

Research Article

Fertility Evaluation of Limed Brazilian Soil Polluted with Scrap Metal Residue

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The aim of this work was to characterize the main inorganic contaminants and evaluate the effect of lime addition, combined with soil dilution with uncontaminated soil, as a strategy for mitigation of these contaminants present in a soil polluted with auto scrap. The experiment was performed in a greenhouse at Campinas (São Paulo State, Brazil) in plastic pots (3 dm^{-3}). Five soil mixtures, obtained by mixing an uncontaminated soil sample with contaminated soil (0, 25, 50, 75, and 100% contaminated soil), were evaluated for soil fertility, availability of inorganic contaminants, and corn development. In addition to the expected changes in soil chemistry due to the addition of lime, only the availability of Fe and Mn in the soil mixtures was affected, while the available contents of Cu, Zn, Cd, Cr, Ni, and Pb increased to some extent in the soil mixtures with higher proportion of contaminated soil. Liming of 10 t ha^{-1} followed by soil dilution at any proportion studied was not successful for mitigation of the inorganic contaminants to a desired level of soil fertility, as demonstrated by the available amounts extracted by the DTPA method (Zn, Pb, Cu, Ni, Cr, Cd) and hot water (B) still present in the soil. This fact was also proved by the phytotoxicity observed and caused by high amounts of B and Zn accumulating in the plant tissue.

1. Introduction

In many parts of the world, soil is still considered as an option for waste disposal, acting simultaneously as a filter that protects the groundwater and as a bioreactor in which many pollutants may be degraded or stored [1]. Thus, inorganic chemical elements accumulate in soil as a result of human activities.

The monitoring and remediation of contaminated soil are relatively new processes in Brazil, introduced less than 20 years ago. The environmental agency of São Paulo State (CETESB) is a pioneer in the country and has identified more than 4,131 contaminated areas in that state, of which at least 13% are contaminated exclusively by the addition of heavy metals to the soil [2].

Soil contamination by heavy metals requires an effective and affordable solution due to their potential toxicity and high persistence [3]. Among the so-called heavy metals, elements such as Cu (copper), Pb (lead), and Zn (zinc) are

important contaminants because high quantities of these elements can decrease crop production and due to the risk of biomagnification and bioaccumulation in the food chain [4, 5]. Other inorganic contaminants that are not as frequently considered, such as B (boron) and Ba (barium), can be extremely toxic to some plants at concentrations only slightly higher than levels that are optimum for others [6].

The boron requirement of plants is small, with a narrow concentration range from deficiency to toxicity. In arid and semiarid areas, B toxicity results from high levels of B in soils and from the addition of B via irrigation [7–9]. Considerable research has shown the potential toxicity of Ba in plants, but such studies were short-term and performed in nutrient solutions [10, 11].

Although a number of techniques have been developed to remove inorganic contaminants from soils, many sites remain untreated due to high economic costs, and mitigation must be considered. Mitigation can be used to reduce further undesirable impacts on chemical and physical soil degradation,

to immobilize contaminants and to enable plant growth in contaminated areas to protect the soil from erosion [12–14]. Liming and the addition of organic materials are considered the most promising mitigation techniques for reducing the availability of heavy metals in soil [15–17].

The aim of this work was to characterize the main contaminants and evaluate the effect of lime addition, combined with soil dilution with uncontaminated soil, as a strategy for mitigation of inorganic contaminants present in a soil polluted with auto scrap residue.

2. Materials and Methods

2.1. Site Description. The studied soil samples were collected from a polluted area located in Piracicaba, São Paulo State, Brazil (22°42'30"S; 47°38'01"W), which was cultivated with sugarcane before the contamination event, which occurred in 2005. The soil studied is a eutrofic technic leptosol in association with an endodystric leptic cambisol. This soil is intensively cultivated with either sugarcane or pastures in the Piracicaba city region (more than 300,000 ha). The climate is classified as Cwa (tropical moist), according to Köppen, with rainy summers and dry winters. June, July, and August are the driest months, the average temperature of the warmest month is higher than 22°C, and the temperature drops below 16°C in the coldest month. The annual average temperature is 21.5°C, and the precipitation is 1,270 mm [18].

Scrap metal residue was discarded on arable land and incorporated unevenly into the soil. After local environmental agency (CETESB) intervention, 10 t ha⁻¹ of dolomitic limestone was applied (April 2005) in an attempt to increase the pH and to precipitate the metals.

The total inorganic contaminant content of the waste and the soil samples was extracted using the nitric acid-microwave oven digestion method EPA-3051, with determination by inductively coupled plasma-optical emission spectrometry (ICP-OES) [19].

The chemical composition of the waste (dry weight basis) was P = 0.6, K = 0.8, Ca = 10.9, Mg = 12.3, and S = 1.5 g kg⁻¹, and Al = 7,449, B = 170, Ba = 919, Cd = 7.4, Pb = 775, Cu = 2,497, Fe = 101,603, Mn = 1,115, Ni = 153, Cr = 178, and Zn = 8,157 mg kg⁻¹.

Due to heterogeneity in the disposal, for all of the research developed within this area, the region was divided into twelve subareas of approximately 2,450 m² each for chemical analysis. Soil samples were taken from the 0 to 20 cm depth layer, dried at room temperature and sieved to 2.0 mm, and the total heavy metal content was analyzed (Table 1). The soil from subarea number four was selected for the experiment because its composition was close to the average for most of the elements found in the sub-areas considered. One uncontaminated soil sample (SC) was obtained in the vicinity of the contaminated area, at the same depth.

2.2. Greenhouse Experiment. The experiment was performed in a greenhouse at Campinas (São Paulo State, Brazil) in plastic pots (3 dm³). Four soil mixtures, obtained by mixing the uncontaminated soil sample (SC) and contaminated soil from

subarea 4 (CA4) to create a gradient of contamination, were evaluated for soil fertility, chemical contaminant availability, and corn development.

The experimental design used randomized complete blocks with five proportions (0, 25, 50, 75, and 100%) of contaminated soil, with five replicates. The soil mixtures were carefully homogenized and incubated at room temperature for 10 days, with the soil moisture maintained at 70% of the soil's water holding capacity (WHC).

After incubation, the soil samples were collected, air dried, and sieved through a 2 mm mesh screen and then submitted to chemical characterizations for soil fertility and available metal content as explained in the site description (Table 3).

The corn cultivar cv. Al Bandeirantes-CATI was seeded at a rate of ten seeds per pot. Seedlings were thinned to five per pot after emergence. During the cultivation, the soil moisture was maintained at 70% field capacity by watering regularly for water loss. The only nutrient added to the pots was nitrogen, as ammonium nitrate, in four applications of 50, 100, 250, and 250 mg pot⁻¹, respectively at 7, 14, 21, and 28 days after emergence.

The plants were harvested 45 days after emergence. The shoots were selected to evaluate the metal phytoavailability.

2.3. Soil Fertility Analyses. Soil fertility attributes were determined by São Paulo State official methods developed at Instituto Agronomico [20] and consisted, briefly, of soil pH measured in a 0.01 mol L⁻¹ calcium chloride solution (pHCaCl₂) with a soil solution ratio of 1:2.5; H+Al extracted by the SMP buffer; phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg) extracted by the mixed ion-exchange resin method with cation determination by AAS and P-determination spectrophotometry using the blue molybdate method; organic matter (OM) oxidized with potassium dichromate and determined by photometry; cation exchange capacity (CEC) and base saturation (SB) obtained by calculation; sulfate (S) extracted by calcium phosphate and determined by turbidimetry; available Zn, Cu, Fe, Mn, Cd, Cr, Ni, and Pb contents extracted with DTPA-TEA solution at pH 7.3 and determined by ICP-AES; and B contents extracted with hot water and determined photometrically with azomethine-H.

2.4. Plant Analyses. After harvesting, the plant material was rinsed thoroughly with tap water, followed by 1% HCl solution and then deionized water. After the excess water flowed off, each sample was placed in a paper bag and dried in a forced air oven at 70°C until a constant weight was achieved; the samples were then weighed and ground in a Wiley-type grinder. Each sample was submitted to oven digestion (incineration) according to Bataglia et al. [21], and the extracts were analyzed for P, K, Ca, Mg, S, B, Cu, Mn, Zn, Fe, Cd, Cr, Ni, and Pb by induced coupled plasma emission spectrometry (ICP-OES) (Varian, Vista MPX, Australia). Nitrogen contents were determined using a sulfuric digestion extract using the steam distillation method [22].

TABLE 1: Heavy metal concentrations of the twelve subareas analyzed.

| Subarea | Ba | Cd | Pb | Total content ^a | | | |
|---------------------|------------|----------------|------------|----------------------------|------------|------------|--------------|
| | | | | Cu | Cr | Ni | Zn |
| mg kg ⁻¹ | | | | | | | |
| SA1 ^b | 311 | 3.6 | 332 | 198 | 110 | 52 | 1,811 |
| SA2 ^b | 696 | 8.8 | 632 | 150 | 15 | 39 | 3,225 |
| SA3 ^b | 322 | 3.2 | 357 | 250 | 118 | 48 | 3,371 |
| SA4 ^b | 619 | 6.4 | 254 | 172 | 105 | 55 | 2,223 |
| SA5 ^b | 327 | 4.0 | 238 | 147 | 99 | 32 | 1,890 |
| SA6 ^b | 306 | 13.5 | 198 | 265 | 130 | 30 | 1,985 |
| SA7 ^b | 263 | 2.1 | 178 | 199 | 102 | 41 | 1,411 |
| SA8 ^b | 314 | 2.2 | 211 | 131 | 114 | 49 | 1,678 |
| SA9 ^b | 881 | 12.6 | 438 | 115 | 198 | 52 | 2,102 |
| SA10 ^b | 365 | 4.0 | 167 | 201 | 85 | 102 | 1,721 |
| SA11 ^b | 487 | 14.2 | 451 | 389 | 190 | 61 | 2,930 |
| SA12 ^b | 291 | 7.0 | 244 | 108 | 112 | 51 | 2,014 |
| Mean | 432 | 6.8 | 308 | 194 | 115 | 51 | 2,197 |
| SC ^c | 109 | <0.1 | 13 | 7 | 34 | 2.0 | 20 |

^aSW-846 3051 method [19].

^bContaminated soil sample.

^cUncontaminated soil sample.

2.5. Data Analysis. The results of the soil and plant analyses were submitted to an analysis of variance ($P < 0.05$). When significant, the results obtained were also examined using regression analysis (linear and quadratic models). The software used was SISVAR 4.0 [23] and XLSTAT Pro 7.0.

3. Results and Discussion

3.1. Soil Analysis. The total contents of Cu—160 mg kg⁻¹, Cr—103 mg kg⁻¹, Ni—47 mg kg⁻¹, Cd—8.2 mg kg⁻¹, Pb—268 mg kg⁻¹, and Zn—2,454 mg kg⁻¹ were above the maximum content commonly found in the soils of São Paulo (Table 2). The total metal content reference levels in soils established by CETESB are (in mg kg⁻¹) Cu—35, 60, 200; Pb—17, 72, 180; Zn—60, 300, 450; Cd—<0.5, 1.3, 3.0; Cr—40, 75, 150; Ni—13, 30, 70, and Ba—75, 150, 300, respectively, for quality (Quality Reference Level—the concentration of a substance in soil that defines a ground as clean or of natural quality. This level should be used as a reference in the prevention of soil pollution and the control of contaminated areas.), prevention (Prevention Level—the concentration of a substance above which changes to soil quality may occur. This level should be used to regulate the introduction of substances into a soil. When this level is exceeded, continued activity shall be subject to further evaluation.), and agricultural intervention (Intervention Level—the concentration of a substance in soil above which potential risks, direct or indirect, to human health may occur. For soil, this level is calculated using the risk assessment procedure to human health exposure scenarios for agricultural, residential, and industrial protection. The area is classified as an investigational contaminated area when the presence of contaminants is found in the soil at concentrations above the intervention

value, indicating the requirement for action to protect the receptors of risk.) [24].

Considering such values, the amounts of Cu, Cr, and Ni fell between the levels of prevention and agricultural intervention. The amounts of Cd and Pb fell between the levels of agriculture and residential intervention. The most critical value was obtained for Zn, which was 50% higher than the industrial prevention level. No reference values are provided for Mn or B by the local environmental agency. However, considering the limits for Austrian soil (100 mg kg⁻¹), the content of boron in the contaminated soil (62 mg kg⁻¹) can be considered high [25]. The concentration of Ba that was found during soil characterization (241 mg kg⁻¹) is close to the intervention level (300 mg kg⁻¹) [24].

The addition of scrap metal residue and lime to the soil (SA-4) also changed some soil attributes when compared to uncontaminated soil obtained from a neighboring area (Table 2). There was an increase in attributes related both to the lime and to the residue, which were rich in elements such as B, Cu, Zn, Ni, Pb, Cd, Cr, and Ba.

The DTPA method, originally proposed by Lindsay and Norvell [26] to evaluate micronutrient availability for agricultural purposes, can also be helpful in monitoring soil contamination with heavy metals [27]. According to Abreu et al. [28], the available micronutrients in Brazil's soils fall into the following ranges (in mg dm⁻³): B—0.01–10.6; Cu—0.1–56; Mn—1–325; Pb—0.00–63.9; and Zn—1–453, while the respective average values for São Paulo State were B—0.32; Cu—2.5; Mn—16; Pb—0.85; and Zn—4.8. Higher values are indicative of anthropogenic inputs, either due to excessive application of fertilizers or urban and industrial wastes resulting from industrial or mining activities. Thus, the available levels of B and heavy metals (Table 3) found in

TABLE 2: Total element content, available content of heavy metals, and fertility evaluation of the original soil samples studied.

| Soil | Soil fertility attributes ^a | | | | | | | | | |
|------------------|--|------|--------------------------|------|-------|--|------|-------------------|----------------------|--------------------|
| | OM g kg ⁻¹ | pH | P mg kg ⁻¹ | K | Ca | Mg mmol _c kg ⁻¹ | H+Al | CEC ^f | SB ^g % | |
| SC ^d | 23.2 | 5.2 | 39.0 | 2.3 | 90.8 | 27.6 | 28.0 | 149.0 | 80.6 | |
| SA4 ^e | 26.6 | 7.5 | 25.0 | 2.8 | 285.0 | 66.8 | 9.0 | 363.0 | 97.6 | |
| | S | B | Cu | Fe | Mn | Zn | Cd | Cr | Ni | Pb |
| | mg kg ⁻¹ | | | | | | | | | |
| SC ^d | 6.4 | 0.23 | 5.3 | 55.0 | 52.3 | 1.9 | 0.1 | <0.1 ^c | 0.6 | 1.5 |
| SA4 ^e | 56.0 | 14.9 | 29.8 | 47.4 | 15.6 | 325.0 | 0.8 | 0.1 | 2.5 | 18.3 |
| | Total content ^b | | | | | | | | | |
| | Cd | Pb | Cu | Cr | Ni | Zn | Ba | B | Mn | Fe |
| | mg kg ⁻¹ | | | | | | | | | g kg ⁻¹ |
| SC ^d | 2.5 | 13.2 | 30.2 | 18.5 | 7.0 | 38.1 | 107 | 1.8 | 544 | 30 |
| SA4 ^e | 8.2 | 268 | 160 | 103 | 47 | 2450 | 241 | 62 | 498 | 66 |

^aKabata-Pendias and Pendias 2001 [25].

^bUSEPA 2007 [19].

^cLower than detection limit.

^dSC: uncontaminated soil.

^eSA4: contaminated soil (subarea 4).

^fCEC: cation exchange capacity.

^gSB: base saturation.

the studied area should be of substantial concern due to their high availability to plants and their potential for entering the food chain.

The available contents of Zn, B, Pb, and Cu in the contaminated soil (SA-4) were 171, 75, 12, and 6 times higher, respectively, than the values found in the uncontaminated soil sample (rate 0%) (Table 3). Even at the lowest rate of contaminated soil used in the soil mixtures (rate 25%), the dilution effect with uncontaminated soil did not sufficiently reduce the contamination levels to reach the São Paulo availability reference values. Because micronutrients are needed by plants in only minute quantities, plant toxicity and other detrimental effects occur with excess amounts [29, 30].

Considering the soil mixtures tested, the soil pH increased from 5.2 (no contaminated soil added, rate 0%) to 7.5 (rate 100%) This increase is due to the corrective action of lime, releasing OH⁻ ions and consuming H⁺. The dissolution of limestone also promoted an increase in Ca and Mg in the soil, indirectly increasing the CEC and SB as well, while reducing H+Al acidity (Table 3). Similar effects have been reported for such soil attributes when high pH residues, such as slag, are used as soil correctives [31, 32].

The phosphorus availability, as measured by the ion exchange method, clearly increased up to the 50% proportion of contaminated soil and decreased for mixtures enriched with it, as reflected by the 2nd order polynomial used to describe the phosphorus availability behavior (Table 3). The lower P availability in soil mixtures with more than 50% contaminated soil may be explained by the presence of high contents of Ca and Mg and the pH liming effects, with the formation of insoluble calcium phosphate [33].

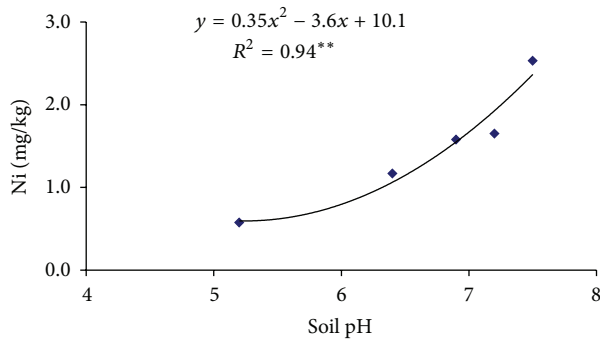
Regression models were developed to better understand the effect of lime addition (increase in soil pH); the increase in contamination by heavy metals in the soil mixtures; soil

dilution effect on micronutrient availability and mobility to plants; and plant uptake (Table 3 and Figure 1, Table 4 and Figure 2). Since the linear behavior can be related directly to the soil dilution effect, deviations from linearity can be identified and attributed to changes in elements mobility in soil and availability to plants promoted by liming.

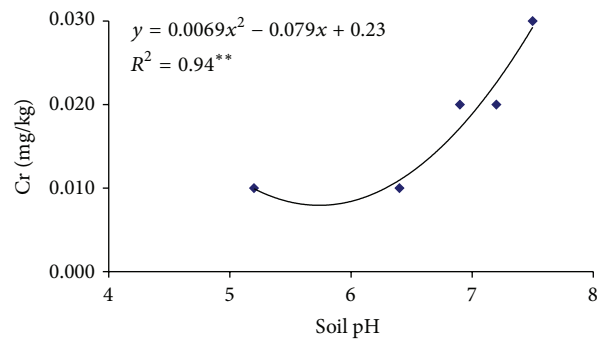
Soil pH is the single factor most consistently cited as the parameter controlling metal solubility and plant availability [36–38]. In general, heavy metal cations and micronutrients, such as Cu and Zn, are mobile under acid conditions, and increasing the pH by liming reduces their bioavailability and mobility in soils. The waste contained high levels of Mn (1,115 mg kg⁻¹) and Fe (101,603 mg kg⁻¹) and the availability of Mn to the plants decreased as the soil pH increased, reducing the element mobility in the soil even in the soil mixtures with higher proportion of contaminated soil (Table 3). Such a decrease also correlates well with the soil pH (Figure 1), but no significant correlation was observed for iron. The availability of most metals is highly reduced at pH levels higher than 6.0, due to the formation of hydroxides or precipitation as carbonates or phosphates.

Despite liming, the available contents of Cu, Zn, Cd, Cr, Ni, and Pb increased to some extent in the soil mixtures with higher proportion of contaminated soil (Table 3). However, most elements available content also correlated well with the increase in soil pH (Figure 1). Thus, one can conclude that liming was not sufficient to immobilize all such metals.

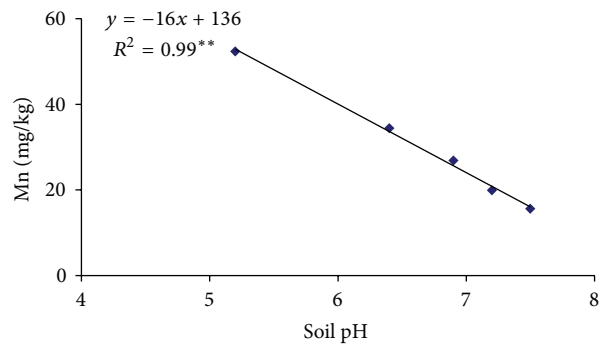
Cadmium is usually very mobile in soils, although it can precipitate at pH values higher than 7.0 as carbonate or phosphate compounds [39]. In contrast, Cu is commonly associated with organic and inorganic compounds, displaying limited mobility in soil, which is further reduced at pH levels higher than 7.0 [25]. Liming has already been tested without success as an alternative to reduce Cd mobility in



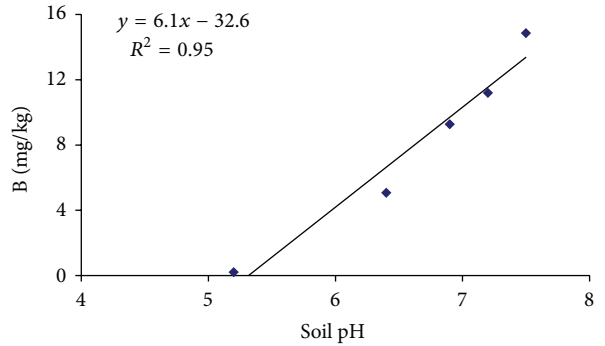
(a)



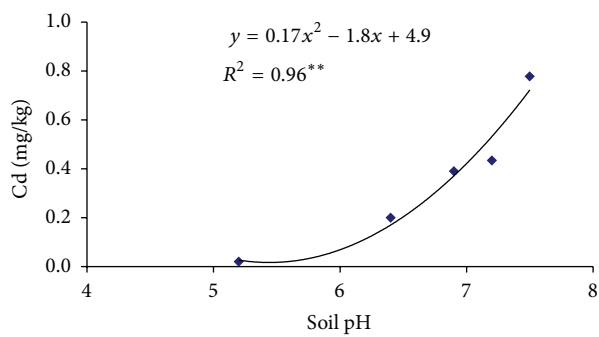
(b)



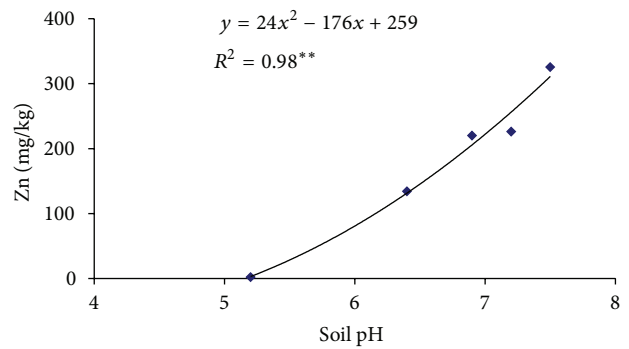
(c)



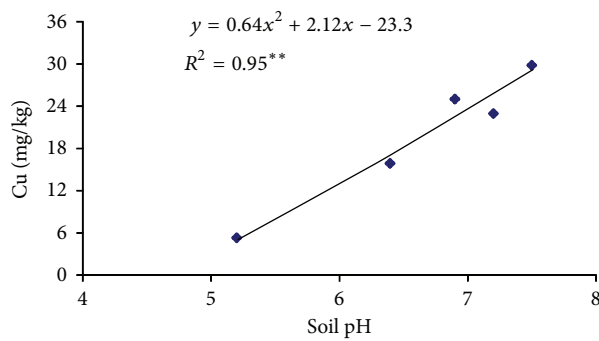
(d)



(e)



(f)



(g)

FIGURE 1: Effect of soil pH on the some elements availability in the soil mixtures tested. **Significant at $P < 0.01$.

TABLE 3: Soil fertility and available content of heavy metals in the soil mixtures used in the experiment (after incubation).

| Attribute | Proportion of contaminated soil (%) | | | | | Equation | Regression coefficient ^a <i>R</i> ² |
|--|-------------------------------------|------|------|------|------|---|--|
| | 0 | 25 | 50 | 75 | 100 | | |
| pH CaCl ₂ | 5.2 | 6.4 | 6.9 | 7.2 | 7.5 | $y = -2.3E - 04x^2 + 4.5E - 02x + 5.3$ | 0.98* |
| OM (g kg ⁻¹) | 23.2 | 23.8 | 25.3 | 25.6 | 26.6 | $y = -3.2E - 05x^2 + 3.8E - 02x + 23.13$ | 0.52* |
| P (mg kg) | 39.0 | 40.6 | 48.2 | 30.0 | 25.0 | $y = 0.3x + 38.7$ | 0.52* |
| K (mmol _c kg ⁻¹) | 2.3 | 2.0 | 2.7 | 2.4 | 2.8 | $y = 5.5E - 05x^2 + 7.5E - 04x + 2.2$ | 0.27* |
| Ca (mmol _c kg ⁻¹) | 90.8 | 193 | 288 | 242 | 285 | $y = 4.7x + 95.1$ | 0.80* |
| Mg (mmol _c kg ⁻¹) | 27.6 | 48.6 | 57.6 | 61.6 | 66.8 | $y = 0.8x + 28.9$ | 0.84* |
| H + Al (mmol _c kg ⁻¹) | 28.0 | 15.8 | 12.2 | 11.4 | 9.0 | $y = 0.003x^2 - 0.4x + 26.9$ | 0.95* |
| CEC (mmol _c kg ⁻¹) ^b | 148 | 259 | 360 | 317 | 363 | $y = 5.1x + 153$ | 0.80* |
| SB (%) ^c | 80.6 | 93.6 | 96.6 | 96.6 | 97.6 | $y = 0.5x + 81.7$ | 0.89* |
| S (mg kg ⁻¹) | 2.4 | 14.4 | 26.0 | 45.0 | 82.2 | $y = 6.6E - 03x^2 + 0.1x + 4.2$ | 0.83* |
| B (mg kg ⁻¹) | 0.2 | 5.1 | 9.3 | 11.2 | 14.9 | $y = -5.5E - 04x^2 + 0.20x - 0.36$ | 0.98* |
| Cu (mg kg ⁻¹) | 5.3 | 15.8 | 25.0 | 22.9 | 29.8 | $y = 0.4x + 5.9$ | 0.87* |
| Fe (mg kg ⁻¹) | 55.0 | 56.8 | 58.8 | 56.2 | 47.4 | $y = 0.2x + 54.3$ | 0.27* |
| Mn (mg kg ⁻¹) | 52.3 | 34.0 | 26.8 | 19.9 | 15.6 | $y = 0.003x^2 - 0.7x + 51.4$ | 0.99* |
| Zn (mg kg ⁻¹) | 1.9 | 134 | 220 | 226 | 325 | $y = 4.6x + 12.9$ | 0.92* |
| Cd (mg kg ⁻¹) | 0.02 | 0.2 | 0.4 | 0.4 | 0.8 | $y = 1.4E - 05x^2 + 5.5E - 03x + 4.9E - 02$ | 0.91* |
| Cr (mg kg ⁻¹) | 0.01 | 0.01 | 0.02 | 0.02 | 0.03 | $y = 1.6E - 07x^2 + 7.9E - 06x + 0.01$ | 0.69* |
| Ni (mg kg ⁻¹) | 0.6 | 1.2 | 1.6 | 1.7 | 2.5 | $y = 2.2E - 05x^2 + 1.5E - 02x + 0.7$ | 0.89* |
| Pb (mg kg ⁻¹) | 1.5 | 12.3 | 35.3 | 24.1 | 18.3 | $y = 0.9x - 0.4$ | 0.41* |

^aSignificant at $P < 0.05$ (*).

^bCation exchange capacity = $Ca^{2+} + Mg^{2+} + K^+ + H^+ + Al^{3+}$.

^cBase saturation = $(Ca^{2+} + Mg^{2+} + K^+ + Na^+ / CEC) * 100$.

soils [40]. The data presented in Table 3 are consistent with both statements, as the available contents of Cd were poorly affected by the soil pH and a low increase in Cu DTPA was observed above a rate of 50% contaminated soil.

Reduction in Zn mobility is usually associated with its adsorption to Al, Fe, and Mn oxides at pH levels higher than 5.5 [41]. A reduction in Zn availability was observed due to dilution of the contaminated soil, but when compared to the pH effect on Cu availability (Figure 1), Zn seemed to be more affected by the lime addition. This finding may be attributed to the higher Zn content in the soil mixtures because the total content of Zn was approximately 15 times higher than that of Cu.

Boron is usually found in soils in its anionic form, which is highly available from pH 5.0 to 7.0 [42] and which corresponds to the range observed in the pot experiment. According to the literature, B availability can be influenced by soil organic matter content and texture [43, 44]. In the present study, because a small increase was observed in the organic matter content of the soil mixtures and a larger increase was observed for the B concentration in the same situation, there is no evidence of an organic matter effect on B availability (Table 3).

The concentration of both OM and B did not seem to be affected by liming (Table 3). A significant linear regression was obtained for OM and available B with increasing amounts of contaminated soil in the soil mixtures (Table 3). However, in both cases, one can conclude that this is exclusively due

to the contribution of the contaminated soil content. A very small deviation was observed when a mass balance of such attributes was performed while considering the contaminated soil proportion in such mixtures.

According to van Raij et al. [34], concentrations of B above 0.6 mg dm^{-3} and of S above 10 mg dm^{-3} in soil are to be considered high for local soils. Values above such limits were observed for all of the proportion tested. In addition, the linear increase in S concentration in the soil mixtures with contaminated soil indicates that changes in pH did not affect the availability of S. A similar effect has been reported in the literature [45].

3.2. Dry Matter Yield and Element Contents in the Corn.

Although symptoms of toxicity in plants were observed, this did not affect the dry matter yield. Visual evaluation of the plants 40 days after emergence evidenced purple and brown spotting, suggesting P deficiency in treatments without contaminated soil (0%). The soil analysis showed lower concentrations of available P as the contaminated soil proportion increased in the soil mixtures (Table 3).

The Zn concentrations in the corn shoots varied from 46.1 to 454 mg kg^{-1} , surpassing the level of 100 mg kg^{-1} considered to be adequate [35] for all proportion studied, except for the 0 proportion (uncontaminated soil). The toxic range for zinc in plants is reported as 100 – 400 mg kg^{-1} [25, 46].

TABLE 4: Dry matter yield, element concentration, and adequate nutritional range for corn grown in the soil mixtures studied.

| Attributes | Proportion of contaminated soil (%) | | | | | Adequate range | Equation | Regression coefficient ^a <i>R</i> ² |
|-----------------------------------|-------------------------------------|------|------|------|------|----------------------|---|--|
| | 0 | 25 | 50 | 75 | 100 | | | |
| Dry matter (g pot ⁻¹) | 13.3 | 12.9 | 12.4 | 12.4 | 13.1 | | — | NS |
| N (g kg ⁻¹) | 29.1 | 27.7 | 26.9 | 27.2 | 26.5 | 27–35 ^b | $y = 2.9E - 04x^2 - 5.2E - 02x + 28.9$ | 0.27* |
| P (g kg ⁻¹) | 1.10 | 0.90 | 0.94 | 1.14 | 1.13 | 2.0–4.0 ^b | $y = 6.1E - 05x^2 - 4.9E - 03x + 1.1$ | 0.28* |
| K (g kg ⁻¹) | 39.3 | 47.9 | 48.1 | 49.7 | 49.9 | 17–35 ^b | $y = 0.3x + 40.2$ | 0.73* |
| Ca (g kg ⁻¹) | 7.3 | 8.6 | 8.9 | 9.1 | 9.1 | 2.5–8.0 ^b | $y = -3.1E - 04x^2 + 4.8E - 02x + 7.4$ | 0.48* |
| Mg (g kg ⁻¹) | 3.6 | 5.1 | 5.6 | 5.7 | 5.8 | 1.5–5.0 ^b | $y = -3.61E - 04x^2 + 5.5E - 02x + 3.7$ | 0.76* |
| S (g kg ⁻¹) | 1.2 | 1.8 | 2.0 | 2.0 | 2.2 | 1.5–3.0 ^b | $y = -1.1E - 04x^2 + 2E - 02x + 1.3$ | 0.75* |
| B (mg kg ⁻¹) | 25.7 | 315 | 572 | 779 | 950 | 10–25 ^b | $y = 12.5x + 24.8$ | 0.91* |
| Cu (mg kg ⁻¹) | 7.5 | 8.9 | 11.6 | 9.8 | 13.0 | 6–20 ^b | $y = -1.2E - 04x^2 + 5.9E - 02x + 7.7$ | 0.51* |
| Fe (mg kg ⁻¹) | 66.8 | 83.4 | 93.0 | 86.0 | 80.5 | 30–250 ^b | — | NS |
| Mn (mg kg ⁻¹) | 112 | 43.8 | 46.0 | 55.2 | 67.5 | 20–200 ^b | $y = 0.02x^2 - 2.23x + 104.4$ | 0.77* |
| Zn (mg kg ⁻¹) | 46.1 | 276 | 328 | 359 | 454 | 15–100 ^b | $y = 6.92x + 71.5$ | 0.81* |
| Cd (mg kg ⁻¹) | 0.22 | 0.34 | 0.32 | 0.26 | 0.42 | 0.1 ^c | — | NS |
| Cr (mg kg ⁻¹) | 0.80 | 0.56 | 1.22 | 0.84 | 0.30 | 0.20 ^c | — | NS |
| Ni (mg kg ⁻¹) | 0.60 | 0.10 | 2.60 | 0.10 | 0.10 | 0.19 ^c | — | NS |
| Pb (mg kg ⁻¹) | 0.58 | 0.82 | 6.32 | 12.1 | 0.70 | 0.02 ^c | $y = 0.3x - 1.5$ | 0.30* |

^aSignificant at $P < 0.05$ (*) and not significant (NS).

^bvan Raij et al. [34].

^cU. C. Gupta and S. C. Gupta [35].

Other symptoms of toxicity and deficiency were observed in the shoots starting at the 25% proportion, such as chlorosis, necrosis, browning, spotting, and death of older leaves. The chlorosis of older leaves with evolution to necrosis has been associated with boron toxicity [42]. Similar symptoms of toxicity in corn due to excess B have also been reported, with toxic effects for most plants in the range of 50–200 mg kg⁻¹ [25, 44, 46]. In the present work, the soil available B concentration increased with the addition of contaminated soil to the mixtures tested. This finding indicates that B availability was not affected by soil pH. Plant analysis supported this statement, as B concentrations were found well above the nutritionally adequate range and accumulated in the corn shoots (Table 4, Figure 2).

Gabos et al. [47], in an experiment using the same contaminated soil employed in this study, tested organic matter amendments for the mitigation of contaminants and used sunflowers as the test plants; they also observed high levels of B, Cu, and Zn in the shoots regardless of treatment (385–374 mg kg⁻¹ for B; 305–289 mg kg⁻¹ for Cu, and 338–473 mg kg⁻¹ for Zn). However, the plants showed no symptoms of B, Cu, or Zn toxicity. According to van Raij et al. [34], levels of 100, 100, and 80 mg kg⁻¹, respectively, for B, Cu, and Zn are considered adequate for sunflowers.

Toxicity in plants has been reported in the literature to occur for Cu from 20–100 mg kg⁻¹, for Mn from 300–500 mg kg⁻¹, and for Pb from 30–300 mg kg⁻¹ [25, 46]. No accumulation effect above the adequate range was observed for the Cu content in the corn shoots for all soil mixtures (Table 4), despite an increasing trend with an increase in available contents in the soil (Figure 2). Although a liming

effect on Mn availability in the soil was clear, liming's nutritional impact on corn did not limit plant development or result in deficiency (Table 4). Lead accumulation in the corn shoots seemed closely related to the available contents of lead in the soil (Tables 3 and 4) but did not reach toxic levels.

Chromium, nickel, and cadmium concentrations in the corn shoots varied from 0.3 to 1.22, 0.1 to 2.6, and 0.22 to 0.42 mg kg⁻¹, respectively, surpassing the level of 0.2 mg kg⁻¹ considered as adequate [35]. According to Macnicol and Beckett [48], levels above 8 mg kg⁻¹ of Ni, 4 mg kg⁻¹ of Cd, 2 mg kg⁻¹ of Cr, and 15–30 mg kg⁻¹ of Pb [25, 49] may cause toxicity in many plants, reducing their production. Although the available contents of Cd, Cr, and Ni were higher in the soil mixtures containing higher proportion of contaminated soil, such metals were not significantly found in the corn shoots (Table 4).

Nitrogen and iron absorption by the plants was not influenced by the rate of contaminated soil in the soil mixtures or by the soil pH.

The correlation coefficients for the proportion of contaminated soil and the Ca, Mg, S, and K concentrations in the shoots of the corn were significant (Table 4), with Ca, Mg, and S found to be within or close to the adequate nutritional range. The Ca and Mg concentrations in the shoots of the corn varied from 7.3 to 9.1 and 3.6 to 5.8 g kg⁻¹, respectively, barely surpassing the levels of 8.0 and 5.0 g kg⁻¹ considered as adequate [35] for all proportion studied except for the 0 rate (uncontaminated soil). The S and Fe concentrations in the shoots of the corn were considered as adequate for all proportion tested [35]. The K concentration in the shoots of the corn varied from 39.3 to 49.9 g kg⁻¹, surpassing the level of

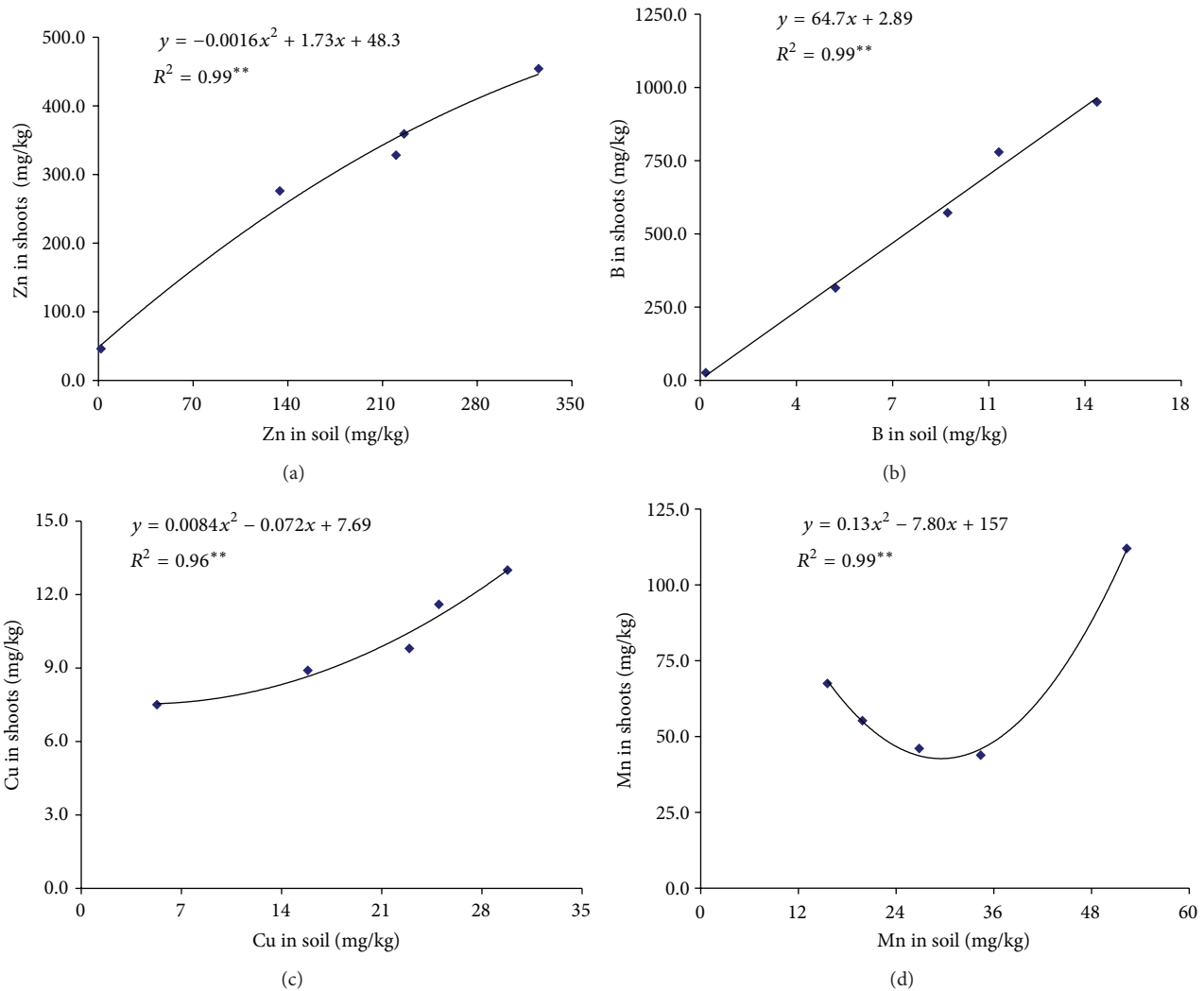


FIGURE 2: Corn shoots uptake and available content of elements in soil. **Significant at $P < 0.01$.

35 g kg^{-1} considered as adequate [35] for all proportion tested (Table 4).

4. Conclusions

The main contaminants present in the scrap metal residue were Ba, Cu, Cr, Ni, Pb, Zn, and B, which increased total concentrations of these elements in the soil above the maximum content commonly found in the soils of São Paulo. Furthermore, the amounts of Zn, Cd, and Pb were above the intervention levels suggesting that a strategy should be made for soil remediation at this area.

Liming of 10 t ha^{-1} followed by soil dilution at any proportion studied was not successful for mitigation of the inorganic contaminants to a desired level of soil fertility, as demonstrated by the available amounts extracted by the DTPA method (Zn, Pb, Cu, Ni, Cr, Cd) and hot water (B) still present in the soil. This fact was also proved by the phytotoxicity observed and caused by high amounts of B and Zn accumulating in the plant tissue.

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