

High thallium concentrations in soils from sites of historical Ag, Pb, and Zn mining in western Małopolska (S Poland)

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Abstract. The aim of this study was to assess thallium concentration in topsoil originating from sites of historical mining of Ag, Pb and Zn in western Małopolska (S Poland). Soil samples were collected from 63 sites, sieved, ground and digested in hot HClO₄. Thallium concentration was measured with an atomic absorption spectrometer. Thallium concentrations averaged 20.84 mg kg⁻¹ and varied from 4.42 to 49.82 mg kg⁻¹. In all studied soils they exceeded values typical for uncontaminated soils (0.02 to 2.8 mg Tl kg⁻¹). This indicates that Tl contamination may threaten the environment and public health. Routine monitoring of Tl contamination in southern Poland is required.

Key words: Thallium, historical Ag-Pb-Zn mining, old heaps, soil

Introduction

Abandoned sites of historical mining and smelting of metal ores may threaten the environment and public health for many centuries after cessation of industrial activities at those sites (Pyatt et al. 2000). Metals are slowly released from deposited waste rock, tailings or slag to the environment through chemical and physical erosion and accumulate in soils and organisms (Pyatt et al. 2000). Historical waste sites are often unknown to local authorities and no reclamation is taken up (Eckel et al. 2001).

Western Małopolska is one of the oldest areas of non-ferrous metal mining in central Europe. Mining of the ores dates back to 12th century, although earlier exploitation cannot be excluded (Molenda 1963). At first, Pb and Ag ores were used, while excavation of Zn ores started in the 16th century, and in the 19th century Zn has become the most important metal mined and processed in this region (Molenda 2000).

Thallium is a highly toxic element often accompanying metal ores. Ores in western Małopolska contain up to 90 mg Tl kg⁻¹ (Zn sphalerite ores) and up

to 1000 mg Tl kg⁻¹ (Fe marcasite ores) (Cabała 2009). Despite its toxicity, Tl is a rarely studied metal and it has not been considered a pollutant for a long time in Poland (Borgmann et al. 1998, Wierzbicka et al. 2004). The aim of this study was to assess total Tl concentrations in soils developed at sites of historical Ag-Pb-Zn mining in Poland.

Materials and Methods

Sixty-three study sites were established in the area of historical Ag-Pb-Zn mining between Krzeszowice, Jaworzno, Libiąż and Olkusz in western Małopolska (S Poland). They were located on S, SW or SE non-forested slopes of old mining heaps (Fig. 1). To our knowledge, the heaps are at least 100-years old. From each site, 3 samples of the top mineral layer to a depth of 15 cm were collected (2-3 m apart) and bulked to obtain one composite soil sample. The soil was sieved (2 mm), air-dried, ground and digested in hot HClO₄. Thallium content was measured by atomic absorption spectrometry (Varian 220 FS).



Fig. 1. A remnant of a typical pit-shaft surrounded by heaps of polluted ore-bearing dolomite located in the area of historical mining of Ag, Pb and Zn in Trzebinia (S Poland).

Results and Discussion

Thallium concentrations in studied soils varied from 4.42 to 49.82 mg kg⁻¹, while average concentration amounted to 20.84 mg kg⁻¹. Soils containing between 20 and 30 mg Tl kg⁻¹ were the most numerous (Fig. 2). The results indicate that total Tl concentrations in soils developed on the old heaps significantly exceeded Tl concentrations found in unpolluted soils. Kabata-Pendias and Pendias (1993) stated that unpolluted soils worldwide contain from 0.02 to 2.8 mg Tl kg⁻¹, while in Poland from 0.01 to 0.4 mg Tl kg⁻¹. This means that the most polluted soil in our study contained ca. 120 times more thallium than unpolluted soils in Poland. High Tl concentrations were also found in soil from 100-year-old waste heap near Olkusz in Poland (not included in our study). Average Tl concentration reached 43 mg kg⁻¹, while the highest Tl concentration equaled to 78 mg kg⁻¹ (Wierzbicka et al. 2004). In turn, in Wiesloch in Germany soils from a nearby of a closed Pb and Zn mine contained 8.8 – 27.8 mg Tl kg⁻¹ (Schoer and Nagel 1980).

High Tl concentration in soil may threaten the environment and human health as Tl accumulates in plants and animals. Dmowski and Badurek (2002) found that plants and fungi growing in the vicinity of a

zinc smelter in Olkusz accumulated elevated Tl contents in comparison to control soils. Vegetables contained 1.28 – 3.70 mg Tl kg⁻¹, whereas natural Tl concentration in plants has been estimated at 0.05 mg Tl kg⁻¹ (Dmowski and Badurek 2002). In turn, the maximum Tl concentrations in kidneys and livers of a bank vole, living in environs of a zinc smelter near Olkusz amounted to 34.27 and 14.53 mg kg⁻¹, respectively, whereas values for animals from unpolluted sites were below the detection limit – 0.07 mg Tl kg⁻¹. In a few animals a loss of hair was observed, which is a characteristic of Tl poisoning (Dmowski et al. 1998).

Our study is important for at least two reasons. Firstly, it dealt with a highly toxic and rarely studied element. As emphasized by Dmowski and Badurek (2002), Tl has been neglected as a pollutant in Poland and the institutions responsible for monitoring environmental quality do not measure Tl routinely, despite its high concentrations in soils and organisms living in contaminated areas in western Małopolska. Secondly, Tl concentrations were measured in soils originated from sites of historical mining, most of which were identified in the field and analyzed for the first time. As indicated by Eckel et al. (2001) documentation and monitoring of sites of former metal processing may be of primary importance. They recognized 430 potential lead-smelting sites from years 1931-1964 unknown to

authorities and preliminary analysis of metal content in soils at 10 sites revealed high Pb contamination, up to 2550 mg kg⁻¹. As showed by Pyatt et al. (2000),

metal-polluted sites of historical ore mining and smelting may affect the surroundings for many centuries after cessation of industrial activities.

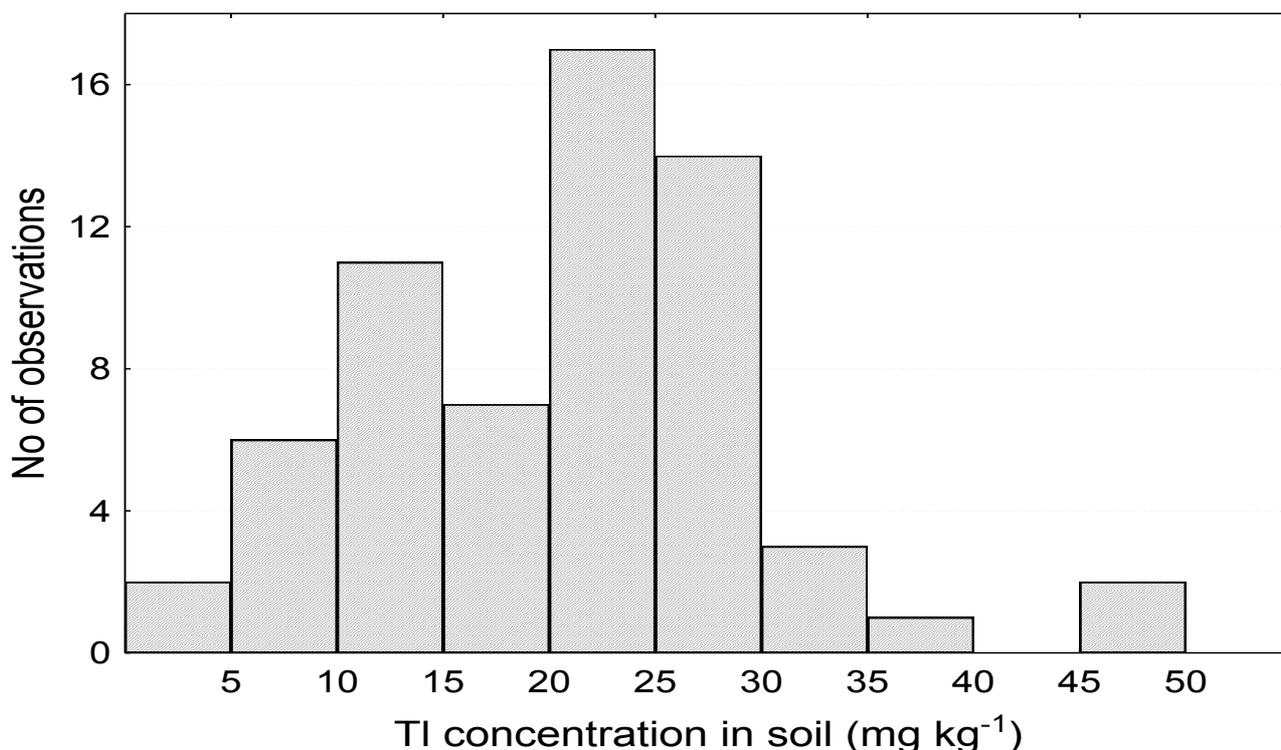


Fig. 2. Histogram presenting thallium contamination of soils developed at sites of historical mining of Ag, Pb and Zn in western Małopolska (S Poland).

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