

Summary of the Doctoral Dissertation

Indicators of environmental risk with chromium compounds originating from the tanning industry for selected valuable natural areas located in the Nowy Sącz district

The aim of the study was to assess the impact of inappropriate reclamation of postindustrial areas, i.e., tanning plants and their landfills, on the presence of excess chromium content in the soil and plant environment in naturally valuable areas. An important part of the work was also the calculation of environmental and health indicators to determine the impact of the already closed tannery landfills on the water-soil environment and on living organisms (humans), with particular emphasis on the size of the health risk associated with changes in the forms of chromium occurrence in the environment.

In the Nowy Sącz district, 5 research areas have been selected which are subject to the legal form of nature protection, i.e., the South Małopolska Protected Landscape Area, the buffer zone of the Poprad Landscape Park, and at the same time where activities related to the tanning industry were carried out in the 60-90s of the twentieth century. These were the following locations: (1) Łącko, (2) Obidza, (3) Stary Sącz, (4) Łabowa plant, and (5) Łabowa landfill. In 2017–2019, the following samples were collected: (i) 113 soil samples from all five areas, (ii) 8 surface water samples from Stary Sącz and Łabowa Zakład, (iii) 8 groundwater samples from the areas of Stary Sącz and Łabowa landfill, (iv) 30 plant samples from two areas of Stary Sącz and Łabowa Zakład. The following determinations were made on the collected soil samples: pH, carbonate content, organic substance content, leaching of chromium by aqueous solution, chromium(III) and chromium(VI) content, phytoprotective form (extraction with EDTA solution), as well as chromium fractions in soils (extraction BCR). Total chromium content was also determined in the samples of surface and ground waters and plants (*Taraxacum officinale* L. and *Agrostis capillaris* L.).

The average total chromium content in soils for all analyzed areas varies from 45 to 39,100 mg·kg⁻¹ and forms the following series: Łącko < Łabowa landfill < Stary Sącz < Obidza < Łabowa factory. The highest total chromium content was determined in a sample taken from the Łabowa plant area (63,900 mg·kg⁻¹), it is the highest value described in the literature so far. In the analyzed soil samples, the dominance of chromium(III) over chromium(VI) (ratio 95:5) was found, which indicates the advantage of the more stable form of this metal, which was also confirmed in the performed BCR sequential extraction.

Total chromium contents determined in surface waters ranged from 0.08 to 5.71 $\mu\text{g}\cdot\text{l}^{-1}$, and generally lower concentrations were recorded in the Stary Sącz area than in samples collected from the Łabowa plant area. The highest total chromium content in groundwater was 7.97 $\mu\text{g}\cdot\text{l}^{-1}$ and it was determined in the ŁSws-6 sample collected from the Łabowa landfill area. In the surface water and groundwater samples, geochemical indicators showed no significant chromium contamination.

Total chromium content found in grasses (*Agrostis capillaris* L.) ranges from 6.14 to 35.3 $\text{mg}\cdot\text{kg}^{-1}$, and in samples of dandelions (*Taraxacum officinale* L.) from 9.65 to 367 $\text{mg}\cdot\text{kg}^{-1}$. The highest levels of this metal were found in plants collected in the immediate vicinity of former buildings related to the tanning industry, i.e., sludge drying beds and the main building of the tannery.

The conducted analyzes showed that the Łabowa plant is the most polluted postindustrial area among the analyzed areas. In the past, the largest tanning plant in the Nowy Sącz district operated in this area. Geochemical indicators of environmental pollution (I_{geo} , CF, Er) showed that the soils collected in the immediate vicinity of the buildings of the former tanneries are moderately and extremely polluted, showing a very high and high degree of ecological risk to the current ecosystems. Health risk estimated on the basis of a model developed by the US Environmental Protection Agency showed that in four out of five analyzed areas, i.e., Obidza, Stary Sącz, Łabowa Zakład and Łabowa landfill, there is a significant non-carcinogenic health risk related to contact with contaminated soil through accidental ingestion and dermal contact.

The paper shows how important is the process of proper reclamation and continuous monitoring of the degree of contamination of soil, especially in zones of anomalous chromium content, where the calculated values of environmental and health indicators exceed safe levels.

Key words: chromium, tanning industry, Nowy Sącz district, geochemical indicators, health risk.