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THE CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SOILS IN RELATION TO THE ORGANIC MATTER FRACTIONAL COMPOSITION

Degradation of soils by chemical compounds is one of the current problems relating to the protection of the Earth's crust (COM(2006)231). This process disturbs the chemical balance, negatively impacts component availability, and limits the biological activity of soils. Soils contaminated with polycyclic aromatic hydrocarbons (PAHs) require special focus due to their low biodegradation potential, long persistence in soils and toxicity to living organisms. The main factor affecting the accumulation of PAHs and their effects on the soil environment is the content of organic matter (OM).

The general aim of the research conducted as part of the present doctoral thesis was to analyse the effects of OM fractional composition on PAH content in soils. Specific objectives of the study included adaptation of OM fractionation methods and evaluation of the implemented methodologies (Objective 1), and selection of OM fractions that may have a considerable impact on PAH accumulation in soils (Objective 2). The scope of the doctoral thesis included analysis of soils from an area that was subject to intense anthropogenic industrial pressure.

Samples of upper layer (0–25 cm) of agricultural soils archived at the Department of Soil Science and Land Conservation at IUNG-PIB were used for Objective 1 implementation. Six types of soils were selected, each with different physical and chemical properties. They were chosen based primarily on the content of organic carbon (C_{org}) and their grain-size composition. The content of OM fractions with considerable environmental impact whose properties may affect PAH accumulation was determined. These fractions included: carbon of humic substance (HS), consisting of low molecular fulvic fraction (FU-C_{org}), fulvic acid fraction (FA-C_{org}), humic acid fraction (HA-C_{org}) and humin fraction (HN-C_{org}); cold water extractable carbon (CWE-C_{org}) and hot water extractable carbon (HWE-C_{org}) as well as black carbon (BC). The process of optimisation and adaptation of OM fractionation, involved introducing modifications to the existing methodologies (the CWE-C_{org} determination method with extended extraction time; the HS determination method including fractionation with FU-C_{org} separated extraction and without FA-C_{org} purification on a DAX polymer resin; the BC determination method with carbonate content determination without addition of a strong acid for decalcification) and establishing validation parameters for the methods applied (precision, repeatability, systematic and proportional error, method correctness).

Assessment of the methods for extraction of the OM analysed fractions (humic substances, cold and hot water extractable carbon, black carbon) provided objective evidence for correctness of the introduced methodologies under conditions of their use, and fulfilment of the qualitative criteria assumed (ISO VIM:2006; ISO/IEC 17025:2018) i.e. correctness, precision and no constant error present in the methods. These validation parameters indicated that the analysis processes were conducted reliably and provided meaningful and credible results that may be applied in the research discussed, which in turn allowed for Objective 2 implementation.

The implementation of Objective 2 included analysis of agricultural soils (upper layer of soil) potentially contaminated with PAHs, subject to strong and prolonged industrial anthropopressure (western sub-region of the Silesian Province, Czerwionka-Leszczyny Commune). Samples were subject to evaluation of basic physical and chemical properties, content of 16 PAHs (16 compounds from the US EPA list, 1976) and analyses of OM fraction content according to developed methods during implementation of Objective 1.

The total content of 16 PAHs in soils from the investigated area varied, and the mean value was slightly higher than in agricultural soils in other contaminated areas. High molecular weight PAHs (≥4 rings in a molecule) of pyrogenic origin dominated in the soils, which was the result of high industrial pressure, mainly related to the mining industry. Low molecular weight PAHs (<4 rings in a molecule) constituted an minor part of the total PAHs content, due to their high volatility and low intensity of petrogenic emission sources.

The total OM content varied depending on land usage. Grasslands and fallow lands had higher C_{org} content than soils from arable lands. Most soils exhibited a high humification index ($HI = HA\text{-}C_{org} / FA\text{-}C_{org}$) and a high humification degree ($DH = (HN\text{-}C_{org} / C_{org})*100$), which indicate a high content of stable forms of OM. Among the investigated fractions, the HS were predominated ($HN\text{-}C_{org} > HA\text{-}C_{org} > FA\text{-}C_{org} > FU\text{-}C_{org}$ in soils of grasslands and fallow lands, and $HA\text{-}C_{org} > HN\text{-}C_{org} > FA\text{-}C_{org} > FU\text{-}C_{org}$ in arable soils), while water extractable carbon fractions ($HWE\text{-}C_{org} > CWE\text{-}C_{org}$) and the "black carbon" fraction (BC) comprised the smallest part of OM.

The content of organic carbon in soils has proved to be the key parameter influencing the assessment of the PAH–OM relation. In soils with low C_{org} content ($C_{org} < 12\ g \cdot kg^{-1}$), the potential of PAH accumulation depends mostly on physical and chemical properties of soils (grain-size composition, pH), while in soils with high C_{org} content ($C_{org} > 12\ g \cdot kg^{-1}$) – mostly on the OM fractional composition. Land usage had also a considerable impact on C_{org} content. Therefore, significant OM–PAH correlations were found in grassland and fallow land soils with a high C_{org} content ($C_{org} > 12$ g·kg^{-1}). Assessment of the OM fractional composition on PAHs accumulation in soils confirmed that the retention of this contaminants (in particular high molecular weight PAHs containing ≥4 rings in a molecule) depends mostly on stable forms of OM, i.e. HN and BC, whereas the impact of other HS fractions, including FU, FA, HA, and the DOC fraction was negative and dependent on their share in the total C_{org} content. Although ambiguous relations between HA and PAHs content were found in the soils (positive correlation with PAHs only in grassland areas and negative correlation between HA-C_{org} and PAHs in soils with high C_{org} content ($C_{org} \geq 12$ g·kg^{-1})), the PCA analysis (Table 47) and literature data (Hu et.al., 2000; Pan et.al., 2006; Pan et.al., 2007) indicates that humic acids co-participate in accumulation processes of the analysed contaminants, playing an intermediate role which, due to the limited scope of research, has not been fully identified.

It has been found that PAH accumulation processes in soil depend significantly on the OM content and their fractional composition, and the mutual relations between numerous factors related to PAH and OM properties.