



Assessment of Composition Changes, Stability Degree and the Potential of Biogas Formation of Sewage Sludge Composts During Maturation Process

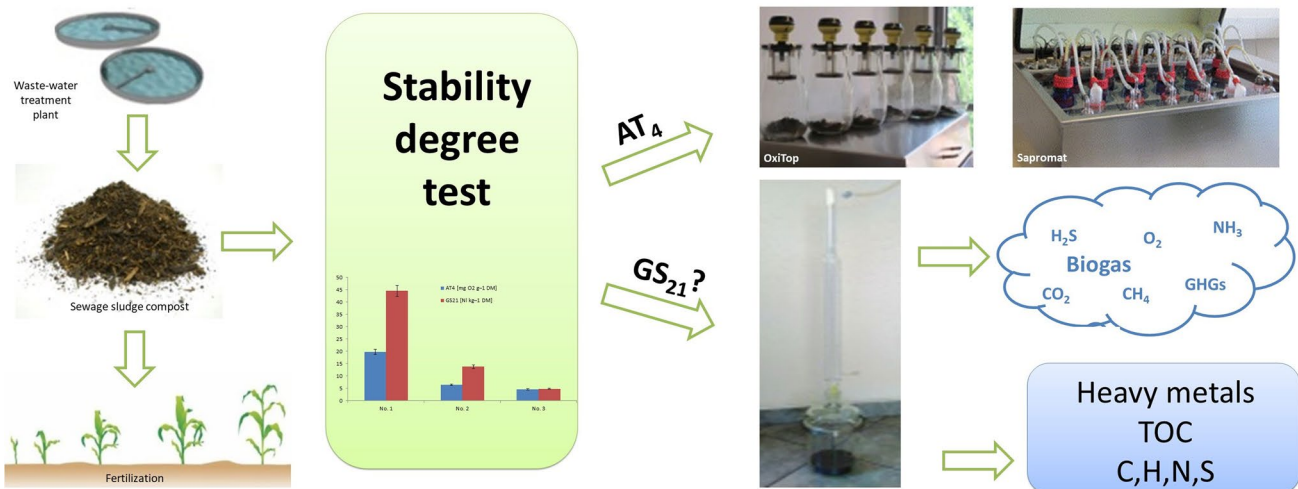
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Abstract

The aim of this study was to assess the degree of stabilization of composted sewage sludge (SSC) during maturation using tests in aerobic and anaerobic conditions, determining the potential for biogas formation and its composition, as well as changes of mobile and bioavailable forms of metals in SSC after treatment. The samples were taken in the second phase of composting, during the maturation process. The biological stability of SSC samples was determined by detecting an incubation test (GS_{21}) and respiration index (AT_4). The potential for biogas formation and composition changes of SSC during maturation were analyzed. It was found that the chemical composition of the tested samples depended on the degree of their maturity. It was found that the both tested methods (AT_4 , GS_{21}) of assessing the stability of waste are sufficient. Treatment under anaerobic conditions did not significantly change the composition of the samples, with the exception of total organic carbon (TOC). A high percentage of methane in biogas for samples at the beginning of the maturation process indicates a high content of biodegradable organic matter in SSC. In addition, the decrease of mobile and bioavailable forms of heavy metals percentage, during the SSC maturation, was found. In order to confirm the results of current study, a long-term field studies should be carried out on the effects of SSCs tested on soils and plants.

Graphic Abstract



Keywords Sewage sludge compost (SSC) · Maturity · Incubation test (GS_{21}) · Respiration index (AT_4) · Biogas potential · Heavy metals

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Abbreviations

AAS	Atomic absorption spectrometry
AT ₄ (RA ₄)	Static respiration index
CHNS	Elementary analysis of C, H, N and S
COU	Cumulative oxygen uptake
CRM	Certified reference material
DM	Dry matter
GB ₂₁	Gas evolution (in German “ <i>Gasbildung</i> ”), fermentation test after 21 days
GHG	Greenhouse gas
GI	Germination index
GS ₂₁	Gas generation sum, incubation test after 21 days
ICiMB	Institute of Ceramics and Building Materials
MBT	Mechanical–biological treatment
MSW	Municipal solid waste
MWWTP	Municipal waste water treatment plant
OUR	Oxygen uptake rate
p.e.	Population equivalent
SS	Sewage sludge
SSC	Sewage sludge compost
TOC	Total organic carbon
WWTP	Waste water treatment plant

Statement of Novelty

Unstable composts used as a fertilizer can cause negative effects in the soil e.g. GHGs emission, phytotoxic risks, low nitrogen and oxygen availability. The degree of compost stabilization is a very important quality parameter and in fact the most difficult to evaluate. In the literature, many different methods have been proposed to measure the compost stability, the most are based on static and dynamic aerobic methods. The novelty of these studies is the additional use of anaerobic test to assess the stability of SSC. Therefore, the potential for biogas formation from compost during maturation was assessed. The potential to produce biogas containing GHGs from matured SSC was found. The usefulness of the GS21 test to assess SSC stability has been proved.

Introduction

Sewage sludge (SS) used in agriculture is the one of the recommended recycling routes. The main processing for agricultural use of SS includes biological treatment as aerobic or anaerobic digestions, respectively composting or methane fermentation for biogas production. The best way is via the addition of SS in a correct dose to improve chemical soil properties. However, agricultural use of untreated SS may pose a risk of soil sanitary contamination and odour emission, and an indirect risk to the environment, due to

the possibility of greenhouse gases (GHGs) emissions after soil application. The problem of GHGs, ammonia, and N₂O emissions during the composting of SS is well known and has been described by many authors [1–5]. In order to reduce GHGs emissions during the composting process, many methods are recommended, e.g. zeolites [1], biochar [2] in a compost mixture or simply covering compost windrows with a thick layer of peat [5]. On the other hand, immature compost or other organic fertilizers that contain biodegradable organic matter may trigger GHGs emissions in soil [6]. Soil fertilization with unstable compost can cause environmental pollution due to its residual biodegradability, nutrient removal from the soil, leaching of heavy metals and phytotoxic risks [7–9]. The stability of compost is an important index for determining the potential impact on the nitrogen and oxygen availability in the soil [10]. For this reason, a suitable composting process management is necessary to obtain a quality product [11]. The stability can be defined as the extent to which readily biodegradable material has been decomposed. According to Alvarenga et al. [12] the maturity of compost is associated with phytotoxicity and influence of plant growth potential. In contrast, the stability of compost is related to microbial activity and to the degree of organic matter decomposition. Each of these parameters, maturity and stability, is assessed using different tests e.g. germination index (GI), production rates of O₂ uptake or CO₂, physico–chemical parameters or microbial activity [11, 13–21]. During composting processes there is a predominant activity of aerobic bacteria; for this reason, respirometric methods are most often used for assessing compost stability. Testing under anaerobic conditions may also be used for this purpose. In some European countries, to test the degree of stability of landfilled waste after mechanical–biological treatment (MBT), static respiration indexes (AT₄, RA₄, RI₄) are used [22, 23]. Furthermore, the incubation test or fermentation test, respectively GS₂₁ or GB₂₁, are used as a complementary indicator for their stability [18]. Binner et al. [24] suggest that both AT₄ and GS₂₁ test are very suitable methods for characterizing the stability of waste. Nowadays, a wide range of biological and chemical tests are readily available for the evaluation of the stability of compost. Biochemical test methods are commonly used, which are based on aerobic respiration indices adopted from assessing the stability of waste after mechanical–biological treatment (MBT) or composted waste [18]. According to European legislation on waste, stabilization means the decomposition of the biodegradable waste fraction in order to minimize odours and stabilize the composition. Stabilized waste should be characterized by a low value of the AT₄ parameter, below 10 mg O₂ g⁻¹ DM [10]. Many tests are used to assess the stability of waste compost [10, 12, 25–28]. In recent years, a number of automated respirometers have become available on the market, each with a proven

capability to measure O_2 consumption. The most popular methods are based on respirometric test using a SaproMat or OxiTop apparatus [25, 29–31]. However, compost stability analysis based on these tests may be insufficient. The biogas production potential, used in Austria and Germany for the analysis of stabilizers, can also be useful for assessing the stability of composts. Additionally, measurement of biogas composition gives an estimation of anaerobic biodegradability and helps in assessing the impact of compost to the environment.

The aim of the study was to assess (I) AT_4 and GS_{21} tests used to assess SSC stabilization, (II) the potential of biogas formation from SSC during maturation, (III) biogas composition in order to predict effects in soil after application of SSC, and (IV) changes of mobile and bioavailable forms of metals in SSC after treatment.

Materials and Methods

Sampling

The materials were taken from a Composting Plant located in Northern Poland Municipal Waste Water Treatment Plant (WWTP) (200,000 p.e.). SS were stabilized in aerobic conditions by composting it in a compost triangular and in sliding windrows with the addition of structural materials (straw, wood chips). Both, a dynamic by flipping and static with aeration channels are used to aerate the composted material. The composting process runs for 6–8 weeks (intensive degradation phase) and then compost is sieved and matured in windrows during 2–3 months in roofed boxes with a concrete floor. For this study, samples were taken only during the second phase of composting (maturation process). The compost samples were collected during maturation: after 2, 8 and 12 weeks of maturation. The waste water treatment plant (WWTP) has a permission of the Ministry of Agriculture to produce and sell SSC to be applied as a fertilizer. Each year 13,000 tonnes of raw SS is composted, furthermore, about 7000 tonnes of fertilizer are produced each year. The parameters of the mixture are as follows: C/N 25/1 and moisture content of about 55% WM. The height of the windrow did not exceed 1.5 m, and the volume of the windrow was over 100 m^3 .

In three sampling periods, samples were taken from the same windrow after 2 (No. 1), 8 (No. 2), and 12 weeks (No. 3) of maturation according to Polish Standards [32–34]. The primary samples were reduced by quartering. The laboratory samples prepared in this way were placed in tightly sealed polypropylene containers and stored at a temperature of $4\text{ }^\circ\text{C}$ during transport to the laboratory. The samples were delivered to the laboratory within 12 h. Fresh samples were ground to obtain a $<20\text{ mm}$ fraction. One part of the

fresh material was used for the test of biological activity and the second part of each sample was air-dried. These samples were ground with an agate mill and sieved and subsequently analyzed according to Polish Standard [35]. The sampling and the TOC, CHNS, AT_4 , GS_{21} and composition of biogas were conducted by an accredited ICiMB laboratory in Opole. The heavy metal analysis were carried out in the laboratory of the Opole University of Technology.

Analysis

The biological stability of SSC samples was determined by using the incubation test (GS_{21}) and respiration index (AT_4). The tests were carried out in triplicate, according to Austrian Standards [36, 37]. The AT_4 index was measured as the cumulative oxygen consumption during 4 days, at $20\text{ }^\circ\text{C}$ using a OxiTop apparatus [31]. The GS_{21} test were carried out at $40\text{ }^\circ\text{C}$ in a water bath, during 21 days of incubation using the specially designed apparatus. The apparatus for analysis of waste stability under anaerobic conditions (GS_{21} test) is presented in Fig. 1. The volume of the sample was about 1.7 L ($\approx 1.5\text{ kg DM}$). The result of analysis was carried out to DM in $105\text{ }^\circ\text{C}$. The GS_{21} test is included in static processes, i.e. without material mixing. The test does not require additional inoculation of the material. During the 21 days of the incubation test, the volume of biogas is analyzed. Additionally, an analysis of biogas composition was carried out. The aim of this part of the research was to assess the potential of biogas formation and analysis of its composition, depending on SSC maturation time. Each of the anaerobic incubation apparatus was equipped with an opening intended for taking gaseous pollutant samples. The concentrations of carbon dioxide (CO_2), oxygen (O_2), methane (CH_4) and the sum of ammonia (NH_3) and hydrogen sulphide (H_2S) were identified with the gas analyzer

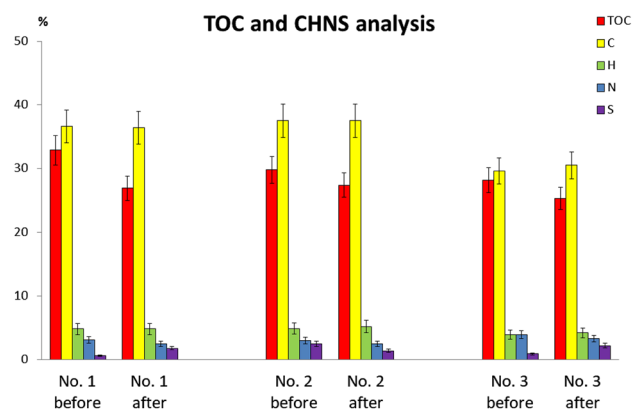


Fig. 1 TOC and CHNS analysis of SSC samples before and after 42 days of incubation test: TOC (red), C (yellow), H (green), N (blue), S (violet). (Color figure online)

Geotech GA5000 (Tusnovics Instruments). The calibration of analyzer was obtained through a separate analysis of pure gas compounds (Linde Gas). The elementary composition (CHNS) of SSC was analyzed using “CHNS Analyzer” (Elementar). The total organic carbon (TOC) was analyzed using “Vario Macro Cube” (Elementar).

Heavy Metals Content

The samples of SSC were taken before and after incubation test (42 days). In the samples the total content and mobile and bioavailable forms of heavy metals (Cd, Pb, Cu, Zn, Cr, Ni, Co, Fe, Mn) were analyzed. A microwave system (Milestone, Start D) was used for sample digestion with *aqua regia* (36% HCl Tracepur[®] and 65% HNO₃ Suprapur[®], Merck). The bioavailable form of heavy metals were determined using acetic acid extraction (0.11 M Ac) (Emsure[®], Merck), according to the method SM&T [38]. The mobile form of heavy metals were determined using a hydrochloric acid (0.5 M HCl) (Tracepur[®], Merck) according to Polish Chemical and Agricultural Stations procedure based on Polish Norm [39]. The extractions were carried out at room temperature. All measurements of metals concentrations and they fractions were made with a Solaar 6 M (Thermo) by FAAS technique. Heavy metal analysis were carried out in triplicate.

Quality Control

Certificate materials were used for quality control/quality assurance: B2273, Cert. No. 41505: (CHNS and TOC) and CRM material: ‘Trace metals—Sewage amended soil’ CRM005–50G (Sigma–Aldrich, Lot: LRAB1009). Each material was tested in a minimum of triplicate assays. Data were processed using STATISTICA 5.0 software and analyzed with ANOVA and *F*-test for mean separation.

Results and Discussion

Stability Degree Tests and Gas Production Potential

The degree of compost stabilization is a very important parameter of its quality and probably the most controversial [40, 41]. The stability assessment is used to determine the end of the stabilization process (maturation), monitoring the process conditions during composting, comparing some composting technologies or predicting distribution in the soil [1, 2, 42]. Whereas the degree of stabilization of waste after biological treatment of MBT is determined in order to assess the potential for decomposition in a landfill. In Poland, waste after stabilization (composting) in a MBT plant is called a stabilizer. Due to there being no legal

regulations in Poland regarding the assessment of the stabilization of waste after treatment, the Austrian standards for stabilization after MBT were used to assess the tested samples. According this standards the limits for stabilizer is: respiration activity (AT_4) < 7 mg O₂ g⁻¹ DM and Gas Generation Sum GS_{21} < 20 NI kg⁻¹ DM. In the current study, the 2 weeks of the maturation sample (No. 1) was characterized by respiration activity AT_4 19.8 mg O₂ g⁻¹ DM and gas generation sum GS_{21} 44.6 NI kg⁻¹ DM. During maturation, the value for both parameters decreased, respectively: after 8 weeks AT_4 6.5 mg O₂ g⁻¹ DM and GS_{21} 13.8 NI kg⁻¹ DM (No. 2) and after 12 weeks 4.6 mg O₂ g⁻¹ DM and 4.9 GS_{21} NI kg⁻¹ DM (No. 3). Decreasing the value of the respiration index (AT_4 , RA_4) is an obvious effect of compost maturation [10, 12, 26, 27]. The results of the AT_4 analysis for the tested samples were compared with the German classification of composts (Table 1).

Therefore, it was found that the tested compost samples could be classified as fresh compost (sample No. 1), finished compost as IV class (sample No. 2) and finished compost as V class (sample No. 3). Differences between class IV and V according to German standards have not been clarified [10]. Based on the AT_4 value it can be stated that the 12 weeks of maturation reduced the value of the AT_4 parameter to a level that results in the sufficient stabilization of the material [10, 40]. Some authors have found that the AT_4 value can be much higher for SSC than for composts from other wastes [12, 25]. In a current study an interesting effect was a high level (44.6 NI kg⁻¹ DM) of GS_{21} for the sample after 2 weeks of maturation (No. 1). Due to the fact that composting is an aerobic treatment of SS, the potential of biogas production in this material should be low. It seems that the SSC after 2 weeks of maturation (No. 1) could be in the final phase of active composting and it could contain a high percentage of biodegradable organic matter, converted into biogas. For tested SSC, the GS_{21} = 13.8 NI kg⁻¹ for the sample after 8 weeks of maturation (No. 2) and GS_{21} = 4.9 NI kg⁻¹ for the sample after 12 weeks of maturation (No. 3) were obtained. Smidt and Parravicini [27] obtained a high GS_{21} value (47 NI kg⁻¹ DM) in anaerobic treated SS and low value for the same SS after additional aerobic treatment (18 NI kg⁻¹ DM). This effect may have been the result of low

Table 1 Classification of the compost samples according to German Standards based on AT_4 analysis [10]

The class of compost	AT_4 (mg O ₂ g ⁻¹ DM)	Product description
I	> 40	Compost raw materials
II	28–40	Fresh compost
III	16–28	Fresh compost
IV	6–16	Finished compost
V	<6	Finished compost

availability of biodegradable organic matter, not the aerobic treatment of SS. The authors [27] also observed that respiration activity (RA_4) and gas generation sum (GS_{21}) correlate in aerobically treated waste materials. In the current study, the basis of Austrian standards for stabilizer (AT_4) < 7 mg O_2 g^{-1} DM and GS_{21} < 20 NI kg^{-1}), it can be stated that samples No. 2 and No. 3 should be stable. However, the tests of biogas generation potential showed a different tendency. The results of biogas composition from SSC samples after 10, 20, 30, 36 and 42 days are presented in Table 2.

In the current study the highest percentage of methane in biogas was determined in sample No. 1 (56.8%), i.e. SSC after 2 weeks of maturation (Table 2). Moreover for this sample a high percentage of CH_4 already at the beginning of the anaerobic treatment was determined. For sample No. 2 (SSC after 8 weeks of maturation) initially the percentage of methane was low (1.3%), but after 30 days increased to 51.8%, i.e. a similar level as in sample No. 1. The lowest amount of methane was produced from an SSC sample after 12 weeks of maturation (No. 3). For all samples, an increase in the percentage of methane in biogas during the incubation test was found, but for sample No. 2, the increase was the most dynamic. A high percentage of methane in biogas indicates high activity of methane microorganisms and high content of biodegradable organic matter in the SSC. It follows that composting of SSC does not reduce the potential for biogas production with a high percentage of methane. For comparison Maulini–Duran et al. [3] found higher methane emissions from SS treated in two stages: fermentation and composting, than from SS treated in one stage (only composting). It is known that methane is produced during the decomposition of the organic matter of the substrate or by reduction of CO_2 by autotrophic methane microorganisms [43]. In the current research, the content of carbon dioxide in biogas depended on the time of maturation of SSC. For sample No. 3, i.e. SSC with the longest maturation time

(12 weeks), the highest percentage of CO_2 was determined (61.3–73.9%). For sample No. 1 and 2 the percentage of CO_2 in biogas decreased during the incubation test, in contrast to sample No. 3. The percentage of oxygen in biogas was very low in all samples (0.1–0.5%). The term *Residue* means other unidentified components of biogas, mainly N_2 and a low percentage of CO , H_2 , H_2O , siloxanes and others. In all samples the percentage of *Residue* decreased during the incubation test. The mature compost (No. 3) characterized the highest percentage of *Residue* in biogas. The highest level of NH_3 and H_2S sum was determined in sample No. 2, i.e. the SSC after 8 weeks of maturation, especially at the beginning of the incubation test (Table 2). The highest concentration of H_2S in the sample No. 2 has a direct relationship with the initial content of S in the CHNS of this sample. It was found that the content of NH_3 and H_2S decreased during the incubation test for all samples. It should be noted that both gases, ammonia and hydrogen sulfide, are inhibitors of biogas production [44]. In addition, they have toxic properties and negatively affect the environment. The concentration of toxic and odorous gases in biogas such as NH_3 and H_2S depends on the composition of the substrate, especially the protein content.

Elementary and TOC Analysis

The content of TOC and CHNS [%] of SSC samples is shown in Fig. 1. The concentration of TOC slightly decreased during the time of SSC maturation from 32.9% after 2 weeks of maturation (No. 1) and 29.8% after 8 weeks of maturation (No. 2) to 28.2% after 12 weeks of maturation (No. 3) (Fig. 1). This effect indicates that biodegradable organic matter was present in samples. The reduction of the TOC content is observed in treated SS, regardless of whether it is a treatment under aerobic or anaerobic conditions [26]. The initial TOC could be lost during maturation when compost

Table 2 Biogas composition after 10, 20, 30, 36 and 42 days of incubation SSC

Sample	Days	CH_4 (%)	CO_2 (%)	O_2 (%)	$\sum NH_3$ and H_2S (ppm)	Residue (%)
1	10	39.1 ± 4	52.7 ± 5	0.1 ± 0.0	1149 ± 138	8.1 ± 0.8
	20	56.8 ± 6	40.6 ± 4	0.2 ± 0.0	320 ± 38	2.4 ± 0.2
	30	54.5 ± 5	42.5 ± 4	0.2 ± 0.0	207 ± 25	2.9 ± 0.3
	36	54.2 ± 5	42.6 ± 4	0.2 ± 0.0	193 ± 23	3.0 ± 0.3
	42	54.6 ± 5	42.7 ± 4	0.2 ± 0.0	173 ± 21	2.5 ± 0.3
2	10	1.3 ± 0.1	73.7 ± 7	0.2 ± 0.0	2191 ± 263	9.2 ± 0.9
	20	23.0 ± 2	67.6 ± 7	0.1 ± 0.0	1073 ± 129	9.2 ± 0.9
	30	51.8 ± 5	44.2 ± 4	0.3 ± 0.0	456 ± 55	3.7 ± 0.4
	36	53.5 ± 5	43.6 ± 4	0.2 ± 0.0	426 ± 51	8.8 ± 0.9
	42	53.5 ± 5	43.9 ± 4	0.2 ± 0.0	384 ± 46	2.5 ± 0.3
3	10	0.5 ± 0	61.3 ± 6	0.2 ± 0.0	364 ± 44	38.0 ± 4
	20	1.3 ± 0.1	73.9 ± 7	0.2 ± 0.0	376 ± 45	24.6 ± 2
	30	11.5 ± 1	71.4 ± 7	0.5 ± 0.0	210 ± 25	16.7 ± 2
	36	14.0 ± 1	72.2 ± 7	0.1 ± 0.0	250 ± 30	13.7 ± 1
	42	18.8 ± 2	69.8 ± 6	0.1 ± 0.0	291 ± 35	11.3 ± 1

windrows were treated by aeration, homogenizing and sieving. The results indicate that the tested SSC contained degradable organic matter, which was used by microorganisms during maturation. However, the decrease in the percentage of TOC was not high, about 14% compared to the original value (No. 1). This may indicate that the minor part of TOC was a biodegradable fraction. Probably the major part of the TOC from the tested composts were complex organic compounds such as humus. In the current study, the reduction of total carbon content from 36.6 to 29.6% during the maturation of SSC was also observed. However, no tendency for H, N or S content during the maturation process of SSC was found, the percentage of these elements was characterized by high variability (Fig. 1). No statistically significant changes in the percentage of elements (CHN) in SSC before and after the incubation test were found. Similar results to the current study were obtained by Dussan and Monaghan [45] in typical ultimate composition analysis of SSC: C 36.5%, H 5.2%, N 5%, S 1.5%. In the current study the S content in the SSC (Nos. 1 and 3) increased after the test under anaerobic conditions (Fig. 1). This effect can be explained that during the anaerobic test, some of the organic matter was transformed into biogas, which resulted in a decrease in the weight of the final product and an increase in the S percentage. The percentage of carbon and hydrogen of tested composts was at a similar level before and after the anaerobic test. Due to the emission of volatile nitrogen compounds (NO_x , NH_3), a slight decrease in the percentage of nitrogen was found.

Heavy Metals

The results of heavy metals content and percentage of mobile and bioavailable forms are presented in Fig. 2. The content of heavy metals in the tested samples was varied. SSCs were characterized by a high content of iron and zinc. The order of the total heavy metal content in the SSC is as follows: $\text{Cd} < \text{Co} < \text{Ni} < \text{Cr}, \text{Pb} < \text{Cu} < \text{Mn} < \text{Zn} < \text{Fe}$. A significant increase in the concentrations of Fe and Mn in the final product after the maturation process was observed. Probably, the composted material was contaminated with those metals during mechanical processing, such as turning flipping, screening, and aerating. A slight increase of total metals content in compost after maturation was found, as effect of organic matter mineralization and the reduction of compost volume. The total content of heavy metals showed no significant variation before and after 42 days of the fermentation process (incubation test). The heavy metals concentrations were generally low in tested SSC samples, and the values were much lower than the limitation for first class compost quality from municipal wastes in Poland [46]. Table 3 presents limits on the content of heavy metals in composts from wastes in accordance with the applicable law in a few countries, including Poland. In Poland, the limits of

heavy metals content in compost from municipal waste are slightly higher than in UK, Germany, France and Canada. US law allows the use of composts in agriculture with higher heavy metal content than in other countries. However, in Poland, in order to use SSC in agriculture, two other legal acts should be included, not only the classification of compost. These legal acts are the Act on Fertilizers and Fertilization [47] which is applicable only for commercial fertilizers and requirement for SS used in agriculture [48]. According to these legal acts, limits on the content of heavy metals are lower than for the first class of composts (Table 3). The total content of heavy metals in the tested samples did not exceed the limits set in Polish standards.

The most important forms of metals in the soil are bioavailable forms, which allows the estimation of the related phyto-toxic and nutritional deficiency effects, and a mobile forms, what indicates the potential of groundwater contamination. Two metal extractants were selected, characterized by the ability to elute mobile forms (0.5 M HCl) and bioavailable forms (0.11 M Ac). The evaluation of the leachability of heavy metals in SSC before and after 42 days of the incubation test are presented in graphs in Fig. 2. The extractabilities of metals obtained with hydrochloric acid (0.5 M HCl) was generally higher than acetic acid (0.11 M Ac) for all metals. Among all metals, zinc was characterized by the highest percentage of leaching by 0.11 M Ac (17–28%) (Fig. 2d). A lower degree of leaching was determined for: Ni 9–15%, Mn 10–15% and Fe 1–10% (Fig. 2f, h, i). The lowest percentage of bioavailable forms was determined for Pb and Cu (2–6%) (Fig. 2b, c). A high variability of bioavailable forms concentration of Co (0–18%) (Fig. 2g) was found. The percentage of bioavailable forms in sample No. 2 was the highest. It seems that during the maturation of the SSC there were changes in the forms of Co. Initially, cobalt could be mobilized between 2 and 8 weeks of SSC maturation. Later, this metal could be immobilized in the SSC. In other studies, the reduction of Co mobility in composted SS was found [49]. In the current study the concentration of Cd and Cr in the 0.11 M Ac extracts was below the limit of quantification, which means that the tested SSCs did not contain bioavailable forms of both metals. There were no significant differences in the percentage of forms bioavailable in SSC samples after the incubation test. The research of other authors shows that heavy metals can be immobilized by chelating or aggregated by microbial hypha during composting SSC, which causes the reduction of bioavailability [7, 13, 50, 51].

Extraction with hydrochloric acid (0.5 M HCl) affects the leaching of metals in mobile forms, associated with carbonate and organic matter in SSC. Hydrochloric acid is capable of dissolving large quantities of microelements, which considerably exceed the nutritional demand of plants. In Poland, the leaching test using HCl for the assessment

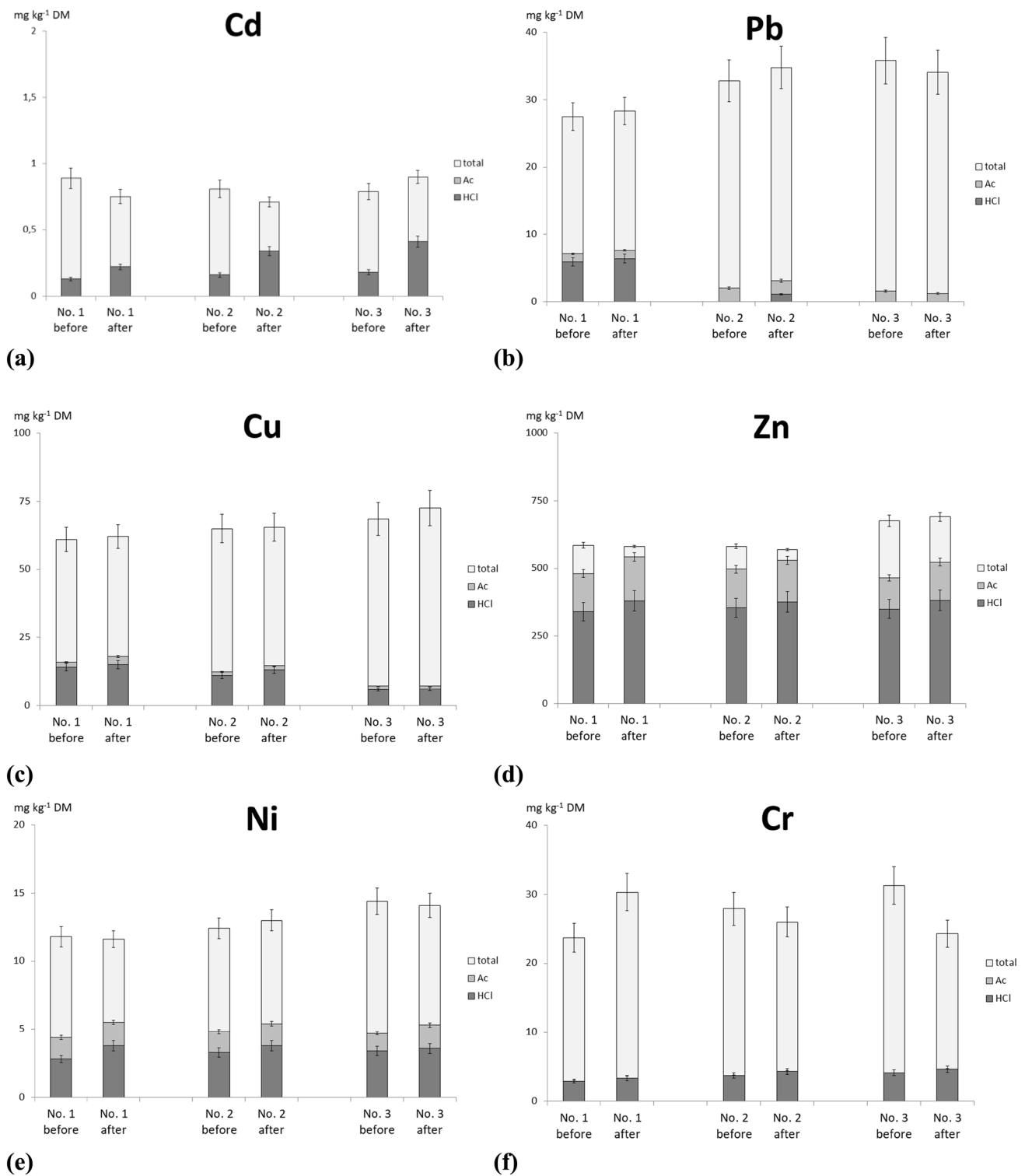


Fig. 2 The heavy metals content (mg kg⁻¹ DM): **a** Cd, **b** Pb, **c** Cu, **d** Zn, **e** Cr, **f** Ni, **g** Co, **h** Fe, **i** Mn in eluate: Ac (medium gray) and HCl (light gray) compared to the total metal content (mg kg⁻¹ DM) (light gray) before and after 42 days of incubation test

of mobile forms of metals in soil and to predict the risk of groundwater contamination is used. The highest percentage of mobile forms was determined for zinc (52–61%) (Fig. 2d).

The percentage of bioavailable and mobile forms of zinc is usually high in SSC [50]. Other metals were characterized by the following percentage of mobile forms: Co (25–40%),

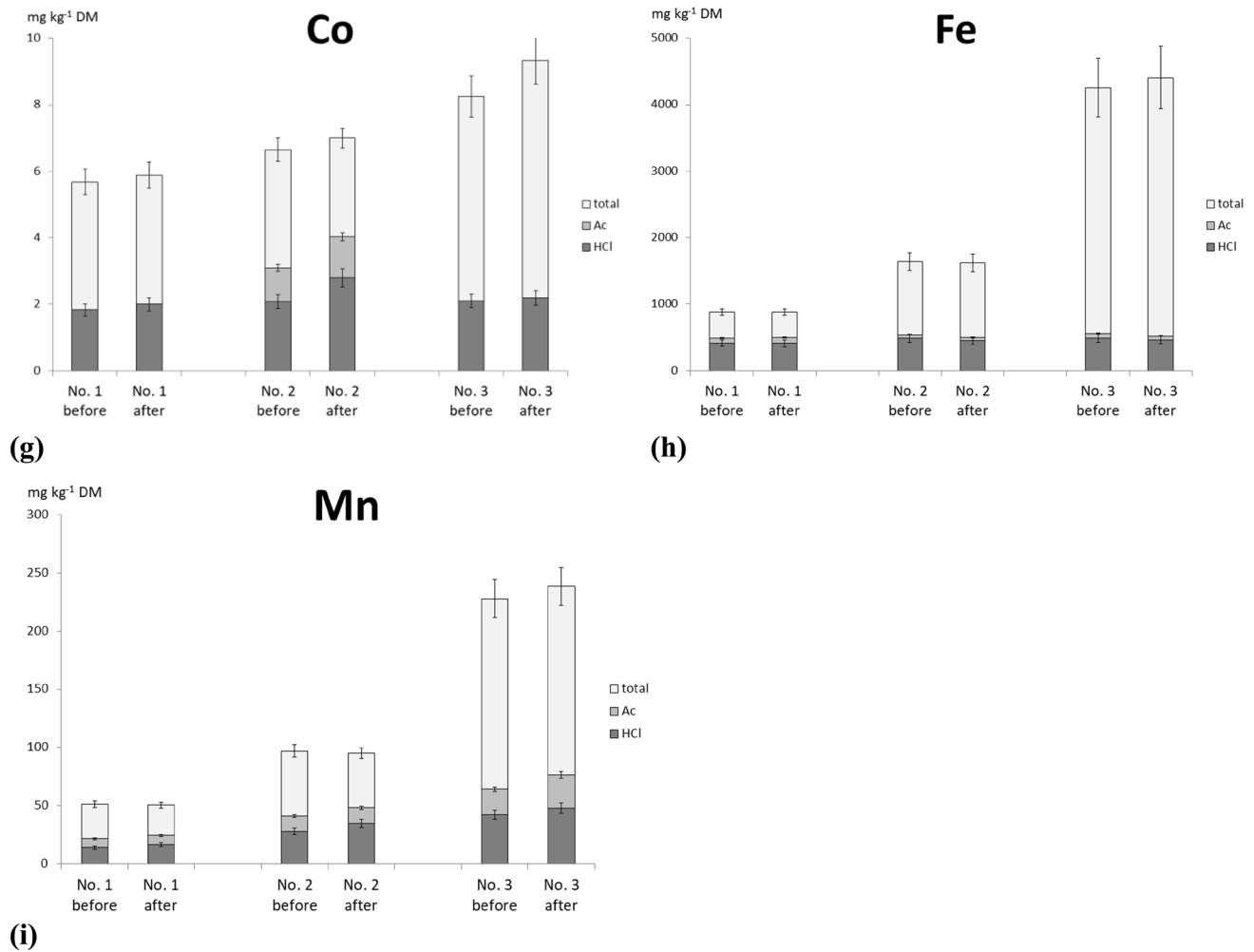


Fig. 2 (continued)

Table 3 The limits of total metal content (mg kg⁻¹ DM) in compost used in agriculture in few countries [8–10, 46–48]

Metal	Compost quality						Others	
	UK	Germany	France	Canada	USA	Poland ^a	Poland ^b	Poland ^c
Cd	1.5	0.7	3	3	39	5	20	5
Pb	200	100	180	150	300	350	750	140
Cu	200	100	300	400	1500	300	1000	–
Zn	400	200	600	700	2800	1500	2500	–
Cr	100	100	120	210	–	300	500	100
Ni	50	50	60	62	420	100	300	60

^aThe first class of quality of compost from municipal waste [46]^bAgricultural use of municipal sewage sludge [48]^cSolid organic fertilizer according to guidelines for fertilizers and fertilization [47]

Ni (24–33%), Mn (18–37%), Fe (10–47%), Cd (15–48%), Cr (12–17%), Cu (8–24%) and Pb (0–23%) (Fig. 2). The percentage of mobile forms of Zn, Ni and Cr did not change significantly during the SSC maturation. A slight decrease in the percentage of mobile forms Co and a significant decrease

in Cu, Pb, Mn and Fe in SSC during maturation was found. It is known that humic substances reduce the mobility of heavy metals [52]. The exception was cadmium, the percentage of Cd increased during the maturation from 15 to 23%. An increase in the percentage of Cd mobile forms after the

incubation test was also found. Cadmium in SS and SSC usually occurs in soluble forms, which can negatively affect plants and soil [50].

Based on the obtained results, it can be stated that for most metals, the maturation caused a reduction in the level of bioavailable and mobile forms. In the current study the metal leaching with both eluents sequence is as follows: Zn > Co > Cd > Mn > Fe > Cu > Pb > Cr. It is known that the composting process increases the complexation of heavy metals. In composts, metals are strongly bound with organic matter and the compost matrix, which limits their mobility and bioavailability. Usually the strong bounded metal in compost is Pb, whereas the least bounded in composted waste and SSC are Cd, Zn, Ni and Cu [50]. In the current study it was found that 42 days of anaerobic treatment of SSC samples during the incubation test did not create significant changes in the percentage of bioavailable and mobile forms of heavy metals (Fig. 2). Due to the low total content of heavy metals and the decrease in the percentage of bioavailable and mobile forms during maturation, the tested SSCs should not have a negative impact on the environment. There is no scientific evidence of negative effect of heavy metals from SSC on soils and plants [50]. Many factors can affect the bioavailability of heavy metals in soil, such as organic matter composition, pH, Fe–Al complex, and other [50, 51].

Conclusions

1. The SSC after 2 weeks of maturation was characterized by a high AT₄ and GS₂₁ value, which may indicate a high percentage of biodegradable organic matter. A significant decrease in both parameters after 12 weeks of maturation was found. The final product of composting (No. 3) should be considered stable, according to Austrian and German requirements. It seems that the analysis of both parameters: AT₄ and GS₂₁ is appropriate to assess the stability of SSC. The use of a single AT₄ analysis may not fully assess the degree of stabilization, as SSC may have the potential to biogas produce under anaerobic conditions.
2. A strong potential to produce biogas of the tested SSC was found. Due to the fact that the highest volume of biogas and the percentage of methane was determined in sample No. 1 and the lowest in sample No. 3, it can be concluded that maturation of SSC reduced the level of anaerobic biodegradation potential. A potential of biogas production can negatively affect the environment, especially after the application of unstable SSC to the soil. In order to reduce the potential of biogas production of SSC in soil, the maturing process should be controlled until significant reduction in GS₂₁ value.
3. The identified potential for biogas production with a high percentage of methane at initial maturation process, may suggest that biodegradable organic matter still remains in the tested compost. It is known that methane is produced during the decomposition of the organic matter of the substrate or by reduction of CO₂ by autotrophic methane microorganisms. A high content of CO₂ in biogas in all samples was found. The percentage of H₂S in biogas depended on the sulphur content in the SSC samples. It was found that the content of NH₃ and H₂S decreased during the incubation test for all samples. This is a positive effect, because both toxic gases are inhibitors of biogas production and they have negative impact on the environment.
4. A low concentration of total heavy metals in tested SSC was found. The metals content did not exceed the permissible standards specified in the Polish law. It can be stated that for most metals, except of cadmium, the maturation caused a reduction in the level of bioavailable and mobile forms. It is known that cadmium in SS and SSC is in soluble forms. Therefore, it is important to reduce the total Cd content in the compost substrate, so as to decrease the risk to the environment after soil application of SSC.
5. On the basis of the research conducted it can be concluded that the methods of assessing the stability of waste based on AT₄ and GS₂₁ test are sufficient. In addition, both tests provide information on the quality of waste and help predict the impact to on environment. Current studies have shown that the SSC samples were chemically stable. At present, there are not many literature reports regarding the assessment of the environmental effects of introducing unstable composts to the soil. In order to confirm the results of current study, a long-term field studies should be carried out on the effects of SSCs tested on soils and plants. The studies assumed that the identified potential of biogas production can affect the composition of compost. However, it was found that after 42 days of anaerobic treatment (incubation test) only the TOC content decreased. On the other hand, the elemental composition, the total content of heavy metals and their mobile and bioavailable forms did not significantly change after 42 days of the incubation test.

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