ZINC AVAILABILITY FOR CORN GROWN ON AN OXISOL AMENDED WITH FLUE DUST

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ABSTRACT: The costs related to the construction and maintenance of industrial landfills, and the environmental risks that they may represent, have increased the interest of several types of industries in studying the possibility of applying residues to agricultural soils. This study evaluates the efficiency of flue dust as a zinc source for corn, and the zinc availability for corn evaluated by four methods. A greenhouse experiment carried out at Campinas, SP, Brazil, evaluated the effect of two zinc sources (flue dust and zinc sulphate), at three rates (5, 50 and 150 mg dm$^{-3}$), in one soil (Rhodic Hapludox) under two pH conditions (5.0 and 6.0). The treatments were arranged in a randomized factorial scheme design with three replications. Zinc availability indexes were determined by the pH 7.3 DTPA, Mehlich-1, and Mehlich-3 methods. The free Zn$^{2+}$ activity in soil solution was calculated by the MINTEQ computer model. The extraction methods and the activity of the free ion Zn$^{2+}$ were equally reliable to evaluate zinc availability in the soil amended with flue dust. More than 70% of the total Zn present in the saturation extract was in the free ion form, and the remainder was mainly complexed to SO$_4^{2-}$ and OH$^-$, independent of soil pH. Flue dust is a zinc supplier to plants. All tested methods were efficient in evaluating Zn availability for corn, independently of soil pH.

Key words: DTPA, heavy metals, industrial wastes, speciation, soil pH

INTRODUCTION

Iron smelters produce several residues that can cause environmental impacts depending on the form and location where they are disposed. Several studies show the potential use of iron smelter industry residues as correctives and fertilizers (Anderson & Parkpian, 1998, Silva, 1999). Among them the flue dust, containing about 12% of Zn originated from the steel production, represents a potential source of this nutrient to plants.

Retention of Zn by the soil is strongly influenced by pH, being greater at high pH (Alcântara & Camargo, 2001), influenced by the metal concentration in the soil (Basta & Tabatabai, 1992), by the CEC (Cunha et al., 1994), by the organic matter content (Lewis & Rule, 2001), and by the soil mineralogical characteristics (Ziper et al., 1988).
Metal availability can be evaluated through the use of appropriate extractants, but the extracted amounts ought to be correlated with the element quantity or concentration in the plant (Abreu et al., 2002). Several studies demonstrated that the DTPA and Mehlich-1 were adequate to evaluate Cd, Ni, Zn and Pb availability (Ribeiro-Filho et al., 2001). However, metal absorption and metal toxicity depend on the chemical species in solution so that plant response generally correlates better with the ion concentration or activity in solution (Parker et al., 1995). The ionic species concentration resulting from metal complexation with inorganic anions can be estimated through chemical balance models implemented in softwares such as MINTEQ and GEOCHEM, among others (Mattigod & Zachara, 1996) that use total dissolved contents as input data. Considering the potential of flue dust as source of zinc to plants and the contradictory results found in literature on the best chemical extraction method to be used to evaluate its availability, the objective of this work was to evaluate flue dust as a zinc source for corn, compared to a commercial Zn source like ZnSO₄, and the use of three traditional extraction methods and a calculation model for free ionic activity, in predicting Zn availability for corn, in two soil pH environments.

**MATERIAL AND METHODS**

A greenhouse experiment was carried out from November 2000 to January 2001 in Campinas, SP, Brazil (22°54'20"S; 47°05'34"W; 674 m above sea level), in order to evaluate the effect of two zinc sources (flue dust and zinc sulphate) at three rates (5, 50 and 150 mg dm⁻³) and two soil pHs (5.0 and 6.0). Treatments were arranged as a randomized design in a factorial 2 × 3 × 3 scheme with three replications. The surface (0-20 cm) layer of the Rhodic Hapludox used in the experiment, presented: Zn = 0.8 mg dm⁻³; organic matter = 27 g dm⁻³; pH = 4.3; CEC = 53.8 mmol dm⁻³; and clay content = 250 g kg⁻¹. The soil to solution ratio for the pH determination was 1:2.

The very fine powdered flue dust used in the experiment was supplied by a steel plant from the São Paulo State and presented the following metal concentrations: Fe = 684; Zn = 122; Mn = 63; Pb = 24; Cr = 60; Al = 3.5; Cu = 2.3; Ni = 0.48 and Cd = 0.13, with pH (in 0.01 mol L⁻¹ CaCl₂) = 9.4, pH (in 0.005 mol L⁻¹ acetic acid) = 9.6. Zn water solubility was determined according to the official method from the Analytical Chemistry International Association and yielded a value of 690 mg kg⁻¹ (Kane, 1995).

At the end of the experiment, the corn was harvested and the shoot washed, oven-dried at 70°C until constant weight, weighed and ground using a Willey mill to pass 60-mesh silve and digested in nitric acid constant weight, weighed and ground using a Willey mill to pass 60-mesh silve and digested in nitric acid.

Zinc concentration in corn shoot varied from 14.4 to 522.8 mg kg⁻¹ (Figure 1), surpassing the level of 95 mg kg⁻¹, considered as toxic (Gupta & Gupta, 1998), for the higher rates of the two zinc sources. Similar results were obtained by Silva (1999) and...
Accioly (1996) for a soil of the Minas Gerais State, Brazil. Plant visual evaluation 40 days after emergence evidenced a yellowing of the younger leaves in treatments that received 150 mg dm\(^{-3}\) of Zn, independently of pH and Zn source, suggesting Zn toxicity (Adriano et al., 1971).

For both zinc sources, the increase in the application rate is accompanied by an increase in corn shoot, regardless of pH, with a linear and significant correlation (Figure 1). However, the flue dust promoted lower zinc concentration in the shoot than zinc sulphate, in contrast with the results of Accioly (1996). With the application of 50 mg Zn dm\(^{-3}\) to the soil, 79 and 152 mg Zn kg\(^{-1}\) of dry matter were recovered from the flue dust and zinc sulphate treatments, respectively.

These results show that, although the flue dust is a zinc supplier to plants, its rate has to be higher than that recommended as zinc sulphate due to its lower solubility. This is be a problem for flue dust containing significant amounts of other heavy metals.

Soil Zn ranged from 0.8 to 94.4 mg dm\(^{-3}\) (DTPA), 2.3 to 109.3 mg dm\(^{-3}\) (Mehlich-1) and 3.5 to 118.6 mg dm\(^{-3}\) (Mehlich-3) (Figure 2). The Mehlich-1 and Mehlich-3 extractants exhibited larger extraction capacity than DTPA, regardless of soil pH (Figure 2), probably because the former extractants released part of adsorbed Zn to oxides, while pH 7.3 DTPA, an alkaline extractant, did not (Ribeiro-Filho et al., 1999).

It should be pointed out that even in the presence of visual symptoms of Zn toxicity in the plants, the Zn concentration in the soil was lower than the suggested value of 130 mg kg\(^{-1}\) considered as toxic by the Inter-Departmental Committee on Redevelopment of Contaminated Land (1987). However, it should be mentioned that this suggested toxic level was obtained with a 0.05 mol L\(^{-1}\) EDTA solution, while in this experiment other extractants were used for metal availability evaluation. The extractants were efficient in evaluating zinc availability for corn plants (Figure 3), in agreement with the results of Accioly (1996) and Amaral et al. (1996), in an experiment with flue dust, having lettuce and corn as test plants using a similar soil. The determination coefficients between DTPA, Mehlich-1, and Mehlich-3 soil extracted Zn and its concentration in corn shoot were smaller for flue dust than that for zinc sulphate.
Taking into account the extractant efficiency regarding soil pH (Figure 4), it was observed that the extractants were efficient in evaluating Zn availability irrespective of the zinc source. A decrease was also verified in its availability with pH increase for both Zn sources, probably due to the decreasing amount of free Zn$^{2+}$ by complex reactions with SO$_4^{2-}$, OH and other ligands (Shuman, 1986) (Table 1).

Flue dust supplied less zinc to corn than zinc sulphate, probably because the former is less soluble. Approximately only 0.6% and 43% of total Zn obtained by the aqua regia extraction of flue dust was respectively soluble in water, and in ammonium neutral citrate. The water solubility is the determinant factor to determine the short-term agronomic efficiency. Several studies have demonstrated that metals added to soils as metal salts are more available than the metals in sewage sludge (Logan & Chaney, 1983) or as oxides (Abreu et al., 1996). Moreover, Zn availability can also be related to the differences in their constituents, once metal salts, like zinc sulphate, just add the anion bound to the metal while flue dust adds metal oxides.

The ionic speciation of the saturation extract of the zinc sulphate and flue dust-treatments is presented at Table 1. The Zn$^{2+}$ free species activity increased with the zinc sulphate or flue dust addition rate at pH 5.0 and decreased only for the flue dust treatment at pH 6.0. The changing soil pH from 5.0 to 6.0 increased more the species ZnSO$_4$º than ZnOHº for both sources of zinc. This can be explained by the greater association of Zn with SO$_4^{2-}$, as with the ZnSO$_4$º ionic pair. The predominant zinc species in solution below pH 7.7 is Zn$^{2+}$, although ZnOHº is more prevalent above this pH and the ZnSO$_4$º ionic pair is predominant in solution below pH 6.0 (Lindsay, 1979).

![Figure 3 - Regression between zinc extracted by: (a) DTPA method at pH 7.3, (b) Mehlich-1 method and (c) Mehlich-3 method and zinc in the corn shoots. ▲, zinc sulphate; ●, flue dust; *, significant at 95% level; **, significant at the 99% level.]

Table 1 - Ionic species percentual distribution in soil solution for two sources of Zn at two pH levels.

| Zn Source | Zn$^{2+}$ | ZnOHº | ZnSO$_4$º | Other
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>mg kg$^{-1}$</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Flue dust</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 5.0</td>
<td>82</td>
<td>0.1</td>
<td>18</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>82</td>
<td>-</td>
<td>15</td>
<td>2.7</td>
</tr>
<tr>
<td>150</td>
<td>89</td>
<td>-</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>ZnSO$_4$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>82</td>
<td>&lt;0.1</td>
<td>17</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>84</td>
<td>&lt;0.1</td>
<td>15</td>
<td>0.9</td>
</tr>
<tr>
<td>150</td>
<td>90</td>
<td>&lt;0.1</td>
<td>9</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Flue dust</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6.0</td>
<td>73</td>
<td>3.1</td>
<td>23</td>
<td>1.3</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>0.5</td>
<td>26</td>
<td>1.4</td>
</tr>
<tr>
<td>150</td>
<td>71</td>
<td>0.3</td>
<td>27</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>ZnSO$_4$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>76</td>
<td>&lt;0.1</td>
<td>23</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>77</td>
<td>3.6</td>
<td>19</td>
<td>0.4</td>
</tr>
<tr>
<td>150</td>
<td>82</td>
<td>&lt;0.1</td>
<td>17</td>
<td>0.6</td>
</tr>
</tbody>
</table>
The Zn\(^{2+}\) activity also decreased considerably when pH changed from 5.0 to 6.0 with a 18 and 8% difference for higher flue dust and zinc sulphate rates, respectively (Table 1). If the free species (Zn\(^{2+}\)) is the predominantly absorbed form (Machado & Pavan, 1987), this might partly explain the lower Zn absorption by corn (Figure 4).

Table 2 - Linear correlation coefficients between Zn availability measured by three extraction methods and Zn\(^{2+}\) estimated by the MINTEQ computer speciation program, and Zn uptake by the plants in a soil amended with flue dust and ZnSO\(_4\) as Zn sources.

<table>
<thead>
<tr>
<th>Zn Source</th>
<th>Zn(^{2+}) (pH 7.3 DTPA)</th>
<th>Zn (Mehlich-1)</th>
<th>Zn (Mehlich-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue dust</td>
<td>0.85**</td>
<td>0.72**</td>
<td>0.69**</td>
</tr>
<tr>
<td>ZnSO(_4)</td>
<td>0.85**</td>
<td>0.92**</td>
<td>0.91**</td>
</tr>
</tbody>
</table>

*, **Significant at 95 and 99% levels, respectively.

Table 3 - Linear correlation coefficients between Zn\(^{2+}\) estimated by the MINTEQ computer speciation program and Zn availability for corn estimated by pH 7.3 DTPA, Mehlich-1 and Mehlich-3, for two sources of Zn at two pH levels.

<table>
<thead>
<tr>
<th>Extraction Method</th>
<th>Zn(^{2+}) activity in saturation paste</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flue dust</td>
</tr>
<tr>
<td></td>
<td>pH 7.3 DTPA</td>
</tr>
<tr>
<td></td>
<td>Mehlich-1</td>
</tr>
<tr>
<td></td>
<td>Mehlich-3</td>
</tr>
</tbody>
</table>

*, **Significant at 95 and 99% levels and non significant, respectively.

In general, the estimated activity of Zn\(^{2+}\) in solution and the three extractants were efficient in evaluating soil Zn availability to corn, whether supplied as flue dust or zinc sulphate, for the two pH values (Table 2, Figure 3).

High correlation was observed between the three extraction methods and Zn\(^{2+}\) ionic activity in the saturation extract at pH 5.0 and 6.0, except for the flue dust treatment at soil pH 6.0, being similar or greater than the correlations obtained for the three studied extractants (Table 3, Figures 3 and 4). Since the activity of an element in the soil solution is just an intensity factor, these results indicate that the quantities, which are capacity factors, were very important for the Zn supply for corn, at the highest soil pH value.

CONCLUSIONS

The flue dust is an efficient source of zinc to corn. The DTPA, Mehlich-1, Mehlich-3 extraction methods and the estimated free zinc activity are equally
reliable to evaluate zinc availability in an Oxisol amended with flue dust.

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