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ABSTRACT OF THE DOCTORAL THESIS

"The Ofh soil subhorizon as a potential geoindicator in environmental quality studies"

Geoindicators are a group of commonly used geological indicators of environmental quality. They enable the assessment of environmental changes based on the analysis of abiotic elements, such as coastline location, volcanic activity, and soil properties. Of the 27 geoindicators, only two directly relate to soil: *"soil erosion and sediments"* and *"soil quality"*. In practice, topsoil is most often used to assess the degree of soil contamination resulting from anthropogenic activity. In temperate climate zone, where vertical soil stratification occurs, this layer is composed of the organic horizon (O) and the humic horizon (A). The organic horizon, in turn, consists of the subhorizons, including the Ol subhorizon (forest litter) and the Ofh subhorizon (organic fermentative humic), which is of particular interest due to its specific structure and properties. This subhorizon forms a mat resembling tangled tobacco fibers, approximately 1-10 cm thick. This mat acts as a "natural sponge" for organic pollutants (including polycyclic aromatic hydrocarbons) and inorganic pollutants (trace elements such as Cd, Hg and Pb). As a result, the Ofh subhorizon is characterized by higher concentrations of pollutants compared to the overlying and underlying horizons, which make it a potential geoindicator of temperate climate soil quality.

The main aim of this study was to assess the suitability of the Ofh subhorizon, due to its specific structure, composition and properties, as a geoindicator for selected trace elements (Cd, Hg and Pb) and polycyclic aromatic hydrocarbons (PAHs). To verify this objective, 130 samples were collected (from the Ofh subhorizon (65 samples) and the lower humic horizon – A (29 samples) and the mixed humic-eluvial horizon AE (36 samples)) from 5 forest areas located near the city of Kielce (south-central Poland). Selected trace elements and major elements (Cd, Hg, Pb, Zn, Ca, Fe, K, Mn, S, Ti) and 16 polycyclic aromatic hydrocarbons (PAHs) were determined in all samples. Additionally, pH and cation exchange capacity (CEC), soil organic matter (SOM) and percentage C and N content. For selected samples, oxygen functional groups (base, carboxyl, lactone, phenolic and carbonyl), amorphous and crystalline fractions were determined and SEM imaging was performed.

The results showed that the Ofh subhorizon was characterized by a lower pH (mean values: Ofh 4.8, A 5.2, AE 5.4) and higher soil organic matter content (Ofh 58.3%, A 20.6%, AE 4.08%) compared to the lower A and AE horizons. In this subhorizon, higher average contents of Cd (Ofh 1.41 mg/kg, A 0.694 mg/kg, AE 0.225 mg/kg), Zn (Ofh 144 mg/kg, A 83,5 mg/kg, AE 43.0 mg/kg) and Hg (Ofh 0.231 mg/kg, A 0.221 mg/kg, AE 0.058 mg/kg) were obtained. Pb dominated in horizon A (Ofh 63.7 mg/kg, A 123 mg/kg, AE 41.1 mg/kg). Considering that the Ofh subhorizon may act as a "sponge" in relation to selected trace elements, the value of the geochemical background (GB) and selected geochemical coefficients (LEF, I_{geo}) were calculated for Zn, Cd, Pb and Hg. The obtained values varied between the tested (sub)horizons and indicated minimal enrichment or no contamination with these metals. The highest contents of the sum of 16 PAHs were obtained in samples from the Ofh subhorizon (Ofh 1547 µg/kg, A 1103 µg/kg, AE 109 µg/kg). In this subhorizon, 6-rings PAHs had the highest percentage contribution, while in horizons A and AE, A had 4- and 5-rings PAHs and AE had 3-rings PAHs, respectively. The calculated PAH diagnostic ratio also varied depending on the (sub)horizons, but in all cases, they indicated the same main sources of these compounds: coal, crude oil and biomass combustion.

The most important factors determining the accumulation properties of the Ofh subhorizon included organic matter content, its decomposition rate expressed by the C/N ratio, pH, CEC and the developed porous structure.

The obtained results provide a basis for a better understanding of accumulation properties of the possibility of using it as a geoindicator of temperate climate soil quality in relation to selected trace elements (Cd, Hg, Zn and in selected cases also Pb) and polycyclic aromatic hydrocarbons.

Keywords: subhorizon-Ofh, geoindicator, soil quality, PAHs, trace elements

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