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Linking heavy metal bioavailability (Cd, Cu, Zn and Pb) in Scots pine needles to soil properties in reclaimed mine areas



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HIGHLIGHTS

- Bioaccumulation of Cd, Cu, Zn, Pb by the pine needles on mine soils was studied.
- Element content of needles is good criterion in the assessment of threats for new ecosystem.
- Correlation of soil microbial activity and needle elements concentration was observed.
- There is no risk of critical levels of trace element in studied reclaimed areas.

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ABSTRACT

This work deals with bioaccumulation of Zn, Pb, Cu and Cd in foliage of Scots pine, grown on mine soils. Regression models were used to describe relationships between pine elements bioavailability and biological (dehydrogenase activity) and physico-chemical properties of mine soils developed at different parental rocks. Concentration of trace elements in post-mine ecosystems did not differ from data for Scots pine on natural sites. We conclude that, in this part of Europe in afforested areas affected by hard coal, sand, lignite and sulphur mining, there is no risk of trace element concentrations in mine soils. An exception was in the case of Cd in soils on sand quarry and hard coal spoil heap located in the Upper Silesia region, which was more due to industrial pressure and pollutant deposition than the original Cd concentration in parental rocks.

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1. Introduction

Post-mining facilities such as open pit quarries, lignite mine spoil heaps, open pit sulphur mine spoil, and hard coal spoil heaps are the consequences of fossil fuels and mineral extraction and are examples of large scale land transformation. Although land area directly affected by mining of minerals is relatively small on a global scale, it can represent substantial portions of some countries or regions. In addition, the influence of mining is increasing, and in comparison to any landscape disturbances its intensity is substantial (Hüttl and Weber, 2001). In Poland, about 61,000 ha have been degraded and disturbed

as of 2012, and approximately 25,000 ha post-mine sites were reclaimed (Dmochowska and Witkowski, 2012).

From an ecological point of view, reclamation is a process of restoring the ecosystem (Hüttl and Bradshaw, 2000; Hüttl and Weber, 2001; Pietrzykowski and Krzaklewski, 2007). Mine-site rehabilitation is presented as an ideal case study for developing an ecosystem starting from point zero on “terra nova” (Hüttl and Weber, 2001). The ecosystem is a basic ecological unit (Golley, 1993) constituting an integrated system of biotic and abiotic elements in which all structure levels contain a set of species ensuring circulation of matter and energy flow. Soil is one of the basic elements of all terrestrial ecosystems and provides links in the biogeochemical cycles in emerging ecological systems (Bradshaw, 1983; Schaaf, 2001). In addition to the macro-elements such as C, N, P, K, Ca, Mg, and S, trace elements are also involved in the biogeochemical cycles and often have toxic interactions (Kabata-Pendias and Pendias, 1992; Allen et al., 1995). Coal and mineral mine spoils and post-mining facilities are comprised of various

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materials belonging to different geological formations (Quaternary, Neogene and Carboniferous deposits and mixture of substrates) and are one type of metal-rich industrial solid waste (Jeng and Bergseth, 1992; Dang et al., 2002). Through mining, large quantities of this kind of waste have been excavated from underground to the surface of the earth. Natural weathering conditions may cause these exposed mine spoils to be broken down into small clay-sized particles and released in to the environment (Haigh, 1992; Dang et al., 2002). Reclaimed mine soils (RMS) developed on these deposits contain different levels of trace elements and contaminants and can be toxic to living organisms (Massey and Barnhisel, 1972; Allen et al., 1995; Dang et al., 2002). Therefore, it is important to monitor the processes of metals released to the environment and their bioavailability during the development of new ecosystems on post-mine sites.

Almost every risk assessment procedure for contaminated soils includes a preliminary evaluation of risks based on the total concentration of contaminants. These concentrations can be compared with soil quality values, from dose–response relationships to the likelihood of harm (Weeks and Comber, 2005; Harmsen, 2007; Pereira et al., 2006). However, the total concentration of a contaminant present in soil is not always related to its availability for uptake by organisms and biological effects (Alexander, 2000; Ehlers and Luthy, 2003; Alvarenga et al., 2009).

Taking that into account, bioavailability is increasingly being used as a key indicator of potential risk that contaminants pose to both environmental and human health (Adriano et al., 2004). However, the concept of bioavailability is not easily defined and it should be described in relation to the assessment of soil functions to be monitored (Alexander, 2000; Ehlers and Luthy, 2003; Adriano et al., 2004; Alvarenga et al., 2012). The concentration-based bioavailability, assessed by chemical methods, is of primary importance from an experimental point of view, but chemical data alone are not sufficient to evaluate the toxic effects of the contaminants and characterize potentially contaminated environments because they do not take into consideration the interactions between contaminants, the matrix and biota (Leitgib et al., 2007; Pereira et al., 2006). To assess the bioavailability of contaminants it is important to monitor plant growth (e.g. *Avena sativa* L., *Brassica ropa* L.), seed germination, earthworm mortality, soil enzymatic activities or conduct bacteria bioassays (Fuentes et al., 2004; Alvarenga et al., 2009). Monitoring the state of the environment through the performance of living organisms (i.e., bioindicators) can be used to measure the cumulative impact of different types of environmental pressure, e.g. air pollution emitted from a range of emission sources, soil and water contamination.

Chemical analyses of Scots pine (*Pinus sylvestris*) needles have been widely used in studies of bioindicators (Dmuchowski and Bytnerowicz 1995; Rautio et al., 1998). This tree species is widely distributed in Europe and Asia (Białobok, 1976) and is commonly used for afforestation of post-mining barrens in central Europe. It has low nutritional requirements and is able to survive on acidic and dry soils and is able to grow on reclaimed mine soil (Baumann et al., 2006; Kuznetsova et al., 2010).

Scots pine is particularly sensitivity to the effects of industrial pollution, making it a good candidate for the role of bioindicator and an excellent model for studying microevolution processes occurring under the influence of anthropogenic pressure (Kurczyńska et al., 1997; Schulz et al., 1999; Rautio, 2003; Saarelaa et al., 2005; Pöykiö et al., 2010). In particular, its needles have proven to be suitable indicators of the deposits of pollutants, including sulphur compound element concentration and metal pollution (Rautio et al., 1998; Kozlov et al., 2000; Lampu and Huttunen, 2003; Pöykiö et al., 2010) and are widely used for biomonitoring purposes in areas around point sources. Authorities have accepted them as a bioindicator (Pöykiö et al., 2010).

The aim of the study is to determine the bioavailability and risk levels of trace elements (Zn, Cu, Cd, Pb) in reclaimed mine soils (RMS).

Bioavailability of elements was measured by concentration in pine needles with interactions of the total concentration in reclaimed mine soils and their physicochemical (particle size distribution, pH, organic matter content, sorption complex) and biological properties. Specifically, we pursued the following objectives.

i – To compare post-mining soil substrates in terms of the total concentration of the trace elements (Zn, Cu, Cd, Pb); ii – to compare the concentration of trace elements in current-year needles with previous-year pine of Scots (*P. sylvestris* L.); iii – to test the correlation between the concentration of trace elements in pine foliage and microbial activity of RMS to assess the utility of Scots pine as a bioindicator species; and iv – to test the correlation between trace elements in foliage and soil properties to indicate influence of these parameters on bioavailability of trace elements to pine in new ecosystem on reclaimed post-mine sites.

2. Material and methods

2.1. Experimental and study sites

This research was conducted in monoculture Scots pine (*P. sylvestris* L.) stands (ranging from 15 to 30 years of age) on four reclaimed post-mining sites in Poland: (1) an external spoil heap following open cast lignite mining at KWB Bełchatów (Bel); (2) a spoil heap at the Smolnica hard coal mine (Smol); (3) a sand quarry at the Szczakowa mine (Szcz); and (4) an external spoil heap at the Piaseczno sulphur mine (Pias) (Fig. 1). A total of 28 sample plots (10 × 10 m) were established in pine stands with 4 replications on 7 different substrate variants: a mixture of Quaternary loamy and gravelly sands which occasionally contains loam, bouldery clay and clay (QLSS); Neogene sandy strata with inclusion of loam and clay, which contain carbonates and sulphides (NS); mudstones, sandstones and carbonaceous shales (CF); Quaternary sands with loam (QLS) and poor Quaternary sands (QS1; mixture of Quaternary sands and Neogene clays (QSNC) and Quaternary sands (QS2)).

The spoil heap Bełchatów (Bel) is located in central Poland (N 51 13.196; E 19 25.569) (Fig. 1). Climate in the area is transitional and changeable due to frequent interactions between polar maritime and continental air masses. The average annual temperature is 7.6 °C and total precipitation is 580 mm. The external spoil heap ranges in height from 120 to 180 m and covers an area of 1480 ha. The heap is built mostly from a mixture of Quaternary loamy and gravelly sands which occasionally contains loam, bouldery clay and clay. There are also areas of Neogene sandy strata with inclusions of loam and clay, which commonly contain carbonates and sulphides in varying amounts. These sands oxidize to be extremely acidic (pH < 4.5), frequently displaying phytotoxic properties (Katur and Haubold-Rosar, 1996). The initial reclamation treatment on the flat summit of the external spoil heap consisted of N–P–K fertilization (N–60, P–70 and K–60 kg · ha⁻¹), and sowing a mixture of grasses and leguminous plants (60 kg · ha⁻¹). The Neogene pyritic strata were neutralized earlier with bog lime incorporated into the surface horizon to a depth of 40 cm.

The Smolnica spoil heap (Smol) is located in Southern Poland's Upper Silesia region (N 50 15.095 E 18 31.284) (Fig. 1). The average annual temperature is 7.7 °C; the annual range is 21 °C; the length of the growing period is 220 days and the average precipitation is 702 mm per year. The site consists of a 60 ha⁻¹ spoil heap, with a flat hilltop and gradual slopes. In these carboniferous dumps, primarily waste rocks from coal processing and cleaning are disposed of, i.e. mostly carboniferous shales and claystones (85–95%) with an addition of mudstones and sandstones (5–15%). From the reclamation point of view, the high proportion of large rock fragments (>20 cm) is important since it negatively affects reclamation success. However, some of the rocks are susceptible to weathering (e.g. some shales) and slate quickly, providing a clayey/silty mine soil of good potential productivity.

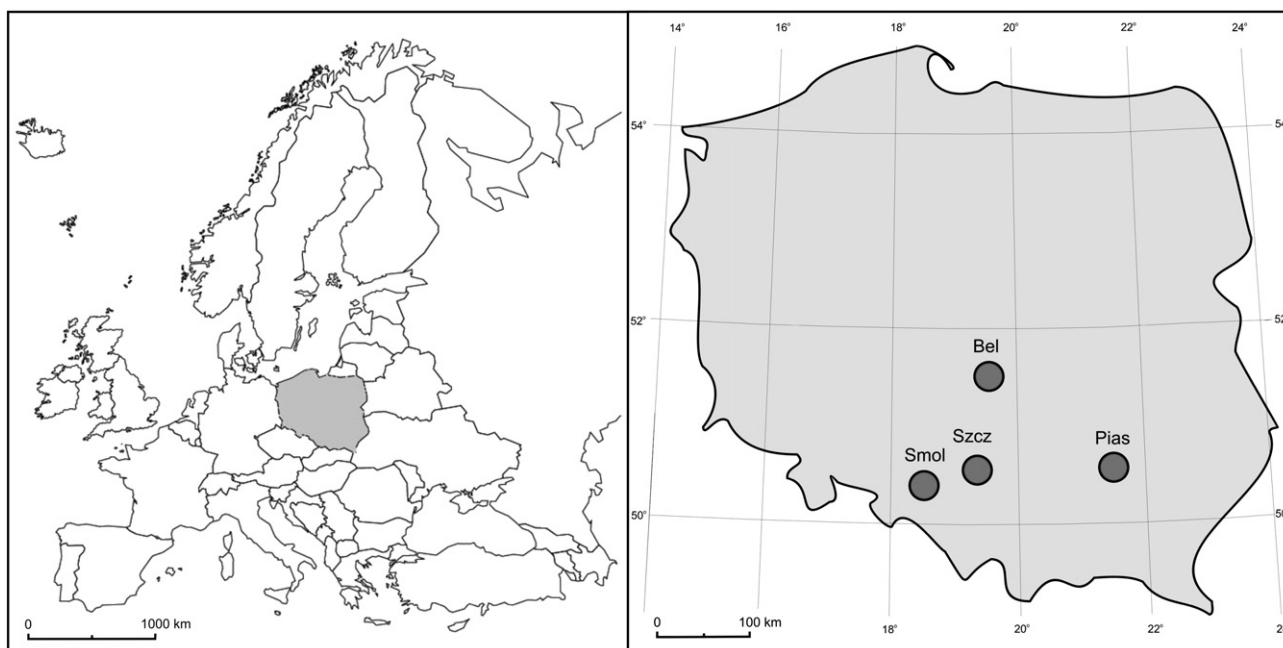


Fig. 1. Location of investigated post-mining sites.

Generally, low content of Ca, P and N and relatively high content of Na, Mg, K and sulphidic materials are characteristic of these spoils. The remaining areas were not fertilized and Scots pine invaded on the spoil heap via primary succession.

The Szczakowa sand mine quarry (Szcz) is also located in the Upper Silesia region (N 50 14.394 E 19 25.140) (Fig. 1). In this region average annual air temperature is 8 °C and the precipitation averages 700 mm per year. A disturbed area of over 2700 ha⁻¹ with an excavated depth of 5 to 25 m resulted from open strip mining. The study sites were located on Quaternary sands with loam and poor Quaternary sands. The reclamation treatments included re-grading the surface and adding organic amendments (approx. 300 m³ ha⁻¹). The organic amendment used was a mixture of local forest litter and mineral A horizons with an average organic C content of 0.3 to 1.0%, selectively collected from the overlying forest soils before mining. Subsequent treatments included a 2-year cycle of N–P–K fertilization (total amount of N–140, P–130 and K–150 kg·ha⁻¹), a 2-year cycle of lupine (*Lupinus luteus* L.) cultivation followed by incorporating the lupine as green manure. Next, the sites were reforested using mainly Scots pine along with Silver birch.

The external spoil heap at the Piaseczno (Pias) open cast sulphur mine is located in Southern Poland, not far from the Wisła River (N 50 33.622 E 21 34.185) (Fig. 1). In this region average annual air temperature is 7.0 °C and average precipitation is 650 mm per year. The site is conical in shape with an area of 120 ha⁻¹ and a height of up to 40 m. The spoil heap mainly consists of Neogene Krakowiec formation clays, mudstone horizons, loose Quaternary sands and Quaternary loamy sands. During revegetation, as the spoil heap gradually stabilized, the mine soils were sown to agronomic crops such as *Papilionaceae* sp. and grasses (e.g. *Lolium* sp.) and mineral fertilization occurred twice (at initiation and then topdressing) with a total application of N–80, P–50, K–60 kg·ha⁻¹. In the most difficult areas where vegetation failures occurred, *Melilotus albus* L. and alfalfa (*Medicago sativa* L.) were sown again. Different tree species were introduced depending on their functional adaptations and macrohabitat conditions. Species such as Pedunculate oak (*Quercus robur* L.) and Sessile oak, (*Quercus petraea* (Mattuschka) Liebl.), Scots pine (with established research plots), and Silver birch (*Betula pendula* L.) were planted on the flatter hilltops.

There is no doubt a very important factor that must be taken into account in the analysis of environmental pollution with heavy metals is the pressure of industrial pollution, especially on new ecosystems developed on post-mine sites. The areas, in which the study sites are located, are characterized by different levels of industrial pollution trace element deposits. The highest degree of industrial pressure is in the Upper Silesia region, where Szczakowa (Szcz) sand quarry and Smolnica (Smol) spoil heap are located. Towards the end of the 1970s and in the 1980s dust fallout in these area exceeded 200 g·m⁻²·yr⁻¹. Average annual SO₂ concentration in this period reached 68 µg·m⁻³. At the beginning of the 1990s there was a marked fall in the magnitude of industrial emissions. Although there was a nearly twofold decrease in the dust fallout, it still exceeded 100 g·m⁻²·yr⁻¹. Only from mid-1990s to 2001 was a gradual decrease in industrial emission reported, with dust fallout falling to approx. 25 g·m⁻²·yr⁻¹. There was also a marked downward trend in heavy metal deposition. Still at the beginning of the 1990s the emission of lead (Pb) increased from 0.044 to 0.125 g·m⁻²·yr⁻¹, zinc (Zn) from 0.212 to 7.089 g·m⁻²·yr⁻¹, and cadmium (Cd) from 0.0026 to 0.0039 g·m⁻²·yr⁻¹. In the mid-1990s deposition of heavy metals significantly decreased and in 2001, in the case of lead, it was slightly above 0.01 g·m⁻²·yr⁻¹, zinc was slightly above 0.10 g·m⁻²·yr⁻¹, and cadmium was below 0.0007 g·m⁻²·yr⁻¹ (Pietrzykowski and Krzaklewski, 2010).

2.2. Soil sampling and analyses

Soil pedons were sampled and analysed, from 28 pits at each of the sample plots to a depth of 110 cm. Additionally, 5 samples were collected from each plot by soil auger (Eijkelkamp set) on a grid. Pits and boreholes were sampled at depths of 0–8 cm (AC organic-mineral horizons exhibiting some features of parent material), 8–110 cm (C–parent materials/rocky spoils). Samples of organic horizons (Olf) (annotated with FAO syntax where l = leaf; f = fermentation/fragmentation layers) were collected after litterfall from 1 × 1 m quadrats with 3 replications for each 100 m². Next, 4 mixed samples for each soil-substrate variants were collected for laboratory testing. The soil samples from AC and C horizons were divided into two parts. One part (from AC horizon) was immediately sieved (2 mm mesh size) and stored field-moist at 4 °C for microbial measurements, the other part was air-dried,

sieved (2 mm mesh size), finely ground and used for chemical analyses. Physicochemical soil analyses were conducted using the procedures of Ostrowska et al. (1991) and Van Reeuwijk (2002). Particle size distribution was determined by hydrometer and sand fractions by sieving. Soil pH was determined in a 1:2.5 1 M KCl solution. Soil organic carbon (C_{org}) and total nitrogen (N_t) were measured with a 'Leco CNS 2000'. Samples containing $CaCO_3$ were washed in 10% HCl to remove carbonates prior to the determination of C_{org} .

To measure exchangeable acidity (Hh) the samples (40 g) were treated with 1 M $Ca(CH_3COO)_2$ using 1:2.5 soil/solution ratio. Suspensions were shaken for 1 h, filtered and titrated with 0.1 M NaOH to pH = 8.2. The exchangeable acidity was calculated from the amount of base used and expressed in $cmol_{(+)}\cdot kg^{-1}$ (Ostrowska et al., 1991). Total Exchangeable Bases (TEB) were calculated as a sum of base cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) extracted in 1 M CH_3COONH_4 (pH = 7). The concentrations of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in the extracts were measured using atomic absorption spectrometry by a Thermo Scientific iCE 3000 Series AA Spectrometer. Cation exchange capacity (CEC) was defined as the equivalent sum of TEB and exchangeable acidity, and the base saturation (BS) as the sum of base cations as a percentage of CEC.

Dehydrogenase activity (DHG) in the soils was determined following the method of Casida et al. (1964) by reduction of 2,3,5-triphenyltetrazolium chloride (TTC). The soil samples (5 g) were amended with 3 ml of 0.2 M $CaCO_3$ and 1 ml of 3% TTC and incubated for 24 h at 37 °C (Casida et al., 1964). The triphenyl formazan (TPF) formed was extracted from the reaction mixture with methanol and assayed colorimetrically at 485 nm with VARIAN, Inc., Cary 300 UV-Vis Spectrophotometers.

2.3. Foliage sample collection and analyses

At each of the twenty eight plots (10 × 10 m), Scots pine branches were sampled and collected during the fall of 2009 from treetops (facing SW) of five healthy-looking (no dead branches or chlorotic/necrotic symptoms). The trees were representative of the trees throughout the plot, i.e. no needle damage or dead branches were evident in the other trees in the plots. The stems collected from the five sample trees per plots were stored in plastic bags in a cold room (4–6 °C) until element analysis. Before the analysis for each of the sampling points, a composite sample was prepared by mixing identical amounts (300 pairs of needles for each research plot) for current-year (2009) needles (hereafter referred to as C needles) and previous-year (2008) needles (C + 1 needles). The samples were then washed in distilled water for about 1 min to remove material deposits on needle surface so that the results of chemical analysis of samples collected in various locations could be compared. After washing, needles were dried for 24 h at 60 °C, ground to a fine powder and stored in plastic vials until chemical analysis.

Total content of Zn, Cu, Cd, and Pb in needles was determined by digestion in a mixture of HNO_3 ($d = 1.40$) and 60% $HClO_4$ acid in a 4:1 ratio (standard procedure described in Ostrowska et al. (1991)); element levels were determined by atomic absorption spectroscopy by a Thermo Scientific iCE 3000 Series AA Spectrometer.

2.4. Statistical analyses

A Kruskal–Wallis nonparametric ANOVA test with multiple comparison procedure (at $p = 0.05$ level) was used to test the differences between mean values of trace element concentration in soil-substrates for current-year (2009) needles (C needles) and previous-year (2008) needles (C + 1 needles).

The relationships between the trace element concentration in pine needles and in the soils (organic horizon Olf and mineral layers 0–8 and 8–50 cm deep) were described using Pearson's correlation matrix. The multiple forward stepwise regression method was used to analyse

the relationship between concentration of individual trace elements (Zn, Cu, Cd and Pb) in pine needles and soil biological activity (DHG) and basic mine soil characteristics (texture, pH, %BS, CEC, TEB, C_{org} content and $C_{org}-N_t$ ratio). The significance of individual independent variables in multiple regression equations was tested using the t test at a significance level of $\alpha = 0.05$. Before including the independent variable in the model its redundancy was estimated by calculating the variance inflation factor (VIF, Eq. (1)) (Fox, 1991).

$$VIF_j = 1/1 - R_j^2 \quad (1)$$

where R_j^2 is the adjusted coefficient of determination between the independent variable j and other independent variables. The accuracy of the developed regression models was analysed using the adjusted coefficient of determination (R_{adj}^2) and the root mean square error (RMSE). Homoscedasticity and the distribution of residual values against values predicted according to the regression models were both analysed graphically and tested using the White test (1980). Assumption of homoscedasticity means that the variance around the regression line does not vary with the effects being modelled. In the case of the absence of homoscedasticity, logarithmic and square root data transformations were used.

Statistical analyses of the results were done using the STATISTICA (StatSoft, 2008).

3. Results

3.1. Soil texture

The mine soils on Smolnica heap (Smol) that developed on carboniferous rocks (CF) had not only a relatively high content of silt (34%) and clay (23%) but also a high percentage ($\geq 70\%$) of rock fragments (>2 mm) derived from sandstone and shale. The soils at the sand quarry Szczakowa (Szc) site (QLS and QS1) on fluvioglacial sands and loamy sands contained 3–10% silt and 1%–5% clay particles (Table 1). Soil developed on quaternary sands (QS2) and sands with admixture of Neogene clays (QSN) at the sulphur mine heap Piaseczno (Pias) contained 3–9% silt and 3–8% clay. Similar clay contents were found also on Bełchatów (Bel) spoil heap in the NS and QLSS soils. However, QLSS soils contained higher amounts of silt particles (up to 28%) (Table 1). The highest content of clay (23%) and silt (34%) fraction was measured in Smolnica CF soil and the lowest (1 and 3% respectively) in Szczakowa QS1 soil (Table 1).

3.2. Chemical and microbial properties of the soils

The highest C_{org} (166.1 $g\cdot kg^{-1}$) and N_t (4.04 $g\cdot kg^{-1}$) contents and the widest C_{org} -to- N_t ratio (41.2) were measured in the Smol soils on CF substrate. In the remaining soils the contents of C_{org} and N_t were much lower and varied from 2.3 to 13.2 $g\cdot kg^{-1}$ and from 0.15 to 0.86 $g\cdot kg^{-1}$, respectively (Table 1). The cation exchange capacity (CEC) was the highest in the Bel mine spoil heap on QLSS substrate (27.7 $cmol_{(+)}\cdot kg^{-1}$) and the Smol spoil heap on CF substrate (21.3 $cmol_{(+)}\cdot kg^{-1}$) (Table 1). The base saturation (%BS) was the highest in the Bel QLSS soils (98.1%) and the lowest on Szc QS1 soils (49.6%). The Smol CF soils had the lowest pH (3.6) and contained significantly more exchangeable acidity Hh (10.7 $cmol_{(+)}\cdot kg^{-1}$) and less TEB (10.6 $cmol_{(+)}\cdot kg^{-1}$) than the Bel QLSS soils (27.2 $cmol_{(+)}\cdot kg^{-1}$) (Table 1).

The soils at the Pias site on QS2 substrate exhibited the highest DHG activity (18.6 $mg\cdot TPF\cdot 100\ g^{-1}\ soil\cdot 24\ h^{-1}$) whereas the lowest activity of this enzyme was measured in the Szc QS1 (0.2 $mg\cdot TPF\cdot 100\ g^{-1}\ soil\cdot 24\ h^{-1}$) (Table 1).

Table 1
Reclaimed mine soil (RMS) physicochemical and microbial characteristics.

Plot (facility and post-mine sites)		Bel ^a		Pias		Szcz		Smol
Substrate (parent rock material)	Horizon and depth (cm)	QLSS	NS	QS2	QSNC	QLS	QS1	CF
<i>Textures</i>								
% coarse fragments >2.0-mm diam.	AC ^b (0–8) and C ^c (8–110)	0 (0 ± 0)	0 (0 ± 0)	5 (0 ± 10)	0 (0 ± 0)	0 (0 ± 0)	0 (0 ± 0)	70 (70 ± 70)
% sand (2–0.05 mm)		68 (56 ± 82)	84 (71 ± 92)	90 (86 ± 93)	88 (80 ± 93)	85 (75 ± 92)	96 (95 ± 97)	44 (40 ± 47)
% silt (0.05–0.002 mm)		28 (15 ± 39)	12 (4 ± 24)	3 (2 ± 4)	9 (4 ± 16)	10 (5 ± 18)	3 (2 ± 4)	34 (32 ± 36)
% clay (<0.002 mm)		4 (1 ± 7)	5 (2 ± 7)	3 (2 ± 5)	8 (4 ± 10)	5 (3 ± 6)	1 (1 ± 2)	23 (21 ± 26)
<i>Chemical parameters</i>								
C _{org} ^d g·kg ⁻¹	AC (0–8)	6.1 (3.4 ± 8.6)	2.7 (2.3 ± 3.3)	4.8 (4.2 ± 5.2)	13.2 (10.6 ± 15.1)	4.6 (3.2 ± 5.9)	2.3 (1.5 ± 4.1)	166.1 (153.9 ± 182.0)
N _t ^e g·kg ⁻¹		0.53 (0.49 ± 0.55)	0.15 (0.12 ± 0.17)	0.35 (0.30 ± 0.42)	0.86 (0.74 ± 0.98)	0.40 (0.33 ± 0.46)	0.30 (0.23 ± 0.43)	4.04 (3.71 ± 4.59)
C _{org} -to-N _t ratio		11.6 (6.3 ± 16.9)	18.8 (17.5 ± 19.4)	13.8 (12.4 ± 16.1)	15.5 (13.7 ± 18.9)	11.2 (9.8 ± 13.2)	7.3 (6.0 ± 9.5)	41.2 (39.7 ± 42.7)
pH _{KCl} (1:2.5)	AC (0–8) and C (8–110)	7.5 (7.2 ± 7.8)	4.7 (2.7 ± 7.4)	5.4 (4.0 ± 7.2)	6.4 (4.0 ± 7.6)	4.6 (4.1 ± 5.2)	6.2 (4.1 ± 8.0)	3.6 (2.8 ± 5.8)
TEB ^f cmol ₍₊₎ ·kg ⁻¹		27.2 (22.7 ± 33.3)	3.3 (1.8 ± 5.3)	2.7 (1.2 ± 5.4)	10.2 (4.7 ± 22.1)	2.1 (1.4 ± 3.1)	1.3 (0.4 ± 2.5)	10.6 (3.9 ± 18.9)
CEC ^g cmol ₍₊₎ ·kg ⁻¹		27.7 (23.2 ± 33.9)	5.5 (3.7 ± 8.2)	3.7 (2.2 ± 6.3)	11.8 (6.2 ± 22.8)	3.1 (2.2 ± 4.4)	2.2 (1.2 ± 3.7)	21.3 (13.3 ± 31.8)
Hh ^h cmol ₍₊₎ ·kg ⁻¹		0.5 (0.4 ± 0.6)	2.2 (0.8 ± 4.8)	1.0 (0.8 ± 1.4)	1.6 (0.7 ± 2.4)	1.0 (0.5 ± 2.0)	0.9 (0.6 ± 1.5)	10.7 (6.1 ± 16.7)
%BS ⁱ		98.1 (97.8 ± 98.5)	61.0 (29.9 ± 81.9)	68.0 (55 ± 84.5)	83.4 (73.5 ± 96.8)	66.7 (46.7 ± 83.2)	49.6 (26.5 ± 66.2)	47.0 (25.5 ± 68.6)
<i>Microbial parameters</i>								
DHG ^j (mg·TPF · 100 g ⁻¹ soil · 24 h ⁻¹)	0–8 (AC)	4.0 (2.9 ± 5.3)	1.5 (1.0 ± 2.0)	18.6 (12.0 ± 26.9)	4.6 (3.4 ± 6.0)	1.4 (0.9 ± 1.9)	0.2 (0.1 ± 0.3)	1.0 (0.7 ± 1.2)

See Section 2.1 for details on post-mine sites and soil-substrate abbreviations. Sample size is 4 for each site variant. Values represent mean and range (in parentheses).

^a Bel—Bełchatów spoil heap.

^b AC—organic–mineral horizons exhibiting some features of parent material at 0–8 cm deep.

^c C—parent materials/rocky spoils at 8–110 cm layers.

^d C_{org}—Soil organic carbon.

^e N_t—total nitrogen.

^f TEB—Total Exchangeable Bases (Ca²⁺, Mg²⁺, K⁺, Na⁺).

^g CEC—Cation Exchangeable Capacity.

^h Hh—exchangeable acidity.

ⁱ %BS—base saturation.

^j DHG—Dehydrogenase activity in AC horizon (0–8 cm).

Table 2
Trace element (Zn, Cu, Pb and Cd) concentrations in reclaimed mine soil (RMS) at different horizon and depth of profile.

Elements mg·kg ⁻¹	Depth (cm) and horizon	Soil-substrate (parent rock material)							
		QLSS ^a	NS	QS2	QSNc	QLS	QS1	CF	
Zn	Olf	59.60 (54.80 ± 61.20) ^{ab}	49.60 (39.30 ± 96.80) ^a	63.50 (44.00 ± 77.00) ^{ab}	65.00 (57.00 ± 82.00) ^{ab}	205.50 (160.00 ± 283.00) ^{ab}	217.50 (207.00 ± 229.00) ^b	142.50 (126.00 ± 201.00) ^{ab}	
	0–8 (AC)	20.28 (17.45 ± 21.65) ^{ab}	9.48 (6.50 ± 10.90) ^a	14.00 (9.00 ± 17.00) ^a	28.00 (22.00 ± 33.00) ^{ab}	35.50 (26.00 ± 70.00) ^{ab}	70.00 (19.00 ± 184.00) ^{ab}	80.00 (72.00 ± 99.00) ^b	
	8–110 (C)	19.05 (16.73 ± 20.68) ^{ab}	9.05 (8.27 ± 10.35) ^a	8.50 (7.00 ± 11.00) ^a	17.50 (11.50 ± 24.50) ^{ab}	16.00 (15.50 ± 32.00) ^{ab}	9.00 (8.00 ± 10.00) ^a	80.25 (57.50 ± 100.00) ^b	
Cu	Olf	6.80 (5.75 ± 7.55) ^a	5.13 (4.60 ± 5.40) ^a	10.05 (6.20 ± 16.40) ^{ab}	11.60 (8.00 ± 12.20) ^{ab}	9.90 (8.30 ± 11.20) ^{ab}	11.40 (10.70 ± 13.10) ^{ab}	18.05 (16.00 ± 21.40) ^b	
	0–8 (AC)	7.45 (4.50 ± 9.25) ^{ab}	4.63 (2.40 ± 7.10) ^{ab}	1.50 (0.00 ± 2.00) ^a	7.0 (4.00 ± 23.00) ^{ab}	4.00 (2.00 ± 19.00) ^{ab}	1.50 (1.00 ± 4.00) ^a	39.50 (38.00 ± 41.00) ^b	
	8–110 (C)	6.44 (4.98 ± 8.90) ^{ab}	4.40 (3.83 ± 11.40) ^{ab}	1.00 (1.00 ± 17.00) ^a	4.00 (2.00 ± 9.00) ^{ab}	3.25 (3.00 ± 3.50) ^{ab}	1.25 (1.00 ± 2.00) ^a	50.25 (45.00 ± 51.50) ^b	
Pb	Olf	9.40 (8.70 ± 10.75) ^a	7.28 (6.35 ± 10.45) ^a	21.05 (18.70 ± 24.10) ^{ab}	18.05 (13.50 ± 21.50) ^{ab}	79.95 (69.60 ± 101.10) ^b	90.85 (69.20 ± 107.40) ^b	39.90 (25.80 ± 44.60) ^{ab}	
	0–8 (AC)	5.30 (4.60 ± 11.50) ^{ab}	4.83 (0.00 ± 5.55) ^a	5.40 (3.90 ± 7.30) ^a	7.23 (6.10 ± 8.30) ^{ab}	15.50 (10.50 ± 33.30) ^{ab}	24.05 (9.80 ± 61.40) ^{ab}	61.50 (47.90 ± 99.30) ^b	
	8–110 (C)	5.95 (4.78 ± 8.50) ^{ab}	2.29 (0.00 ± 5.33) ^a	1.15 (0.15 ± 1.60) ^a	3.73 (2.58 ± 7.25) ^{ab}	6.23 (5.20 ± 6.80) ^{ab}	5.98 (3.05 ± 6.35) ^{ab}	50.73 (29.05 ± 81.90) ^b	
Cd	Olf	0.35 (0.20 ± 0.55) ^a	0.78 (0.65 ± 1.00) ^{ab}	0.95 (0.60 ± 1.00) ^{ab}	0.75 (0.50 ± 1.00) ^{ab}	2.90 (2.50 ± 4.00) ^b	2.90 (2.60 ± 3.10) ^b	1.65 (1.10 ± 1.70) ^{ab}	
	0–8 (AC)	0.20 (0.05 ± 0.35) ^a	0.05 (0.00 ± 0.10) ^a	0.53 (0.20 ± 0.55) ^a	0.05 (0.00 ± 0.55) ^a	0.38 (0.20 ± 0.60) ^a	0.73 (0.10 ± 2.35) ^a	0.00 (0.00 ± 0.05) ^a	
	8–110 (C)	0.15 (0.13 ± 0.20) ^a	0.06 (0.03 ± 0.13) ^a	0.26 (0.08 ± 0.50) ^a	0.28 (0.00 ± 0.38) ^a	0.06 (0.00 ± 0.15) ^a	0.15 (0.03 ± 0.23) ^a	0.00 (0.00 ± 0.20) ^a	

Sample size is 4 for each site variant. Values represent median and range (in parentheses) trace element concentrations. In a given row, values followed by the same letters are not significantly different at $p = 0.05$.

^a See Section 2.1 for details on abbreviation for soil-substrate.

3.3. Trace elements' concentration in soil

The concentration of trace elements in the studied reclaimed mine soils varied considerably between analysed substrates, and in the case of certain post-mine facilities within the analysed sample plots. The analysis showed that the distributions of trace elements are not normal (Shapiro–Wilk test at $p = 0.05$), therefore, the comparison of the mean values of concentration using parametric tests is not appropriate. Thus, the significance of differences was compared using Kruskal–Wallis nonparametric ANOVA test with multiple comparison procedure.

The distribution of trace element concentrations in soil profiles, especially for Zn and Cd, indicates a clear downward trend from the organic layer (Olf) and AC horizon (0–8 cm deep) to the deeper horizon C of the parent rock (8–110 cm deep). The content of zinc (Zn) in Olf was 280.0 mg·kg⁻¹, copper Cu was 21.0, lead (Pb) was greater than 107.4 mg·kg⁻¹, and cadmium (Cd) was up to 4.0 mg·kg⁻¹ and in AC horizon (0–8 cm deep) up to 99.0 mg·kg⁻¹, 41.0 mg·kg⁻¹, 99.3 mg·kg⁻¹ and 2.35 mg·kg⁻¹, respectively (Table 2). In the deeper parent rock horizon C (8–110 cm), the concentration of Zn reached 100 mg·kg⁻¹, Cu was up to 51.5 mg·kg⁻¹, Pb was up to 81.9 mg·kg⁻¹ and Cd was up to 0.5 mg·kg⁻¹. All these cases, with the exception of Cd, were observed in the CF substrates (Table 2).

In almost all cases, exceptional Cu in Olf and Pb in AC horizon, the highest trace element concentrations were observed on sand quarry Szczakowa, which was developed on QLS and QS1 deposits (Table 2). In Szczakowa sandy mine soils it is easier for trace metals to migrate into the soil, which could be seen for example in the case of Zn in QLS, where high concentration (32.0 mg·kg⁻¹) in the C horizon was recorded (Table 2).

Higher concentration of Cu and Pb was observed in parent rock horizon C (8–110 cm deep) than in the organic layer (Olf) in more fertile substrates like QLSS on Bechatów spoil heap and CF on Smolnica spoil heap. These soils are characterized by higher % of clay and silt content, CEC and %BS (Tables 1 and 2). The high concentration of trace elements in the C horizon of RMS on Smolnica spoil heap (CF) is due to its geological origin in carboniferous deposits.

3.4. Trace elements concentration in pine needles

The trace element (Zn, Cu, Pb and Cd) concentrations in the pine needles growing on different soil-substrates in mine sites are presented in Fig. 2. The average Zn concentration in the C-needles ranged from 32.9 to 76.6 mg·kg⁻¹ and in C + 1-needles from 36.7 to 113.5 mg·kg⁻¹. The average Cu concentration ranged from 3.0 to 27.9 mg·kg⁻¹ and 2.2 to 5.5 mg·kg⁻¹; Pb from 0.8 to 3.2 and 2.6 to 10.9 mg·kg⁻¹; and Cd from 0.1 to 1.0 and 0.2 to 1.1 mg·kg⁻¹ (Fig. 2). The average needle Zn, Cu and Pb concentrations were significantly higher (at $p = 0.05$) in older needles (C + 1) than current year needles (C) (Fig. 1a, b, c). In the case of needle Cd concentration, the average value was also higher (however not significantly at $p = 0.05$) in older needles (C + 1-year) than younger (current C) needles, but only in the case of substrate groups QLS, QSNc and QS2 (Fig. 2d). In the case of the rest of the substrates QLSS, NS, CF and QS1, older needles accumulate more cadmium than younger needles (Fig. 2d).

3.5. Relationships of trace elements in pine needles and soil properties

To describe the bioavailability of trace elements the relationships between individual element (Zn, Cu, Cd and Pb) concentrations in pine needles (older needles and current year needles) and mine soil characteristics were considered in two cases: with 1) basic soil characteristics (% of clay and silt sized fractions, pH, BS, CEC, TEB, C_{org} content and C_{org}-N_t ratio) in addition to biological activity (DHG), and 2) trace elements concentrations in soils at different

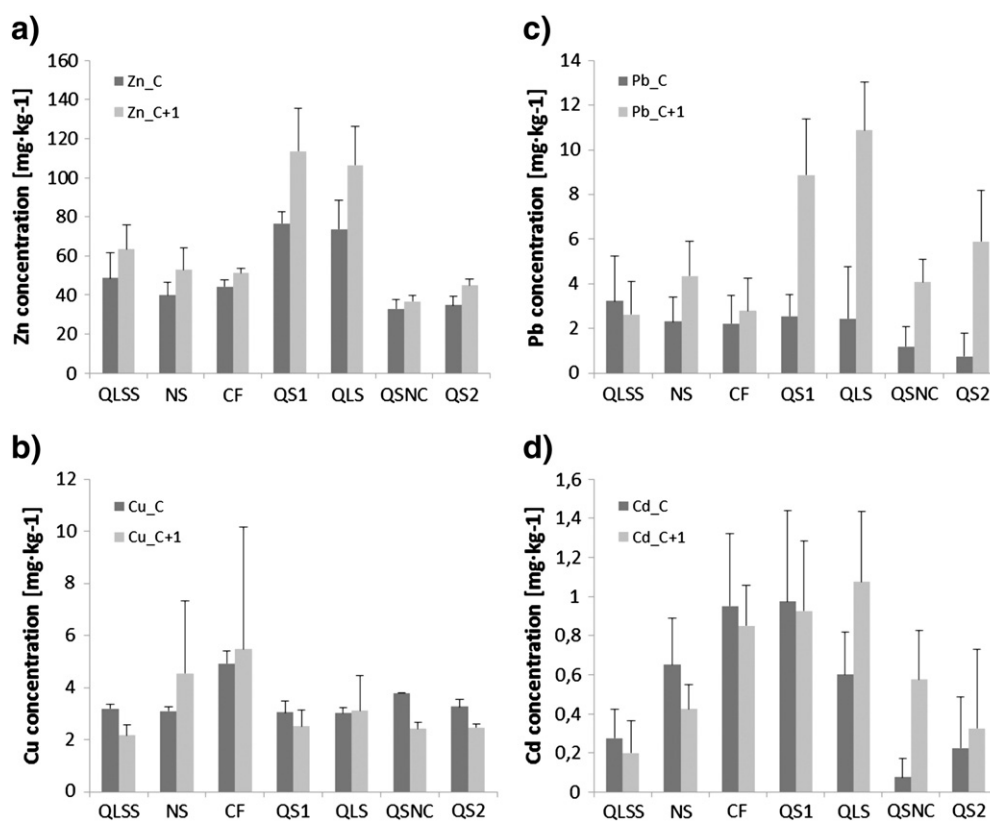


Fig. 2. Trace element concentration (mean + standard deviation) of (a) Zn, (b) Cu, (c) Pb, and (d) Cd in C and C + 1 needles. Sample plots are shown on the x axis.

depths (organic horizon O1f and mineral layers 0–8 and 8–50 cm deep). Therefore, for each element four regression models were developed (two for older needles and two for current needles).

The results indicate that among mine soil characteristics there was a significant correlation between pine needles individual trace element concentration and clay % content, organic carbon (C_{org}) content, pH and soil sorption complex properties (CEC and TEB). The results indicate that Zn concentration in current pine needles (variable Zn_{SoC}) was correlated positively with clay % content in the mineral soil layer (8–110 cm deep) and negatively with dehydrogenase activity (DHG), whereas C_{org} and CEC levels were significant only at $p = 0.10$ probability level. These soil parameters explained close to 40% variance ($R^2_{adj} = 0.399$) (Eq. (2)).

$$Zn_{SoC} = 75.807 - 2.818 \times \% \text{clay} - 1.609 \times \text{DHG}_{0-8} + 3015.287 \times C_{org0-8} - 0.352 \times \text{CEC}_{0-8} \quad (2)$$

Zinc concentration in C + 1 needles (variable Zn_{SoC+1}) was significantly correlated with clay % content in mineral soil layer (8–110 cm deep), dehydrogenase activity (DHG) and pH_{KCl} (8–110) at $p = 0.05$ level and C_{org} at $p = 0.10$ level. Above-mentioned characteristics explain about 45% of Zn_{SoC+1} variability (Eq. (3)).

$$Zn_{SoC+1} = 166.457 - 7.309 \times \% \text{clay}_{8-110} - 2.022 \times \text{DHG}_{0-8} + 5509.288 \times C_{org0-8} - 9.290 \times \text{pH}_{\text{KCl}_{8-110}} \quad (3)$$

Copper concentration in current year needles (variable Cu_{SoC}) was significantly correlated with organic carbon content (C_{org}) and pH_{KCl} in the AC horizon (0–8 cm deep) (explained 84% of the variance; $R^2_{adj} = 0.847$) (Eq. (4)) and in older needles (Cu_{SoC+1}) with pH_{KCl} in

all mineral horizons (0–8 and 8–110 cm deep) (explained 38% of the variance; $R^2_{adj} = 0.386$) (Eq. (5)).

$$Cu_{SoC} = 2.6318 + 147.462 \times C_{org} - 0.0851 \times \text{pH}_{\text{KCl}_{8-110}} \quad (4)$$

$$Cu_{SoC+1} = 5.8981 - 1.5562 \times \text{pH}_{\text{KCl}_{8-110}} - 1.17329 \times \text{pH}_{\text{KCl}_{0-8}} \quad (5)$$

Lead concentration in older needles (Pb_{SoC+1}) was significantly correlated with complex exchangeable capacity (CEC) in the soil mineral layer (8–110 cm deep) (explained variance up to above 60%, $R^2_{adj} = 0.604$) (Eq. (6)):

$$Pb_{SoC+1} = 7.7337 - 0.219024 \times \text{CEC}_{8-110} \quad (6)$$

Cadmium concentration in current year needles (Cd_{SoC}) was significantly correlated with soil dehydrogenase activity (DHG) ($R^2_{adj} = 0.44$) (Eq. (7)).

$$Cd_{SoC} = 0.6716 - 0.0307 \times \text{DHD}_{0-8} \quad (7)$$

In the case of older needles, Cd concentration (Cd_{SoC+1}) is correlated with Total Exchangeable Bases (TEB) and DHG in the AC horizon (0–8 cm) (Eq. (8)). Above-mentioned characteristics explain about % of the variability in Cd_{SoC+1} , however DHG is significant at the $p = 0.10$ level.

$$Cd_{SoC+1} = 0.8536 - 0.017648 \times \text{TEB}_{0-8} - 0.019527 \times \text{DHD}_{0-8} \quad (8)$$

The results of this study indicate that, in measurements of these post-mine ecosystems, there were no significant correlations between trace element concentrations in soil (by depth) and in needles (by age). An exception was the significant relationship between Cu concentration in current year needles and in the mineral soil layers (0–8 and 8–110 cm

deep) ($R = 0.84$ and 0.86). It is very interesting that there is a significant correlation between the concentration of trace elements in pine needles and organic layer (Olf) (Pearson's correlation coefficient R from 0.52 for Cd to 0.75 for Pb) (Table 3). The concentration of trace elements in organic layer is mostly connected with industrial pressure and deposition of pollutants, thus, similar to relationships with biological activity (DHG), it confirms usefulness of pine foliage as a bioindicator for trace element risk assessment and ecological monitoring.

4. Discussion

The toxicity of heavy metals for plants is generally known (Godbold and Hüttermann, 1985; Kabata-Pendias and Pendias, 1992), although the mechanism of toxic interaction itself has not yet been fully explained. Especially in the case of the forest ecosystem it is difficult to explicitly define the role of the respective pollutants in its degradation. It results from the existence of a series of connections and interdependences among the forest ecosystem components, as well as complex activity of emitted contamination constituents. For example, in forest soils, the negative effects of metal pollution on microbial processes stem from more than just one single metal species (Åkerblom et al., 2007). It is difficult to propose a threshold for toxic concentration of Zn, Cu, Cd and Pb (Phälsson, 1989), however on the basis of research on the destructive influence of heavy metals on forests, the following threshold concentrations of the accumulation in the layers of organic soils of coniferous forest sites for the industrial regions of Southern Poland have been established: cadmium (Cd)— $50 \text{ mg} \cdot \text{kg}^{-1}$, copper (Cu)— $150 \text{ mg} \cdot \text{kg}^{-1}$, zinc (Zn)— $500 \text{ mg} \cdot \text{kg}^{-1}$, and lead (Pb)— $1500 \text{ mg} \cdot \text{kg}^{-1}$ (Zwoliński, 1995). In general, $500 \text{ mg} \cdot \text{kg}^{-1}$ is considered a critical threshold for total concentration of heavy metals (Zn, Cd, Pb, Cu) in the soil of coniferous forest sites (norms accepted for the Upper Silesia and Legnica–Głogów Industrial Region, Southern Poland (Zwoliński, 1995).

The observed zinc, cadmium and lead concentration in the topsoil layers (0–8 cm) according to Kabata-Pendias classification (Kabata-Pendias et al., 1993) corresponds to the lowest level (0) of trace element concentration on a 6° scale. For three of the given mine soils (QS2, QSNc and QLS substrates), the concentration of Cd was at most $0.60 \text{ mg} \cdot \text{kg}^{-1}$ which corresponds to the first level on a scale of zero to six, i.e. second lowest contamination. Only for one case (QS1 on Szczakowa sand quarry) Cd and Zn concentration in the topsoil layer corresponds to the second level (i.e. the slightly contaminated soil).

Copper is one of the most important microelement necessary for plant nutrient supply. Elevated concentration of copper should be considered a positive factor in the case of RMS and depends on the original concentration of Cu in parent rock substrates of mine soils.

High concentrations of Zn, Pb and Cd in the organic layer (Olf) clearly show the strong influence of the industrial pressure and high deposition containing heavy metals in Upper Silesia region and post-mine sites such as the sand mine and quarry Szczakowa and Smolnica spoil heap. This phenomenon is due to the high affinity of trace

elements in the soil organic matter (SOM) in upper layers. The presence of heavy metal concentration in the soil profile decreasing by depth verified the high accumulation of these elements in the organic and organic–mineral topsoil layers (Greszta and Godzik, 1964; Godbold and Hüttermann, 1985; Zwoliński, 1995). This is due to a high ability of sorption and accumulation of heavy metals by organic material and mineral–humus soil complexes (Kabata-Pendias and Pendias, 1992). High concentration of trace elements in organic layer (Olf) is particularly harmful in the case of sandy soils that developed on the QLS and QS1 deposits, the most susceptible to degradation (Kabata-Pendias and Pendias, 1992). In sandy mine soils there is also easier migration of trace metals into the soil, which could be seen for example in the case of QLS variant in C horizon, compared to another soil-substrates.

Based on the observed soil trace element concentrations it may be concluded that in the studied mine soils there is no direct threat of heavy metal contamination. However, the main degrading factor in the investigated soils, especially in sand quarry located in the region of Upper Silesia, may be the concentration of cadmium in topsoil layer. Cadmium is one of the most mobile elements in the soil environment among the group of heavy metals (Kabata-Pendias and Pendias). In this study, cadmium concentration was no higher than the critical norm for forest site soils, i.e. $50 \text{ mg} \cdot \text{kg}^{-1}$ (Zwoliński, 1995).

It should be stressed, however, that detrimental effects of pollutants should be determined not only by the total concentration of trace elements, but also by their potential synergistic interactions, even at low individual concentrations. There is no completely unambiguous method of determining the biologically available fraction of the metals in the soil (Phälsson, 1989). The total concentration of a contaminant present in soil is not always related to its availability for uptake by organisms and biological effects (Alexander, 2000; Ehlers and Luthy, 2003; Adriano et al., 2004; Alvarenga et al., 2012). Taking that into account, the potential risk posed by the bioavailability of contaminants in new post-mine ecosystems to both environmental and human health was assessed based on the pine needle element (Zn, Cu, Pb and Cd) concentrations.

In most cases, concentrations of Zn, Cu, Pb and Cd in the pine needles were higher in comparison to data from the area at a low pollution site (e.g. Białowieża Primeval Forest) where the following concentrations were observed: 40.9 , 2.9 , 1.29 and $0.25 \text{ mg} \cdot \text{kg}^{-1}$, respectively (Dmuchowski and Bytnerowicz, 1995). In the case of Zn, Pb and Cd in needles of pine growing on QS1 and QLS substrates on Szczakowa sand quarry (Zn, Pb and Cd) and CF on Smolnica coal refuse spoil heap (Cd), the concentrations were especially high. As mentioned, these post-mining ecosystems are located in the Upper Silesia region which is under strong industrial pollution pressure, usually higher than mean values for Europe (Dmuchowski and Bytnerowicz, 1995).

According to literature (Kochian, 1991), the trace element concentrations increase from C to C + 1-needles. Trends of

Table 3
Correlations (Pearson's correlation coefficients) between mineral soil (0–8 and 8–110 cm depth) and organic layer (Olf) element (Zn, Cu, Pb and Cd) concentrations and element concentration in pine needle (older needles C + 1 and current year needles C) in post-mine ecosystems on reclaimed sites.

	Zn (Olf)	Zn (0–8 cm)	Zn (8–110 cm)	Cu (Olf)	Cu (0–8 cm)	Cu (8–110 cm)	Pb (Olf cm)	Pb (0–8 cm)	Pb (8–110 cm)	Cd (Olf)	Cd (0–8 cm)	Cd (8–110 cm)
Zn _{SoC} -needles	0.723 ^a	0.332	−0.113									
Zn _{SoC} + 1-needles	0.722 ^a	0.229	−0.203									
Cu _{SoC} -needles				0.687 ^a	0.841 ^a	0.860 ^a						
Cu _{SoC} + 1-needles				0.228	0.360	0.349						
Pb _{SoC} -needles							0.090	0.129	0.040			
Pb _{SoC} + 1-needles							0.750 ^a	−0.068	−0.332			
Cd _{SoC} -needles										0.515 ^a	−0.078	−0.416 ^a
Cd _{SoC} + 1-needles										0.734 ^a	0.208	−0.343

^a Significant at $p = 0.05$.

increasing Zn, Pb, and Cd accumulation with needle age was noted by Kurczyńska et al. (1997) in a study of bioindicators of heavy metal pollution in the environment. In our studies similar trends were observed in the case of Zn, Cu and Pb concentrations. The average value of needle Cd concentration was also higher in older needles than that in current needles, but only on some substrates. These disorders may result from the phenomenon of translocation since heavy metals are phloem-mobile elements, they are resorbed from older to younger needles as the needles age. This is particularly relevant, in addition to cadmium, nickel and copper as well (Marschner, 1995). Similarly, it has been found in the areas strong contaminated with heavy metals in the vicinity of Monchegorsk smelter complex on the Kola Peninsula in Russia (Rautio, 2003).

The results indicate that of the measured mine soil characteristics, pine needles' individual trace element concentration was significantly correlated with clay % content, organic carbon (C_{org}) content, pH and soil sorption complex properties (CEC and TEB). In terms of natural soils there is a correlation between bioavailability of trace elements and soil pH, organic matter content and texture, especially with respect to clay fraction content. In addition, the results indicate that in most cases, except Cu, there were no correlations between soil–plant trace element concentration. However, positive relationship of Zn and Cd concentrations in pine needles with microbial activity (DHG) confirms the bioindicator value of pine foliage chemical composition and trace element risk assessment of developed post-mine ecosystems. Additionally, the relationship between trace element pine needle concentration and the organic layer (Olf) indicates that industrial pressure and deposition of pollutants are important considerations in these developed post-mine ecosystems, especially in the region of Upper Silesia.

5. Conclusion

The results from this study show that there was no excessive concentration of trace elements on mine soils developed on Quaternary, Tertiary and Carboniferous deposits. An exception was seen in cadmium in soils that developed on sand quarry (SzcZ-QLS and QS1) and hard coal spoil heap (Smol-CF) in the Upper Silesia region which were influenced more by industrial pressure and pollutant deposition than original Cd concentrations in the soil-substrates.

Trace element (especially Zn and Cd) content of needles is a good indicator of bioavailability and is a valid criterion in the assessment of emerging threats to developed post-mine ecosystems. Evidence of this lies in the observed correlation between soil microbial activity (expressed by dehydrogenase activity in upper soil layer) and the content of trace elements in the organic layer (Olf) as a result of industrial pressure.

We conclude that there is no risk of critical levels and bioavailability of trace element concentration in reclaimed and afforested areas affected by open strip mining (sand quarries, lignite and sulphur mining spoil heaps) and hard coal mining (spoil heaps) built from dominant substrates common to this part of Europe (i.e. Quaternary, Tertiary and Carboniferous sediments).

Conflict of interest statement

No conflict of interest.

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