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SUMMARY OF THE DOCTORAL DISSERTATION

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Study content of trace elements and rare earths elements in sewage sludge from selected wastewater treatment plants in Poland

Sewage sludge is the organic-mineral solid phase produced during the wastewater treatment process. It is estimated that it accounts for about 1-2% or even 3% of the total volume of wastewater flowing into the wastewater treatment plants and contain more than half of the total pollutant load contained therein. The processes of sludge treatment, stabilization, dewatering, and management are all crucial elements of the operation of a wastewater treatment plant. That said, they also cause many problems. Improper and inefficient sludge management can pose a real threat to the environment and human health.

So far, most of the research which has been devoted to sewage sludge has focused on studying its fertilizer value (nitrogen, phosphorus). identifying the composition of organic matter, and determining the total content of heavy metals (including cadmium, copper, nickel, lead, zinc, mercury, and chromium) as well as the forms of their occurrence that determine their mobility and bioavailability. The occurrence of other trace elements and rare earth elements in sewage sludge has practically remained unaddressed.

The research work undertaken in this study was primarily aimed at expanding the knowledge on the occurrence of trace elements in sewage sludge, providing data on the occurrence of REEs in the sludge from diverse wastewater treatment plants - both in terms of types of wastewater treated and of technological processes used. Specific objectives included the comparison of the various trace element and REE content in the sewage sludge produced at municipal and industrial installations, assessing the contamination of the sewage sludge by said trace elements and REEs, based on the values of their geoaccumulation index (I_{geo}), development of a normalization of the obtained REE results concerning sedimentary rocks, soils and subsoils from the area of Poland, discussion of the enrichment/depletion of this group of elements in sewage sludge , as well as determination of the relationship (correlation) between the measured major elements, trace elements, and REE in municipal and industrial sewage sludge.

The study used 49 sludge samples (11 from industrial wastewater treatment plants and 38 from municipal wastewater treatment plants) collected in 2013-2014 during the implementation of the project *Variability of phase composition and content of trace elements and rare earth elements in sewage sludge from selected wastewater treatment plants* sponsored by the funds allocated to PIG-PIB for statutory activities . Content measurements of major elements (Al, Ca, Fe, K, Mg, Na, P, and S) and of trace elements (Ag, As, Ba, Cd,

Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Sr, Ti, V and Zn) were performed by inductively coupled plasma optical emission spectrometry (ICP-OES). Mercury was analyzed using atomic absorption spectrometry (AAS). For samples for which results were obtained outside the method's measurement range, atomic absorption spectrometry combined with cold vapor generation (CV-AAS) was used. Total organic carbon (TOC) was determined by coulometric titration, while tests for rare earth elements were performed by inductively coupled plasma mass spectrometry (ICP-MS).

In sludge from industrial wastewater treatment plants, the highest average contents among the major elements were calcium (median 15.84%) and total organic carbon (median 2.07%), while the lowest median values were recorded for potassium (0.08%) and sodium (0.177%). In municipal sewage sludge, the highest median concentration values were indicated for total organic carbon (median 21.30%) and calcium (median 3.54%), while the lowest second quartile values were found for sodium (0.093%) and potassium (0.23%).

Based on the analysis of trace element results, it was found that sludge from industrial wastewater treatment plants contained on average the highest levels of manganese (median 1,112 mg/kg), zinc (median 466 mg/kg), and copper (median 225 mg/kg). In contrast, the studied sludge from municipal wastewater treatment plants had the highest median values for zinc (829 mg/kg), manganese (284 mg/kg) and copper (215 mg/kg).

The average of total REE content in sludge from industrial wastewater treatment plants was 9.47 mg/kg, while sludge from municipal wastewater treatment plants had a median value of total REE content of 13.5 mg/kg (elements for which the percentage of results below the determination limit was at least 50% were not included in the calculations). The median concentration of yttrium in sludge produced in industrial facilities was calculated to be 2.1 mg/kg, while the municipal sewage sludge had an average concentration of 2.2 mg/kg.

Based on the calculated values of the coefficient of variation of the quarter deviation, it was found that sludge from industrial wastewater treatment plants was characterized by a much greater range of variation in the occurrence of the determined elements than sludge from municipal installations. A very strong variation in content relative to the median in the studied set of industrial sludge samples indicated iron, total organic carbon, arsenic, cobalt, copper, mercury, manganese, molybdenum, nickel, lead, tin, titanium, zinc, rare earth elements (except cerium) and yttrium. Sludge from municipal wastewater treatment plants, had no significant variation observed in the content of any of the elements. The observed greater variation in elemental content in sludge from industrial wastewater treatment plants is a consequence of the very large differences in the chemical composition of the wastewater generated by the industrial plants (resulting primarily from the business profile, as well as the technologies and raw materials used). The lower variability in the occurrence of the elements in municipal sludge is mainly due to the introduction of domestic wastewater into the sewage system.

The studied sludge from municipal and industrial wastewater treatment plants showed statistically significant differences in the average content (medians) of calcium, potassium, magnesium, sodium, phosphorus, total organic carbon, arsenic, barium, cadmium, manganese, lead, strontium, titanium, and vanadium. For other elements, including REE, there were no significant differences between the medians of their content in municipal and industrial sewage sludge.

Normalization of REE content in samples from both, industrial and municipal wastewater treatment plants showed that they were less abundant in rare earth elements when compared against the standards used: the Post-Archean Australian Shale (PAAS)-normalized rare earth element (REE) patterns of geochemical standards with soils and subsoils from Poland. A slight deviation from this rule was observed only in the case of sludge from the Wastewater Treatment Plant of the Chemical Plant „Siarkopol" Tarnobrzeg S.A.

The normalization results did not reveal regularities regarding the occurrence of europium and cerium anomalies for any of the tested sets of sewage sludge samples. It was also found that there was no clear fractionation into LREE and HREE in the two studied collections. The calculated values of the La/Yb(PAAS) ratio for individual samples from industrial facilities ranged from 0.55 to 1.45, while those from municipal wastewater treatment plants ranged from 0.74 to 3.14.

5 out of the 38 municipal sewage sludge samples contained higher concentrations of heavy metals than the permissible values specified in the Regulation of the Minister of the Environment of February 6, 2015, on the use of municipal sewage sludge. In 4 of the samples, the exceedances involved one metal (Zn), while in 1 sample, an above-normal content of two metals (Zn and Cr) was determined.

Significant positive correlation was found between arsenic and cadmium, cadmium and lead, and copper and molybdenum in the studied sludge from industrial wastewater treatment plants. In municipal sewage sludge none of the major and trace elements correlated very strongly. Very influential and strong positive correlations were observed between rare earth elements, REE, and yttrium in both groups.