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ORIGINAL PAPER

# EFFECT OF PROCESSING TEMPERATURE APPLIED TO MIXTURES OF SEWAGE SLUDGE AND PLANT WASTE ON THE CONTENT OF MACRO- AND MICROELEMENTS IN THE PRODUCT AND ON THE LUMINESCENCE OF *VIBRIO FISCHERI**

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## Abstract

The aim of the research was to determine the effect of temperature and addition of plant material to sewage sludge on the efficiency of thermal treatment of biomass. Another goal was to assess the content of selected macro- and microelements in the end product, taking into account the possibility of their agricultural use. The input material for the research consisted of anaerobically stabilized, dehydrated sewage sludge. The experimental design consisted of: sewage sludge + bark (SS + B), sewage sludge + wheat straw (SS + WS), sewage sludge + sawdust (SS + S). The mixtures were thermally treated in a chamber furnace, under anaerobic conditions. Two temperature settings were applied: 300°C and 600°C; the exposure time in both cases was 15 minutes. Thermal, anaerobic transformation of organic matter at a temperature up to 600°C causes even a twofold increase in the content of ash elements in the product. An increase in the nitrogen content can only be obtained under conditions of low-temperature transformation of a mixture of sewage sludge with organic materials. Using the temperature of 600°C for the transformation of organic materials caused an increase in the content of easily hydrolyzing nitrogen as well as forms of phosphorus, potassium and sodium extracted with water in comparison to mixtures transformed at the temperature of 300°C. Of the analyzed trace elements, only the content of water-soluble forms of zinc (apart from mixture of sewage sludge and straw) increased along with the increase in temperature of the transformation process, which

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indicates higher zinc bioavailability. In terms of fertilization, as a result of increasing the processing temperature applied to sewage sludge with the addition of different mass of plant origin, a lower value product is obtained due to nitrogen losses and a decrease in the availability of some elements for plants. The extracts from the mixtures were not toxic to bacteria. Stimulation of the luminescence of *V. fischeri* was observed in the research.

**Keywords:** biochar, sewage sludge, chemical composition, microtox test.

# INTRODUCTION

Sewage sludge management is currently becoming one of the greatest challenges for mankind (Fytili, Zabaniotou 2008). Among many attempts made to elaborate a way to treat and manage sewage sludge, relatively little attention has been paid to processes of thermal treatment of these materials (Jakubus 2012, Gondek 2010, Iżewska 2009). Thermal methods that sewage sludge has been subjected to until now have concerned mainly combustion and co-combustion. Currently, the so-called alternative methods are becoming more and more important. These methods include degassing, wet oxidation or pyrolysis (Agrafioti et al. 2013).

When analyzing the suitability of sewage sludge for thermal disposal, attention should be paid to the chemical composition of combustible mass, share of mineral substances, content of volatile parts, humidity and, finally, to the chemical composition of residues. Chemical composition is particularly important in the case of treatment based on the degassing process when, among other things, a solid product of the process (often called biochar) is the final output (Jahirul et al. 2012, Park et al. 2014). Biochar is defined as a product rich in carbon obtained from plant biomass and organic waste under conditions of no or little air access.

Properties of biochar vary significantly and depend on the kind of biomass, size of molecules and on conditions of conducting the thermal treatment, such as the following: duration of the process, type of reaction atmosphere, or temperature (which is of great importance for the chemical composition of the created product) (Antal, Grøbli 2003).

Taking into account different properties of biochar, the chemical composition is an important determinant for its use, aside from its physical parameters. Direct thermal treatment of sewage sludge may lead to excessively high concentrations of trace elements, which will limit the usability of the end product. Addition of other organic materials (e.g. sawdust, bark or cereal straw) to sewage sludge may solve this problem by diluting the content of trace elements and improving physical parameters of sewage sludge, mainly its structure, which will have a beneficial effect on the efficiency of the process (Gondek et al. 2014).

When considering the natural (including agricultural) use of the product of sewage sludge thermal treatment, the level of trace elements, beside the content of macroelements, is an important element of the evaluation of its suitability. On the other hand, Menendez et al. (2012) claim that as a result of sewage sludge thermal treatment, trace elements can occur in carbonate forms, which inhibits their leaching. According to some research, a beneficial effect of biochar used for soil amendment on the amount of grown plant biomass can be noted (Yamato et al. 2006, Chan et al. 2007). Assuming the natural use of such materials, the content of bioavailable forms and relations among individual elements also need to be assessed. These features influence the efficiency at which plants take up different components.

According to Chan et al. (2007), biochar is a more stable source of nutrients for plants than manure or compost. Results of research carried out by Beesely et al. (2011) as well as Nigussie et al. (2012) indicate that biochar added to poor and degraded soils may contribute to the improvement of their fertility and productivity. In this context, attention should also be paid to the fact that biochar may be a valuable substrate for reconstruction of the humus layer of soils destroyed as a result of industrial activities.

On the other hand, many studies have shown that chemical analysis is not a sufficient tool for an assessment of the risk connected with the use of biochar as a soil fertilizer and amending substance (Oleszczuk et al. 2013). Biochar application to soil raises concerns about soil's environmental quality, associated with some of its components. Ecotoxicological studies with the focus on bioavailable biochar components in soil may prove to be useful for that purpose. The use of bioassays in the assessment of biochar added to soil may expand the knowledge on the potential ecological risk resulting from the presence of various components in biochar, their bioavailability and interactions. The Microtox test is a standard biosensor measurement technique for ecotoxicity testing of water, soil, sediments, sludge, composts and biochar (Mamindy-Pajany et al 2011, Baran, Tarnawski 2013, Kopeć et al. 2013, Gondek et al. 2014). The test uses luminescent bacteria *Vibrio fischerii*.

The aim of the research was to determine the effect of temperature and addition of plant material to sewage sludge on the efficiency of thermal treatment of biomass and on the content of selected macro- and microelements as well as the luminescenece of *Vibrio fischeri*.

## MATERIAL AND METHODS

The input material for the research consisted of anaerobically stabilized, dehydrated sewage sludge collected at the Sewage Treatment Plant located in Krakow.

Wheat straw used in the research came from a farmstead. Sawdust and bark from coniferous trees were obtained as waste material from the processing of timber. The plant materials used in the research came from Małopolska, a region in the south of Poland.

The content of dry matter, organic matter, ash as well as macro- and microelements is presented in Tables 1-3.

In order to improve physical properties, sewage sludge was mixed with plant material in a 1:1 weight ratio with respect to dry matter. The experimental design consisted of: sewage sludge + bark (SS + B), sewage sludge + wheat straw (SS + WS), sewage sludge + sawdust (SS + S). The content of dry matter, ash as well as macro- and microelements in the untreated mixtures is presented in Tables 4-6.

Table 1

The content of dry matter, organic matter and ash in sewage sludge and plant materials used in the experiment

| Material | Dry weight | Organic matter | Ash |
|---|---|---|---|
| | (g kg$^{-1}$) | (g kg$^{-1}$ DW) | |
| Wheat straw (WS) | 990 ± 24 | 968 ± < 1 | 32± < 1 |
| Sawdust (S) | 989 ± 24 | 993 ± < 1 | 7± <1 |
| Bark (B) | 988 ± 23 | 553 ± 3 | 447± 3 |
| Sewage sludge (SS) | 236 ± 6 | 493 ± 4 | 507± 4 |

± standard deviation, $n$ = 4

Table 2

The content of macroelements in plant materials and sewage sludge used in the experiment

| Material | N | P | K | Ca | Mg | Na |
|---|---|---|---|---|---|---|
| | (g kg$^{-1}$ DW) | | | | | |
| Wheat straw (WS) | 4.94±0.14 | 0.75±0.01 | 5.25±0.06 | 2.51±0.08 | 0.41±0.01 | 0.11±0.01 |
| Sawdust (S) | 1.17±0.01 | 0.16±0.10 | 0.80±0.29 | 1.41±0.03 | 0.10±0.01 | 0.10±0.01 |
| Bark (B) | 4.67±0.01 | 0.75±0.21 | 1.31±0.04 | 6.57±0.13 | 0.40±0.01 | 0.17±0.02 |
| Sewage sludge (SS)* | 26.1±0.71 | 35.1±1.84 | 3.12±0.06 | 33.1±1.12 | 4.72±0.19 | 0.87±0.03 |
| Sewage sludge (SS)** | 6.62±0.07*** | 0.29±0.01 | 0.73±0.01 | 11.8 ±1.43 | 2.75±0.21 | 0.52±0.01 |

± standard deviation, $n$ = 4; * total forms; ** water soluble forms; *** N extracted 0.25 M $H_2SO_4$

Table 3

The content of microelements in sewage sludge and plant materials used in the experiment

| Material | Cu | Zn | Fe | Mn |
|---|---|---|---|---|
| | (mg kg$^{-1}$ DW) | | | |
| Wheat straw (WS) | 2.83±0.10 | 36.0±0.2 | 136±12 | 32.4±0.6 |
| Sawdust (S) | 2.25±0.40 | 17.3±0.3 | 417±26 | 138±2 |
| Bark (B) | 7.19±1.00 | 49.0±3.8 | 2468±318 | 231±3 |
| Sewage sludge (SS)* | 330±6 | 1751±69 | 35499±1021 | 390±1 |
| Sewage sludge (SS)** | 3.08±0.18 | 84.1±8.8 | 104±6 | 41.7±7.4 |

± standard deviation, $n$ = 4; * total forms; ** water soluble forms

Table 4

The dry weight and ash in mixtures before conversion of mixtures

| Material | Dry weight | Ash |
|---|---|---|
| | (g kg$^{-1}$) | (g kg$^{-1}$ DW) |
| Sewage sludge + bark (SS+B) | 351±6 | 406±12 |
| Sewage sludge + wheat straw (SS+WS) | 312±9 | 206±5 |
| Sewage sludge + sawdust (SS+S) | 302±7 | 225±9 |
| CV (%) | 8 | 32 |

± standard deviation, $n = 4$

Table 5

The residue after thermal conversion of mixtures

| Material | Residue at 300°C | Residue at 600°C |
|---|---|---|
| | (g kg$^{-1}$ DW) | |
| Sewage sludge + bark (SS+B) | 714±10 | 614±40 |
| Sewage sludge + wheat straw (SS+WS) | 535±13 | 431±10 |
| Sewage sludge + sawdust (SS+S) | 530±14 | 423±10 |
| CV (%) | 17 | 22 |

± standard deviation, $n = 4$

Table 6

The content total forms of maroelements in mixtures of sewage sludge and plant materials before thermal conversion

| Material | N | P | K |
|---|---|---|---|
| | (g kg$^{-1}$ DW) | | |
| Sewage sludge + bark (SS+B) | 20.3±1.3 | 15.3±1.2 | 2.07±0.04 |
| Sewage sludge + wheat straw (SS+WS) | 18.7±1.2 | 14.0±0.3 | 3.56±0.01 |
| Sewage sludge + sawdust (SS+S) | 20.6±1.7 | 16.8±0.8 | 1.59±0.11 |
| CV (%) | 5 | 9 | 43 |
| Material | Ca | Mg | Na |
| Sewage sludge + bark (SS+B) | 18.5±0.8 | 2.11±0.10 | 0.47±0.03 |
| Sewage sludge + wheat straw (SS+WS) | 14.6±0.1 | 1.89±0.10 | 0.42±0.01 |
| Sewage sludge + sawdust (SS+S) | 16.5±0.6 | 2.15±0.14 | 0.45±0.01 |
| CV (%) | 12 | 7 | 6 |

± standard deviation, $n = 4$

The mixtures were thermally treated in a chamber furnace, under anaerobic conditions. Two temperature settings were applied: 300ºC and 600ºC; the exposure time in both cases was 15 minutes. After completing the procedure, the materials were left in the furnace to cool (ambient temperature).

Once a sample of the material had been mineralized in concentrated sulfuric acid, the total nitrogen content was determined by a modified Kjeldahl method (Kalembasa et al. 1989). The total content of the other elements was determined after incinerating the sample in a chamber furnace at 450°C for 12 hours. After cooling, the residue was treated with a mixture of concentrated nitric and perchloric (3:2) (v/v) acids, and then left at room temperature for 24 h (Kopeć et al. 2013). Concentrations of P, K, Ca, Mg, Na, Zn, Cu, Fe, Mn were determined in the solution using the ICP-OES method and a Perkin Elmer Optima 7300 DV apparatus.

The content of easily hydrolyzing forms of nitrogen in untreated sewage sludge as well as in the mixtures after thermal treatment was determined after extraction (24 h) with $H_2SO_4$ solution of the concentration of 0.25 mol $dm^{-3}$ (Kalembasa 1998).

The content of mobile forms of macro- and microelements in untreated sewage sludge and in the mixtures after thermal transformation was determined after 24-hour extraction with redistilled water. Determinations of the content of the analyzed elements were immediately carried out in the extracts. The determinations were performed using the ICP-OES method on a Perkin Elmer Optima 7300 DV apparatus (Oleszczuk 2007).

Acute toxicity of the extracts (1:20) was determined based on the measurement of the luminescence intensity of *Vibrio fischeri* bacteria. Light emission of these bacteria is a function of the luciferase enzyme system controlled by the lux genes and the light output is related to respiratory activity. The test uses reagents (*V. fischeri*) purchased from Strategic Diagnostics Inc. (Polish distributor, Tigret). A standard test procedure was applied in the extract samples: 81.9% Screening Test. The samples were analyzed in Microtox® M500 analyzers (MicrobicsCorporation 1992). Luminescence was measured at 490 nm before and after 5 min incubation of the bacterial suspension with each of the tested samples, and then toxicity effect I (%) was calculated according to the equation: $I = (1 - L_s/L_c)\ 100(\%)$, where: $I$ – toxicity (%), $L_s$ – luminescence intensity of a sample, $L_c$ – luminescence intensity of the control. Three replicate samples were tested.

The standard deviation (SD) value was calculated for the results and – in order to determine the variantion within the analyzed population – the coefficient of variation (CV) was calculated as the share of standard deviation (SD) in the arithmetic mean of the analyzed properties.

## RESULTS AND DISCUSSION

The materials used in the research differed not only in chemical parameters (Tables 1-3), but also in the source of their origin. Of all the materials used in the research, sewage sludge had the lowest content of dry matter and organic matter, and the highest content of ash. Wheat straw, sawdust and bark, all of which were components for preparing mixtures with sewage sludge, had a small amount of water, which was an important factor that made it possible to change physical properties of the mixtures (Kim et al. 2003). The plant materials used as components to prepare the mixtures contained considerable amounts of organic matter (Table 1). A relatively lower amount of ash particles was determined in those materials. The determined content of individual components in the plant materials used for preparing the mixtures with sewage sludge did not deviate from values reported by other authors (Ghetti et al. 1996). The ash content of bark was an exception due to the contamination of this material with mineral substances in the production process.

The levels of trace elements determined in sewage sludge depended on the type of sewage, which is confirmed by other authors (Walter et al. 2006). The sewage sludge contained significantly higher amounts of the analyzed elements (apart from potassium in wheat straw) in comparison to the content determined in the other materials. The share of easily hydrolyzing forms of nitrogen and the most mobile forms of the other determined macroelements in the total content of sewage sludge was varied and significantly greater than this share in the case of microelements (Tables 2, 3).

Of the plant materials used as components to prepare the mixtures with sewage sludge, the highest amounts of copper, zinc, iron and manganese were determined in bark from coniferous trees (Table 3). The determined content of microelements in the plant materials used in the research did not deviate from the content recorded by other authors (Saidur et al. 2011).

The dry matter content in the mixtures of sewage sludge with plant materials (especially in the mixture of sewage sludge and bark) was higher than the dry matter content determined in untreated sewage sludge (SS) – Tables 1, 4. The prepared mixtures differed also in the ash content (Table 4), which was lower that the one determined in untreated sludge as a result of mixing sewage sludge with materials of plant origin which had a lower content of mineral components.

As a result of the thermal treatment of the prepared mixtures, various amounts of the residue were obtained. These quantities depended on the plant component that was used to prepare the mixture and on the temperature of the process (Table 5). Less residue, regardless of the component added to the sewage sludge, was recorded at 600°C, which was due to greater losses of substances, including non-organic compounds, that undergo oxidation at this temperature (Karayildirim et al. 2006). Thipkhunthod et al. (2006) also obtained various amounts of residue after thermal treatment of different kinds of sewage sludge. As the quoted authors stated, differences in mass loss of pyrolyzed sewage sludge can result from quantitative and qualitative differences between components, including the ash content. This is an important conclusion, especially because the sewage sludge used in the present research was mixed with plant materials that varied not only in the organic matter content but also in the stability of organic compounds. In their research, Hossain et al. (2011) showed that apart from the quantitative and qualitative composition another factor which decided about the mass loss of materials subjected to thermal treatment was the temperature at which the process was conducted.

The total content of the elements determined in the untreated mixtures of sewage sludge and plant materials were lower than the ones determined in untreated sewage sludge, which was a result of dilution (Tables 6, 7).

Table 7

The content of total forms of trace elements in mixtures of sewage sludge and plant materials before thermal conversion

| Material | Cu | Zn | Fe | Mn |
|---|---|---|---|---|
| | (mg kg$^{-1}$ DW) | | | |
| Sewage sludge + bark (SS+B) | 141±12 | 941±71 | 20592±104 | 297±9 |
| Sewage sludge + wheat straw (SS+WS) | 132±8 | 866±70 | 18100±155 | 173±1 |
| Sewage sludge + sawdust (SS+S) | 149±11 | 996±65 | 20650±530 | 247±11 |
| CV (%) | 6 | 7 | 7 | 26 |

± standard deviation, $n$ = 4

As seen from the research conducted by Hossain et al. (2011), the content of trace elements increases during pyrolysis depending on the applied temperature, which corresponds with mass loss. In the authors' own research, the temperature was set at 300°C and 600°C. According to Song and Guo (2012), the suggested temperature of pyrolysis of materials for agricultural purposes should be approximately 300°C. An increase in the temperature of pyrolysis caused a distinct increase in the content of zinc and copper in the end material, whereas no changes in the cadmium content were detected (Hossain et al. 2011).

The thermal treatment of the prepared mixtures at the temperature of 300°C resulted in an increase in the content of all the analyzed elements (Tables 8, 9). Regardless of the addition of plant material, setting the temperature at 600°C during the process caused an increase in the content of all the elements, except nitrogen, in comparison to the content determined in the mixtures prior to the treatment and in comparison to the content determined in the mixtures subjected to the thermal treatment at the temperature of 300°C. In their research on the effect of temperature on the content of nutrients of plants in biochar from sewage sludge, Hossain et al. (2011) found that an increase in temperature during the process caused a decrease in the nitrogen content as well as the enrichment of biochar with trace elements. According to Gaskin et al. (2008), mineral composition of biochar depends on the kind of substrate used in the process. The quoted authors con-

Table 8

The content of total forms of macroelements in mixtures of sewage sludge and plant materials after thermal conversion

| Material | N | | P | | K | |
|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C |
| | (g kg$^{-1}$ DW) | | | | | |
| (SS+B) | 23.3±0.4 | 14.4±0.1 | 20.3±0.1 | 26.3±1.3 | 2.75±0.05 | 3.40±0.15 |
| (SS+WS) | 24.4±1.6 | 16.8±2.4 | 27.7±0.9 | 37.9±0.5 | 6.76±0.40 | 8.99±0.09 |
| (SS+S) | 24.4±1.2 | 16.8±1.5 | 29.8±0.3 | 38.5±0.2 | 3.01±0.09 | 3.76±0.11 |
| CV (%) | 3 | 9 | 19 | 20 | 54 | 58 |
| Material | Ca | | Mg | | Na | |
| (SS+B) | 24.6±0.8 | 30.2±1.6 | 2.76±0.02 | 3.49±0.13 | 0.58±0.01 | 0.74±0.02 |
| (SS+WS) | 27.9±1.3 | 38.3±0.7 | 3.62±0.18 | 4.99±0.01 | 0.77±0.02 | 1.07±0.01 |
| (SS+S) | 29.8±0.3 | 40.8±3.0 | 3.78±0.09 | 4.84±0.05 | 0.74±0.01 | 0.99±0.01 |
| CV (%) | 10 | 15 | 16 | 19 | 15 | 18 |

± standard deviation, $n$ = 4

Table 9

The content of total forms of trace elements in mixtures of sewage sludge and plant materials after thermal conversion

| Material | Cu | | Zn | | Fe | | Mn | |
|---|---|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C |
| | (mg kg$^{-1}$ DW) | | | | | | | |
| (SS+B) | 180±1 | 238±9 | 1161±86 | 1425±61 | 25327±607 | 29993±541 | 388±1 | 457±18 |
| (SS+WS) | 251±1 | 342±1 | 1519±32 | 1914±97 | 30073±762 | 36154±340 | 316±6 | 411±4 |
| (SS+S) | 259±5 | 348±1 | 1582±30 | 1965±72 | 31890±758 | 36885±112 | 406±15 | 518±4 |
| CV (%) | 19 | 20 | 16 | 17 | 12 | 11 | 13 | 12 |

± standard deviation, $n$ = 4

firm an increase in the content of such components as potassium, calcium or magnesium, at the same time indicating that using a higher temperature results in an increase in the content of mineral components in biochar. It results from some depletion of substance of organic character. When analyzing changes in the nitrogen content in materials subjected to thermal treatment, Gaskin et al. (2008) showed that losses of this element can be within a wide range and are significantly conditioned by the kind of organic matter being transformed. As shown by the quoted authors (Gaskin et al. 2008), greater nitrogen losses occurred in thermally treated poultry droppings, which probably resulted from the oxidation of ammonia nitrogen as well as easily decomposed compounds such as uric acid. The quoted authors obtained considerably lower losses of nitrogen when thermally treating pine shavings, which was a consequence of the lower content of N in this material as well as the occurrence of this element in complex structures that are not easily transformed into volatile compounds. The content of easily hydrolyzing nitrogen (extracted with sulfuric acid of the concentration of 0.25 mol $dm^{-3}$) in organic materials after thermal treatment varied mainly due to the temperature of the treatment (Table 10). Using the temperature of 600°C for the transformation of organic materials caused a reduction in the content of easily hydrolyzing nitrogen in comparison to mixtures transformed at the temperature of 300°C by 23.6% (SS+B), 32.9% (SS+SW), and 27.4% (SS+S) – Table 10. Setting the higher temperature of treating organic materials

Table 10

The content of N extracted and water soluble forms of P and K in sewage sludge and mixtures of sewage sludge and plant materials after thermal conversion

| Material | N extracted 0.25 mol $dm^{-3}$ $H_2SO_4$ | | P | | K | |
|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C |
| | (mg $kg^{-1}$ DW) | | | | | |
| (SS+B) | 1.57±0.09 | 1.20±0.04 | 83±2 | 2±0.8 | 240±10 | 140±10 |
| (SS+WS) | 1.46±0.13 | 0.98±0.01 | 118±29 | 4±0.3 | 790±80 | 610±170 |
| (SS+S) | 1.46±0.03 | 1.06±0.03 | 86±7 | 2±0.1 | 160±10 | 70±20 |
| CV (%) | 3 | 5 | 20 | 43 | 86 | 107 |

± standard deviation, *n* = 4

caused a decrease in the content of water-soluble forms of phosphorus, potassium and sodium. Compared to the content determined in the material subjected to transformation at the temperature of 300°C, the content of phosphorus forms extracted with water decreased the most. Transformation of the mixtures of sewage sludge with plant materials at the temperature of 600°C caused an increase in the content of soluble forms of calcium and magnesium, and at the same time the increase in the content of soluble forms of Mg was significantly greater than that of soluble forms of Ca (Table 11).

Table 11

The content of water soluble forms of Ca, Mg and Na in sewage sludge and mixtures of sewage sludge and plant materials after thermal conversion

| Material | Ca | | Mg | | Na | |
|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C |
| | (g $kg^{-1}$ DW) | | | | (mg $kg^{-1}$ DW) | |
| (SS+B) | 6.31±0.21 | 6.80±0.30 | 0.30±0.02 | 0.40±0.02 | 82±5 | 78±5 |
| (SS+WS) | 6.07±0.09 | 7.06±0.41 | 0.41±0.07 | 0.88±0.19 | 159±34 | 99±26 |
| (SS+S) | 7.34±0.44 | 7.39±0.24 | 0.20±0.03 | 0.87±0.10 | 82±6 | 56±15 |
| CV (%) | 12 | 4 | 35 | 38 | 41 | 28 |

± standard deviation, *n* = 4

When comparing the concentrations of the macroelements in the transformed mixtures, regardless of the applied temperature, it was found that the determined content of all the studied macroelements was lower than in the untreated sewage sludge. The study of GASKIN et al. (2008) indicates that the kind of substrate does not have a great influence on the content of available macroelements, and that their content corresponds with the total content of the elements. Of all the trace elements determined in the materials (apart from the mixture assigned the symbol WS), it was only the content of water-soluble forms of zinc that was higher after the treatment at 600°C than the one determined in the mixtures treated at the temperature of 300°C (Table 12). Inconclusive results regarding the effect of adding plant

Table 12

The content of water soluble forms of Cu, Zn, Fe and Mn in sewage sludge and mixtures of sewage sludge and plant materials after thermal conversion

| Material | Cu | | Zn | | Fe | | Mn | |
|---|---|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C |
| | (mg kg$^{-1}$ DW) | | | | | | | |
| (SS+B) | 0.28±0.09 | 0.23±0.02 | 6.02±0.59 | 10.1±0.44 | 5.04± 1.88 | 0.18± 0.01 | 70±4 | 19±1 |
| (SS+WS) | 0.26±0.04 | 0.28±0.08 | 9.30±1.55 | 9.27±0.58 | 2.95± 1.19 | 0.23± 0.04 | 21±1 | 15±2 |
| (SS+S) | 0.21±0.02 | 0.11±0.01 | 12.7±1.81 | 15.1±1.48 | 4.12± 0.6 | 0.09± 0.01 | 34±7 | 10±4 |
| CV (%) | 14 | 42 | 36 | 27 | 26 | 43 | 61 | 31 |

± standard deviation, $n$ = 4

material to sewage sludge were obtained. However, the experiment indicates that as a result of adding plant materials to sewage sludge as well as thermal treatment of the mixtures, a decrease in the mobility of the trace elements appeared in comparison to the untreated sewage sludge. Results from the tests conducted by HE et al. (2010) suggest that pyrolysis temperature above 350°C improves the stability of forms of such trace elements as Zn and Cu. According to GONDEK et al. (2014), the process of thermal treatment of mixtures of sewage sludge with plant materials generally favoured an increase in the content of forms of the analyzed trace elements extracted with water. This resulted from a loss of unstable aliphatic bonds and formation of more stable aromatic bonds, which KLOSS et al. (2012) showed in their research.

The research showed that the extracts prepared from the mixtures were non-toxic to *Vibrio fischeri* (Table 13). Moreover, stimulation of luminescence

Table 13

Non-toxicity of extracts from sewage sludge and mixtures of sewage sludge and plant materials to *Vibrio fischeri*

| Material | SS+B | | SS+WS | | SS+S | | SS |
|---|---|---|---|---|---|---|---|
| | 300°C | 600°C | 300°C | 600°C | 300°C | 600°C | |
| inhibition *Vibrio fischeri* (%) | -6±2.3 | -14 ±1.5 | -24 ±2.5 | -19 ±1.8 | -17 ±1.2 | -15 ±2.5 | 10 ±1.5 |

± standard deviation, $n$ = 4

of the test organism was found. The extract samples showed negative mean values of toxicity. Namely, the luminescence intensity of *V. fischeri* increased after exposure to the extracts as a result of their lower toxicity compared with the reference medium (NaCl solutions). Inhibition of luminescence of *V. fischeri* at a level of 9% was found only in extracts from sewage sludge (SS). In literature, the stimulating effect of sublethal or low concentrations of toxic chemicals on an organism's metabolism is referred to as hormesis (Christofi et al. 2002). Noteworthy, the concentrations of trace elements found in the extracts in our research were low (Table 12). Hormesis has been found to be common in the widely used *Vibrio fischeri* luminescence bioassays (Fulladosa et al. 2005). Samples showing hormesis are currently considered to be non -toxic. Hormesis is a widespread phenomenon in the exposure of luminescent bacteria to metals because the bacteria *V. fischeri* are generally less sensitive to metals than to plant and animal cells (Cedergeen, Blain 2009, Shen et al. 2009). In the research by Shena et al. (2009), distinct hormesis was observed via luminescence assay for all tested metals (Cu, Zn, Cd, Cr) at low concentrations. Luminescence stimulation by exposure to zinc, cadmium and chromium was also found by Christofi et al. (2006), who showed more intensive luminescence induced by low concentrations of these metals. Stimulation of luminescence of *V. fischeri* bacteria was observed in environmental research when analyzing samples of pore water from bottom sediments and a river (Baran, Tarnawski 2013). In both cases, low concentrations of heavy metals were found in the samples. However, hormesis is rarely mentioned and accepted in mainstream toxicology (Shen et al. 2009). A reason why hormesis is not often found in organism-based bioassays is probably due to the fact that inhibitory concentrations of substances are more frequently observed (Fulladosa et al. 2005). The arising problem is that the result of hormesis may be dismissed as an experimental error and ignored in toxicity calculations.

## CONCLUSIONS

1. Thermal, anaerobic transformation of organic matter at a temperature up to 600°C causes even a twofold increase in the content of ash elements in the product.

2. An increase in the nitrogen content can only be obtained under conditions of low-temperature transformation of a mixture of sewage sludge with organic materials.

3. Using the temperature of 600°C for the transformation of organic materials caused an increase in the content of easily hydrolyzing nitrogen as well as forms of phosphorus, potassium and sodium extracted with water in comparison to mixtures transformed at the temperature of 300°C.

4. Of all the analyzed trace elements, only the content of water-soluble forms of zinc increased along with the increase in temperature of the transformation process of all materials (apart from the mixture of sewage sludge and straw), which indicates higher zinc bioavailability.

5. In terms of fertilization, as a result of increasing the temperature of treating sewage sludge with the addition of varied organic mass, a product with a lower fertilizing value is obtained due to nitrogen losses and a decrease in the availability of some elements for plants.

6. The extracts from the tested mixtures were not toxic to bacteria. Stimulation of the luminescence of *V. fischeri* was observed in the research.

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