Dissolved Organic Carbon and Metals Release in Amended Mine Soils

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Past mining activities in Mazarron, SE Spain left a legacy of derelict landscapes devoid of vegetation and seasonal formation of salt efflorescence. Soils in these landscapes contain high amounts of Fe-oxyhydroxides, sulphates, and potentially leaching of toxic metals (e.g., 27,515 mg zinc kg^{-1} soil) due to extreme acidic conditions. Leaching experiments were carrying out with to determine the influence of dissolved organic carbon (DOC) from pig manure-amendment on release of metals in mine soils. The columns were amended with single (3,750 kg N/ha-yr) and double doses of pig manure, and leached weekly with distilled water for 21 weeks (W1-W21). Relationships between DOC and metals concentrations in initial leachates (W1-W11) showed positive significant correlations for cadmium (Cd), zinc (Zn) and copper (Cu), while lead (Pb) had negative correlation. After additional dose (W12-W21), significant positive correlations were observed for Cu, Pb and Zn, and low and negative relation for Cd. Our results suggest that complexation between metals and organic matter may play a role in the mobility of metals in mine soils.

INTRODUCTION

The environmental impacts of the long-history of mining activities in Mazarrón, southeast Spain has generated mine tailings stored in terraced silt ponds (or balsas). Balsas are associated with problem-soils such as extreme acidity and salinity, and elevated contents of metals such as Cd, Cu, Pb, and zinc (Zn) where establishment of vegetation as a management option to stabilize these environmentally-problematic landscape features is quite challenging. However, successful re-vegetation of mine wastes is proven to be one of the best reclamation techniques for mine tailings available to date (e.g., Norland & Veith, 1995; Freitas et al., 2004).

The mobility of the metals as complexes with soil organic matter (SOM) cannot be attributed solely to DOM in solution but also to pH, redox, dissolved organic carbon (DOC), speciation (binding form), and reaction kinetics. Leachability of metals also depends on their total concentrations in the soil and on the soil physicochemical properties and environmental factors (Li & Shuman, 1997).

The movement of metals in soils has received considerable attention because even a slow transport through soil and subsoil materials may result in an increased content of metals in the groundwater. Boyle and Fuller (1987) found that Zn leaching through soil columns was enhanced by elevated (DOC); Lamy et al. (1993) also observed that the mobility of Cd was enhanced by an increase amounts of soluble SOM. Dowdy & Volk (1983) suggested that the movement of heavy metals in soils would occur in sandy, acid, low-organic matter soil, subjected to heavy rainfall or irrigation. Other authors have also found positive correlations between organic carbon and Zn and Cu in leachates (McBride et al., 1997; Ashworth & Alloway, 2004).

The use of pig manure to reclaim acidic mine soils in southeast Spain is promising because Murcia province generates an estimated 8 millions m3 of waste residues from the pork industry (CAAMA, 2003). This generation of large volume of pig slurry aggravates disposal problem for many pig producers. Using pig manure as soil amendment will address two environmental problems in southeast Spain – disposal of industrial wastes from pig production and reclamation of acidic mine soils.
The objective of this paper is to describe the relationship between the release of dissolved organic carbon (DOC) and metals in leachates generated from undisturbed soil column amended with pig manure.

MATERIALS AND METHODS

Leaching experiments

The leaching column experiment were carried out according to the principles described by Mihaljevic et al., (2004), Ashworth & Alloway (2004), Doye & Duchesne (2003), Camobreco et al., (1996), and recommended by ISO/DIS 18772, (2006). Undisturbed soil columns were taken from soils in the vicinity of silt pond. Soils were extracted using transparent metacrylate cylinder 60 cm long, 25 cm inside diameter, and 35 cm thick. Soil columns were amended with single (3,750 kg N/ha-yr) and double doses of pig manure applied in the surface 0 to 10 cm depth. The applied doses were calculated from the 3,580 kg N/ha/yr the mean nitrogen (N) content of soils, and the agronomic rate of N-requirement (170 kg N/ha/yr) (Directiva 91/676/CEE). Leachings were carried out weekly using distilled water at a rate of 8 mL min-1 to simulate the annual critical rainfall events (50 L m^{-2}) in the study area. Experiment was carried out for 21 weeks (W); W1-W11 for single dose and W12-W21 for double dose. Leachates were collected each week were filtered with a Whatman nº 42 paper, and filtered liquid was refrigerated at 5 ºC while awaiting chemical analysis.

Analytical methods

Selected chemical properties of soils and pig manure were determined following the routine methods for soil analyses. Chemical composition of leachates was determined following analytical techniques suggested in APHA (1998). We analyzed the leachates for pH, electrical conductivity (EC), redox potential (Eh), and soluble metals and ion contents. Total dissolved organic carbon (DOC) was

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Leaching week	pH	EC (dS m^{-1})	Eh (mV)	Cd (mg L^{-1})	Cu (mg L^{-1})	Pb (mg L^{-1})	Zn (mg L^{-1})	DOC (mg L^{-1})
W1	1.80 (0.08)a	18.13 (2.15)a	583 (24,9)a	18.31 (4.8)a	97.8 (7.2)a	0.60 (0.4)a	2520 (413)a	25.25 (1.3)a
W11	2.57 (0.14)b	4.79 (0.33)b	412 (47)b	0.10 (0.02)b	3.18 (2.26)b	1.92 (0.5)b	22.10 (4.10)b	15.34 (1.6)b
W21	2.87 (0.19)ba	4.26 (0.49)b	448 (59)b	0.04 (0.01)c	1.16 (0.43)b	0.83 (0.7)ba	5.59 (0.64)c	15.00 (2.9)ba

n: number of observations in a group, w1 (n=3), w11 (n=3), w21 (n=2). Means followed by similar letter are not significantly different

Tabla 1. Characteristics of leachates in single and double doses of pig manure-amendment columns

measured using a TOC – V-CSH Shimadzu (Kyoto-Japan). We determined the following elements in soils and pig manure: Cd, Cu, Pb, Zn, and Cd, Cu, Pb, Zn, iron (Fe), manganese (Mn), nitrate (NO_3^-), DOC, sulphate (SO_4^{-2}), chloride (Cl^-), sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) for leachates. Statistical comparison of the chemical composition of soils and leachates from columns subjected to single and double doses of pig manure was conducted using ANOVA.

Results and Discussion

Characteristics of leachates from leaching experiment

Table 1 summarises the composition of leachates obtained in soil columns subjected to single (W1 to W11) and double doses (W12 to W21). The results showed that initial acidity was very high due to the oxidation of pyritic minerals. pH in leachates slightly increased from 1.8 to 2.6 after week 11 and to pH 2.9 at the end of the experiment (W21). Leaching caused a significant reduction ($p < 0.05$) in EC in single dose (W1-W11). EC values was highest in the first leaching events due to the washing of soluble salts from pig manure amendment and soil but declined from 18.1 to 4.8 and 4.3 dS m^{-1} in single and double doses, respectively. Redox potential remained in the range 400 to 450 mV for both single and double doses.

The total contents of Cu and Zn in leachates were relatively high at the beginning of the experiment, and decreased steadily over time, whereas Pb and Cd contents remained low (*Table 1*). We think that the reductions in Cu, Cd and Zn concentrations in leachates were due to increase CEC resulting from the increased in soil organic matter. The release of DOC through soil washing processes was significant ($p<0.01$) at the first 6 weeks, and then remained around 15 mg L^{-1}. After 21 weeks of leaching, all metals reached low values, and were slightly over the threshold established by FAO for irrigation water (Cd:0.01; Cu:0.20; Pb:5.0; Zn:2.0 in mg L^{-1}).

Cadmium, Cu, Pb and Zn concentrations in the leachates with time are shown in *Fig. 1*. The contents of metals in the leachates significantly decreased with time during W1-11, and seemed to reach steady state except for Pb that exhibited gradual increase in single dose and decreased in double dose. Significantly higher amounts of soluble Zn, followed by Cu, Cd and Pb, were found in leachates generated during the first 6 weeks (W1-W6) than similar period (W12-W18) in columns amended with double dose. In W6-W11, soluble Cu, Cd and Zn showed fluctuations in low values that continuously decreased even alter the addition of double dose. Pb concentration of the leachates was low because it is normally retained in the solid phases (Dunnivant et al., 1992); while high Zn values in leachates were due to its high solubility and mobility (Guisquiani et al., 1992; Alloway, 2003). The low pH (< 3.0) in leachates might also contribute to the mobilization of metals in the soil (Ashworth & Alloway, 2004).

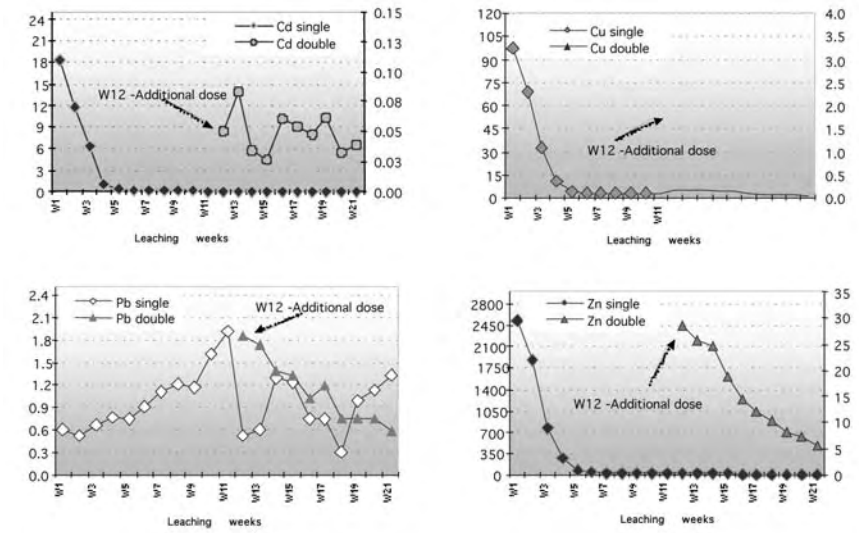

Fig. 1. Evolution of metals in leachates from undisturbed mine soil columns amended with pig manure subjected to 21 weeks of leaching.

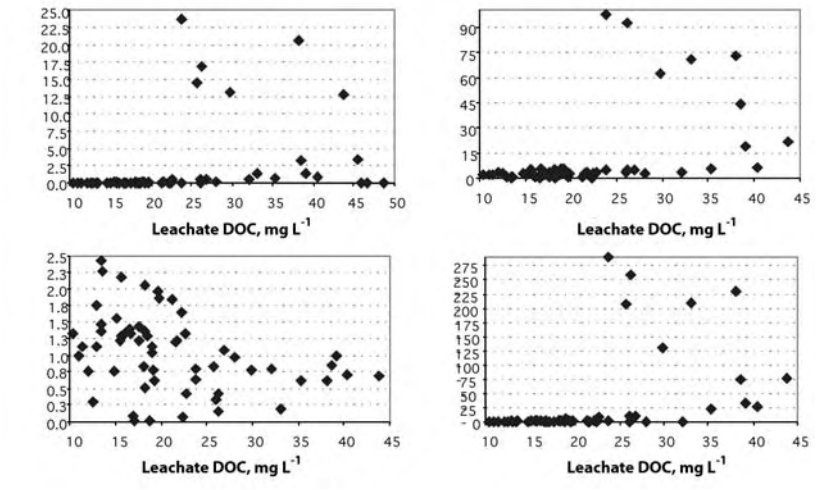

Fig. 2. Relationships between Cd, Cu, Pb, and Zn concentrations and dissolved organic carbon in leachates from pig manure-amended mine soil column.

	DOC			
	Cd	*Cu*	*Pb*	*Zn*
Single dose (W1-W11)	0,882 **	0,673*	-0,873**	0,782**
Single dose (W12-W21)	0,240	0,342	-0,252	0,324
Double dose (W12-W21)	-0,181	0,879**	0,596	0,588

**(p < 0.05), and **(p < 0.01) indicate significant differences between coefficients.*

Tabla 2. The Rho de Spearman correlation matrix between DOC and metals for single and double doses in pig manure-amended columns.

Relationship between DOC and metals

The relationships between Cd, Cu, Pb and Zn concentrations and DOC are presented in *Fig. 2.* The scatter of data for Cd, Cu and Zn against DOC for the entire data set were similar and exhibited no distinct relationships at first glance. However, large number of observations showed positive relationships especially when few (n=5) high values were excluded from the plots. In contrast, there seemed to be a negative relationship between Pb and DOC. The Rho de Spearman matrix (*Table 2*) showed that correlations between Cd and Pb against DOC are more significant than that of Cu and Zn and may indicate that Cd and Pb in the soil solutions can form more stable complexes than Cu and Zn ions.

Comparison of the release of metals in DOC in single and double doses is given in Table 2. In W1-W11, we observed significant positive correlations for Cd, Zn and Cu, and significantly negative relation for Pb. In double dose pig manure, Cd, Pb and Zn concentrations exhibited no significant relationships DOC in leachates, while Cu had significant correlation (r: 0.88).

Our observations suggest that when organic carbon is added to soils (e.g., pig manure amendments), leaching of Zn and Cd, followed by Cu increase, whereas Pb tends to be retained in the soil. We would like to emphasize that although pig manure amendment increased the amounts of Zn, Cd and Cu in leachates, metal contents in leachates were low and were just slightly over the threshold established by FAO for irrigation water (Cd:0.01; Cu:0.20; Pb:5.0; Zn:2.0 in mg L^{-1}).

CONCLUSIONS

We examined the relationships between DOC and Cd, Cu, Pb and Zn in leachates from undisturbed mine soils amended with pig manure. The main conclusions derived from this study are: 1) there are significant positive correlations exist between DOC and Cd, Zn and Cu and significant negative relation for Pb in the single dose application (W1 to W11). 2) additional application (i.e., double dose) of pig manure at week 12 showed no significant correlation between Cd, Pb and Zn and significant relationship for Cu and DOC in leachates, and. 3) pig manure amendment increased DOC in leachates that may contribute to increase release of metals from mine soil. However, metals in leachates remained low and just slightly above FAO guidelines.

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