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### **pt. Analiza rozmieszczenia cyny i molibdenu w glebach południowej części Wyżyny Śląskiej w aspekcie antropogenicznego zanieczyszczenia środowiska**

#### **ABSTRACT**

The purpose of the study was to determine tin and molybdenum concentrations in the soils of the Silesian Upland (SW Poland), compiling a geochemical map at the scale of 1:25 000. Both elements may be used as environmental pollution markers. The knowledge about their distribution within the environments (including soils) of Poland was insufficient, mainly due to limited analytical capabilities. Analysis of bioavailability and mobility of tin and molybdenum, carried out by sequential extraction, allowed determining the degree of bonding of these elements to a given fraction.

Soil samples were collected in 2007–2008 within a regular grid of 250 x 250 m (16 samples/km<sup>2</sup>) in the area of Katowice, Mysłowice, Bieruń Stary and Imielin map sheets under the project “Detailed Geochemical Map of Upper Silesia” at the scale of 1:25 000, conducted by the Polish Geological Institute National Research Institute.

The concentration of tin and molybdenum was determined in 9858 soil samples, 5223 from a depth of 0.0–0.3 m, and 4635 from a depth of 0.8–1.0 m, using ICP–OES after *aqua regia* digestion. The additional analyses were done in soils with anomalous content of tin and/or molybdenum. In this case, 33 soil samples from a depth of 0.0–0.3 m, and 27 soil samples from a depth of 0.8–1.0 m were collected from 33 selected sampling sites. After *aqua regia* digestion the samples were analysed by ICP-OES to determine the concentration of tin, molybdenum and other elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, V and Zn). Determination of the pH was also performed. Three samples from a depth of 0.0–0.3 m were brought under analysis of bioavailability and mobility of tin and molybdenum by sequence extraction using a modified BCR procedure.

In the soils of the surface layer, the tin content was in the range of <2–295 mg/kg, and at a depth of 0.8–1.0 m its content varied between <2 and 1,460 mg/kg. The regional geochemical background of tin in soils from both depths did not exceed 2 mg/kg.

The molybdenum concentration in soil from the depth of 0.0–0.3 m was <0.5–28.0 mg/kg, while from the depth of 0.8–1.0 m it varies in the range of 0.5–9.8 mg/kg. The regional geochemical background of molybdenum in soils from both depths was estimated as <0.5 mg/kg.

Tin anomalies (2–16 mg/kg) were detected in the north-western part of the research area (in the most industrialized districts of Katowice, Mysłowice and Sosnowiec), in the area of the Jaworzno Power Station, and in the vicinity of the paper mill in Czułów (district of Tychy). Much larger areas of those anomalies in the topsoil suggest that the main source of tin was industrial activity. The first area was contaminated probably due to the historic activity of a zinc smelter, the second one by the emission of coal-fired power plants, and the third one by the discharge of wastewater from the mill.

Molybdenum anomalies (0.5–1.7 mg/kg) are more extensive in the surface layer, as compared with the tin anomalies, which can be attributed mainly to its anthropogenic origin. In the north-western part of the research area, molybdenum anomalies coincide with tin anomalies, indicating the historical zinc metallurgy as a source of Mo. The increased content of molybdenum in the Ziemowit coal mines (in Łędziny) and Murcki (Katowice) is associated with the exploitation and storage of mining waste as well as industrial coal combustion. Local enrichment of alluvial soils in tin and molybdenum in the wetlands of the Gostynia, Przemsza, Przyrwa and Mleczna rivers are probably the source of industrial waste discharges.

Significant divergences in the comparison of the results of tin and molybdenum content from the same sites in different years are probably related to the high variability of the investigated material (mainly by the presence of bulk soil) and the limited extent of the maximum content of the analysed elements.

The assessment of soil pollution by tin and molybdenum, carried out using geochemical indicators, has shown that contamination by these metals was strong only in a few sampling sites. Sites with elevated levels were found in the Czułów paper mill area and in the area of allotment (parcel) gardens and railway embankments in Katowice. All of these regions are the areas of anthropogenic bulk soils that, apart from the natural components, contain significant admixture of foreign materials.

Both the soil's depth ranges show clear correlations of tin and molybdenum with other elements. In the case of tin, the correlations with lead, arsenic and copper were significant, while as regards molybdenum, a significant correlation was observed with chromium, iron and nickel. The coexistence of tin with these elements is probably related to their historical presence in the waste from the zinc smelter. In turn, the correlations of molybdenum were attributed mainly to the presence of these elements in coal ash, and to the interplay of waste from power plants and steelworks.

The mineral composition of the investigated soils is dominated by quartz and clay minerals, which are accompanied by feldspars and carbonates. In some samples, additional

minerals, e.g. mullite and maghemite, are present. This indicates the anthropogenic origin of the material.