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An investigation of rare earth elements in sewage sludge generated in Poland

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Abstract: According to Statistics Poland, an average of around 1 million tonnes DM of sewage sludge has been generated in Poland annually over the past several years, of which approximately 30% has been used in nature, e.g. in agriculture, to grow plants for compost production, or for land reclamation (Statistics Poland 2004–2022). Most research on sewage sludge has focused on investigating its fertilizing value (nitrogen, phosphorus), identifying the composition of organic matter and determining the total content of heavy metals (including primarily cadmium, copper, nickel, lead, zinc, mercury and chromium) and the forms of their occurrence that determine their mobility and bioavailability. The occurrence of rare earth elements (REEs) in sewage sludge has hardly been addressed in research, even though their presence in production processes and everyday objects is increasingly common. The results presented in this article of studies of the concentrations of individual REEs in sewage sludge from selected industrial and municipal wastewater treatment plants located in Poland indicate that they are significantly lower than the average lanthanide level in the Earth's crust. This may suggest that anthropogenic sources of REEs do not affect the composition of the wastewater and sludge studied. The calculated median concentration of ∑REE in sludge from industrial wastewater treatment plants is 9.47 mg/kg, whereas in municipal sewage sludge, the midpoint value for REE concentration is 13.5 mg/kg. Normalization of the obtained results with respect to Post-Archean Australian Shale (PAAS) and to topsoil and subsoil from Poland shows that the sludge is generally depleted in REE relative to the standards used. An assessment of the contamination of sewage sludge with rare earth elements, based on the calculated values of the geoaccumulation index (I_{geo}) for these elements, also shows that the content of lanthanides in the studied sewage sludge is lower than in the soils of Poland.

Keywords: sewage sludge, rare earth elements, industrial/ municipal wastewater treatment plants

INTRODUCTION

Geochemically, rare earth elements, also called lanthanides or abbreviated REEs, comprise 15 metals with ordinal numbers ranging from 57 (La) to 71 (Lu). Due to their high chemical (resulting from their specific electron shell structure) and geochemical similarity, REEs occur in nature isomorphically (excluding radiogenic promethium), mainly as trivalent cations (exceptions are Ce, which can also occur as the Ce^{4+} ion, and Eu, which can occur as the Eu^{2+} ion) and show an affinity to combine with oxygen (e.g. Kabata-Pendias & Mukherjee 2007, Paulo & Krzak 2015). The average concentration of total REEs in the Earth's crust is approximately 120–190 mg/kg (Long et al. 2010, Paulo & Krzak 2015). Of all REEs, cerium (average 60 mg/kg), lanthanum (average 30 mg/kg) and neodymium (average 28 mg/kg) show the highest concentrations. Thulium and lutetium, despite being the least abundant of the lanthanides (average 0.5 mg/kg), are nevertheless found in the Earth's

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crust in higher concentrations than elements such as antimony, bismuth, cadmium or thallium (Gambogi & Cordier 2012).

Rare earth elements have been used on an industrial scale since the 1960s. As their separation and purification are demanding analytically and technically, initially the so-called mischmetal, i.e. an unseparated REE mixture also known as a cerium mixture, was mainly used (Charewicz 1990, Gupta & Krishnamurthy 2005, Paulo & Krzak 2015). Currently, production processes use either elements in the free (metallic) state, or their compounds (mainly oxides) (Paulo & Krzak 2015), and demand for REEs is steadily increasing. USGS data (2022) shows that the global REE production in 2018 was 190,000 metric tonnes of REO equivalent. Estimates for 2023 indicate a value of 350,000 tonnes (USGS 2024). In terms of the main applications of REE, industries related to magnet production, metallurgy, and catalyst production dominate the market structure. Other industries for which REEs are crucial are the production of polishing agents, glass and ceramics, batteries and luminophores. In addition to these sectors, REEs are also used, e.g., in medicine or in the production of fertilizers (e.g. Goodenough et al. 2017, Filho et al. 2023). REEs are seen as one of the most important strategic raw materials, enabling both the transformation of traditional industries towards low-emission technologies and the development of advanced and latest national defence technologies (Zhang 2022, Liu et al. 2023).

Natural processes are the main factors responsible for the occurrence of REEs in the environment. However, the rapid development of REE technologies and the resulting demand for these metals are making anthropogenic sources increasingly important in the distribution of lanthanides. In addition to the mining and processing sectors, rare earth elements can be released into waters and soils as a result of waste disposal, the use of phosphate fertilizers, as well as with wastewater. It is evidenced by, e.g., a positive gadolinium anomaly observed in surface and tap waters of large cities (Verplanck et al. 2010, Wysocka et al. 2018, Balaram 2019, Wysocka et al. 2023).

The potential presence of rare earth elements in wastewater also makes it reasonable to identify their occurrence in sewage sludge that constitutes approximately 1–2% or even 3% of the total volume of wastewater flowing into treatment plants and contains more than half of their total pollution load (Oleszkiewicz 1998, Bień & Wystalska 2011). The processes of sludge treatment, stabilization, dewatering and management are an important element of the operation of wastewater treatment plants but can also bring about many problems. Inappropriate and ineffective sludge management can pose a genuine hazard to the environment and human health, especially if sludge is used for natural purposes (in agriculture, for the reclamation of degraded land, or for the production of compost). In this context, it should be noted that REEs of anthropogenic origin usually enter the environment in biologically bioavailable forms and can therefore alter the existing biogeochemical balance in a given environment (Zhang & Shan 2001). Previous results of research on the effects of REEs on soils and plant and animal organisms are ambiguous and it is likely that they may not be representative of actual environmental conditions because most experiments were conducted under laboratory conditions (Tommasi et al. 2021).

Research on the occurrence of lanthanides in sewage sludge has been conducted to varying extents, among others, in Japan (Kawasaki et al. 1998), Sweden (Eriksson 2001), China (Suanon 2017, Nkinahamira 2019) and Switzerland (Kaegi et al. 2021), while in Poland the issue is poorly developed. However, taking into account the need for sustainable development and the growing importance of the concept of the circular economy, the issue seems to be an intriguing one. Furthermore, in terms of the natural use of sewage sludge and especially in agriculture, more data on its chemical composition, and thus its potential pollutant load, may provide an important clue when taking measures aimed at maintaining the chemical balance of soil ecosystems and their biodiversity.

The paper presents the results of a study of REE content in 49 sewage sludge samples from selected industrial and municipal wastewater treatment plants in Poland. The calculations and tests were performed to compare the variation in REE content in sewage sludge generated in municipal and industrial installations. An assessment of REE contamination of the studied sewage sludge was also carried out on the basis of I_{geo} geoaccumulation index values, taking the lanthanide content of Poland's soils as the geochemical background. The enrichment/depletion of the sewage sludge with rare earth elements was assessed on the basis of REE contents normalized with respect to PAAS and to topsoil and subsoil from the area of Poland. In addition, relationships (correlations) between REEs in municipal and industrial sewage sludge were analysed.

MATERIALS AND METHODS

Collection of sewage sludge samples

Sludge samples were collected from nine industrial wastewater treatment plants representing the following industries: chemical (fertilizer production) (IWTP 1 and IWTP 2), pulp and paper (IWTP 3–6), electrical engineering (IWTP 7), metallurgy (IWTP 8) and mining and metallurgy (IWTP 9), and from 28 municipal wastewater treatment plants (MWTP 10–37) located in Poland.

The fieldwork was carried out between October and December 2013 and in July 2014. Fresh sludge samples were collected from installations whose owners and/or operators agreed to collect material for testing, after dewatering. At 12 treatment plants, where older batches of sludge were temporarily stored, additional sludge samples were taken (marked with "*"). A total of 49 sludge samples were taken for testing, including 11 samples from industrial treatment plants and 38 samples from municipal treatment plants. As the selection of sampling sites (based on the consents of the owners and/or operators of the treatment plants) did not comply with the principles of representativeness, hence the samples discussed in this article are non-representative ones.

Each sludge sample was collected in 0.5 litre plastic (polypropylene) containers (directly, e.g. by placing the container under the machine press or using a plastic spatula).

Analytical methods

The sludge material was collected and delivered to the Central Chemical Laboratory of the Polish Geological Institute – National Research Institute for testing. In accordance with the research procedures, air-dry sediment samples were grated and dissolved in *aqua regia* ($3HCl + HNO_3$), and then the contents of rare earth elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer ELAN II DRC apparatus. The limit of determination of the method was 0.5 mg/kg for La, Ce, Pr and Nd, and 0.05 mg/kg for Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

Methods of results evaluation and interpretation

Statistical processing of the study results was carried out using Microsoft Office Excel 2010 spreadsheet and the STATISTICA 12 software. Taking into account the different nature of municipal sewage sludge and that produced in industrial wastewater treatment plants (determined, in particular, by the type and composition of wastewater from which the sludge is derived), selected measures of descriptive statistics were first calculated for the elements studied: arithmetic mean, geometric mean, median, percentiles (25 and 75), and standard deviation. If the content of the determined element was below the limit of determination of the analytical method, a value equal to half the detection limit was taken in the calculation of its measures, although the actual concentrations in some samples may have been lower. Considering elements for which the percentage of results below the limit of determination exceeded 50% (praseodymium in industrial sewage sludge samples and thulium and lutetium in industrial and municipal sludge samples), the calculation of selected measures of descriptive statistics was abandoned. The normality of the distribution of the determined variables was then examined using the Shapiro–Wilk test. As the test result for some elements (despite data transformation) was negative, positional statistical measures and non-parametric tests were used to interpret the results.

The coefficient of variation of the quartile deviation (positional coefficient of variation) – V, was used to assess the variation in the content of rare earth elements in industrial and municipal sewage sludge, calculated according to the formula:

$$V = \frac{Q}{M_e} \cdot 100\% \qquad (1)$$

where: Q – quartile deviation, M_e – median.

To test the hypothesis that there is no shift in the distributions taken for comparison, i.e. that the differences between the medians of the variables in the sample sets (in sludge from industrial wastewater treatment plants and in sludge generated in municipal installations) are not significant, the Mann–Whitney U test was applied.

An attempt was made to assess the sludge contamination with REE by calculating the geoaccumulation index (I_{geo}), which is widely used in geochemistry. Introduced by Müller (1969), the parameter is described by the equation:

$$I_{\text{geo}} = \log_2 \cdot \frac{C_n}{1.5B_n} \tag{2}$$

where: C_n – concentration of the element under study, B_n – geochemical background value of the element.

Originally, the I_{geo} index was used to assess the degree of metal contamination in water sediments, but many authors also use it to determine the contamination level in sewage sludge (e.g. Duan et al. 2017, Chen 2019, Li et al. 2019, Nkinahamira et al. 2019, Tytła 2019, Latosińska et al. 2021, Sundha et al. 2022). In this paper, the median value of REEs in Poland's soils, calculated from data selected from the *Geochemical Atlas of Europe* (De Vos et al. 2006), is used as the geochemical background for the studied REEs.

In order to verify the occurrence of the relationship between the variables in sludge samples from industrial and municipal wastewater treatment plants, and to determine it, the Spearman's rank correlation coefficient rho (ρ) was calculated; however, elements for which more than 50% of results were below the limit of determination were ignored.

REE contents are usually presented as normalized values relative to reference values in the material taken as a reference standard (e.g. in meteorite, sedimentary rocks, soil). Therefore, in this publication, the results obtained for REE contents in sludge from industrial and municipal wastewater treatment plants were normalized relative to the average REE content of Post-Archean Australian Shale (PAAS) (Taylor & McLennan 1985). The PAAS is characterized by a negative europium anomaly relative to the chondrites and shows enrichment with LREE (La-Eu) relative to HREE (Gd-Lu). Studies have shown that the REE content is generally higher in younger sediments (Nance & Taylor 1976); hence, this method is considered representative in the studies of hypergenic processes, including environmental studies. Taking into account the natural use of sewage sludge, the determined REE contents were also normalized in relation to the average content of these elements in Poland's topsoil and subsoil.

RESULTS AND DISCUSSION

The contents of rare earth elements in sludge samples collected from industrial wastewater treatment plants were characterized by a wide range of variability (Fig. 1A). The sludge from industrial wastewater treatment plants contained an average of 9.47 mg REE/kg. Lanthanum was found in the concentration range from 0.8 to 67.1 mg/kg, cerium – from 1.8 to 69.4 mg/kg, praseodymium concentrations ranged from below the limit of determination to 12.6 mg/kg, neodymium – from 0.8 to 51.2 mg/kg, samarium – from 0.18 to 10.13 mg/kg, europium – from 0.05 to 2.46 mg/kg, and gadolinium – from 0.19 to 11.25 mg/kg. The minimum contents of terbium, holmium, thulium and lutetium were below the limit of determination of the method used, while the maximum concentrations of these elements were, respectively: 1.65 mg/kg, 2.41 mg/kg, 0.93 mg/kg, and 0.95 mg/kg. The concentrations of dysprosium, erbium and ytterbium were 0.17–10.65 mg/kg, 0.09–7.21 mg/kg, and 0.08–5.84 mg/kg, respectively. The highest concentrations of rare earth elements were found in samples from a treatment plant receiving wastewater from the chemical industry (fertilizer production), with the ΣREE of 253.8 mg/kg (sample IWTP 2*) and 141.2 mg/kg (sample IWTP 2), respectively. In the sludge sample from another treatment plant receiving wastewater generated by a chemical plant (IWTP 1), ΣREE content were much lower and attained a value 34.9 mg/kg. The lowest content was determined in a sample from the IWTP 3 treatment plant, which receives wastewater from paper production (ΣREE 4.6 mg/kg). Other sludge generated by facilities operating in the pulp and paper industry contained rare earth elements in the range of 7.5–10.4 mg/kg. A similar range of lanthanides content was found in sludge from the treatment plants of the mining and metallurgy industry (5.1–8.5 mg/kg) and metallurgy (9.1 mg/kg), while a sample from the wastewater treatment plant from an electrical engineering factory contained 21.3 mg/kg REE.

The samples of municipal sewage sludge contained (Fig. 1B) 1.3–6.6 mg/kg of lanthanum and 2.3–11.3 mg/kg of cerium. Praseodymium concentrations were found ranging from below the limit of determination to 1.5 mg/kg, neodymium – from 0.9 to 5.9 mg/kg, samarium – from 0.17 to 1.21 mg/kg, europium – from 0.03 to 0.28 mg/kg, and gadolinium – from 0.22 to 1.15 mg/kg. The minimum contents of terbium, holmium, thulium and lutetium were below the limit of determination of the method, while the maximum concentrations of these elements were 0.16 mg/kg, 0.18 mg/kg, 0.06 mg/kg, and 0.06 mg/kg, respectively. Dysprosium was present in the range of 0.13–0.91 mg/kg, erbium – 0.07–0.50 mg/kg and ytterbium – 0.07–0.42 mg/kg. The concentration of total rare earth elements in the sludge samples from municipal wastewater treatment plants varied between 5.6 and 28.9 mg/kg, while the median ΣREE was 13.5 mg/kg.

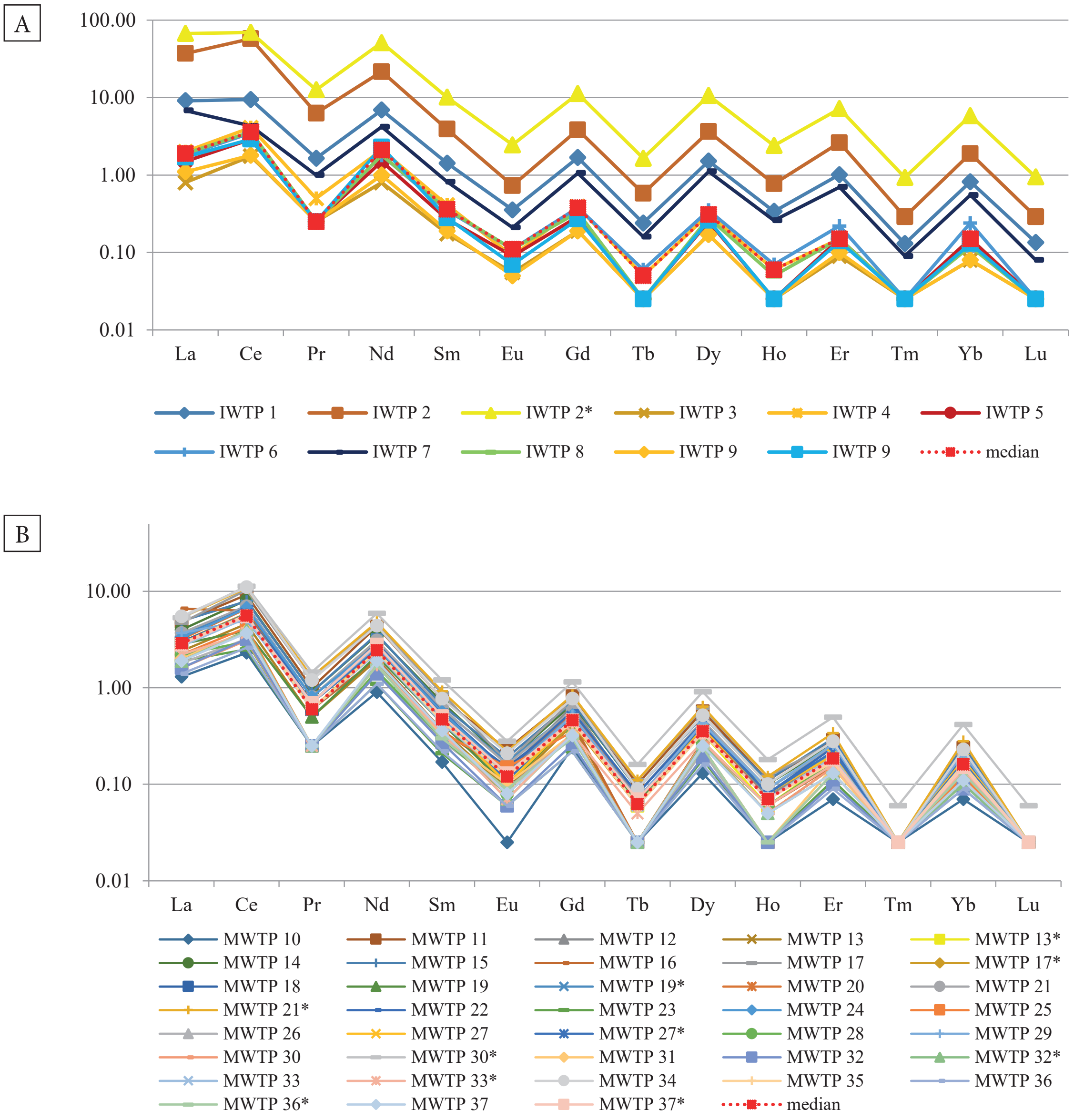


Fig. 1. *Rare earth element contents [mg/kg] of sludge samples from industrial (A) and municipal (B) wastewater treatment plants*

A review of the literature indicates that publications on the REE content in sewage sludge from industrial installations are scarce. The paper by Kawasaki et al. (1998) presents, among others, the results of a study of sludge generated by wastewater treatment processes from food ($n = 10$) and chemical ($n = 10$) industry plants. The contribution by Gao et al. (2012) provides information on REE content of a single sludge sample from an industrial wastewater treatment plant. By comparing the results obtained by the present author, it was found that the mean and median values of individual REEs for the studied set of sludge samples from industrial wastewater treatment plants in Poland are higher than in sludge from the chemical industry, studied by Kawasaki et al. (1998). This statement should be supplemented with the information that the calculated central measures were influenced by relatively high REE contents in the IWTP 2 and IWTP 2* samples. The concentrations of some REEs, especially lanthanum and cerium, were more than twice as high as their concentrations in the sample studied by Gao et al. (2012), while the median values of the other REEs calculated for the studied group of sludge were lower.

The literature on the occurrence of REEs in municipal sewage sludge is somewhat more extensive, and the results obtained by the author were compared to the results of studies conducted in Switzerland (Kaegi et al. 2021), Sweden (Eriksson 2001) and Japan (Kawasaki et al. 1998). The data summarized in Table 1 show that the cluster of municipal sewage sludge samples studied by the author is characterized generally by the lowest concentrations of rare earth elements. The sum of the average contents of the individual REEs calculated for the cluster (13.5 mg/kg d.m.) was 1.8–3.7 times lower than in the groups taken for comparison (Switzerland 24.54 mg/kg, Japan 30.5 mg/kg, and Sweden 50.77 mg/kg). Although the Swedish sewage sludge in general showed the highest enrichment with rare earth elements, the highest average cerium content was found in sludge from Switzerland. The elevated level of this element was associated with the influx of industrial wastewater into several of the studied installations (Kaegi et al. 2021).

The calculated values of the coefficient of variation of the quartile deviation (V) (Table 2) indicate that sludge from industrial installations is characterized by a very strong variation in the occurrence of most REEs; only cerium shows a strong variation from the median in a narrowed area of variation.

Table 1

Comparison of the concentrations of REE in municipal sewage sludge with the results from studies by other authors

Element	**Medians of the concentrations of REEs in municipal sewage sludge**			
	This study	**Kaegi et al. (2021)**	**Eriksson (2001)**	**Kawasaki et al. (1998)**
	$n = 38$	$n = 63$	$n = 47$	$n = 14$
	[mg/kg]			
La	3.1 (2.9)	10.90 (7.05)	16 (13)	6.70 (6.17)
Ce	5.7 (5.6)	26.24 (10.26)	24 (20)	14.1 (12.5)
Pr	0.6 (0.6)	1.12 (0.93)	2.8 (2.5)	1.48 (1.47)
Nd	2.6 (2.5)	4.09 (3.41)	11 (8.0)	6.00 (5.86)
Sm	0.49 (0.47)	0.94 (0.67)	1.8 (1.3)	1.02 (1.01)
Eu	0.13 (0.12)	0.20 (0.15)	0.30 (0.26)	not tested
Gd	0.49 (0.46)	0.87 (0.67)	2.0 (1.7)	1.18 (1.05)
Tb	0.06 (0.07)	0.11 (0.09)	0.34 (0.26)	0.16 (0.16)
Dy	0.37 (0.36)	0.61 (0.51)	1.7 (1.3)	0.93 (0.87)
Ho	0.07 (0.07)	0.12 (0.10)	0.40 (0.35)	0.19 (0.18)
Er	0.20 (0.19)	0.35 (0.30)	1.0 (0.9)	0.57 (0.54)
Tm	(<0.05)	0.05 (0.04)	0.21 (0.16)	0.08 (0.08)
Yb	0.17 (0.16)	0.36 (0.32)	1.1 (0.9)	0.54 (0.53)
Lu	(<0.05)	0.05 (0.04)	0.19 (0.14)	0.08 (0.08)

Table 2
Variation in REE content in sludge from industrial and municipal wastewater treatment plants based on the coefficient of variation of the quartile deviation (V)

Element	**Coefficient of variation of the quartile deviation [%] in the studied sludge samples**	
	from industrial wastewater treatment plants	**from municipal wastewater treatment plants**
La	200	29
Ce	92	27
Pr	233	42
Nd	129	24
Sm	161	24
Eu	132	25
Gd	186	26
Tb	210	38
Dy	205	25
Ho	258	29
Er	290	27
Tm	not calculated	not calculated
Yb	233	22
Lu	not calculated	not calculated

LEGEND

$V > 100\%$	very high variation
$45\% \leq V \leq 100\%$	high variation
$25\% \leq V < 45\%$	moderate variation
$V < 25\%$	very low variation

In sludge from municipal wastewater treatment plants, the observed variation in the content of most REEs is moderate – the exceptions are neodymium, samarium and ytterbium, whose concentrations in the studied set are characterized by low variation with respect to the median.

The Mann–Whitney U test showed no significant difference in the average REE content between sludge from municipal and industrial wastewater treatment plants.

Assessment of sewage sludge contamination by rare earth elements

The geoaccumulation index was calculated for individual rare earth elements in the studied sewage sludge samples by taking the median value of REEs in soils of Poland, calculated from data selected from the *Geochemical Atlas of Europe* (De Vos et al. 2006), as geochemical background values.

The I_{geo} index of nine out of 11 industrial sludge samples indicated the absence of REE contamination (Table 3). Moderate REE contamination (Class 2) was found in sample IWTP 2 (from a treatment plant receiving wastewater generated from fertilizer production). The other sample from the same installation (IWTP 2*) shows moderate to high contamination with REE (Class 3). In comparison, none of the tested sludge samples from municipal wastewater treatment plants was contaminated by REE.

Table 3
Geoaccumulation index (I_{geo}) values calculated to assess the degree of sewage sludge contamination with REE

Sample no.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE Class
IWTP 1	−0.575	−1.585	−0.910	−0.734	−0.523	−0.059	−0.237	−0.392	−0.370	−0.305	−0.302	−0.791	−0.767	−0.684	0
IWTP 2	1.452	1.015	0.980	0.913	0.928	0.961	0.952	0.881	0.889	0.874	1.073	0.366	0.438	0.366	2
IWTP 2*	2.307	1.284	1.980	2.158	2.301	2.714	2.506	2.389	2.438	2.521	2.534	2.047	2.066	2.078	3
IWTP 3	−4.083	−3.985	−3.413	−3.842	−3.513	−2.644	−3.381	−3.392	−3.531	−3.807	−3.790	−2.907	−4.124	−2.907	0
ITWP 4	−2.761	−2.797	−2.676	−2.450	−2.325	−2.059	−2.344	−2.655	−2.664	−2.807	−3.053	−2.907	−3.317	−2.907	0
IWTP 5	−3.176	−3.297	−3.413	−2.935	−2.928	−2.059	−2.771	−3.392	−2.975	−3.807	−3.053	−2.907	−3.217	−2.907	0
IWTP 6	−2.913	−3.026	−3.413	−2.672	−2.554	−1.769	−2.381	−2.392	−2.489	−2.585	−2.501	−2.907	−2.539	−2.907	0
ITWP 7	−0.996	−2.729	−1.676	−1.450	−1.325	−0.837	−0.901	−0.977	−0.824	−0.692	−0.831	−1.322	−1.343	−1.492	0
IWTP 8	−2.835	−2.985	−3.413	−2.672	−2.513	−1.769	−2.585	−3.392	−2.811	−3.070	−3.053	−2.907	−3.539	−2.907	0
IWTP 9	−3.624	−3.985	−3.413	−3.520	−3.435	−2.907	−3.381	−3.392	−3.531	−3.807	−3.638	−2.907	−4.124	−2.907	0
MWTP 10	−3.800	−4.023	−3.812	−4.122	−4.112	−4.044	−3.577	−3.907	−4.352	−4.209	−4.636	−3.170	−4.755	−3.248	0
MWTP 11	−1.915	−2.023	−2.076	−1.866	−1.933	−1.106	−1.805	−2.170	−2.220	−2.335	−2.585	−3.170	−2.977	−3.248	0
MWTP 12	−2.413	−2.502	−2.590	−2.485	−2.445	−1.822	−2.140	−2.684	−2.805	−2.794	−3.051	−3.170	−3.475	−3.248	0
MWTP 13	−2.915	−3.023	−3.076	−2.970	−2.990	−2.459	−2.770	−3.907	−3.298	−3.472	−3.536	−3.170	−3.862	−3.248	0
MWTP 13*	−2.642	−2.714	−2.812	−2.707	−2.676	−2.170	−2.639	−2.907	−2.965	−3.209	−3.273	−3.170	−3.755	−3.248	0
MWTP 14	−2.178	−2.207	−2.228	−2.163	−2.050	−1.542	−2.075	−2.322	−2.352	−2.472	−2.743	−3.170	−3.103	−3.248	0
MWTP 15	−1.886	−2.243	−2.228	−2.122	−2.155	−1.381	−2.013	−2.322	−2.380	−2.335	−2.536	−3.170	−2.918	−3.248	0
MWTP 16	−1.456	−2.569	−2.812	−2.970	−3.030	−1.929	−2.671	−3.907	−3.245	−3.209	−3.443	−3.170	−3.562	−3.248	0
MWTP 17	−1.946	−1.860	−1.812	−1.800	−1.740	−1.542	−1.953	−2.032	−2.098	−2.209	−2.688	−3.170	−3.103	−3.248	0
MWTP 17*	−2.593	−2.664	−2.590	−2.648	−2.585	−2.307	−2.770	−2.907	−2.883	−2.987	−3.273	−3.170	−3.655	−3.248	0
MWTP 18	−2.593	−2.714	−2.812	−2.648	−2.615	−1.722	−2.490	−2.684	−2.805	−2.794	−3.121	−3.170	−3.392	−3.248	0
MWTP 19	−2.642	−3.261	−3.076	−2.833	−2.773	−2.307	−2.639	−2.684	−2.695	−2.624	−2.743	−3.170	−3.314	−3.248	0
MWTP 19*	−2.371	−2.397	−2.397	−2.338	−2.293	−1.542	−2.330	−2.492	−2.561	−2.624	−2.858	−3.170	−3.240	−3.248	0
MWTP 20	−2.500	−2.502	−2.397	−2.434	−2.392	−1.822	−2.408	−2.684	−2.843	−2.987	−3.195	−3.170	−3.475	−3.248	0
MWTP 21	−2.291	−2.417	−2.397	−2.338	−2.245	−1.629	−2.304	−2.492	−2.529	−2.624	−2.799	−3.170	−3.240	−3.248	0
MWTP 21*	−1.772	−1.792	−1.697	−1.707	−1.676	−1.170	−1.770	−2.032	−2.053	−2.209	−2.355	−3.170	−2.755	−3.248	0
MWTP 22	−2.456	−2.459	−2.590	−2.434	−2.367	−1.822	−2.330	−2.492	−2.593	−2.794	−2.858	−3.170	−3.240	−3.248	0
MWTP 23	−3.252	−3.903	−3.812	−3.833	−3.807	−3.044	−3.703	−3.907	−3.883	−4.209	−3.984	−3.170	−4.240	−3.248	0

MWTP 24	–2.456	–2.481	–2.397	–2.485	–2.392	–1.929	–2.462	–2.684	–2.731	–2.794	–3.051	–3.170	–3.392	–3.248	0
MWTP 25	–3.041	–3.154	–3.812	–3.122	–3.112	–1.722	–3.033	–3.907	–3.468	–4.209	–3.743	–3.170	–3.977	–3.248	0
MWTP 26	–3.330	–3.547	–3.812	–3.485	–3.392	–2.459	–3.118	–3.907	–3.593	–4.209	–3.743	–3.170	–4.103	–3.248	0
MWTP 27	–2.693	–2.765	–2.812	–2.648	–2.527	–2.307	–2.639	–2.684	–2.767	–2.794	–3.121	–3.170	–3.392	–3.248	0
MWTP 27*	–2.642	–2.689	–2.590	–2.648	–2.472	–2.170	–2.519	–2.684	–2.695	–2.794	–2.984	–3.170	–3.475	–3.248	0
MWTP 28	–3.041	–3.640	–3.812	–3.385	–3.293	–2.629	–3.118	–3.907	–3.298	–3.209	–3.355	–3.170	–3.755	–3.248	0
MWTP 29	–2.291	–2.903	–2.590	–2.537	–2.585	–2.044	–2.462	–2.684	–2.626	–2.624	–2.743	–3.170	–3.170	–3.248	0
MWTP 30	–3.500	–3.593	–3.812	–3.205	–3.155	–2.629	–3.075	–3.907	–3.298	–3.472	–3.536	–3.170	–3.562	–3.248	0
MWTP 30*	–1.772	–1.727	–1.491	–1.410	–1.281	–0.822	–1.317	–1.492	–1.545	–1.624	–1.799	–2.170	–2.170	–2.248	0
MWTP 31	–3.178	–3.261	–3.812	–3.205	–3.200	–2.307	–3.118	–3.907	–3.468	–4.209	–3.536	–3.170	–4.103	–3.248	0
MWTP 32	–3.500	–3.547	–3.812	–3.485	–3.445	–3.044	–3.462	–3.907	–3.805	–4.209	–4.121	–3.170	–4.392	–3.248	0
MWTP 32*	–3.252	–3.261	–3.812	–3.122	–3.070	–2.822	–3.118	–3.907	–3.352	–3.472	–3.743	–3.170	–4.240	–3.248	0
MWTP 33	–2.745	–2.819	–2.812	–2.769	–2.773	–2.044	–2.639	–2.907	–2.965	–2.987	–3.195	–3.170	–3.562	–3.248	0
MWTP 33*	–3.041	–3.337	–3.812	–3.205	–3.112	–2.822	–3.075	–3.170	–3.245	–3.209	–3.443	–3.170	–3.755	–3.248	0
MWTP 34	–1.719	–1.765	–1.812	–1.833	–1.933	–1.237	–1.896	–2.322	–2.352	–2.472	–2.636	–3.170	–3.039	–3.248	0
MWTP 35	–2.642	–2.714	–2.812	–2.707	–2.708	–2.044	–2.703	–2.907	–2.965	–2.987	–3.355	–3.170	–3.562	–3.248	0
MWTP 36	–3.693	–3.846	–3.812	–3.833	–3.740	–3.044	–3.703	–3.907	–4.053	–4.209	–4.273	–3.170	–4.392	–3.248	0
MWTP 36*	–3.252	–3.299	–3.812	–3.205	–3.293	–2.459	–3.256	–3.907	–3.468	–4.209	–3.743	–3.170	–3.862	–3.248	0
MWTP 37	–3.252	–3.337	–3.812	–3.044	–3.030	–2.629	–3.162	–3.907	–3.409	–3.472	–3.743	–3.170	–4.103	–3.248	0
MWTP 37*	–2.693	–2.765	–2.590	–2.485	–2.527	–1.929	–2.639	–2.684	–2.923	–2.987	–3.273	–3.170	–3.655	–3.248	0

LEGEND

I_{geo} value	Environmental Class	Designation of environmetal quality
$I_{geo} \le 0$	0	unpolluted
$0 < I_{geo} \le 1$	1	unpolluted to moderately polluted
$1 < I_{geo} \le 2$	2	moderately polluted
$2 < I_{geo} \le 3$	3	moderately to strongly polluted
$3 < I_{geo} \le 4$	4	strongly polluted
$4 < I_{geo} \le 5$	5	strongly to extremely polluted
$I_{geo} > 5$	6	extremely polluted

Correlations of REE content in sludge from industrial and municipal wastewater treatment plants

The Spearman's rank coefficient values calculated for the individual pairs of variables under study are summarized as a correlation matrix (Fig. 2). They indicate that rare earth elements in sludge from industrial wastewater treatment plants generally show very strong and strong positive correlations with each other (correlation coefficient value ρ is from 0.83 to 1.00), with the exception of praseodymium, thulium and lutetium, for which no correlation index has been calculated as more than 50% of determinations were below the limit of determination. Very strong and strong positive correlations were also found between REEs in the sludge generated by municipal installations (excluding thulium and lutetium, for which correlation coefficients have not been calculated). The occurrence of strong and very strong positive correlations between REEs in municipal sewage sludge is also documented by other authors (Suanon et al. 2017, Vriens et al. 2017). Positive correlations between metals may suggest that they had similar levels of contamination, the same sources (or a single major source) of origin and exhibited similar transport behaviour (Suresh et al. 2011, Tytła 2020).

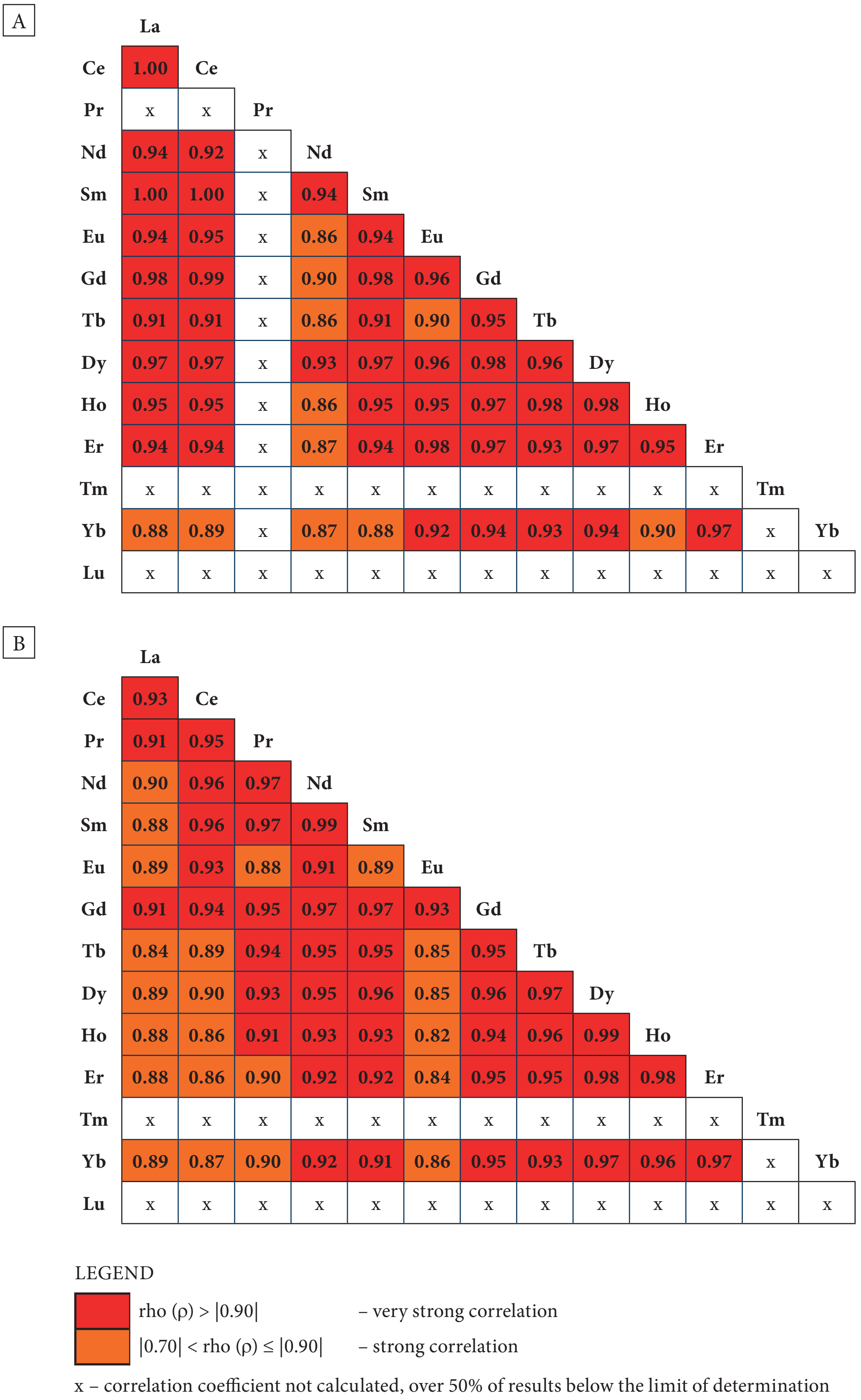
REE enrichment/depletion of sludge generated from industrial and municipal wastewater treatment plants

Applying the normalization to sedimentary rocks (PAAS) (Fig. 3A), the sewage sludge from industrial treatment plants was found to be depleted in rare earth elements – only sample IWTP 2* from an installation treating chemical plant wastewater (from fertilizer production) showed a slight enrichment with REE relative to the standard used. Values of the La/Yb(PAAS) index ranged from 0.55 to 1.45, indicating poor and, for some samples, even reverse REE fractionation. The calculated median of the La/Yb(PAAS) ratio (0.91) indicates the existence of a slight dominance of HREE over LREE in the studied set of samples from industrial wastewater treatment plants. Normalization against PAAS showed the presence of a weak positive europium anomaly (Eu/Eu*(PAAS)) in all sludge samples from industrial installations – Eu/Eu*(PAAS) values ranged from 1.06 to 1.42, excluding sample IWTP 2 (Eu/Eu*(PAAS) = 0.89).

Eu and Ce anomalies are often used as a tool to monitor redox conditions in various environmental components, including seawater and freshwater, rocks and soils. The studies show that although the occurrence of the above-mentioned anomalies is mainly dependent on the redox potential (Eh), other parameters, including pH and temperature, may also be important in forming them. The occurrence of REE anomalies in sewage sludge, as well as in wastewater, is poorly recognised in the literature, and the lack of pH and Eh measurements further precludes the possibility of drawing conclusions about the observed phenomenon. As sewage sludge is produced in wastewater treatment processes, it can be surmised that the physicochemical parameters of the wastewater and the conditions under which the sludge is formed are important elements that influence the content and fractionation of REEs.

Normalization performed on the topsoil and subsoil from Poland (Fig. 3B, C) also showed a general depletion of the industrial sludge in REE. A deviation in this respect was found in the case of samples IWTP 2 and IWTP 2*, which may suggest that the raw materials used in the plant's production processes contain rare earth elements. Alongside, it was observed that the depletion relative to topsoil was slightly lower than that relative to subsoil.

Normalization of the REE content to sedimentary rocks (PAAS) performed for sludge from municipal wastewater treatment plants showed its depletion in rare earth elements (Fig. 4A). Similar results were obtained in Switzerland (Kaegi et al. 2021), where sludge from 63 municipal installations was studied. This may suggest that wastewater generated in households and public facilities is not a significant REE carrier. The La/Yb(PAAS) ratio ranged from 0.74 to 3.14, and values indicative of reverse REE fractionation (enrichment with HREE) were found only in samples MWTP 30 and MWTP 30*. The calculated median of the La/Yb(PAAS) ratio (1.34) indicates the existence of a slight quantitative prevalence of LREE over HREE in the studied data set.



A

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	1.00												
Pr	x	x											
Nd	0.94	0.92	x										
Sm	1.00	1.00	x	0.94									
Eu	0.94	0.95	x	0.86	0.94								
Gd	0.98	0.99	x	0.90	0.98	0.96							
Tb	0.91	0.91	x	0.86	0.91	0.90	0.95						
Dy	0.97	0.97	x	0.93	0.97	0.96	0.98	0.96					
Ho	0.95	0.95	x	0.86	0.95	0.95	0.97	0.98	0.98				
Er	0.94	0.94	x	0.87	0.94	0.98	0.97	0.93	0.97	0.95			
Tm	x	x	x	x	x	x	x	x	x	x	x		
Yb	0.88	0.89	x	0.87	0.88	0.92	0.94	0.93	0.94	0.90	0.97	x	
Lu	x	x	x	x	x	x	x	x	x	x	x	x	x

B

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ce	0.93												
Pr	0.91	0.95											
Nd	0.90	0.96	0.97										
Sm	0.88	0.96	0.97	0.99									
Eu	0.89	0.93	0.88	0.91	0.89								
Gd	0.91	0.94	0.95	0.97	0.97	0.93							
Tb	0.84	0.89	0.94	0.95	0.95	0.85	0.95						
Dy	0.89	0.90	0.93	0.95	0.96	0.85	0.96	0.97					
Ho	0.88	0.86	0.91	0.93	0.93	0.82	0.94	0.96	0.99				
Er	0.88	0.86	0.90	0.92	0.92	0.84	0.95	0.95	0.98	0.98			
Tm	x	x	x	x	x	x	x	x	x	x	x		
Yb	0.89	0.87	0.90	0.92	0.91	0.86	0.95	0.93	0.97	0.96	0.97	x	
Lu	x	x	x	x	x	x	x	x	x	x	x	x	x

LEGEND

🟥 rho (ρ) > |0.90| – very strong correlation

🟧 |0.70| < rho (ρ) ≤ |0.90| – strong correlation

x – correlation coefficient not calculated, over 50% of results below the limit of determination

Fig. 2. *Matrix of correlation coefficients for industrial sludge (A), n = 11, p < 0.05 and for municipal sludge (B), n = 38, p < 0.05*

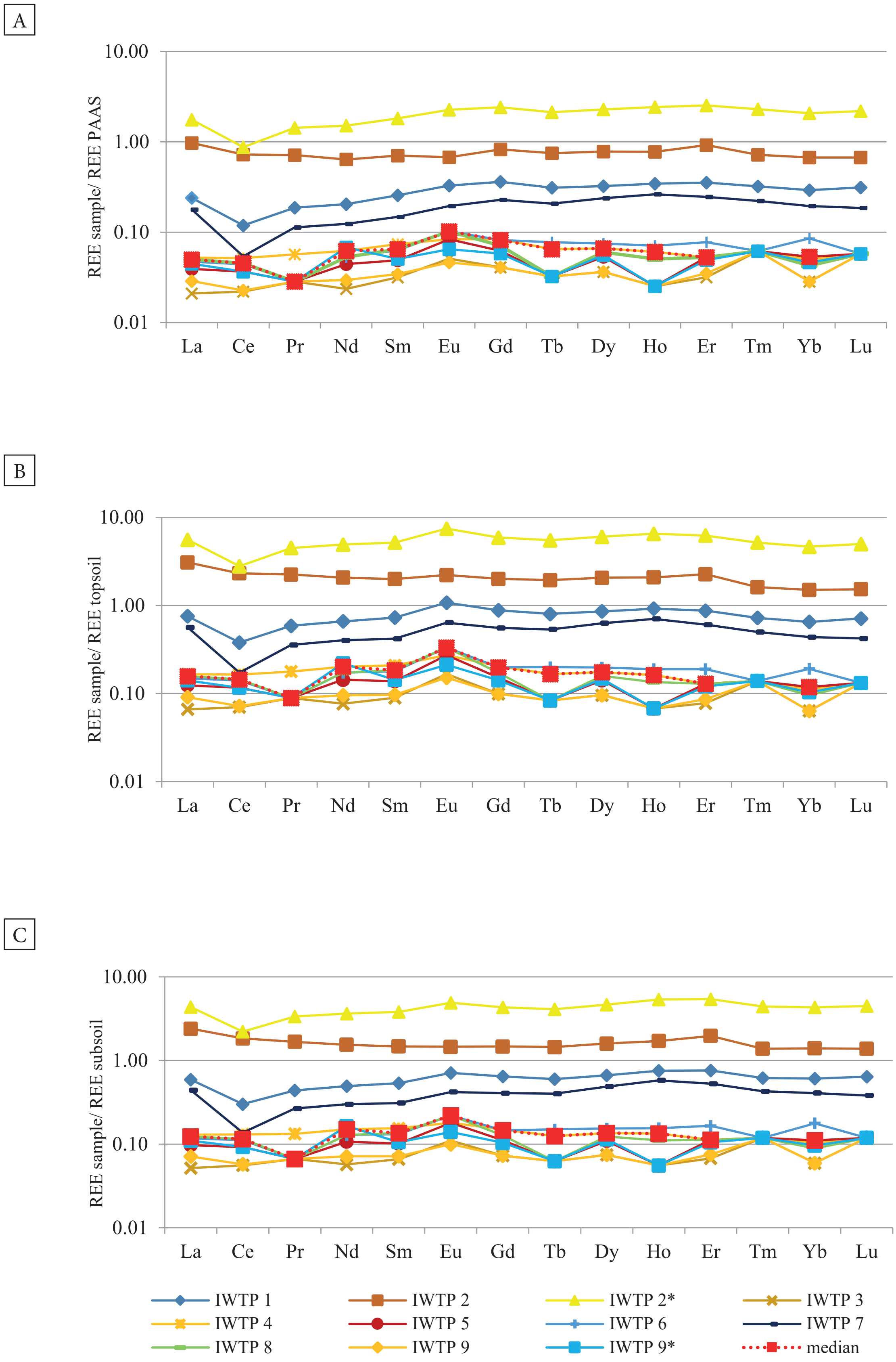


Fig. 3. *REE content [mg/kg] in sewage sludge samples from industrial treatment plants normalized to PAAS (A) and to topsoil (B) and subsoil (C) from the area of Poland*

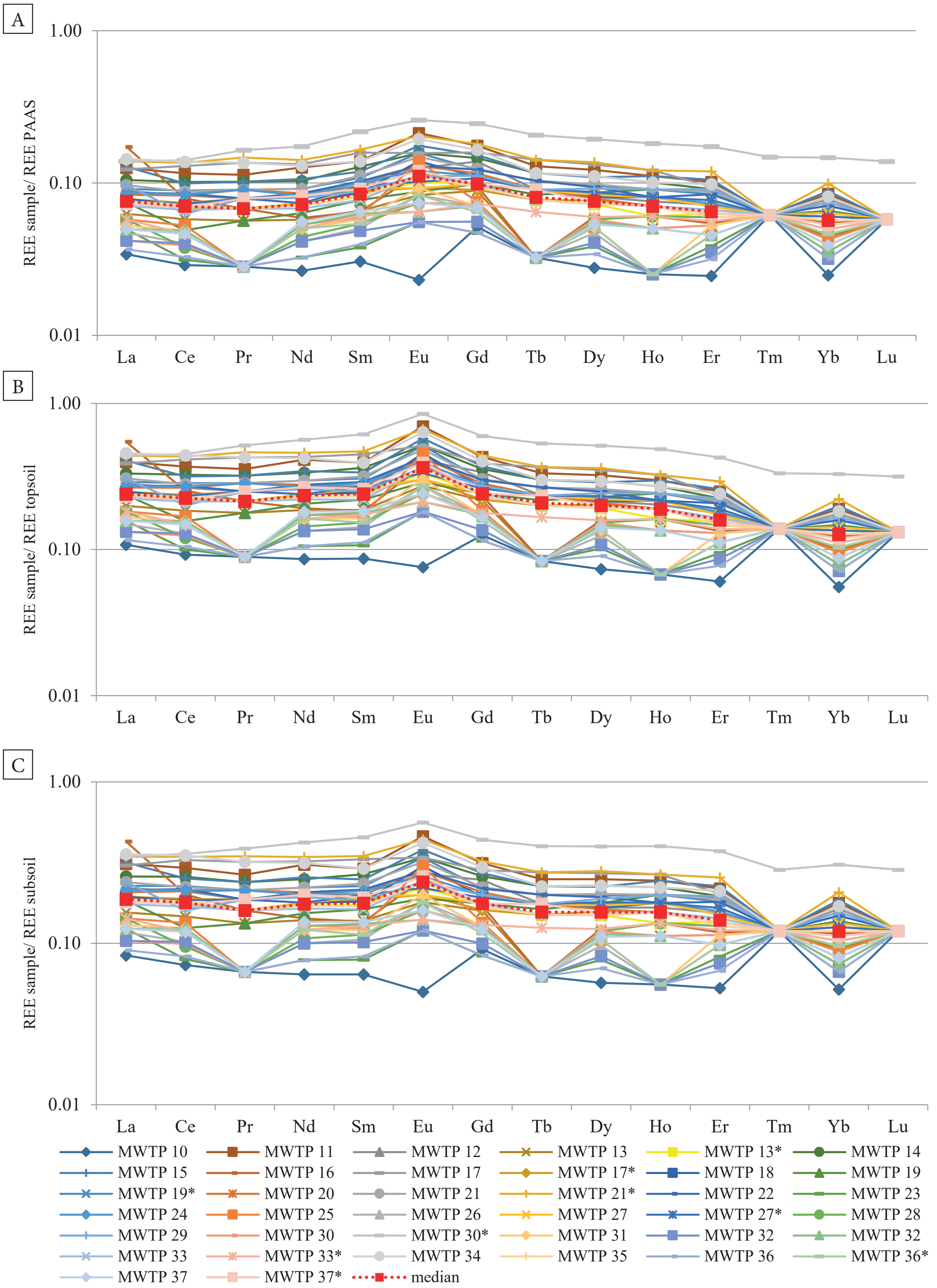


Fig. 4. *REE content [mg/kg] in sewage sludge samples from municipal sewage treatment plants normalized to PAAS (A) and to topsoil (B) and subsoil (C) from the area of Poland*

PAAS normalization showed that sludge from municipal wastewater treatment plants is characterized generally by the presence of a weak positive europium anomaly – the median of the Eu/Eu*(PAAS) ratio was 1.22, and the Eu/Eu*(PAAS) ratios for individual samples ranged from 0.58 to 2.05. Values <1 were obtained for five samples: MWTP 10, MWTP 17, MWTP 27, MWTP 32 and MWTP 33* from different treatment plants. These were both mechanical-biological treatment plants (MWTP 10, MWTP 17) and enhanced nutrient removal mechanical-biological plants. These plants were characterized by a variable load expressed by the population equivalent (p.e.): from 2,457 (MWTP 10) to 160,000 (MWTP 27). The proportion of industrial wastewater in the treated wastewater stream was also varied: from none (MWTP 10 and MWTP 33*) to 34% (MWTP 32). The parameters analysed in the study do not allow indicating the factors determining the occurrence of this phenomenon.

Normalization of the REE content to topsoil and subsoil of Poland in municipal sewage sludge showed that the studied samples are less abundant in rare earth elements while considering these standards as well (Fig. 4B, C). This suggests that the natural use of municipal sewage sludge will not result in the anthropogenic enrichment of soils with rare earth elements.

CONCLUSIONS

The present studies indicate that the content of rare earth elements in sewage sludge generated in Poland is relatively low. Sludge from both municipal and industrial wastewater treatment plants is characterized by a lower lanthanide content than the average content in the Earth's crust. However, the calculated values of the coefficient of variation of the quartile deviation showed that sludge from industrial wastewater treatment plants has a much greater range of variation in REE occurrence than sludge from municipal installations. The greater variation in the elemental content in sludge from industrial wastewater treatment plants may be a consequence of the very large differences in the chemical composition of the wastewater generated by industrial plants (resulting primarily from the business profile, as well as from the technologies and types of raw materials used). In general, however, the difference between the median values REEs of the studied sets of municipal and industrial sludge samples is not significant statistically, as indicated by the Mann–Whitney U test result. Therefore, it can be concluded with a high degree of probability that the REEs present in the sludge are most likely derived from natural sources and that their concentrations are not a criterion for distinguishing between sludge from municipal and industrial installations.

The very strong and strong positive correlations between rare earth elements are undoubtedly a consequence of the chemical (including geochemical) similarity between the metals of this group and suggest that they have a common origin in the sludge.

The results of the chemical tests and its analyses performed suggest that the sludge tested will generally not generate negative pressure on the environment due to its REE content. The geoaccumulation index values calculated taking into account the average content of lanthanides in Poland's soils indicate no contamination of municipal sewage sludge and most of that from industrial installations by REE. Similar results were also provided by the normalization of REE content performed for Australian shale (PAAS) and for topsoil and subsoil of Poland: the sludge was characterized by depletion with rare earth elements in comparison with the standards used. The slight deviation observed in the case of sludge from a treatment plant receiving wastewater generated by fertilizer production may be related to the types of raw materials used in the production process at the plant. On this basis, it can be concluded that the chemical composition of sewage sludge generated by some industries needs to be more precisely identified, especially when the sludge will be used for purposes connected with nature.

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