SJSS
SPANISH JOURNAL OF SOIL SCIENCE

Planting trees and amending with waste increases the capacity of mine tailings soils to retain Ni, Pb and Zn

Plantar árboles y enmendar con residuos incrementa la capacidad de los suelos de escombrera de mina para retener Ni, Pb y Zn

Plantar árvores e emendar com resíduos incrementa a capacidade dos solos de resíduos orgânicos de mineração pra reter Ni, Pb e Zn

Received: 02.06.2014 | **Revised:** 22.10.2014 | **Accepted:** 31.10.2014

AUTHORS

Asensio V.[@ 1, 2]
vfandino@cena.usp.br

Forján R.[1]

Vega F.A.[1]

Covelo E.F.[1]

[@] Corresponding Author

[1] Department of Plant Biology and Soil Science, Faculty of Biology, University of Vigo, As Lagoas-Marcosende. 36310 Vigo, Pontevedra, Spain.

[2] Present address: Department of Plant Nutrition, CENA, Universidade de São Paulo (CENA-USP), Av. Centenário 303. 13400-970, Piracicaba, SP, Brasil.

ABSTRACT

The sorption capacity for Ni, Pb and Zn of mine tailings soil with and without reclamation treatment (tree planting and waste amendment) was evaluated using the batch adsorption technique. It is important to determine the capacity of waste-amended soils to retain Ni, Pb and Zn, as the sludges used usually have high concentrations of these metals. The results obtained in the present study showed that the untreated mine tailings soil had a low capacity for Ni, Pb and Zn retention. The sorption capacity for Pb increased significantly in all of the treated soils, without any significant differences between them. The treatment that most increased the sorption capacity for Ni and Zn was planting with trees and amending with waste simultaneously, as this increased the concentration of both organic and inorganic carbon, exchangeable calcium, soil pH and effective cation exchange capacity.

RESUMEN

Se evaluó la capacidad de un suelo de escombrera de mina con y sin tratamientos de recuperación (plantación de árboles y enmienda de residuos) para sorber Ni, Pb y Zn mediante la técnica de sorción "batch". Es importante determinar la capacidad de sorción de Ni, Pb y Zn de suelos enmendados con residuos, ya que los lodos que son utilizados suelen presentar elevadas concentraciones de dichos metales. Los resultados obtenidos en este trabajo mostraron que el suelo de mina sin tratar tenía baja capacidad para retener Ni, Pb y Zn. La capacidad de sorción de Pb se incrementó significativamente en todos los suelos tratados, sin diferencias significativas entre ellos. El tratamiento que más aumentó la capacidad de sorción para Ni y Zn fue plantar árboles y enmendar con residuos al mismo tiempo, ya que incrementó la concentración de carbono orgánico e inorgánico y de calcio intercambiable, el pH del suelo y la capacidad de intercambio catiónico efectiva.

RESUMO

Avaliou-se a capacidade de sorção do Ni, Pb e Zn por um solo de minas com e sem tratamentos de remediação (plantação de árvores e correção com resíduos orgânicos) usando a técnica de adsorção "batch". É importante determinar a capacidade dos solos corrigidos com resíduos orgânicos para reter Ni, Pb e Zn porque as lamas utilizadas para esse fim apresentam geralmente altos teores destes metais. Os resultados obtidos neste trabalho mostraram que o solo de minas sem tratamento apresentava uma baixa capacidade para reter Ni, Pb e Zn. A capacidade para reter o Pb aumentou significativamente em todos os solos tratados, sem diferenças significativas entre eles. O tratamento que mais aumentou a capacidade de sorção do Ni e Zn foi a plantação de árvores simultaneamente com a aplicação de resíduos orgânicos, já que conduziu a um aumento da concentração de carbono orgânico e inorgânico, do cálcio de troca, do pH do solo e da capacidade de troca catiónica efetiva.

DOI: 10.3232/SJSS.2014.V4.N3.02

1. Introduction

Soils in mining areas are usually physically, chemically and biologically degraded. In addition to these problems, soils associated with metal mines are also polluted by metals. A number of strategies have been developed over the years in order to improve the low quality of these soils and to prevent the surrounding areas from becoming polluted. The most popular reclamation treatments for mine soils involve planting vegetation with plants and amending with wastes (Tandy et al. 2009; Dary et al. 2010; Barrutia et al. 2011; Karami et al. 2011). It has been demonstrated that these treatments significantly increase the quality of mine soils by improving their physical structure, concentration of organic matter and nutrients and by promoting microbial growth and functionality (Rodríguez-Jordá et al. 2012; Asensio et al. 2013b; Asensio et al. 2013a; Asensio et al. 2014). However, the waste used to reclaim mine soils (especially sewage sludge) frequently contains considerable concentrations of Ni, Pb and Zn that enter the soils (Nyamangara 1998; Singh and Agrawal 2008; Asensio et al. 2013c). Sorption studies of mine soils that have been, or are going to be, reclaimed using sewage sludge must take into account the extra input of these metals in the soils.

In spite of the numerous articles that have been published on the effect of planting vegetation or amending mine soils with waste (Bendfeldt et al. 2001; Brown et al. 2003; Shrestha and Lal 2008; Baker et al. 2011), the effect of these treatments on the metal sorption capacity of soils has not been properly reported. The term “sorption” involves the loss of a metal ion from an aqueous to a contiguous solid phase, and consists of three important processes: adsorption, surface precipitation and fixation (Apak 2002; Bradl 2004). Planting trees and amending with waste should increase the sorption capacity of mine soils, as they increase the concentration of soil colloids with a known heavy metal retention capacity, such as clay, inorganic carbon and organic matter (Filcheva et al. 2000; Bendfeldt et al. 2001; Alvarenga et al. 2008; Asensio et al. 2013b). On the other hand, the Fe and Mn oxides that are usually found in high concentrations in soils associated with metal mines also have a high sorption capacity (Vega et al. 2006). In order to determine whether this is capable of creating new conditions for retaining metals, it is necessary to test the combination of organic matter, clay, carbonates and Fe and Mn oxides from both the mine soils and the reclaiming treatments.

For all the reasons indicated above, the main objective of the present study was to compare the sorption capacity of Ni, Pb and Zn of a mine tailings soil from a depleted Cu mine that was ameliorated by tree planting, waste amendment, or both treatments. Samples of the same soil were taken from a vegetated site, an amended site, a vegetated and amended site, and an untreated site. The trees used were *Pinus pinaster* Aiton and *Eucalyptus globulus* Labill. The amendments used were made of sewage sludge and paper mill residues. Previous data have shown that most of the metal found in samples from treated sites was contained in the residual fraction of the soil, i.e. bound to the clay fraction (Asensio et al. 2013c). The present study aimed to go further, by examining whether treated mine tailing soils were capable of retaining relatively high concentrations of Ni, Pb and Zn. This would make it possible to estimate whether the availability of metals could be reduced when mine soils are amended with waste rich in metals.

KEY WORDS
Metals, mine soil, sorption, soil recovery

PALABRAS CLAVE
Metales, suelo de mina, sorción, recuperación de suelos

PALAVRAS-CHAVE
Metais, solo de minas, sorção, remediação dos solos

2. Materials and Methods

2.1. Description of the study area and soil sampling

The sampling site is located in the Touro mine in Galicia, Northwest Spain (Lat/Lon (Datum ETRS89): 8º 20' 12.06'' W 42º 52' 46.18'' N). Copper was extracted from the Touro mine for 14 years, between 1973 and 1988. The tailings at this mine are materials left over after extracting copper from the ore. The unconsolidated material could be considered a Spolic Technosol according to the latest version of the FAO classification (FAO 2014).

Four sites in the mine tailings zone (M) were selected in order to evaluate the effect of tree vegetation (v) and waste amendments (w):

1. M1 as the control site (untreated). This soil covered an area of 1.20 ha and had an AC horizon 20 cm deep.

2. M2v as the vegetated site, where *Pinus pinaster* Aiton trees had been planted 21 years before the sampling date. This soil covered an area of 0.60 ha. M2v had an A horizon 4 cm deep (labelled as M2Av) and an AC horizon 20 cm deep (M2Bv).

3. M3w as the amended site, where sewage and paper mill residues were added 6 months before sampling. The different types of waste were added by trucks and then spread on the soil surface. The final depth of this new layer was around 3m, covering an area of 0.8 ha. The amount of waste added was around 158 tons per ha.

4. M4vw as the amended + vegetated site, where eucalyptuses were planted and waste was added at the same time, 10 years before sampling. The amount of added wastes was 297 tons per ha, and the final depth of this new layer was around 70 cm, covering an area of 1.5 ha.

The waste used had pH values of 7-11.5, total organic C of 120-230 g kg^{-1}, total Cu of 100-500 mg kg^{-1}, and total Zn of 130-870 mg kg^{-1} (Camps Arbestain et al. 2008). Sites M3w and M4vw were only amended once, and there were no reapplications.

On 9 March 2010, five soil samples were randomly collected using an Eijelkamp sampler at each selected site from areas spaced sufficiently far apart to be representative. The whole depth of each horizon was sampled and then stored in polyethylene bags, dried at room temperature and sieved to < 2 mm before being analysed. The single horizon of all of the soils was sampled except from M2, in order to observe possible changes in the subsurface horizon.

2.2. Soil physical and chemical analyses

Some of the characteristics of the selected soils that generally influence metal sorption are summarized in **Table 1**. The procedure of Kroetsch and Wang (2008) was used to determine particle size distribution (sand, silt and clay percentages). Mineralogical analysis of the clay fraction was carried out by X-ray diffraction of crystalline powder in a Siemens D-5000 diffractometer (Brindley and Brown 1980). Exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, Al^{3+}, Fe^{2+} and Mn^{2+}) were extracted with 0.1 M $BaCl_2$ (Hendershot and Duquette 1986) and their concentrations determined by ICP-AES (Perkin-Elmer Optima 4300 DV, USA). Effective cation exchange capacity (ECEC) was calculated by adding up the total cation concentrations. Soil pH was determined with a pH electrode in 1:2.5 water to soil extracts. The method developed by Mehra and Jackson (1958) was used to determine the free oxide concentrations. Aluminium, iron and manganese were determined in the extract by ICP-AES. Both soil organic and inorganic carbon (SOC and IC) were determined in a solid module (Shimadzu SSM-5000, Japan) coupled with a TOC analyser (Shimadzu TNM-1, Japan). Dissolved organic carbon (DOC) was extracted with bidistilled H_2O according to Sánchez-Monedero et al. (1996) and the OC in the supernatant was determined with a TOC analyser. The different chemical organic matter fractions namely humin carbon (Humin C), carbon in the fulvic (C_{FA}) and the humic acids (C_{HA}) were extracted first with 0.1M $Na_4P_2O_7$ and then with 0.1M NaOH, by following the method described in De Blas et al. (2010) and Asensio et al. (2014). Pseudototal nickel (Ni), lead (Pb) and zinc (Zn) concentrations were extracted with *aqua regia* by acid digestion in a microwave oven (Milestone ETHOS 1, Italy). The certified reference material CRM026-050 was also analysed in parallel with samples to check the analysis.

2.3. Sorption experiment and construction of isotherms

The sorption capacity was evaluated after carrying out sorption experiments using the batch method described by Alberti et al. (1997) and Gomes et al. (2001) modified by Harter and Naidu (2001). Single-metal solutions of Ni^{2+}, Pb^{2+} and Zn^{2+} were used as nitrates (0.03, 0.05, 0.08, 0.1 and 0.5 mmol L^{-1}) containing 0.01M $NaNO_3$ as background electrolyte (Vega et al. 2009). Tri-metal equimolar solutions of $Ni^{2+} + Pb^{2+} + Zn^{2+}$ as nitrates were also prepared with the same background electrolyte (0.01M $NaNO_3$) to evaluate the competition for binding sites. The concentration of each metal in the tri-metal solution had the same concentration (which was the same as those of the single-metal solutions). We added 25 mL of the “sorption solutions” to 1.5 g of soil samples in polyethylene tubes and then shook them in a rotatory shaker for 24h at 25 ºC. After centrifuging for 10 min at 3000 rpm the supernatant was filtered through Whatman 42 paper (pore size 0.45 µm). The supernatants were analysed for Ni, Pb and Zn concentrations by ICP-AES (Perkin-Elmer Optima 4300 DV). All of the sorption experiments were performed in triplicate, and the data shown is the average of these three replicates. Each concentration sorbed by each soil sample was calculated as the difference between the concentration added (from sorption solution) and the concentration in the solution after equilibration (24 h shaking) with the soil. To minimize the effect of the background electrolyte, the sorbed concentrations were corrected by subtracting the values obtained in additional experiments with a sorption solution only composed of 0.01M $NaNO_3$.

We also calculated the distribution of each metal (*i*) for each sorption solution concentration (*c*) by following equilibration in each stage. This distribution was expressed in terms of the quotient:

$$K_d = \frac{C_{i,soil}}{C_{i,solution}} \tag{1}$$

where $C_{i,soil}$ is the concentration of metal *i* on the soil (µmol g^{-1}) and Ci,solution is the concentration of metal *i* in solution (µmol L^{-1}) (Anderson and Domsch 1989; Covelo et al. 2008). This K_d was calculated for each experimental replicate at each concentration of metal for all of the soils. We then calculated the mean of three replicates in order to obtain one value for each metal concentration.

The obtained isotherms were fitted, wherever possible ($R^2 > 0.6$), with the Langmuir and Freundlich equations (Vega et al. 2008). The Langmuir equation used is as follows:

$$\frac{C}{C_S} = \frac{1}{\beta_L K_L} + \frac{C}{\beta_L} \tag{2}$$

The linearized Freundlich equation used is the following:

$$logC_s = \frac{logK_F + (logC)}{n} \tag{3}$$

where *C* is the metal concentration in solution at equilibrium (µmol L^{-1}); Cs is sorbed metal per gram at equilibrium (µmol g^{-1}); β_L is the maximum sorption capacity (µmol g^{-1}), corresponding to the adsorption of a complete monolayer; K_L is the Langmuir constant (L µmol^{-1}), which reflects the energy of sorption; K_F (L g^{-1}) is the Freundlich constant, which reflects sorption capacity; and *n* is an adimensional parameter reflecting the intensity of sorption.

Finally, the overall capacity of the soils to sorb Ni, Pb or Zn was evaluated as the slope K_r according to Vega et al. (2008). This K_r is obtained from the regression equation $C_{s,i} = K_r C_{p,i}$, where $C_{s,i}$ is sorbed metal *i* (µmol) per gram of soil at equilibrium, and $C_{p,i}$ is potentially sorbable metal *i* (i.e., the amount of metal *i* in the solution before contact with the soil) also per gram of soil.

2.4. Statistical analyses

All of the analytical determinations were performed in triplicate, and the data were statistically treated using the program SPSS 15.0

for Windows. Analyses of variance (ANOVAs) and homogeneity of variance tests were carried out. In case of homogeneity, a post-hoc least significant difference (LSD) test was carried out; otherwise Dunnett's T3 test was performed. Student's t-test was carried out to calculate the sorption selectivity sequences. All data was previously subjected to the Kolmogorov-Smirnov test for normality. Bivariate correlation analyses were also carried out according to Pearson's method. The obtained correlation (r) and the used probability (95% confidence = $P < 0.05$) are given in the results or discussion section. An independent t-test was carried out in order to compare the obtained K_r and to be able to establish the selectivity sequences of sorption.

3. Results

3.1. Soil characteristics

The mine soil from the untreated site (M1) is extremely acid according to the USDA (1998) (**Table 1**). The site vegetated with pines for 21 years (M2v), the site amended with waste (M3w) and the site simultaneously vegetated and amended (M4vw) have a significantly higher pH than M1.

The percentage of clay fraction, crystalline minerals, concentration of soil organic carbon (SOC) and both aluminium and manganese oxides (Al_2O_3 and MnO) were significantly higher in the treated soils than in M1 (**Table 1**). On the contrary, the concentrations of iron oxides (Fe_2O_3)

Table 1. Selected physical and chemical properties of the studied soils

	M1	M2Av	M2Bv	M3w	M4vw
Texture	**Sandy loam**	**Sandy loam**	**Sandy loam**	**Sandy clay loam**	**Sandy loam**
Sand (%)	69.1±30.4a	51.1±4.7e	59.3±6.1d	66.2±23.8b	60.8±2.9c
Silt (%)	20.1±4.9e	32.2±6.2a	25.4±9.1c	23.5±4.5d	26.1±1.9b
Clay (%)	10.9±3.9c	16.7±1.4a	15.3±1.7a	10.3±1.9c	13.1±0.9b
Crystalline minerals (%)	4.7–10.9	7.1–16.7	8.1–8.1	6.4–10.3	6.9–13.1
Exchangeable Ca ($cmol_{(+)}$ kg^{-1})	0.13±0.05e	9.73±0.64c	7.56±1.16d	11.81±0.76b	20.62±1.32a
ECEC ($cmol_{(+)}$ kg^{-1})	3.8±0.2e	12.0±1.1c	9.4±1.2d	20.8±2.6b	26.7±1.8a
pH_{H2O}	3.6±0.05e	6.6±0.4b	5.2±0.4d	5.8±0.1c	8.2±0.1a
Al_2O_3 (g kg^{-1})	3.2±0.2e	11.6±0.5b	4.7±0.2d	15.5±0.2a	7.8±0.4c
Fe_2O_3 (g kg^{-1})	132±6a	74.8±2.4c	111±2b	22.1±0.4d	7.4±0.3e
MnO (g kg^{-1})	0.02±<0.01e	1.8±0.03b	0.5±0.2d	1.2±0.1c	4.5±0.2a
IC (g kg^{-1})	0.3±0.01b	0.3±0.5b	0.3±<0.01b	0.3±0.01b	33.5±2.7a
SOC (g kg^{-1})	3.2c	35.1a	6.6b	56.3a	54.8a
DOC (g kg^{-1})	u.l.	u.l.	0.02±<0.01c	1.2±0.04a	0.3±0.1b
Humin C (g kg^{-1})	3.92d	17.95b	3.93d	16.10c	37.94a
C_{FA} (g kg^{-1})	0.60±0.17d	6.14±0.99b	0.90±0.25d	13.97±0.11a	2.66±0.10c
C_{HA} (g kg^{-1})	0.87±0.08e	6.67±0.21b	2.00±0.17d	21.11±1.79a	4.71±0.32c
Pseudototal Ni (mg kg^{-1})	15.27±3.24d	121±5a	31.43±10.68c	55.57±8.08b	128±24a
Pseudototal Pb (mg kg^{-1})	19.31±1.68d	24.75±1.4c	16.00±3.37d	71.04±9.03a	34.38±2.31b
Pseudototal Zn (mg kg^{-1})	78.19±26.83c	176±25b	59.69±8.76c	307±51a	135±8b

Note: Mean and 95% confidence interval (CI) for three independent replications. Values followed by different letters in each row of each mine area differ significantly with $P < 0.05$. u.l.: undetectable level. EC: electrical conductivity. ECEC: effective cation exchange capacity. IC: inorganic carbon. SOC: soil organic carbon. DOC: dissolved organic carbon. Humin C: carbon in the humin. C_{FA} and C_{HA}: carbon in fulvic and humic acids.

were higher in the control soil than in the treated ones. Dissolved organic carbon (DOC) was only detectable in all of the treated soils except in M2Av, probably because it was lixiviated to M2Bv.

3.2. Sorption isotherms of Ni, Pb and Zn

The individual and competitive nickel isotherms (**Figure 1**) were L-type for the control (M1) and the vegetated soils (M2Av and M2Bv), and C-type for the amended (M3w and M4vw) according to Giles et al. (1974). These isotherms indicate that the amended soils had the highest affinity for Ni. The individual and competitive Pb isotherms (**Figure 1**) were L-type for M1 and H-type for all of the treated soils according to Giles et al. (1974). Note that the isotherms obtained for all of the treated soils were similar. The H-type indicates a high initial affinity of the treated soils for this metal. The high affinity of soils for Pb has been previously reported by other authors (Sauvé et al. 2000; Fontes and Gomes 2003; Vega et al. 2006).

The individual and competitive zinc isotherms were H-type for all of the treated soils and L-type for the control. These isotherms indicate that M4vw soils had the highest affinity for Zn and M1 the lowest.

It is interesting to observe that the isotherms of the subsurface horizon at the vegetated site (M2Bv) were similar to the ones from its topsoil (M2Av) instead of the ones from the control soil (**Figure 1**).

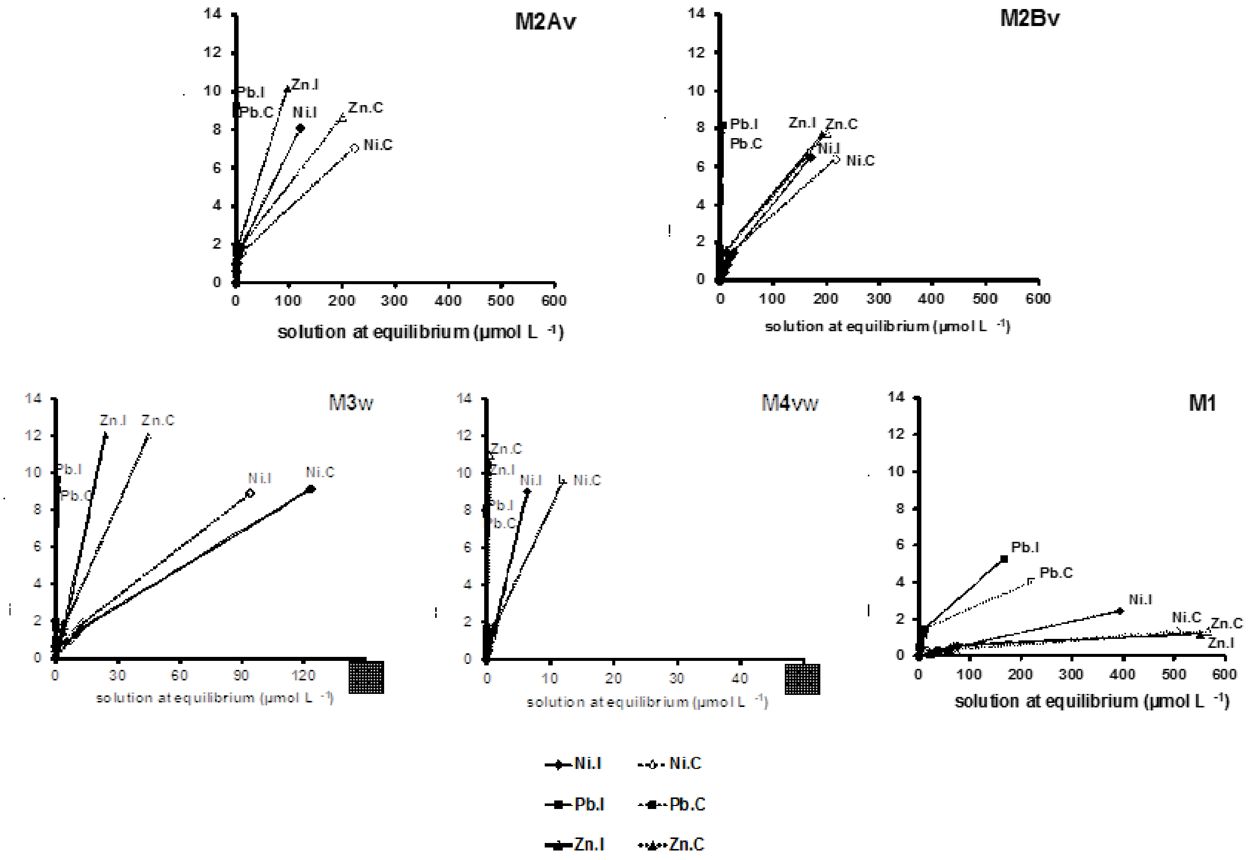

Figure 1. Isotherms of the different soil samples (M1, M2Av, M2Bv, M3w and M4vw) for Ni^{2+}, Pb^{2+} and Zn^{2+} in individual (I) and competitive (C) sorption.

3.3. Sorption capacity and selectivity sequences

With the aim of establishing comparisons between the sorption capacities of the soil samples, different parameters such as K_d, the constants of the Langmuir and Freundlich models (β_L and K_F, respectively) and K_r (Vega et al. 2008) were used. The calculations for the sorption and retention capacity using the distribution coefficient K_d as proposed by different authors (Gomes et al. 2001; Covelo et al. 2007a) are not always suitable to clearly discriminate and compare the individual and competitive sorption capacities (Vega et al. 2008).

Table 2. Fitting sorption isotherms for Ni^{2+}, Pb^{2+} and Zn^{2+} according to the best fitting model

Metal	Type of sorption	Soil	Langmuir fitting (R^2)	Freundlich fitting (R^2)
Ni	individual	M1	**0.007**	0.991
		M2Av	0.981	0.985
		M2Bv	0.983	0.992
		M3w	0.979	0.993
		M4vw	**0.482**	0.997
	competitive	M1	0.875	0.901
		M2Av	0.958	0.932
		M2Bv	0.914	0.923
		M3w	**0.660**	0.915
		M4vw	0.719	0.826
Pb	individual	M1	0.953	0.99
		M2Av	1	0.794
		M2Bv	1	0.788
		M3w	1	0.796
		M4vw	1	1
	competitive	M1	0.992	0.941
		M2Av	1	**0.64**
		M2Bv	1	**0.64**
		M3w	1	**0.64**
		M4vw	1	1
Zn	individual	M1	0.860	0.807
		M2Av	0.965	0.906
		M2Bv	0.939	0.953
		M3w	**0.103**	0.970
		M4vw	1	1
	competitive	M1	0.797	0.758
		M2Av	0.986	0.962
		M2Bv	0.960	0.955
		M3w	**0.538**	0.999
		M4vw	1	0.854

Note: Values in bold type indicate that $R^2 < 0.7$.

Focussing on the Langmuir and Freundlich models, a high fitness correlation was obtained in most cases ($R^2 > 0.7$), which indicates that the constants derived (Table 2) can be used for evaluating the sorption capacities. However, the sorption data did not fit well with either of the models in all of the cases, i.e., Ni, Pb and Zn in both individual and competitive sorption. For this reason, it was only possible to use the Freundlich model for comparing Ni and Zn sorption while the Langmuir model was only useful for the Pb sorption data. Therefore, the constant K_F from the Freundlich equation was used for Ni and Zn sorption, while the maximum sorption capacity obtained from the Langmuir model (β_L) was used for Pb (Table 3). According to the K_F for Ni and Zn, the soil with both treatments (M4vw) has the highest sorption capacity both in individual and competitive situations (significant, $P < 0.05$). In the case of Pb, the soil with the highest β_L is M3w. The soil with the lowest sorption in all cases (Ni, Pb and Zn; individual and competitive sorption) is the untreated soil.

Table 3. Maximum capacity of sorption for Ni^{2+}, Pb^{2+} and Zn^{2+} from the studied soils according to the best fitting isotherm model

Metal	Type of sorption	Best fitting model	Soil	Equation	Max. sorption
Ni	individual	Freundlich	M1	$y = 1.0354x - 2.2725$	$K_F = 0.005$e
			M2Av	$y = 0.5943x - 0.3133$	$K_F = 0.486$b
			M2Bv	$y = 0.8372x - 1.03$	$K_F = 0.093$d
			M3w	$y = 0.8594x - 0.7231$	$K_F = 0.189$c
			M4vw	$y = 0.9485x + 0.1909$	$K_F = 1.552$a
	competitive	Freundlich	M1	$y = 0.5237x - 1.353$	$K_F = 0.044$e
			M2Av	$y = 0.3981x - 0.1529$	$K_F = 0.703$b
			M2Bv	$y = 0.4103x - 0.2482$	$K_F = 0.565$c
			M3w	$y = 0.5645x - 0.344$	$K_F = 0.453$d
			M4vw	$y = 0.7831x + 0.0929$	$K_F = 1.239$a
Pb	individual	Langmuir	M1	$y = 0.1657x + 4.2761$	$\beta_L = 6.04$e
			M2Av	$y = 0.1079x$	$\beta_L = 9.27$b
			M2Bv	$y = 0.122x + 2E-17$	$\beta_L = 8.20$c
			M3w	$y = 0.1041x$	$\beta_L = 9.61$a
			M4vw	$y = 0.123x$	$\beta_L = 8.13$d
	competitive	Langmuir	M1	$y = 0.2305x + 4.2242$	$\beta_L = 4.34$e
			M2Av	$y = 0.1127x$	$\beta_L = 8.87$b
			M2Bv	$y = 0.1259x$	$\beta_L = 7.94$c
			M3w	$y = 0.1104x$	$\beta_L = 9.06$a
			M4vw	$y = 0.1293x$	$\beta_L = 7.73$d
			M2Av	$y = 0.5206x - 0.0253$	$K_F = 0.943$b
			M2Bv	$y = 0.7276x - 0.7368$	$K_F = 0.183$d
			M3w	$y = 1.0803x - 0.3938$	$K_F = 0.404$c
			M4vw	-	$K_F = 1.000$a
	competitive	Freundlich	M1	$y = 0.4346x - 1.1989$	$K_F = 0.063$e
			M2Av	$y = 0.4671x - 0.1241$	$K_F = 0.751$b
			M2Bv	$y = 0.4589x - 0.1977$	$K_F = 0.634$c
			M3w	$y = 0.8052x - 0.2533$	$K_F = 0.558$d
			M4vw	$y = -3.2627x - 0.0188$	$K_F = 0.958$a

Note: Values followed by different letters in each row of each mine area differ significantly with $P < 0.05$.

According to the calculated K_r, M4vw showed the highest sorption capacity of Ni and Zn for both individual and competitive experiments (**Table 4**). For the individual sorption of Pb, all of the treated soils statistically had the same K_r, which was significantly higher than in the untreated soil. The highest K_r values for competitive Pb were from the amended soils (M3w and M4vw) with values ranging from 0.98 to 1.00 ($K_r = 1$ means the maximum sorption capacity). The untreated soil (M1) showed the lowest K_r in all cases (**Table 4**). The K_r values in the subsurface horizon at the vegetated site were similar to the values for its topsoil, instead of those from the control soil.

According to the calculated K_r, the general soil sequence according to the both the individual and competitive sorption capacity for Ni, Pb and Zn was M4vw ≥ M3w ≥ M2Av ≥ M2Bv > M1. The small differences among them can be observed in **Table 4**.

3.4. Influence of soil properties on metal sorption

The data obtained for evaluating the sorption capacity (β_L, K_F and K_r) were correlated with the data for a number of soil physico-chemical soil characteristics (**Table 1**). There was a significantly positive correlation between the β_L, K_F and K_r (for Ni, Pb and Zn, in both individual and competitive sorption) and the following soil characteristics: pH, exchangeable Ca^{2+}, CECe, Al and Mn oxides, organic C (SOC), and humin C ($P < 0.05$ in all cases). The concentration of inorganic C (IC) had a significantly positive correlation with the values of K_r and K_F for Ni.

4. Discussion

4.1. Influence of reclamation treatments on Ni, Pb and Zn retention

The parameters used to estimate the sorption capacity of soils (K_r, β_L and K_F) indicated that the untreated soil (M1) had a very low capacity for Ni, Pb and Zn retention (**Tables 3** and **4**). Nevertheless, it can be seen that this capacity increases in the vegetated (M2v), amended (M3w) and vegetated + amended soil (M4vw).

The metal selectivity sequences according to K_r for individual and competitive sorption can be also observed in detail in **Table 4**. The general selectivity sequence is Pb ≥ Zn ≥ Ni.

The treatment that increased the sorption capacity the most for Ni and Zn was simultaneous tree planting and amendment with waste, as the soil with both treatments (M4vw) had the highest K_r and K_F values for the sorption of these metals (**Tables 3** and **4**). In the case of Pb, amendment with waste was the treatment that most increased the sorption capacity of soils, since there were no significant differences between the K_r of M3w and M4vw for this metal. Moreover, the β_L for Pb was higher in M3w than in M4vw. This higher sorption capacity of the amended soils in comparison with the soils that were only vegetated or untreated was due to the highest concentration of soil components with high retention capacities in M3w and M4vw. It has previously been demonstrated that the soil components with the highest sorption capacity are usually organic matter, clay minerals and carbonates (Stahl and James 1991; Temminghoff et al. 1997; Vega et al. 2006; Covelo et al. 2007b). Soil M4vw had one of the highest SOC concentrations and the highest IC and Mn oxide concentrations of all of the soils. M4vw had a higher retention capacity for Ni, Pb and Zn than M2Av, despite having a lower percentage of clay than M2Av. These results indicate that organic matter and inorganic C played a key role in the retention of metals in the reclaimed mine soils. The statistical data support this hypothesis with the significantly positive correlation obtained between β_L, K_F and K_r for Ni, Pb and Zn (in both individual and competitive sorption) and the

Table 4. Kr for the individual and competitive sorption of Ni^{2+}, Pb^{2+} and Zn^{2+}, preference order of sorption for each metal and selectivity sequences by each soil

		M1	M2Av	M2Bv	M3w	M4vw	Preference order
Individual sorption	Kr Ni	0.267d	0.785b	0.689c	0.827b	0.988a	M4vw > M3w = M2Av > M2Bv > M1
	Kr Pb	0.665b	1.000a	0.990a	0.998a	1.000a	M4vw = M3w = M2Av = M2Bv > M1
	Kr Zn	0.120e	0.851c	0.699d	0.961b	1.000a	M4vw > M3w > M2Av > M2Bv > M1
Competitive sorption	Kr Ni	0.140d	0.632c	0.639c	0.792b	0.980a	M4vw > M3w > M2Av = M2Bv > M1
	Kr Pb	0.513c	0.949b	0.962b	0.998a	1.000a	M4vw = M3w > M2Av = M2Bv > M1
	Kr Zn	0.126d	0.700c	0.698c	0.932b	0.999a	M4vw > M3w > M2Av = M2Bv > M1
Individual selectivity sequence		Pb>Ni>Zn	Pb>Ni>Zn	Pb>Zn>Ni	Pb>Zn>Ni	Pb=Zn>Ni	—
Competitive selectivity sequence		Pb>Ni=Zn	Pb>Ni=Zn	Pb>Zn>Ni	Pb>Zn>Ni	Pb=Zn>Ni	—

Note: Mean of the mean of three replications. Values followed by different letters in each row of each mine area differ significantly with $P < 0.05$.

SOC and humin C concentrations ($P < 0.05$ in all cases). Furthermore, IC was significantly positively correlated with the values of K_r and K_F for Ni. Another important reason why M4vw has a higher sorption capacity for metals than M2Av was the higher pH and CECe values of the soil with both treatments in comparison with the soil that was only vegetated. It is known that soil pH plays a crucial role in metal sorption and solubility (Weng et al. 2001) and that high pH and CEC favours metal sorption in soils. Moreover, the Pearson's correlations that were calculated indicate that there were significantly positive correlations between the soil pH and CECe and the K_r for Ni, Pb or Zn ($P < 0.01$ in all cases).

Planting trees also significantly increased the sorption capacity for Ni, Pb and Zn in the mine soil, since M2Av had significantly higher values of β_L, K_F and K_r than the untreated site M1 (Tables 3 and 4). The maximum sorption values were significantly much lower in M2Av than in M4vw, in spite of the highest clay percentage in M2Av. This is probably because of the lower SOC and pH in this soil than in M4vw, which seem to be more important parameters than clay in the retention capacity of metals by the studied soils.

4.2. Sorption capacity and selectivity sequences

The metal that was sorbed the most in the individual and competitive sorption was Pb for all of the soils except for M4vw, whose retention capacity was the same for Pb and for Zn. This is the opposite of what we expected, as lead is usually the most strongly sorbed metal by soils and sediments (Fontes and Gomes 2003; Fan et al. 2007; Vega et al. 2008; Seo et al. 2008). Therefore, there may be some factor promoting Zn sorption in M4vw compared to the other studied soils. This vegetated + amended soil can be distinguished from the other soils by its much higher concentration of exchangeable calcium (Table 4), and it being the only one where calcite ($CaCO_3$) was detected. It is possible that Pb^{2+} and Zn^{2+} precipitated as $PbCO_3$ and $ZnCO_3$, sorbed onto calcite, exchanged by Ca^{2+} or that all of the processes occurred in M4vw. It is known that both Pb and Zn can be sorbed onto calcite and can even precipitate if their ion activity product is exceeded (Papadopoulos and Rowell 1989; Zachara et al. 1989; Elkhatib et al. 1991; Izquierdo et al. 2013). It is also known that Zn unavailability is due to the sorption of Zn by carbonates, precipitation of Zn in form of hydroxide or carbonates, or even the formation of insoluble calcium zincate (Adriano 2001).

The high SOC concentration in M4vw also influenced the higher sorption capacity compared to the other soils. Several statistical correlations help to support this hypothesis: the positive correlations obtained between the exchangeable Ca^{2+} and the K_r for Pb and Zn in both the individual and competitive sorption ($P < 0.01$ in all cases), and the positive correlations obtained between the metal sorbed in each experiment (Ni, Pb and Zn, individual and competitive sorption) and the corresponding released Ca^{2+} ($P < 0.01$ in all cases). However, this exchange between Pb or Zn and Ca may occur when the concentration of these metals reaches around 0.5 M, because at lower concentrations, the amount of Ca released was undetectable (Figure 2). It is likely that low concentrations of Pb^{2+} or Zn^{2+} in the soil solution were sorbed by the soil elements (organic matter, minerals or oxides) and when their concentration is high enough, the exchange with Ca^{2+} occurred. All of these arguments suggest that when amending degraded soils, it is important to use wastes that not only have a high concentration of organic carbon or clays, but also of carbonates.

The amount of Zn sorbed was always higher than the amount of Ni in all of the treated soils in the individual experiments, while the opposite occurred in the untreated soils, where Ni was sorbed more than Zn.

As with the individual sorption experiments, the same happened in the competitive experiments, except in soils M1 and M2Av, where the sorption capacity of Ni and Zn was statistically the same. This implies that the sorption of each studied metal was not significantly affected by the presence of the others.

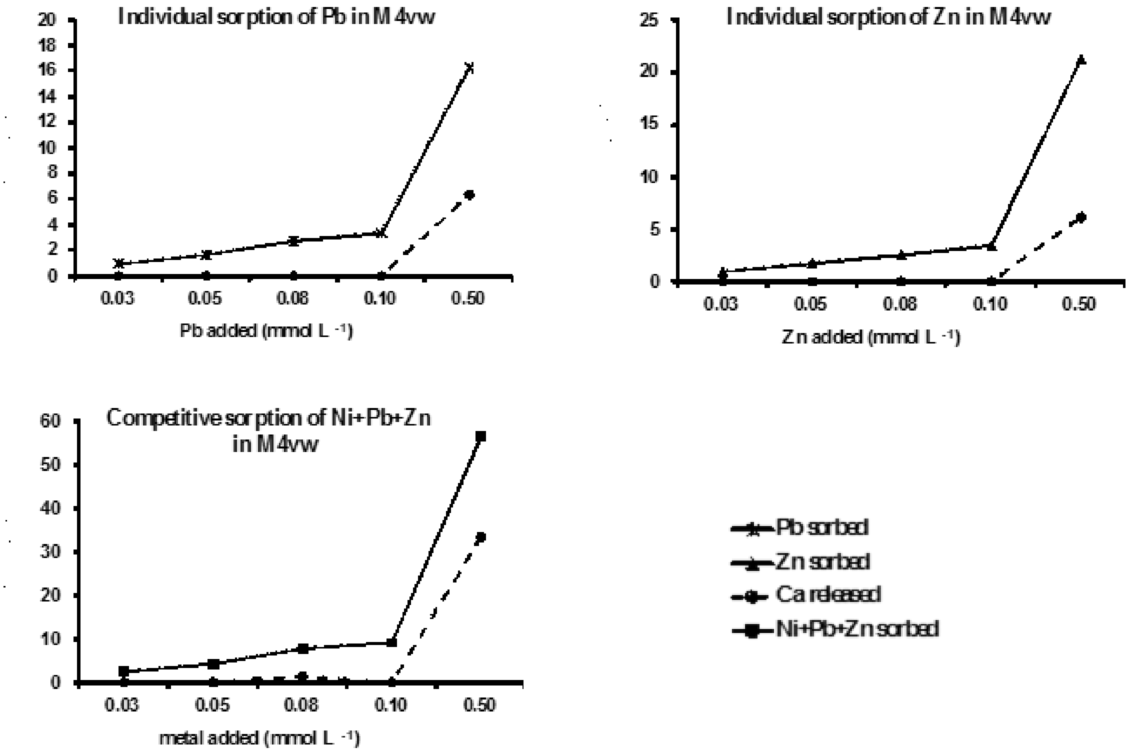

Figure 2. Concentrations of Pb and Zn sorbed in the individual batch experiment as well as Ni + Pb + Zn sorbed in the competitive experiment, together with the concentrations of Ca^{2+} displaced in each situation.

5. Conclusions

Regardless of the possible supply of Ni, Pb and Zn to degraded soils from the sewage or paper mill residues used as amendments, the soils treated with these types of waste had a high sorption capacity to retain these metals. This would prevent Ni, Pb and Zn from occurring in mobile form in the amended sites, even if they are present in a high concentration in the soils. The sorption capacity of the soils amended with waste can be attributed to their high concentration of organic and inorganic carbon, as well as their high pH and effective cation exchange capacity. The high concentration of calcium in the amended and vegetated soil, which came from the sewage and paper mill residues that were added, considerably increased the capacity of the soils to retain metals as Ca^{2+} can be exchanged with Ni, Pb or Zn. Therefore, the treatment that most increased the capacity of the mine soils to retain Ni, Pb and Zn was the amendment with organic wastes rich in calcium and planting of vegetation.

6. Acknowledgements

The authors would like to thank the anonymous reviewers for helping to improve the manuscript with their valuable comments.

REFERENCES

- Adriano DC. 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals. 2nd edition. New York: Springer Verlag. 867 p.

- Alberti G, Cristini A, Loi A, Melis P, Pilo G. 1997. Copper and lead sorption by different fractions of two Sardinian soils. In: Prost R, editor. Contaminated Soils: Third Int. Conf. on the Biogeochemistry of Trace-Elements. Paris: INRA Editions.

- Alvarenga P, Palma P, Gonçalves AP, Baiao N., Fernandes RM, de Varennes A, Vallini G, Duarte E, Cunha-Queda AC. 2008. Assessment of chemical, biochemical and ecotoxicological aspects in a mine soil amended with sludge of either urban or industrial origin. Chemosphere 72(11):1774-1781. doi: 10.1016/j.chemosphere.2008.04.042.

- Anderson TH, Domsch KH. 1989. Ratios of microbial biomass carbon to total organic carbon in arable soils. Soil Biol Biochem. 21:471-479. doi: 10.1016/0038-0717(89)90117-X.

- Apak R. 2002. Adsorption of heavy metal ions on soil surfaces and similar substances. In: Hubbard AT, editor. Encycl. Surf. Colloid Sci. New York, USA: Marcel Dekker. p. 385-417.

- Asensio V, Covelo EF, Kandeler E. 2013a. Soil management of copper mine tailing soils - sludge amendment and tree vegetation could improve biological soil quality. Sci Total Environ. 456-457:82-90. doi: 10.1016/j.scitotenv.2013.03.061.

- Asensio V, Vega FA, Andrade ML, Covelo EF. 2013b. Tree vegetation and waste amendments to improve the physical condition of copper mine soils. Chemosphere 90:603-610. doi: 10.1016/j.chemosphere.2012.08.050.

- Asensio V, Vega FA, Covelo EF. 2014. Effect of soil reclamation process on soil C fractions. Chemosphere 95:511-518. doi: 10.1016/j.chemosphere.2013.09.108.

- Asensio V, Vega FA, Singh BR, Covelo EF. 2013c. Effects of tree vegetation and waste amendments on the fractionation of Cr, Cu, Ni, Pb and Zn in polluted mine soils. Sci Total Environ. 443:446-53. doi: 10.1016/j.scitotenv.2012.09.069.

- Baker LR, White PM, Pierzynski GM. 2011. Changes in microbial properties after manure, lime, and bentonite application to a heavy metal-contaminated mine waste. Appl Soil Ecol. 48:1-10. doi: 10.1016/j.apsoil.2011.02.007.

- Barrutia O, Artetxe U, Hernández A, Olano JM, García-Plazaola JI, Garbisu C, Becerril JM. 2011. Native plant communities in an abandoned Pb-Zn mining area of Northern Spain: Implications for phytoremediation and germplasm preservation. Int J Phytoremediation 13(3):256-270. doi: 10.1080/15226511003753946-.

- Bendfeldt ES, Burger JA, Lee Daniels W, Daniels WL. 2001. Quality of amended mine soils after sixteen years. Soil Sci Soc Am J. 65:1736-1744. doi: 10.2136/sssaj2001.1736-.

- Bradl HB. 2004. Adsorption of heavy metal ions on soils and soils constituents. J Colloid Interface Sci. 277:1-18. doi: 10.1016/j.jcis.2004.04.005.

- Brindley GW, Brown G. 1980. Crystal structures of clay minerals and their X-ray identification. London, UK: Mineralogical Society.

- Brown SL, Henry CL, Chaney R, Compton H, DeVolder PS. 2003. Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. Plant Soil 249(1):203-215.

- Camps Arbestain M, Madinabeitia Z, Anza Hortalà M, Macías-García F, Virgel S, Macías F. 2008. Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. Waste Manag. 28(12):2653-2666. doi: 10.1016/j.wasman.2008.01.008.

- Covelo EF, Vega FA, Andrade ML. 2007a. Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in acid soils II. Soil ranking and influence of soil characteristics. J Hazard Mater. 147:862-70. doi: 10.1016/j.jhazmat.2007.01.108.

- Covelo EF, Vega FA, Andrade ML. 2007b. Heavy metal sorption and desorption capacity of soils containing endogenous contaminants. J Hazard Mater. 143:419-430.

- Covelo EF, Vega FA, Andrade ML. 2008. Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction. J Hazard Mater. 159:342-347.

- Dary M, Chamber-Pérez MA, Palomares AJ, Pajuelo E. 2010. “In situ” phytostabilisation of heavy metal polluted soils using Lupinus luteus inoculated with metal resistant plant-growth promoting rhizobacteria. J Hazard Mater. 177:323-330. doi: 10.1016/j.jhazmat.2009.12.035.

- De Blas E, Rodríguez-Alleres M, Almendros G. 2010. Speciation of lipid and humic fractions in soils under pine and eucalyptus forest in northwest Spain and its effect on water repellency. Geoderma 155:242-248. doi: 10.1016/j.geoderma.2009.12.007.

- Elkhatib EA, Elshebiny GM, Balba AM. 1991. Lead sorption in calcareous soils. Environ Pollut. 69:269-76.

- Fan Q, He J, Xue H, LÜ C, Liang Y, Saruli, Sun Y, Shen L. 2007. Competitive adsorption, release and speciation of heavy metals in the Yellow River sediments, China. Environ Geol. 53(2):239-251. doi: 10.1007/s00254-007-0638-5.

- FAO. 2014. World reference base for soil resources 2014. Rome: FAO. 191 p.

- Filcheva E, Noustorova M, Gentcheva-Kostadinova S, Haigh MJ. 2000. Organic accumulation and microbial action in surface coal-mine spoils, Pernik, Bulgaria. Ecol Eng. 15:1-15. doi: 10.1016/S0925-8574(99)00008-7.

- Fontes MPF, Gomes PC. 2003. Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils. Appl Geochemistry 18:795-804.

- Giles CH, Smith D, Huitson A. 1974. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J Colloid Interface Sci. 47:755-765.

- Gomes PC, Fontes MPF, da Silva AG, Mendonça E, Netto R. 2001. Selectivity Sequence and Competitive Adsorption of Heavy Metals by Brazilian Soils. Soil Sci Soc Am J. 65(4):1115-1121. doi: 10.2136/sssaj2001.6541115x.

- Harter RD, Naidu R. 2001. An Assessment of Environmental and Solution Parameter Impact on Trace-Metal Sorption by Soils. Soil Sci Soc Am J. 65:597-612. doi: 10.2136/sssaj2001.653597x.

- Hendershot WH, Duquette M. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Sci Soc Am J. 50:605-608.

- Izquierdo M, Tye AM, Chenery SR. 2013. Lability, solubility and speciation of Cd, Pb and Zn in alluvial soils of the River Trent catchment UK. Environ Sci Process Impacts 15:1844-1858. doi: 10.1039/c3em00370a.

- Karami N, Clemente R, Moreno-Jiménez E, Lepp NW, Beesley L. 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. J Hazard Mater. 191(1-3):41-48. doi: 10.1016/j.jhazmat.2011.04.025.

- Kroetsch D, Wang C. 2008. Particle size distribution. In: Carter MR, Gregorich GR, editors. Soil Sampl. Methods Anal. Canadian Society of Soil Science. Boca Raton, FL, USA: CRC Press. p. 713-726.

- Mehra OP, Jackson ML. 1958. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals. 7(1):317-327. doi: 10.1346/CCMN.1958.0070122.

- Nyamangara J. 1998. Use of sequential extraction to evaluate zinc and copper in a soil amended with sewage sludge and inorganic metal salts. Agric Ecosyst Environ. 69:135-141. doi: 10.1016/S0167-8809(98)00101-7.

- Papadopoulos P, Rowell DL. 1989. The reactions of copper and zinc with calcium carbonate surfaces. J Soil Sci. 40:39-48.

- Rodríguez-Jordá MP, Garrido F, García-González MT. 2012. Effect of the addition of industrial by-products on Cu, Zn, Pb and As leachability in a mine sediment. J Hazard Mater. 213-214:46-54. doi: 10.1016/j.jhazmat.2012.01.049.

- Sánchez-Monedero MA, Roig A, Martínez-Pardo C, Cegarra J, Paredes C. 1996. A microanalysis method for determining total organic carbon in extracts of humic substances. Relationships between total organic carbon and oxidable carbon. Bioresour Technol. 57(3):291-295.

- Sauvé S, Martínez CE, McBride M, Hendershot W. 2000. Adsorption of free lead (Pb^{2+}) by pedogenic oxides, ferrihydrite, and leaf compost. Soil Sci Soc Am J. 64:595-599.

- Seo DC, Yu K, DeLaune RD. 2008. Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: batch and column experiments. Chemosphere 73:1757-1764. doi: 10.1016/j.chemosphere.2008.09.003.

- Shrestha RK, Lal R. 2008. Land use impacts on physical properties of 28 years old reclaimed mine soils in Ohio. Plant Soil 306:249-260. doi: 10.1007/s11104-008-9578-4.

- Singh RP, Agrawal M. 2008. Potential benefits and risks of land application of sewage sludge. Waste Manag. 28:347-358. doi: 10.1016/j.wasman.2006.12.010.

- Stahl RS, James BR. 1991. Zinc sorption by B horizon soils as a function of pH. Soil Sci Soc Am J. 55:1592-1597.

- Tandy S, Healey JR, Nason MA, Williamson JC, Jones DL. 2009. Remediation of metal polluted mine soil with compost: Co-composting versus incorporation. Environ Pollut. 157(2):690-697. doi: 10.1016/j.envpol.2008.08.006.

- Temminghoff EJM, Van der Zee SEATM, de Haan FAM. 1997. Copper Mobility in a Copper-Contaminated Sandy Soil as Affected by pH and Solid and Dissolved Organic Matter. Environ Sci Technol. 31:1109-1115. doi: 10.1021/es9606236.

- USDA. 1998. Soil quality indicators: pH.

- Vega FA, Covelo EF, Andrade ML. 2006. Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics. J Colloid Interface Sci. 298:582-592. doi: 10.1016/j.jcis.2006.01.012.

- Vega FA, Covelo EF, Andrade ML. 2009. Effects of sewage sludge and barley straw treatment on the sorption and retention of Cu, Cd and Pb by coppermine Anthropic Regosols. J Hazard Mater. 169:36-45. doi: 10.1016/j.jhazmat.2009.03.060.

- Vega FA, Covelo EF, Andrade ML. 2008. A versatile parameter for comparing the capacities of soils for sorption and retention of heavy metals dumped individually or together: results for cadmium, copper and lead in twenty soil horizons. J Colloid Interface Sci. 327:275-286. doi: 10.1016/j.jcis.2008.08.027.

- Weng L, Temminghoff EJM, Van Riemsdijk WH. 2001. Contribution of Individual Sorbents to the Control of Heavy Metal Activity in Sandy Soil. Environ Sci Technol. 35:4436-4443. doi: 10.1021/es010085j.

- Zachara J, Kittrick J, Dake L, Harsh J. 1989. Solubility and surface spectroscopy of zinc precipitates on calcite. Geochim Cosmochim Acta 53:9-19. doi: 10.1016/0016-7037(89)90268-8.