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Inconspicuous waste heaps left by historical Zn–Pb mining are hot spots of soil contamination

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ABSTRACT

This study discovers and surveys sites left by former Zn–Pb mining in western Małopolska (S Poland), focusing on old heaps of mining waste rock located in agricultural land and suburban wasteland. Topsoil samples were taken from 73 heaps and described using many parameters, including heavy metal contamination (the content of total, EDTA-extractable, $BaCl_2$-extractable and water-extractable metals), macronutrient content, pH and texture. At five sites, a short transect was delineated from heaps towards their surroundings to estimate the impact of the heaps on the adjacent agricultural soil. The total heavy metal concentration in the heap soil varied greatly across sites, ranging from 5 to 522 mg Cd kg^{-1}, from 94 to 23,006 mg Pb kg^{-1}, from 6 to 51 mg Tl kg^{-1} and from 394 to 70,435 mg Zn kg^{-1}. These values were very high compared to that measured in the soil of the control areas: 2–5 mg Cd kg^{-1}, 13–67 mg Pb kg^{-1}, 1–17 mg Tl kg^{-1} and 63–476 mg Zn kg^{-1}. The extractability of heavy metals from heap soil decreased in the following order: Cd > Pb > Zn > Tl (EDTA) and Cd > Zn > Pb ~ Tl ($BaCl_2$). For the most mobile metal (Cd), the extractability averaged 43% and 5% for the EDTA and $BaCl_2$ extractants, respectively. A factor analysis reduced 33 soil physicochemical parameters to five factors that explained 72% of the variance in the data. Factor 1 represented heavy metal contamination (concentrations of both total and mobile Cd, Pb and Zn), factor 2 represented organic matter accumulation, reflecting the most likely age of a heap, factor 3 represented the total concentration of Ca, Mg and Tl derived from weathering of the waste material — mostly dolomite and calcite, factors 4 and 5 represented soil particles of different sizes. In the transect study, the amount of total and EDTA-extractable heavy metals in soil generally decreased when increasing the distance from the heaps, but still remained high in agricultural soil sampled 10 m from the foot of the heaps. The results of this study suggest that remnants of the historical Zn–Pb ore mining are "hot spots" of persistent soil contamination and may pose an environmental problem, especially those located in the inhabited areas; their status should be monitored by the local authorities.

1. Introduction

The areas where metal mining and smelting are currently under development or where these activities recently ceased are traditionally the focus of environmental research; these modern industrial sites cause serious and extensive heavy metal contamination (Bech et al., 1997; Chehregani et al., 2009; Li et al., 2014; Lim et al., 2008; Stefanowicz et al., 2008). These sites pose a great challenge for engineers dealing with the minimization of environmental risk while facilitating risk assessments due to the existence and availability of essential data: precise location of pollution sources, estimations of pollutant emissions or predictions of the trend in industrial production.

In contrast, historical metal mining and smelting sites (abandoned tens or hundreds of years ago) have been investigated to a much lesser extent. The papers on this subject do not offer proof that these areas do not threaten the environment and human health; the adverse effects of these sites may be significant while persisting for centuries (Pyatt et al., 2000) because metals cannot be degraded. These areas can be very extensive. Thornton (1996) estimated that Pb contamination in Britain resulting from former mining and smelting activity covers up to 4000 km^2 of urban and agricultural land. Extremely high soil concentrations of Pb found there in places, such as 22,800 μg g^{-1} (Cotter-Howells and Thornton, 1991), undoubtedly make this land hazardous to live. The main obstacle opposing the study of the impact of historical metal mining and smelting is the lack of accurate information on the location of potential contamination "hot spots". Traces of anthropogenic

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activities, such as mine shafts, spoil heaps or excavations, quickly disappear from the landscape (e.g., due to erosion) and official records. For instance, Eckel et al. (2001) identified old Pb-smelting sites (from 1931 to 1964) in the area of the United States via historical research, finding that approximately 430 of them were unknown to federal authorities; their preliminary data suggested that these sites pose a threat to public health due to the Pb contamination.

Western Małopolska is a region in southern Poland where relics of medieval and more recent metal mining and extraction industries still can be discovered. One of the most common types is old Zn–Pb ore excavation sites. These sites are small (on average 0.5–2 m high and from several to tens of m in diameter), inconspicuous (usually masked by vegetation) heaps of waste rock (Fig. 1) locally termed “warpie” (Łabęcki, 1841; Nowak et al., 2011; Turnau et al., 2006). These sites often take the shape of a ring encircling a shallow pit due to the methods used when operating deposits; the ore was mined using shafts, separated from the gangue (mining waste), and the gangue was piled up around shafts. The heaps may occur singly or in groups; in the latter case, they form a bumpy, undulating surface. The heaps are prone to erosion and disappear over time. Therefore the oldest Zn–Pb mining sites cannot be visually detected. We estimate that the heaps surveyed in this study come predominantly from the 19th and the first half of the 20th century. Most areas with a high density of old heaps (e.g., 50 per square km) were afforested long ago, avoiding destruction due to human activity (e.g., settlement expansion); they have been studied recently by Pietrzykowski et al. (2011) and Aleksander-Kwaterczak and Ciszewski (2013), who rated these sites as heavily polluted. Relatively few heaps have survived in non-forested areas. Their investigation seems to be urgent because they occur in arable fields, pastures, gardens and in the immediate vicinity of houses, potentially posing a threat to local inhabitants. Moreover, they have remained completely neglected by environmental studies.

The aim of the study was to investigate the level of heavy metal contamination in the soil at historical mining sites for Zn–Pb ores (old heaps of mining waste) found in the non-forested areas. The concentration of both total and mobile Cd, Pb, Tl and Zn in soil was measured, and other soil parameters that may affect the mobility of heavy metals were determined (main study). At selected sites, the soil was sampled along the transect of increasing distance from a heap to evaluate the influence of the mining waste on the surrounding agricultural soil (transect study).

2. Study area

The study was situated in the south-eastern part of the Silesia–Cracow Upland (southern Poland) and covered an area of ca. 750 km^2 (Fig. 2). This old mining region is known for its rich Zn–Pb ore deposits of Mississippi Valley type occurring in Triassic and Devonian rocks (Cabala et al., 2009; Leach et al., 2001). Sulphides of Zn (sphalerite, wurtzite), Pb (galena) and Fe (pyrite and marcasite) are primary ore minerals; their partial oxidisation formed smithsonite, cerusite, monheimite and limonite (Cabala, 2001). The ores contain an average of 4–6% Zn, 1–3% Pb and 5–8% Fe (Cabala et al., 2009), as well as known amounts of Cd, Tl, Ag and As. The gangue minerals are largely composed of dolomite and calcite; in total, they constitute ca. 70% of the mining output (Cabała, 2009).

The beginnings of metal mining in this region date back to the 11th century, although earlier exploitation cannot be excluded (Rozmus, 2010). At first, Pb and Ag were mined, while the Zn-rich waste material was piled up or left in mine shafts. The Zn ore exploitation began in the 16th century; since the 19th century, Zn has become the most important metal mined and processed in the region (Molenda, 2000). In medieval times, only the near-surface deposits were mined. The development of mine dewatering techniques and metal smelting methods enabled the exploitation of deep-localized ore deposits and the reuse of metal-rich waste (Molenda, 1978). Modern metal industry developed in the second half of the 20th century near Olkusz (the mining and metallurgical plant “Bolesław”) and Chrzanów (the mining plant “Trzebionka”). The recent disposal of mining waste and aerial deposition led to severe heavy metal contamination in the soil within a large radius of the plants. The environmental effect of this contamination has been studied by many authors (e.g., Chrastný et al., 2012; Kapusta et al., 2011; Słomka et al., 2012; Stefanowicz et al., 2010, 2012; Turnau et al., 2006; Verner et al., 1996; Żmudzki and Laskowski, 2012).

Fig. 1. Remains of a heap of waste material left at an old mining shaft — an example of a study site.