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The Residual Cu and Zn in Tropical Soils Two Decades after Amendment with Industrial Waste, Calcite and Cassava-Leaf Compost

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ABSTRACT

Heavy metal concentrations in soils may decrease over time, correlating with key soil variables such as pH, cation exchange capacity (CEC), clay, and organic carbon (organic C) content. The residual Cu and Zn were studied in tropical soils about 20 years after amendment with heavy metal containing industrial waste. Soils amended one time in 1998 with industrial waste, calcite, and cassava-leaf compost were employed as models and analysed for topsoil and subsoil Cu, Zn and several soil properties including pH, CEC, clay and organic C content in 2018. The highest Cu and Zn were detected in high heavy metal plots with the highest waste amendment, lowered by calcite and/or compost. The lower subsoil Cu and Zn were strongly affected by topsoil Cu and Zn. Single variable linear regression showed that the soil Cu and Zn had good relationships with the soil organic C and clay content. The inclusion of soil pH, CEC, clay and organic C content in multiple linear regression analysis improved their correlation coefficients, in which the correlation coefficients of Zn were higher than Cu. Long-term reaction in soils reversed the positive correlation of Cu – pH and Zn – pH in 1998 to the negative correlations in 2018. The soil Cu can be predicted with 33.8% accuracy with equation $Cu = -61 - 11.6 (pH) + 0.47 (CEC) + 2.71 (Clay) + 41.7 (Org\ C)$ ($R^2 = -0.338$) while the soil Zn with accuracy 39.2% by equation $Zn = -26.2 - 8.73 (pH) - 0.276 (CEC) + 1.95 (Clay) + 24.0 (Org\ C)$ (R^2). This results could be utilized to monitor the dynamic of Cu and Zn contamination in soil.

Keywords: Heavy Metals; CEC; Clay; Organic C; Soil Reaction

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1. Introduction

Labile fractions of heavy metals in soils are controlled by soil adsorption capacity; therefore, they are probably greatly affected by soil cation exchange capacity (CEC), clay content, organic carbon (organic C), and, most importantly, by soil pH that greatly affect the soil clay mineral and organic material surfaces and CEC^[1–12]. The increase in soil pH, clay, organic C and CEC increases the soil adsorption capacity and, thereby, decreases the soil heavy metal labile fractions. The soil heavy metal labile fractions include the soluble and low energy bound adsorbed and precipitated heavy metal cations. Therefore, numerous evidence revealed that the extractability and mobility of soil heavy metals are low in soils treated with lime and/ or organic matter^[2,8–11,13–17]. Salam et al. (2021)^[1] demonstrated that the high Diethylene Triamine Penta Acetic Acid (DTPA) extracted Cu and Zn in tropical soils amended one time with heavy metal-containing waste was consistently lowered by 5 Mg ha⁻¹ calcite and/or by 5 Mg ha⁻¹ cassava-leaf compost observed for time intervals of 3, 5, 10 and 20 years after amendment^[11]. Even though the total extracted Cu and Zn decreased with time, the calcite and compost effects were consistently observed for 20 years.

The above reasoning underlines the fact that high concentrations of heavy metals of industrial waste origin were significantly lowered by calcite and/or organic compost amendment^[11]. The presence of higher amount of soil negative charges due to the synergic effects of calcite and the functional groups of casava-leaf compost may have increased the immobilization of heavy metal cations by adsorption and precipitation processes. Lately, it has also been reported that biochar, a pyrolyzed plant material, was also proven to decrease the soil heavy metal labile fractions, as suggested by several soil workers^[4,10,16,18–22]. It is suggested that biochar shows high porosity and potential to increase soil pH and negative charges that may enhance soil adsorption capacity. However, unlike biochar, the decreasing effects of calcite and organic compost were shown to attenuate with time, as shown by^[11,13]. Salam et al. (2021) clearly revealed that the residual Cu and Zn in the 60 Mg waste ha⁻¹ plots decreased over 20 years to 17–53% for Cu and to 12–33% for Zn^[11]; their concentrations were

consistently lower with lime and/or compost treatments. These changes in soil heavy metal labile fractions relate to the decay of organic matter and the decrease in soil pH due to cation leaching to soil sublayers, metal movement out of the soil system and the probable excretion of H⁺ and organic acids by crop plant roots over almost 20 years as reported by previous studies^[23–30].

Since soil CEC, pH, clay and organic C are also influential, the changes in soil heavy metal labile fractions are most probably controlled and relate to these soil properties^[31]. In devising the effects of several key factors in controlling the DTPA extracted heavy metal micronutrients Fe, Mn, Zn and Cu in humid tropical acid soils, Supriatin & Salam (2024) found that the labile Cu was controlled by soil exchangeable Mg, exchangeable Ca and soil clay fraction with a multiple linear regression equation $DTPA\ Cu = -2.67 + 0.57\ (Exch,\ Ca) + 3.48\ (Exch,\ Mg) - 0.01(\% \text{ Clay})(R^2 = 0.72)$ ^[31], in which it was shown that DTPA Cu was positively affected by exchangeable Ca and Mg but negatively affected by soil clay fraction. They also reported that the DTPA Zn was positively affected by soil organic C and total Zn but negatively affected by soil clay fraction with a multiple regression equation $DTPA\ Zn = 0.97 + 2.46\ (Org.\ C) + 0.02\ (Total\ Zn) - 0.03\ (Clay)(R^2 = 0.49)$. The attenuation in soil pH and organic C and changes in CEC and probably in clay content and other controlling factors with time may have occurred in relation to the changes in soil heavy metal labile fractions. Data on these relationships for tropical soils polluted with heavy metals is absent. Therefore, the changes in Zn and Cu labile fractions in tropical soils that had been amended with industrial waste containing heavy metals were evaluated in this research.

2. Materials and Methods

2.1. Soil Treatments, Sampling and Analyses

Soils amended with heavy metals historically loaded through industrial waste were analysed to evaluate their Cu and Zn residual contents almost 20 years after amendments and their relations to the major controlling soil variables including soil pH, organic C and clay contents and CEC. The soil plots were situated in Sidosari, Natar, South Lampung, Indonesia. The soils were factorially one-time

treated with 0–60 Mg ha⁻¹ industrial waste, 0–5 Mg ha⁻¹ calcite and 0–5 Mg ha⁻¹ compost of cassava-leaf replicated thrice after land preparation by conventional tillage to 15 cm depth intended to lower heavy metals concentrations of waste origin in soils ^[11].

As detailed by Salam et al. (2021), measuring 30.5 m x 26.5 m with a slope of 2.5–3.0%, the experimental field was part of an active upland agricultural land ^[11]. The soil was an Ultisol characterized by textural fractions 41.2% sand, 26.0% silt, and 32.8% clay (with a textural class of Sandy Clay Loam), organic C content 1.28 g kg⁻¹, pH 5.11, and Cu and Zn 1.28 and 1.60 mg kg⁻¹, respectively. The average rainfall in South Lampung, Indonesia, was fairly high; the total rainfall in 2015 was 1,628 mm per year with 143 rainy days. Industrial waste used was a metal-ware industrial waste sampled from CV Star Metal Wares Jakarta characterized by high Cu, Zn and Ni. The total contents of Cu were 754 mg kg⁻¹, Zn 44.6 mg kg⁻¹, Pb 2.44 mg kg⁻¹, Cd 0.12 mg kg⁻¹, and pH 7.30. Before being treated in soils, the industrial waste was brought to air-dryness and ground to pass a 1 mm sieve and given one time at 3 levels: 0, 15, and 60 Mg ha⁻¹ (**Table 1**). Lime as CaCO₃ (calcite) was given one time at 0 and 5 Mg ha⁻¹. Organic compost was developed from cassava (*Mannihot utilisima*) leaf prepared as reported by Salam (2000) ^[2], also given one time at 0 and 5 Mg ha⁻¹. Rates of industrial waste, lime, and cassava-leaf compost were determined through several preliminary laboratory and glass-house experiments conducted in 1995–1998, as reported by Salam (2000) ^[2]. The rates of industrial waste were determined to set the heavy metal level into 3 categories: control, low heavy metal LHM, and high heavy metal HHM, particularly for Cu, which was analyzed as the highest in the waste. The soil extracted Cu of more than 100 mg kg⁻¹ was considered high. Lime at 5 Mg CaCO₃ ha⁻¹ was intended to increase the soil pH to about 1 unit higher than the initial value determined by the titration method.

Salam (2021) designed an experimental unit (field plot) measured 4.5 m long and 4.0 m wide, with distances of 1.0 m between blocks and 0.50 m between plots ^[32]. The experimental plots in the field were arranged in a Completely Randomized Block Design (CRBD) with 3 replicates. Borders were imaginary, permanently marked only in several points using metal sticks painted red, to

make it easier in plowing, planting and plant maintenance and, therefore, it was very possible for the soil masses to move between plots and blocks during soil tillage (plowing and harrowing). The industrial waste was incorporated into topsoils by broadcasting on the soil surface and mixed thoroughly by soil tillage at 0 – 15 cm. One week after waste incorporation into soil, cassava-leaf compost and calcite were both also given into 0 – 15 cm depth by broadcasting and soil tillage. The experimental plots were then planted with various crops since 1998, first with corn, and then dryland paddy, cassava, and peanut, and some time left bare in between. Plowing and harrowing before planting were conducted twice, each in the direction E – W and N – S and vice versa. The experimental plots have been well maintained since 1998. Soil sampling for this research was taken from topsoil (0–15 cm) and subsoil (15 – 30 cm) in January 2018 or about 20 years after waste amendment. Detail of each treatment is depicted in **Table 1**.

Table 1. Soil Treatments with One-Time 0–60 Mg ha⁻¹ Industrial Waste, 0–5 Mg ha⁻¹ Calcite and 0–5 Mg ha⁻¹ Cassava-Leaf Compost in July 1998 and Sampled in 2018.

Treatment	Units	Treatment Combinations (Waste – Calcite – Compost in Mg ha ⁻¹)
1	W ₀ L ₀ C ₀	0 – 0 – 0
2	W ₀ L ₀ C ₁	0 – 0 – 5
3	W ₀ L ₁ C ₀	0 – 5 – 0
4	W ₀ L ₁ C ₁	0 – 5 – 5
5	W ₁ L ₀ C ₀	15 – 0 – 0
6	W ₁ L ₀ C ₁	15 – 0 – 5
7	W ₁ L ₁ C ₀	15 – 5 – 0
8	W ₁ L ₁ C ₁	15 – 5 – 5
9	W ₂ L ₀ C ₀	60 – 0 – 0
10	W ₂ L ₀ C ₁	60 – 0 – 5
11	W ₂ L ₁ C ₀	60 – 5 – 0
12	W ₂ L ₁ C ₁	60 – 5 – 5

W = Waste in Mg ha⁻¹: 0 (W₀ or Control), 15 (W₁ or Low Heavy Metals LHM) and 60 (W₂ or High Heavy Metals HHM); L = Calcite in Mg ha⁻¹: 0 (L₀) and 5 (L₁) and C = Compost in Mg ha⁻¹: 0 (C₀) and 5 (C₁), Replicated Thrice.

Soil samples were screened to 2-mm-size after air drying, grinding and a thorough mixing. Soil samples were analysed for clay fraction and organic C by conventional methods (hydrometer and Walkley and Black) in addition to analyses on the available Cu and Zn extracted by DTPA method employing flame atomic absorption spectrophotometry, soil pH (pH electrode) and CEC (batch

method)^[32].

2.2. Statistical Analyses and Model Development

Differences among treatments were compared using standard error of the mean (SEM) calculated by Microsoft Excel Application. Significances were confirmed when the difference between the two means was greater than 2 x SEM.

The relationships between DTPA extracted Cu and Zn with soil pH, CEC, clay and organic C were analysed using single variable and multivariable simple linear regression employing Microsoft Excel Application at $p > 0.05$. The single variable regression analysis for each independent variable (pH, CEC, Clay, or Organic C) was expressed with the following equations with a and b as constants and M as the related heavy metals (Cu or Zn):

$$M = a + b(\text{pH})$$

$$M = a + b(\text{CEC})$$

$$M = a + b(\text{Clay})$$

$$M = a + b(\text{Org C})$$

The equations for multivariable linear regressions for more than one independent variable (pH, CEC, Clay, or Organic C) were expressed as follows with a, b, c, d and e as constants and M as the related heavy metals (Cu or Zn):

$$M = a + b(\text{pH}) + c(\text{CEC})$$

$$M = a + b(\text{pH}) + c(\text{Clay})$$

$$M = a + b(\text{pH}) + c(\text{Org C})$$

$$M = a + b(\text{CEC}) + c(\text{Clay})$$

$$M = a + b(\text{CEC}) + c(\text{Org C})$$

$$M = a + b(\text{Clay}) + c(\text{Org C})$$

$$M = a + b(\text{pH}) + c(\text{CEC}) + d(\text{Clay})$$

$$M = a + b(\text{pH}) + c(\text{CEC}) + d(\text{Org C})$$

$$M = a + b(\text{pH}) + c(\text{Clay}) + d(\text{Org C})$$

$$M = a + b(\text{CEC}) + c(\text{Clay}) + d(\text{Org C})$$

$$M = a + b(\text{pH}) + c(\text{CEC}) + d(\text{Clay}) + e(\text{Org C})$$

3. Results

3.1. Effects of Calcite and Compost on Residual Cu and Zn

As shown in **Table 2**, the residual Cu and Zn in topsoil after about 20 years of amendment of industrial waste were, in general, highest in high heavy metal HHM plots followed by low heavy metal LHM plots, which were both higher than the non-treated plot. This trend was similar to that in 1998 but at a lower magnitude^[2]. This trend in general also occurred in subsoil, particularly in HHM plots. The residual Cu and Zn in subsoils were greatly affected by those in topsoil, as indicated by high correlation in these two soil layers (**Figure 1**). The residual subsoil Cu is well correlated with that in topsoil ($R^2 = 0.91^*$) and so the subsoil Zn with the topsoil Zn ($R^2 = 0.62^*$).

Table 2. The Effect of Waste, Lime and Compost on the DTPA-Extracted Cu and Zn.

Treatment Units		Treatment Combinations (Waste – Calcite – Compost in Mg ha ⁻¹)	Cu		Zn		pH	
			Topsoil	Subsoil	Topsoil	Subsoil	Topsoil	Subsoil
			 mg kg ⁻¹					
1	W ₀ L ₀ C ₀	0 – 0 – 0	10.6 ^{abcd}	1.06 ^a	11.1 ^{bcd}	1.00 ^a	5.08 ^a	5.14 ^{ab}
2	W ₀ L ₀ C ₁	0 – 0 – 5	18.7 ^{de}	10.8 ^c	15.9 ^{def}	2.11 ^{ab}	5.35 ^f	5.33 ^{ef}
3	W ₀ L ₁ C ₀	0 – 5 – 0	29.5 ^f	12.3 ^c	22.3 ^g	2.71 ^{ab}	5.18 ^c	5.44 ^g
4	W ₀ L ₁ C ₁	0 – 5 – 5	6.81 ^{abc}	0.28 ^a	8.85 ^{abc}	0.00 ^a	5.17 ^c	5.30 ^{de}
5	W ₁ L ₀ C ₀	15 – 0 – 0	13.6 ^{bcd}	0.74 ^a	19.7 ^{fig}	0.00 ^a	5.09 ^{ab}	5.12 ^a
6	W ₁ L ₀ C ₁	15 – 0 – 5	5.38 ^{ab}	1.04 ^a	8.09 ^{ab}	0.25 ^a	5.17 ^c	5.20 ^{bc}
7	W ₁ L ₁ C ₀	15 – 5 – 0	4.68 ^a	0.43 ^a	4.04 ^a	0.21 ^a	5.30 ^{ef}	5.32 ^{ef}
8	W ₁ L ₁ C ₁	15 – 5 – 5	15.2 ^{cd}	2.92 ^{ab}	9.48 ^{bc}	6.11 ^b	5.13 ^{abc}	5.32 ^{ef}
9	W ₂ L ₀ C ₀	60 – 0 – 0	63.4 ^g	51.0 ^d	38.0 ^h	28.64 ^c	5.09 ^{ab}	5.24 ^{cd}
10	W ₂ L ₀ C ₁	60 – 0 – 5	25.4 ^{ef}	9.97 ^c	19.7 ^{fig}	2.54 ^{ab}	5.14 ^{bc}	5.47 ^g
11	W ₂ L ₁ C ₀	60 – 5 – 0	18.6 ^{de}	0.50 ^a	16.7 ^{ef}	0.45 ^a	5.29 ^{de}	5.23 ^c
12	W ₂ L ₁ C ₁	60 – 5 – 5	17.4 ^{de}	2.83 ^{ab}	13.7 ^{cde}	1.85 ^{ab}	5.24 ^d	5.37 ^f
SEM			±4.39	±3.96	±2.47	±2.21	±0.02	±0.03

Values sharing the same character in one column are not significantly different at $\alpha = 0.05$.

Similar to those in 1998 ^[2], the decreasing effects of calcite and/or organic compost on extracted Cu and Zn are clear (**Table 2**), even though the magnitude of the effects is much weaker than those in 1998. The residual topsoil Cu in HHM plots was 63.4 mg kg⁻¹, which was significantly lowered by about 54.9, 70.7 and 72.6% by (calcite), (compost), and (calcite + compost) treatments, respectively. In LHM plots, the decreases were respectively 60.5 and 65.6% by (calcite) and (compost) and increased about 11.8% by (calcite and compost) treatments. For topsoil Zn, the residual Zn in Control HHM plots was 38.0 mg kg⁻¹, which was significantly decreased by about 48.1, 56.1, and 64.0%, respectively, by (calcite), (compost) and (calcite + compost) treatments. While in LHM plots, the residual Zn was significantly decreased from 19.7 mg kg⁻¹ to about 58.9, 79.5, and 51.9%, respectively, by (calcite), (compost)

and (calcite + compost) treatment.

Even at low magnitudes, the effects of waste, calcite, and compost on soil pH were evidenced in 2018 (**Table 2**). The soil pH significantly increased by (waste), (calcite), (compost) and (calcite + compost). As shown in **Figure 2**, a negative relationship between the residual Cu and pH ($R^2 = 0.079$) and the residual Zn and pH ($R^2 = 0.114$), a normal relationship for many soils as reported by several previous research ^[1], were clearly observed. This pattern is different from that in 1998, which showed a positive relationship, which is not usual for many soils. This positive relationship in 1998 was caused by a disequilibrium that suddenly increased soil Cu and Zn by waste treatment. After reaching an equilibrium in 2018 or about 20 years the relationship was back to normal, i.e., the soil Cu and Zn concentrations decreased with the increase in soil pH.

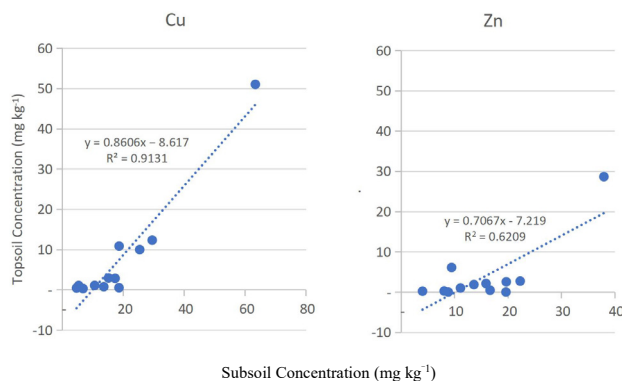


Figure 1. The Relations of Residual Cu and Zn in Topsoil and Subsoil.

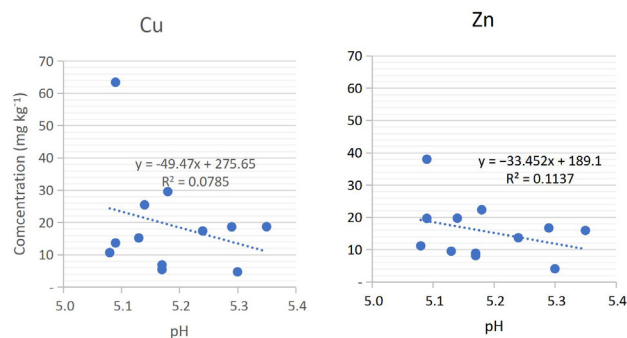


Figure 2. The Relations of Residual Cu and Zn to Soil pH in 2018.

3.2. Linear Relations of Residual Cu and Zn with Several Key Soil Properties

There were weak relations between the residual Cu and Zn with the soil pH, CEC, clay and organic C (**Table 3**). The highest correlation coefficient was observed for the

residual Cu and organic C ($R^2 = 0.207^{ns}$) and the residual Zn with organic C ($R^2 = 0.238^{ns}$). Other soil properties (pH, CEC, and clay) showed weaker correlations with both residual Cu and Zn. The inclusion of other soil variables in addition to Organic C improved the correlation coefficients. For example, the correlation coefficient between

the residual Cu and organic C was 0.207^{ns}, improved to 0.265^{ns} with the inclusion of organic C and pH, to 0.333^{ns} with the inclusion of Organic C and Clay, and finally to 0.338^{ns} with the inclusion of all four soil variables evaluated, i.e., pH, CEC, Clay and Organic C. The correlation coefficient between the residual Zn and organic C was 0.238^{ns}, improved to 0.176^{ns} with the inclusion of organic C and pH, to 0.382^{ns} with the inclusion of Organic C and Clay, and finally to 0.392^{ns} with the inclusion of all four

soil variables evaluated, i.e., pH, CEC, Clay and Organic C. These values indicate that these four soil variables encompassed the control of about 33.8% of the residual Cu and 39.2% of the residual Zn. In addition to organic C, the residual Cu and Zn were also greatly determined by clay content, as seen by the increase in their correlation coefficients from 0.207^{ns} to 0.333^{ns} for Cu and from 0.238^{ns} to 0.392^{ns} for Zn by the inclusion of soil clay content (**Table 3**).

Table 3. The Single and Multiple Linear Regression Relationships of Topsoil Cu and Zn to pH, CEC, Clay and Organic C.

Soil Properties	Linear Regression Relationships	R ²
Cu		
pH	$\text{Cu} = 276 - 49.5 (\text{pH})$	0.079 ^{ns}
CEC	$\text{Cu} = 13.2 + 0.53 (\text{CEC})$	0.005 ^{ns}
Clay	$\text{Cu} = 27.1 + 0.461 (\text{Clay})$	0.049 ^{ns}
Organic C	$\text{Cu} = -20.4 + 34.7 (\text{Org C})$	0.207 ^{ns}
pH + CEC	$\text{Cu} = 268 - 48.7 (\text{pH}) + 0.35 (\text{CEC})$	0.081 ^{ns}
pH + Clay	$\text{Cu} = 197 - 40.0 (\text{pH}) + 0.91 (\text{Clay})$	0.085 ^{ns}
pH + Organic C	$\text{Cu} = 203 - 42.7 (\text{pH}) + 33.0 (\text{Org C})$	0.265 ^{ns}
CEC + Clay	$\text{Cu} = -55.3 - 0.64 (\text{CEC}) + 2.53 (\text{Clay})$	0.054 ^{ns}
CEC + Organic C	$\text{Cu} = -46.2 + 1.71 (\text{CEC}) + 40.3 (\text{Org C})$	0.257 ^{ns}
Clay + Organic C	$\text{Cu} = -138 + 3.41 (\text{Clay}) + 42.2 (\text{Org C})$	0.333 ^{ns}
pH + CEC + Clay	$\text{Cu} = 194 - 39.5 (\text{pH}) - 0.06 (\text{CEC}) + 0.962 (\text{Clay})$	0.085 ^{ns}
pH + CEC + Organic C	$\text{Cu} = 158 - 38.4 (\text{pH}) + 1.51 (\text{CEC}) + 38.2 (\text{Org C})$	0.304 ^{ns}
pH + Clay + Organic C	$\text{Cu} = -87.5 - 8.08 (\text{pH}) + 3.15 (\text{Clay}) + 41.3 (\text{Org C})$	0.335 ^{ns}
CEC + Clay + Organic C	$\text{Cu} = -136 + 0.317 (\text{CEC}) + 3.18 (\text{Clay}) + 42.7 (\text{Org C})$	0.335 ^{ns}
pH + CEC + Clay + Organic C	$\text{Cu} = -61.0 - 11.6 (\text{pH}) + 0.47 (\text{CEC}) + 2.71 (\text{Clay}) + 41.7 (\text{Org C})$	0.338 ^{ns}
Zn		
pH	$\text{Zn} = -3.78 + 3.67 (\text{pH})$	0.002 ^{ns}
CEC	$\text{Zn} = 16.2 - 0.05 (\text{CEC})$	0.000 ^{ns}
Clay	$\text{Zn} = -23.7 + 1.22 (\text{Clay})$	0.055 ^{ns}
Organic C	$\text{Zn} = -8.21 + 20.9 (\text{Org C})$	0.238 ^{ns}
pH + CEC	$\text{Zn} = 193 - 33.8 (\text{pH}) - 0.17 (\text{CEC})$	0.115 ^{ns}
pH + Clay	$\text{Zn} = 157 - 29.5 (\text{pH}) + 0.37 (\text{Clay})$	0.117 ^{ns}
pH + Organic C	$\text{Zn} = 146 - 29.4 (\text{pH}) + 19.8 (\text{Org C})$	0.176 ^{ns}
CEC + Clay	$\text{Zn} = -36.0 - 0.94 (\text{CEC}) + 193 (\text{Clay})$	0.090 ^{ns}
CEC + Organic C	$\text{Zn} = -17.6 + 0.63 (\text{CEC}) + 23.0 (\text{Org C})$	0.259 ^{ns}
Clay + Organic C	$\text{Zn} = -79.0 + 2.03 (\text{Clay}) + 25.4 (\text{Org C})$	0.382 ^{ns}
pH + CEC + Clay	$\text{Zn} = 121 - 24.8 (\text{pH}) - 0.574 (\text{CEC}) + 0.947 (\text{Clay})$	0.128 ^{ns}
pH + CEC + Organic C	$\text{Zn} = 131 - 28.0 (\text{pH}) + 0.481 (\text{CEC}) + 21.4 (\text{Org C})$	0.338 ^{ns}
pH + Clay + Organic C	$\text{Zn} = -10.5 - 10.8 (\text{pH}) + 1.69 (\text{Clay}) + 24.2 (\text{Org C})$	0.390 ^{ns}
CEC + Clay + Organic C	$\text{Zn} = -82.6 - 0.39 (\text{CEC}) + 2.31 (\text{Clay}) - 24.7 (\text{Org C})$	0.389 ^{ns}
pH + CEC + Clay + Organic C	$\text{Zn} = -26.2 - 8.73 (\text{pH}) - 0.276 (\text{CEC}) + 1.95 (\text{Clay}) + 24.0 (\text{Org C})$	0.392 ^{ns}

4. Discussion

The residual Cu and Zn in the amended soils with industrial waste heavy metals in Sidosari, Natar, and South Lampung, Indonesia, after about 20 years, remained significant (Salam et al., 2021). It was reported that the residual Cu and Zn in the 60 Mg waste ha^{-1} plots decreased over 20 years to 17 – 53% for Cu and to 12 – 33% for Zn, which were relatively high, i.e., 20.7 – 64.7 mg kg^{-1} for Cu and 13.4 – 38.8 mg kg^{-1} for Zn with the highest were in control plots and the lowest were in plots treated with lime and cassava-leaf compost. It is obvious that the effectiveness of lime and cassava leaf compost in lowering soil heavy metal was still evident in 2018, after about 20 years. Lime as CaCO_3 in soil water dissociated into Ca^{2+} and CO_3^{2-} ions, which synergically displaced the important potential soil acidity sources, i.e., exchangeable H and Al and neutralized them into H_2CO_3 and $\text{Al}(\text{OH})_{3(s)}$, which finally increased the soil pH and also increased the soil exchanges sites, of both the indigenous exchange sites and those introduced by cassava-leaf compost amendment. All these processes may have finally lowered the labile fractions of heavy metals in soils through activated adsorption and precipitation mechanisms. In addition to adsorption process that was enhanced by pH increase, the precipitation of these heavy metals by OH^- and CO_3^{2-} ions was also probable, synergically working in lowering the soil labile fractions of heavy metals [33].

Current analysis showed that the residual Cu and Zn in lime and/or cassava-leaf compost treated plots were significantly lower, showing that the effects of calcite and/or compost pertained for almost 20 years even though the magnitude of Cu and Zn concentrations in soils were relatively much lower. The decrease in soil pH caused by various possible mechanisms like soil acidification through crop plants' H^+ and organic acid root excretions and major cation Ca^{2+} and Mg^{2+} leaching did not significantly affect the substantial role of lime materials in lowering the residual soil heavy metal concentrations [23,24,27,28]. This suggests that in these soils, the effects of liming materials may remain for quite long time in decreasing the risk of heavy metals in soils. Liming materials other than calcite like dolomite, phosphatic fertilizers etc, may behave similarly.

Even though organic compost may decay quickly [13,23,34], data showed that its effects in decreasing the soil heavy metals remained after about 20 years. It is unexpected that soil heavy metal treatment with organic materials may cause long-term effect. The importance of organic matter was also shown by the close relationship of the residual Cu and Zn with the soil organic C, which was higher than the relationships with other soil controlling properties like soil pH, CEC, and clay. The other soil properties reported controlling the residual Cu and Zn in soils were shown to improve the correlation coefficients, but only soil clay improved more significantly. The improvement by the inclusion of soil CEC and pH was miniscule.

The relationships between the soil residual Cu and Zn with soil pH were weak. However, the general trend of the relationship was clear, like those reported previously, i.e., the residual Cu and Zn decreased with the increase in soil pH [1,2,35]. Salam & Helmke (1998) clearly showed that the logarithmic total Cu and Cd decreased with pH at pH 4 to 6, and the logarithmic Cu^{2+} and Cd^{2+} decreased with pH at pH 4 – 7 [1]. Other researchers also reported that the total dissolved heavy metals were high at low pH and low at high pH [11,35,36]. This means that addition of any liming materials or lime-like materials, like phosphatic fertilizers, that may increase soil pH, may also decrease the soil heavy metal concentrations in soils, generating a negative heavy metal concentration – pH correlation. This trend was significantly different from the relationship of the soil Cu and Zn with soil pH in 1998, which showed a positive correlation. This demonstrates that high inputs of heavy metals and soil amendment in 1998 may have disturbed the soil chemical relations and showed a disturbed relationship, i.e., the positive relationship between soil residual Cu and Zn with pH. After about 20 years, the new equilibrium was reestablished showing a negative relationship between soil residual Cu and Zn with pH, which is a normal relationship between heavy metal concentrations and pH in most soils [1,2,36,37].

Overall, the multivariable linear regression equation clearly shows that the soil labile Cu in these heavy-metal polluted tropical soils was positively affected by the soil cation exchange capacity, clay fraction and organic C content but negatively affected by soil pH and can be predicted with 33.8% accuracy with equation $\text{Cu} = -61.0 - 11.6 \text{ pH} + 0.47 (\text{CEC}) + 2.71 (\text{Clay}) + 41.7 (\text{Org C})$ ($R^2 = 0.338$). The soil labile Zn was also clearly shown to

be positively controlled by soil clay fraction and organic C content but negatively affected by soil pH and CEC and can be predicted with accuracy of about 39.2% by equation $Zn = -26.2 - 8.73 (pH) - 0.276 (CEC) + 1.95 (Clay) + 24.0 (Org\ C)$ ($R^2 = 0.392$). Other soil key controlling variables must be included in developing these mathematical models to improve their accuracies. One interesting phenomenon observed is that the soil labile Cu and Zn were both negatively related to soil pH, which was previously discussed to be the normal relationship in most soils.

5. Conclusions

The highest Cu and Zn were observed in high heavy metal HHM plots with the highest waste, followed by low heavy metal LLM plots with low industrial waste amendment, which were, like in 1998, both significantly lowered by calcite and/or cassava-leaf compost treatment. The lower subsoil Cu and Zn were strongly affected by topsoil as indicated by high correlation of topsoil to subsoil Cu or Zn. The soil Cu and Zn in general did not relate to soil pH and CEC, but they showed better relationship with the soil organic C and clay. The inclusion of soil pH, CEC, clay and organic C in multiple linear regression improved their correlation coefficients, in which the correlation coefficients of Zn were higher than Cu. Long-time reaction in soils reversed the abnormal positive correlation of Cu – pH and Zn – pH in 1998 to negative correlation in 2018, a normal relationship in soils.

The soil labile Cu in these heavy-metal polluted tropical soils was positively affected by soil cation exchange capacity, clay fraction and organic C content but negatively affected by soil pH and can be predicted with 33.8% accuracy with equation $Cu = -61.0 - 11.6 pH + 0.47 (CEC) + 2.71 (Clay) + 41.7 (Org\ C)$ ($R^2 = 0.338$). The soil labile Zn was positively controlled by soil clay fraction and organic C content but negatively affected by soil pH and CEC and can be predicted with accuracy of about 39.2% by equation $Zn = -26.2 - 8.73 (pH) - 0.276 (CEC) + 1.95 (Clay) + 24.0 (Org\ C)$ ($R^2 = 0.392$). Other soil key controlling variables must be included in developing these mathematical models to improve their accuracies. Based on this long term study results, it is suggested to study microbial roles in long-term metal stability in soil to have more comprehensive understanding of the behaviour and fate of heavy

metals in soil.

Author Contributions

Abdul Kadir Salam was a team leader and principal investigator; Galih Susilowati was student researcher that conducted field and laboratory analysis; Nanik Sriyani designed and supervised the field experiment and prepared and handling manuscript revision; Hery Novpriansyah was a student research adviser.

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Data Availability Statement

Data are available to the corresponding author upon request.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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