Heliyon 6 (2020) e05502

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Do soil amendments used to improve agricultural productivity have consequences for soils contaminated with heavy metals?

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ARTICLE INFO

Keywords:
Copperbelt
Lime
Manure
Mine tailings
Bioavailable metals
Agricultural soil science
Environmental analysis
Environmental assessment
Environmental chemistry
Environmental geochemistry
Environmental hazard
Environmental health
Environmental management
Soil science

ABSTRACT

This study presents an analysis of the effects of manure and lime commonly used to improve agricultural productivity and evaluates the potential for such soil amendments to mobilise/immobilise metal fractions in soils contaminated from nearby mine tailings in the Zambian Copperbelt. Lime and manure were applied at the onset of the study, and their effects were studied over two planting seasons, i.e. 2016-17 and 2017–18. Operationally defined plant-available Cd, Cu, Ni, Pb and Zn in the soil, were determined by extraction with DTPA-TEA (diethylenetriaminepentaacetic acid-triethanolamine) and 0.01 M $Ca(NO_3)_2$, before, and after, applying the amendments. In unamended soils, Cd was the most available and Ni the least. Lime application decreased extractable Cd, Cu, Ni, Pb and Zn. The response to lime was greater in soils with an initially acidic pH than in those with approximately neutral pH values. Manure increased DTPA extractable Zn, but decreased DTPA and $Ca(NO_3)_2$ extractable Cd, Cu and Pb. Combined lime and manure amendment exhibited a greater reduction in DTPA extractable Cd, Ni, Pb, Zn, as well as for $Ca(NO_3)_2$ extractable Cd compared to separate applications of lime and manure. The amendments had a significant residual effect on most of the soil fractions between season 1 and 2. The results obtained in this study showed that soil amendment with minimal lime and manure whilst benefiting agricultural productivity, may significantly reduce the mobility or plant availability of metals from contaminated agricultural soils. This is important in contaminated, typical tropical soils used for crop production by resource poor communities affected by mining or other industrial activities.

1. Introduction

Mine tailings are a significant source of heavy metal contamination for soils in their proximity (Gevorgyan et al., 2015; Li and Yang, 2008). In Zambia, historical and current mining operations have resulted in large areas of land been occupied by mine tailings and other mine waste piles (Leteinturier et al., 2001; Lindahl, 2014). The Copperbelt of Zambia has about 45 tailings dumps/dams covering approximately 9,125 ha of land (Lindahl, 2014). This poses a loss of opportunity for productive land use but, due to land scarcity in urban areas, it is common to see food crops grown around these waste dumps (Kneen et al., 2015; Kříbek et al., 2014; Mapani et al., 2009).

Research has shown that crops grown in soils which are contaminated by heavy metals tend to accumulate greater concentrations of metals compared to those grown in uncontaminated soils (Angelova et al., 2010; Antonijević and Marić, 2008; Chenery et al., 2012). There is a perceived risk to consumers of excessive heavy metal ingestion from such crops. Therefore, determining the concentrations of trace metals in soils that are in close proximity to pollution sources is important for agricultural management and for human health. The total concentration of heavy metals in soil is a useful indicator of the level of soil contamination.

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https://doi.org/10.1016/j.heliyon.2020.e05502
Received 29 July 2020; Received in revised form 21 September 2020; Accepted 10 November 2020

However, the *bioavailability* (availability for plant uptake) of metals is also influenced by transient soil properties such as pH (Lombi et al., 2003) and organic matter content (Angelova et al., 2013). Soil pH is often cited as a 'master variable' affecting the bioavailability of metal redox-speciation and their strength of adsorption to soil colloidal functional groups (Rieuwerts et al., 1998).

Manipulation of pH and the sorption capacity of soils using soil amendments has formed the basis for in-situ immobilisation of heavy metals on contaminated soils (Abd El-Azeem et al., 2013). For land used for growing crops, amendments such as lime, fertilisers, manure or incorporation of crop residues are often used for moisture retention or to improve the availability of essential elements (e.g. Zn, Se) for crop health and for the consumer (Vondráčková et al., 2017; Ligowe et al., 2020; Manzeke Muneta et al., 2020). In Zambia's farming systems, lime and manure are recommended amendments for improving soil acidity and fertility, but usually only small doses are applied by most farmers due to cost constraints. Although several liming (Gray et al., 2006; Vondráčková et al., 2013; Yi et al., 2010) and organic-based materials (Conder et al., 2001; Kubátová et al., 2016) have been reported to affect the bioavailability of metals in soils, their effect, when applied at agronomic rates, on contaminated soils used for crop production is not well documented. Furthermore, there is little understanding of the longevity of the applied amendments as their residual effect is often not evaluated. Lombi et al. (2003), observed an increase in lability of Cd, Cu and Zn when previously lime- and beringite-amended soils were re-acidified.

Various operationally defined bioavailable fractions are extractable with 0.005M DTPA-TEA, 0.05M EDTA, 0.01M Ca salts and 0.43M HNO_3. Chemical extractions intended to extract the entire bioavailable reservoir of metal should be effective enough to extract the labile pool while not mobilising non-labile forms (Garforth et al., 2016). DTPA and EDTA extractions are commonly used to determine plant available trace elements in soils, especially in low pH soils. By contrast, soluble concentrations may be estimated by extraction with dilute solutions of neutral Ca salts. Calcium chloride (0.01 M) is commonly used but chloride ions are known to enhance dissolution of Cd by chloro-complexation (Garforth et al., 2016), thus, calcium nitrate may be a better alternative where Cd bioavailability is of interest. Therefore, this study aimed to investigate the consequences of typical agricultural amendments of lime and manure on the bioavailability of heavy metals in agriculturally productive soils contaminated to varying degrees by the close proximity of mine tailings in the Zambian Copperbelt, building on previous work by Lark et al. (2017) and Hamilton et al. (2020). To achieve this aim, the following objectives were: i) evaluate the bioavailability and mobility of metals in agricultural soils using DTPA- and $Ca(NO_3)_2$ extractants at locations representative of varying degrees of contamination in relation to the mine tailings; ii) determine how the bioavailable metals are affected by the application of lime and manure at typical agricultural amendment rates, and iii) assess the residual effect of the amendments after one growing season.

2. Materials and methods

2.1. Study area

The study was carried out in Mugala village which lies adjacent to a large (711 ha) mine tailings dam (Figure 1a), north of Kitwe town in the Copperbelt province of Zambia (12°47′20″S and 28°06′10″E). The main occupation of the people in this community is subsistence farming; they grow a wide variety of crops including leafy vegetables, tubers and cereals (Nakaona et al., 2019). The farm area is north-west of the tailings dam. The area is in climatic region III of Zambia which is characterised by high rainfall (above 1000 mm per annum). Subsequently, the soils in the area are highly weathered, with low pH and organic matter. The soils in this area are classified as Rhodic Ferrasols according to the World Reference Base (Soil Survey Unit, 1991). Physical and chemical soil properties are shown in Table 1.

2.2. Field experimentation

A field experiment was set up across two seasons commencing in 2016-17 to 2017-18 season. The objective of the experiment was to examine the effects of liming and manuring treatments, and to compare their effects in locations which varied in their proximity to the tailings dam. Four 10 × 25-m fields assigned as B1 to B4 (Figure 1a and 1b), were selected for use, two were close to the Dam (about 100–200 m) and two further from the Dam (about 300–400 m). They were selected on the basis of previous reconnaissance sampling of the land around the Dam farmed by residents of Mugala village (Hamilton et al., 2020; Lark et al., 2017). Four 4.5 × 10 m plots, separated by 1 m, were established in each field. Then each plot was randomly and independently assigned one of four treatments: lime, chicken manure, lime and manure, and the control were no amendment was applied (Figure 1b). The land was prepared as per farmer practice in this area, where crops are planted on ridges. Each plot had six 10 m long ridges, spaced 90 cm apart. Lime (limestone with neutralizing capacity of 98.7% CCE) and chicken manure (designated 'manure') treatments were only applied in the first season (2016/17) and their residual effect was observed in the subsequent season. Both amendments were applied only within the ridge. Lime was applied on 23 November 2016, at a rate equivalent to 2 t ha^{-1}, while manure was applied a month later (21 December, 2016), at a dry weight equivalent to 5 t ha^{-1}.

2.3. Sampling and sample preparation

Topsoil samples (0–20 cm) were collected from each plot, just before the treatments were applied and at the end of each of the two consecutive cropping seasons, i.e. six months after inception (S1) and after 18 months (S2). Soil samples were taken from a sub-plot made by eliminating a meter from either end of each ridge (row) and the two border rows in each plot. Two soil samples were collected per plot from the corners of 90 × 90 cm squares and then combined into one aggregated sample before being transported to the laboratory where they were air dried at room temperature, sieved to <2 mm and stored in paper bags. A sub-sample of each soil for total heavy metals analysis was milled using an agate mortar and pestle and packed in paper bags.

2.4. Soil and manure characterisation

The following soil properties were determined: pH, total organic carbon, loss on ignition (LOI), Dissolved organic carbon (DOC), Fulvic acids (FA), Humic acids (HA), cation exchange capacity (CEC) and particle size. The manure properties determined included: LOI, DOC, FA, HA and pH. For all parameters, except LOI, 2 mm mesh sieved soils were used. The soil pH was determined in 0.01 M $CaCl_2$ suspensions at a soil: solution ratio of 1:2.5, soil organic carbon was determined by the Walkley and Black method (Nelson and Sommers, 1982), LOI was done at 450 °C on 1 g of soil, using a <53 μm particle size. Dissolved organic carbon was determined in 0.01M $Ca(NO_3)_2$ suspension at a soil to solution of 1:12.5, and analysed on a Shimadzu TOC-L Total organic carbon analyser. Fulvic and humic acids were determined using the Shimadzu TOC-L Total organic carbon analyser in suspensions of 0.1M NaOH solutions, at soil to solution ratio of 1:10. The combined FA + HA concentrations were first determined in the suspensions, then HA was precipitated out by adding 1M HNO_3 and FA concentration was determined. Cation exchangeable capacity was determined in extracts of 1N ammonium acetate (Rhodes, 1982) and analysed on a Perking Elmer Analyst 400 Atomic Absorption Spectrometer. Particle size was determined using a laser diffraction particle size analyser (Coulter Beckman LS13 320). A cut-off of 8 μm was used for clay particles to allow samples to be placed on the soil textural triangle originally constructed using sedimentation techniques (Konert and Vandenberghe, 1997).

All chemicals used in the analysis of soils in this experiment were analytical grade with high purity (Sup. Table 1).

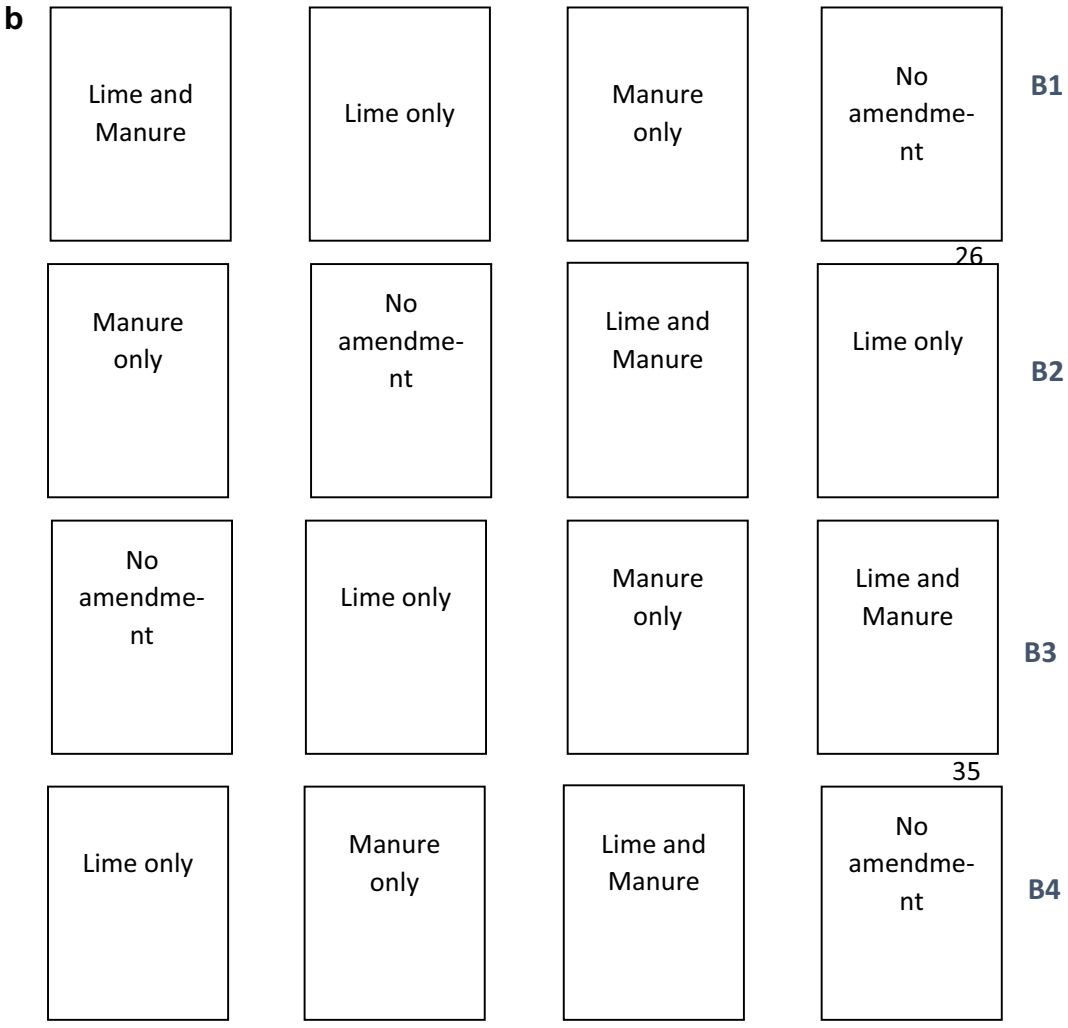

Figure 1. a: Image of the study area showing location of the fields and their proximity to the tailings dam (in gray). Locations B1 and B2 were considered as far from the dam (site D1), while B3 and B4 were considered as close to the dam (site D2); b: Treatments layout per block (B1 – B4).

Table 1. Soil chemical and physical parameters prior to addition of the amendments.

Proximity to tailings dam	Field	Organic carbon (%)	LOI (%)	pH	CEC ($cmol_C/kg$)	Texture (%clay)
Far (~300–400m) (D1)	B1	1.42–1.83	2.6–3.5	5.2–5.6	8.2–13.5	Clay loam (29.8)
	B2	1.55–1.92	3.1–3.7	5.1–5.3	10.1–13.3	Clay Loam (27.2)
Close (~100–200m) (D2)	B3	1.1–2.11	2.4–3.2	6.4–6.7	9.0–13.6	Clay loam (28.5)
	B4	1.55–1.96	3.1–3.6	6.3–7.2	12.1–21.0	Loam (23.9)

Table 2. Average values of M_{Total}, M_{DTPA} and M_{Sol} metal fractions in the soil prior to addition of soil amendments of lime and manure.

Soil fraction	Block	Metal concentrations (four replications±standard error)				
		Cd	Cu	Ni	Pb	Zn
M_{Total} (mg kg^{-1})	B1	0.12 ± 0.01	874 ± 84	36 ± 1.6	9.4 ± 0.5	32 ± 2
	B2	0.11 ± 0.01	935 ± 31	44 ± 1.6	10.2 ± 0.2	32 ± 0.6
	B3	0.11 ± 0.01	947 ± 66	41 ± 0.9	9.6 ± 0.5	26 ± 1.2
	B4	0.09 ± 0.01	979 ± 85	40 ± 1.5	8.1 ± 0.3	24 ± 1.5
	Mean	0.11	934	40.9	9.3	28.5
	Background values for Kitwe (Kříbek et al., 2010)	0.1	289	<5	<10	10
	FAO/WHO max allowable	3	100	50	100	300
M_{DTPA} (mg kg^{-1})	B1	0.04 ± 0.003	128 ± 10	0.04 ± 0.002	0.6 ± 0.02	1.7 ± 0.1
	B2	0.03 ± 0.003	140 ± 12	0.03 ± 0.005	0.6 ± 0.04	1.4 ± 0.1
	B3	0.04 ± 0.002	173 ± 13	0.06 ± 0.008	0.5 ± 0.02	1.0 ± 0.2
	B4	0.03 ± 0.002	226 ± 6	0.03 ± 0.011	0.4 ± 0.1	1.3 ± 0.2
	Mean	0.03	167	0.04	0.5	1.4
M_{Sol} (µg L^{-1})	B1	0.32 ± 0.1	72 ± 13	1.54 ± 0.43	0.05 ± 0.01	19 ± 3.8
	B2	0.45 ± 0.1	68 ± 9	1.79 ± 0.44	0.07 ± 0.01	17 ± 4.5
	B3	0.11 ± 0.1	37 ± 7	0.60 ± 0.1	0.06 ± 0.02	27 ± 5.5
	B4	0.37 ± 0.1	41 ± 15	2.92 ± 0.5	0.59 ± 0.11	18 ± 6.5
	Mean	0.31	55	1.71	0.19	20.3
	Manure	0.002	2.09	1.03	0.048	17.8

Table 3. Soil pH and organic matter content (means of four replicates±standard errors) at baseline and at the end of each season (S1 and S2).

*Treatment	pH			LOI (%)		
	Baseline	S1	S2	Baseline	S1	S2
L0M0 (control)	6.0 ± 0.48	6 ± 0.47	6 ± 0.50	5.39 ± 0.32	5.44 ± 0.32	5.01 ± 0.49
L1M0 (lime)	5.6 ± 0.30	6.6 ± 0.18	6.4 ± 0.26	5.43 ± 0.44	5.73 ± 0.26	5.03 ± 0.67
L0M1 (manure)	6.0 ± 0.47	6.1 ± 0.41	6.1 ± 0.48	4.9 ± 0.25	6.12 ± 0.42	6.18 ± 0.41
L1M1 (lime/manure)	6.0 ± 0.40	6.5 ± 0.27	6.9 ± 0.18	5.4 ± 0.44	6.28 ± 0.32	6.21 ± 0.63

* Treatments do not apply to the baseline data.

2.5. Acid digestion for total soil metal concentration (M_{Total})

Soil samples for total metal analysis were acid-digested on a block digestion unit and analysed using ICP-QQQ-MS (Agilent 8900 ICP-QQQ-MS) as described in Watts et al. (2019) and Sach et al. (2020). Soil samples (0.25 g) were dissolved in a mixed acid solution (2.5 mL HF, 2 mL HNO_3, 2.5 mL H_2O_2) on a programmable hot block. Subsequent total elemental analyses of the acid digests were carried out using ICP-MS. A collision cell gas (He) was used to reduce polyatomic interferences for Ni, Cu, Zn, Cd, and Pb; internal standards employed to correct for signal drift included Sc, Ge, Rh, In, Te and Ir. An ISIS-3 sample introduction loop (Agilent Technologies, USA) was used to minimise the volume of sample (500 µL) presented to the ICP-MS to reduce the risk of carryover between samples. Limits of detection are presented in Sup. Table 2 at the top of each column and analytical performance data are presented in full for certified reference materials at the bottom of each column for each determinant demonstrating good analytical performance (BGS 102, BCR-2 and 2711).

2.6. DTPA extractions (M_{DTPA})

Five grams of soil were extracted with 10 ml of DTPA-TEA-$CaCl_2$ solution (designated 'DTPA') according to the method of Lindsay and Norvell (1978). Concentrations of Cd, Cu, Ni, Pb and Zn were determined by ICP-QQQ-MS with matrix-matched calibration and quality control standards.

2.7. $Ca(NO_3)_2$ extractions (M_{Sol})

Two grams of soil were suspended in 25 ml of 0.01M $Ca(NO_3)_2$ solution and equilibrated on a shaker for 3 days before centrifuging and filtering to <0.2 µm. Concentrations of Cd, Cu, Ni, Pb and Zn were

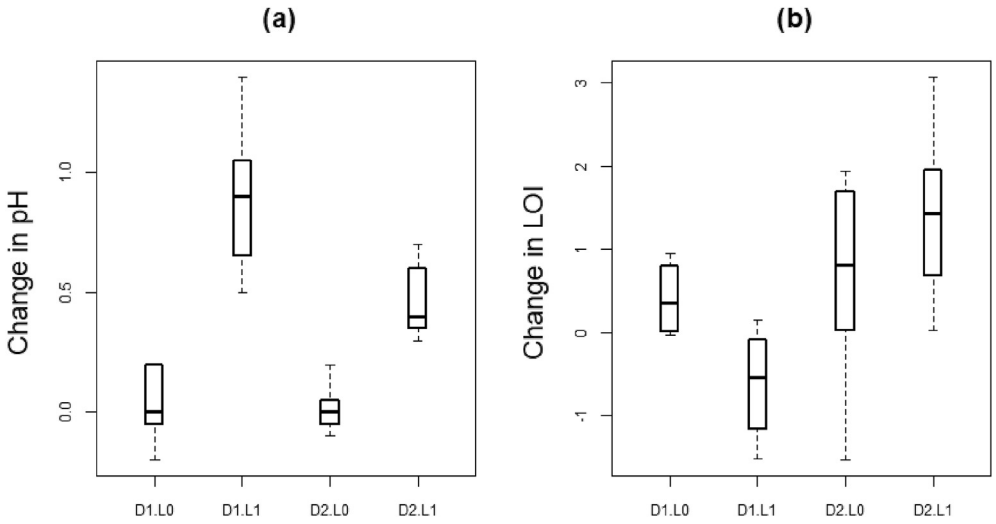

Figure 2. Boxplot showing response of a) pH and b) LOI to the interaction of lime and the distance to the tailings (Dam). D1 and D2 represent blocks which were far and close to the tailings respectively, L0 and L1, represent plots without and with lime treatment respectively. The change was calculated as the difference from baseline values, therefore values above zero signify an increase and vice versa.

determined by ICP-QQQ-MS with matrix-matched calibration and quality control standards.

2.8. Distribution coefficient (Kd)

The distribution coefficient which is an index describing the distribution of metal ions between the solid and the solution phase in soil was determined using the following equation.

$$Kd = \frac{M\_DTPA}{M\_Sol} \quad \text{Eq. 1}$$

Where Kd is the distribution coefficient in L kg^{-1}, M_DTPA (mg kg^{-1}) and M_Sol (mg L^{-1}) are heavy metal concentrations determined by DTPA and $Ca(NO_3)_2$ respectively.

2.9. Data analysis

Data were analysed on the R platform (R Core Team, 2017). Because of the hierarchical structure of the experiment, with the treatments randomised within each field, and replication for the investigation of the proximity to the tailings dam (designated the 'Dam' effect) at the level of field, the data were analysed with a linear mixed model using the lme function in the nlme library for the R platform (Pinheiro et al., 2017). Random effects were 'Field', and 'Plot within Field' and the fixed effects were 'Dam' (close or far), 'season', 'lime', 'manure' and their interactions. The response variables of interest were soil pH, organic matter and the different soil-metal fractions. Differences between each season and the baseline were computed for each variable to determine the change (either reduction or increase).

3. Results

3.1. General soil characteristics

Table 1 shows the range of some initial chemical and physical characteristics of the soils in each field. The organic carbon content of the soil ranged from moderate to high (Hazelton and Murphy, 2007). The cation exchange capacity (CEC) ranged from low to moderate and the pH range (5.1–7.2) was moderately acidic to neutral (Hazelton and Murphy, 2007). The clay content of the soil ranged from around 24%–30%.

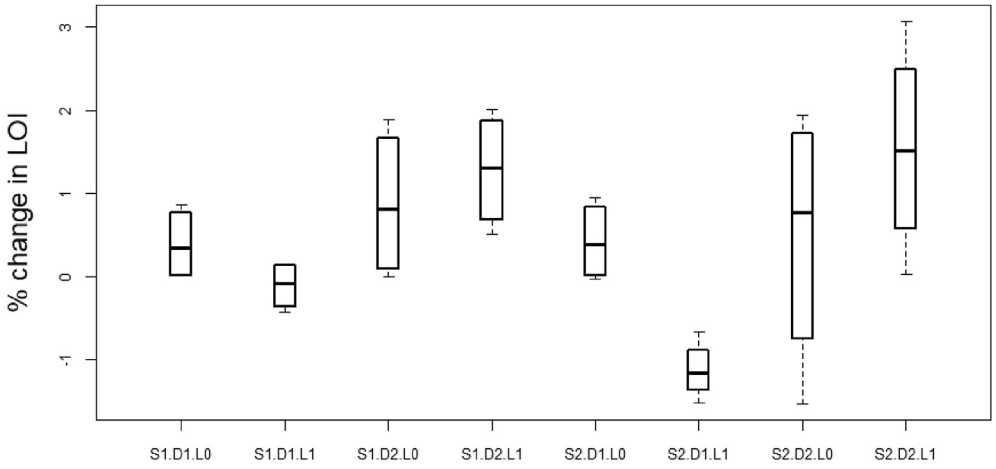

Figure 3. Boxplot showing response of LOI to lime, per season (S) with distance to the tailings (D). S1 and S2 represent seasons 1 and 2, D1 and D2 represent blocks which were far and close to the tailings, L0 and L1 represent plots without and with lime treatment respectively. The change was calculated as the difference from baseline values, so values above zero signify an increase and vice versa.

Table 4. DOC and humic acid composition of manure and soil before application of the amendments.

Parameter	Manure	Soil
DOC (mg L^{-1})	1390	2.6
FA (mg kg^{-1})	39,100	1,490
HA (mg kg^{-1})	26,300	5,210

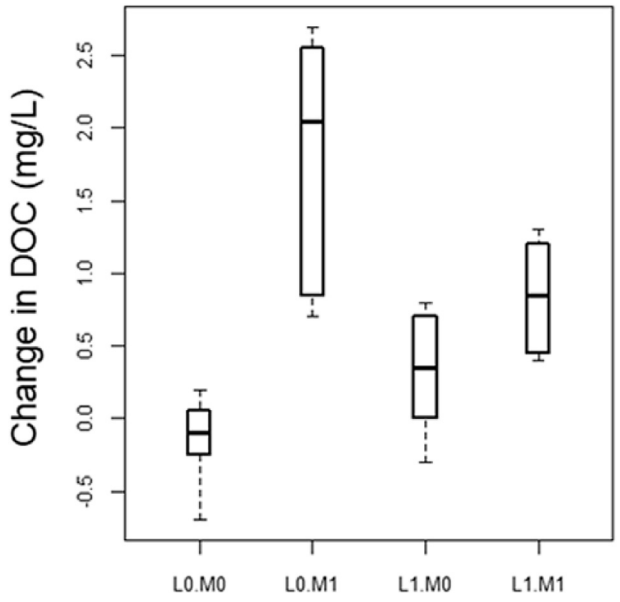

Figure 4. Boxplots showing the response of soil DOC to the treatments. L0.M0, L1.M0, L0.M1 and L1.M1 represent zero, lime, manure and, lime and manure interaction plots respectively. The change is calculated as the difference from baseline values, so values above zero signify an increase and negative values, a reduction. The treatment effects are inferred by comparison to the zero-treatment plot.

Fields B1 and B2, which were further from the tailings dam, were in the moderately acidic pH range (pH 5.1–5.6), which is expected in unamended Ferralsols. The fields which were closer to the tailings dam (B3 and B4) were, however, in the slightly acidic to neutral pH range (6.3–7.2), contrary to expectation for this soil type. This is because of proximity to the tailings which are treated with lime prior to disposal in the dam. Soil organic carbon content did not show a systematic trend but displayed very little variation across the blocks.

3.2. Heavy metal concentrations of soil before application of lime and manure

Table 2 shows the average concentrations of metals extracted by acid digestion (M_{Total}), DTPA (M_{DTPA}) and 0.01 M $Ca(NO_3)_2$ (M_{Sol}) representing total, exchangeable and soluble fractions respectively. Average background total concentrations of the soil in Kitwe according to (Kříbek et al., 2010) have also been included.

3.3. Effect of lime and manure on soil chemical properties and bioavailable metals

Lime was applied at 2 t ha^{-1} in order to raise the pH of the most acidic soils in the study into the agronomic range (pH > 6 but not exceeding 7.5), while manure was applied at 5 t ha^{-1} Table 3 presents the mean values of pH, and LOI as an estimate of organic matter, in the soil before and after application of amendments. The statistical effect of lime and manure on the soil chemical properties are shown in Sup. Tables 3 and 4.

3.3.1. Soil pH

Table 3 shows soil pH values of the baseline samples and for seasons S1 and S2. Soil pH was significantly increased by lime application ($p \leq 0.0001$) while the effects on pH of manure, and the interaction of lime and manure, were not significant (Sup. Table 3). In season S1, lime increased pH from 5.6 to 6.6, and to 6.4 in S2. There was a significant interaction of lime and Dam ($p = 0.0266$), with a larger response to lime in blocks further from the tailings (D1) compared to blocks which were closer (D2), as shown in Figure 2a. This is because of a much lower initial pH in D1 than in D2 which resulted in a larger response to liming. There was no significant main effect of manure on soil pH.

3.3.2. Soil organic matter

Soil organic matter was estimated by LOI. Liming did not have a significant effect on LOI, while manure ($p = 0.0004$) increased it, from 4.9 % in the baseline, to 6 % in both seasons S1 and S2 respectively (Table 3). The increase in soil LOI from manure treatment is due to the high LOI of the manure (47 %). The estimate of total soil organic matter, from LOI measurements, of chicken manure reported in this study is in agreement with 50 % organic matter content reported by Duruigbo et al. (2007). There was no significant interactive effect of lime and manure on LOI.

The response of LOI was significantly different between plots which were further (D1) and closer (D2) to the tailings. As shown in Figure 2b, treatment with manure led to a larger increase in LOI in plots which were closer to the tailings than those which were further. Otherwise, liming led to contrasting effects between D1 and D2, with a reduction in LOI being seen in D1 and no change in D2 (Figure 3). This is perhaps an effect of stimulated mineralization or solubilization of organic matter as pH was increased in the acidic soils of D1. Curtin et al. (1998), observed a rapid increase in mineralization rate of organic matter when acidic soils (pH 5.7) were limed, but this rate declined over time at higher pH.

The DOC composition of the manure used in this study is shown in Table 4. Manure increased the DOC concentration (Figure 4), but did not change the distribution of FA and HA of the soil.

3.3.3. Residual effect of the treatments

There were no significant main effects of the season; the average soil pH and organic matter content did not differ between seasons S1 and S2. However, organic matter (LOI) was larger in season S2 than S1 in limed plots in D2, whereas it was smaller in S2 than S1 in D1, as shown in Figure 3.

3.3.4. Bioavailable metals

Figure 5(a-e) shows values of M_{DTPA} for Cd, Cu, Ni, Pb and Zn in soil subject to the various treatments. For Cd_{DTPA}, manure ($p = 0.0062$) and the interaction of lime and manure ($p = 0.0032$) had significant effects, while lime alone did not (Sup. Table 5). Manure, with, and without, lime reduced Cd_{DTPA} compared to its baseline values, suggesting that the treatments had immobilised Cd. Cd_{DTPA} was reduced by 2 % and 11 % in season S1, and 13 % and 21 % in S2 by manure and manure with lime respectively. A significant interaction of lime and the Dam was realised, with a reduction in D1, and an increase in D2 (Figure 6a).

Significantly lower Cu_{DTPA} was observed in the limed ($p = 0.0003$) soils than in the baseline soil samples, while manure had no significant effect. A significant interaction of lime and manure ($p = 0.0001$) was also observed (Sup. Table 6). This implies that Cu was immobilised by lime addition and the combined use of lime and manure. The reduction caused by lime was 8% in season S1 and 7% in S2; the combination of lime and manure reduced it even further, by 20% in both seasons.

No significant main effects of either lime or manure were observed for Ni_{DTPA} but their interaction was significant with a p-value of 0.0067 (Sup. Table 6), again suggesting a synergistic effect of the amendments. In season S1, Ni_{DTPA} was increased by 14%, while the opposite was

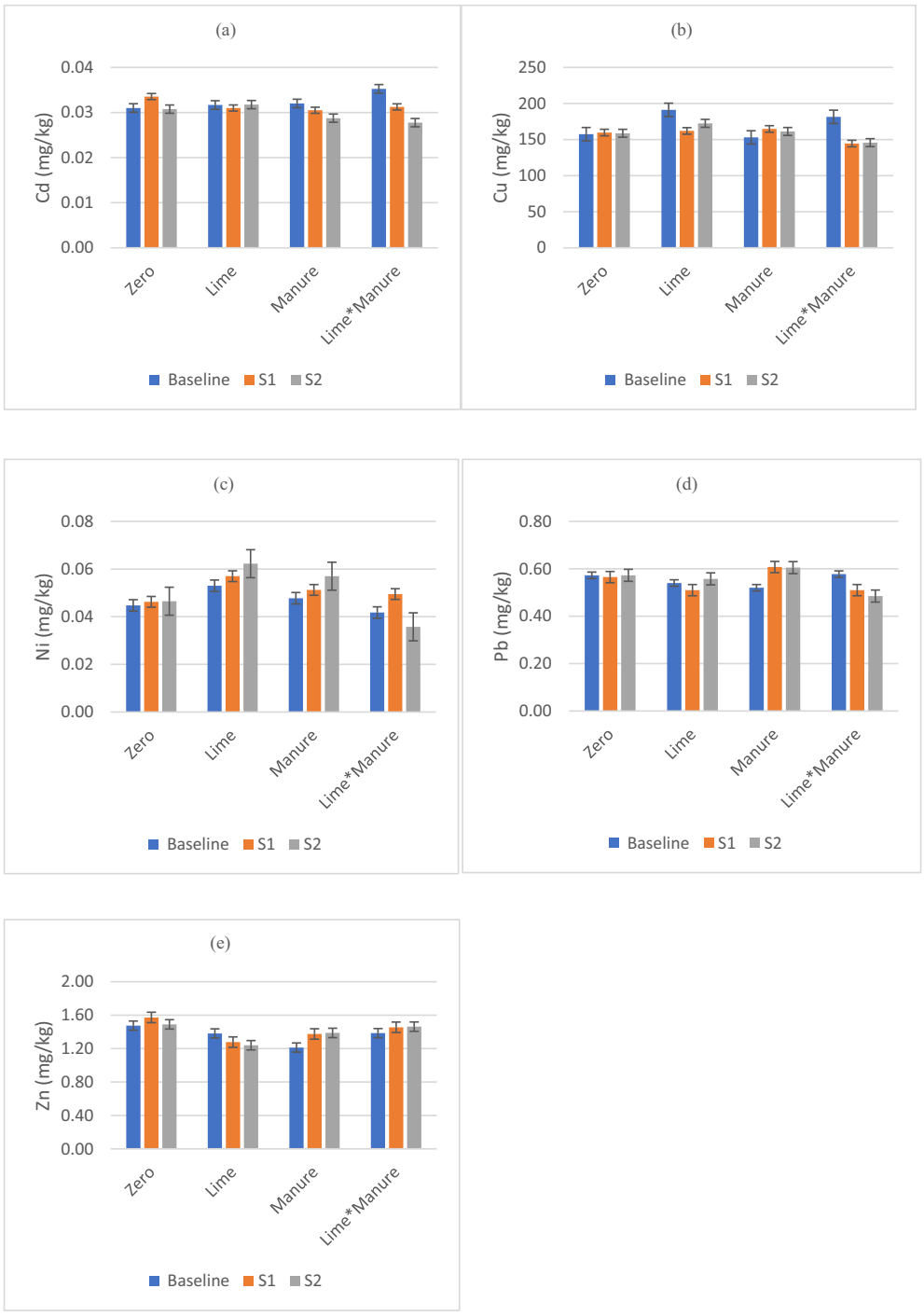

Figure 5. (a–e): M_{DTPA} concentration in each treatment. S1 and S2 represent season 1 and 2 respectively. Treatment effects are inferred from the comparison of the concentration obtained in a season under a treatment to its baseline concentration.

observed in S2. Similarly, to Cd_{DTPA}, Ni was immobilised by liming in D1 and mobilised in D2 (Figure 6b).

Manure showed a significant increase in Pb_{DTPA} ($p = 0.05$), while the effect of lime alone was not significant (Sup. Table 8). A significant interaction of lime and manure ($p = 0.0008$) was also observed. Relative to their baseline, manure increased Pb_{DTPA} by 5% in both seasons, while the combination of lime and manure led to reductions of 7% and 15% in S1 and in S2 respectively. Similarly to Cd_{DTPA} and Ni_{DTPA}, a significant interaction of the Dam with lime was observed for Pb_{DTPA}, with contrasting effects of lime between D1 and D2 (Figure 6c).

Only manure had a significant effect ($p = 0.0334$) on Zn_{DTPA} (Sup. Table 9). Manure increased Zn_{DTPA} by 18% and 19% in seasons S1 and S2, respectively. These results suggest that Zn in the soil was complexed by organic matter. Otherwise, the manure applied in this study had a large total concentration of Zn (434 mg/kg) relative to the concentrations in the soil, therefore, it is plausible that manure could account for some of the increase in Zn_{DTPA}. There was a significant main effect of the Dam on Zn_{DTPA} where an increase was seen in D2 while no change was seen in D1 (Figure 6d). This result could be attributed to enhanced solubilisation of organic matter in the high pH soils in D2, therefore releasing DOM complexed Zn.

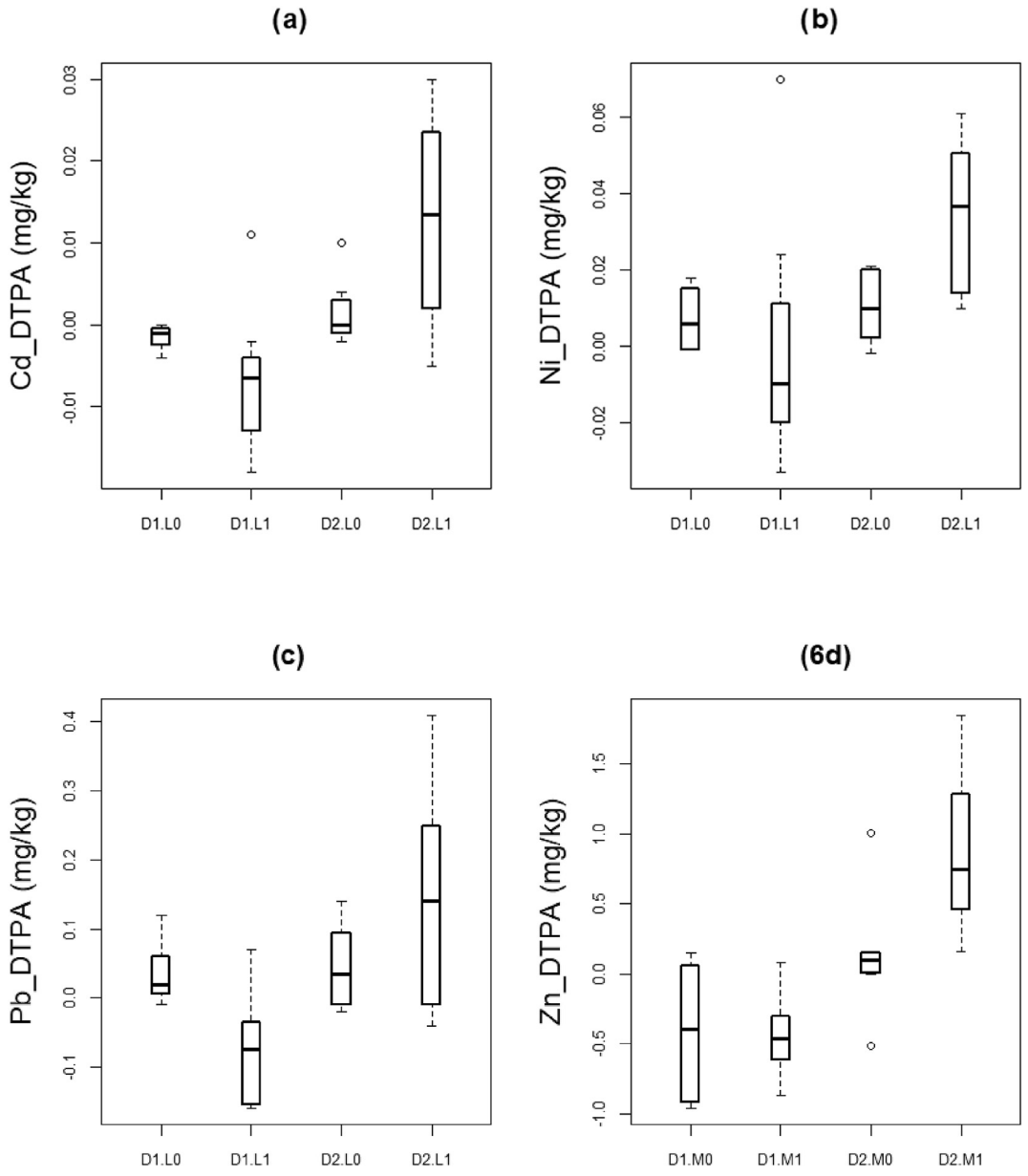

Figure 6. (a–d): Box plots showing response of: Cd_{DTPA} (a), Ni_{DTPA} (b), Pb_{DTPA} (c) to the interaction of lime and the Dam, and Zn_{DTPA} (d) to the interaction of manure and the Dam. D1 and D2 represent blocks which were far and close to the tailings respectively, L0 and L1, and M0 and M1 represent plots without and with lime (L)/ manure (M) treatment respectively. The change was calculated as the difference from baseline values, therefore values above zero signify an increase and vice versa.

No significant differences were observed between season S1 and S2 except under manure for Cu_{DTPA}. This implies that the treatments had a significant residual effect within the timeframe of the study.

Similar trends of the effect of the amendments on M_{DTPA} were observed for M_{Sol} (Sup Tables 10–14).

3.3.5. Distribution coefficient

Figure 7 shows the seasonal Kd of Cd, Cu, Ni, Pb and Zn for each soil amendment determined according to Eq. (1). The values for the various metals varied over two orders of magnitude and were approximately 30–90 L kg^{-1} for Cd, 800–7000 L kg^{-1} Cu, 15–150 L kg^{-1} Ni, 1500–4000 L kg^{-1} Pb and 50–300 L kg^{-1} Zn.

4. Discussion

4.1. Bioavailability of unamended soils

All values of M_{Total}, except for Cu_{Total}, were below the FAO maximum permissible limits for agricultural soils (FAO/WHO, 1984; WHO, 1993). From the background values shown, it is clear that significant contamination of soils with Cu has occurred, while the other metals are close to background concentrations. When expressed as a proportion of M_{Total}, % M_{DTPA} decreased in the order Cd > Cu > Pb > Zn > Ni. Thus, Cd was the most extractable metal with DTPA, ranging from 20-36 % of Cd_{Total}, while Ni was the least extractable (Ni_{DTPA} < 1 %). A similar trend was also reported by Römkens et al. (2009) and Izquierdo et al. (2012) who

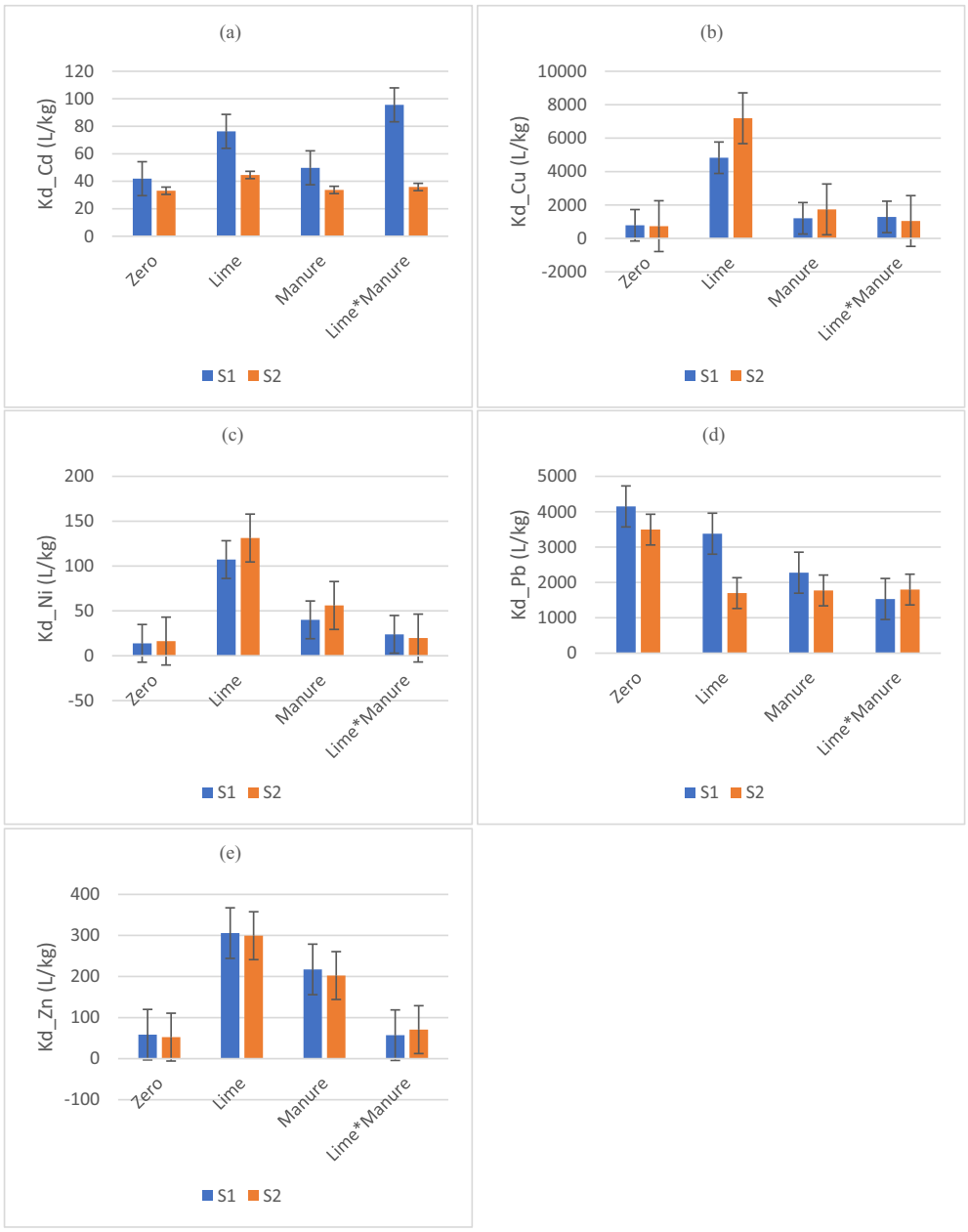

Figure 7. (a–e): Distribution coefficients (Kd) of Cd (a), Cu (b), Ni (c), Pb (d), Zn (e) under each treatment, per season. S1 and S2 represent season 1 and 2 respectively.

used isotopic dilution to determine 'labile' heavy metal concentrations, or 'E-value', in soils (M_E). Cadmium is reported to have a relatively low affinity for most binding phases in the soil compared to other trace metals (Shaheen, 2009) and is therefore the most available even in soils with only background concentrations (Liu et al., 2013). Contrastingly, Ni has been reported to bind strongly to amorphous iron oxides (Malinowska, 2017) and so considering that the soils for this study are rich in Fe oxides, this could explain the low extractability of Ni_{DTPA} seen. Cu_{DTPA} was 13–22 % of Cu_{Total}, while $\%Pb_{DTPA}$ and $\%Zn_{DTPA}$ were 4–7 % and 3–7 %, respectively. The proportion extracted by 0.01 M $Ca(NO_3)_2$ solution (M_{Sol}) decreased in the order: $\%Cd_{Sol} > \%Zn_{Sol} > \%Cu_{Sol} > \%Pb_{Sol} \geq \%Ni_{Sol}$.

The effect of organic matter on contaminant or nutrient availability is highly influenced by the different forms or fractions of organic matter. The reactivity of DOC is influenced by the proportion of fulvic and humic acids contained within it (Boechat et al., 2016). Fulvic acids (FA) are soluble at all pH conditions while humic acids (HA) are only soluble at alkaline pH values. Both humic substances are able to complex cations via their surface functional groups which include carboxyl and hydroxyl groups, but FAs are more chemically reactive as they contain a greater density of these surface functional groups than HAs. Schnitzer and Kerndorff (1981) cited pH as a determining factor regarding whether FA forms soluble or insoluble complexes with metals. According to its HA:FA ratio of 0.7, it can be classified as 'fulvic-humic', while the soil is 'humic' at a ratio of 3.5 (Angelova et al., 2013). With an increase in DOC of the soil due to manure, the solubility of heavy metals which are complexed with it is expected.

4.2. *Effect of amendments on bioavailable metals*

Lime and manure increased the pH and sorption capacity of the soil respectively, thereby enhancing the adsorption of the heavy metals into specific 'unavailable' soil fractions. An increase in pH favours adsorption and precipitation of metal hydroxides and carbonates (Lombi et al.,

2003). The reduction of Cd_{DTPA} by manure was greater when lime was present. Kumarpandit et al. (2017) also reported immobilisation of Cd by the combination of lime and manure which translated into reduced uptake by spinach grown in contaminated soils. The immobilisation of Cd_{DTPA} by organic amendments was also reported by Angelova et al. (2013), who attributed it to an increase in the cation exchange capacity (CEC) of the soil as the organic matter content increased. Immobilisation by lime in the presence of manure which was also observed for Cu, Ni and Pb is likely an indication of the formation of more stable metal-organo complexes. Angelova et al. (2013) reported a reduction in Cu_{DTPA}, in compost and vermicompost treated soils, attributed to formation of stable complexes with HA, which are less soluble than FA. Immobilisation of Ni by increasing the pH through liming and complexation with organic matter has been reported (de Macedo et al., 2016; Malinowska, 2017; Ren et al., 2015; Wallace et al., 1977; Weng et al., 2002). However, Pb is preferentially complexed by DOM which may explain the increase in Pb_{DTPA} under the manure treatment. Weng et al. (2002) noted that complexation with DOM was more significant for Cu and Pb than for Cd, Ni and Zn. All the studied heavy metals except Zn were immobilized by the combination of lime and manure, and in Cd, Cu and Pb which were also affected by application of the single amendments, the combination of lime and manure had a much larger effect than with either lime or manure alone. This shows a synergistic effect of lime and manure in reducing the availability of heavy metals. The average reduction in M_{DTPA}, for seasons S1 and S2, by combined lime and manure followed the order Cu_{DTPA} (20%)> Cd_{DTPA} (13%)>Pb_{DTPA} (11%)>Ni_{DTPA} (7%).

The effect of lime on Cd_{DTPA}, Ni_{DTPA} and Pb_{DTPA} was however contrasting between D1 and D2, with D1 being reduced and an increase or no change in D2. In the acidic soils of D1, the increase in pH due to liming led to increased adsorption of the heavy metals, while in the higher pH soils in D2, liming did not advantage adsorption of heavy metals. These results suggest that pH was the predominant immobilising factor in acidic soils, while at pH > 6, DOM was more important.

4.3. Distribution coefficient (Kd)

Metal elements with larger Kd values have more ions adsorbed onto the soil solid phase than in the soil solution while smaller Kd values imply that there are more ions in solution phase than on the adsorption surfaces. In unamended soils, the order of Kd values of the studied metals was; Pb > Cu > Zn > Cd > Ni. This index is important for determining the fate of heavy metals in the soil environment (Carlon et al., 2004; Yuan, 2003). The amendments applied led to an increase in the Kd of Cd, Cu, Ni and Zn (Figure 7). This shows that the amendments caused an increase in the adsorption of the metals, which would reduce their mobility and availability for uptake by plant. Conversely, the Kd for Pb was reduced in amended soils. This shows that more Pb was released into the solution which would then be available for plant uptake and/or leaching down to groundwater.

5. Conclusions

The most bioavailable metal in the studied soils was Cd, which had a DTPA extractable quantity of about 20–36% of the total and Ni was the least at <1%.

The extractable metal concentrations were reduced by liming whereas a binary effect of manure was observed, causing an increase in Pb and Zn, and a decrease in Cd. The increase in Pb and Zn caused by manure addition may increase their availability to crops and therefore rise in the food chain. However, a synergistic reducing effect of lime and manure was seen for all metals. This is important for agriculture in this area as the quantities of lime and manure which were applied in this study were typical of local practice for agricultural amendments and did not adversely affect agronomic soil properties and so should not threaten crop production. The amendments were more effective in reducing extractable metals in soils with pH ≤ 5.6, and therefore, even at agriculturally applied rates, have benefits in immobilising heavy metals in contaminated tropical soils such as Oxisols and Ultisols. The amendments had a positive residual effect on DTPA extractable metals.

It is apparent that organic amendments in combination with liming may reduce the bioavailability of heavy metals as shown in this study. Therefore, in instances where there is little option but to farm crops on contaminated soils, lime and manure applied at lower agricultural rates, may still reduce plant availability of harmful elements without adversely affecting the soil's productivity.

Declarations

Author contribution statement

Belinda Kaninga, Michael J. Watts, Murray Lark; Elliott M. Hamilton: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Benson H. Chishala, Kakoma K. Maseka, Godfrey M. Sakala; Amanda Gardner: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Andrew Tye, Scott D. Young: Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the Royal Society-Department for International Development (DfID) for funding the work under the Project-AQ140000, “Strengthening African capacity in soil geochemistry for agriculture and health’’.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2020.e05502.

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