Chapter 17
Sludge Amendment and Tree Vegetation Could Improve the Quality of Mine Soils

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17.1 Introduction

Reclaiming areas where mining has previously carried out is necessary in order to restore mine soils. Mine tailings occupy huge areas, requiring substantial resources to improve the quality of their soils. Planting vegetation is a common practice to reclaim mine areas (Chodak and Niklińska 2010; De Varennes et al. 2010; Shrestha and Lal 2008), although in most cases this is not enough due to the severely degraded condition of these soils (extreme pH, nutrient deficiency, poorly aerated). Amending with organic residues has proven to be a cheap and effective treatment to increase soil quality (Bendfeldt et al. 2001; Brown et al. 2003; Hemmat et al. 2010), as well as being a good way to reuse wastes.

In 1988, work began on recovering the depleted copper mine at the village of Touro (Galicia, Northwest Spain, Fig. 17.1). The mine soils were partially reclaimed by planting trees at the end of the copper extraction, although another company has been carrying out work to restore the whole area since 2000. This reclamation process involves planting pine trees (*Pinus pinaster* Aiton) and eucalypts (*Eucalyptus globulus* Labill) and amending with organic wastes (mainly sewage sludge and paper mill residue).

There are three main categories of soil quality indicators: chemical, physical and biological (Carter et al. 1997). We propose a method for developing soil quality

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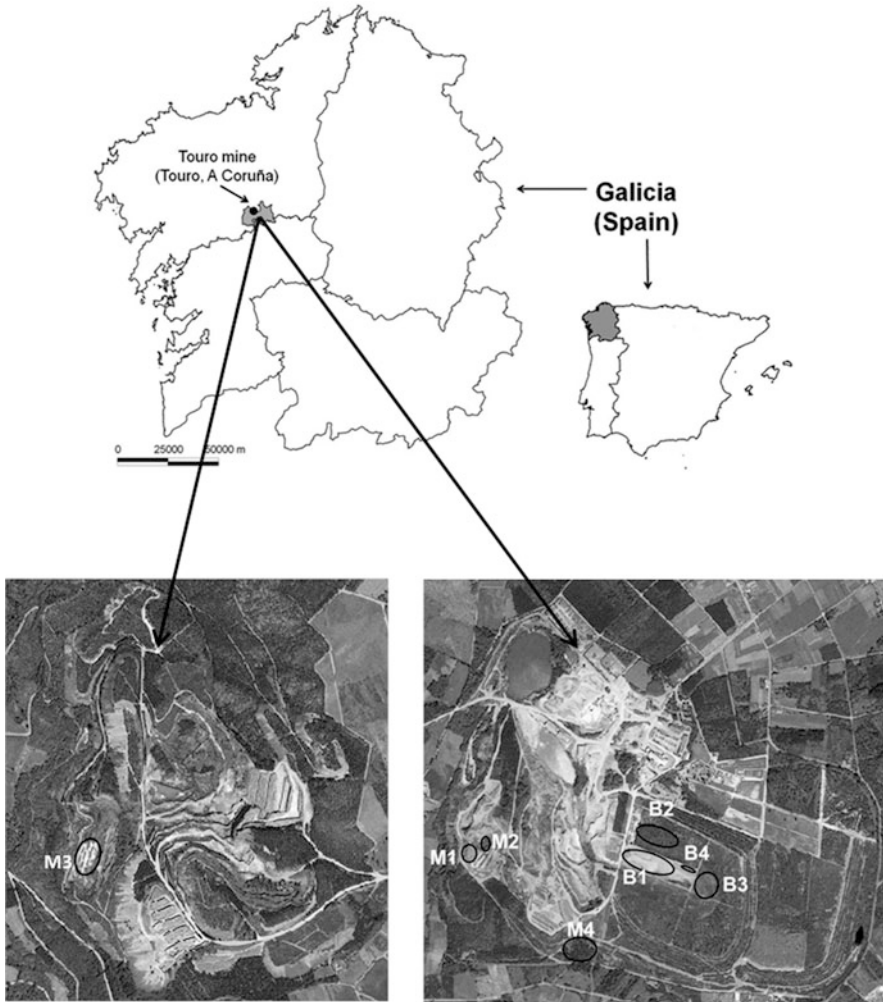e-mail: emmaf@uvigo.es

Fig. 17.1 Location of sampled areas in Touro mine. Source: ©Instituto Geográfico Nacional de España

indexes (SQI) for two types of mine soils (settling pond and mine tailing) reclaimed by planting trees and/or amending with wastes and to assess the quality of these soils under field conditions.

We hypothesised that vegetating with *E. globulus* Labill and *P. pinaster* Aiton and amending with sludges at the same time may increase the soil quality in mine soils polluted by metals.

17.2 Materials and Methods

17.2.1 Soil Sampling

The sampling area is located at the mine in Touro (Galicia, Northwest Spain) (Lat/Lon (Datum ETRS89): 8° 20′ 12.06″ W 42° 52′ 46.18″ N) (Fig. 17.1). The climate of the experimental site is Atlantic (oceanic), with precipitation reaching 1,886 mm per year (with an average of 157 mm per month) and a mean daily temperature of 12.6 °C. The average relative humidity is 77 % (AEMET 2012).

Copper was extracted from the Touro mine between 1973 and 1988 (15 years). This activity left behind a settling pond (71 ha) and a huge mine tailing (larger than 700 ha). Nowadays, apart from the extraction of material for road construction, the former mining areas are being reclaimed. Settling ponds are created by the accumulation of waste after the process of metal concentration in flotation banks. Mine tailings are the accumulation of thick material after mining activity. The settling pond in the Touro mine was created with waste from the copper flotation process, but today it is completely emerged and dry. There is an active oxidation zone near the surface where vegetation does not grow. The unvegetated or amended areas in the mine tailing were also completely bare. In order to evaluate the effectiveness of treatments in the settling pond and mine tailing, four areas were selected in each zone (Table 17.1, Fig. 17.1). The soil samples are described in greater detail below. Five soil samples were randomly collected in points sufficiently spaced to be representative of each site on 9 March 2010. Samples were stored in polyethylene bags, dried at room temperature and sieved to < 2 mm prior to being analysed. All soils had only one horizon, except two of them, where both horizons were sampled (described below). Soils were classified according to the latest version of the FAO (2006).

Table 17.1 Location, depth and reclamation of soil samples

Zone	Name	Horizon	Treatment	Time of treatment
Settling pond	B1	AC	None	—
	B2v	AC	Tree vegetation	21 years
	B3v	AC	Tree vegetation	6 years
	B4Aw	AC	Waste amendment	5 months
	B4Bw	C	None	—
Mine tailing	M1	AC	None	—
	M2Av	AC	Tree vegetation	21 years
	M2Bv	C	None	—
	M3w	AC	Waste amendment	6 months
	M4vw	AC	Trees + wastes	10 years

17.2.2 Settling Pond Samples

The control sample from the settling pond (B1) was in an untreated area. B1 is a Spolic Technosol located 336 m above sea level, covering an area of 1.9 ha with an AC horizon 40 cm deep.

The second sampled area (B2v) was chosen for its old vegetation. Pine trees (*P. pinaster* Aiton) were planted here in 1989 (21 years ago). B2v is also a Spolic Technosol, with spontaneous vegetation: eucalyptus (*E. globulus* Labill), gorse (*Ulex* sp.), heather (*Erica* sp.), *Agrostis* sp. and bryophytes. The B2v soil covers 6200 m^2 and is 340 m above sea level, with an AC horizon 20 cm deep.

The third sample (B3v) was chosen because of its young vegetation, in order to compare it with B2v and to observe the effect of trees over time. The B3v area was vegetated with eucalyptus in 2004 and is also a Spolic Technosol. This area also has spontaneous vegetation: pine trees (*P. pinaster* Aiton), *Agrostis* sp., broom (*Cytisus* sp.), *Acacia* sp. and bryophytes. The B3v soil covers 1.15 ha and is 335 m above sea level, with an AC horizon 20 cm deep.

The fourth sample (B4w) was located in a recently amended area. Sewage sludge mixed with paper mill residue had been added 5 months before the sampling date. This waste was directly added with trucks and then spread on the soil surface, without being mixed in with the mine soil. The final depth of this new layer was 20 cm, with a volume of 280 t per ha. The properties of this amendment are similar to those reported by Camps et al. (2008). The general characteristics of the added waste were pH 8–10, more than 150 g kg^{-1} of total organic C, more than 100 mg kg^{-1} of total Cu and more than 300 mg kg^{-1} of total Zn. Only spontaneous herbaceous vegetation grew on B4w, measuring 100 m^2 and at a height of 339 m above sea level. B4w was an Urbic Technosol with two horizons: AC (B4Aw) and C (B4Bw). B4Bw was also sampled to compare it with the untreated sample (B1) as it was considered to be analogous of the control soil. B4Aw was 20 cm deep, and B4Bw was 40 cm deep.

As the use of waste amendments in this area began only 5 months before the sampling date, there are no samples that are representative of the long-term effects of amendment or both treatments at the same time (vegetation and amendment).

17.2.3 Mine Tailing Samples

The control sample in the mine tailing (M1) was in an untreated area and is classified as Spolic Technosol. M1 was 336 m above sea level and covered an area of 1.20 ha, with an AC horizon 20 cm deep.

The second sampled area (M2v) was chosen because of its old vegetation, as it was vegetated with pine trees in 1989. It also had spontaneous vegetation: gorse (*Ulex* sp.), heather (*Erica* sp.), *Agrostis* sp. and bryophytes. This soil is also a Spolic Technosol, covering an area of 0.60 ha and 340 m above sea level, with an AC horizon 20 cm deep. The C horizon of this soil was also sampled to be compared

with the untreated one (M1), as it is similar to the original bare soil but with the amendment on top of it. The AC horizon was named M2Av and the C horizon M2Bv. M2Av was 4 cm deep and M2Bv was 20 cm deep.

The M3w soil is an Urbic Technosol created with sewage sludge and paper mill residue. These sludges were added 6 months before the sampling date by trucks, and then spread on the soil surface. The final depth of this new layer was around 3 m, covering an area of 0.8 ha. The amount of wastes added was around 158 t per ha. These wastes were the same as those used in the settling pond. This soil was 178 m above sea level and only had natural herbaceous vegetation.

The fourth area (M4vw) was selected because it was vegetated and amended at the same time. This area was vegetated with eucalyptus and amended in 2000 with the same type of wastes as M3w. The amount added in M4vw was 297 t per ha and the final depth of this new layer was around 70 cm. This area also had spontaneous vegetation (gorses, brambles, pine trees and bryophytes). The M4vw soil is also an Urbic Technosol, measuring 1.5 ha and 336 m above sea level.

17.2.4   Analytical Methodology

17.2.4.1   Physical Properties

Samples were air-dried, passed through a 2 mm sieve and homogenised in a vibratory homogeniser for solid samples (Fritsch Laborette 27 rotary sampler divider) prior to analysis. A portion of each sample was sieved at 10 mm to determine aggregate size distribution.

Standard procedures were used to estimate both soil stoniness (Eriksson and Holmgren 1996) and particle size distribution (Day 1965). Particle and bulk density (BD) were determined following standard procedures (Hao et al. 2008). Porosity was calculated as the difference between both densities as a percentage.

Aggregate size distribution was determined by sieving 50 g of >10 mm aggregates in a set of five sieves (5, 2, 1, 0.25 and 0.05 mm). The mean weight diameter (MWD) obtained of each sample was related to the stability of the aggregates (Le Bissonnais 1996).

The determination of water-stable aggregates (WSA) was carried out with standard equipment (Eijkelkamp Wet Sieving Apparatus) (Asensio et al. 2013).

17.2.4.2   Chemical Properties

Soil reaction was determined with a pH electrode in 1:2.5 water to soil extracts, while 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 their concentrations determined by ICP-AES (Perkin-Elmer Optima 4300 DV). Effective cation exchange capacity (CECe) was

calculated by adding up the total cation concentrations. The method developed by Mehra and Jackson (1960) was used to determine the free oxide concentrations. Aluminium, iron and manganese were determined in the extract by ICP-AES.

Both total and inorganic carbon (TC and IC) were determined in a module for solid analysis (SSM-5000) coupled with a TOC analyser (Shimadzu TNM-1, Japan). Soil organic carbon (SOC) contents were calculated from the difference TC−IC. Dissolved organic carbon (DOC) was extracted with bidistilled H_2O according to (Sanchez-Monedero et al. 1996) and the OC in the supernatant was determined with a TOC analyser (Shimadzu TNM-1, Japan).

The different chemical organic matter fractions labelled as humin C, humic acids (C_{HA}) and fulvic acids (C_{FA}) were separated following the method described in De Blas et al. (2010). Microbial biomass carbon (C_{mic}) was determined by the fumigation-extraction method according to (Joergensen 1996). Organic C in the fumigated and non-fumigated extracts was determined in a TOC analyser. The microbial biomass C was calculated as $C_{mic} = E_C/k_{EC}$, where E_C is the difference between organic C extracted from fumigated soils and organic C extracted from non-fumigated soils and k_{EC} is a constant. For soils with pH > 4.5, k_{EC} is 0.45 and when pH < 4.5, $k_{EC} = 0.30$ (Joergensen 1996; Vance et al. 1987).

Pseudototal concentrations of Cr, Cu, Ni, Pb and Zn were extracted with aqua regia by acid digestion in a microwave oven (Milestone ETHOS 1). The certified reference material CRM026-050 was analysed in parallel with samples to check the effectiveness and precision of the extraction analysis. Chromium, copper, nickel, lead and zinc were extracted with acidified 0.01 M $CaCl_2$ (Houba et al. 2000). The chemical form of heavy metals extracted with 0.01 M $CaCl_2$ is operationally defined as phytoavailable (Houba et al. 2000). Pseudototal and $CaCl_2$-extractable heavy metal concentrations were compared with the Generic Reference Level (GRL) established for Galician soils (Macías and Calvo de Anta 2009).

The total bioavailable phosphorus content was determined by the Olsen method (Olsen et al. 1954). The 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 analysed by potentiometric titration with a titrator equipment (702 SM Titrino, Metrohm).

17.2.4.3 Statistical Analyses

All analytical determinations were performed in triplicate and the data obtained were statistically treated using the program SPSS 15.0 for Windows. Statistical analyses were performed by separating the data from the settling pond soils from the mine tailing, as the characteristics of the control soils at each zone are significantly different. Analyses of variance (ANOVAs) 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 done when data were not parametric. An independent *t*-test was done to compare each control soil (B1 or M1) with their respective analogous (B4Bw or M2Bv). A correlated bivariate analysis was carried out from all soil samples in each zone.

Soil quality index proposed by Asensio et al. (2013) by totalling the scores of the minimum data set (MDS) selected through a principal component analysis (PCA) proved to be a valid and useful tool. These results revealed that the quality of these reclaimed soils should be determined by analysing both physical and chemical characteristics. In the case of settling pond sites, stoniness, pH, Al^{3+}, CECe, MWD, SOC, humin C, C_{HA}, C_{FA}, TN, clay, K $CaCl_2$ (extracted with $CaCl_2$), Mn $CaCl_2$, Ni $CaCl_2$, Zn $CaCl_2$ and pseudototal both Ni and Pb should be analysed. In the case of mine tailing sites, it is necessary to analyse stoniness, pH, BD, WSA, humin C, C_{HA}, C_{FA}, TN, C_{mic}, Ca $CaCl_2$, Mn $CaCl_2$, Zn $CaCl_2$ and pseudototal both Pb and Zn. The establishment of this set of key parameters for assessing the quality of reclaimed mine soils will help to save time and money by analysing a large number of soil characteristics.

To eliminate the effect of different units of variables, the PCA was carried out using the correlation matrix on the standardised values of the measured soil properties (Shukla et al. 2006). The principal components (PC) obtained had eigenvalues >1 and were subjected to varimax rotation with Kaiser. The variables selected for the minimum data set (MDS) to elaborate the soil quality index (SQI) were the highest weighted from each PC. We defined highly weighted as being within 10 % of the highest factor loading (using absolute values) (Andrews et al. 2002). When more than one variable was retained within a PC, we calculated their correlations to determine whether the variables could be considered redundant and, therefore, eliminated from the MDS (Andrews et al. 2002). If the highly weighted variables were not significantly ($p < 0.05$) correlated or the correlation was considered spurious (significantly affected by the reclamation treatments), then each was considered important and was retained in the MDS. The scores for values of each selected variable were created by assigning negative scores to values unfavourable for soil living organisms or hazardous for the environment, neutral value (zero) for values that do not affect positive or negative and finally positive scores for values that affect positive. The consideration of "negative" or "positive" for values were decided according to the references cited for each soil characteristic in Table 17.1. The scores of each selected MDS variable were then summed for each soil to obtain the soil quality index (SQI), based on the equation proposed by (Amacher et al. 2007) as follows:

$$SQI = \frac{\sum individual\ soil\ characteristic\ score\ value}{maximum\ possible\ total\ SQI\ for\ characteristics\ measured} \times 100 \quad (17.1)$$

Thus, missing characteristics do not contribute to the index. The highest score of the index is 100 %, which indicates very high soil quality. Scores around 0 or negative indicates very low quality.

Factor time is included in the SQI proposed due to sites where the same treatment applied in different years is used.

17.3　Results and Discussion

The untreated areas in the mine in Touro (Tables 17.2 and 17.3) were physically degraded: low porosity, high density and less than 50 % of water-stable aggregates. Both planted trees and added waste amendments significantly changed these physical properties in the mine soils, although each treatment did so a different way. The planted vegetation increased soil porosity and, consequently, decreased the bulk density. On the other hand, the added amendments increased the percentage of MWD and WSA probably due to the addition of organic matter from the wastes added to the soil. It was seen that the simultaneous use of both treatments improved the physical condition of the mine soils better than the use of only one treatment. Waste supplies organic matter and roots increase porosity and the percentage of small aggregates. The best treatment for improving the physical quality of mine soils is to plant trees and to add organic wastes at the same time.

The control soils (B1 and M1) had an extremely acidic pH (according to the USDA 1998) (Tables 17.4 and 17.5). The soil pH was still acidic 21 years after tree planting, but in amended sites the pH rose to 6–8, probably due to their high organic

Table 17.2 Physical characteristics of the settling pond soils

	Settling pond soils				
	B1	B2v	B3v	B4Aw	B4Bw
Stoniness (%)	$20.1 \pm 5.7d$	$34.9 \pm 8.2b$	$30.9 \pm 7.2c$	$81.2 \pm 11.2a$	$11.3 \pm 1.9e$
Sand (%)	$69.3 \pm 13.5b$	$69.1 \pm 0.7c$	$65.1 \pm 17.5d$	$45.8 \pm 10.9e$	$71.1 \pm 17.1a$
Silt (%)	$21.1 \pm 0.1c$	$19.9 \pm 0.5d$	$24.6 \pm 2.2b$	$27.9 \pm 1.9a$	$19.7 \pm 2.2e$
Clay (%)	$9.5 \pm 1.5d$	$11.1 \pm 0.3b$	$10.3 \pm 2.5c$	$26.1 \pm 6.1a$	$9.2 \pm 3.1e$
Texture	Sandy loam	Sandy loam	Sandy loam	Sandy clay loam	Sandy loam
Particle density (g cm^{-3})	$2.8 \pm <0.1b$	$2.3 \pm <0.1d$	$2.5 \pm <0.1c$	$1.9 \pm <0.1e$	$3.1 \pm <0.1a$
BD (g cm^{-3})	$1.7 \pm 0.1a$	$0.8 \pm 0.07c$	$1.5 \pm 0.02b$	$0.3 \pm 0.1e$	$0.7 \pm 0.07d$
Porosity (%)	38.4e	65.7c	40.6d	83.2a	77.6b
MWD (mm)	$1.2 \pm 0.2d$	$2.1 \pm 0.2b$	$2 \pm 0.2c$	$4.8 \pm 0.3a$	$0.9 \pm 0.2e$
WSA (%)	$43.3 \pm 0.3c$	$82.1 \pm 0.3b$	$97.6 \pm 0.1a$	$93.2 \pm 4.2a$	$44.4 \pm 4.3c$

Mean ± confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$

u.l. undetectable level, *WSA* water-stable aggregates, *MWD* mean weight diameter, *BD* bulk density

Table 17.3 Physical characteristics of the mine tailing soils

	Mine tailing soils				
	M1	M2Av	M2Bv	M3w	M4vw
Stoniness (%)	$53.1 \pm 8.7b$	$22.9 \pm 6.4e$	$41.1 \pm 3.5d$	$56.2 \pm 6.9a$	$46.8 \pm 7.7c$
Sand (%)	$69.1 \pm 30.4a$	$51.1 \pm 4.7e$	$59.3 \pm 6.1d$	$66.2 \pm 23.8b$	$60.8 \pm 2.9c$
Silt (%)	$20.1 \pm 4.9e$	$32.2 \pm 6.2a$	$25.4 \pm 9.1c$	$23.5 \pm 4.5d$	$26.1 \pm 1.9b$
Clay (%)	$10.9 \pm 3.9d$	$16.7 \pm 1.4a$	$15.3 \pm 1.7b$	$10.3 \pm 1.9e$	$13.1 \pm 0.9c$
Texture	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam
Particle density ($g\ cm^{-3}$)	$2.8 \pm <0.1a$	$2.3 \pm <0.1d$	$2.7 \pm <0.1b$	$2 \pm <0.1e$	$2.4 \pm <0.1c$
BD ($g\ cm^{-3}$)	$1.1 \pm 0.05b$	$1.9 \pm 0.03a$	$1.9 \pm 0.02a$	$0.9 \pm 0.05c$	$0.8 \pm 0.1d$
Porosity (%)	$58.3b$	$19.1e$	$31d$	$53.1c$	$64.7a$
MWD (mm)	$2.8 \pm 0.3c$	$1.3 \pm 0.1e$	$3.5 \pm 0.8b$	$3.8 \pm 0.1a$	$2.3 \pm 0.4d$
WSA (%)	$49.1 \pm 5.9b$	$58.4 \pm 6.3a$	$76.9 \pm 5.7a$	$83.6 \pm 6.0a$	$83.8 \pm 9.5a$

Mean $\pm$ confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$

u.l. undetectable level, *WSA* water-stable aggregates, *MWD* mean weight diameter, *BD* bulk density

carbon concentrations. The effective cation exchange capacity (CECe) significantly increased in the settling pond after amending with wastes but in the mine tailing only after the use of both treatments. The concentrations of aluminium (Al_2O_3) and manganese (MnO) oxides are higher in the treated soils than in the controls, whereas the opposite happens with iron oxide (Fe_2O_3). The soil total nitrogen concentration significantly increased with the use of both treatments, especially with waste amending.

The control sites (B1 and M1) were poor in both soil organic and inorganic carbon (SOC and IC) (Tables 17.4 and 17.5), since they had no carbon sources i.e., vegetation, animals, microorganisms or organic amendments. The SOC concentration was extremely low in both B1 and M1 in comparison to undisturbed sites with similar conditions (formed over schist and vegetated with pines and eucalyptus) in the surrounding area ($92–126\ g\ kg^{-1}$) (De Blas et al. 2010). In the control soils, most of the SOC was still in the free organic matter (FOM) fraction and therefore was non-humified (Tables 17.4 and 17.5). Moreover, the microbial biomass C (C_{mic}) was very low in comparison with microbially active soils (1–4 %) (Anderson and Domsch 1990; Kandeler et al. 1996; Sparling 1992) showing that the organic matter in the untreated sites has not been biologically degraded. Planting trees significantly increased the total C concentration, even 6 years after starting this reclamation treatment (Tables 17.4 and 17.5). The inorganic C concentrations in the vegetated soils did not change significantly in comparison to control soils, and the increase in soil C was due to the organic C inputs. Most of the SOC in the vegetated sites was still in the FOM (Tables 17.4 and 17.5).

Both the organic and inorganic C concentration significantly increased in the mine soils after being amended with wastes (Tables 17.4 and 17.5). The carbon concentration shifted between the amended sites due to the heterogeneity of the

Table 17.4 Chemical characteristics of the settling pond soils

	Settling pond soils				
	B1	B2v	B3v	B4Aw	B4Bw
pH H_2O	3.8 ± 0.04d	4.8 ± 0.05b	4.7 ± 0.03b	6.9 ± 0.3a	4.3 ± 0.3c
TC (g kg^{-1})	1.7 ± 0.9e	10.7 ± 1.2c	11.4 ± 1.3b	115 ± 10a	1.8 ± 0.8d
SOC (g kg^{-1})	1.4d	10.4b	11.1b	112a	1.5c
IC (g kg^{-1})	0.3 ± 1.3b	0.3 ± 0.01b	0.3 ± 0.05b	3.7 ± 1.9a	0.3 ± <0.01b
DOC (g kg^{-1})	0.01 ± 0.007d	0.09 ± 0.01bc	0.1 ± 0.03b	1.2 ± 0.2a	0.03 ± 0.01 cd
Humin C (g kg^{-1})	0.51 ± 0.01d	4.23 ± 0.03c	4.64 ± 0.02b	59.55 ± 0.01a	0.3 ± 0.02e
C_{FA} (g kg^{-1})	0.65 ± 0.07c	2.03 ± 0.17b	2 ± 0.01b	12.3 ± 0.69a	0.48 ± 0.01c
C_{HA} (g kg^{-1})	0.89 ± 0.17c	2.16 ± 0.19b	1.89 ± 0.29b	36.60 ± 1.45a	0.68 ± 0.18c
C_{mic} (mg kg^{-1})	8.8 ± 11.6e	181 ± 57b	130 ± 26c	247 ± 38a	19.1 ± 10d
TN (g kg^{-1})	0.14 ± 0.03d	0.58 ± <0.06b	0.58 ± 0.04b	3.71 ± <0.73a	0.32 ± <0.06c
NH_4^+	100 ± 25b	120 ± 25b	110 ± 25b	1,500 ± 27a	120 ± 26b
$NO_2^- + NO_3^-$	20 ± 2b	340 ± 50ab	450 ± 25a	140 ± 26b	120 ± 26b
C/N	11.9c	18.4b	11.3d	115a	1.8e
EC (ms cm^{-1})	0.1 ± <0.1c	0.03 ± <0.1d	0.03 ± <0.1d	0.4 ± <0.1a	0.1 ± <0.1b
P (Olsen)	u.l.	u.l.	u.l.	424 ± 25.8a	18.98 ± 0.8b
P ($CaCl_2$-ext.)	u.l.	u.l.	u.l.	68.28 ± 1.38	u.l.
K ($CaCl_2$-ext.)	21.7 ± 1.61e	91.25 ± 3.85b	64.6 ± 0.65c	333 ± 7.99a	33.5 ± 5.36d
Ca ($CaCl_2$-ext.)	u.l.	u.l.	u.l.	704 ± 125a	135 ± 60b
Mg ($CaCl_2$-ext.)	13.38 ± 0.62e	41.40 ± 1.45c	34.97 ± 0.97d	777 ± 3.97a	60.5 ± 8.74b
Al ($CaCl_2$-ext.)	171 ± 5.7b	223 ± 10.7a	252 ± 6.8a	0.68 ± 0.3d	170 ± 5.6c
Mn ($CaCl_2$-ext.)	2.15 ± 0.05d	22.10 ± 0.65b	61.1 ± 1.42a	4.04 ± 0.13c	3.72 ± 0.94c
CECe (cmol kg^{-1})	2.1 ± <0.1b	2.5 ± <0.1b	2.4 ± <0.1b	58.4 ± 2.9a	2.2 ± 0.1b

Al_2O_3 (g kg^{-1})	$2.54 \pm 0.1d$	$7.41 \pm 0.1b$	$5.06 \pm {<}0.1c$	$15.08 \pm 0.3a$	$2.38 \pm {<}0.1d$
Fe_2O_3 (g kg^{-1})	$88.3 \pm 4.1a$	$38.9 \pm 0.6b$	$28.6 \pm 0.1c$	$23.1 \pm {<}0.1d$	$27.9 \pm 0.5c$
MnO (g kg^{-1})	$0.02 \pm {<}0.1c$	$0.6 \pm {<}0.1b$	$0.8 \pm {<}0.1a$	$0.8 \pm {<}0.1a$	$0.06 \pm {<}0.1c$

Mean $\pm$ confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$

Abbreviations: *u.l.* undetectable level, *CECe* effective cation exchange capacity, *IC* inorganic carbon, *SOC* soil organic carbon, *DOC* dissolved organic carbon, *Humin C* humin carbon, C_{FA} fulvic acid carbon, C_{HA} humic acid carbon, C_{mic} microbial biomass carbon, *TN* total nitrogen, NH_4^+ ammonium, $NO_2^- + NO_3^-$ nitrates and nitrites, *EC* electric conductivity, $CaCl_2$-*ext.* extractable with $CaCl_2$

Table 17.5 Chemical characteristics of the mine tailing soils

	Mine tailing soils				
	M1	M2Av	M2Bv	M3w	M4vw
pH H_2O	3.6±0.05e	6.6±0.4b	5.2±0.4d	5.8±0.1c	8.2±0.1a
TC (g kg^{-1})	3.5±1.0e	35.3±1.5c	6.9±1.2d	56.6±3.0b	88.3±6.1a
SOC (g kg^{-1})	3.2c	35.1a	6.6b	56.3a	54.8a
IC (g kg^{-1})	0.3±0.01b	0.3±0.5b	0.3±<0.01b	0.3±0.01b	33.5±2.7a
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})	3.92±0.02d	17.95±0.01b	3.93±0.02d	16.1±0.03c	37.94±0.04a
C_{FA} (g kg^{-1})	0.6±0.17e	6.14±0.99b	0.89±0.25d	13.97±0.11a	2.66±0.1c
C_{HA} (g kg^{-1})	0.87±0.08d	6.67±0.21b	1.99±0.17d	21.11±1.79a	4.71±0.32c
C_{mic} (mg kg^{-1})	7.6±1.4e	64.2±23.3b	12.5±2.4d	669±155a	53.1±2.2c
TN (g kg^{-1})	0.25±0.04d	0.74±0.28b	0.28±0.04d	3.7±0.34a	0.6±0.28c
NH_4^+	40±26b	80±27b	30±25b	391±12a	40±5b
$NO_2^- + NO_3^-$	60±27b	460±25a	130±25ab	220±25ab	100±25ab
C/N	3.5e	35.3c	6.9d	56.6b	88.3a
EC (ms cm^{-1})	0.1±<0.1c	0.1±<0.1c	0.1±<0.1c	1.9±0.2a	0.2±<0.1b
P (Olsen)	u.l.	14.1±6.1c	3.7±1.5d	265±16.4a	125±13.9b
P (CaCl$_2$-ext.)	29.61±0.30e	154±7.41c	59.65±5.00d	230±2.85a	184±9.20b
K (CaCl$_2$-ext.)	159±43.2d	1,106±43.9b	761±20.3c	1,210±39.1b	1,929±91.3a
Ca (CaCl$_2$-ext.)	53.12±3.1e	158±3.61d	208±6.68c	813±27.18a	300±9.97b
Mg (CaCl$_2$-ext.)	184±11.1a	155±53.4b	81.57±10.0c	6.8±0.4d	0.15±0.2d
Al (CaCl$_2$-ext.)	17.2±2.46b	93.12±17.93a	20.98±3.58b	4.31±0.34c	u.l.
Mn (CaCl$_2$-ext.)	0.24±0.03d	2.4±0.02a	1.43±0.1c	1.89±0.16b	u.l.
CECe (cmol kg^{-1})	3.8±0.1e	12.0±0.4c	9.4±0.5d	20.8±1.1b	26.7±0.7a

Al_2O_3 (g kg^{-1})	$3.22 \pm <0.1$e	11.65 ± 0.2b	$4.67 \pm <0.1$d	$15.53 \pm <0.1$a	7.82 ± 0.1c
Fe_2O_3 (g kg^{-1})	132 ± 2.4a	74.8 ± 0.9c	111 ± 0.8b	22.1 ± 0.1d	7.4 ± 0.1e
MnO (g kg^{-1})	$0.02 \pm <0.1$e	$1.8 \pm <0.1$b	$0.5 \pm <0.1$d	$1.2 \pm <0.1$c	$4.5 \pm <0.1$a

Mean $\pm$ confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$

Abbreviations: *u.l.* undetectable level, *CECe* effective cation exchange capacity, *IC* inorganic carbon, *SOC* soil organic carbon, *DOC* dissolved organic carbon, *Humin C* humin carbon, C_{FA} fulvic acid carbon, C_{HA} humic acid carbon, C_{mic} microbial biomass carbon, *TN* total nitrogen, NH_4^+ ammonium, $NO_2^- + NO_3^-$ nitrates and nitrites, *EC* electric conductivity, $CaCl_2$-*ext.* extractable with $CaCl_2$

wastes used, which had TOC concentrations that vary between 150 and 230 g kg^{-1} (Camps Arbestain et al. 2008). In fact, the organic C concentration was only within the range observed in undisturbed soils in the surroundings in one of the two amended sites (Tables 17.4 and 17.5). Therefore, if it is necessary to add organic C to soils, it is necessary to analyse the wastes for C prior to their use as amendments in order to achieve the optimal concentration for soils.

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 *Eucalyptus globulus* Labill and *Pinus 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 was undetectable in either site (Tables 17.4 and 17.5). 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. Nevertheless, 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 (Tables 17.4 and 17.5). However, the site amended and vegetated for 10 years had a deficient N concentration and lower ammonium concentration that the recently amended sites.

Settling pond and mine tailing soils in the untreated mine sites (B1 and M1, respectively) were polluted by Cr and Cu (Tables 17.6 and 17.7). Pollution by these heavy metals should not be an environmental problem in the Touro mine soils at the present time, as the phytoavailable concentration was below the Generic Reference Level (Tables 17.6 and 17.7). The GRL for Galicia (Macías and Calvo de Anta 2009) established the following threshold limit values for metals in soils: 40 mg kg^{-1} for cobalt, 80 mg kg^{-1} for chromium, 50 mg kg^{-1} for copper,

Table 17.6 Metal content of the settling pond soils

		Settling pond soils				
		B1	B2v	B3v	B4Aw	B4Bw
Cr	CaCl₂- extractable (mg kg^{-1})	u.l.	u.l.	u.l.	u.l.	u.l.
Cu		12.6 ± 0.1a	1.6 ± <0.1c	6.7 ± 0.1b	0.7 ± <0.1d	13.4 ± 0.3a
Ni		u.l.	0.2 ± <0.1b	0.4 ± <0.1a	u.l.	u.l.
Pb		u.l.	0.4 ± <0.1a	0.4 ± <0.1a	u.l.	u.l.
Zn		u.l.	0.2 ± <0.1 cd	0.4 ± <0.1c	0.9 ± <0.1b	1.6 ± 0.3a
Cr	Pseudototal (mg kg^{-1})	**194 ± 2.8a**	86.3 ± 7.1 cd	71.8 ± 3.1d	**94.1 ± 5.6c**	**136 ± 18.1b**
Cu		**310 ± 8.1b**	63 ± 5.8c	75.3 ± 7.5c	**467 ± 21.1a**	**338 ± 16.1b**
Ni		16.2 ± 1.1c	66.7 ± 1.1a	55.6 ± 9.5b	50.5 ± 1.2b	15.6 ± 0.7c
Pb		19.1 ± 1.4c	31.9 ± 3.9bc	32.1 ± 1.7b	**97.1 ± 6.2a**	16.9 ± 0.6c
Zn		41.4 ± 0.7c	90.2 ± 8.3b	89.5 ± 10.4b	**538 ± 25.1a**	45.9 ± 1.9c

Mean ± confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$

u.l. undetectable level, *CaCl₂-ext.* extractable with CaCl₂. Values in bold are over the GRL—Generic Reference Level—established for Galician soils (Macías and Calvo de Anta 2009)

75 mg kg^{-1} for nickel and 200 mg kg^{-1} for zinc. However, in order to prevent the future bioavailability of Cr and Cu, it is important to observe whether planting trees or amending with wastes decreased the concentration of these heavy metals in the soils. The effect of the treatments will not be the same in each mine area due to the different soil characteristics of the settling pond and mine tailing (Tables 17.4 and 17.5).

Planting eucalyptus or pines decreased pseudototal Cr and Cu concentrations in the settling pond and mine tailing soils (Tables 17.6 and 17.7). The accumulation of Cr and Cu in M2Av can be explained because this horizon comprises the first 4 cm of soil, and heavy metal concentrations in soils usually decrease with depth. In fact, the subsuperficial horizon in this soil (M2Bv) had significantly less Cu than the untreated mine tailing and a similar Cr concentration (Tables 17.6 and 17.7). Nickel, lead and zinc concentrations in the vegetated soils behaved in the opposite way to chromium and copper. The sites with tree vegetation (B2v, B3v and M2Av) had more pseudototal Ni, Pb and Zn than the untreated sites.

Amending with wastes decreased the pseudototal Cr concentration in the mine soils, even to values below the GRL for Galicia in the mine tailing area (Table 17.7). Although the amended sites were still polluted by copper, a marked decrease in its concentration was observed in the mine tailing soil (M3w). However, the amended settling pond site (B4Aw) had a higher Cu concentration than its control (Table 17.6). Copper extracted from amended soil samples is attributable to the added wastes, since it has previously been reported that the sewage sludges and paper mill residues used contain more than 100 mg kg^{-1} of total Cu (Camps Arbestain et al. 2008). The results indicate that heavy metal concentrations in the wastes used could vary between batches, due to the heterogeneity caused by different production times. In spite of the high pseudototal Cu concentration in amended soils, this heavy metal was strongly retained and not available in the short term in amended sites, since very low concentrations were observed in the CaCl$_2$-extractable form (Tables 17.6 and 17.7). Pseudototal Ni, Pb and Zn concentrations were also higher in the soils treated with wastes than in the controls. The amended soils had Pb and Zn concentrations that were higher than the soil pollution limits for Galicia (Tables 17.6 and 17.7).

The use of both treatments at the same time (tree vegetation and waste amendments) decreased Cr and Cu concentrations in the mine soils more than the use of a single treatment (Tables 17.6 and 17.7) . Pseudototal Ni, Pb and Zn concentrations also increased with the use of both treatments, especially nickel, as they were in higher concentration than in M3w, even exceeding the GRL for Galicia (Table 17.7). It was clearly shown that Ni, Pb and Zn were added by the wastes used.

Table 17.7 Metal content of the mine tailing soils

		Mine tailing soils				
		M1	M2Av	M2Bv	M3w	M4vw
	CaCl$_2$-extractable (mg kg^{-1})					
Cr		u.l.	u.l.	u.l.	u.l.	u.l.
Cu		17.2 ± 0.9b	**93.1 ± 7.2a**	20.9 ± 1.4b	4.3 ± 0.1c	u.l.
Ni		0.2 ± <0.1d	2.4 ± <0.1a	1.4 ± <0.1c	1.9 ± <0.1b	u.l.
Pb		u.l.	u.l.	u.l.	u.l.	u.l.
Zn		0.8 ± <0.1d	9.2 ± 0.1b	1.7 ± <0.1c	26.8 ± 0.3a	u.l.
Cr	Pseudototal (mg kg^{-1})	**118 ± 18.6b**	138 ± 9.9a	**118 ± 3.1b**	68.9 ± 3.4c	31.7 ± 2.2d
Cu		**911 ± 63.7b**	**1,921 ± 126a**	**537 ± 31.8c**	**350 ± 20.8d**	**51.1 ± 3.5e**
Ni		15.3 ± 1.3d	**121 ± 1.9a**	31.4 ± 4.3c	55.6 ± 3.2b	**128 ± 10.1a**
Pb		19.3 ± 0.7d	24.7 ± 0.5c	16 ± 1.3d	71.1 ± 3.6a	34.4 ± 0.9b
Zn		78.2 ± 10c	176 ± 10.3b	59.7 ± 3.5c	**307 ± 20.5a**	135 ± 3.5b

Mean ± confidence interval (CI) of the mean of three replications. Values followed by different letters in each row differ significantly with $p < 0.05$
u.l. = undetectable level; CaCl$_2$-ext. = extractable with CaCl$_2$. Values in bold are over the GRL—Generic Reference Level—established for Galician soils (Macías and Calvo de Anta 2009)

17.3.1 Soil Quality in the Settling Pond Sites

The percentage of soil quality index (% SQI) was very low in the untreated settling pond site (B1), since most of the soil quality indicators were zero or had a negative score. The application of both types of reclamation treatments (planting pines and eucalyptus or amending with wastes) significantly increased the SQI at the settling pond (Fig. 17.2). The treatment that most increased the quality was amending with wastes, as it increased soil pH, CECe, MWD, concentrations of all chemical forms of soil organic C, total N concentration, clay percentage and phytoavailable K concentration (Tables 17.2,17.3,17.4,17.5,17.6 and 17.7). The increase of all these variables was due to the characteristics of the wastes used (sewage sludges and paper mill residues). The treatment consisting of planting trees also increased the
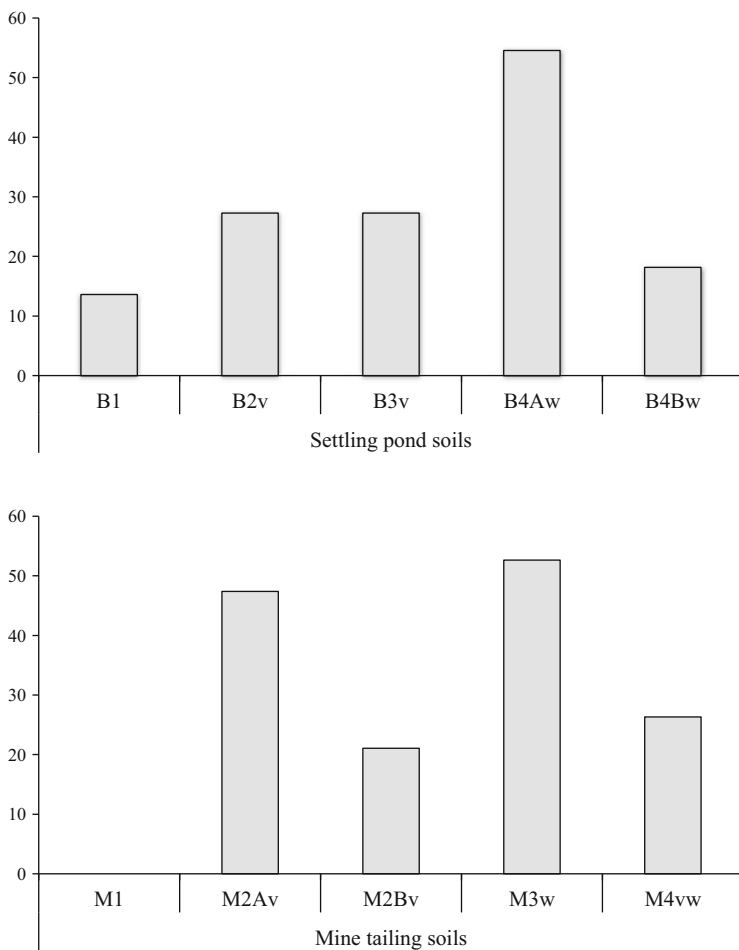

Fig. 17.2 Soil quality index (SQI) of the settling pond and mine tailing soils

quality of the settling pond soil, although less than by amending with wastes. The SQI increased by vegetating with trees basically due to the increase in soil pH, MWD and $CaCl_2$-extractable Mn. There was no difference in the % SQI between the two vegetated sites, despite the fact that one had been vegetated for 6 years and another for 21. It is likely that by planting pines or eucalyptuses alone, it is not possible to increase the quality of settling pond soils as much as by amending with wastes (according to the proposed index), although more studies under field conditions should support this hypothesis.

17.3.2 Soil Quality in the Mine Tailing Sites

The soil quality index percentage was also very low in the untreated mine site at the mine tailing zone (M1), as most soil quality indicators were zero or had negative values. The application of both types of reclamation treatments also significantly increased the SQI at this mine zone, and once again the treatment that most increased this index was the recent addition of wastes (M3w site). However, the site with both trees and wastes for 10 years showed lower SQI than the sites with only one treatment. The use of reclamation treatments (alone or in combination) increased the SQI of mine tailing because they increased pH, WSA, humin C and $CaCl_2$-extractable Ca concentrations. In addition, the recently amended site (M3w) increased the concentration of $CaCl_2$-extractable Zn, C_{FA}, C_{HA}, TN and C_{mic}.

17.3.3 Comparison of Reclamation Treatment Effects Between Both Mine Zones

The application of waste amendments to mine soils was the treatment that most increased the SQI in both the settling pond and the mine tailing, although its effect was different in each zone. The soil characteristics that contributed the most to increasing the SQI after waste amending were pH, CECe, $CaCl_2$-extractable K, Ca and Zn, clay, MWD, WSA, all chemical forms of organic C, total N and C_{mic}. However, all these variables were not selected for the SQI of both mine zones. The variables CECe, $CaCl_2$-extractable K, clay and MWD were only selected for the SQI of settling pond soils. On the other hand, WSA, $CaCl_2$-extractable Ca and C_{mic} were only selected for mine tailing soils. This is because the variables that were only selected for the settling pond SQI increased their values after waste amendments more at this mine zone than at the mine tailing. At the same time, those selected only for the mine tailing increased their values more in this mine zone. The high concentration of pseudototal Pb decreased the SQI in the amended settling pond site and the pseudototal Zn in the amended mine tailing. This indicates that the wastes used must be analysed prior to being added to soils. The differences in the

soil characteristics of the amended sites (B4Aw and M3w) are due to the heterogeneity caused by different production times of the used wastes.

Planting trees also increased the SQI at both mine zones and, like the other reclamation treatment, had a different influence in each zone. The scores of pH and $CaCl_2$-extractable Mn at the vegetated sites contributed towards increasing the SQI in both mine zones. Humin C concentration of the vegetated sites, although it was selected for both SQI, only contributed to increase the index in the mine tailing. The MWD was only selected for the settling pond SQI because its value increased more at the vegetated site in this mine zone, while WSA and $CaCl_2$-extractable Ca were selected in the vegetated mine tailing site.

17.4   Conclusions

In order to assess the quality of any type of soil, a soil quality index (SQI) created by totalling the scores of the minimum data set (MDS) selected through a principal component analysis (PCA) proved to be a valid and useful tool. This index was tested in a settling pond and a mine tailing soil reclaimed by planting trees and amending with sewage sludges and paper mill residues. Our results revealed that the quality of these reclaimed soils should be determined by analysing both physical and chemical characteristics. In the case of settling pond sites, stoniness, pH, Al^{3+}, CECe, MWD, SOC, humin C, C_{HA}, C_{FA}, TN, clay, K $CaCl_2$ (extracted with $CaCl_2$), Mn $CaCl_2$, Ni $CaCl_2$, Zn $CaCl_2$ and pseudototal both Ni and Pb should be analysed . In the case of mine tailing sites, it is necessary to analyse stoniness, pH, BD, WSA, humin C, C_{HA}, C_{FA}, TN, C_{mic}, Ca $CaCl_2$, Mn $CaCl_2$, Zn $CaCl_2$ and pseudototal both Pb and Zn. The establishment of this set of key parameters for assessing the quality of reclaimed mine soils will help to save time and money by analysing a large number of soil characteristics.

In applying the proposed SQIs, we observed that the untreated mine sites had a very low quality and that the treated sites had a significantly higher index. The reclamation treatment that most increased the SQI of the mine soils was the recent addition of wastes. However, we recommend the regular addition of sewage sludges and paper mill residues to degraded sites because their favourable effect on soils decreases over time.

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