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Enzyme activity as an indicator of soil-rehabilitation processes at a zinc and lead ore mining and processing area

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ABSTRACT

The activities of soil enzymes in relation to the changes occurring in the soil on a degraded area in southern Poland after zinc and lead mining were analyzed. An evaluation of the usefulness of urease and invertase activities for estimating the progress of the rehabilitation processes in degraded soil was performed. The data show that the soil samples differed significantly in organic carbon (0.68–104.0 g kg^{-1}) and total nitrogen (0.03–8.64 g kg^{-1}) content in their surface horizons. All of the soil samples (apart from one covered with forest) had very high total concentrations of zinc (4050–10,884 mg kg^{-1}), lead (959–6661 mg kg^{-1}) and cadmium (24.4–174.3 mg kg^{-1}) in their surface horizons, and similar concentrations in their deeper horizons. Nevertheless, the amounts of the soluble forms of the above-mentioned heavy metals were quite low and they accounted for only a small percentage of the total concentrations: 1.4% for Zn, 0.01% for Pb and 2.6% for Cd. Urease activities were ranked as follows: soil from flotation settler (0.88–1.78 μg N–NH_4^+ 2 h^{-1} g^{-1}) < soil from old slag heaps (1.77–2.51 μg N–NH_4^+ 2 h^{-1} g^{-1}) < soil undisturbed by mining activity (2.14–5.73 μg N–NH_4^+ 2 h^{-1} g^{-1}). Invertase activities were similar in soil that was undisturbed by mining and in soil from old slag heaps, ranging from 20.5 to 77.1 mg of the inverted sugar, but they were much lower in soil from the flotation settler (0.12–6.95 mg of the inverted sugar). The results demonstrated that heavy pollution with Zn, Pb and Cd slightly decreased the activities of urease and invertase. It is thought that it resulted from the enzyme reactions occurring in slightly acidic or alkaline soil conditions. Under such conditions, heavy metals occur mainly in insoluble forms. The activities of these enzymes are strongly dependent on the content and decomposition of organic matter in the soil.

1. Introduction

The mining and processing of non-ferrous metal ore results in local geo-mechanical transformation, and in environmental pollution by these metals. In the Olkusz area of southern Poland, zinc (Zn) and lead (Pb) ore mining and metallurgy have been carried out since the 14th century, which has resulted in environmental degradation of the surrounding area. Over time, the technology for obtaining and processing ores has changed, which has resulted in the accumulation of waste rock dumps, flotation-waste stockpiles and mounds that contain mixtures of these materials. These materials originate from different output periods and have been left to the spontaneous succession of plants or have, in some cases, been rehabilitated (Ciarkowska and Hanus-Fajerska, 2008; Skubała, 2011).

Soil enzymes play a fundamental role in organic matter decomposition and in plant nutrient cycling. The activities of enzymes that participate in nitrogen transformation, such as urease, can be used as a measure of the intensity of nitrogen transformation that is occurring in a given environment and can indicate the availability of different nitrogen compounds to plants (Ianelli et al., 2012). The activity of the enzyme invertase reflects the soil's ability to break down sucrose and free simple sugars, which are the main energy sources of soil microorganisms (Frankenberger and Johanson, 1983).

Soil enzyme activity is often used as an indicator of the functioning of soil ecosystems. In addition, enzymes are potential indicators of anthropogenic activities in soil environments. Furthermore, enzyme activities can be used to show the effectiveness of soil-rehabilitation treatments or to reflect soil quality following the restoration of soil environments that were destroyed by industrial processes (Hinojosa et al., 2004; Izquierdo et al., 2005). Thus, enzyme activity can be used to indicate soil

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improvements that occur during rehabilitation efforts after mining (Finkenbein et al., 2013; Schimann et al., 2012). However, to our knowledge there are relatively little data available from studies of the relationship between enzyme activity and soil properties under specific conditions that include chronic pollution with Zn, Pb and Cd, soils of different age, and soils with a diversified vegetation cover. Our work will provide new insight into the use of urease and invertase activities as bioindicators for monitoring the soil-rehabilitation processes in such environments. The innovative aspect will be to consider the crucial role of soil microbial processes when evaluating the level of alteration during restoration processes which may serve to planning management.

The aim of this work was to use a measure of soil enzyme activities to evaluate the progress of soil restoration in areas that were degraded by Zn and Pb ore mining.

2. Materials and methods

2.1. Soil sampling sites

Soil samples were collected from the Olkusz area, which has Zn and Pb ore deposits that probably originated from the Silesia-Krakow Upland in southern Poland. Mounds of waste rock and excavations at various stages of reclamation can be found in the area as a result of ore mining and processing by the opencast method. In the last 40 years, metals have been acquired by the flotation method. The wastes collected from this process were collected on a flotation settler with an area of approximately 110 ha.

For these experiments, material from 10 sites located near Olkusz (N50° 17′ E19° 29′) was sampled (Fig. 1). The sites are listed below.

- The two following sites were located in areas that were not impacted by mining: M1 is a meadow that is densely covered with grassy flora, including *Agrostis* sp. L, *Lolium* sp. L, *Festuca* sp. L, *Deschampsia* sp. P. B., and *Calamagrostis* sp. Adans., and F2 is an overgrown mixed forest that is dominated by *Pinus silvestris* L., *Fagus sylvatica* L., *Betula pendula* Roth, *Vaccinium* sp. L, *Deschampsia* sp. P. B., and *Calamagrostis* sp. Adans.
- The next two sites (W3 and W4) were located on so-called "warpies", which are places from which ores were manually collected in the 14th century. Today, these areas are covered with flora that is similar to *Festuco-Brometea*. In addition, several trees are present, of which the *P. silvestris* L. and *B. pendula* Roth species are dominant.
- The next site (D5) was located on a slag heap of waste rock and Zn and Pb ore waste that was more than 100 years old. This site was covered by calamine grass from the class *Violetea Calaminarie*, such as *Armeria maritima* (Mill.) Willd. and *Biscutella laevigata* L.
- The five following sites were located on the flotation settler: S6 was located on the most recently utilized portion, which was on the slope and had no flora cover; S7 was located on a portion that had had several years to settle after hydro-seeding with *Agrostis* sp. L, *Lolium* sp. L, and *Festuca* sp. L enriched with straw and sewage sludge; S8 was located on the slope of the settler that was planted three years ago with *B. pendula* Roth seedlings; S9 was located on the slope of the settler that had a rare grassy cover (with a share of *Agrostis* sp. L, *Lolium* sp. L, and *Festuca* sp. L.) following 10 years of succession; and S10 was located on the oldest part of the settler, which had been covered by flora resulting from natural succession for 40 years. This area was grassy and contained species that were characteristic of calamine flora (*A. maritima* Mill.) Willd, *Silene vulgaris* (Moench) Garcke, and *Gypsophila fastigiata* L. Approximately 15% of the flora in this area was comprised of the trees *B. pendula* Roth and *P. silvestris* L.

2.2. Study methods

Five samples were collected from each site from each of the two following layers: 0–10 cm and 10–40 cm. Individual samples at a given depth were combined to give a representative sample of each site. Chemical and physical analyses were performed using the following methods.

- Soil texture was determined according to Polish Norms PN-R-04032 and PN-R-04033 (1998).
- pH values were determined potentiometrically (Tan, 2005).
- Total and inorganic carbon concentrations and total nitrogen (N_{tot}) concentrations were determined with an automatic carbon and nitrogen analyser (TOC-TN 1200 Thermo Euroglas).

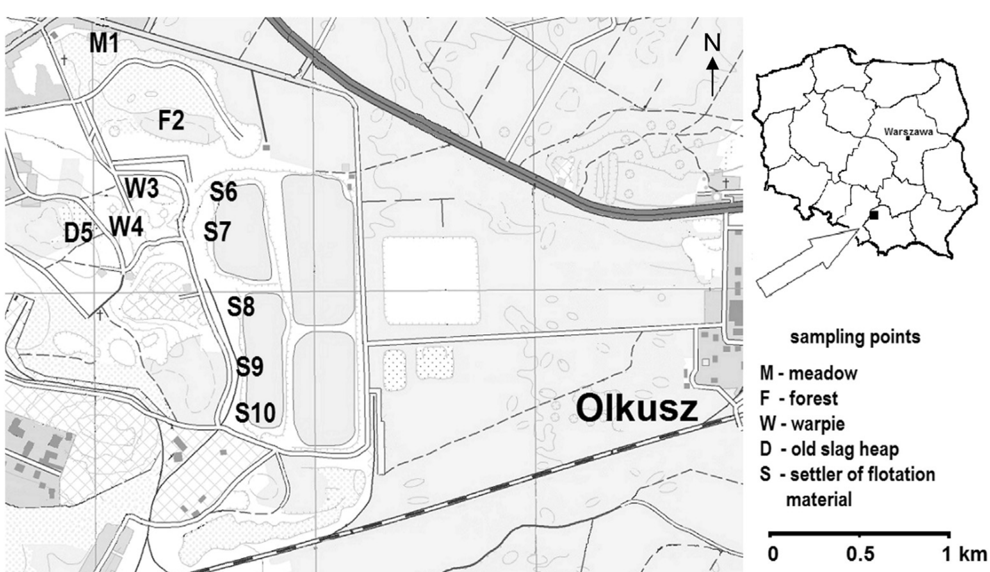

Fig. 1. Map of the studied area.