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Soil solution concentrations and chemical species of copper and zinc in a soil with a history of pig slurry application and plant cultivation

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ABSTRACT

Successive pig slurry applications may increase soil copper (Cu) and zinc (Zn) concentrations and change the proportions of free chemical species in solution when combined with plant cultivation. The aim of this study was to assess the soluble, available, and total Cu and Zn concentrations and the distribution of their chemical species in the solution in a Hapludalf soil with a history of pig slurry application and plant cultivation. The study was conducted in undisturbed soil columns that originated from an 8-year-long experiment conducted at the experimental unit of the Federal University of Santa Maria in Santa Maria, southern Brazil. The soil was a Typic Hapludalf soil fertilized with pig slurry at rates of 0, 20, 40, and 80 $m^3\,ha^{-1}$. The soil was collected from depth intervals of 0–0.05, 0.05–0.1, 0.1–0.2, 0.2–0.3, 0.3–0.4, and 0.4–0.6 m before and after cultivation with black oat and maize in a greenhouse to assess the total and available Cu and Zn concentrations and to extract the solution. The soil solution concentrations of the main cations, anions, and dissolved organic carbon (DOC) and pH were assessed. The distribution of Cu and Zn chemical species was assessed using the Visual Minteq software. The history of 21 pig slurry applications increased the concentration of Cu and Zn in surface soil intervals, but the concentration of Cu also increased in the soil solution at depth. The phytotoxicity caused by Cu and Zn may not occur even after several years of pig slurry application because the plants provide soil conditions in which chemical species complexed with dissolved organic carbon predominate and Cu and Zn in free forms are present only in small amounts.

1. Introduction

Pigs on farms in southern Brazil number approximately 22.02 million, representing approximately 54% of the total pig stock in Brazil and generating high volumes of pig slurry (ABIPECS, 2013). The state of Rio Grande do Sul (RS) in southern Brazil contains 17% of the national stock, which produces approximately 38.000 m^3 of pig slurry per day (FEPAM, 2004). This slurry is primarily used as fertilizer in agricultural production to provide nutrients, including nitrogen (N), phosphorus (P), and potassium (K), to crops (Brunetto et al., 2012; Couto et al., 2015; Guardini et al., 2012; Scherer et al., 2010). However, successive applications of high doses of pig slurry may lead to increased levels of other soil elements, particularly those present in high concentrations in the slurry (Adeli et al., 2008; Lourenzi et al., 2014; Scherer et al., 2010) or those required in small amounts by plants, including heavy metals such as copper (Cu) and zinc (Zn) (Adeli et al., 2008; Legros et al., 2013; Mallmann et al., 2014; Tiecher et al., 2013).

Cu and Zn are retained in the soil through physicochemical bonds with varying degrees of energy, and the availability and soil sorption capacity are controlled by the amount and type of clay minerals; iron (Fe), aluminum (Al), and manganese (Mn) oxides and hydroxides; carbonates; and organic matter, in addition to the pH and cation exchange capacity (CEC) (Bradl, 2004; McBride, 1994). The adsorption of heavy metals supplied to soils by external sources initially occurs at the most avid adsorption sites, with greater affinity of Cu for the functional groups of organic constituents, given its electron configuration, and of Zn for certain

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mineral constituents (Brunetto et al., 2014; Croué et al., 2003). However, frequent pig slurry applications may lead to saturation of these surface functional groups, increasing the metal concentration in the soil solution and the available concentrations, which may increase the risk of toxicity to plants and transfer via leachate, thereby increasing the contamination of surface water bodies, or via percolation, thereby increasing the contamination of subsurface waters (Fernández-Calviño et al., 2012; Legros et al., 2013).

Plants and microorganisms absorb Cu and Zn from the soil solution, preferably in inorganic chemical forms that are coordinated to water molecules, classified as free species (Cu^{2+} and Zn^{2+}) (McBride, 1994). However, the bioavailability and mobility of heavy metals are dependent not only on the total concentration in the soil solution but also on the chemical species contained therein. This occurs because heavy metals, in addition to their free forms, may act as central cations forming complexes and ion pairs with various organic and inorganic ligands, which are soluble in the soil solution and controlled by the soil and soil solution characteristics, particularly by the concentrations of dissolved organic compounds (DOC) and by the pH (Kim et al., 2010; Nolan et al., 2003; Pérez-Esteban et al., 2014; Ren et al., 2015). Species complexed with inorganic ligands (OH^-, $CO_3{}^{2-}$, $PO_4{}^-$, $SO_4{}^{2-}$, and $NO_3{}^-$) in solution in agricultural soils are typically present in low concentrations, as reported by Pérez-Esteban et al. (2014), who reported concentrations of less than 1% Cu and 3% Zn complexing with inorganic binders, indicating that Cu and Zn in solution in agricultural soils are free species and species complexed with organic compounds (Kim et al., 2010; Meers et al., 2006; Nolan et al., 2003; Pérez-Esteban et al., 2014). The formation of species complexed with organic compounds, particularly Cu, which forms more stable complexes, may reduce their availability and increase their mobility in soil (Ashworth and Alloway, 2008; Weng et al., 2002).

Identifying the Cu and Zn chemical species in the soil solution is critical to best assess their availability and mobility when multi-element fertilizers such as pig slurry are added to the soil and the soil is planted with annual crops. Plants have the ability to modify the chemical characteristics of the solution near the root system through the absorption and accumulation of elements in the phytomass. In addition, the exudation of ions and organic compounds, including amino acids and low-molecular-weight organic acids, affects the pH and the solubility and distribution of heavy metal species (Kim et al., 2010; Li et al., 2013). The availability of metals in the soil has been analyzed in many studies using chemical extraction methods. However, these methods might not provide adequate values of bioavailability because they do not take into account whether the chemical species are free or complexed with organic or inorganic ligands. Thus, knowledge of the distribution of chemical species is required for a better diagnosis of the bioavailability of metals in the soil, and such knowledge can be obtained using specific software (Girotto et al., 2010a; Kim et al., 2010; Marcato et al., 2009; Yeh et al., 2009).

The aim of this study was to assess the soluble, available, and total Cu and Zn concentrations and the distribution of their chemical species in the solution in a Hapludalf soil subjected to pig slurry applications and plant cultivation.

2. Materials and methods

2.1. Soil, pig slurry, and cultivation

Undisturbed soil columns originating from a long-term experiment were used in the present study conducted at the Federal University of Santa Maria (Universidade Federal de Santa Maria, UFSM) in Santa Maria, Rio Grande do Sul, Brazil (29°43′12″S, 53°43′4″W). The experiment was conducted in the field from 2000 to 2008 under no-tillage in a Typic Hapludalf soil (Soil Survey Staff, 2006) that had the following characteristics in the 0–0.1-m depth interval prior to starting the experiment: 170 g kg^{-1} clay, 300 g kg^{-1} silt, 530 g kg^{-1} sand, 16 g kg^{-1} organic matter (OM), determined by oxidation with dichromate (Tedesco et al., 1995), pH in water (1:1) 4.7, 15 mg kg^{-1} available P (Mehlich-1-extractable), 96 mg kg^{-1} exchangeable K (Mehlich-1-extractable), and 0.8, 2.7, and 1.1 cmol$_c$ dm^{-3} exchangeable Al, Ca, and Mg, respectively (1 mol L^{-1} KCl extractable) (Tedesco et al., 1995).

Crops were planted in the following sequence during the study: black oat (*Avena strigosa* S.), maize (*Zea mays* L.), and radish (*Raphanus sativus* L.) in 2000/2001 and 2001/2002; black oat, pearl millet (*Pennisetum americanum* L.), and black turtle bean (*Phaseolus vulgaris* L.) in 2002/2003; black oat + common vetch (*Vicia sativa* L.) and maize in 2003/2004 and 2004/2005; black oat, black turtle bean, and sunn (*Crotalaria juncea* L.) in 2005/2006; and black oat and maize in 2006/2007. The treatments consisted of applying pig slurry as the only source of nutrients by surface broadcasting at doses of 0, 20, 40, and 80 m^3 ha^{-1} preceding each crop planting for a total of 19 applications during the 8 years of cultivation. The experimental designed was one of randomized blocks with 3 replicates.

The total concentrations of N, P, and K in the pig slurry were measured after digestion of 2-mL samples *in natura* with 2 mL of H_2SO_4 and 1 mL of H_2O_2 (Tedesco et al., 1995). For determinations of the total Ca, Mg, Cu, and Zn, the pig slurry was oven-dried at 65 °C to a constant weight to measure the dry matter (DM). Afterward, 0.1 g was ground and digested in 3.0 mL of HNO_3 plus 1 mL of $HClO_4$ (EMBRAPA, 1997). The total organic carbon (C) content of the pig slurry was determined from sub-samples of finely ground DM using an elemental autoanalyzer (FlashEA 1112, Thermo Finnigan, Italy). Based on the resulting concentrations of chemical elements and the application rates of pig slurry, the amounts applied in the 19 applications in the field and 2 in the greenhouse were determined, as shown in Table 1.

Table 1
Amounts of chemicals applied through pig slurry (PS) with 19 applications in the field experiment and in the cultivation of black oat and maize crops in the greenhouse.

Rate PS (m^3 ha^{-1})	C (Mg ha^{-1})	N (kg ha^{-1})	P (kg ha^{-1})	K (kg ha^{-1})	Ca (kg ha^{-1})	Mg (kg ha^{-1})	Cu (kg ha^{-1})	Zn (kg ha^{-1})
Applied in 19 applications performed in the field experiment								
0	–	–	–	–	–	–	–	–
20	4.69	951	624	364	327	378	17.1	21.4
40	9.39	1902	1248	727	654	756	34.2	42.8
80	18.78	3804	2497	1455	1308	1513	68.4	85.6
Applied in the cultivation of black oat and maize in the greenhouse								
0	–	–	–	–	–	–	–	–
20	0.91	152	80	50	82	54	2.13	5.58
40	1.82	304	160	100	164	108	4.26	11.15
80	3.64	608	320	200	328	216	8.52	22.30