Note

HEAVY METALS IN A DEGRADED SOIL TREATED WITH SLUDGE FROM WATER TREATMENT PLANT

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ABSTRACT: The application of water treatment sludge (WTS) to degraded soil is an alternative for both residue disposal and degraded soil reclaim. This study evaluated effects of the application of water treatment sludge to a Typic Hapludox soil degraded by tin mining in the National Forest of Jamari, State of Rondonia, Brazil, on the content of heavy metals. A completely randomized experimental design with five treatments was used: control (n = 4); chemical control, which received only liming (n = 4); and rates D_{100}, D_{150} and D_{200}, which corresponded to 100, 150 and 200 mg of N-sludge kg^{-1} soil (n = 20), respectively. Thirty days after liming, period in which soil moisture was kept at 70% of the retention capacity, soil samples were taken and analyzed for total and extractable Fe, Cu, Mn, Zn, Cd, Pb, Ni, and Cr. The application of WTS increased heavy-metal contents in the degraded soil. Although heavy metals were below their respective critical limits, sludge application onto degraded areas may cause hazardous environmental impact and thus must be monitored.
Key words: soil reclaim, tin mining, Mehlich 1, environmental pollution

METAIS PESADOS EM SOLO DEGRADADO TRATADO COM LODO DE ESTAÇÃO DE TRATAMENTO DE ÁGUA

RESUMO: A aplicação do lodo de estação de tratamento de água (LETA) em solos degradados é uma alternativa tanto para disposição desse resíduo como para a recuperação do solo. Neste trabalho avaliaram-se os efeitos do LETA nos teores de metais pesados em um Latossolo degradado por mineração de cassiterita na Floresta Nacional do Jamari, RO, Brasil. Utilizou-se delineamento experimental inteiramente casualizado com cinco tratamentos: testemunha (n = 4); testemunha química, que recebeu apenas calagem (n = 4) e doses D_{100}, D_{150} e D_{200} (respectivamente 100, 150 e 200 mg de N kg^{-1} solo na forma de LETA), aplicadas antes da calagem (n = 20). Após 30 dias da calagem, período em que o solo contido nos vasos foi mantido com teor de umidade próximo à capacidade de retenção, coletaram-se amostras de solo, que foram analisadas com relação aos teores totais e extraíveis de Fe, Cu, Mn, Zn, Cd, Pb, Ni e Cr. A aplicação de LETA aumentou os teores dos metais pesados do solo. A aplicação deste tipo de lodo em áreas degradadas pode causar impacto ambiental e, portanto, deve ser monitorada.
Palavras-chave: recuperação de solo, mineração de estanho, Mehlich 1, poluição

INTRODUCTION

The water treatment sludge (WTS), indiscriminately returned to watercourse, causes alterations in the flora and the fauna (Cordeiro, 1999) because it contains sand, silt and clay, humic and mineral substances, chemical coagulants, heavy metals and, depending on the water source, pathogenic microorganisms. Minimizing the negative environmental effects of this residue is a great challenge. Alternatives for use of WTS are cement manufacturing, brick making, disposal in sanitary earthwork, composting (with yard waste or sewage sludge), soil potting, and soil disposal (agriculture, forest, soil reclaim) (AWWA, 1999, Morita et al., 2002).

The main advantage of the agricultural use of WTS is the improvement of the physical characteristics of soils resulting from large amounts of clay present in the residue (Skene et al., 1995). Application of WTS improves soil aggregation, raises pH, supplies nutrients to plants, increases water retention capacity, and soil aeration. Therefore, in some parts of the world, WTS in already applied onto agricultural soil, as is the case of Atlanta and New Jersey in the USA (AWWA, 1999), and Portugal in the European Union.

Data on application of WTS to agricultural soils in Brazil is scarce, and demand research to define advantages and risks of this soil management practices. The objective of this study was to evaluate the effects of the application of WTS to a degraded soil from tin mining in the National Forest of Jamari, state of Rondonia, Brazil, on soil's heavy metals contents.

MATERIAL AND METHODS

Place, experimental design and treatments

The study was developed in a greenhouse (25-28°C) in Jaboticabal, SP, Brazil. Trials were set up in a completely randomized design, with five treatments: T = control, soil degraded (n = 4); Tc = chemical control, soil degraded + liming (n = 4); D_{100}, D_{150} and D_{200} = liming + 100, 150 and 200 mg of N-WTS for kg of soil (n = 20).

Characterization of the degraded soil and the WTS

Before mining activity, the area's soil was classified as Typic Hapludox. Samples for the study were collected at the 0-20 cm layer, and presented the following physico-chemical properties: pH (0.01 mol L^{-1} $CaCl_2$) = 4.9; organic matter = 3 g dm^{-3}; P (resin extractor) = 8 mg dm^{-3}; K = 0.5 $mmol_c$ dm^{-3}; Ca = 5.0 $mmol_c$ dm^{-3}; Mg = 2.0 $mmol_c$ dm^{-3}; H+Al = 12 $mmol_c$ dm^{-3}; sum of bases = 7.5 $mmol_c$ dm^{-3}; CEC = 19.5 $mmol_c$ dm^{-3} and bases saturation = 38%. Chemical analysis were carried out according to Raij et al. (1996).

WTS samples were collected in the Water Treatment Plant of Araraquara (SP), which works under conventional treatment, using iron chloride as coagulant agent. A suction pump was installed at the end of the treatment unit, and was turned on during sludge discharge for ten consecutive days. The composite sample was conditioned in a 1000-L fiber container. Superficial water was discharged through a siphon in a daily basis, and when the residue reached circa 98% moisture, it was removed from the container, conditioned in plastic bags, taken to the experimental unit, and stored in 500-L fiber container. During 20 days, the container was kept open along the day, and the water layer was siphoned out to bring sludge moisture to about 94%, when a sample for chemical and physical characterizations was taken. The physico-chemical properties of the prepared sludge was: moisture = 98%, organic-C = 10.5 g kg^{-1}, total-N = 2.2 g kg^{-1}, P = 1.3 g kg^{-1}, K = 2.2 g kg^{-1}, Ca = 121 g kg^{-1}, Mg = 4.3 g kg^{-1}, S = 4.1 g kg^{-1}, Fe = 167040 mg kg^{-1}, Zn = 65.6 mg kg^{-1}, Cu = 149 mg kg^{-1}, Mn = 1683 mg kg^{-1}, Pb = 8.4 mg kg^{-}), Cr = 86 mg kg^{-1}, Ni = 27 mg kg^{-1}, Cd = 6.1 mg kg^{-1}, clay = 260 g kg^{-1} silt = 315 g kg^{-1}, and sand = 425 g kg^{-1}. Organic-C was determined by wet oxidation (Dabin, 1976); the total-N by the Kjeldahl method, and other elements by AAS in the extract of digestion with HNO_3, HCl and H_2O_2 (USEPA, 1995). Granulometric analysis was carried out as recommended by EMBRAPA (1997).

Experimental procedures

Pots with 6 kg capacity were filled with 5 kg of degraded soil. Rates of the prepared WTS were applied to the soil surface daily during 15 days, according to the water retention capacity. After application of half doses of each treatment, the soil was removed from the pots, placed on trays, homogenized and then returned to the respective pot, and the other half of the WTS dose was applied. The soil was again removed from the pots, placed on trays, dried at room temperature, passed through a soil mill, homogenized and returned to the respective pots.

After the application of the WTS, soils of the Tc, D_{100}, D_{150}, D_{200} received 3.3; 3.6; 3.7 and 3.9 g dolomitic limestone (total relative neutralization power = 131%), respectively, corresponding to a field application equivalent to 2 t ha^{-1} to raise bases saturation to circa 70%. After liming, the pots were wetted with distilled water to reach circa 70% of water retention capacity, covered with paper, and incubated at greenhouse conditions for 30 days, period in which the water lost by evaporation was replaced every two days. After the incubation, soil was removed from these pots, placed on plastic trays, air dried and sieved to 2 mm. A sample from each treatment was used for heavy metal analysis.

Heavy metals analysis and pH determination

Total contents of Cu, Fe, Mn, and Zn were determined in the extract of the nitric-percloric digestion by AAS using air-acetylene flame; total contents of Cd, Pb, Ni and Cr were determined in the extract of the digestion with HNO_3, HCl and H_2O_2 (USEPA, 1995) by AAS using air-acetylene flame (Cd, Pb and Ni) or nitrous acetylene-oxide (Cr). Extractable micronutrients and heavy metals were determined by the Mehlich 1 extractor (Jones Jr., 1990) and analyzed by AAS as described; pH was measured in water, using the ratio 1:2.5 (soil:water).

Data analysis

Data were submitted to analysis of variance (P = 0.05) and, the Tukey test was used for comparison of means (P = 0.05) (Banzatto & Kronka, 1992).

RESULTS AND DISCUSSION

Fe, Cu, Mn, Zn and Ni contents

Total contents of Fe, Cu and Mn increased with the application of WTS, effect that was not observed for the total contents of Zn (Table 1). The extractable contents of these micronutrients increased as a function of WTS doses. Total iron contents increased more than the other metals. Total Fe contents ranged between the ordinary limits found for Brazilian soils. For instance, a Typic Hapludox presents more than 36% Fe_2O_3 (Embrapa, 1999).

The WTS presents large quantities of Fe in the soluble form (Elliot et al. 1990). There are two explanations for high content found for extractable Fe in this study. First, a effect of the coagulant used (iron chloride) in the water treatment sludge and second, the action of the Mehlich-1 extractor, that contains a mixture of two

Table 1 - Total and extractable contents of heavy metals plant nutrients in a degraded soil by tin mining amended with water treatment sludge.

Treatment	Ni	Fe	Cu	Mn	Zn
			Total Heavy Metals (mg kg^{-1} dry basis)		
T	4.68 a	61072 a	41.28 ab	198.63 a	79.63 a
T_c	4.85 a	59716 a	37.98 a	199.50 a	89.75 a
D_{100}	5.84 a	70277 a	51.22 bc	371.23 b	111.84 a
D_{150}	5.66 a	76620 a	54.96 c	387.80 b	93.72 a
D_{200}	6.14 a	90277 b	56.34 c	373.78 b	88.22 a
			Extractable Heavy Metals (mg kg^{-1} dry basis)		
T	0.30 a	6.63 a	0.23 a	4.67 a	0.33 a
T_c	0.80 a	7.89 a	0.30 a	4.67 a	1.6 a
D_{100}	0.72 b	5801 b	6.54 b	59.58 b	2.30 b
D_{150}	0.84 c	8254 c	7.87 c	71.26 c	3.06 c
D_{200}	0.85 c	9695 d	10.17 d	90.40 d	3.84 d

T = control (degraded soil); Tc = chemical control (degraded soil + limestone); D_{100}. D_{150} and $D_{200=}$ = application of 100, 150 and 200 mg of N-WTS kg^{-1} of degraded soil + limestone. Means followed by the same letter in the same column and same form of heavy metal are not different by Tuckey's test at $P < 0.05$.

strong acids (H_2SO_4 and HCl) and may solubilize partialy insoluble forms of Fe in the soil (Simonete & Kiehl, 2002), possibly not available to plants (Amaral Sobrinho et al., 1993). This last effect is enhanced when pH is above 6.6 (Camargo et al., 1982). In the control treatment, pH was small than 6.6, which may have resulted in the low contents of Fe recorded. Moreover, the degraded soil probably had low contents of extractable Fe.

WTS application increased the total copper contents in the three tested doses; values lied within limits found by Fageria et al. (2002) for Brazilian soils. Oliveira & Mattiazzo (2001) recorded an average 40 mg kg^{-1} total Cu in soils amended with sewage sludge. Comparing to values observed by Galvão (1999) to savannah soils treated with WTS, the contents of extractable Cu were very high. These extractable contents increased proportionally to the increment of WTS doses. WTS increased total and extractable contents of Mn, but only the extractable Mn increased proportionally to WTS doses (Table 1). For soils with pH (in water) above of 6.6 and treated with limestone Camargo et al. (1982) observed increasing contents of Mn when Mehlich-1 extractor was used. Those authors found values of extractable Mn varying from 87.4 to 120 mg kg^{-1}, corroborating findings of this study, where extractable contents of Mn were 90 mg kg^{-1} in the higher WTS doses. The total contents of Zn ranged as expected for Brazilian soils (Muraoka et al., 1984) and differences among treatments were not detected. The extractable contents of Zn increased with the WTS doses, and values ranged as expected for soils of the state of São Paulo (Camargo et al., 1982), and for sandy soils treated with WTS (Elliot & Singer, 1988).

Regarding Ni, the extractable contents increased with WTS application. The average contents were considered low, probably because of the adsorption, so the risks to environmental impacts are low (McGrath, 1995). Practically all the Ni added to oxidic soils with pH next to 7.0 is adsorbed and, probably occurred an increase in the adsorption of Ni when the values of soil pH were above 7.0 (Mellis et al., 2004).

Cd, Cr and Pb contents

Total Cd, Cr and Pb contents recorded for treatments with WTS were below the limits established by USEPA (1995) and by the legislation of CETESB (1999) for the state of São Paulo (Table 2). Although no difference has been detected in the total contents of Pb, the contents of Cd and Cr increased in some doses of WTS, but without a clear relation dose-effect. In regard to the extractable contents, treatments that received WTS always presented higher contents of those heavy metals. A negative relationship was observed between Cd contents and WTS doses, while Cr increased with increasing WTS doses. This effect was less clear regarding Pb therefore there was not a linear relation. Cd was the more extracted heavy metal by Mehlich 1 extractant, in comparison to the total contents (Table 2). Annual applications of WTS could cause phytotoxicity to cultivated plants, once Cd should be in high concentrations, even in a soil with alkaline reaction, as observed by Hinesly et al. (1984).

The extractable fractions of Pb and Cr were lower than 1% of the total. Probably, this low extraction is associated to the high value of pH, as suggested by Davies (1995) and Elliot & Singer (1988). As a matter of fact, pH value in the different treatments were T = 5.5; Tc = 6.1; D_{100} = 7.6; D_{150} = 7.8 and D_{200} = 7.9, indicating that soils of the treatments that received WTS were alkaline. Despite of the potential benefits of WTS, applied to the

Table 2 - Total and extractable contents of heavy metals plant nutrients in a soil degraded by tin mining amended with water treatment sludge.

Treatment	Cd	Cr	Pb
	Total Heavy Metals (mg kg^{-1} dry basis)		
T	0.78 b	40.15 ab	69.86 a
T_c	0.82 b	46.65 ab	52.84 a
D_{100}	0.98 c	51.76 b	74.22 a
D_{150}	0.65 ab	47.50 ab	72.38 a
D_{200}	0.77 a	41.34 a	75.49 a
	Extractable Heavy Metals (mg kg^{-1} dry basis)		
T	0.07 a	0.08 a	1.47 a
T_c	0.08 a	0.08 a	1.50 a
D_{100}	0.55 d	1.27 b	2.49 c
D_{150}	0.47 c	1.46 c	2.44 c
D_{200}	0.40 b	1.59 d	2.20 b

T = control (degraded soil); Tc = chemical control (degraded soil + limestone); D_{100}. D_{150} and $D_{200=}$ = application of 100, 150 and 200 mg of N-WTS kg^{-1} of degraded soil + limestone. Means followed by the same letter in the same column and same form of heavy metal are not different by Tuckey's test at $P < 0.05$.

soil (increase in pH, addition of nutrients and clay), negative effects have been found as adsorption of phosphorus and phytotoxicity with aluminum (AWWA, 1999). In the state of New Jersey (U.S.A.), 100% of the residues of water treatment plants contain aluminum (AWWA, 1999). Moreover, Elliot et al. (1990) observed that, although WTS presents low metal contents, they are in a mobile form and present potential for environment contamination.

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