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Changes in the Phytoavailability of Nutrients in Mine Soils after Planting Trees and Amending with Wastes

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Abstract The purpose of the present study was to evaluate the effect of planting trees (*Pinus pinaster* or *Eucalyptus globulus*) and amending with wastes (sewage sludges and paper mill residues) on the nutrient content of mine soils and under field conditions. The studied soils were located in a settling pond and a mine tailing within a former copper mine. The soil samples were analyzed for several physico-chemical characteristics and the concentration of nutrients. The untreated settling pond soil had levels of N and K adequate only for the growth of eucalyptuses and pines, and moreover, the concentration of Ca and P were undetectable. The untreated mine tailing soil presented the same condition, also with adequate levels of Ca and Mg for eucalyptuses and pines. Planting these trees increased the concentration of Mg in the settling pond up to adequate levels only for such trees. Amending with wastes increased the phytoavailable concentration of all nutrients up to adequate levels for most plant species. In conclusion, it is recommended to amend mine soils with wastes rich in nutrients and re-amend after some time because they raise them up to adequate levels for most plants but are depleted over time. It is possible to increase the concentration of all nutrients in mine soils by adding organic wastes, even to values adequate for most plant species.

Keywords Mine soil · *Eucalyptus globulus* · Phytoavailable nutrients · *Pinus pinaster* · Waste amendments

1 Introduction

Mine soils usually have severe limitations for plants to develop, including lack of nutrients (Asensio et al. 2011; Kramer et al. 2000; Vega et al. 2005; Yang et al. 2003). In order to increase the content of nutrients in phytoavailable form in mine soils, a large amount of amendment also provide organic matter and slowly release nutrients. For this reason, organic wastes have been widely used as amendments in mine reclamation (Pérez-de-Mora et al. 2007; Pichtel et al. 1994; Santibáñez et al. 2007; Schwab et al. 2007; Zanuzzi et al. 2009), as they are inexpensive and produced in large volumes. Moreover, amendments of biosolids would also provide organic matter and slow-release nutrients (Harrison et al. 1995). Numerous studies have already evaluated the effect of organic amendments on metal-polluted mine soils (Conesa et al. 2007; Karami et al. 2011; Lottermoser et al. 2008; Vega et al. 2004, 2005; Yang et al. 2003), but only a few have focused on soil nutrient content (Kramer et al. 2000; Nikolic et al. 2011). More information is required on the influence of adding organic wastes to soils on nutrient concentration and phytoavailability. Therefore, the aim of this study was to evaluate the effect of organic waste amendments on the nutrient content of two metal-polluted mine soils, with the added value of carrying out the study under

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field conditions and with tree vegetation. Some important chemical and physical properties of the soils, such as nutrient availability, are strongly determined by vegetative cover (Sardans and Peñuelas 2013). The present study focuses on the effect of both type of treatments (tree vegetation and waste amendments) on the concentration and phytoavailability of nutrients in two types of mine soils (settling pond and mine tailing). We hypothesize that the use of both treatments at the same time is the best way to increase the phytoavailable concentration of nutrients in soils.

2 Material and Methods

2.1 Description of the Study Area and Soil Sampling

The sampling area is located in a mine in Touro (Galicia, Northwest Spain; Fig. 1) (Lat/Lon (Datum ETRS89): 8° 20′ 12.06″ W, 42° 52′ 46.18″ N). The climate of the experimental site is Atlantic (oceanic). Precipitation reaches 1,886 mm per year (with an average of 157 mm per month) and the mean daily temperature is 12.6 °C. The average of relative humidity is 77 % (AEMET 2013).

Previous studies have shown that the soils in this location are poor in nutrients (Asensio et al. 2011; Vega et al. 2005). However, these studies have not analyzed the nutrient concentration in detail. Copper was mined at the mine in Touro for 14 years (1973–1988), and since then, another company has extracted material for road construction. When copper mining ended, the soils were only partially reclaimed by planting trees in some locations. The development of these trees has been very slow and deficient. In order to promote and support the establishment and growth of plants in 2000, the company “Tratamientos Ecológicos del Noroeste” (TEN) began to amend some mine sites with wastes. At the same time, they planted *Pinus pinaster* Aiton and *Eucalyptus globulus* Labill. The amendments used were made mainly o sewage sludge and residues from paper mills.

Two soil zones at the Touro mine were sampled: the settling pond (B) and the mine tailing (M). In order to evaluate the effectiveness of tree vegetation (v) and waste amendment (w) treatment, four sites were selected in each mine zone (Fig. 1, Table 1). The selected soils have already been described in detail by Asensio et al. (2013). Briefly, the four sites sampled in the settling pond were *B1* as the control sample (without treatment), *B2v* as the soil vegetated with pines (*P. pinaster* Aiton) for 21 years, *B3v* as the soil vegetated with eucalyptuses (*E. globulus* Labill) for 6 years and *B4w* as the soil amended with sewage sludges and paper mill residues for 5 months. All of the soils only had one horizon AC except B4w, where the two horizons, A and AC, were sampled (*B4Aw* and *B4Bw*). Since the use of waste amendments in the settling pond began 5 months before the sampling date in this zone, there are no representative samples of the long-term effects of the amendment or both treatments at the same time (vegetation and amendment). The four sites sampled in the mine tailing were *M1* as the control, *M2v* as the soil vegetated with pines for 21 years, *M3w* as the soil amended with the same type of wastes than B4w for 6 months and M4vw as the soil vegetated with eucalyptus and amended with wastes 10 years ago. The two soil horizons in M2v were sampled (*M2Av* and *M2Bv*). The general characteristics of the used wastes were pH of 8–10, total organic C ranges from 150 to 230 g kg^{-1}, total Cu higher from 100 to 500 mg kg^{-1} and total Zn from 130 to 870 mg kg^{-1} (Camps Arbestain et al. 2008). Five subsamples per soil were randomly collected on 9 March 2010 from places spaced enough to be representative of each site. The samples were stored in polyethylene bags, dried at room temperature, and sieved to <2 mm prior to analysis.

2.2 General Characterization of the Soil Samples

Standard procedures were used to determine soil stoniness (Eriksson and Holmgren 1996), particle size distribution (Kroetsch and Wang 2008) and bulk density (Hao et al. 2008). The soil characteristics that are most commonly related to nutrient concentration and phytoavailability were also determined (Table 2). Soil pH was determined with a pH electrode in 1:2.5 water to soil extracts. Electrical conductivity (EC) was determined according to Porta (1986). 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 element concentrations were determined by ICP-OES (Perkin-Elmer Optima 4300 DV). Exchangeable acidity (H^{+}) was determined by using a 1-M KCl replacing solution and titration to a phenolphthalein end

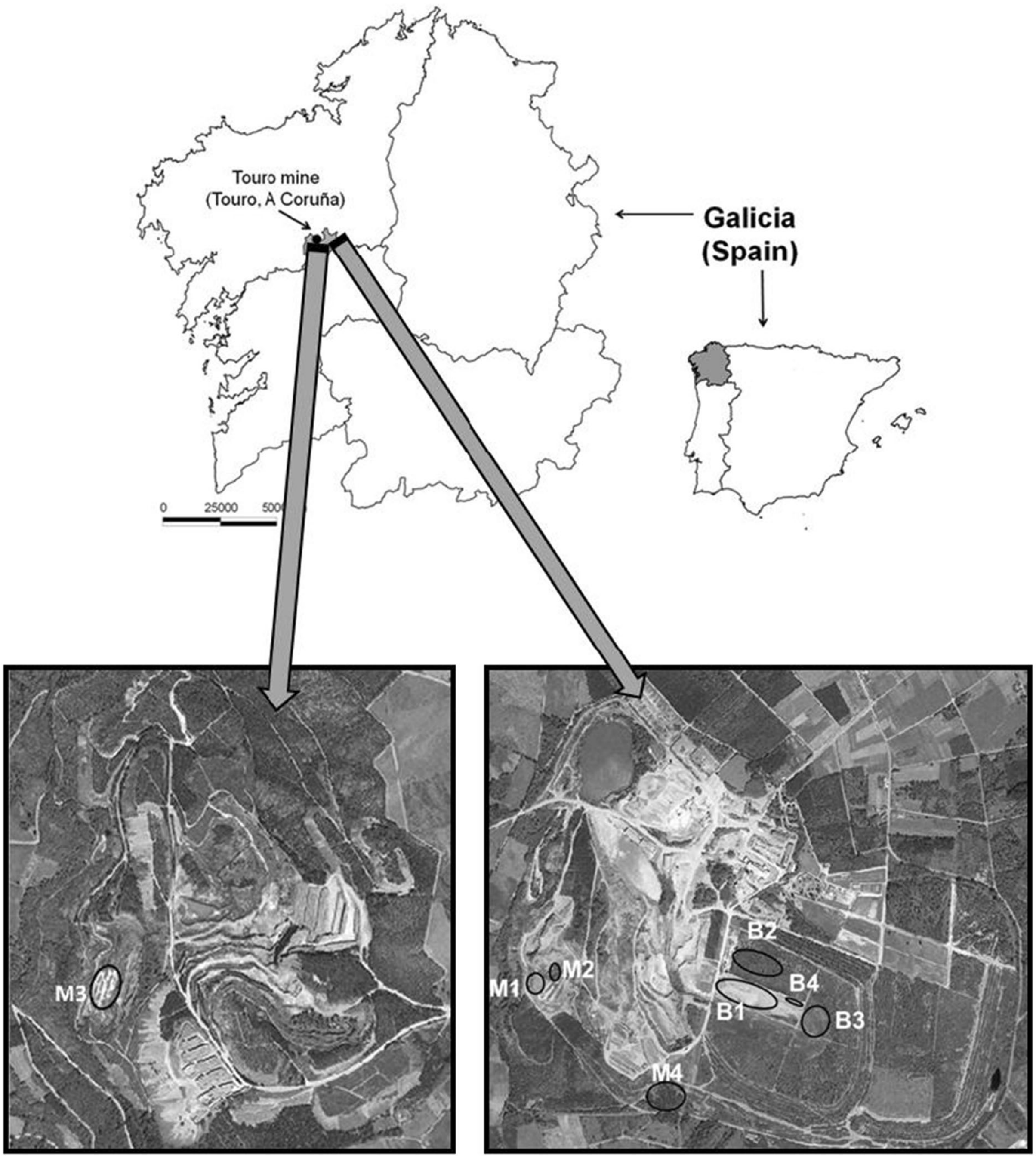

Fig. 1 Location of sampled sites in Touro mine. Map source: ©Instituto Geográfico Nacional de España

point (Thomas 1982). Effective cation exchange capacity (CECe) was calculated with the total cation concentration and the total CEC (CECt) by summing up CECe and exchangeable acidity. Soil organic carbon (SOC) was determined in a solid module (SSM-5000) coupled with a TOC analyzer (TNM-1, Shimadzu).

2.3 Soil Nutrient Concentrations

The potential phytoavailable concentration of Al, Ca, Cu, K, Mg, Mn, Ni, P and Zn were estimated by using 0.01 M $CaCl_2$ as extractant, according to Houba et al. (2000). The chemical form of metals extracted with

Table 1 Location, plot size, dose of amendment, type of vegetation and reclamation treatment of the studied soils

Mine zone	Label	Plot size	Dose of amendment	Vegetation	Horizon (depth, cm)	Treatment	Time of treatment
Settling pond	B1	1.9 ha	None	None	AC (40)	None	–
	B2v	6,200 m^2	None	*Eucalyptus globulus* Labill, *Ulex* sp., *Erica* sp., *Agrostis* sp. and bryophytes	AC (20)	Vegetation	21 years
	B3v	1.15 ha	None	*Pinus pinaster* Aiton, *Agrostis* sp., *Cytisus* sp., *Acacia* sp. and bryophytes	AC (20)	Vegetation	6 years
	B4Aw	100 m^2	280 tons ha^{-1}	Herbaceous	AC (20)	Amendment	5 months
	B4Bw				C (40)	None	–
Mine tailing	M1	1.20 ha	None	None	AC (20)	None	–
	M2Av	0.60 ha	None	*Ulex* sp., *Erica* sp., *Agrostis* sp. and bryophytes	AC (4)	Vegetation	21 years
	M2Bv				C (20)	None	–
	M3w	0.8 ha	158 tons ha^{-1}	Herbaceous	AC (3)	Amendment	6 months
	M4vw	1.5 ha	297 tons ha^{-1}	*Ulex* sp., *Rubus* sp., *P. pinaster* Aiton and bryophytes	AC (70)	Vegetation + amendment	10 years

0.01 M $CaCl_2$ is operationally defined as phytoavailable (Houba et al. 2000). Total bioavailable phosphorus content was determined by the Olsen method (Olsen et al. 1954). Total Kjeldahl-N (TN) was determined according to Bremner (1996). The three inorganic N (IN) fractions, which are NH_4^+–N (ammonium), NO_2^-–N (nitrites) and NO_3^-–N (nitrates), were extracted with 2 M KCl and distilled with their respective reagents: ammonium with MgO and nitrates + nitrites with Devarda's alloy (Bremner and Keeney 1965). To determine total and inorganic N contents, an aliquot of each extract was analyzed by potentiometric titration with titrator equipment (702 SM Titrino, Metrohm).

2.4 Statistical analyses

All analytical determinations were performed in triplicate, and the data obtained were statistically treated using the SPSS 15.0 programme for Windows. Statistical analyses were performed by separating the data from the settling pond soils from the mine tailing, as each zone has its own control soil. Analyses of variance (ANOVA) and test of homogeneity of variance 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. The Mann-Whitney test was performed when the data were not parametric. An independent *t* test was performed to compare each control soil (B1 or M1) with their respective theoretically analogue (B4Bw or M2Bv). A correlated bivariate analysis was carried out, as well as a principal component analysis (PCA) with data from all soil samples in each zone.

3 Results

3.1 General Characteristics of the Soil Samples

The values of the physico-chemical characteristics of the mine soils such as stoniness, particle size distribution, bulk density, pH, SOC, EC, CECe, base saturation and Al saturation of the vegetated and/or amended sites were significantly different ($P<0.05$) to their respective control/untreated B1 or M1 (Table 2) and its corresponding subsurface analogous horizons B4Bw and M2Bv. The percentage of clay fraction was significantly higher in the treated soils, whereas the bulk density was lower (Table 2). The untreated sites showed extremely acid soil pH according to the USDA (1998); in the vegetated and amended sites, the pH value was significantly higher. The effective and total cation exchange capacity (CECe and CECt) significantly increased in the settling pond after amending with wastes (B4Aw) and after the use of both treatments at the same time in the mine tailing (M4vw), which was due to the increase in the concentration of the basic cations (percentage of base saturation) and decrease in Al^{3+} (Al saturation). The SOC also significantly increased in the mine sites

Table 2 Selected characteristics of the soil samples

	Settling pond soils					Mine tailing soils				
	B1	B2v	B3v	B4Aw	B4Bw	M1	M2Av	M2Bv	M3w	M4vw
Stoniness (%)	20.1±5.7d	34.9±8.2b	30.9±7.2c	81.2±11.2a	11.3±1.9e	53.1±8.7b	22.9±6.4e	41.1±3.5d	56.2±6.9a	46.8±7.7c
Sand (%)	69.3±13.5b	69.1±0.7c	65.1±17.5d	45.8±10.9e	71.1±17.1a	69.1±30.4a	51.1±4.7e	59.3±6.1d	66.2±23.8b	60.8±2.9c
Silt (%)	21.1±0.1c	19.9±0.5d	24.6±2.2b	27.9±1.9a	19.7±2.2e	20.1±4.9e	32.2±6.2a	25.4±9.1c	23.5±4.5d	26.1±1.9b
Clay (%)	9.5±1.5d	11.1±0.3b	10.3±2.5c	26.1±6.1a	9.2±3.1e	10.9±3.9d	16.7±1.4a	15.3±1.7b	10.3±1.9e	13.1±0.9c
Texture	Sandy loam	Sandy loam	Sandy loam	Sandy clay loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam
Bulk density (g cm^{-3})	1.7±0.1a	0.8±0.07c	1.5±0.02b	0.3±0.1e	0.7±0.07d	1.1±0.05b	1.9±0.03a	1.9±0.02a	0.9±0.05c	0.8±0.1d
SOC (g kg^{-1})	1.4d	10.4b	11.1b	112a	1.5c	3.2c	35.1a	6.6b	56.3a	54.8a
pH H_2O	3.8±0.04d	4.8±0.05b	4.7±0.03b	6.9±0.3a	4.3±0.3c	3.6±0.05e	6.6±0.4b	5.2±0.4d	5.8±0.1c	8.2±0.1a
pH KCl	3.64±0.05d	3.79±0.01b	3.84±0.1b	6.66±0.2a	3.76±0.04c	3.21±0.01e	6.01±0.08b	4.42±0.09d	5.68±0.08c	7.87±0.06a
EC (ms cm^{-1})	0.10±0.04c	0.03±0.01d	0.03±<0.01d	0.40±0.1a	0.11±0.02b	0.15±0.02c	0.12±0.03c	0.15±0.02c	1.95±0.5a	0.22±0.02b
CECe	2.1±0.2b	2.5±0.1b	2.4±0.1b	58.4±7.3a	2.2±0.4b	3.8±0.2e	12.0±1.1c	9.4±1.2d	20.8±2.6b	26.7±1.8a
CECt	2.08±0.2b	2.53±0.1b	2.43±0.1b	58.38±7.3a	2.20±0.3b	3.78±0.2e	12.01±1.1c	9.37±1.2d	21.06±2.6b	26.79±1.8a
Base saturation (%)	16.27±2.4e	40.52±0.9d	24.61±1.5b	100±0a	36.67±7.1c	20.86±3.6d	100±0a	93.59±1.5c	98.67±0.1b	99.89±0.01ab
Al saturation (%)	83.73±2.5a	59.48±0.2d	75.39±1.5b	0	63.33±7.1c	79.14±3.6a	0	6.41±1.5b	0	0

Mean ± confidence interval (CI) of the mean of three replicates. Values followed by different letters in each row differ significantly with $P<0.05$. Soils description is shown in Table 1

EC electrical conductivity, *SOC* soil organic carbon after the application of the treatments, especially after waste amending.

3.2 Soil Macronutrient Concentrations (N, P, K, Ca and Mg)

The untreated mine soils (B1 and M1) had a very low phytoavailable ($CaCl_2$-extractable) concentration of Ca, K and Mg as well as organic and inorganic N compared to the optimum values (Table 3). Moreover, the concentration of phosphorus in B1 and M1 was below the detection limits both by extracting with $CaCl_2$ and the Olsen method. Nevertheless, the concentrations of most macronutrients significantly increased ($P<0.05$) after the reclamation treatments applied to the soils (tree vegetation and waste amendments) at both mine zones (settling pond and mine tailing), even in the subsuperficial horizons (B4Bw and M2Bv).

The total N concentration (TN) increased to around 500 mg kg^{-1} both after planting trees (B2v, B3v and M2Av) and also using the two treatments (M4vw) and to around 3,500 mg kg^{-1} after recent waste amendment (B4Aw and M3w) (Table 3). The subsurface horizons (B4Bw and M2Bv) also had a significantly higher TN concentration than their respective control sites (B1 and M1). Most of the TN in the vegetated soils and the subsurface horizons were inorganic, particularly nitrates and nitrites, whereas the majority of the TN in the amended soils (B4Aw, M3w and M4vw) was organic (Table 3). Despite this, the amended soils had a higher concentration of ammonium, nitrates and nitrites than the vegetated soils. Regarding the C/N ratio, it was lower than 6 in B4Bw and M1 and higher than 30 in B4Aw, M2Av and M3w (Table 3).

The concentration of phytoavailable P increased to 30–70 mg kg^{-1} in the mine soils after recent waste amendment and 7 mg kg^{-1} after the application of the two treatments, but it was still below the detection limits in the soils vegetated with trees (Table 3). The soils where phytoavailable P was detected showed a higher concentration of this nutrient by extracting with the Olsen method, and some soils where $CaCl_2$-extractable P was not detected had between 3 and 20 mg kg^{-1} of Olsen P.

The potassium in phytoavailable form increased to 230–330 mg kg^{-1} in the mine soils after recent waste amendment and 35–125 mg kg^{-1} after tree planting. The use of the two treatments increased phytoavailable K in an intermediate form (150 mg kg^{-1} more than its control soil) (Table 3).

The concentration of phytoavailable Ca in the amended soils was 700–1,000 mg kg^{-1} more than in their controls. The vegetated sites showed different behaviour depending on the mine zone. The vegetated sites at the settling pond had no phytoavailable Ca (as the control), but the vegetated at the mine tailing had almost 1,000 mg kg^{-1} more than its control. The site with the two treatments (M4vw) showed the highest phytoavailable Ca concentration (Table 3).

The magnesium concentration in phytoavailable form increased around to 760 mg kg^{-1} after recent amendment, 22–100 mg kg^{-1} after vegetating with trees and 250 mg kg^{-1} after the use of the two treatments (Table 3).

3.3 Soil Micronutrient Concentrations (Al, Cu, Mn, Ni and Zn)

The phytoavailable Al concentration was high in the two control soils (B1 and M1), with similar values in both (around 180 mg kg^{-1}). The concentration significantly decreased in the vegetated soil at the mine tailing (30 mg kg^{-1} less than in the control) and especially in the sites recently amended and with the two treatments (170 mg kg^{-1} less). However, the vegetated sites at the settling pond (B2v and B3v) had an even higher concentration than B1 (more than 200 mg kg^{-1}) (Table 3).

The concentration of phytoavailable Cu decreased from 12 to 17 mg kg^{-1} in the two control soils to 2–7 mg kg^{-1} in the treated soils except in the vegetated soil at the mine tailing, where it increased to 90 mg kg^{-1}.

The two untreated sites had the lowest phytoavailable concentrations of Mn, Ni and Zn of the soils of their respective mine zone (Table 3). The concentration of phytoavailable Ni increased significantly more with the tree vegetation than with the waste amendments, whereas the opposite occurred with the Zn concentration.

4 Discussion

The minimum concentration of each soil nutrient necessary for plant development depends on the type of soil function (i.e. agriculture and forestry) and the plant species growing on it. The soils of this study are used for forestry or have legume species and will not be agricultural because of their acidic pH and pollution

Table 3 Nutrient concentrations (mg kg^{-1}) in the soil samples and the optimum for *Eucalyptus globulus* Labill and most plant species

	Settling pond samples					Mine tailing samples					*Eucalyptus globulus* Labill	Most plant species
	B1	B2v	B3v	B4Aw	B4Bw	M1	M2Av	M2Bv	M3w	M4vw		
TN	140±30d	580±60b	580±40b	3,710±73a	320±60c	250±40d	740±280b	280±40d	370±340a	600±280c	20	1000–1,500
IN	100±10d	570±30b	560±30b	1,650±170a	250±30c	110±60b	550±20a	160±60b	600±70a	150±11b	—	—
ON	20c	10d	20c	2,060a	70b	140d	190c	120e	3,080a	450b	—	—
NH_4^+	100±25b	120±25b	110±25b	1,500±27a	120±26b	40±26b	80±27b	30±25b	391±12a	40±5b	—	—
$NO_2^- + NO_3^-$	20±2b	340±50ab	450±25a	140±26b	120±26b	60±27b	460±25a	130±25ab	220±25ab	100±25ab	—	—
C/N	11.86d	18.34c	19.66b	30.97a	5.68e	13.82e	47.92b	24.64c	15.32d	150a	24	24
P (Olsen)	u.l.	u.l.	u.l.	424±25.8a	18.98±0.8b	u.l.	14.1±6.1c	3.7±1.5d	265±16.4a	125±13.9b	25	10–20
P ($CaCl_2$-ext.)	u.l.	u.l.	u.l.	68.28±1.38	u.l.	u.l.	u.l.	u.l.	29.17±0.12a	7.15±0.20b	25	10–20
K ($CaCl_2$-ext.)	21.7±1.61e	91.25±3.85b	64.6±0.65c	333±7.99a	33.5±5.36d	29.61±0.30e	154±7.41c	59.65±5.00d	230±2.85a	184±9.20b	8	150–250
Ca ($CaCl_2$-ext.)	u.l.	u.l.	u.l.	704±125a	135±60b	159±43.2d	1,106±43.9b	761±20.3c	1,210±39.1b	1,929±91.3a	81	1,000–2,000
Mg ($CaCl_2$-ext.)	13.38±0.62e	41.40±1.45c	34.97±0.97d	777±3.97a	60.5±8.74b	53.12±3.1e	158±3.61d	208±6.68c	813±27.18a	300±9.97b	28	60–180
Al ($CaCl_2$-ext.)	171±5.7b	223±10.7a	252±6.8a	0.68±0.3d	170±5.6c	184±11.1a	155±53.4b	81.57±10.0c	6.8±0.4d	0.15±0.2d	–	–
Cu ($CaCl_2$-ext.)	12.6±0.27a	1.58±0.06c	6.70±0.23b	0.72±0.02d	13.4±0.92a	17.2±2.46b	93.12±17.93a	20.98±3.58b	4.31±0.34c	u.l.	–	0.6–50[a]
Mn ($CaCl_2$-ext.)	2.15±0.05d	22.10±0.65b	61.1±1.42a	4.04±0.13c	3.72±0.94c	1.92±0.01d	56.04±2.14b	40.72±3.75c	208±13.13a	2.59±0.22d	–	1.5–not defined[a]
Ni ($CaCl_2$-ext.)	u.l.	0.20±0.03b	0.43±0.03a	u.l.	u.l.	0.24±0.03d	2.4±0.02a	1.43±0.1c	1.89±0.16b	u.l.	–	Not defined–75[a]
Zn ($CaCl_2$-ext.)	u.l.	0.19±0.11 cd	0.40±0.01c	0.88±0.03b	1.61±0.72a	0.83±0.08d	9.17±0.33b	1.68±0.17c	26.8±0.79a	u.l.	–	1.0–200[a]

Mean ± confidence interval (CI) of the mean of three replicates. Values followed by different letters in each row differ significantly with $P<0.05$. Soil description is shown in Table 1. The optimum values for *E. globulus* were established by Madeira and Pereira (1990) and the values for most plant species were collected by Marx et al. (1999). The values for *E. globulus* are also valid for pines (Fölster and Khanna 1997)

u.l. undetectable level, *TN* total N, *IN* inorganic N, *ON* organic N, NH_4^+ ammonium, $NO_2^- + NO_3^-$ nitrates + nitrites

[a] Minimum value according to Marx et al. (1999) and threshold value of soil pollution according to Macías and Calvo de Anta (2009)

by metals. Forest species do not require a high nutrient concentration as agricultural species, and the species that have been planted in the mine (*P. pinaster* Aiton and *E. globulus* Labill) have low requirements of Ca, Mg and P (Brañas et al. 2000). The purpose of the applied treatments (the plantation of the mentioned tree species and the addition of waste amendments) in the studied mine sites was to reclaim the quality of the soils, which includes correcting the soil nutrient concentration. The undisturbed soils located at the region where the studied sites are located (Galicia, Fig. 1) are acid and poor in nutrients except in phosphorus, whose concentration is rather high (Alvarez et al. 2008; Temes 1985). Because of this, the treatments applied to the mine soils must increase the concentration of some nutrients, even exceeding the typical values of Galician soils. Despite the fact that any research studies have found linear correlation between the concentration of nutrients in soils and the taken up by plants, the goal concentrations of nutrients for the soils studied in the present work are the range of suitable concentrations in soils for the proper development of most plant species.

4.1 Effect of the Treatments in the Mine Soil Macronutrient Concentrations

The concentrations of soil macronutrients (N, Ca, K, Mg and P) that are optimum for *E. globulus* were established by Madeira and Pereira (1990) in kilograms nutrient per hectare soil. For an easier comparison with the data from the present study, the concentrations were calculated for each soil in milligrams nutrient per kilogram soil (Table 3). As it is known that conifers need a lower concentration of nutrients than eucalypts (Fölster and Khanna 1997), the values calculated can be also valid for pines. Regarding the nutrients required by other plant species, Marx et al. (1999) established the adequate concentrations as indicated in Table 3. According to these values, the soil at the untreated settling pond site (B1) had a sufficiently high N and K concentration for *P. pinaster* and *E. globulus* growth, but an insufficient concentration of Ca, Mg and P for these species and an insufficient concentration of all macronutrients for other plants (Table 3). The soil reclamation treatment consisting of planting these tree species at the B2v and B3v sites significantly increased the concentration of $CaCl_2$-extractable Mg up to optimum levels for pines and eucalypts, but not for other plant species, or Ca and P for any of them. Nevertheless, the treatment consisting on amending with wastes (sewage sludges and paper mill residues) for a short time (5–6 months) at the B4w-settling pond site increased all macronutrients up to adequate levels for all plant species except Ca, which only increased to optimum levels for pines and eucalypts. The soil at the untreated mine tailing site (M1) had an optimum concentration of N, Ca, Mg and K for pines and eucalyptus, but insufficient for other plants (Table 3). Moreover, M1 had a concentration of available P below the method detection limits. Only the amendment with wastes (M3w and M4vw sites) increased the concentration of P, Ca, K and Mg up to adequate levels for all plants. However, the nitrogen concentration only reached the adequate value in the recently amended site (M3w). Moreover, only the recently amended soils at both mine zones (B4Aw and M3w) had significantly high concentrations of NH_4^+ and of organic N, which indicate a future source of inorganic N. Other authors have previously reported that the wastes used (sewage sludge and paper mill residues) have high nutrient concentrations (Calace et al. 2005; N'Dayegamiye 2006; Tripathy et al. 2008). On the other hand, the soil that was amended with wastes but also vegetated with eucalypts for 10 years had an inadequate TN concentration and significantly lower concentration of NH_4^+ than M3w. This indicates that eucalypts take up ammonium over time and that the addition of wastes that are rich in this nutrient is necessary at regular intervals. Conifers and eucalypt species have preferential absorption of ammonium (NH_4^+) in relation to nitrates (NO_3^-) (Adams et al. 1982). The selection of this type of trees was only for economic reason. These tree species are not the best to improve the nutrient status of soils and enhance further colonization by other plants, so we recommend that other species are selected in the future.

The optimal C/N ratio in the OM is 24. Ratios greater than 30 result in immobilization, and less than 20 result in mineralization (Zechmeister-Boltenstem and Zechmeister-Boltenstem 2007). According to the C/N ratio of the soils, only M2Bv is within the optimum. The ratio of B1, B2v, B3v, B4Bw, M1 and M3w indicates mineralization of N. However, the mineralization process is almost depleted in all of them except the amended because their organic N concentrations were low. The C/N ratio of B4Aw, M2Av and M4vw indicated immobilization of N, which is due to the limiting effect of the amount of nitrogen. The differences observed in the nitrogen processes (mineralization and immobilization) in the studied soils could be due to differences in soil microorganisms, pH and organic carbon concentration. In fact, a highly significantly positively correlation was obtained between C/N and soil pH (r>0.88 in both mine sites, P<0.01) and organic C (r>0.93 in both mine sites, P<0.01).

4.2 Effect of the Treatments on the Mine Soil Micronutrient Concentrations

The concentrations of soil micronutrients that must be checked because they are usually found in a deficient concentration for plants are copper, manganese and zinc. The minimum concentration of these nutrients for most plant species to grow properly were defined by Marx et al. (1999) (Table 3). Due to the possible pollution by metals in the studied soils, it was also necessary to check that the concentration of Cu, Ni and Zn was not above the pollution threshold value for soils. The threshold values for Galician soils were established by Macías and Calvo de Anta (2009) (Table 3). According to these values, the concentrations of phytoavailable Cu were adequate in all soils except in the vegetated soil at the mine tailing, as its topsoil had a higher value than the pollution threshold limit. This is probably due to the accumulation of Cu in the surface horizon of this soil, as the subsurface (M2Bv) had a significantly lower concentration (Table 3).

The phytoavailable concentration of manganese was adequate in all soils. Nevertheless, it is important to observe that the untreated soils had a low concentration and that both reclamation treatments significantly increased it. The phytoavailable concentration of Zn was only deficient in B1 and M4vw, where it was below the method detection limits. The treatment that most increased the phytoavailable Zn concentration was the addition of wastes. The concentration of Ni in phytoavailable form was very low or below the method detection limits in all soils, which indicates that the wastes used as amendments (sewage sludges and paper mill residues) did not add hazardous contents of this metal to soil.

The aluminium concentration in exchangeable or soluble form can affect the soil pH and, therefore, plant growth. In fact, the soils B1, B2v, B3v and M1 had an acid pH because of their high phytoavailable Al concentration and percentage of Al saturation (Tables 2 and 3), which is supported by the significantly negative correlation between soil pH–$CaCl_2$-extractable Al and pH–Al saturation (r<−0.8, P<0.01 in all cases for both mine zones). The amendment with wastes and the plantation of trees at the mine tailing decreased the Al concentration and, as a result, increased soil pH.

4.3 PCA for the Settling Pond Soils

The concentrations of the analyzed nutrients were selected in order to perform a PCA for the settling pond samples (Table 4). The two principal components obtained accounted for 89 % of the total variance. According to the position of the samples in the scatter plot (Fig. 2), the nutrient concentration significantly changed in the treated soils in comparison to the control (B1), except in the subsurface horizon at the recently amended site (B4Bw), probably because 6 months was not long enough for any substantial changes to occur. The scatter plot shows that both B1 and B4Bw are not influenced by the concentration of any of the soil nutrients. On the contrary, there is positive influence of most nutrients (TN, ON, ammonium, Olsen P, phytoavailable Ca, K, Mg and P) in the topsoil of the recently amended soil (B4Aw). Moreover, there is a negative correlation with Al concentration. The two vegetated soils (B2v and B3v) are positively influenced by the phytoavailable concentrations of Al, Mn, Ni and nitrates + nitrites, but negatively by Cu.

Table 4 The component score coefficients matrix from the PCA for the two mine zones

Indicators	Settling pond		Mine tailing	
	PC1	PC2	PC1	PC2
Total N	0.96	0.28	0.92	0.33
Organic N	0.98	0.15	0.87	0.42
NH_4^+	0.98	0.17	0.79	0.14
$NO_2^- + NO_3^-$	−0.32	0.79	0.15	−0.04
Olsen P	0.99	0.14	0.73	0.67
Al	−0.98	0.19	−0.33	−0.87
Ca	0.97	0.05	0.16	0.62
Cu	−0.49	−0.76	0.11	−0.85
K	0.94	0.34	0.70	0.47
Mg	0.98	0.17	0.84	0.53
Mn	−0.48	0.79	0.97	0.15
Ni	−0.53	0.81	0.72	−0.056
P	0.98	0.17	0.82	0.54
Pb	−0.54	0.81	–	–
Zn	0.32	−0.35	0.99	0.09

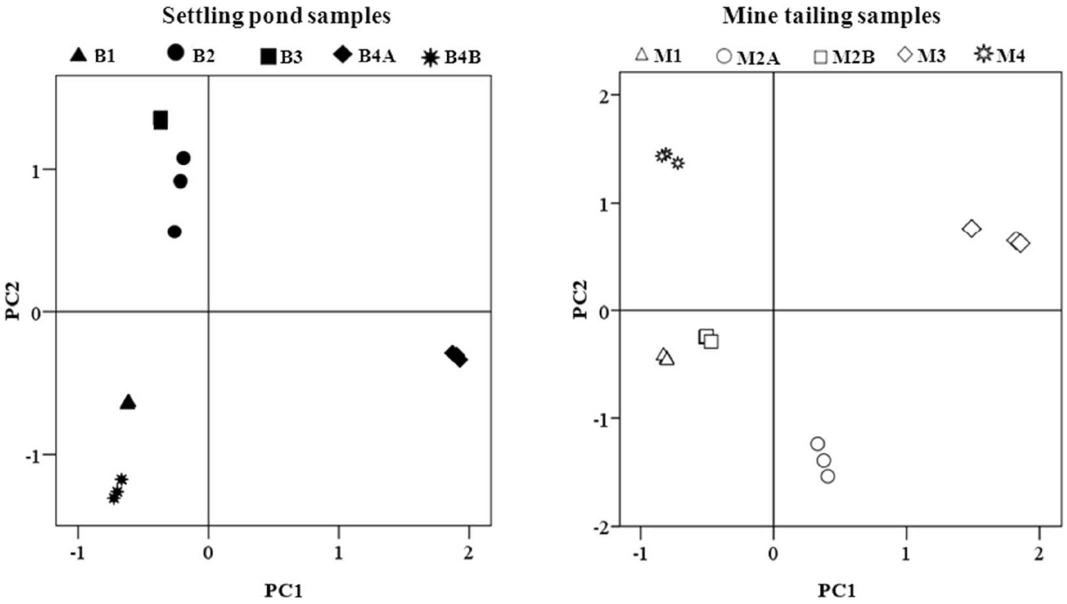

Fig. 2 Scatter plot with the two principal components obtained in the PCA (PC1 and PC2) referred to both the settling pond and the mine tailing samples

4.4 PCA for the Mine Tailing Soils

The concentrations of the analyzed nutrients were also selected to perform a PCA for the mine tailing samples (Table 4). The two principal components obtained accounted for 79 % of the total variance. According to the position of the samples in the scatter plot (Fig. 2), the treated soils significantly changed their nutrient concentration in comparison to the control (B1), except the subsurface horizon at the vegetated site (M2Bv). The component score coefficients matrix obtained (Table 4) shows that M1 and M2Bv are not influenced by any of the nutrient contents, as was observed in the settling pond. The surface horizon in the vegetated site (M2Av) and the recently amended soil (M3w) is positively influenced by the $CaCl_2$-extractable (phytoavailable) concentration of most nutrients (TN, ON, ammonium, Olsen P, phytoavailable K, Mg, Mn, Ni, P and Zn). In addition, M3w is negatively influenced by the phytoavailable concentration of Al and Cu. Finally, the soil with the two treatments (M4vw) is also negatively influenced by Al and Cu contents, but it is not positively influenced by any nutrient.

5 Conclusions

The settling pond and the mine tailing soils at the sites without reclamation treatment contain optimum levels of total N and K for the growth of *E. globulus* Labill and *P. pinaster* Aiton, but not for other plant species. The phytoavailable concentration of Ca and Mg was only optimum for eucalypts and pines and only in the mine tailing. Moreover, both the phytoavailable and Olsen P were below the method detection limits in either site. The reclamation treatment consisting of planting these tree species increased the concentration of Mg in the settling pond up to adequate levels for eucalypts and pines, but not for other plants. However, the growth of both eucalyptuses and pines was slow, and their trunks were thin in the sites without amendment. The treatment consisting of amending with wastes (sewage sludges and paper mill residues) was able to increase the phytoavailable concentration of all macro- and micronutrients (N, P, K, Ca, Mg, Cu, Mn and Zn) up to adequate levels for most plant species. However, the site amended and vegetated for 10 years had a deficient N concentration and lower ammonium concentration than the recently amended sites. Because of this, we recommend periodically amending of mine soils with wastes rich in nutrients because they raise them to adequate levels for most plants, but are depleted over time. The periodicity of this amending should be determined by future research studies. We also suggest the use of wastes with a balanced C/N ratio in order to avoid the immobilization of N in soils and with a low Al concentration in the case of soils from metal mining, as its high concentration promotes acid soil pH.

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