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

Marcin Pietrzykowski [a,b,*], Jarosław Socha [c], Natalie S. van Doorn [d]

[a] Department of Forest Ecology, Forest Faculty, University of Agriculture in Krakow, Al. 29 Listopada 46, Pl. 31-425 Krakow, Poland
[b] Virginia Polytechnic Institute and State University, Department of Crop and Soil Environmental Science, 244 Smyth Hall, Blacksburg, VA 24061, USA
[c] Department of Biometry and Forest Productivity, Forest Faculty, University of Agriculture in Krakow, Al. 29 Listopada 46, Pl. 31-425 Krakow, Poland
[d] Department of Environmental Science, Policy and Management, 130 Mulford Hall, University of California, Berkeley, CA 94720, USA

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.

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

* Corresponding author at: Department of Forest Ecology, Forest Faculty, University of Agriculture in Krakow, Al. 29 Listopada 46, Pl. 31-425 Krakow, Poland.
E-mail addresses: rlpietrz@cyf-kr.edu.pl, mpietrzy@vt.edu (M. Pietrzykowski), rlsocha@cyf-kr.edu.pl (J. Socha), Natalies@berkeley.edu (N.S. van Doorn).

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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; Lamppu 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 (Katzur 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 $kg \cdot ha^{-1}$), and sowing a mixture of grasses and leguminous plants (60 $kg \cdot ha^{-1}$). 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.