Sulaimani Journal for Pure and Applied Sciences Vol. 27 Issue 2 (2025) 52-64.

Journal homepage https://sjpas.univsul.edu.iq

Sulaimani Journal for Pure and Applied Sciences

ISSN:1812-4100

Original Article

Assessment of Lead and Cadmium Mobility in Calcareous Soil Under the Impact of Farmyard Manure (FYM) and Wastewater Irrigation

Manal Z. Fatihi[a,*] and Khalida A. Hassan[a]

[a] *Department of Soil and Water, College of Agriculture, University of Duhok, Duhok, Kurdistan Region, Iraq.*

ARTICLE INFO

Article History:
Received: 30/07/2025
Revised: 14/09/2025
Accepted: 19/10/2025
Published online: 25/12/2025

Key Words:
Manure
Lead
Cadmium
Mobility
Calcareous soil
Wastewater

ABSTRACT

The leachability as well as the distribution of cadmium (Cd) and lead (Pb) were studied in two different calcareous soils treated with sheep manure (FYM) and wastewater (WW). The FYM thoroughly mixed with surface soils at three levels (F0, F20, and F40 g kg^{-1}), and the treated soils were incubated for 45 days. Soil columns were subjected to the intermittent leaching for ten times (seven days' intervals) using waste water, and the leachates were collected for analysis of pH, EC, Pb, Cd, anions, and cations. The soils in the columns were divided into two depths (0-12 cm and 12-24 cm) and then analyzed. Results showed that EC, Na^{+}, Cl^{-}, K^{+} and SO$_4^{-2}$ of incubated soils increased due to manure application. Pb was higher in the soil treated with 20 g kg^{-1}, while Cd levels were very low (0.0189–0.0339 mg kg^{-1}). Wastewater application lowered the leachate pH of both soils and sharply increased EC. Cd concentrations slightly decreased, while Pb of the leachates across all treatments remained between (0.0218–0.0274 mg kg^{-1}). Comparing the two depths of the soil, Pb concentrations were consistently lower in the 12–24 cm layer compared to 0–12 cm, indicating Pb retention in surface soil, with limited downward mobility. However, Cd concentrations increased in the 12–24 cm layer under wastewater irrigation, especially at F20 WW (0.0243 mg kg^{-1}) and F40 WW (0.0281 mg kg^{-1}). This confirms the vertical movement of soluble Cd and the potential environmental risks of Cd migration under combined wastewater and organic amendments in calcareous soils.

1. Introduction

The contamination of agricultural soils with heavy metals is an increasingly critical environmental issue due to their toxic nature, persistence, and ability to bioaccumulate in crops (Roy and McDonald, 2014). Among these contaminants, lead (Pb) and cadmium (Cd) are particularly concerning because they are non-biodegradable and can persist in soil for decades, ultimately affecting soil fertility, groundwater quality, and human health (Odeh, 2023; Hooda and Alloway, 1993). These metals can accumulate in the food chain, posing serious health threats, particularly in developing regions where untreated wastewater is commonly used for irrigation (Aftab et al., 2023). With rampant inflation in anthropogenic activities, the release of toxic metals into the environment is increasing day by day. According to an estimate by (Singh et al., 2003), global annual release of Pb and Cd into the environment is 783,000 and 22,000 metric tons, respectively. In addition, wastewater from different sources (domestic, municipal and industrial) plays a significant role in the release of heavy metals like Pb and Cd. (Azizullah et al., 2011) revealed that about 2 million tons of sewage sludge

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* Corresponding author.
E-mail address: manal.zaki@uod.ac (M. Fatihi)

and effluents are polluting the world's water per day, and can persist in the environment for long periods, posing serious threats to soil health, food safety and human well- being (Kumar et al., 2017). Furthermore, metals such as cadmium (Cd) and lead (Pb) have no biological role and are hazardous for the environment even when available in small quantities or above the maximum recommended limits (Khan et al., 2021; Ji et al., 2022; Liu et al., 20021; Azam et al., 2021).

It was revealed that Several metals, such as lead (Pb), are extremely harmful to both humans and ecosystems (Alalwan et al., 2020; Charkiewicz and Backstrand, 2020). Toxic concentrations of all trace metals damage cell membranes, disrupt cellular processes and affect the three-dimensional structure of an enzyme (Ten Have et al.,2021). Due to its neurotoxic and cancer-causing effects, trace metal toxicity is a major issue for people all over the world (Kumar et al., 2019). Human heavy metal consumption is linked to cancer, kidney problems, blood acidity, development retardation, and finally mortality. In recent years, an estimated 12.6 million people have died worldwide from more than 100 diseases caused by unhealthy environments such as contaminated soils (WHO, 2016).

Heavy metals in soils originate from various anthropogenic activities, including wastewater irrigation, industrial waste disposal, excessive fertilizer application, Geological formation, and atmospheric deposition (Elbana and Selim, 2010). These metals do not degrade over time, meaning their accumulation in soils is irreversible unless effective remediation strategies are employed (Jalali and Latifi, 2018). Cadmium is found in some phosphate fertilizers (Triple super phosphate, mono super phosphate and diammonium phosphate) as an impurity, which accumulates in soils over time (Jalali and Khanlari, 2006), it is a toxic element and has great solubility (Gubrelay et al., 2013), while Pb contamination is often linked to vehicular emissions, industrial smelting, and coal combustion, which deposit Pb into soils through precipitation (Ma et al., 2021; Nordbery et al., 2007) due to its low solubility. The amount of anthropogenic Cd entering the mobile fraction is of great importance, as this fraction is believed to be more bioavailable (Alloway, 1991; Riise et al., 1994), but Pb is much less mobile (Camobreco et al., 1996).

Wastewater (WW) is also one of the major sources of heavy metal contamination in agricultural soils, which is widely practiced in many regions due to water scarcity and increasing demand for agricultural production (Rattan et al., 2005; Shaheen et al., 2017). (Majid et al., 2018) reported in their study that large numbers of wastewater effluent and sewage outlets, which may contain different transitional heavy metals, are discharged directly into sources of surface water without any pretreatment. Wastewater contains a mixture of industrial effluents, sewage sludge, and household waste, leading to high concentrations of Pb, Cd, Ni, Zn, Cu, and Cr in irrigated soils (Murtaza et al., 2010). Several studies have highlighted that long-term wastewater irrigation significantly increases the mobility and bioavailability of heavy metals, posing potential risks for plant uptake and groundwater contamination (Jalali and Khanlari, 2006; Ma et al., 2021).

Using wastewater in irrigating calcareous soils, which characterized by high calcium carbonate ($CaCO_3$) content, plays a crucial role in controlling heavy metal mobility (Al-Wabel et al., 2011). The presence of $CaCO_3$ modifies soil pH, alters metal adsorption capacity, and influences metal precipitation into stable forms. While Pb tends to be strongly retained in calcareous soils due to its strong adsorption to soil particles and low solubility in alkaline conditions, Cd remains highly mobile due to its weaker affinity for carbonate precipitation and cation exchange sites. Jalali and Khanlari, (2006) and Al-Wabel et al., (2011) observed that Cd remains more soluble "even in $CaCO_3$-rich soils" and competes with Ca^{2+} ions for exchange sites, leading to greater desorption under conditions of high calcium availability (Aziz et al., 2017). Both metals can be absorbed by plant roots, but Cd is more bioavailable, leading to higher accumulation in leafy vegetables and grains (Shaheen et al., 2017). Pinto et al., (2015) reported that availability of metals depends on the physical, chemical properties of the soil including "CEC, PH, and OM".

However, long-term wastewater irrigation can lead to soil salinity buildup, structural degradation, and gradual acidification, which increases Cd leaching and bioavailability. The application of organic amendments such as farmyard manure (FYM) is a common practice to enhance soil fertility and structure (Westerman and Bicudo, 2005), but FYM also affects heavy metal mobility by modifying soil pH, increasing organic matter content, and altering microbial activity. FYM enhances Pb retention but may increase Cd solubility due to competition with Ca^{2+} ions (Aziz et al., 2017). The presence of organic matter from wastewater and manure can either increase or decrease metal mobility depending on the metal-organic binding strength (Jalali and Latifi, 2018). Ma et al., (2021) reported that Pb has a high affinity for clay minerals, humic acids, and Fe/Mn oxides, further limiting its leaching potential. While (Shaheen et al., 2017) reported that organic matter from wastewater and manure can increase Cd solubility, making it more available for plant uptake.

Similarly, (Malik et al., 2021) reviewed the effectiveness of organically amended chickpea and wheat straw in the immobilization of Cd and Pb, and Tordoff et al., (2000) reported that mature compost, rich in humified OM, can effectively immobilize heavy metals, thereby reducing their environmental mobility. So FYM, which is environmentally safe, was used in this study to reduce the impact of these pollutants through the processes of adsorption, stabilization, complex formation, oxidation-reduction or precipitation. The reuse of wastewater for irrigation of agricultural field has been a common practice in many parts of the world (Jun et al., 2018; Assad et al., 2022). In Duhok city the farmers are obliged to use wastewater, without any pretreatment, for irrigation of their fields to produce vegetables, because availability of renewable water resources for irrigation is poor and is worsening over time. This wastewater is heavily contaminated with heavy metals (Sulaivany and Al-Mezori,2006), which tend to accumulate in soil. Thus, the interaction between wastewater, $CaCO_3$, and farmyard manure (FYM) plays a complex role in determining Pb and Cd mobility in calcareous soils, which this study aims to investigate, because the soil calcium carbonate content especially active CaCO3 causes decrees in availability of Cd and Pb due to precipitation them in the form of carbonate or hydroxyl of Cd and Pb.

Understanding heavy metal movement from contaminated calcareous soils which widely spread in Kurdistan Region, is crucial for assessing environmental risks. Because of a lack of research, such soils require detailed study on the effect of farmyard manure and wastewater on heavy metal retention and mobility in soil. Therefore, the objective of this research was to evaluate the effect of different rates of farmyard manure on ability and capacity of two different calcareous soils to retain and mobilize both Pb and Cd elements when irrigated with wastewater.

2. Materials and methods

Two different calcareous soils were collected from distinct agricultural locations differing in $CaCO_3$ content (14.77and 28.77%), representing Semel(S1) and Derabin(S2), respectively. Each soil was air-dried, gently crushed to pass through a 4 mm sieve, and stored for incubation processes. A portion from each soil was passed through a 2 mm sieve for routine analysis. The initial physicochemical properties of the soils were shown in Table 2. A brief description of analytical methods was: Electrical Conductivity (EC) measured using a conductivity meter model (BC3020) and expressed by dS m^{-1} according to (Rowell, 1996), and pH determined using a pH meter model (BP3001) as described by (Jackson, 1958). Major Cations: Calcium and magnesium were determined by titration with (EDTA 2Na) (0.01N) with the presence of murexide (ammonium purareate) and EBT as an indicator (Rowell, 1996). Sodium (Na^{+}) and Potassium (K^{+}) were determined using a flame photometry model (JENWAY/PFP7).

Titration method using 0.02N HCl with phenolphthalein as an indicator for the determination of Bicarbonate (HCO_3^-) (Estefan *et al.,* 2013). Soil particle size distribution determined by the hydrometer method, and equivalent calcium carbonate was measured by calcimeter.

Sheep manure (FYM) was obtained from a local source (Agricultural Engineering Sciences college experiments field), air-dried, and finely ground before incorporation into the soils. The manure was applied at three different levels: F0 (Control): No manure (0 g.kg^{-1} soil), F20 (Low level): 20 g kg^{-1} soil, and F40 (High level): 40 g kg^{-1} soil. The farmyard manure was thoroughly mixed with the soils, which were then incubated for forty-five days. The soil was kept moist by adding tap water as needed. After the given time, the soil was air dried, crushed, and sieved through a 4 mm sieve to ensure uniform distribution before being packed into PVC soil columns. A soil sample was taken from each treatment and analyzed for pH, EC, Cd, Pb, after sieving from a 2 mm sieve. Waste water sample was collected from industrial area of Kashi in Semel, Duhok Governate, located on 36^{0}98'53.08" N, Latitude and 42^{0}78'65.61" E, Longitude. Some chemical properties of wastewater (WW) and manure are given in Tables 3 and 1.

PVC columns (10 cm diameter × 30 cm height) were used for the soil leaching experiment. The columns were assembled as follows: a filter paper and a perforated plate were placed at the bottom to allow free drainage. The amount of soil packed into columns was 2.58 Kg, at a fixed bulk density in both treatments, which was 1.3 g cm^{-3}, ensuring uniform compaction. Prior to leaching, the soil columns were saturated from the base with wastes water or tap water for four days using capillary rise; saturation was taken as complete when the upper filter paper was entirely wetted. Each treatment was replicated three times (n = 3), leading to a total of 18 experimental units (2 soil types × 3 manure levels × 3 replicates for waste water treatment), in addition to three extra columns from each soil with three FYM levels using tap water.

The columns were subjected to successive leaching; each leaching event was conducted once a week over a period of ten weeks. During each event a fixed volume of wastewater was applied to each column. The leachate was collected 24 hours after application in polyethylene bottles. The collected leachate was filtered and stored at 4°C until analysis. Each collected leachate sample was analyzed for the following parameters: pH: measured using a digital pH meter; Electrical Conductivity (EC): determined using a conductivity meter, in addition to some cations and anions. Pb and Cd concentrations, measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). All analyses were conducted following standard methods for water and wastewater analysis (APHA, 1976). The factorial experiment was arranged in a completely randomized design (CRD) with two factors: Factor 1: Soil type (2 levels), Factor 2: FYM levels (3 levels: 0, 20, and 40 g kg^{-1} soil).

Table 1. Some characteristics of farmyard manure.

Properties	Units	FYM
pH (1:2)		8.04
EC	dS m^{-1}	0.972
TN	g kg^{-1}	21.85
O.M		291.23
O.C		168.93
Total Cadmium (Cd)	mg kg^{-1}	0.3300
Total Lead (Pb)		5.6800

3. Results and discussion

Tables 2 and 3 show some soil Physicochemical and wastewater properties. S1 soil was richer in clay and had higher CEC and buffering capacity, while the sand content of S2 is higher, with lower CEC. Pb concentration was much higher in S1 than S2. High EC in wastewater indicated a strong potential for effect on soil. The concentrations of Pb and Cd in the farmyard manure were 5.6800 and 0.3300 (mg kg^{-1}) respectively (Table 1).

Table 4 shows the chemical properties and heavy metal content for Semel (S1) and Derabin (S2) soils treated with 20 and 40 (g kg^{-1} soil) of FYM after incubation. The pH values of all samples ranged from 7.93 to 8.04, reflecting the $CaCO_3$ dominance, with slight buffering from FYM. S2F20 had the lowest pH (7.93), while S1F40 reached 8.04; calcareous soils tend to resist drastic pH changes, even under organic additions (Kabata and Pendias, 2001).

Table 2. Some physical and chemical properties of the studied soils.

Soil character	Units	Semel soil (S1)	Derabin soil (S2)
pH		8.13	7.96
EC at 25 C°	dS m^{-1}	0.281	0.502
Ca^{2+}	Soluble ions mmolc L^{-1}	1.9	4.00
Mg^{2+}		1.3	1.01
Na^{+}		0.31	0.16
K^{+}		0.12	0.20
CO_3^{2-}		0	0
HCO_3^{-}		1.86	1.66
Cl^{-}		0.183	0.216
SO_4^{2-}		1.587	3.494
CEC	Cmolc kg^{-1}	28	23
O.M	g kg^{-1}	10.66	14.38
Total $CaCO_3$		147.05	287.7
Active $CaCO_3$		83.1	105
Pb	mg kg^{-1}	1.0247	0.4419
Cd		0.0094	0.0255
Bulk density	g cm^{-3}	1.37	1.38
Clay	g kg^{-1}	557.5	399.5
Silt		387	263
Sand		55.5	337.5
Texture class		Clay	Clay Loam

Table 3. Some properties of the studied wastewater.

Properties	Units	Waste water
pH		8.63
EC at 25 C°	dS m^{-1}	4.29
Ca^{2+}	mmolc L^{-1}	5.21
Mg^{2+}		2.35
Na^{+}		34.883
K^{+}		0.340
CO_3^{2-}		0.933
HCO_3^{-}		3.066
Cl^{-}		1.533
SO_4^{2-}		37.251
COD	mg L^{-1}	4540
BOD		744
Lead (Pb)	mg L^{-1}	0.0276
Cadmium (Cd)		0.0074

The pH of soil pre-incubation was slightly alkaline, typical of calcareous regions, but after incubation, little decrease in pH occurred. FYM maintained alkaline pH; this consistent with (Kabata and Pendias, 2001), who found that high $CaCO_3$ and bicarbonates buffer acid-base fluctuations. While (Park et al., 2011) stated that organic inputs can increase soil pH temporarily during decomposition**.** (Wang and Kuzyakov, 2024) reviewed that organic matter inputs can lead to short-term increases in soil pH due to microbial activity and the release of base cations during decomposition.

Electrical Conductivity (EC) ranged from 1.083 to 1.173 dSm^{-1}, indicating increase in EC value due to FYM application. EC was highest in S2F40 (1.173 dSm^{-1}), suggesting salt accumulation from mineralization of manure. Bhanwaria et al., (2022) observed that the application of organic manures, such as farmyard manure (FYM) and vermicompost, significantly enhanced the soil's electrical conductivity compared to control treatments. The increase in EC was attributed to the decomposition of organic matter, which releases soluble salts into the soil solution.

Table 4. Some chemical properties of the studied soil after incubation period with sheep manure (FYM).

Treatment	p H	EC	Pb	Cd	Ca^{+2}	Mg^{+2}	K^{+}	Na^{+}	Cl^{-}	CO_3^{-2}	HCO_3^{-}	SO_4^{-2}
Units		$dS\ m^{-1}$	$mg\ kg^{-1}$		$mmol_c\ L^{-1}$							
S1F20	8.02	1.163	2.0322	0.0261	6.7	4.7	0.282	1.935	2.55	0.00	3.30	7.767
S1F40	8.04	1.104	1.5479	0.0339	5.8	5.2	0.307	1.826	2.50	0.00	2.80	7.833
S2F20	7.93	1.083	0.9051	0.0300	6.4	4.0	0.307	1.782	2.45	0.00	2.65	7.389
S2F40	8.03	1.173	0.4477	0.0189	6.7	4.6	0.435	1.891	2.00	0.00	3.20	8.426

Sodium concentration was remained stable (1.782–1.935 $mmole_c$. L^{-1}), and Cl^- concentration was also relatively stable across all treatments, but there was a clear increase in their concentrations compared to their initial values. potassium concentration (K^+) increased in the S2F40 treatment, indicating manure contributed to K mineralization. SO_4^{2-} rose sharply in S2F40 (8.426 mmolec. L^{-1}), possibly due to decomposition of sulfur-rich organics. Organic amendments are known to release soluble ions like SO_4^{2-} and K^+ during incubation (Wang et al., 2014).

As shown in Figure 1, Pb concentrations were higher in S1 than S2. In S2 Pb dropped significantly after incubation, showing strong immobilization under F40; this might be due to the high active $CaCO_3$ (Table 1), or FYM might improves Pb immobilization over time (Park et al., 2011). (Mourid, 2014) concluded that the retention of heavy metals depends on the amount of active calcium carbonate and clay content. Moreover, Moreno, (2006) and Sparks, (1995) stated that Pb forms strong inner-sphere complexes with soil particles, especially in calcareous soils. The percentages of increase for Pb after incubation were 49.5% and 33.8% for S1F20 and S1F40, respectively; however, it was 51.2% for S2F20 and only 1.34% for S2F40.

After the 45-day incubation period, cadmium concentrations remained low across all treatments, ranging from 0.0189 to 0.0339 mg.kg^{-1}(Fig.2). Cd increased by 64.1%, 72.3% and 37.7%, in S1F20, S1F40, and S2F20, respectively, after the incubation period; however, S2F40 showed a percentage decrease of 6.31%. The highest Cd concentration was observed in the S1F40 treatment, suggesting possible mineralization or ligand exchange. This aligns with (Hooda and Alloway, 1998), who reported that Cd remains more bioavailable in soil due to its weak sorption affinity, particularly in calcareous soils. Despite Cd's higher mobility compared to Pb, its concentration was still within acceptable post-incubation ranges, indicating only minor risk of leaching under the tested conditions. However, Qadir et al., (2007) stated that saline wastewater may enhance Cd solubility in alkaline conditions.

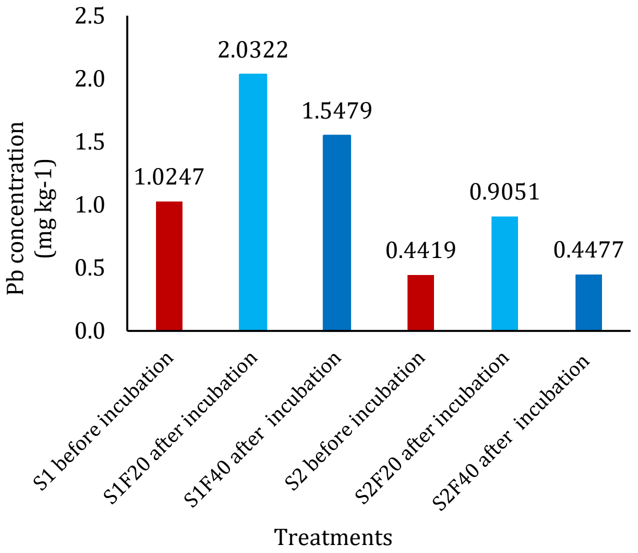

Figure 1. Pb concentration before and after incubation period for the different treatments.

Table 5 illustrates the mean values of pH, EC, Cd, and Pb of ten pour volumes after irrigating the incubated soils with wastewater. In control treatments, pH remained slightly alkaline, consistent with the calcareous nature of the soil. However, wastewater (WW) irrigation lowered pH slightly in both soils, more noticeably in S1, likely due to organic acid input from FYM or ionic replacement effects and nitrification from wastewater nutrients. (Qadir et al., 2007) and (Al-Wabel, 2011) reported that saline or organ-laden irrigation can temporarily reduce pH even in buffered calcareous soils. Both soils leachates showed a pronounced increase in EC under wastewater and FYM application. S2 reached slightly higher EC, indicating more rapid salt accumulation due to its higher sand content and lower buffering capacity. Salinity buildup was most severe under F40WW, a combination of high salt content in wastewater and increased ion retention from FYM. EC rose sharply, with S2F20 WW showing the highest salinity, implying a greater leaching risk. This finding supports the observation of (Ayers and Westcot, 1985), who reported that EC above 4 dS m^{-1}classifies soil as saline, reduce crop performance and increase heavy metal availability.

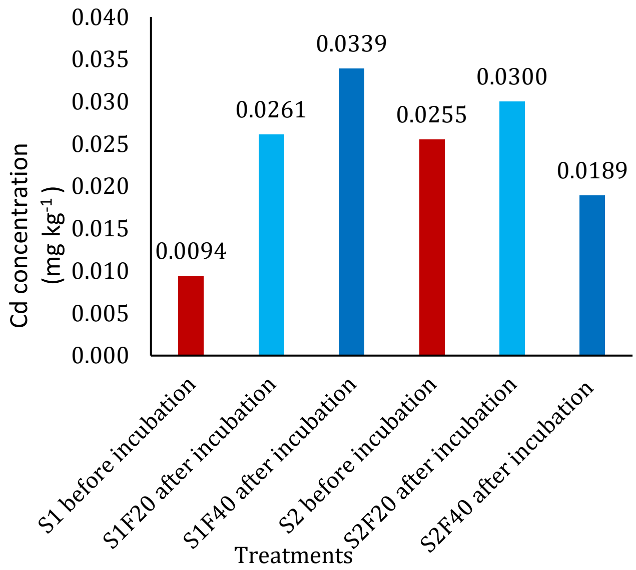

Figure 2. Cd concentration before and after incubation period for the different treatments

Cadmium concentrations slightly decreased under wastewater and FYM, especially in S1. This indicates Cd immobilization through complexation with manure-derived organic matter, or sorption onto mineral surfaces activated by FYM. Cd was more responsive in S1 (the clay-rich soil), showing stronger decreases under FYM and WW than in S2. (McLaughlin et al., 2000) and (Hooda and Alloway, 1998) mentioned that organic matter and clay enhance Cd retention and reducing leaching. While S1 (clayey) showed a steady decline in Cd with both FYM addition and wastewater irrigation, reaching the lowest at S1F20 WW (0.0046 mg kg^{-1}). Cd removal was less efficient in S2 compared to S1. Interestingly, S2F20 control peaked (0.0070 mg kg^{-1}), possibly due to insufficient organic stabilization or complex competition at moderate FYM levels. The stronger response in S1 confirms that texture and CEC improve Cd retention; this consistent with (Hooda and Alloway, 1998) and (McLaughlin et al., 2000). Although Cd mobility controlled by pH, OM, clay, and salinity, the mobility reduced under higher OM and clay content, possibly mobilized through complexation with dissolved organic matter (McLaughlin et al., 2000; Park et al., 2011).

Table 5. Mean values of pH, EC, Cd and Pb of ten pour volumes in the leachates after washing with wastewater

Soil	Treatments	pH	EC	Cd	Pb
Units			dS m^{-1}	mg kg^{-1}	
S$_1$	F$_0$ c	8.45	0.923	0.0068	0.0242
	F$_{20}$ c	8.67	1.655	0.0066	0.0263
	F$_{40}$ c	8.54	1.713	0.0058	0.0274
	F$_0$ ww	8.29	5.118	0.0056	0.0218
	F$_{20}$ ww	8.39	7.254	0.0046	0.0241
	F$_{40}$ ww	8.40	10.717	0.0053	0.0274
S$_2$	F$_0$ c	8.23	1.062	0.0064	0.0231
	F$_{20}$ c	8.63	1.676	0.0070	0.0264
	F$_{40}$	8.63	1.858	0.0068	0.0264
	F$_0$ ww	8.22	10.395	0.0055	0.0264
	F$_{20}$ ww	8.43	12.407	0.0054	0.0252
	F$_{40}$ ww	8.47	11.611	0.0060	0.0232

lead levels were relatively stable across all treatments and less influenced by WW/FYM treatments. Its concentrations remained within a narrow range across all treatments (0.0218–0.0274 mg kg^{-1}). This supports the strong retention of Pb in calcareous soils due to precipitation as Pb-carbonates or sorption to stable organic and mineral surfaces. (McBride, 1995) and (Cao et al., 2009) noted that Pb mobility is inherently low in alkaline soils. (Gubrelay et al., 2013) mentioned that Cd exhibits higher mobility than Pb. However, addition of FYM in S1 increased Pb concentrations, with both the F40 control and WW reaching the same peak (0.0274 mg kg^{-1}), while in S2 wastewater with FYM slightly decreased Pb from (0.0264 to 0.0232 mg kg^{-1}). (Mourid, 2014) reported that cattle manure greatly increased Pb concentrations in leachates. In S1, FYM possibly mobilized Pb through complexation with dissolved organic matter (DOM), while in S2, (the sandy texture), Pb probably immobilized due to carbonate precipitation (Cao et al., 2009; Al-Wabel et al., 2011).

The effect of FYM and WW on Pb mobility in the surface and subsurface of the S1 was shown in Figure 3. The data revealed that across all treatments, Pb concentrations were lower in WW-treated soils than in controls. The most pronounced Pb reduction was in F20, from 1.9124 (control) to 1.1531 (WW). This suggests that FYM with WW had a strong mobilizing effect on Pb under the moderate addition, likely due to a balance between enhanced sorption sites and limited mobilization via dissolved organic carbon (DOC) complexation. The surface Pb concentrations slightly exceeded subsurface values at higher FYM treatments (especially F40), indicates minor Pb mobility under intense organic matter conditions. The availability of heavy metals decreases with increasing retention of heavy metals by clay or calcite and/or soil OM (Elliot & Denny, 1982; Jone and Leyval, 2001; Park et al., 2011).

Considering the FYM effect, control treatments show slight increase in Pb concentration; there were small differences between FYM treatments, i.e., F0 control (0–12 cm) Pb was equal to 1.8958 and F40 control (0–12 cm) Pb was equal to 1.9644. However, under WW, Pb concentrations do not increase linearly with FYM; in fact, F20 WW (0–12 cm) recorded the lowest Pb at 1.1531 and F40 WW increased slightly to 1.4691, suggests that moderate FYM (F20) with WW is optimal for Pb stabilization. (McBride, 1995) and (Alloway, 2013) stated that FYM enhances retention by improving soil structure and binding capacity, releasing dissolved organic carbon (DOC) which can either immobilize or mobilize Pb depending on its type and concentration. The behavior of Pb in the figure suggests dominance of adsorption and precipitation in surface soils and minimal leaching, confirming environmental stability of Pb in these conditions.

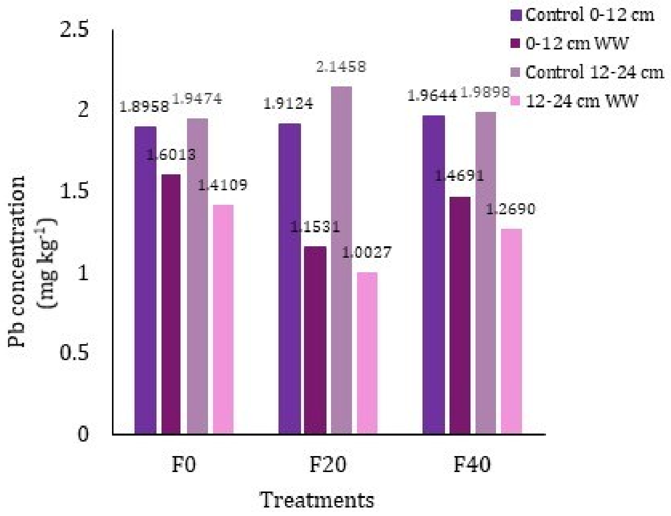

Figure 3. Pb concentrations, surface VS subsurface (S1).

Figure 4 shows the Pb concentration in (S2), which was higher in the surface layer across both control and wastewater treatments. Soluble Pb for F0 increased from 1.2942 to 2.4000 in (0–12 cm) and from 0.5820 to 1.3562 in (12–24 cm). This increase may be due to wastewater-borne organics or Potential re-adsorption enhanced by dissolved organic carbon (DOC) or increased ionic competition from WW. This supports Pb's known low leaching capacity, leading to surface accumulation due to strong affinity for carbonates and organic matter and Limited mobility under alkaline conditions (Al-Wabel et al.,2011; Alloway, 1991).

By taking FYM influence, in general, increasing FYM from F0 to F40 decreases Pb concentrations. Low FYM may not supply enough binding material, while high FYM (F40) may mobilize some Pb through complexation (Cao et al., 2009). F20 emerges as the intermediate, showing moderate soluble Pb-potentially a better balance between mobilization and retention.

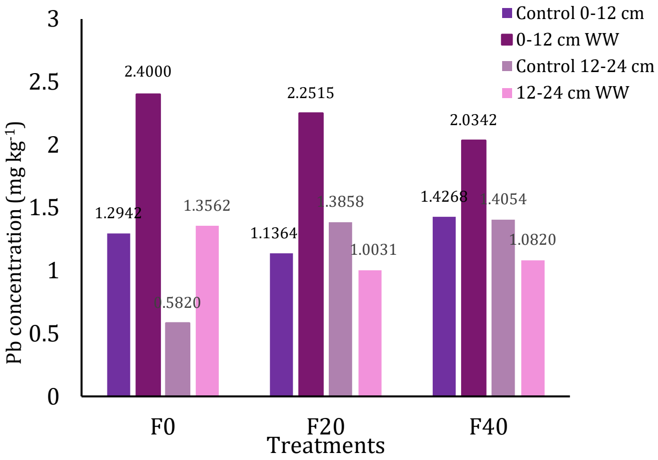

Figure 4. Pb concentration surface VS subsurface (S2).

When comparing soil types, higher mobility of Pb in S2 is probably due to its sandy texture and lower binding capacity, consistent with (Park et al., 2011). While S1 (clayey) retained Pb more consistently but showed less vertical mobility, confirming Pb's preference for surface retention. This finding support those of (Park et al., 2011), highlighting the role of texture and organic inputs in Pb behavior.

As shown in Figure 5, the Cd of S1 increases with wastewater addition. In F0 (0–12 cm), Cd increased from 0.0008 to 0.0047, and in F40 from 0.0056 to 0.0401. This is expected, as Cd in wastewater is in soluble or weakly adsorbed forms and may be mobilized by salinity-induced ion exchange or dissolved organic carbon (DOC) complexation from FYM or wastewater.

Considering depth distribution, Cd concentrations increased in the 12–24 cm layer under wastewater irrigation, especially at F20WW (0.0243 mg kg^{-1}). (Hinz and Selim, 1994) discussed the down movement of metals, and they concluded that Cd was the greatest in soils with lower OM and clay content. Cd's presence at depth (12–24 cm) raises environmental concerns due to its bioavailability and leaching risk in groundwater. This finding supported by (Park et al., 2011) and (McLaughlin et al., 2000) on its behavior in calcareous systems. (Cavallaro and McBride, 1978) found that adsorption of Cd decreased in the presence of 0.01 M $CaCl_2$, and they attributed that to the competition with Ca for adsorption sites.

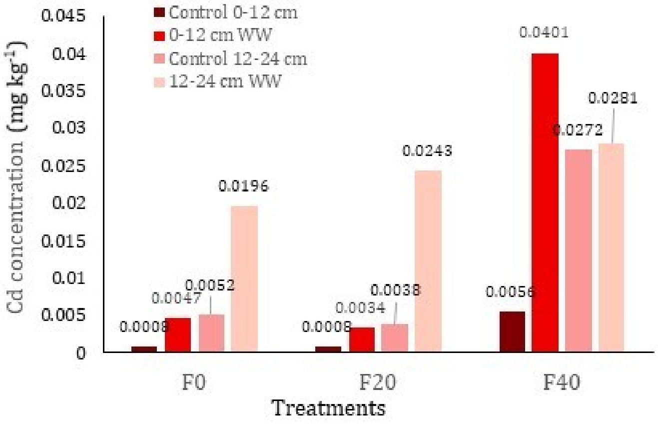

Figure 5. Cd concentration surface VS subsurface (S1).

Taking treatment effect (FYM rates) under control, Cd concentrations were negligible, but under WW treatment, Cd mobility increased with FYM rate, peaking at F40 (0–12 cm) to 0.0401 mg kg^{-1} and at (12–24 cm) to 0.0281 mg.kg^{-1}. Cao et al., (2009) reported that high organic amendments can either stabilize or remobilize Cd, depending on soil saturation, DOC type, and competing ions.

In general, Cd in S2 was also increased under WW treatment (Fig. 6). The increase for F0 (0–12 cm) was from 0.0050 to 0.0117 and for F20 from 0.0010 to 0.0095. F40 treatment behaved differently; there was high Cd in the control (0.0154 mg kg^{-1}), but WW application slightly increased the Cd concentration to 0.0165.

Showing depth trends, in contrast to S1, Cd in S2 was not consistently higher at depth. F0 control had high value Cd (0.0011 mg kg^{-1}) in the (12-24 cm). This mixed trend shows weaker Cd retention in S2's sandy texture. (McLaughlin et al., 2000) and (Park et al., 2011) explain that, Cd is highly mobile particularly in sandy, low-OM soils and DOC from manure can either enhance solubility or promote stabilization depending on saturation and pH. (Mourid, 2014) revealed that in calcareous soil, the CEC and clay content were the most important soil properties affecting Cd adsorption behavior.

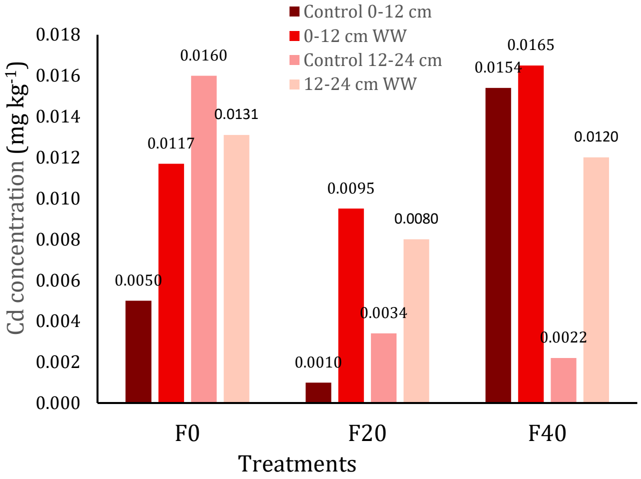

Figure 6: Cd concentration surface VS subsurface (S2).

4. Conclusion

The study showed that Pb is relatively immobile in calcareous soils, especially in clay-rich S1, due to strong sorption to carbonates and organic matter. Moderate FYM application (F20) with wastewater was most effective in stabilizing Pb. In contrast, Cd was more mobile, particularly under wastewater irrigation and higher FYM rates, due to increased DOC and ionic competition. Sandy soil (S2) showed greater metal mobility and leaching risk than S1. Overall, soil texture, FYM rate, and wastewater quality must be carefully managed to minimize heavy metal mobility and environmental risk.

Conflict of interest.

The Authors do not declare conflict of interest.

CRediT authorship contribution statement.

Acknowledgments.

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