To attain the desired viscosity for the grinding process, 48 ml of isopropyl alcohol was added to the sample. The grinding was executed in cycles of 3 minutes, followed by a 10-minute pause to mitigate excessive pressure accumulation. After the completion of three cycles, the external temperature of the bowl was monitored to ensure it did not exceed 70°C.

The ground samples were subjected to analysis of their properties and elemental composition through transmission electron microscopy (TEM), scanning electron microscopy (SEM), and SEM in conjunction with energy-dispersive X-ray spectroscopy (EDX).The surface area of the nanoparticles was determined using the Brunauer-Emmett-Teller method (Brunauer et al., 1938).Fourier-transform infrared spectroscopy (FTIR) was also utilized to investigate the functional groups related to the complex interactions of heavy metals, specifically copper and lead in nano-wastewater treatment residuals (nWTR). All measurements adhered to established protocols that are standard in the field of nanomaterial research.

Field lysimetric experiments

To assess the impact of co-application of nWTRs and biosolids on agronomic performance, plant available water, and environmental quality, field lysimeter experiment was carried out utilizing a drainage lysimeter system equipped with a leachate outlet at the base, allowing for drainage collection under ambient atmospheric pressure. The experiment took place at the Soil Salinity & Alkalinity Laboratory in Abees, Alexandria (Fig. 1). The location is situated at latitude of 31° 2" N and a longitude of 29° 6" E, with an elevation approximately 2.50 meters below sea level. The site experiences an average annual rainfall of 200 mm, and the relative humidity during daytime is around 67.30%. The mean maximum temperatures recorded in August and September ranged from 30.9°C to 29.6°C. The lysimeters utilized measured 0.6 m in width, 0.6 m in length, and 0.75 m in depth. The lysimeters used in the experiment measured 0.6 x 0.6 x 0.75 meters and were filled with Borg alarab calcareous soil. Different application rates of biosolids (0% and 30 $g.kg^{-1}$) and nWTRs (0%, 0.1%, 0.2%, and 0.3% by weight) were applied and thoroughly mixed with the soil. Corn seeds of the single hybrid 176 variety were sown for two growing seasons (2017and 2018). The field lysimeter experiment included three replicates of each treatment, along with a control (soil without any biosolid or nWTR amendments). In total, there were 24 lysimeters (1 soil type x 4 nWTR application rates x 2 biosolid application rates x 3 replicates. Seedlings were thined to four in each lysimeter. Irrigation was done with tap water, and the amount of water applied was calculated based on the maize's water requirements. Throughout the growth period, no nutritional disorders were noted. Soil samples were collected prior to sowing and after harvesting. The plant shoots and grains were gathered, then thoroughly washed with running tap water and rinsed three times using de-ionized water. The plant tissues were subsequently dried in a forced-air drying oven at 65°C for 48 hours, and the dry matter yield was recorded.

Assessment of Plant Biomass

Plant tissues were processed using a stainless steel mill. Sub-samples of the ground plant material underwent ashing in a muffle furnace at a temperature of 450 °C for duration of 6 hours (Jones, 2001). The resulting ash was then dissolved in a 1:1 solution of nitric acid and subsequently diluted to a constant volume with de-ionized water for the analysis of Copper (Cu), and Lead (Pb) (Murphy and Riley, 1962). The absorption levels of Copper (Cu), and Lead (Pb) by the plants (measured in $mg.kg^{-1}$) were calculated, along with the concentrations of these metals in the plant tissues and the total dry matter weight.

Evaluation of Bioavailable Copper (Cu) and Lead (Pb) in Soil Solution and Leachate

The extraction of soil solution was performed both before and after the harvest, following the methodology outlined by Elkhatib et al. (1987). Bioavailable copper (Cu) and lead (Pb) were extracted using DTPA as described by Lindsay and Norvell (1978) and subsequently analyzed through atomic absorption spectroscopy (contrAA 300).To investigate the impact of nWTR treatments on the mobility of Cu and Pb in biosolids-amended soils, drainage water was collected in plastic containers connected via tubing to the bottom outlet of each lysimeter. The volume of drainage was recorded after each collection, and samples of the drainage water were analyzed chemically for metal content. Concentrations of Cu and Pb were measured in both treated and control soils, as well as in soil leachates and plant tissues .An analysis of variance (ANOVA) was performed to evaluate the statistical significance of treatment effects on crop yield, extractable Cu and Pb , pH, and water holding capacity (WHC). This analysis utilized Fisher's least significant difference method at a significance level of 0.05, as per the guidelines of the SAS Institute (1994).

Figure 1. Layout of field lysimeter experiment (60x 60 x 75cm)

Water Holding Capacity (WHC)

The water holding capacity of the examined soils was assessed prior to and following treatments over two growing seasons, utilizing the methodology outlined by Skene et al. (1995).

Fractionation of Cu, and Pb

A fractionation analysis of Cu and Pb in soils treated with biosolids was carried out both before and after the application of nWTR treatments, using the sequential extraction method outlined by Tessier et al. (1979). This approach was employed to classify the Cu and Pb in the soil into five separate fractions: exchangeable Cu and Pb; carbonate-bound Cu and Pb; Cu and Pb absorbed by Fe-Mn oxides; Cu and Pb bound to organic matter; and residual Cu and Pb. The concentrations of Cu and Pb in the extraction solutions were measured using ICP/MS.

Speciation Modeling Utilizing MINEQL+

In the analysis of pore water samples, several parameters were evaluated, such as soil pH, electrical conductivity, concentrations of major ions, toxic metals, and soluble Cu and Pb. The speciation of Cu and Pb in the soil pore water was modeled using MINEQL+ (version 4.6), based on the measured concentrations of these metals and other elements, along with pH, temperature, log K, pCO_2, pO_2, pE, and the calculated ionic strength, following the approach described by Schecher and McAvoy (2003).

Statistical and Mathematical Analyses

The analysis of variance (ANOVA) was conducted to assess the statistical significance of treatment effects on crop yield, extractable copper (Cu), and lead (Pb), as well as the accumulation of metals, pH, and water holding capacity (WHC). This was performed using Fisher’s least significant difference method at a significance level of 0.05 (SAS Institute, 2002).

RESULTS AND DISCUSION

Properties of the studied soil, biosolids and water treatment residuals

The overall physicochemical properties of the soil, biosolids, and WTR are summarized in Table 1.The calcareous soil used in the study was alkaline whereas the WTRs and biosolids were slightly alkaline and slightly acidic, respectively. The OM and $CaCO_3$ contents of the calcareous soil were high. High OM contents (5.7 %) were observed in the WTRs, greater than OM contents in Egyptian agricultural soils. The salinity of the WTRs was <4 dSm^{-1}, and the CEC was 34.78 cmol $(+)kg^{-1}$ indicating that WTRs could be a source of cationic nutrients.The WTRs also have been shown, via scanning electron microscopy (SEM), to be of various shapes and sizes and are highly porous (Fig. 1). Using SEM, Yang et al. (2006) compared WTRs to pure aluminum hydroxide and noted that the WTRs were virtually amorphous, having no distinct shape or form, in contrast to pure aluminum hydroxide ،which exhibited a regular crystalline structure.The OM content of the biosolids was 492 g/kg. The total concentrations of Cu and Pb in the soils and WTRs were low and the available concentrations of Cu and Pb, extracted by DTPA were very low compared with the general toxic levels of crops (Alloway 1995). The application of sewage sludge provided a source of heavy metals and enriched the soils in relatively mobile and available forms (Pengxing et al.1997).

Elemental composition and morphology of nWTR

The scanning electron microscopy (SEM) image of nWTR is presented in Fig. 2a. The samples exhibited spherical shapes with diameters ranging from 45 to 96 nm. The SEM-EDX analysis spectrum(Fig. 2c) indicated a predominance of iron (Fe), silicon (Si), and aluminum (Al) within the nWTR. Additionally, sulfur (S) present in nWTR may serve as a potential electron donor for Cd or Pb. The X-ray diffraction pattern of nWTR,(Fig. 2c) showed no crystalline forms of Fe–Al (hydr) oxides, instead identifying amorphous silicon oxide and Al-Fe (hydr) oxides as the primary mineral phases.

The specific surface area (SSA) of nWTR was measured at 129.0 m^2/g, while the total pore volume (TPV) was recorded at 0.51 cm^3/g. Notably, the SSA and TPV values of nWTR were 2-3 times greater than those of bulk WTR. This elevated SSA and TPV may provide nWTR nanoparticles with highly reactive surface sites conducive to the retention of Cd and Pb.

Table 1. Some physical and chemical characteristics of studied soil, WTRs and biosolids

Characteristics	Units	Borg Al-Arab SOIL	WTRs	Biosolids
pH		8.08 ± 0.06	7.45 ± 0.06	6.69 ± 0.03
EC	dSm^{-1}	2.92 ± 0.06	1.67 ± 0.04	11.25 ± 0.12
$CaCO_3$	$g\ kg^{-1}$	356.80 ± 2.60	-	–
Sand	$g\ kg^{-1}$	740.00 ± 3.70	-	–
Silt	$g\ kg^{-1}$	101.50 ± 1.90	-	–
Clay	$g\ kg^{-1}$	158.50 ± 3.20	-	–
Texture		S.L	-	–
O.M†	$g\ kg^{-1}$	4.60 ± 0.15	57.00 ± 2.00	450.00 ± .67
KCl-Al	$mg\ kg^{-1}$	0.08 ± 0.02	28.18 ± 1.03	4.22 ± 0.13
Olsen-P	$mg\ kg^{-1}$	18.70 ± 0.80	24.00 ± 2.00	48.60±1.62
CEC	$Cmol(+)kg^{-1}$	26.00 ± 2.02	34.78 ± 0.34	73.57±0.51
Total Elements:				
N	$g\ kg^{-1}$	-	4.20 ± 0.13	32.00 ±1.6
P	$g\ kg^{-1}$	-	1.90 ± 0.15	4.60 ± 0.12
K	$g\ kg^{-1}$	-	2.20 ± 0.21	1.90 ± 0.08
Al	$g\ kg^{-1}$	-	38.01 ± 0.93	3.10 ± 0.23
Ni	$mg\ kg^{-1}$	17.02 ± 0.03	9.40 ± 0.07	108.0±1.01
Pb	$mg\ kg^{-1}$	62.20 ± 0.35	76.00 ± 0.17	143.00±0.64
Cu	$mg\ kg^{-1}$	24.06 ± 0.07	49.00 ± 0.02	128.00±0.44
Cd	$mg\ kg^{-1}$	4.50 ± 0.03	3.00 ± 0.02	4.00 ±0.15
DTPA-Extractable Metals:				
Ni	$mg\ kg^{-1}$	7.17 ± 0.05	2.49 ± 0.07	12.12 ±0.24
Pb	$mg\ kg^{-1}$	5.69 ± 0.12	1.58 ± 0.04	62.13 ±0.22
Cu	$mg\ kg^{-1}$	4.98 ± 0.03	1.20 ± 0.1	11.83 ±0.15
Cd	$mg\ kg^{-1}$	0.26 ± 0.04	0.09 ± 0.02	0.72 ±0.04

† : pH measured in sample/water suspension(1:2.5) by pH-meter instrument(CRISON); ND: not determined; EC: electrical conductivity; O.M: organic matter ; CEC: cation exchange capacity ;
S.C.L: sandy clay loam; L.S.: loamy sand; S.L.: sandy loam

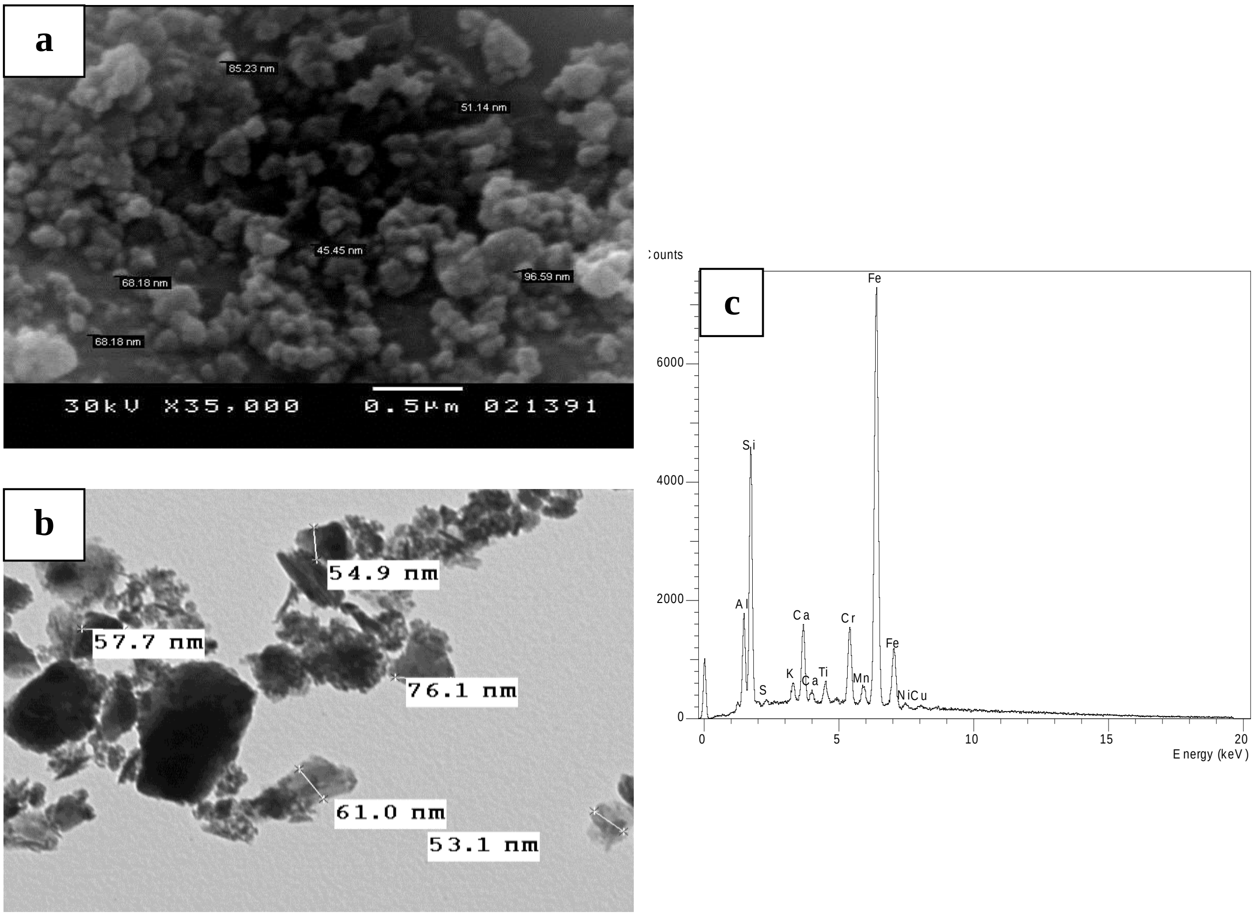


Fig 2. Scanning electron microscopy (SEM) image (a) transmission electron microscopy (TEM) image (b) and energy dispersive X-ray (EDX) spectrum (c) of nWTRs

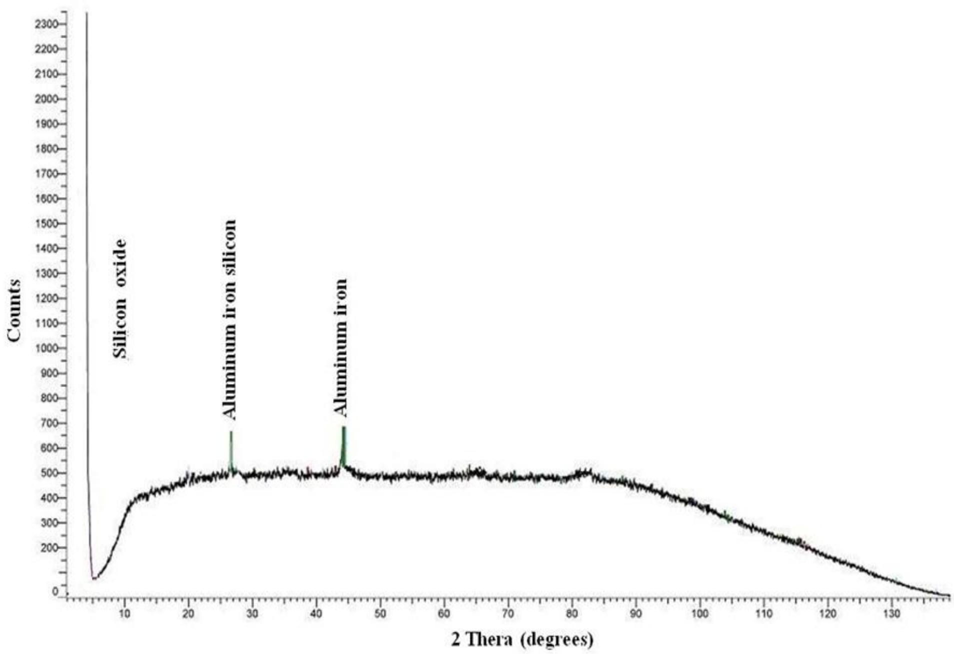


Fig 3. X-ray diffraction (XRD) analysis of nWTRs

Evaluation of plant biomass influenced by biosolids and nWTRs

The effect of nWTRs on the overall dry weight yield, encompassing both grain and stover, of corn plants grown in biosolids-treated calcareous soil over two successive growing seasons is depicted in Fig. (4). Notable increases in total biomass production of corn were recorded during both the first and second growing seasons, attributed to the application of biosolids (3%) and a mixture of biosolids (3%) with WTRs (2%), as well as nWTRs applied at rates of (0.1%) and (0.2%), with a least significant difference (L.S.D.) of 0.01and0.05.These findings align with the research conducted by Mahdy et al. (2012), which indicated an enhancement in dry matter production following the use of nano-water treatment residuals alongside biosolids.

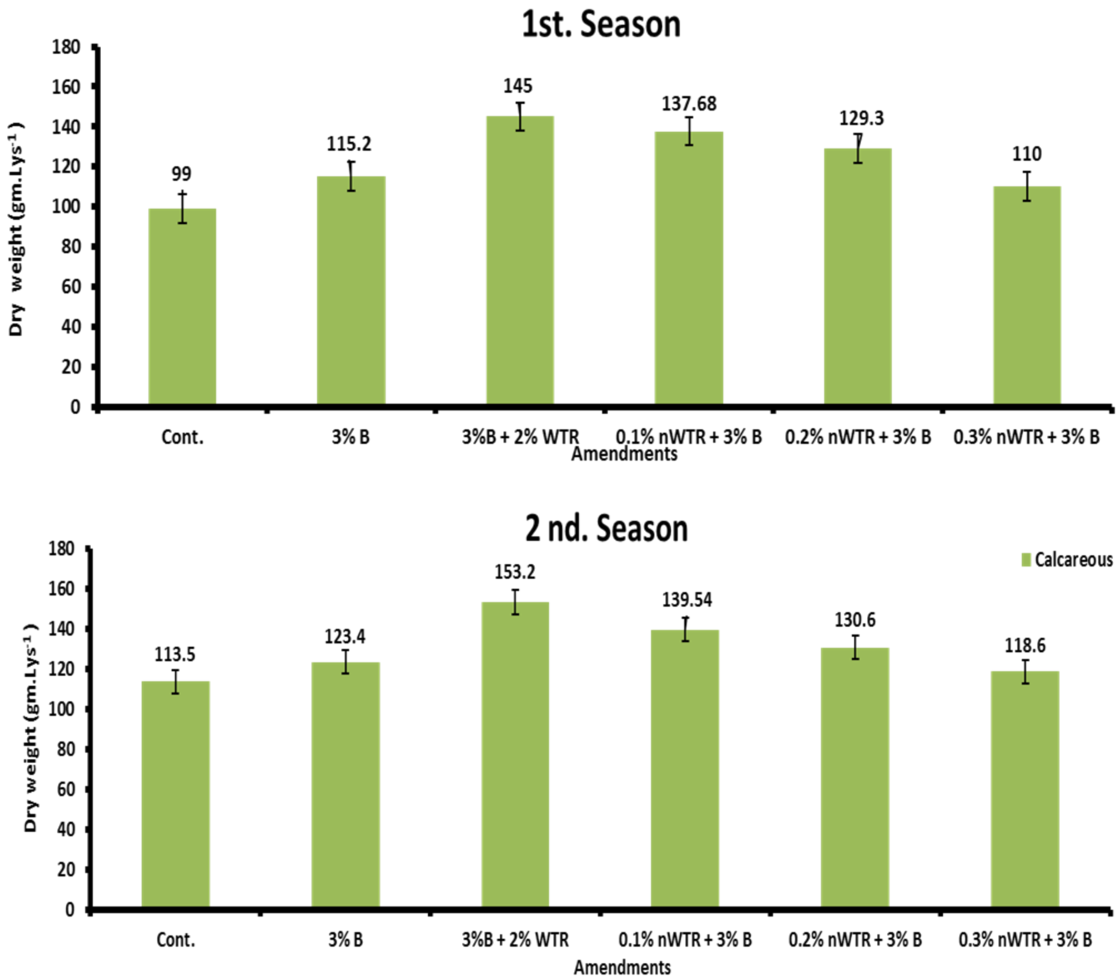


Fig.4. Effects of nWTRs on total dry weight yield of corn plants grown on biosolids-treated calcareous soil

F-test: Soil **, Treatment **, ** is significant at 0.01 probability level.
1st season (L.S.D. at 0.05) =15.04 , (L.S.D. at 0.01) = 20.61 S.E= 7.16 2nd season (L.S.D. at 0.05) =14.14 , (L.S.D. at 0.01) = 19.38 S.E= 6.73

The application of biosolids and nWTRs affected copper concentration in corn plants

During the first and second seasons, the concentrations of copper (Cu) in tissues of plants grown in calcareous soils showed a significant increase compared to the control group when treated with 3% B, 3% B combined with 2% WTRs, and 3% B combined with 0.1% nWTRs. Conversely, the application of 0.2% nWTRs and 0.3% nWTRs resulted in a significant decrease in Cu levels (Fig. 5).

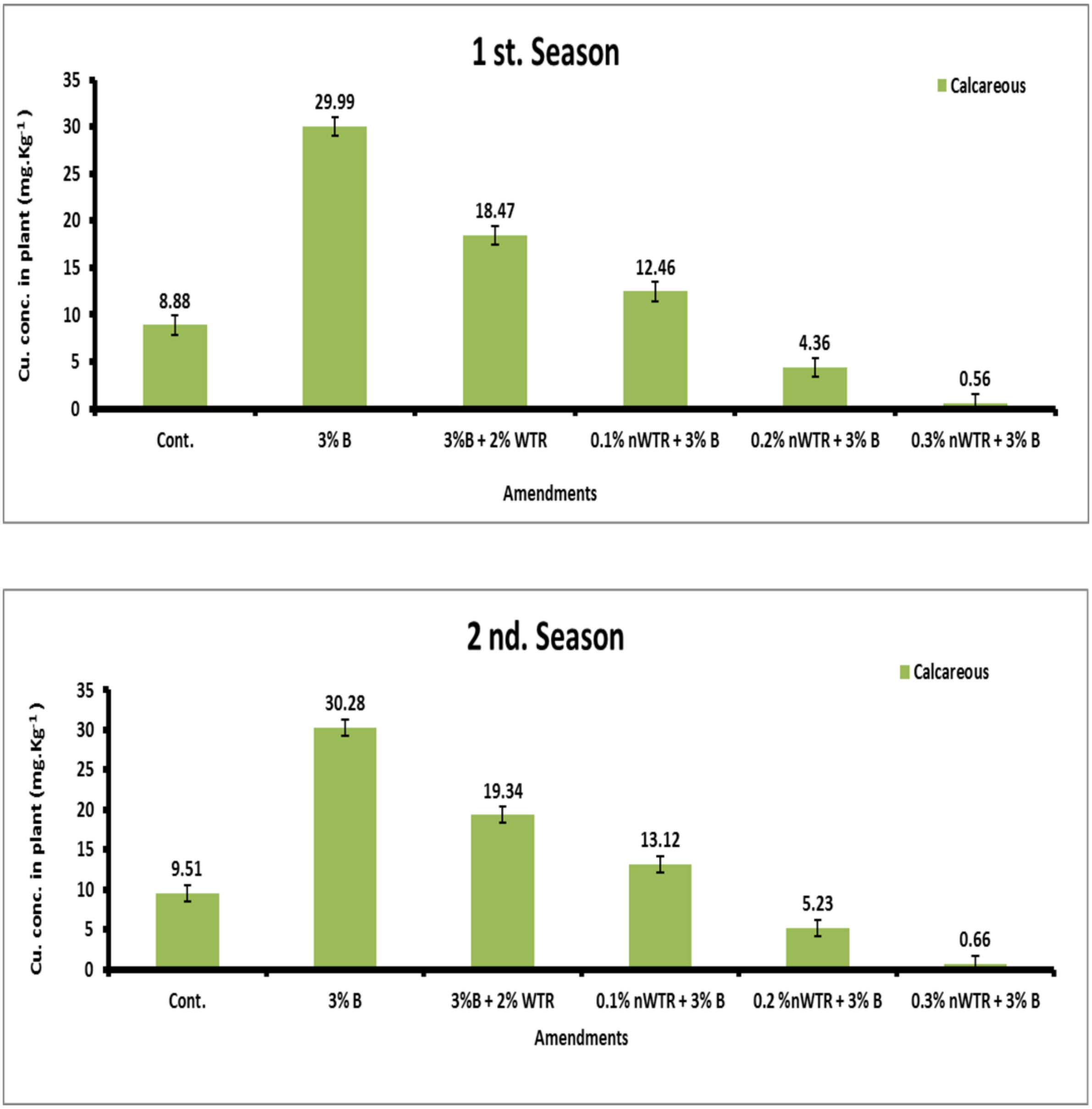


Fig. 5. Effects of nWTRs on Cu concentrations in corn plants grown on biosolids-treated calcareous soil

F-test: Soil **, Treatment **, **Soil*Treatment** --** is significant at 0.01 probability level and (--) = N.S

1st. season L.S.D.(0.05) = 3.05 , L.S.D.(0.01) = 4.18, S.E= 1.45

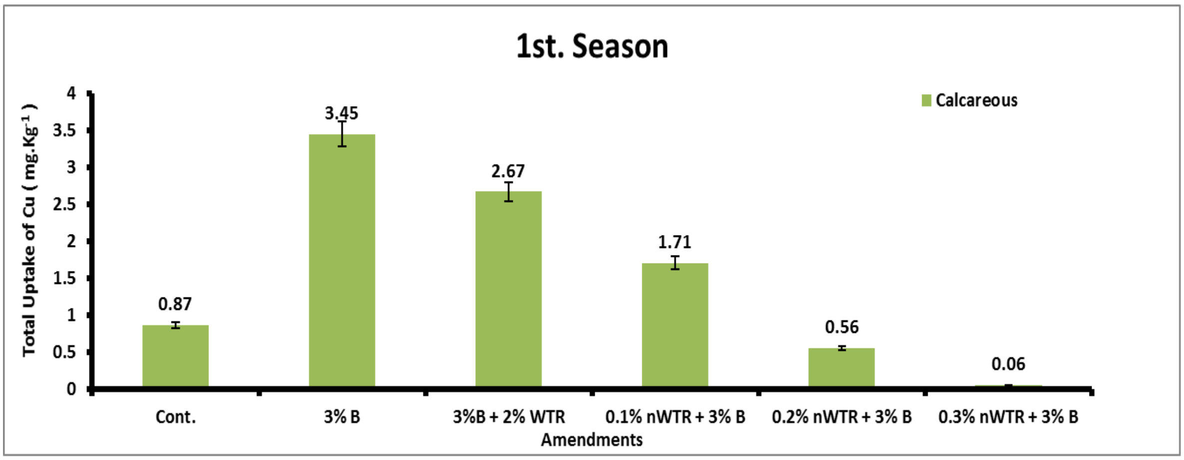
2nd. season L.S.D.(0.01) = 2.35, L.S.D.(0.01) = 3.23, S.E= 1.10

The overall absorption of copper by the tissues of corn plants influenced by biosolids and (nWTRs)

The impact of co-applying biosolids and nano-water treatment residues (nWTRs) on copper (Cu) uptake by corn plants grown in calcareous soils is illustrated in Figure 6. In the first growing season, the maximum copper uptake by corn tissues was 3.45 mg/kg, achieved with 3% biosolids, while the lowest uptake (0.06 mg/kg) occurred with 0.3% nWTRs. In the second season, the highest uptake increased slightly to 3.73 mg/kg with 3% biosolids, while the lowest was 0.07 mg/kg with 0.3% nWTRs.

The reduced copper uptake observed with nWTRs may be attributed to the presence of amorphous aluminum oxides in the treated soils, which provide additional sorption sites for copper ions. This sorption occurs in a two-step process: an initial rapid adsorption to the surface followed by slower, more stable binding, which significantly reduces copper availability to plants. Research by Scheckel and Sparks (2001) supports this, showing that hydrous amorphous surfaces greatly influence the mobility of contaminants. Even at the low application rate of 0.1% nWTRs, a substantial reduction in copper availability was observed.

Compared to untreated control soil, which had a baseline copper uptake of 0.87mg/kg, the application of 3% biosolids significantly increased copper uptake, while 0.3% nWTRs decreased it. These results suggest that nWTRs can effectively immobilize copper in soils with high metal content, offering a potential strategy for managing copper levels in calcareous soils, especially in arid regions. Repeated applications of nWTRs could further enhance copper immobilization, benefiting both soil health and agricultural productivity.



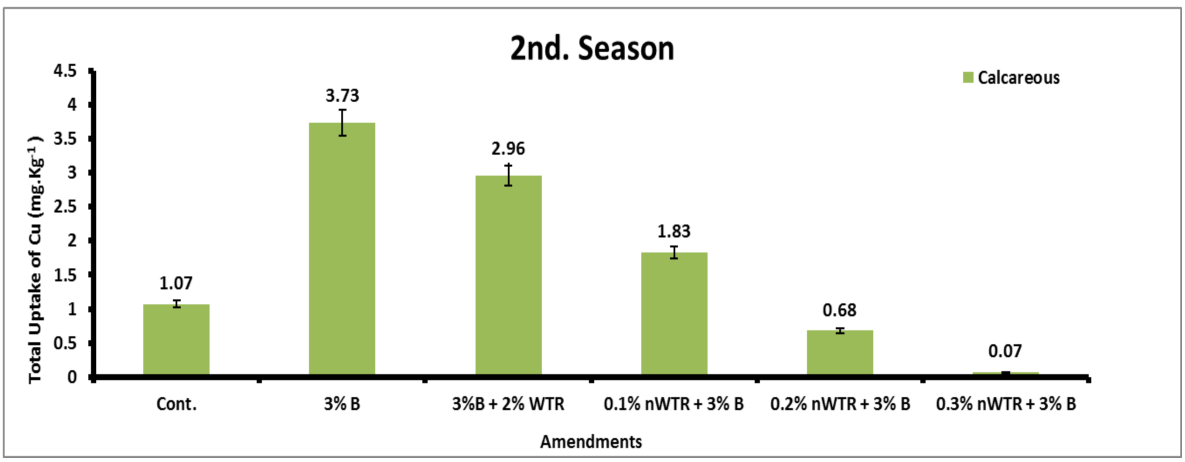


Fig.6. Effects of nWTRs on the uptake of Cu by corn plants grown on biosolids-treated soils

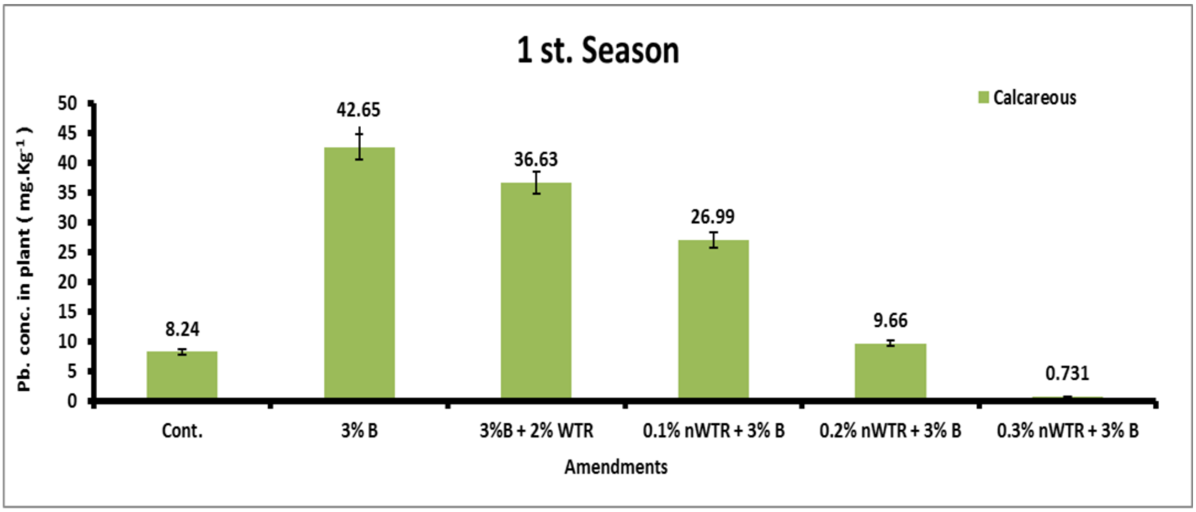
F-test: Soil **, Treatment **, **Soil*treatment --**

** is significant at 0.01 probability level and (--) = N.S

1st. season	L.S.D.(0.05) = 1.4	L.S.D.(0.01) = 1.92	S.E= 0.67
2nd. season	L.S.D. (0.05) = 1.89	L.S.D.(0.01) = 2.6	S.E = 0.90

Lead concentration in corn plants influenced by co-applying biosolids and nWTRs

The impact of co-applying biosolids and water treatment residuals (WTR) or nano water treatment residuals (nWTR) on lead (Pb) levels in corn plants cultivated in calcareous soil is depicted in Figure (8). The data presented in this figure indicate that the Pb concentrations in the plant tissues were markedly higher compared to the control group following the application of 3% biosolids, 3% biosolids combined with 2% WTRs, and 0.1% nWTRs. In contrast, the use of 0.3% nWTRs led to a significant reduction in Pb levels in the soils examined throughout the two growing seasons, when compared to the control.



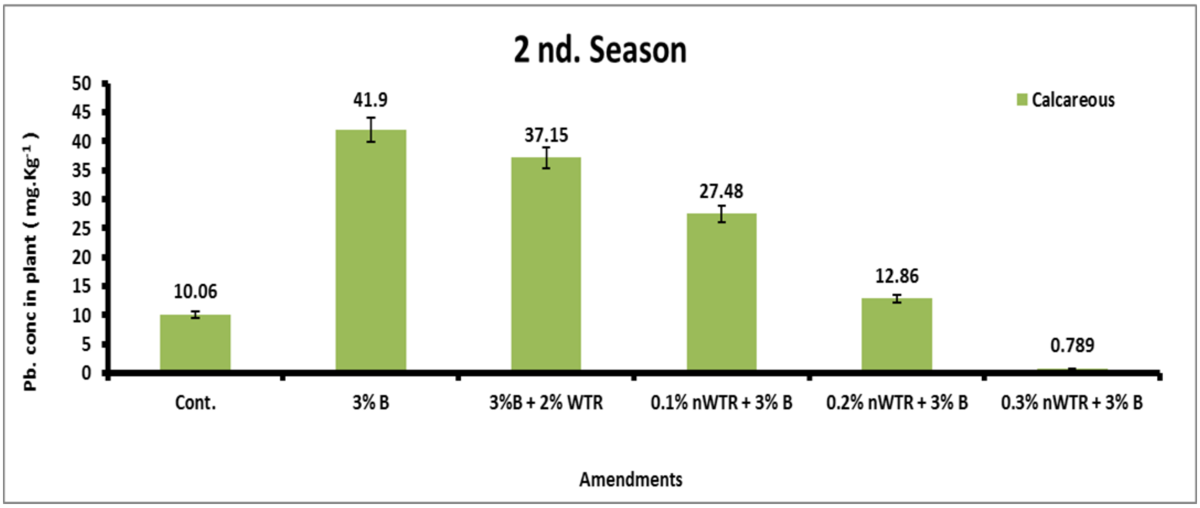


Fig.8. Effects of nWTRs on Pb concentrations in corn plants grown on biosolids-treated soils

F-test: Soil **, Treatment **, and Soil*Treatment * is significant at 0.05 probability level , ** is significant at 0.01 probability level

1st.season: L.S.D(0.05)=3.79 , L.S.D.(0.01)=5.19 S.E = 1.80

2nd. Season : L.S.D (0.05) = 3.50 , L.S.D.(0.01) = 4.79 S.E = 1.66

Lead uptake by corn plants influenced by co-applying biosolids and nWTRs

The impact of co-application of biosolids and nWTRs on the total lead (Pb) absorption by corn in calcareous soil is illustrated in Figure (9). In the first season, the maximum Pb uptake recorded in plant tissues was 5.31 mg/kg, resulting from the application of 3% biosolids combined with 2% WTRs. Conversely, the minimum Pb uptake observed was 0.08 mg/kg, attributed to the application of 0.3% nWTRs. In the second season, the highest Pb uptake in plant tissues increased to 5.69 mg/kg, again due to the application of 3% biosolids and 2% WTRs, while the lowest uptake was 0.09 mg/kg, linked to the 0.3% nWTRs application. The exceptional properties of nWTRs, such as their extensive surface area, significant retention capacity, and stability, make them highly effective for the remediation of soils contaminated with metals. In contrast, conventional bulk WTRs exhibit limited reactivity towards pollutants. To address this limitation, Elkhatib et al. (2015) initiated the development and application of nWTRs for the remediation of soil and water. Various retention studies have demonstrated that the ability of nanostructured WTRs to retain arsenic (As), mercury (Hg), cadmium (Cd), and chromium (Cr) from polluted wastewater surpasses that of bulk WTRs by factors of 16.7, 13, 16.8, and 15, respectively (Elkhatib & Moharem, 2015; Elkhatib et al., 2019; Hamadeen et al., 2022). Consequently, we propose that the creation of nanostructured super sorbents from the cost-effective byproducts of the water industry (WTRs) would significantly enhance the remediation capabilities of their bulk counterparts for soils contaminated with lead.

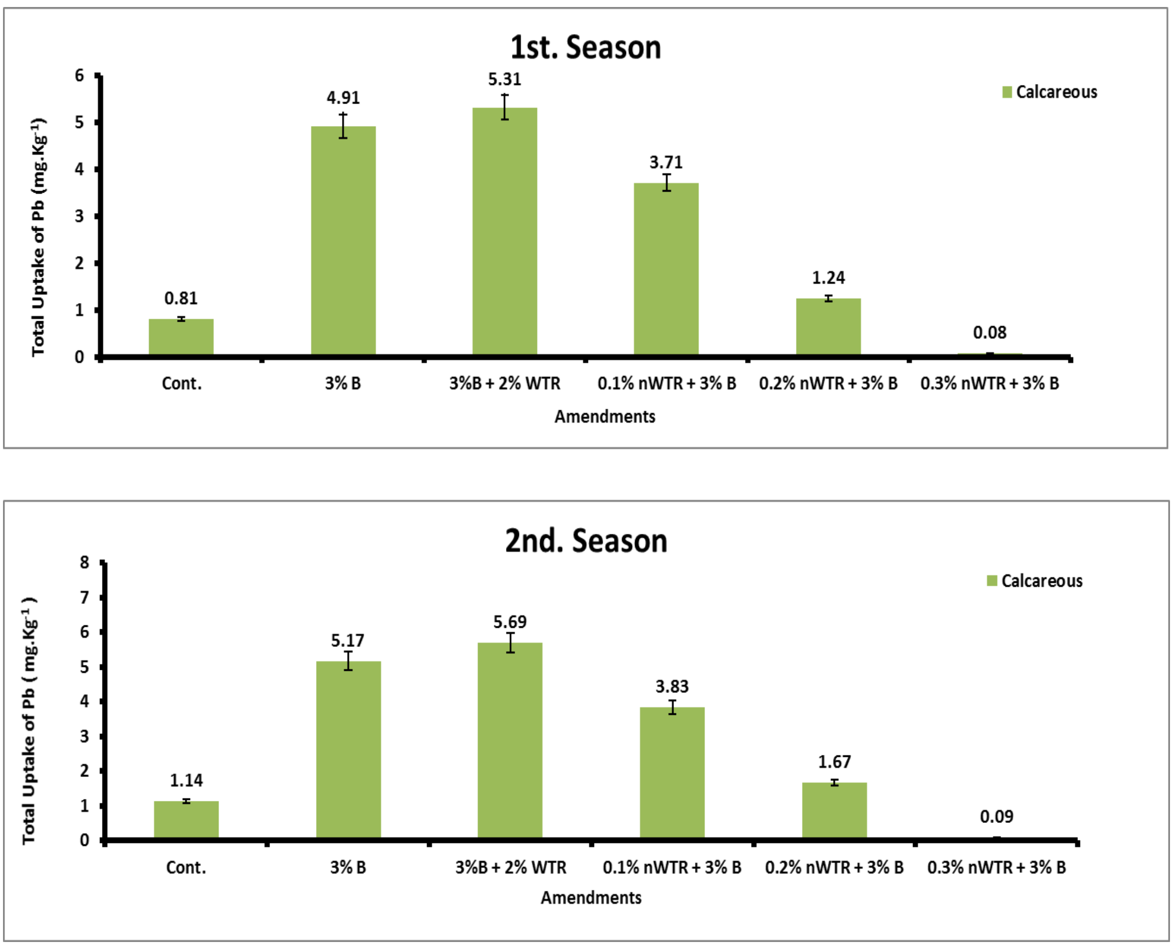


Fig.9. Effects of nWTRs on the uptake of Pb by corn plants grown on biosolids-treated soils

F-test: Soil **, Treatment **, **Soil*Treatment --**

** is significant at 0.01 probability level , and (--) = N.S

1st. season L.S.D. (0.05) = 3.28 L.S.D.(0.01) = 4.50 S.E = 1.56

2nd. season L.S.D. (0.05) = 2.68 L.S.D.(0.01) = 3.67 S.E = 1.27

Soluble copper and lead in soil solution influenced by co-applying biosolids and nWTRs

The concentration of copper (Cu) and lead (Pb) in the soil solution typically reflects their adsorption onto the solid phase of the soil. However, factors such as the presence of dissolved organic matter (DOM), pH, and ionic strength can cause the concentration of these metals to exceed what would be expected from simple adsorption equilibrium (Tipping et al., 2003). In soil systems, more than 90% of the copper and lead in solution is often associated with DOM, which plays a crucial role in complexation and metal mobility.

Figures 10 and 11 illustrate the impact of nano water treatment residues (nWTRs) on soluble Cu and Pb levels in calcareous soil amended with biosolids (B), WTRs, and nWTRs. The application of 3% biosolids (B) and a combination of 3% B with 2% WTRs significantly increased soluble Cu and Pb levels compared to the control group. In contrast, the addition of 0.1%, 0.2%, and 0.3% nWTRs consistently decreased the availability of these metals in the soil solution during both the first and second growing seasons. These reductions in soluble Cu and Pb concentrations were statistically significant (L.S.D., $p \leq 0.05$).This decrease in metal availability can be attributed to the adsorption of Cu and Pb onto the large surface area and active sites provided by the nWTRs, which include hydroxyl (O–H) and aluminum-oxide (O–Al–O) groups that facilitate metal binding. These findings are consistent with those reported by Moharem (2019), who observed similar reductions in DTPA-desorbed metals following the application of nWTRs over multiple wetting-drying cycles. Furthermore, Elkhatib et al. (2019) highlighted the efficacy of nWTRs in removing heavy metals from the soil solution, primarily due to their high surface area and sorptive capacity. Taken together, these results suggest that nWTRs can be a promising land amendment for mitigating the hazardous effects of heavy metals in soils treated with biosolids. Therefore, incorporating nWTRs with biosolids during land application is recommended as a strategy to reduce metal bioavailability and environmental risk.

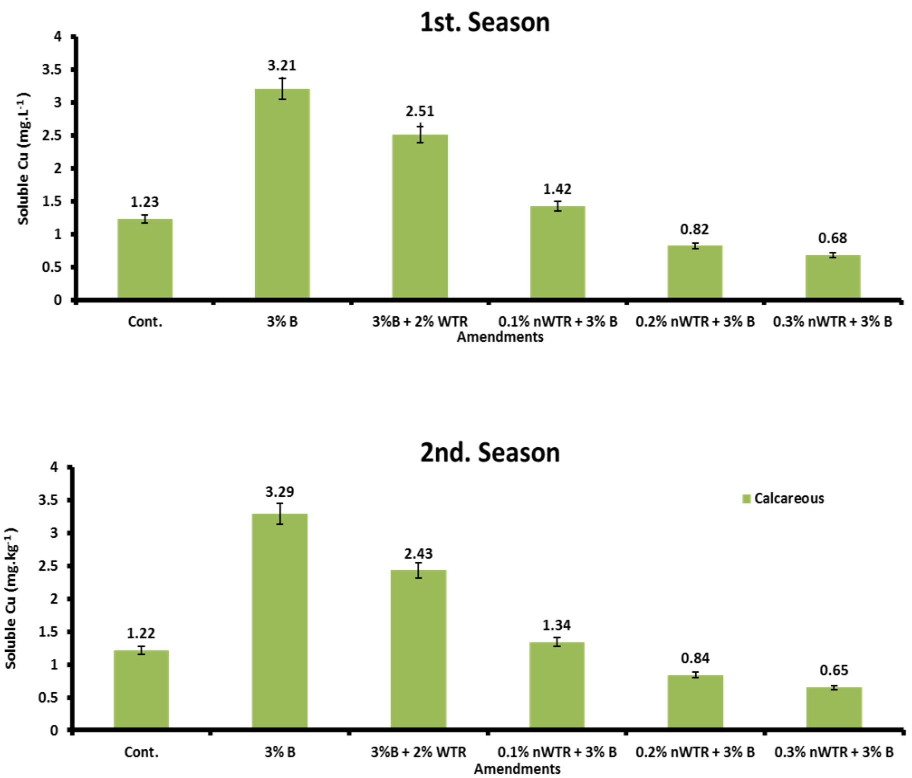


Fig.10. Impact of nWTRs on the concentration of soluble copper in the soil solution of calcareous soil treated with biosolids, WTRs, and nWTRs

F-test: 1 st. season :- Soil **, Treatment **, and T*S (--);**2nd. Season:** Soil **, Treatment **, and T*S **

* is significant at 0.05 probability level ** is significant at 0.01 probability level and (--) = N.S

1st. season L.S.D.(0.05) = 0.45 L.S.D.(0.01) = 0.62 S.E = 0.10

2nd. season L.S.D (0.05) = 0.18 L.S.D.(0.01) = 0.24 S.E = 0.04

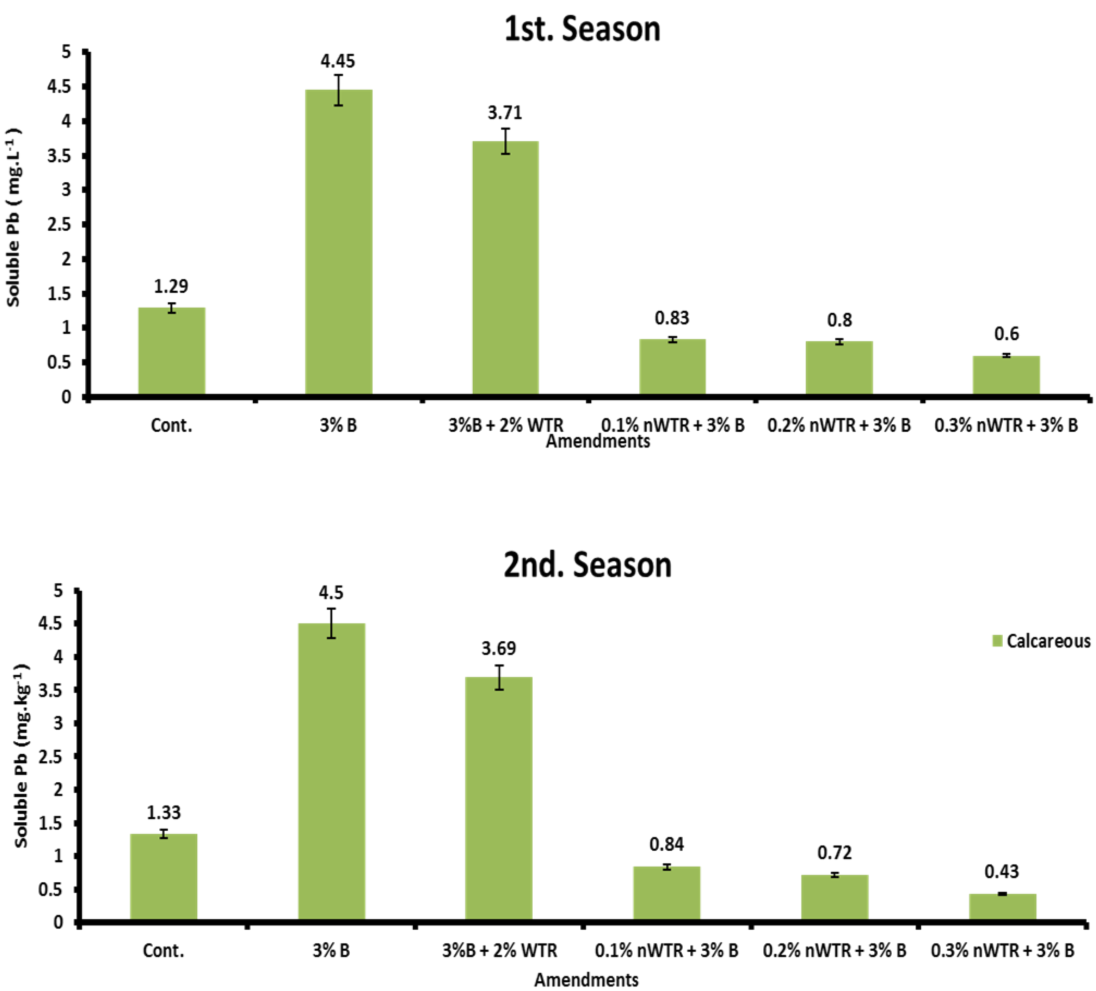


Fig.11. Impact of nWTRs on the concentration of soluble copper in the soil solution of calcareous soil treated with biosolids, WTRs, and nWTRs

F-test: Soil **, Treatment **, ** is significant at 0.01 probability level

1^{st}. season L.S.D.(0.05) = 0.12 L.S.D.(0.01) = 0.16 SE = 0.05

2^{nd}. season L.S.D.(0.05) = 0.24 L.S.D.(0.01) = 0.33 S.E = 0.11

Effect of nWTRs on water holding capacity (WHC) of biosolids-treated studied calcareous soil for two growing seasons

The water holding capacity (WHC) of the calcareous soil was evaluated before and after the application of various amendments over two consecutive growing seasons (Table 2). Results demonstrated that all treatments, biosolids, water treatment residues (WTRs), and nano water treatment residues (nWTRs),significantly enhanced the WHC of the soil compared to the untreated control.

In the first growing season, the application of 3% biosolids increased the WHC from 87.82 to 129.36%, while the incorporation of 0.3% nWTRs resulted in a more pronounced improvement, raising the WHC to 183.27%. A similar trend was observed in the second season, where 3% biosolid application increased WHC from 88.38 to 130.17%, and 0.3% nWTRs elevated it further to 188.30%. These increases were statistically significant at the 0.05 level (L.S.D.).

The observed improvements in WHC can be attributed to the organic matter content in biosolids and the fine particle size and high surface area of nWTRs, which enhance soil structure, porosity, and water retention. Among the treatments, nWTRs exhibited the greatest effect on increasing WHC, likely due to their superior physicochemical properties, which facilitate the formation of micro-aggregates and enhance soil moisture retention capacity. Furthermore, the interaction effects between biosolids and nWTRs also contributed significantly to improving WHC, as confirmed by statistical analysis.

Table 2. Effect of biosolids, water treatment residues (WTRs), and nano water treatment residues (nWTRs) on the water holding capacity (WHC) of calcareous soil over two growing seasons

TREATMENT	W.H.C. (1st. Season)
Cont.	87.82
3% B	129.36
3%B + 2% WTR	132.48
0.1 nWTR + 3% B	146.11
0.2 nWTR + 3% B	176.34
0.3 nWTR + 3% B	183.27
L.S.D 0.05	**15.63**
L.S.D 0.01	**21.42**
TREATMENT	**W.H.C. (2nd. Season)**
Cont.	88.38
3% B	130.17
3%B + 2% WTR	132.45
0.1 nWTR + 3% B	143.64
0.2 nWTR + 3% B	169.17
0.3 nWTR + 3% B	188.3
L.S.D 0.05	**46.76**
L.S.D 0.01	**64.06**

Values represent the mean WHC percentage before and after treatment application. Statistically significant differences between treatments and the control are indicated by the least significant difference (L.S.D., $p \leq 0.05$).

These findings suggest that the use of nWTRs, either alone or in combination with biosolids, can substantially enhance the water retention capacity of calcareous soils, thereby improving their suitability for agricultural production in arid and semi-arid regions.

Fractionation of copper in biosolids-amended calcareous soil as influenced by the application of nano-water treatment residues(nWTRs)

The fractionation of copper (Cu) in biosolids-amended calcareous soil was investigated using the sequential extraction procedure developed by Tessier et al. (1979), a well-established method for evaluating the speciation and mobility of heavy metals in soils. This technique differentiates Cu into various geochemical fractions, providing critical insight into its environmental behavior. In this context, copper associated with the residual (RS) fraction is considered to be the most stable and least bioavailable, while the non-residual (NORS) fractions—including exchangeable, carbonate-bound, Fe/Mn oxide-bound, and organic-bound forms are more mobile and potentially accessible to plants. The distribution of Cu across these fractions thus serves as an important indicator of its ecological risk and long-term stability in soil environments (Moharem et al., 2013; Elkhatib et al., 2017).

In unamended (control) soil, the residual Cu fraction accounted for 22% of the total Cu in the first growing season and increased slightly to 26% in the second season. Upon the application of biosolids at a rate of 3%, a significant decrease in the residual fraction was observed—dropping to 22% and 21% in the first and second seasons, respectively. This substantial reduction suggests that biosolid amendments enhance the transformation of Cu into more bioavailable and labile forms, potentially increasing the risk of metal uptake by plants or leaching into groundwater. Conversely, the application of nano water treatment residues (nWTRs) at a rate of 0.3% to biosolids-amended soil resulted in a notable shift in Cu speciation towards more stable forms. The residual Cu fraction increased markedly, reaching 81% and 77% in the first and second growing seasons, respectively. These findings indicate that nWTRs play a significant role in immobilizing copper, thereby reducing its bioavailability. This behavior is consistent with earlier studies, which have demonstrated the high affinity of nWTRs for heavy metals, attributed to their large surface area, high reactivity, and capacity to form stable complexes (Elkhatib and Moharem, 2015).

Further analysis revealed that the sequential distribution of Cu in nWTR-treated soils followed the order: Residual > Oxide-bound > Carbonate-bound > Exchangeable > Organic-bound, in both growing seasons. This pattern reinforces the effectiveness of nWTRs in promoting the stabilization of Cu within less mobile soil fractions. Overall, these results highlight the potential of nWTRs as a sustainable soil amendment for mitigating Cu mobility in biosolids-amended calcareous soils, thereby reducing environmental risk and enhancing soil health.

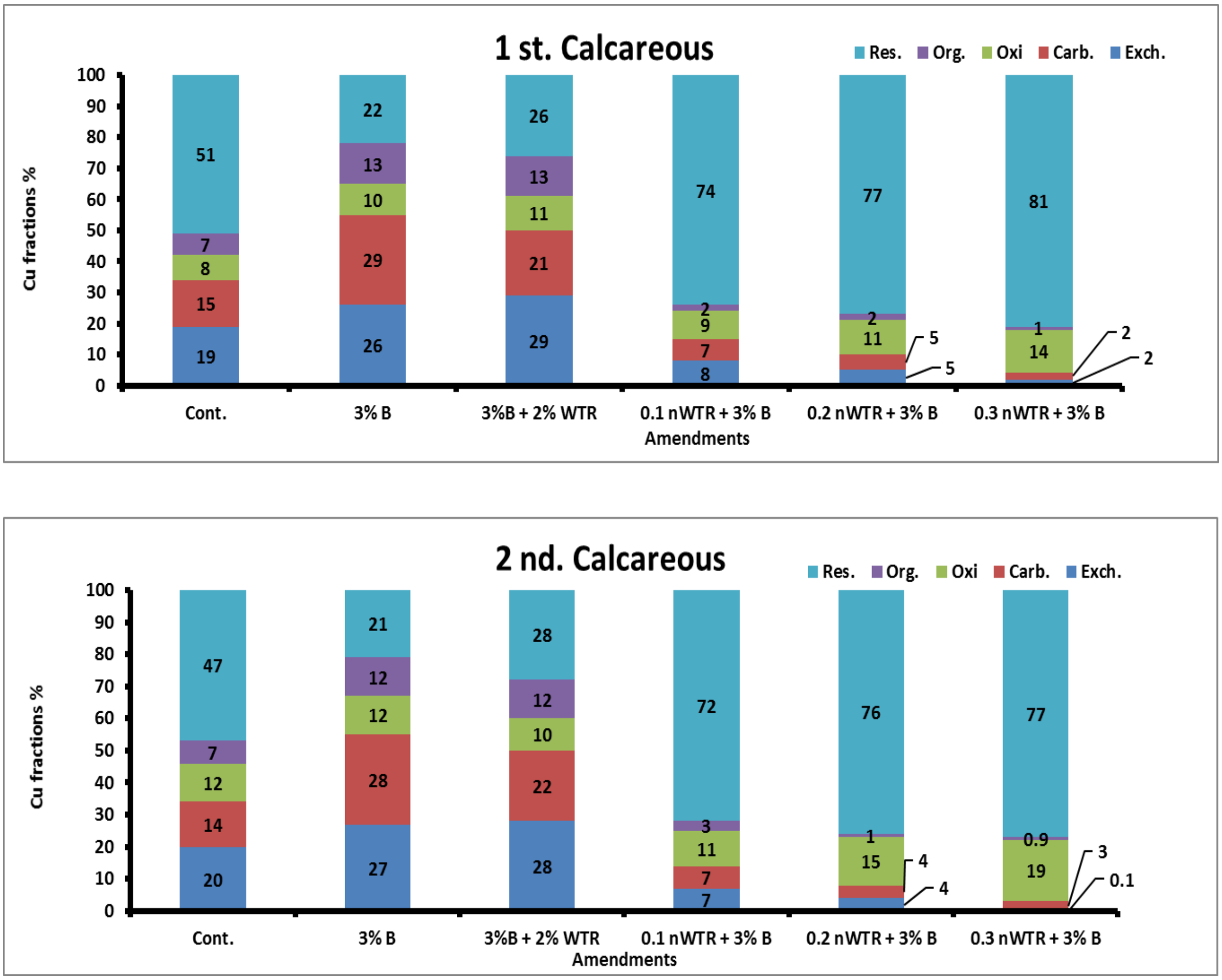


Fig.12. Relative percentages of Cu fractions for the calcareous soils amended with 3%Bio solids and as affected by 2%WTRs or nWTR at rates of 0·1% , 0.2% and 0·3% by weight

(WTR, water treatment residual) ; (nWTR, water treatment residual nanoparticles ; (Res, residual fraction; Org, organic matter; Oxi, Oxides fractions; Carb, Carbonates fractions; Exch., Exchangeable fractions)

Fractionation of Lead in Biosolids-Amended Calcareous Soil as Influenced by Nano-Water Treatment Residues (nWTRs)

The effect of nano-water treatment residues (nWTRs) on the geochemical fractionation of lead (Pb(II)) in calcareous soil amended with biosolids and WTRs was evaluated, with results presented in Figure 13. The application of nWTRs, particularly at a rate of 0.3%, significantly altered the distribution of Pb fractions, decreasing the concentrations of labile forms (exchangeable, carbonate-bound, oxide-bound, and organic-bound Pb) and increasing the proportion of the residual fraction.In untreated control soils, the residual Pb fraction accounted for 51% and 49% of the total Pb in the first and second growing seasons, respectively. Upon application of 0.3% nWTRs, this fraction increased markedly to 79% in both seasons, indicating greater stability and reduced mobility of Pb. The Non-residual fractions decreased as follows:

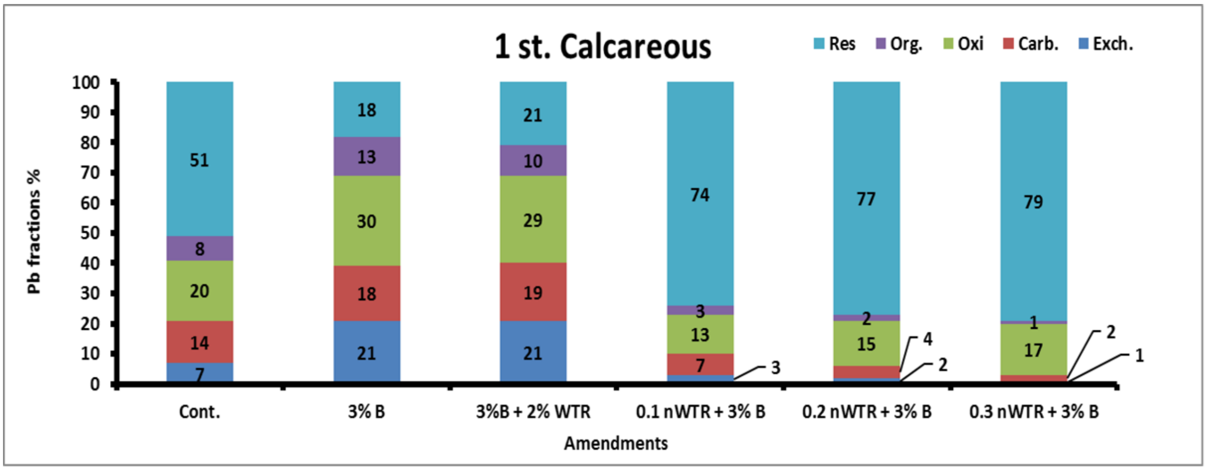
[1] **Oxide-bound Pb:** Reduced from 21% and 22% (control) to 17% and 18% in the first and second seasons, respectively.

[2] **Carbonate-bound Pb:** Declined from 14% (both seasons) to 2% and 1.5%.

[3] **Organic-bound Pb:** Decreased from 14% to 1% in both seasons.

[4] **Exchangeable Pb:** Declined from 7% and 8% to 1% and 0.5%, respectively.

This redistribution of Pb from mobile to more stable fractions suggests that nWTRs effectively immobilize Pb in biosolid-amended calcareous soils. These findings are consistent with prior studies (Moharem et al., 2013; Elkhatib et al., 2015a, b, c), which reported the ability of nWTRs to convert heavy metals such as Cu and Pb into less bioavailable forms. Overall, the distribution of Pb fractions following nWTR application followed the order: **Residual** > **Oxide** > **Carbonate** > **Organic** > **Exchangeable**, for both growing seasons. This trend highlights the effectiveness of nWTRs in enhancing the environmental safety of biosolid-amended soils by promoting Pb stabilization.



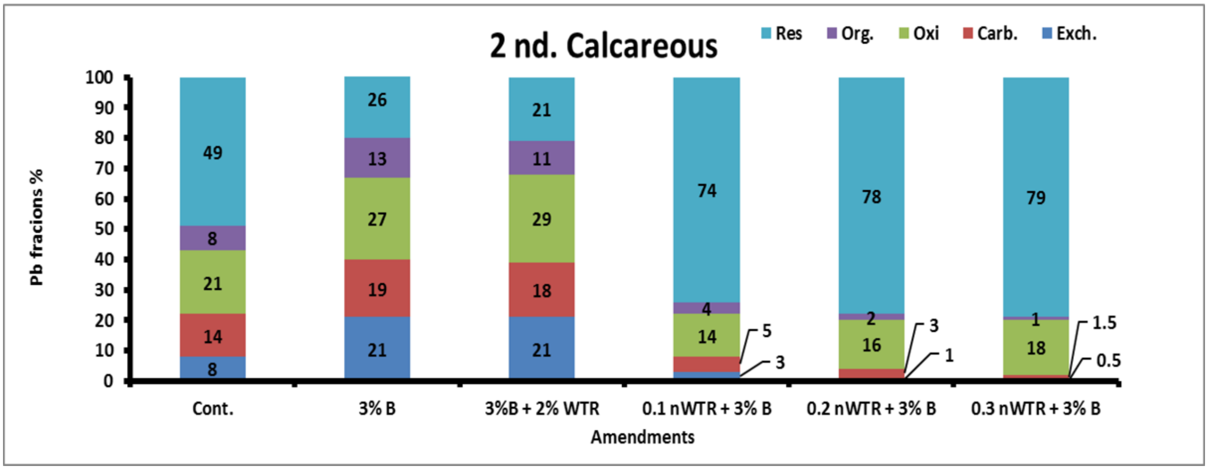


Fig. 13.The relative percentages of lead (Pb) fractions in calcareous soils that have been amended with 3% biosolids and influenced by the addition of nWTR at weight rates of 0.1%, 0.2%, and 0.3%.

(WTR, water treatment residual) ; (nWTR, water treatment residual nanoparticles ; (Res, residual fraction; Org, organic matter; Oxi, Oxides fractions;Carb, Carbonates fractions; Exch., Exchangeable fractions)

Copper and lead species in soil solution of amended calcareous soil

The chemical speciation MINEQL+ 4.6 program (Schecher & McAvoy, 2003) was utilized to calculate Cu and Pb species in the soil solution of calcareous soil amended with Biosolids, WTRs and/or nWTR (Tables3 and 4).

Copper species

Table 3 summarizes the percentage distribution of copper species in the soil solution of calcareous soils amended with biosolids (3%B), water treatment residues (WTRs), and nano-water treatment residues (nWTRs) at varying rates (0.1%, 0.2%, 0.3%). The total Cu(II) is expressed as a sum of four main species: free Cu^{2+} ions, tenorite (CuO), $Cu(OH)^{+}$, and $Cu(OH)_2$ (aq).In all treatments, Cu^{2+} remained the dominant form, accounting for nearly all of the soluble copper in treatments without nWTRs. Specifically, Cu^{2+} constituted 99.1% of the total copper in the control, 3% biosolids, and 3% biosolids + 2% WTR treatments. Slight reductions in free Cu^{2+} concentrations were observed with increasing nWTR dosages: 0.7%, 0.3%, and 0.2% in the 0.1%, 0.2%, and 0.3% nWTR treatments, respectively. As nWTR application increased, there was a corresponding rise in the proportion of hydroxylated and solid-phase copper species, particularly $Cu(OH)^{+}$ and $Cu(OH)_2$(aq), although they remained minor components overall (each ≤ 0.1%). These findings suggest that nWTRs promote the transformation of copper from its free ionic form (Cu^{2+}) which is highly mobile and bioavailable—to more hydrolyzed or precipitated forms, such as $Cu(OH)^{+}$, $Cu(OH)_2$(aq), and CuO (tenorite). This shift becomes more pronounced with higher nWTR application rates, especially at 0.2% and 0.3%.

The significant reduction in Cu^{2+} from 0.9% in the control to 0.2% at the 0.3% nWTR treatment highlights the potential of nWTRs to reduce the lability and toxicity of copper in soil solutions. This behavior is likely attributed to the high surface area, reactive hydroxyl groups, and aluminum/iron oxides in nWTRs, which serve as sorption sites and precipitation nuclei for Cu species (Moharem et al. 2013). Furthermore, the slight increase in $Cu(OH)^{+}$ and $Cu(OH)_2$(aq) suggests pH modulation and hydrolytic transformation, which are consistent with the presence of alkaline constituents in nWTRs. The appearance of CuO only in nWTR-treated soils is also notable, as it points toward the formation of sparingly soluble mineral forms that further reduce copper mobility.

Environmental and practical implications:

The reduced proportion of free Cu^{2+} in nWTR-treated soils suggests lower bioavailability to plants and microorganisms, which is advantageous for mitigating phytotoxicity in biosolids-amended calcareous soils. These findings reinforce the immobilization capacity of nWTRs and their potential application in sustainable soil remediation strategies, especially in areas impacted by biosolid land application

Lead species

Table 4 displays the percentage distribution of different lead (Pb) species in the soil solution of calcareous soil amended with biosolids, water treatment residuals (WTRs), and nano-water treatment residuals (nWTRs). The data indicate a clear shift in lead speciation dynamics with the application of nano water treatment residues (nWTRs). Notably, the concentration of free ionic lead (Pb^{2+}),the most bioavailable and toxic species, declined sharply from 1.6% in the control to just 0.1% with 0.3% nWTR, underscoring the strong immobilizing effect of nWTR on lead. Simultaneously, $Pb(OH)_2$ (aq), a more stable and less mobile species, emerged as the dominant form across all treatments, with its proportion increasing slightly from 97% to 98.2%, likely due to enhanced pH buffering and surface adsorption facilitated by nWTRs. Interestingly, the carbonate-bound species $Pb(CO_3)_2^{2-}$ appeared only in the presence of nWTRs, albeit in trace amounts (0.1%), suggesting a potential for carbonate precipitation in the calcareous soil environment enhanced by the amendment(Elkhatib and Moharem,2015). Meanwhile, $PbOH^{+}$ concentrations remained relatively constant (1.4–1.6%), indicating a steady, albeit minor, role in overall lead speciation. Collectively, these shifts point to the effectiveness of nWTRs in transforming lead into less bioavailable and more geochemically stable forms, thereby improving soil safety and reducing environmental risks.

Environmental and practical implications

The findings of this study carry significant environmental and practical implications, particularly for the safe management of heavy metals in biosolids-amended calcareous soils. The marked reduction in the bioavailable fraction of lead (Pb^{2+}) following the application of nano-water treatment residues (nWTRs) highlights their strong potential as an eco-friendly soil amendment for mitigating heavy metal toxicity. By transforming lead into more stable hydroxide and carbonate forms, nWTRs not only reduce the immediate risk of metal uptake by plants but also limit leaching into groundwater, contributing to long-term soil and water quality protection.

Table3. Distribution of copper species (% of total Cu(II)) in soil solution of amended calcareous soil

Calcareous soil						
NAME	**Cont.**	**3B%**	**3%B + 2%WTRs**	**nWTRs 0.1%**	**nWTRs 0.2%**	**nWTRs 0.3%**
Cu (+2)	0.9	0.9	0.8	0.7	0.3	0.2
Tenorite (CuO)	99.1	99.1	99.1	99.2	99.5	99.6
$Cu(OH)^{+}$	0	0	0	0.1	0.1	0.1
$Cu(OH)_{2\ (aq)}$	0	0	0	0	0.1	0.1
TOTAL Cu(2+)	100	100	100	100	100	100

Table 4. Distribution of Lead species (% of total Pb (II)) in soil solution of amended calcareous soil

Calcareous soil						
NAME	**Cont.**	**3B%**	**3%B + 2%WTRs**	**nWTRs 0.1%**	**nWTRs 0.2%**	**nWTRs 0.3%**
Pb(2+)	1.6	1.3	1.1	0.4	0.2	0.1
PbOH (+)	1.4	1.5	1.5	1.5	1.6	1.6
$PbSO_4$ (aq)	0	0	0	0	0	0
$Pb(OH)_2$ (aq)	97	97.2	97.4	98	98.1	98.2
$PbCO_{3\ (aq)}$	0	0	0	0	0	0
$Pb(CO_3)_2^{-2}$	0	0	0	0.1	0.1	0.1
TOTAL Pb (2+)	100	100	100	100	100	100

From a practical standpoint, the ability of low-dose nWTRs (as little as 0.3%) to significantly stabilize lead suggests that they are a cost-effective and scalable solution for remediating contaminated or biosolid-treated lands. Their use aligns with sustainable agricultural practices by promoting the reuse of industrial by-products and reducing reliance on synthetic or chemical stabilizers. Furthermore, the immobilization of heavy metals through such amendments supports safe crop production, particularly in arid and semi-arid regions where calcareous soils are widespread and biosolids are commonly used to enhance soil fertility. In summary, nWTRs offer a dual benefit: enhancing soil health while addressing a critical environmental challenge. Their application could be instrumental in achieving cleaner production goals and ensuring safer use of biosolids in agriculture.

CONCLUSIONS

The application of nano-water treatment residuals (nWTRs) represents a promising and sustainable strategy for mitigating the environmental risks associated with biosolids application in calcareous soils, particularly in arid regions. The nWTRs significantly reduced the bioavailability and mobility of copper and lead by transforming them from reactive and labile forms into stable residual and hydroxide species. The most notable improvements were observed with the 0.3% nWTR application, which achieved up to a 92% reduction in free ionic forms of Cu^{2+} and Pb^{2+} in soil solution and enhanced metal retention in less mobile geochemical fractions. Moreover, nWTRs contributed to a measurable reduction in metal uptake by maize, demonstrating their effectiveness in limiting metal transfer through the food chain. The physical and chemical characteristics of nWTRs, especially their high surface area, reactive Al/Fe oxides, and sorptive capacity, enabled these benefits even at low application rates. These results reinforce the practical viability of reusing water treatment byproducts as nano-amendments for soil remediation. Furthermore, incorporating nWTRs with biosolids during land application can enhance soil quality, minimize heavy metal risks, and support safe and sustainable agricultural practices, offering a circular approach to waste reuse and environmental protection.

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ديناميكية النحاس و الرصاص المستمد من المخلفات الصلبة الحيوية(الحمأة)المضافة إلى الأراضي الجيرية : تأثير المواد النانومترية المشتقة من مخلفات معالجة مياه الشرب

اضافة *حمأة* الصرف الصحي الى الأراضى الزراعية يمكن أن تسبب مخاطر بيئية وصحية سلبية. ويرتبط هذا بشكل أساسي بتراكم المعادن الثقيلة السامة مثل *النحاس والرصاص*.لذلك تبحث هذه الدراسة في ديناميكيات النحاس (Cu) والرصاص (Pb) الناتجة من اضافة الحمأةالى الأراضي الجيرية وتُقييّم اثراضافةالمواد النانومترية المُشتقة من مخلفات صناعةمعالجة مياه الشرب (nWTRs) فى الحد من التأثير السلبى للحمأة على البيئة. وقدأُجريت تجربة ميدانية ليسيمترية باستخدام تربة جيرية مُعدّلة بـ ٣% من الحمأة وبمعدلات (0.1%) ، 0.2%، 0.3%) من مخلفات معالجة المياه النانومترية (nWTRs) وزراعة نبات الذرة بها فى موسمين متتاليين. وأوضحت

النتائج ان اضافة الحمأة الى الأرض الجيرية بمعدل ٣% أدى الى زيادة معنوية في صلاحية كل من النحاس والرصاص وتركيزاتهما الذائبة في المحلول الأرضى وامتصاص النبات لهذين العنصرين فى كل من الموسمين. في المقابل، أدى اضافة (nWTRs)الى الأرض المعاملة بالحمأة إلى خفض مستويات النحاس والرصاص الذائبةفى المحلول الأرضى والمتاحة للنبات معنويا،وذلك بتحويلهم من الصور المتاحة و النشطة كيميائيا الي صور غير متاحة متبقية وخاصةً عند معدل ٠,٣%.ولقد عززت نتائج تجربة الإستخلاص المتتالى تحول صورالنحاس والرصاص من الصور المتاحة للإمتصاص بواسطة النبات(قابلة للتبادل، مرتبطة بالكربونات، مرتبطة بالأكسيد) الى الصورة غير المتاحة(المتبقى) وارتفاع نسبتهما من ٢٢% إلى ٨١% للنحاس، ومن ٥١% إلى ٧٩% للرصاص.كما أظهرت نمذجة الصور الكيميائية باستخدام +MINEQL انخفاضًا كبيرًا في أيونات النحاس والرصاص الحرة، مع زيادة تكوين صور الهيدروكسيد والكربونات الأقل حركة في التربة المعدلة. و توضح هذه النتائج أن المواد النانومترية المُشتقة من مخلفات صناعةمعالجة مياه الشرب (nWTRs تعمل بشكل فعال على تثبيت النحاس والرصاص في التربة المعدلة بالحمأة من خلال تغيير صورها وصلاحيتها للإمتصاص بواسطة النبات، وبالتالي خفض المخاطر البيئية وتعزيز استدامة إعادة استخدام المخلفات الصلبة الحيوية في الزراعة و حماية البيئة.