Athens Institute for Education and Research

ATINER

ATINER's Conference Paper Series ERT2014-1379

REE in Sewage Sludge from Selected Pulp and Paper Plants in Poland

Paulina Kostrz-Sikora
Specialist
Polish Geological Institute
Poland

Izabela Bojakowska
Professor
Polish Geological Institute
Poland

Stanisław Wołkowicz
Professor
Polish Geological Institute
Poland

An Introduction to ATINER's Conference Paper Series

ATINER started to publish this conference papers series in 2012. It includes only the papers submitted for publication after they were presented at one of the conferences organized by our Institute every year. The papers published in the series have not been refereed and are published as they were submitted by the author. The series serves two purposes. First, we want to disseminate the information as fast as possible. Second, by doing so, the authors can receive comments useful to revise their papers before they are considered for publication in one of ATINER's books, following our standard procedures of a blind review.

Dr. Gregory T. Papanikos
President
Athens Institute for Education and Research

This paper should be cited as follows:

Kostrz-Sikora, P., Bojakowska, I. and Wołkowicz, S., (2015) **"REE in Sewage Sludge from Selected Pulp and Paper Plants in Poland",** Athens: ATINER'S Conference Paper Series, No: **ERT2014-1379.**

Athens Institute for Education and Research
8 Valaoritou Street, Kolonaki, 10671 Athens, Greece
Tel: + 30 210 3634210 Fax: + 30 210 3634209 Email: info@atiner.gr
URL: www.atiner.gr
URL Conference Papers Series: www.atiner.gr/papers.htm

ISSN: **2241-2891**
04/03/2015

REE in Sewage Sludge from Selected Pulp and Paper Plants in Poland

Paulina Kostrz-Sikora
Izabela Bojakowska
Stanisław Wołkowicz

Abstract

Volume reduction and proper treatment and use of sewage sludge are high on the list of current priorities of environmental policy. This is especially the case of industrial sewage sludge, often highly varying in chemical and physical as well as sanitary properties.

Due to those differences, usability of sludge depends on results of obligatory safety tests of its chemical and bacteriological composition. Therefore, these tests do not cover a wide range of parameters, which can provide valuable information about sludge properties and usability.

The present study covered samples of sewage sludge from four wastewater treatment plants of pulp and paper plants in Poland. The samples were analyzed for concentration of rare earth elements (REE) by inductively coupled plasma mass spectroscopy (ICP-MS). The obtained results showed concentrations of LREE to be higher than those of HREE. In the case of the LREE group, concentrations of cerium, lanthanum and neodymium appeared the highest, ranging from 0.8 to 4.1 ppm. Concentrations of the remaining LREE were markedly lower, below 0.41 for europium and samarium and merely reaching the detection limit of the applied analytical method (0.5 ppm) for praseodymium in one sample only. The highest concentrations of elements of the HREE group, between 0.17 and 0.39 ppm, were recorded for gadolinium and dysprosium. Concentrations of the remaining HREE (terbium, holmium, erbium and ytterbium) range from 0.24 to less than 0.05 ppm whereas those of thulium and lutetium appeared lower than detection limit (0.05 ppm) in all the studied samples. Normalized concentrations of the lanthanum – neodymium group in the studied sewage sludge were found to be 1.5 to over 6 times higher than in chondrite. Further course of plots shows decrease in relative content of the remaining REE, down to values significantly lower than in chondrite. The recorded REE distributions normalized to the Post-Archean Australian Shale (PAAS) (Figure.1b) (McLennan, 2001) appear to be at the level from 0.02 to 0.1 of REE content in PAAS standard. It may be concluded that the REE contents recorded in the studied sludge from the pulp and paper industry are very low in comparison with those of fine-grained sedimentary rocks. Impoverishment of the studied sewage sludge in REE was also shown by normalization to arable soils of Poland as concentrations of the above mentioned elements correspond to 0.03 to 0.4 of their contents in topsoil.

Keywords: rare earth elements, sewage sludge, pulp and paper plants

Introduction

In Poland, the volume of sewage sludge has been steadily growing. According to the Local Data Bank of Central Statistical Office, sewage sludge generated at industrial treatment facilities reached an amount of 418 581 Mg, which the peak level in the last five years. Almost 29 percent of all sludge is disposed in landfills or other facilities and about 10 percent subjected to thermal treatment. The share of sludge used as a fertilizer in agriculture and for land reclamation for agricultural and other purposes exceeds 29 percent. In the latter case, the sludge has to meet obligatory criteria and standards for land application, such as pollutant ceiling concentration limits and bacteriological ones.

However, the obligatory criteria and standards do not comprise a wide range of parameters which may provide valuable information on properties of sewage sludge, including that concerning its potential negative as well as positive impact on environment. This is the case of information on concentrations of some trace elements, including REE. Concentrations of REE in sludge still remain poorly known, despite of the fact that their presence may bear important effects on disposal sites as well as usability of that material for fertilizing farm lands and in soil recultivation. Here it is worth to refer to results of Chinese studies on influence of REE on soils and plants. The studies showed that the use of REE-containing fertilizers can enhance crop production and quality of crops. However, this can also have some negative side effects as an increase in concentration of REE in soil environment may induce contamination of food-chain and endanger the ecosystem safety (Zhang and Shan, 2001). Any direct evidence for toxic effect of elements of the lanthanide series on plants is still missing but it may be stated that they exert a negative influence on cell membrane of vascular plants and calcium metabolism of microorganisms (Kabata – Pendias and Mukherjee, 2007). It should be noted that REE of anthropogenic origin usually get into soil in easily assimilable form which opens a possibility of change of biochemical equilibrium in a given soil environment (Zhang and Shan, 2001). There is also growing evidence on adverse influence of these elements on human health as shown by some cases of pneumonia due to a long-term exposure to volatile REE compounds emitted in the workplace. The studies under in vivo conditions also showed that REE may lead to some morphological changes and adverse effects, in particular to the liver (Rim at al., 2013).

The paper presents some partial results of an applied research project of assessing concentrations of trace elements and those of the REE group in sludge from selected sewage treatment plants. This project was aimed to determining and analysis of chemical composition of sludge sediments generated in municipal, municipal-industrial and industrial sewage treatment facilities. The attention is focused here on results of studies on concentrations of REE in sludge sediments generated in the course of treatment of liquid waste products disposed by pulp and paper plants.

Materials and Methodology

The sludge sediment samples were collected from 4 industrial sewage treatment facilities of pulp and paper plants differing in the scale of production, applied technologies and manufactured products. The main products of these plants include: copy paper for copying and laser printers, offset printing and other printing and writing papers grades (Plant no. 1), industrial paper for wrapping and packaging and industrial, consumer and carrier bags and testliner cardboard paper with wavy and flat sheets (Plant no. 2), recycled paper for wavy sheets of cardboard, recycled cardboard and industrial paper for wrappings (Plant no. 3), and half-parchment, industrial paper for wrappings and ecological paper (Plant no. 4).

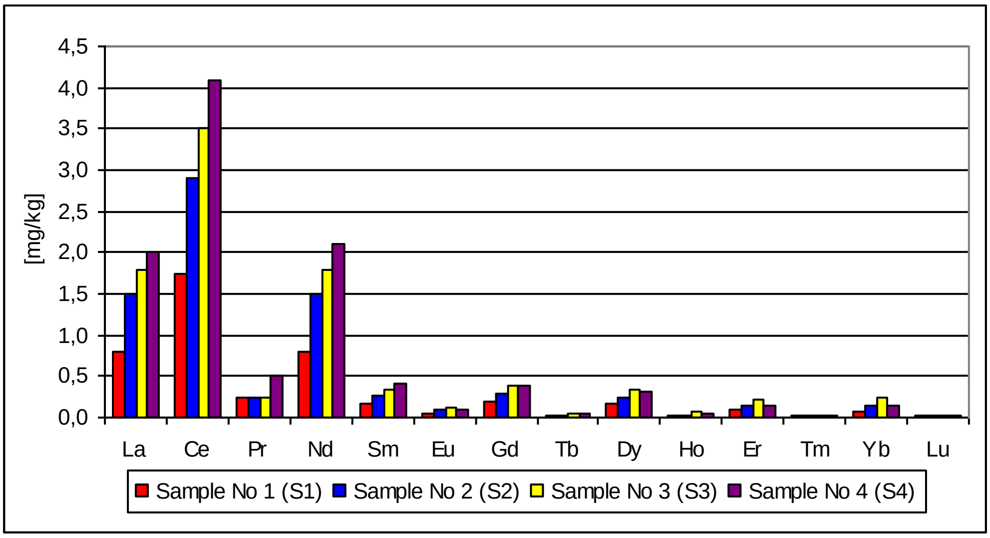
At each sewage treatment facility, random samples of sludge were collected using polypropylene containers with a capacity of about 0.7 liter. Samples representative for the flow of sludge were obtained by merging and mixing thoroughly the sampled material. The samples were marked with symbols S1, S2, S3 and S4, where number stands for treatment facility at which a given sample was taken. Samples S1, S2, S3 were taken in the form of dewatered sediment and S4 – as wet concentrate.

The collected samples were analyzed in the Central Chemical Laboratory of the Polish Geological Institute - National Research Institute (PGI-NRI). This laboratory has authorization of the Polish Centre for Accreditation (Certificate no. AB 283) which confirms that it fulfills standards and requirements of the Polish Normative PN/EN ISO/IEC 17025 for testing chemistry and physico-chemical properties of water, sewage, soils, sediments, environmental and geological samples and plant material. In accordance with procedures, sediment samples were air dried, powdered and dissolved in aqua regia. Concentration of REE was determined by inductively coupled plasma mass spectrometry method (ICP-MS) using PerkinElmer Elan DRC II ICP-MS System. In this paper, the term REE refers to lanthanum and 13 remaining elements of the lanthanide series, except for radiogenic promethium which is unknown to occur in nature. The detection limit of this method is 0.5 mg/kg for La, Ce, Pr and Nd and 0.05 mg/kg for the remaining elements (Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

Results and their Analysis

The obtained results showed that REE are mainly represented in the studied sludge sediments by those assigned to the light REE group (LREE), that is lanthanum, cerium and neodymium (see Figure 1).

Figure 1. *Contents of REE in the Studied Samples*



Of these elements, cerium was found to occur in the highest concentrations, ranging from 1.8 ppm in sample S1 to 4.1 ppm in sample S4. Concentrations of lanthanum were found to range from 0.8 to 2.0 ppm, being almost identical as those of neodymium (except for a small difference of the order of 0.1 ppm in sample S4). Contents of the remaining LREE (praseodymium, samarium and europium) appeared to be clearly lower. Concentrations of praseodymium reached detection limit of the used analytical method (0.5 ppm) only in sample S4 whereas those of samarium appeared to be the lowest (0.18 ppm) in sample S1 to rise to 0.41 ppm in sample S4. Concentrations of europium were found to range from 0.06 to 0.11. It is worth to note that the highest concentrations of europium were recorded in sample S3 whereas concentrations of all the remaining LREE were found to be the highest in sample S4 (Table 1).

Table 1. *Concentrations of REE in the Studied Samples of Sewage Sludge Sediments*

Elements	Sample No. 1 (S1)	Sample No. 2 (S2)	Sample No. 3 (S3)	Sample No. 4 (S4)
	[mg/kg]			
La	0.8	1.5	1.8	2.0
Ce	1.8	2.9	3.5	4.1
Pr	<0.5	<0.5	<0.5	0.5
Nd	0.8	1.5	1.8	2.1
Sm	0.18	0.27	0.35	0.41
Eu	0.06	0.09	0.11	0.09
Gd	0.19	0.29	0.38	0.39
Tb	<0.05	<0.05	0.06	0.05
Dy	0.17	0.25	0.35	0.31
Ho	<0.05	<0.05	0.07	0.06
Er	0.09	0.15	0.22	0.15
Tm	<0.05	<0.05	<0.05	<0.05
Yb	0.08	0.15	0.24	0.14
Lu	<0.05	<0.05	<0.05	<0.05

Analysis of concentrations of heavy REE (HREE) in the studied samples showed that the most common elements of this group include gadolinium, dysprosium and erbium. Concentrations of gadolinium range from 0.19 to 0.39 ppm, being similar to those of dysprosium – ranging from 0.17 to 0.35 ppm. The highest concentration of the latter was recorded in sample S3. The case of erbium was similar as its highest concentration (0.22 ppm) was recorded in that sample and the lowest one (0.09 ppm) – in sample S1. Concentrations of the remaining HREE turn to be lower, at the level of detection limit (0.05 ppm) in the case of thulium and lutetium as well as terbium and holmium in samples S1 and S2. In sample S3 the concentrations of these two latter elements were equal 0.06 and 0.05 ppm, respectively, and in sample S4 – 0.07 and 0.06 ppm (Table 1).

The obtained results were subsequently compared with those of municipal sewage sludge from Japan and Sweden and industrial sewage sludge generated by the chemical and food industry in Japan (Table 2) (Kawasaki et al., 1998; Eriksson, 2001).

Table 2. *Comparison of Concentrations of REE in Sewage Sludge Generated by the Pulp and Paper, Chemical and Food Industry and Municipalities in Poland, Japan and Sweden*

Elements	Type and origin of sewage sludge				
	Pulp and paper industry sludge (Poland)	**Chemical industry sludge (Japan)**	**Food industry sludge (Japan)**	**Sewage sludge (Japan)**	**Sewage sludge (Sweden)**
	Our studies	**(Kawasaki A. et al., 1998)**			**(Eriksson J., 2001)**
	Mean value [mg/kg]				
	n=4	**n=10**	**n=10**	**n=14**	**n=47**
La	1.53	2.46	0.89	6.70	16
Ce	3.06	2.69	1.83	14.1	24
Pr	0.31	0.48	0.22	1.48	2.8
Nd	1.55	2.04	0.91	6.00	11
Sm	0.30	0.36	0.17	1.02	1.8
Eu	0.09	*	*	*	0.30
Gd	0.31	0.48	0.17	1.18	2.0
Tb	0.04	0.06	0.03	0.16	0.34
Dy	0.27	0.39	0.14	0.93	1.7
Ho	0.05	0.09	0.03	0.19	0.40
Er	0.15	0.26	0.08	0.57	1.0
Tm	0.03	0.03	0.01	0.08	0.21
Yb	0.15	0.19	0.09	0.54	1.1
Lu	0.03	0.03	0.01	0.08	0.19

* Europium was omitted in determinations

Analysis of the data given in Table 2 made it possible to state that mean concentrations of REE in industrial sewage sludge are comparable and generally of similar order of magnitude. The studied sludge from the pulp and paper industry is characterized by higher mean concentrations of cerium than those from chemical and food industries. At the same time, mean values of concentrations of the remaining REE appear lower, being close or identical in the case of thulium and lutetium as those obtained for sludge from chemical plants. In turn, all the REE concentrations recorded in sludge of the pulp and paper industry appear higher than those recorded in sludge discharged by the food industry.

The results obtained for municipal sewage sludge are found to be much more diversified. The values recorded in Sweden (Eriksson, 2001) appear almost twice as high as REE concentrations in Japanese material (Kawasaki, 1998). The differences are the highest in the case of lanthanum, thulium and lutetium as their concentrations in Swedish material are over two times higher than in the municipal sludge from Japan. Nevertheless, REE concentrations in both Swedish and Japanese material generally attain much higher values (often even several times higher) than those obtained for all the industrial sludge samples (see Table 2). Concentrations of individual REE in the studied sludge from the pulp and paper industry are from 2.6 (in the case of Tm and Lu) to 4.7 times lower (in the case of Pr) than those in municipal sludge from Japan and from 3.3 (Eu) to 10.4 times (La) lower than in the Swedish material.

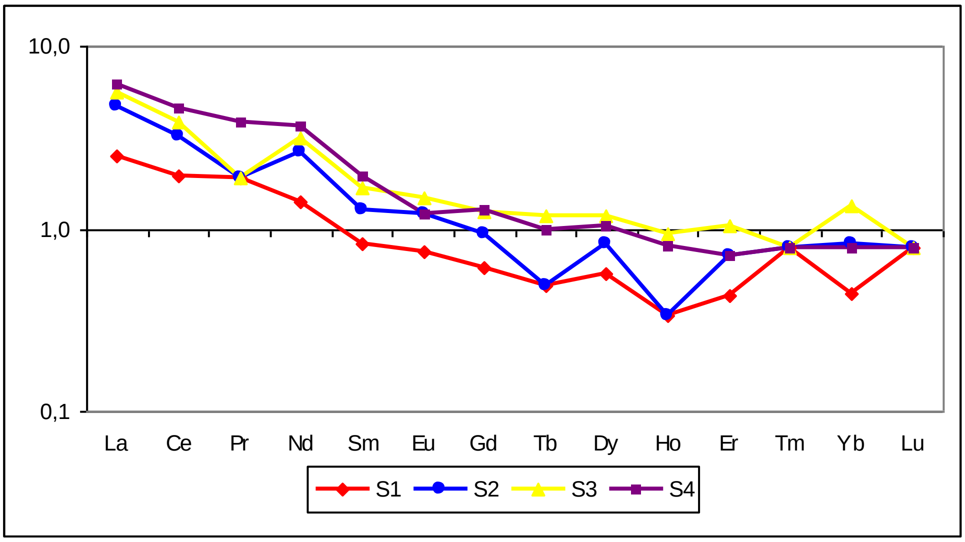
Normalized Values of REE Concentrations in the Studied Sewage Sludge

From the point of view of regulations, sewage sludge used for agricultural purposes or land reclamation represents an anthropogenic material. Nevertheless, an attempt was made to determine the level of REE mineralization of that sludge. This was done by normalization of the obtained results to REE concentrations in chondrite (Schmidt et al., 1963) and Post-Archaen Australia Shale (PAAS) (McLennan, 2001) and mean concentrations in topsoil of Poland as given in Geochemical Atlas of Europe (De Vos, Tarvainen (red.) et al., 2006).

Normalization to Chondrite

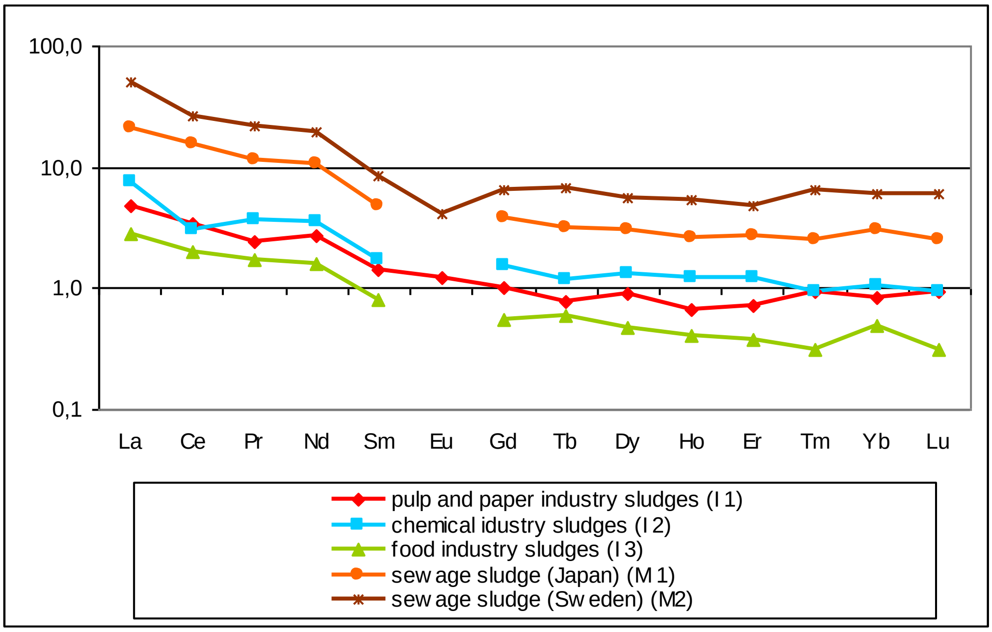
Analysis of normalized REE/chondrite graph (Figure 2) confirms fairly high differentiation of REE concentrations in the studied samples. Concentrations of lanthanum, cerium, praseodymium and neodymium are from 1.5 to over six times higher than in chondrite. In turn, further course of the graph shows that these relative values are dropping down to oscillate around or below the level 1.0 in its part corresponding to HREE. In that part of the graph it is also worth to note a clear positive neodymium anomaly related to concentrations recorded in two samples (S2 and S3)

Figure 2. *Normalized REE/Chondrite Graph (Schmidt et al., 1963) for REE Concentrations in the Studied Sludge*



Normalization of mean concentrations of REE in the studied sludge, municipal sewage sludge and sludge generated by other industries (Kawasaki et al., 1998; Ericsson, 2001) in relation to chondrite is given below (Figure 3).

Figure 3. *Normalized REE/Chondrite Graph (Schmidt et al., 1963) for REE in Municipal and Industrial Sludge*



Graphs I2, I3 and M1 do not show normalized values of Eu because determinations of concentrations of that element were beyond the scope of the present study

The course of graphs shown in Figure 3 is generally characterized by clear repeatability and high variability. All the graphs reflect enrichment of the sludge in LREE in comparison with HREE.

Graphs for municipal sewage sludge from Sweden (M2) and Japan (M1) show the largest enrichment in REE in relation to chondrite. All the REE are here enriched and normalized mean concentrations of LREE (La – Nd series) are from 50 (La in graph M2) to 10 times higher (Nd in graph M1) than in chondrite. Even the lowest concentrations of elements of the HREE series appear 4.7 (Er in graph M2) to 2.5 times higher (Tm in graph M1) than in chondrite. Graph M2 also shows a small negative europium anomaly. However, this phenomenon cannot be traced in graph M1 because of the lack of determinations of concentrations of that element in results of studies carried out by Kawasaki et al. (1998).

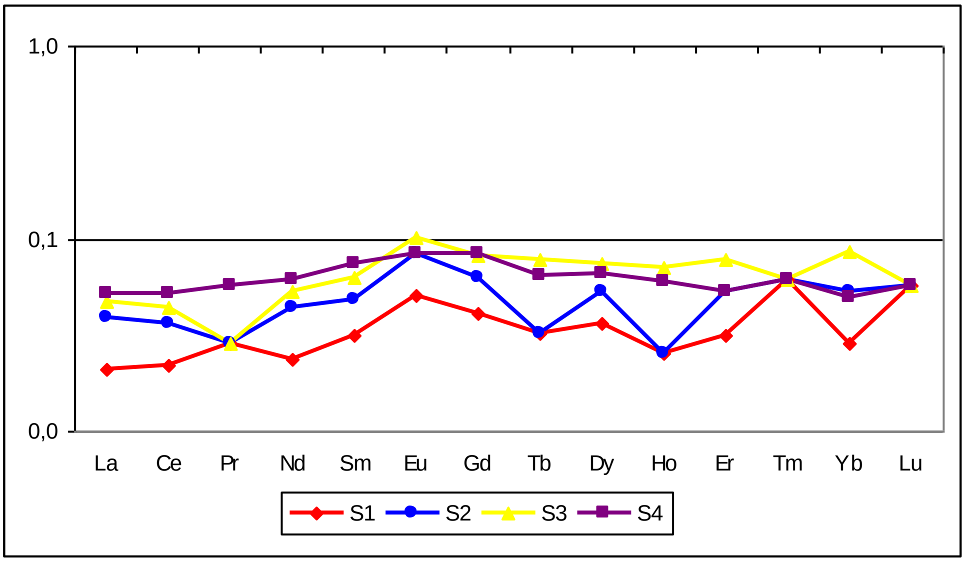
Graphs drawn for REE concentrations in industrial sludge show much higher variability. These sediments are characterized by concentrations of the La - Sm series (LREE) somewhat increased in relation to chondrite and falling in the range from 7.6 to 1.7. Further course of that graph shows REE concentrations gradually decreasing to oscillate around the level 1.0. The exceptions are here Tm and Lu with concentrations dropping below 1.0 in graph I2.

The course of graph I3 shows normalized concentrations of REE in sludge generated by the food industry. In that graph, only concentrations of the La – Nd series (LREE) are slightly higher than in chondrite whereas those of all the remaining REE appear somewhat lower. The course of graph I1, drawn for sludge of the pulp and paper industry, looks identical. This graph shows a small enrichment of LREE, higher than that in sludge sediments of the food industry (graph I3) but lower than in those of the chemical industry (graph I2). Mean concentrations of lanthanum and europium in the studied sediments appear 4.7 and 1.2 times higher than in chondrite, respectively. Further course of this graph displays progressively lower relative concentrations of HREE, oscillating around the level 1.0 for Gd and 0.6 for Ho.

Normalization to PAAS

Normalization of the obtained values to results of determination of REE concentrations in the Post-Archaen Australian Shale (PAAS) (McLennan, 2001) (Figure 4) showed that contents of REE in the studied sewage sludge correspond merely to 0.002 to one-tenth of those of Australian shale. Therefore, the obtained values may be regarded as very low in comparison with those for fine-grained sedimentary rocks.

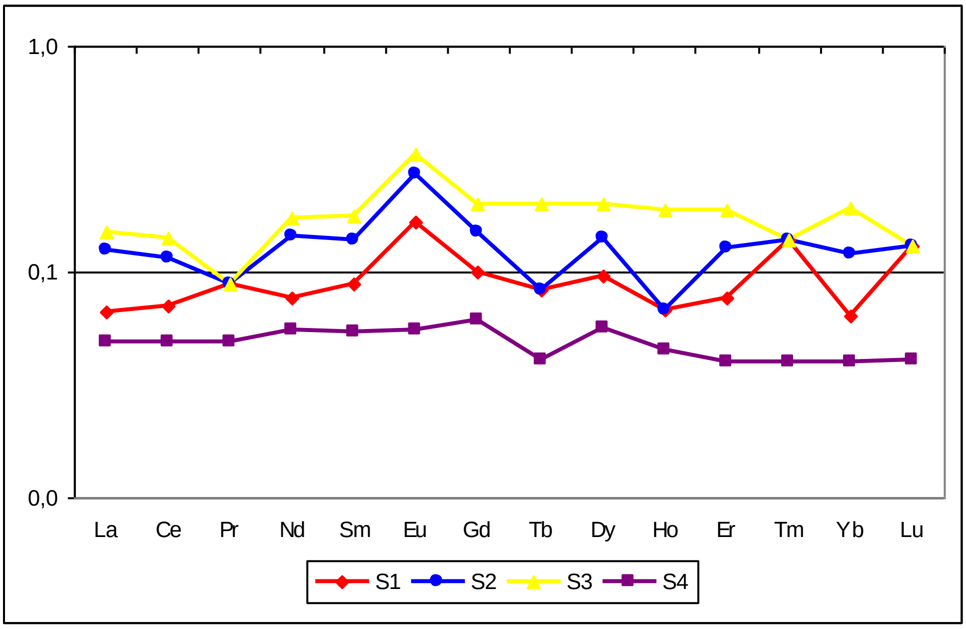
Figure 4. *Normalized REE/ PAAS Graph (McLennan, 2001) for REE in the Studied Sewage Sludge*



Normalization to Topsoil of Poland

The obtained results were also normalized in relation to mean concentrations of REE in topsoil of Poland as given in Geochemical Atlas of Europe (De Vos, Tarvainen (red.) et al., 2006) (Figure 5.). The course of graph shows that summative concentrations of REE in the studied sludge are generally low, ranging from 0.04 to 0.3 of those recorded in topsoil. The lowest concentrations of REE in relation to those of topsoil may be noted in graph for sample S3 and the highest – in graph for sample S4.

Figure 5. *Normalized Graph of REE/Topsoil of Poland for REE in the Studied Sludge*



Conclusions

The studies on sludge sediments from industrial sewage treatment facilities of the pulp and paper industry showed that they yield REE in concentrations ranging from 4.5 to 10.4 ppm. The recorded concentrations of individual REE are comparable with those obtained in the course of studies on sewage sludge generated by the food and chemical industries in Japan. It should be noted that mean concentrations of REE in municipal sewage sludge are at least two times higher than in the industrial sludge (Kawasaki et al., 1998; Eriksson, 2001). The highest concentrations were recorded for municipal sewage sludge in Sweden.

Normalization of the obtained results in relation to mean concentrations of REE in soils of Poland has also shown concentrations in the studied sludge to be markedly lower than in the topsoil.

Therefore, it may be concluded that the recorded REE concentrations are sufficiently low to allow for use of the studied sludge as fertilizers in agriculture and land reclamation.

References

De Vos W., Tarvainen T. (Chief-editors), Salminen R., Reeder S., De Vivo B., Demetriades A., Pirc S., Batista M.J., Marsina K., Ottesen R.-T., O'Connor P.J., Bidovec M., Lima A., Siewers U., Smith B., Taylor H, Shaw R., Salpeteur I., Gregorauskiene V., Halamic J., Slaninka I., Lax K., Gravesen P., Birke M., Breward N., Ander E.L., Jordan G., Duris M., Klein P., Locutura J., Bel-lan A., Pasieczna A., Lis J., Mazreku A., Gilucis A., Heitzmann P., Klaver G., Petersell V., 2006. Geochemical Atlas of Europe. Part 2 - Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications; Geological Survey of Finland Espoo

Eriksson J., 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, percipitation and in oil and crops, Swedish EPA Rep 5159, Stockholm

Główny Urząd Statystyczny – Bank Danych Lokalnych DOI=http://stat.gov.pl/bdl/app/strona.html?p_name=indeks

Kabata – Pendias A., Mukherjee A.B., 2007. Trace Elements from Soil to Human, Springer-Verlag Berlin, p.141

Kawasaki A., Kimura R., Arai S., 1998. Rare earth elements and other trace elements in wastewater treatment sludges, Soil Science and Plant Nutrition, 44:3, 433-441 DOI= http://dx.doi.org/10.1080/00380768.1998.10414465

McLennan S. M., 2001. Relationships between the Trace Element Composition of Sedimentary Rocks and Upper Continental Crust, Geochemistry Geophysics Geosystems, Vol. 2, No. 4, pp. 1-24. DOI=http://onlinelibrary.wiley.com/doi/10.1029/2000GC000109/abstract

Rim K.T., Koo K.H., Park J.S., 2013. Toxicological Evaluations of Rare Earths and Their Health Impacts to Workers: A Literature Review, Saf. Health Work 2013;4:12-26, DOI= http://dx.doi.org/10.5491/SHAW.2013.4.1.12

Schmidt R.A., Smith R. H., Lasch J. E., Mosen A. W., Olehy D. A. and Vasilevshis J., 1963. Abundances of Fourteen Rare Earth Elements, Scandium, and Yttrium in Meteoritic and Terrigenous Matter, Geochimica et Cosmochimica Acta, Vol. 27, No. 6, pp. 577-622.

Zhang S., Shan X., 2001. Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application, Environmental Pollution Vol. 112 (3), p. 395-405, DOI= http://dx.doi.org/10.1016/S0269-7491(00)00143-3