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Comparative analysis of sewage sludge from two sewage treatment plants: in Mrozy and Siedlce (Mazowieckie Province)

Porównawcza analiza osadów ściekowych z dwóch oczyszczalni ścieków w Mrozach i Siedlcach (województwo mazowieckie)

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Słowa kluczowe: osad ściekowy, składniki odżywcze, materia organiczna, metale ciężkie, radiocez

Abstract
Selected parameters of sewage sludge from two different sewage treatment plants: a rural one (in Mrozy) and a municipal one (in Siedlce) were compared. Samples from a mechanical–biological sewage treatment plant (Mrozy) showed a higher content of nitrogen and lower content of phosphorus, potassium and magnesium than the samples from the sewage treatment plant with the tertiary enhanced nutrient removal (Siedlce). The C/N ratio was 7.5 and 11.7, respectively. No differences were noted in the content of zinc in analysed samples. From among analysed metals (Cu, Zn, Fe and Mg), magnesium occurred in the greatest amounts in easily available form. The presence of ^{137}Cs was found in sewage sludge from both treatment plants.

Streszczenie
W pracy porównano skład chemiczny osadów ściekowych wytwarzanych w dwóch różnych oczyszczalniach ścieków: w oczyszczalni wiejskiej (Mrozy) i miejskiej (Siedlce). Ustalono, że próbki z oczyszczalni mechaniczno-biologicznej (Mrozy) charakteryzują się wyższą zawartością azotu, niższym poziomem fosforu, potasu i magnezu w porównaniu do próbek z oczyszczalni z podwyższonym usuwaniem biogenów (Siedlce). Stosunek C/N wynosił odpowiednio 7.5 do 11.7. Nie odnotowano różnic w zawartości cynku w badanych próbkach Spośród metali: Cu, Zn, Fe i Mg w największych ilościach w formach biodostępnych dla roślin występował magnez. W osadach z obu oczyszczalni odnotowano także obecność izotopu ^{137}Cs.

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1. INTRODUCTION

The amounts of sewage sludge have been recently found to systematically increase in Poland [GUS 2012]. It is thus necessary to monitor the quality of sewage sludge to recommend its proper utilisation. Chemical composition of sewage sludge is rarely investigated in sewage treatment plants. Sewage is very often used, without inspection, in agriculture as an organic fertiliser.

Sewage sludge is characterised by the abundance of organic matter and nutrients. The content of organic matter, total nitrogen and total phosphorus may vary across a wide range (e.g., Bauman-Kaszubska, Sikorski 2011; Cebula 1994; Czekała 2008; Piotrowska, Wolna-Maruwka 2010). Moreover, sewage sludge can be a rich source of heavy metals [Czekała 2008; Gawdzik, Gawdzik 2012; Gondek 2006; Jakubus, Czekała 2001; Wilk, Gworek 2009]. This is possible when the sludge contains a lot of industrial wastes.

The quality of sewage treatment depends on the type of treated waste waters and the type of sewage treatment plant. Chemical and biological composition of sewage sludge determine the method of its treatment and utilisation [e.g. Bauman-Kaszubska, Sikorski 2011; Bień et al. 2011; Szwedziak 2006].

The aim of this study was to compare the chemical composition of sewage sludge produced in two different sewage treatment plants: a rural (Mrozy) and a municipal (Siedlce) plant. The rural plant receives only communal sewage, while in Siedlce, both communal and industrial sewage is treated. We hypothesised that the content of organic matter and nutrients are not related to the location of sewage treatment plant, but the sludge may differ in heavy metals content.

The studies aimed to determine:

a. The content of dry matter, organic matter, organic carbon, total nitrogen and total phosphorus,
b. The content of magnesium, iron, copper and zinc in the easily available and acid-extractable forms,
c. The activity of ^{137}Cs and ^{40}K isotopes calculated on the basis of radiometric measurements,
d. pH of sewage sludge.

Measuring the content of zinc in sewage sludge from Siedlce sewage treatment plant seemed important because of the operation of the galvanizing line in the plant; other metals were chosen randomly. The analysis of ^{137}Cs content in sewage sludge seemed interesting also owing to the fact that after the Chernobyl accident, radioactivity in Siedlce region was significantly increased in comparison with other parts of the country [Chibowski 1994], while cesium isotope can still be detected in the diet of the inhabitants of the region [Królak and Karwowska 2010].

2. MATERIAL AND METHODS

Samples of sewage sludge used in the study were taken from two sewage treatment plants: in Mrozy and in Siedlce, located in Mazowieckie Province.

The sewage treatment plant in Mrozy serves 8600 inhabitants of the Mrozy community area. It is a mechanical–biological sewage treatment plant operating in the system of deep fine bubble sewage aeration based on diffusers; its maximum sewage treatment capacity is 600 m^3/per day but actually it purifies about 74 000 m^3 domestic sewage annually (ENI– 4200). The plant was modernised in 2010.

The other sewage treatment plant is situated in Siedlce and serves about 77 000 inhabitants (ENI– 120 000). There are a few industrial companies in the town. Industrial sewage produced by the companies is treated in the companies' on-site plants. The biological sewage treatment plant with enhanced nitrogen and phosphorus removal has about 22 000 m^3/per day throughput. The process of sewage aeration is similar to the one in the Mrozy plant. The plant is now being modernised.

Sewage sludge dewatering in the Mrozy plant is done with the use of a press, while in Siedlce, after leaving the settlement tanks, sewage sludge goes through the process of anaerobic sludge digestion at a temperature of 35°C. In the process, methane is produced, which is then dewatered with a press.

Fresh sludge samples stored at a drain plot for 1–2 days were taken from heaps and various places in the pile in the period December 2009–July 2010 in Siedlce and September 2011–April 2012 in Mrozy. Five separate subsamples were taken from one heap, then they were mixed and an average sample was taken for analysis.

This material was analysed for basic physical and chemical properties using standard methods:

a. dry matter – the samples were dried overnight at 105°C,
b. organic matter – determined as a loss on ignition at 550°C for 12 h,
c. organic carbon – by wet dichromate oxidation with sulphuric acid,
d. reaction – pH was measured in water with a glass electrode in water suspension (1:2.5 ratio),
e. total nitrogen with the phenylhypochlorite method [Solórzano 1969],
f. Total phosphorus with the molybdenum blue method [Standard Methods 1999].

The content of metals: magnesium, iron, copper and zinc in easily available and acid-extractable forms were analysed with AAS, after the extraction of sewage sludge in 1 M CH_3COONH_4 (pH=6), and mineralisation in nitric acid with hydrogen peroxide respectively.

Moreover, the activity of ^{137}Cs and ^{40}K isotopes was determined in fresh samples of sewage sludge with the use of γ-spectrometric method and semiconductor spectrometer with coaxial germanium detector made by Canberra Company. Spectrum analysis was carried out with the use of Genie 2000 Applications Software. The content of potassium in dry mass was calculated based on the activity of ^{40}K in wet mass, the content of dry mass in wet mass and the equivalence of 31.7 Bq ^{40}K to 1 g potassium.

The analyses were repeated twice. Results were processed with the Statistica 9.0 software. The normality of data was tested using Shapiro–Wilk test. Differences between the mean content of individual elements and soil pH in sewage sludge from two sewage sludge plants were tested using Student's t-test (normal distribution) and Mann–Whitney U test (non-normal distribution).

3. RESULTS

The sewage sludge was highly hydrated. The content of water in the majority of samples from two sewage sludge plants exceeded 80%. Most of the other analysed physical–chemical parameters in sewage sludge were statistically different and dependent on the site (Fig. 1). The content of organic matter, organic carbon and total nitrogen were higher in samples from Mrozy, but the content of total phosphorus and pH values were lower in comparison to the samples from Siedlce.

The concentration of metals (Fe, Mg, Cu and Zn) and the activity of isotopes ^{40}K and ^{137}Cs in sewage sludge fromthe two sites are presented in Table 1. From among analysed metals (magnesium, iron, copper and zinc), magnesium was specific for its relatively large, easily available form. Its amount extracted with ammonium acetate constituted about 40% (44.0% in samples from Mrozy and 35.5% in samples from Siedlce) of the total acid-extractable magnesium. The content of copper and zinc in easily available forms in sewage sludge was below 10% of the total. Respective proportion for Cu was 8.9% in Mrozy and 4.9% in Siedlce and for Zn – 3.6% and 4.3%, respectively. The content of easily available iron was very low, less than 0.2% of the total acid-extractable form.

Furthermore, considerably greater activity in sewage sludge was measured for natural isotope ^{40}K than for artificial isotope ^{137}Cs. Based on potassium activity, we calculated that the mean concentration of potassium in sewage sludge was 2.11 g kg^{-1} d.m. in Mrozy and 3.98 g kg^{-1} d.m. in Siedlce. The mean contents of cesium and potassium did not significantly differ between the sewage sludge from Mrozy and Siedlce.

4. DISCUSSION

The results obtained in this study show that the values of the analysed parameters were within the range reported in literature (for example: Bauman-Kaszubska, Sikorski 2011; Cebula 1994; Czekała 2008; Gondek 2006; Kazanowska, Szaciło 2012; Siuta 2003). The mean values of the parameters showed noticeable differences depending on the location of the investigated sludge samples. The differences in the content of organic matter, organic carbon,

Table 1. The concentration of chosen metals and the activity of isotopes ^{40}K and ^{137}Cs in sewage sludge from two cites: Mrozy and Siedlce

Parameter	Unit	Mrozy (n=6)			Siedlce (n=5)			Statistical test	
		mean	range	SD	mean	range	SD	test	Statistical value
Fe	g kg^{-1} d.m	5.26	3.27–6.49	1.16	10.63	9.88–11.39	0.75	U Mann–Whitney	Z= −3.51***
Mg		4.26	3.59–4.78	0.38	8.28	7.61–8.93	0.47		Z = −3.66***
Cu	mg kg^{-1} d.m	137.5	128.0–144.9	5.87	149.5	143.2–164.3	6.62	t-Student	t = −4.22***
Zn		1308.9	1070.5–1680.7	208.5	1297.9	1134.9–1447.1	152.3	U Mann–Whitney	ns
^{40}K	Bq kg^{-1} w.m	12.3	8.9–16.1	2.75	23.67	11.8–46.9	12.13		
^{137}Cs		2.8	0.7-7.4	3.15	3.1	1.3–5.6	1.86		

* p<0.05, ** p<0.01, *** p< 0.001, ns – not significant

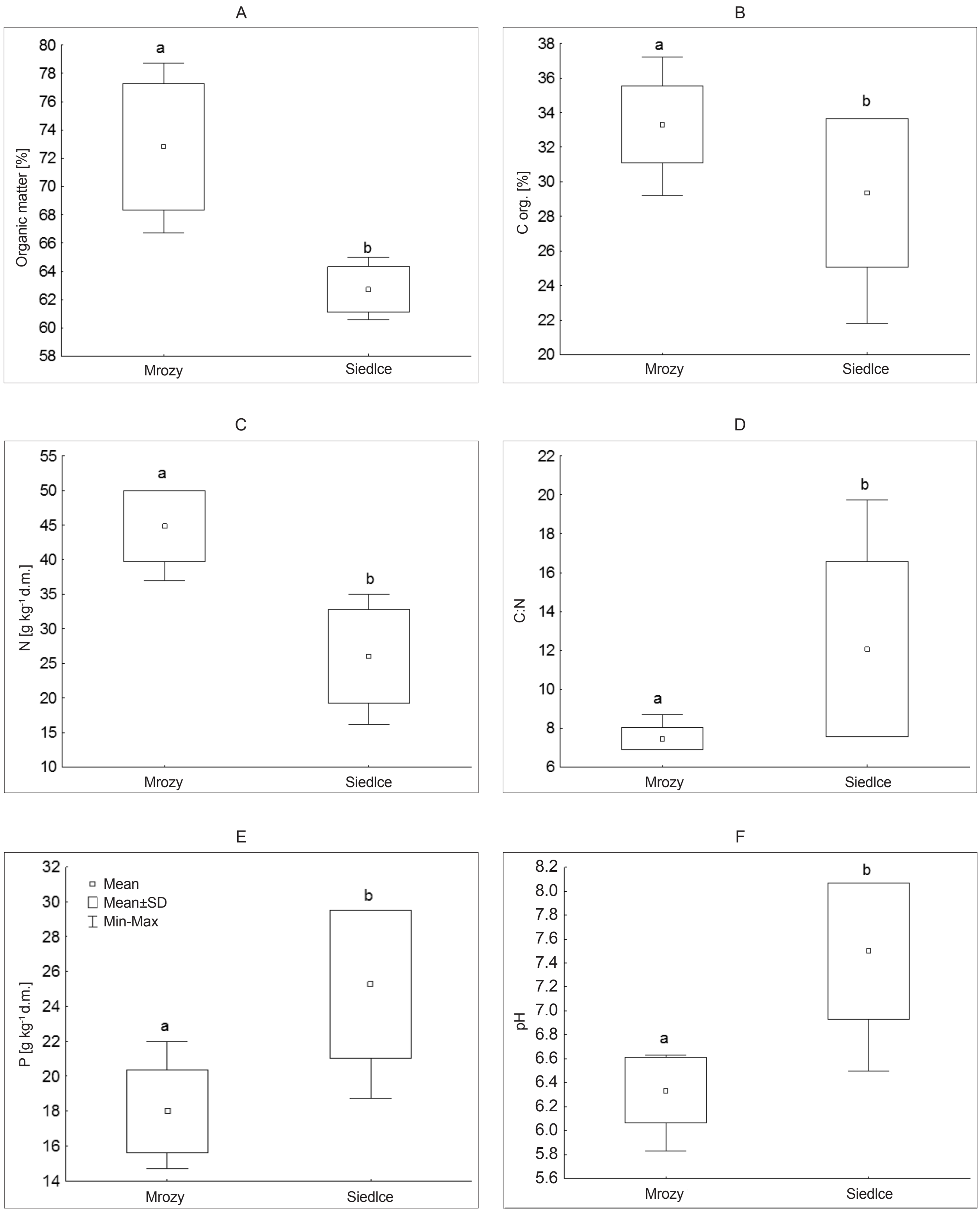

Fig. 1. The values of chosen physical and chemical parameters of sewage sludge from sewage treatment plants in Mrozy and Siedlce.

A – The content of organic matter (Student's t-test, $t = 2.36$, $p < 0.05$)

B – The content of organic carbon (Mann-Whitney U test, $Z = 2.16$, $p < 0.01$)

C – The concentration of nitrogen total (Student's t-test, $t = 6.3$, $p < 0.001$)

D – C: N ratio (Mann-Whitney U test, $Z = -2.46$, $p < 0.05$)

E – The concentration of phosphorus total (Student's t-test, $t = -4.6$, $p < 0.001$)

F – Reaction (Mann-Whitney U test, $Z = -2.65$, $p < 0.01$)

total nitrogen, total phosphorus and pH between samples from Mrozy and Siedlce were particularly significant. As a result, different technologies were applied to treat waste waters. Observed differences resulted from different technologies applied in sewage treatment. In Mrozy, there is a biological sewage treatment plant. In Siedlce, a biological sewage treatment plant is equipped with facilities for enhanced nitrogen and phosphorus removal. Nitrogen is removed to the atmosphere as N_2 owing to the activity of micro-organisms such as: *Achrombacter, Aerobacter, Bacillus, Pseudomonas stutzeri, Pseudomonas celsis* [Sadecka 2010]. Phosphorus is incorporated in the biomass of dephosphatizing micro-organisms [Dymaczewski et al. 1997]. As a result, the sewage sludge from Siedlce contained less nitrogen but more phosphorus compared with that from Mrozy.

The differences in pH between samples can be the result of the type of waste waters and the technology used for their treatment.

Sewage sludge is a rich source of nitrogen, phosphorus and organic matter. This is shown in both the literature [Bauman-Kaszubska, Sikorski 2011; Cebula 1994; Czekała 2008; Piotrowska, Wolna-Maruwka 2010] and in our results. Therefore, it can be utilised as an organic fertiliser [Wilk, Gworek 2009]. Szwedziak [2006] reported that when used for agricultural purposes, sewage sludge can be a rich source of macro-elements for plants. Our study indicated that the content of potassium and magnesium was higher in the samples from Siedlce than in those from Mrozy. Magnesium was largely present in sewage sludge in the form available for plants. Bioavailability among the other metals from sewage sludge was low (a few percent for Cu, Zn or below 1% for Fe). Similar results were reported by Gawdzik [Gawdzik 2012; Gondek 2006; Jakubas and Czekała 2001]. The authors indicated that the dominant forms of heavy metals (including Cu and Zn) are immobile compounds. The contents of copper and zinc in the two sampled sites were below the threshold levels (1000 mg Cu kg^{-1} and 2500 mg Zn kg^{-1}) given in the Regulation of the Minister of Environment [Rozporządzenie 2010]. It should be noted that the content of zinc was similar in sewage sludge from the two sewage treatment plants. At the beginning of this analysis, we hypothesised that the content of heavy metals in samples from Siedlce should be higher than in those from Mrozy. In Siedlce, a few industrial companies, for example, zinc-processing firm Mostostal-Siedlce, are located. Our results did not support this hypothesis. The higher content of iron in samples from Siedlce in comparison with those from Mrozy can occasionally be a result of the application of iron salt to remove phosphate from waste waters.

The observed activity of ^{137}Cs in sewage sludge is worth emphasising. This shows that radiocesium may occur in the diet of people from the study region, which was also remarked by Królak and Karwowska [2010]. It is worth mentioning that literature sources lack information concerning ^{137}Cs radioactivity in sewage sludge, while the results presented here show that the natural use of sewage sludge does not cause a significant increase in soil radioactivity.

Chemical composition of sewage sludge is very important in choosing the ways of its agricultural application. The results show that the sewage sludge from both sites (Mrozy and Siedlce) can be used for soil and plant fertilisation and for the reclamation of degraded soil, but it needs appropriate stabilisation. The course of sludge stabilisation is determined by the C/N ratio. The optimum C/N ratio for nutritional requirements of plants is estimated at 10–15 [Jędrczak 2008]. The C/N ratio in sewage sludge from Siedlce (11.7) fell within this range. The C/N ratio in samples from Mrozy (7.5) indicated that the sewage sludge should be stabilised, for example by adding adequate substances in order to improve final product properties.

Appropriate use of sewage sludge should be reviewed to assess its chemical and microbiological composition, although the latter was not investigated in our studies.

5. CONCLUSIONS

Sewage sludge from Siedlce is characterised by better chemical properties in comparison with sewage sludge from Mrozy in view of their use for natural purposes due to lower level of nitrogen, higher level of phosphorus and magnesium and the optimum C/N ratio.

The content of copper and zinc in sewage sludge from the two sites is below the threshold values set for sludge utilisation for natural and agricultural purposes.

The activity of ^{137}Cs in sewage sludge reaching several Bq kg^{-1} indicates the occurrence of radiocesium in the diet of people from the study region, while the natural use of sewage sludge does not increase cesium radioactivity in soils.

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