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ORIGINAL PAPER

AGRONOMIC EVALUATION OF DRIED SEWAGE SLUDGE AND SEWAGE SLUDGE ASH AS SOURCES OF NUTRIENTS FOR MAIZE*

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Abstract

The aim of this study was to determine whether dried sewage sludge (SS) and sewage sludge ash (SSA) from municipal sludge processed in a mono-incineration plant in Olsztyn (Poland) are good sources of P and other nutrients for maize (*Zea mays* L.). The effect of fertilization with dried SS and SSA on heavy metal accumulation in soil and plants was also determined. The pot experiment comprised 9 fertilizer treatments: control; 12.5 g, 25.0 g and 37.5 g of SSA DM per kg soil DM; 12.5 g, 25.0 g and 37.5 g of SS DM per kg soil DM; 62.5 mg of P as $Ca(H_2PO_4)_2$ per kg soil DM; 62.5 mg of P as $Ca(H_2PO_4)_2$ + 62.5 mg of Mg as $MgSO_4$ $7H_2O$ per kg soil DM. A dose of P as $Ca(H_2PO_4)_2$ covered the requirements of plants for P. In all the treatments, maize plants were additionally fertilized with equal amounts of N (as NH_4NO_3) and K (as KCl). Dried municipal SS and SSA were characterized by a high concentration of plant-available P, Mg and low concentrations of toxic trace elements, such as Cd, Pb, Ni, Cr and Hg. Fertilization with SS and SSA exerted a significant yield-forming effect. The weight of maize harvested from treatments fertilized with SS and SSA was approximately 5-fold higher than that noted in the control treatment. Sewage sludge ash and SS were very good sources of P and Mg for plants. The tested waste products significantly increased P and Mg uptake by plants and the content of available P in soil. Sewage sludge and SSA did not lead to a significant increase in heavy metal concentrations in soil or in plants.

Keywords: phosphorus, sewage sludge ash, heavy metals, magnesium, fertilization, yield.

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INTRODUCTION

Each year, enormous amounts of sewage sludge (SS) are produced around the world, and combined production in Europe, North America and Japan exceeds 30 million t/a (Krüger, Adam 2015). Massive quantities of SS pose a serious problem because they are very difficult to recycle. Thermal processes are the main method which significantly reduces SS mass. Furthermore, attempts are being made to limit other less safe and less effective methods of handling municipal SS, such as landfilling and agricultural processing. Recent years have witnessed a rapid increase in the application of thermal processing methods, in particular drying and mono-incineration. The number of SS drying and incineration plants has increased, mainly in large urban centers (Środa et al. 2012, Henclik et al. 2014, Krüger, Adam 2015, Gorazda et al. 2017). Sludge drying is not the ultimate treatment method, but it considerably decreases the volume and mass of SS and contributes to its sanitation. The process decreases transport costs, facilitates storage and modifies SS parameters to an extent that enables land application and incineration of SS, but it is an energy-intensive process (Bień 2012, Środa et al. 2012).

Sludge incineration is the most effective treatment method. The process leads to a radical 10-fold decrease in sludge mass, in addition to which it increases the concentrations of P and other macronutrients (Mg and Ca), and eliminates dangerous organic pollutants (Harrison et al. 2006, Kauffman et al. 2014, Gorazda et al. 2017). Incineration is the main method of SS treatment in many countries, and the production of ash from SS incineration can be expected to increase rapidly in the future. Many European countries as well as Japan and China are conducting intensive research into the use of sewage sludge ash (SSA) in the production of high-quality phosphorus fertilizers (Mattenberger et al. 2008, Adam et al. 2009, Nanzer et al. 2014, Gorazda et al. 2017).

Sewage sludge ash often contains high levels of heavy metals. In addition, many researchers have argued that the bioavailability of P in SSA is low (Franz 2008). For this reason, they are searching for effective and low-cost methods of eliminating heavy metals from SSA and improving the solubility of P. Novel fertilizers recycled from SSA are characterized by satisfactory P solubility, safe heavy metal levels and high effectiveness which is comparable to that of conventional phosphorus fertilizers (Adam et al. 2009, Donatello, Cheeseman 2013, Nanzer et al. 2014, Gorazda et al. 2017). However, SSA processing technologies are still expensive.

Sewage sludge and SSA can be effectively used as important sources of P and other plant nutrients, and they can partially replace conventional mineral fertilizers. SS and SSA are regarded as slow-release P fertilizers (Vogel et al. 2015). The P content of SS is estimated at 15-30 g kg^{-1} DM, and it increases to 39-112 g kg^{-1} DM in SSA. The suitability of SSA for recovering

P has been demonstrated in Germany which in 2012 produced around 300 000 t of SSA containing 19 000 t of P, i.e. approximately 13% of P used in mineral fertilizers in German agriculture (Krüger, Adam 2015).

The application of SSA in the production of phosphorus fertilizers requires thorough knowledge of its composition. The high content of heavy metals in SSA often exceeds safe levels for mineral fertilizers; therefore, SSA cannot be directly applied as fertilizers. For this reason, attempts are being made in many countries to develop effective and relatively inexpensive technologies for removing heavy metals from SSA (Adam et al. 2009, Krüger, Adam 2015, Herzel et al. 2016, Gorazda et al. 2017). Furthermore, according to many researchers, SSA contains forms of P that are not sufficiently available to plants, and additional processing is required to convert them into more readily available compounds (Adam et al. 2009, Krüger, Adam 2015, Herzel et al. 2016).

The aim of this study was to determine whether dried SS and SSA from municipal sludge processed in a mono-incineration plant in Olsztyn (Poland) are good sources of P and other plant nutrients. The effect of fertilization with dried SS and SSA on heavy metal accumulation in soil and plants was also determined.

MATERIALS AND METHODS

A pot experiment was conducted in the greenhouse of the University of Warmia and Mazury in Olsztyn, Poland, to determine whether ash from the incineration of municipal sewage sludge (SSA) can be recovered for fertilization purposes, and to compare the effectiveness of SSA with that of municipal sewage sludge (SS). The fertilizer value of SS and SSA was evaluated. The experiment comprised 9 fertilizer treatments with 4 replications: control treatment, 12.5 g, 25.0 g and 37.5 g of SSA DM per kg soil DM; 12.5 g, 25.0 g and 37.5 g of SS DM per kg soil DM; 62.5 mg of P as $Ca(H_2PO_4)_2$ per kg soil DM; 62.5 mg of P as $Ca(H_2PO_4)_2$ + 62.5 mg of Mg as $MgSO_4$ $7H_2O$ per kg soil DM. A dose of 62.5 mg of P kg^{-1} soil DM as $Ca(H_2PO_4)_2$ covered the requirements of plants for P. Every pot was additionally fertilized with 0,55 g of N as NH_4NO_3 and 0.55 g of K as KCl per kg soil DM in all the treatments.

Dried municipal sewage sludge (SS) and sewage sludge ash (SSA) used in the experiment were obtained from the Łyna wastewater treatment plant and the Sludge Thermal Processing System in Olsztyn. The dried sludge is obtained in a traditional thermal drying process of dewatered sewage sludge, and it is completely sanitized. The DM content of dried SS is estimated at 80-90%. The temperature of sludge is 75-90°C during the drying process. SSA is produced by dried sewage sludge incineration in a modern fluidised bed furnance. The sewage sludge mono-combustion process eliminates organic carbon nearly completely (Corg. content is reduced below 3%). The dried SS and SSA used in the experiment were collected five times for 5 consecutive months, and then mixed thoroughly. The chemical composition of SS and SSA is presented in Table 1.

Table 1

Chemical composition of dried sewage sludge (SS) and sewage sludge ash (SSA) from Olsztyn (Poland) and SSA from various countries.
The heavy metal limit values of fertilizer ordinances in some European countries

Parametr	Unit	Olsztyn (Poland)		SSA from various countries[1, 2]	Limit values of fertilizer ordinance			Limit values for SS
		SS	SSA		Austria[2]	Germany[2]	Poland[3]	Poland[4]
Organic matter	(g kg^{-1} DM)	590	35.1	–	–	–	–	–
N	(g kg^{-1} DM)	64.7	< 10	–	–	–	–	–
P	(g kg^{-1} DM)	27.4	83.3	39 -112	–	–	–	–
K	(g kg^{-1} DM)	3.2	8.9	4 - 23	–	–	–	–
Ca	(g kg^{-1} DM)	37.3	111.0	89 - 163	–	–	–	–
Mg	(g kg^{-1} DM)	7.1	20.3	11 - 22	–	–	–	–
S	(g kg^{-1} DM)	7.8	5.4	–	–	–	–	–
Cd	(mg kg^{-1} DM)	1.37	0.54	<0.4 - 4.7	15	50#	50	20
Cr	(mg kg^{-1} DM)	48.8	106.0	70 - 130	667	300	100	500
Ni	(mg kg^{-1} DM)	26.9	58.9	39.5 - 98.0	100	80	60	300
Pb	(mg kg^{-1} DM)	13.4	38.2	89.9 - 264	100	150	140	750
Hg	(mg kg^{-1} DM)	0.59	0.044	<0.1 - 0.23	1	1	2	16
Zn	(mg kg^{-1} DM)	1020	1965	910 - 2181	–	–	–	2500
Cu	(mg kg^{-1} DM)	304	778	417 - 1267	–	–	–	1000

[1] Franz (2008); [2] Adam et al. (2009); [3] *Regulation...* 2008; [4] limit values for SS intended for crop fertilization;
mg Cd kg^{-1} P_2O_5

Pots were filled with 9.0 kg of soil with the grain-size composition of loamy fine sand according to the USDA textural soil classification. The experimental soil was characterized by a moderate content of available P (67.6 mg P kg^{-1} soil), a very low content of available Mg (8.1 mg Mg kg^{-1} soil), a low content of available K (67.5 mg K kg^{-1} soil), and pH of 5.7 in 1 M KCl. Contents of trace elements (extraction in 1 M HCl) were as followed: 140.96 mg Mn, 7.13 mg Zn, 1.61 mg Cu, 0.078 mg Cd, 24.71 mg Pb, 0.350 mg Ni, 0.336 mg Cr and 1325.21 mg Fe kg^{-1} soil.

Nine kilograms of soil were mixed with 100 g, 200 g and 300 g of SS DM or SSA DM. Additionally, soluble P treatments were included in which $Ca(H_2PO_4)_2$ was mixed into soil at a dose of 0.5 g P per pot, and one treatment in which 0.5 g of P as $Ca(H_2PO_4)_2$ and 0.5 g of Mg as $MgSO_4 \cdot 7H_2O$

per pot were added. The experimental plant was maize (*Zea mays* L.) harvested in the milk stage. After germination, four plants were left in each pot.

Before sowing, equal amounts of N and K were added to each pot. Nitrogen was applied in the form of NH_4NO_3 at a dose of 0.4 g N per pot, and K was applied in the form of KCl at 0.4 g per pot. During the growing season, 4.0 g of N per pot in the form of NH_4NO_3 and 4.0 g of K per pot in the form of KCl were additionally applied as top-dressing fertilization.

Chemical analyses of SS and SSA were performed by SGS Poland, an accredited environmental laboratory. The elemental composition (Cu, Zn, Mn, Pb, Cd, Cr, Ca, Mg, K, P) of SS and SSA was determined with inductively coupled plasma-optical emission spectrometry (ICP-OES, standard EN ISO 11885). Mercury (Hg) content was determined by AAS (standard KJ-I-5.4-36), nitrogen (N) content was determined with the Kjeldahl method (KJ-I-5.4-97), sulfur (S) content was determined according to Standard EN ISO 16994, and organic matter content (loss on ignition of dry mass) was determined according to Standard EN-12879.

Soil samples were air-dried and passed through a 2-mm sieve. They were analyzed for pH in 1 M KCl (soil : solution ratio of 1 : 2.5) by the potentiometric method, the content of available P and K – by the Egner-Riehm method (DL), and available Mg – by the Schachtschabel method. The heavy metal (Cu, Zn, Mn, Pb, Cd, Cr) content of soil samples was determined by atomic absorption spectrometry (AAS) on a Shimadzu AA-6800 spectrophotometer on soil samples extracted in 1 M HCl with a 1 : 10 soil solution ratio (Gembarzewski et al. 1987).

Dried and ground plant samples (separately from each pot) were mineralized: (a) in a mixture of concentrated HNO_3, $HClO_4$, and H_2SO_4 (at a ratio of 40 : 10 : 1) for analyses of trace element concentrations (Cu, Zn, Mn, Pb, Cd, Cr), (b) in concentrated H_2SO_4 with the addition of 30% H_2O_2 for analyses of P, Ca and Mg content. The content of P in mineralized samples was determined by the vanadomolybdate method. The concentrations of K and Ca were determined by flame emission spectrometry, and the content of Mg and trace elements – by atomic absorption spectrometry in both mineralized plant samples and soil samples.

The results were processed by one-way ANOVA for completely randomized orthogonal designs. Differences between means (significance level of 1%) were estimated by the Tukey's HSD test. Statistical analyses were performed using PC Statistica v. 10.0 program.

RESULTS AND DISCUSSION

Dried SS comprised solid granules with a diameter of 5 mm and length of 3-5 mm, which were not susceptible to crumbling. Sewage sludge ash is also produced in the form of granular substance to minimize dust emissions.

Dried SS and SSA can be easily applied as fertilizers, and they have a considerable advantage over raw SS, which is characterized by undesirable physical parameters. Dried SS and SSA had a relatively high content of P. The concentration of P was determined at 27.4 g P kg^{-1} DM of dried SS and 83.3 g P kg^{-1} DM of SSA (Table 1). The P content of SSA from Polish incineration plants ranges from 78 g P kg^{-1} DM to 122 g P kg^{-1} DM. The highest values are similar to the P content of less abundant phosphate rocks (Gorazda et al. 2017). Sewage sludge and SSA are also rich sources of other macronutrients. The analyzed SS from Olsztyn contained 7.1 g Mg kg^{-1} DM and 7.8 g S kg^{-1} DM, and SSA contained 20.3 g Mg kg^{-1} DM and 5.4 g S kg^{-1} DM.

The concentrations of Cd, Pb and Hg in SSA from Olsztyn were determined at 0.54 mg Cd, 38.2 mg Pb and 0.044 mg Hg kg^{-1} DM, and were considerably below the norm for mineral fertilizers in Poland and other EU countries (Krüger, Adam 2015). The low content of Cd in SSA makes this waste material a particularly attractive alternative to mineral phosphorus fertilizers. Soil monitoring studies in the EU have revealed a progressing increase in the Cd content of soils. Mineral phosphorus fertilizers produced from imported African phosphorite are a considerable source of this carcinogenic metal. In mineral phosphorus fertilizers applied in the EU and Norway, the average content of Cd was determined at 62 mg Cd kg^{-1} P (Smolders 2017). In this study, the Cd content of the analyzed SSA was determined at only 6.48 mg Cd kg^{-1} P, which is a highly satisfying result in view of the reported increase in the Cd content of European soils. The concentrations of Ni and Cr in the tested SSA did not exceed the safe limits for mineral fertilizers and were similar to those of triple superphosphate, TSP (Xu et al. 2012). In a study by Kumpiene et al. (2016), the incineration of SS from municipal wastewater treatment plants in Sweden improved the Cd/P ratio of ashes 2- to 5-fold relative to the initial SS. The low Cd content of ashes (4-13 mg Cd kg^{-1} P) makes this material a particularly attractive alternative to mineral fertilizers.

The content of Cu and Zn in SSA from Olsztyn was high at 778 mg Cu kg^{-1} DM and 1965 mg Zn kg^{-1} DM, but safe thresholds were not exceeded (according to the Polish Standards). Sewage sludge ash was characterized by a lower content of Cd and Hg than SS, but the concentrations of Zn, Cu, Cr, Ni and Pb were nearly twice as high, having been condensed during the incineration of organic matter contained in SS.

The above results indicate that ashes from incinerated municipal SS, in particular sludge from plants that treat non-industrial wastewater, constitute safe fertilizers in terms of their heavy metal content. Both the chemical analysis of SSA and the pot experiment revealed that SSA is relatively abundant in P, Mg and S, and is also a good source of Cu and Zn for crops, in particular on light soils which are deficient in these micronutrients.

According to Herzel et al. (2016), more than half of SSA from German sludge incineration plants cannot be used directly for fertilization due to high concentrations of one or more heavy metals, which can probably be attributed to the co-incineration of industrial sludge.

The dried SS from Olsztyn was characterized by very low levels of Cd, Pb, Hg, Ni and Cr (Table 1). Despite relatively high concentrations of Cu and Zn in SS, the Cu content was 3-fold lower and the Zn content was more than two-fold lower than the safe thresholds set for SS intended for crop fertilization in Poland. Other authors have also noted that not all dried SS and SSA require expensive methods of removing toxic trace elements. The SSA and SS from two Swedish wastewater treatment plants, examined by Kumpiene et al. (2016), had lower Cd content (4-49 mg Cd kg^{-1} P) than the weighted average content of Cd in mineral fertilizers (68 mg Cd kg^{-1} P) in 9 EU countries (EFSA 2009). Other critical elements, such as Cu, Pb and Zn, in the SS and SSA were within the Swedish standards.

In the present study, the content of Pb, Cu and Zn in SSA was 2.5-fold to 2.8-fold higher compared with the respective initial values in SS, but the concentration of Pb did not exceed the threshold value for mineral fertilizers, and the concentrations of Zn and Cu were below the limits for SS intended for crop fertilization in Poland (Table 1).

The tested SS and SSA significantly stimulated the yields (Table 2). The weight of maize harvested from treatments fertilized with SS and SSA was approximately 5-fold higher than in the control treatment. Lower doses of dried SS (12.5 g and 25.0 g kg^{-1} of soil) exerted significantly greater yield-forming effects than SSA, but the resulting differences in plant biomass were not very high. The highest SS dose (37.5 g kg^{-1} of soil) resulted in weaker

Table 2

Effect of sewage sludge (SS) and sewage sludge ash (SSA) fertilization on green mass yield of maize, content and uptake of P, K and Mg by plants

Fertilizer treatments Dose per kg soil DM*	Yield	Content (g kg^{-1} DM)			Uptake (mg pot^{-1})		
	(g DM pot^{-1})	P	K	Mg	P	K	Mg
Control	55.81*d*	3.03*c*	25.92*a*	2.86*a*	169.1	1446.6	159.6
12.5 g DM SSA	258.48*b*	1.01*g*	9.22*cd*	1.67*d*	261.1	2383.2	431.7
25.0 g DM SSA	268.86*b*	1.22*f*	9.82*cd*	1.87*cd*	328.0	2640.2	502.8
37.5 g DM SSA	258.73*b*	1.31*f*	10.63*c*	1.91*bc*	338.9	2750.3	494.2
12.5 g DM SS	291.55*a*	1.72*e*	8.76*d*	1.94*bc*	501.5	2554.0	565.6
25.0 g DM SS	290.27*a*	2.37*d*	9.52*cd*	2.13*b*	687.9	2763.4	618.3
37.5 g DM SS	197.80*c*	3.28*b*	14.73*b*	1.67*d*	648.8	2913.6	330.3
62.5 mg P – $Ca(H_2PO_4)_2$	62.33*d*	4.02*a*	26.45*a*	2.85*a*	250.6	1648.6	177.6
62.5 mg P – $Ca(H_2PO_4)_2$ 62.5 mg Mg – $MgSO_4$	272.11*ab*	2.39*d*	9.14*d*	2.10*b*	650.34	2487.1	571.4

* Every pot was additionally fertilized with 4.4 g N and 4.4 g K in all the treatments.
Mean values in the same column followed by different letters indicate significant differences according to the Tukey's test (p<0.01).

plant growth at the beginning of the growing season, which led to a significant decrease in final yield in that treatment. The SSA dose had no significant effect on maize yield. The yield-forming effects of SS have been confirmed in numerous studies. Sewage sludge ash has also been found to exert positive effects on crop yields (BIERMAN, ROSEN 1994*a*, IŻEWSKA, WOŁOSZYK 2015).

Maize yields in treatments fertilized with mineral P and Mg only (62.5 mg P $kg^{-1}$of soil in the form of $Ca(H_2PO_4)_2$ and 62.5 mg Mg $kg^{-1}$of soil in the form of $MgSO_4$) were similar to the yields in treatments fertilized with SS or SSA. The yield in the treatment fertilized with mineral P in the form of $Ca(H_2PO_4)_2$ only was significantly lower than the yield in treatments fertilized with SS or SSA. This indicates that the plant growth in the above treatment and in the control treatment was inhibited mainly by very low levels of Mg and, possibly, S in soil. Dried SS and SSA were very good sources of both Mg and P, which was confirmed by the observations of the plant growth. In the control treatment and the treatment where only mineral P in the form of $Ca(H_2PO_4)_2$ was applied, the plant growth was strongly inhibited and severe symptoms of chlorosis were observed on maize leaves, which suggests that these changes were caused mainly by Mg and S deficiency in soil. The results of other studies confirm that both dried SS and SSA are an attractive alternative to conventional mineral phosphorus fertilizers, and that their effectiveness is comparable to that of TSP (BIERMAN, ROSEN 1994*a*,*b*, VOGEL et al. 2015, ANDRIAMANANJARA et al. 2016, MACKAY et al. 2017). In a study by KUMPIENE et al. (2016), P contained in SSA (in particular in SSA from sludge incinerated at a temp. of 950°C) was more available to plants than P contained in SS. As a result, plants fertilized with SSA were characterized by greater biomass than the plants fertilized with SS. The biomass and P content of plants were also more strongly correlated with the content of available P in soil than with the content of P in the soil solution.

In addition to P, the tested SS and SSA also supplied significant amounts of Mg, S and micronutrients to soil. Light soils are often deficient in these elements, which could also have inhibited the growth and development of plants. All the tested treatments were supplied with large amounts of N and K fertilizers; therefore, these nutrients were not responsible for the inhibited plant growth in the control treatment and in the treatment with mineral P fertilization in the form of $Ca(H_2PO_4)_2$, but without SS or SSA fertilization. However, high doses of K could have exacerbated the Mg deficit in plants in these treatments.

The results of other studies also indicate that SSA could be an important source of P as well as Mg, Ca, S, Cu and Zn, leading to improvement in the yield and chemical composition of crops. According to BIERMAN, ROSEN (1994*a*), fertilization with SSA increased the concentrations of P, Ca, Mg, Cu and Zn in maize, lettuce and soil after harvest. Sewage sludge ash also increased the $S\text{-}SO_4$ content of soil. In the work of IŻEWSKA, WOŁOSZYK (2015), SSA fertilization increased P and S concentrations in maize grain.

In treatments fertilized with dry SS or SSA, P uptake by maize plants was many-fold higher than in the control treatment, which indicates that the examined waste was an effective fertilizing material (Table 2). However, plants fertilized with SS were characterized by a significantly higher concentration of P than those fertilized with SSA. Higher doses of SS also led to a significant increase in the P content of plants. The highest P uptake was noted at the SS dose of 25.0 g kg^{-1} of soil. The highest dose of SS (37,5 g kg^{-1} of soil) increased the concentration of P in plants, but it also induced a significant decrease in maize yield which, consequently, significantly reduced P uptake by plants. Sewage sludge ash was a less abundant source of P for plants than SS. In the treatments with SSA fertilization, P uptake and P concentration in plant tissues were significantly lower than in the treatments fertilized with SS. However, SSA was also a good source of P for plants. In the treatments fertilized with 25 g and 37.5 g of SSA per kg soil, P uptake was approximately two-fold higher than in the control treatment.

The bioavailability of P is crucial for effective use of SSA as raw fertilizer material. Phosphorus bioavailability can be evaluated based on its solubility in neutral ammonium citrate solution (PNAC). In a study by Krüger, Adam (2015), the majority of the tested SSA were characterized by PNAC values in the range of 18.4% to 55.8%. According to the cited authors, the above values do not justify the direct use of SSA as fertilizers where PNAC of 100% is required. Therefore, the bioavailability of P in SSA should be enhanced in most cases. In the present study, the P contained in SSA was highly available to plants, and maize fertilized with SSA did not display symptoms of P deficiency.

Vogel et al. (2015) also observed that dried SS and SSA are good sources of P for plants. In the cited study, fertilization with dried SS and SSA increased both P uptake by various plant species and the content of readily available forms of P in soil, and exerted similar effects to TSP. Research shows that even P compounds with relatively low solubility (present in SSA) can be mobilized in soil by crops and microorganisms, and that standard methods of P extraction from soil do not always reflect the complex biological processes that take place in soil (Dakora, Phillips 2002, Eichler-Löbermann et al. 2007, Requejo, Eichler-Löbermann 2014). Vogel et al. (2015) demonstrated that the bioavailability of P from SSA was satisfactory, and it increased significantly during the 55-day experiment. The authors concluded that both SS and SSA can be regarded as fertilizers with slow P release, and that they are particularly suited for soils with lower pH. Mackay et al. (2017) also found that dried SS and SSA constitute effective fertilizers. In a study by Kumpiene et al. (2016), the P contained in SSA (in particular in ash incinerated at 950°C) was characterized by even higher bioavailability than that obtained from SS, and it created superior yield-forming effects to SS. In addition, the incineration of SS also significantly increased the concentration of easily soluble P (P-AL).

Not all SSA and novel fertilizers produced from SSA produce similar effects to commercial phosphorus fertilizers. In a pot experiment with spring barley, both SSA and thermo-chemically treated SSA were less effective P fertilizers than TSP and the sewage sludge from which they originate (Lemming et al. 2017). However, the lower fertilizing effectiveness of SSA could be attributed to a relatively short growing season of spring barley and the characteristics of this cereal species. In the present experiment, control plants and plants fertilized with P in the form of $Ca(H_2PO_4)_2$ only were also characterized by high P content, but total P uptake by maize was very low, which can be attributed to very low plant biomass in the above treatments.

The results of this experiment indicate that SS and SSA were also good sources of Mg for plants. Magnesium uptake was significantly higher in the treatments supplied with the tested waste than in the control treatment (Table 2). An increase in SS and SSA dose from 12.5 g to 25.0 g also contributed to a significant, but small increase in the Mg content of green forage maize. The lowest Mg uptake was noted in the control treatment and in the treatment fertilized with mineral P ($Ca(H_2PO_4)_2$) only. In the above treatments, plant growth was very strongly inhibited and severe symptoms of chlorosis were observed on maize leaves due to Mg deficiency in soil, which provides additional evidence that SS and SSA effectively minimized Mg deficiency in soil.

The results of the present study also show that SS and SSA are good sources of K for plants. Potassium uptake increased significantly after the application of SS and SSA, and K concentration increased with a rise in the dose of SS and SSA. The high K content of plants in the control treatment and in the treatment where only mineral P ($Ca(H_2PO_4)_2$) was applied resulted from increased concentration of K in the very low plant biomass in these treatments.

Both SSA and SS also contributed to a significant increase in plant-available P in soil after harvest (Table 3.). The SSA dose of 37.5 g DM per kg of soil increased the content of available P four-fold relative to the initial content (from 65 to 262 mg P kg^{-1} soil). Higher doses of SS and SSA significantly increased the concentration of available P in soil. The above indicates that the P contained in SS and SSA was easily converted to plant-available forms. Similar results were reported by other authors (Bierman, Rosen 1994a, Vogel et al. 2015). Bierman et al. (1995) observed that SSA increased P and S levels in the soil solution. The concentration of P in the soil solution was also strongly correlated (r = 0.92) with P accumulation in sweet maize (*Zea mays* L.) plants. Fertilization with the tested waste products also contributed to a significant increase in the content of available Mg in soil after maize harvest. Sewage sludge ash promoted soil deacidification. The SSA dose of 37.5 g kg^{-1} of soil increased soil pH from 5.70 to 5.98 (Table 3). The deacidifying properties of SSA were also observed

Table 3

Effect of dried sewage sludge (SS) and sewage sludge ash (SSA) fertilization on content of available P, K and Mg in soil after maize harvest

Fertilizer treatments Dose per kg soil DM*	pH_{KCl}	Content (mg kg^{-1} soil)		
		P	K	Mg
Control	5.35*d*	41.3*g*	246.5*ab*	52.7*d*
12.5 g DM SSA	5.73*b*	120.7*d*	125.5*de*	53.6*d*
25.0 g DM SSA	5.87*a*	231.9*b*	133.0*d*	72.6*c*
37.5 g DM SSA	5.98*a*	261.9*a*	148.6*c*	103.9*b*
12.5 g DM SS	5.14*e*	53.5*fg*	113.6*e*	46.7*d*
25.0 g DM SS	5.05*e*	95.3*e*	114.5*e*	67.1*c*
37.5 g DM SS	5.08*e*	206.6*c*	235.0*b*	120.4*a*
62.5 mg P – $Ca(H_2PO_4)_2$	5.27*d*	64.8*f*	250.7*a*	50.2*d*
62.5 mg P – $Ca(H_2PO_4)_2$ 62.5 mg Mg – $MgSO_4$	5.49*c*	42.9*g*	112.2*e*	51.3*d*

* Every pot was additionally fertilized with 4.4 g N and 4.4 g K in all the treatments.
Mean values in the same column followed by different letters indicate significant differences according to the Tukey's test (p<0.01).

by other authors (Bierman, Rosen 1994*a*, Bierman et al. 1995). In contrast, SS exerted acidifying effects. The SS dose of 37.5 g per kg of soil decreased soil pH from 5.70 to 5.08.

Sewage sludge ash did not lead to the excessive accumulation of heavy metals in plants (Table 4). In most treatments fertilized with SSA, the content of trace elements, in particular Mn, Zn and Cd, in maize plants was significantly lower than in the control treatment. Only a minor increase in the concentration of Pb was noted. An increase in the SSA dose from 12,5 g to 37,5 g per kg soil DM did not induce a significant increase in the heavy metal content of maize. Similar results were reported in other studies (Bierman, Rosen 1994*a*, Bierman et al. 1995), where SSA fertilization did not lead to significant changes in the concentrations of heavy metals in plants. The tested SS did not promote heavy metal accumulation in maize, either. Plants fertilized with SS were characterized by lower or similar concentrations of Zn, Fe, Cd, Ni and Cr relative to control plants, and a somewhat higher concentration of Pb. The only exception was Mn, whose content in plants increased substantially after the application of SS and continued to rise significantly with an increase in the SS dose. Despite the high increase in the Mn content of plants fertilized with SS, the highest Mn concentration of 278 mg Mn kg^{-1} DM (after the application of 37.5 g of SS) did not exceed the safe limit for most field crops. Manganese absorption by plants usually increases in acidic soils (pH<5.5) which are characterized by high organic matter content and excessive moisture content. The high concentration of Mn in plants fertilized with SS was associated with the

Table 4

Effect of dried sewage sludge (SS) and sewage sludge ash (SSA) fertilization on heavy metal content of green forage maize

Fertilizer treatments Dose per kg soil DM*	Content (mg kg^{-1} DM)							
	Fe	Mn	Zn	Cu#	Cd	Pb	Ni	Cr
Control	68.59*b*	70.86*cd*	40.85*d*	3.164	0.091*b*	1.073*a*	2.454*b*	2.095*ab*
12.5 g DM SSA	54.98*a*	43.01*ab*	17.35*a*	2.480	0.022*a*	1.843*abc*	2.056*ab*	1.812*a*
25.0 g DM SSA	51.99*a*	32.99*a*	17.40*a*	2.853	0.028*a*	1.776*abc*	1.971*a*	2.058*ab*
37.5 g DM SSA	53.80*a*	31.87*a*	17.44*a*	2.534	0.018*a*	1.959*bc*	2.115*ab*	2.060*ab*
12.5 g DM SS	63.68*b*	91.06*d*	21.62*b*	2.261	0.036*a*	2.464*c*	2.150*ab*	2.295*bc*
25.0 g DM SS	62.92*b*	210.63*e*	28.88*c*	2.130	0.084*b*	1.766*abc*	2.054*ab*	2.154*abc*
37.5 g DM SS	81.99*c*	277.68*f*	38.90*d*	2.910	0.135*c*	1.537*ab*	2.063*ab*	2.272*bc*
62.5 mg P – $Ca(H_2PO_4)_2$	63.51*b*	62.90*bc*	38.49*d*	2.800	0.094*bc*	1.945*bc*	2.359*ab*	2.542*c*
62.5 mg P – $Ca(H_2PO_4)_2$ 62.5 mg Mg – $MgSO_4$	50.02*a*	49.28*abc*	15.97*a*	2.102	0.019*a*	1.084*a*	2.068*ab*	1.998*ab*

* Every pot was additionally fertilized with 4.4 g N and 4.4 g K in all the treatments;
# non significant differences according to the Tukey's test (p<0.01).
Mean values in the same column followed by different letters indicate significant differences according to the Tukey's test (p<0.01).

presence of Mn in sludge introduced to soil and with a decrease in soil pH, which mobilized Mn in soil. In contrast, SSA fertilization decreased the Mn content of plants. In plants fertilized with 25.0 g of SSA per kg soil DM, Mn concentration was approximately 7-fold lower than in plants supplied with an equivalent dose of SS. Bierman, Rosen (1994*a*) also found that the content of the available forms of Mn in soil decreased after fertilization with SSA. Considerable differences in the Mn content of soil and plants after SSA and SS fertilization resulted from the deacidifying properties of SSA, the acidifying effects of SS and the supply of easily mobilized forms of Mn with SS. The highest SS dose also significantly increased the concentrations of Fe and Zn in plants. Similarly to Mn, the above increase can be attributed to the acidifying effects of SS, which mobilized Fe and Zn in soil, as well as the increased supply of Fe and Zn introduced with a high dose of that waste product.

Sewage sludge ash did not lead to the excessive accumulation of heavy metals in soil (Kabata-Pendias 1995). However, the concentrations of Fe, Mn, Zn, Cu, Pb, Ni and Cr in soil generally increased with a rise in the SSA dose (Table 5). The tested waste induced the greatest increase in the content of Cu and Zn, whereas the concentration of Pb increased significantly only in response to the highest SSA dose. In a study by Bierman et al. (1995), SSA increased the concentration of Cd and Zn in the soil solution, but did not lead to a significant increase in the content of other trace metals (Cu, Pb, Ni, Mn, Ba and Cr) in the soil solution. Furthermore, trace metal levels were

Table 5

Effect of sewage sludge (SS) and sewage sludge ash (SSA) fertilization on heavy metal content of soil (extraction in 1 M HCl) after harvesting maize

Fertilizer treatments Dose per pot*	Content (mg kg^{-1} DM)							
	Fe	Mn	Zn	Cu	Cd#	Pb	Ni	Cr
Control	1311.5*c*	138.8*de*	6.788*ab*	1.893*abc*	0.033	24.98*a*	0.352*a*	0.369*ab*
12.5 g DM SSA	1347.3*c*	148.0*ef*	9.659*d*	4.277*e*	0.018	26.62*a*	0.381*a*	0.392*ab*
25.0 g DM SSA	1457.3*e*	150.9*f*	13.414*f*	7.275*f*	0.019	25.34*a*	0.783*c*	0.567*bc*
37.5 g DM SSA	1509.1*f*	156.6*f*	14.464*g*	7.864*g*	0.034	41.39*b*	0.736*bc*	0.653*bc*
12.5 g DM SS	1232.5*ab*	129.1*cd*	7.210*bc*	2.055*bc*	0.022	20.06*a*	0.723*bc*	0.198*a*
25.0 g DM SS	1254.3*b*	124.2*bc*	7.895*c*	2.197*c*	0.029	26.20*a*	0.830*c*	0.396*ab*
37.5 g DM SS	1404.4*d*	109.7*a*	10.835*e*	2.695*d*	0.062	45.85*b*	0.696*bc*	0.738*c*
62.5 mg P – $Ca(H_2PO_4)_2$	1204.8*a*	136.2*d*	7.078*bc*	1.714*ab*	0.048	24.49*a*	0.450*ab*	0.599*bc*
62.5 mg P – $Ca(H_2PO_4)_2$ 62.5 mg Mg – $MgSO_4$	1209.7*ab*	124.5*ab*	6.040*a*	1.602*a*	0.018	22.32*a*	0.342*a*	0.360*ab*

* Every pot was additionally fertilized with 4.4 g N and 4.4 g K in all the treatments, # non significant differences according to the Tukey's test (p<0.01).
Mean values in the same column followed by different letters indicate significant differences according to the Tukey's test (p<0.01).

either weakly correlated (r = 0.49 for Zn; r = 0.36 for Cd) or not significantly correlated with plant accumulation.

In the present study, SS from the wastewater treatment plant in Olsztyn did not promote the excessive accumulation of heavy metals in soil after harvest. In most cases, soil levels of Zn, Pb, Fe, Cr and Cu increased significantly only in response to the highest SS dose. However, in the above treatment, the concentrations of Zn, Fe, Cd, Cr and Cu were within a range that corresponded to their natural levels ("0" class of pollution) (KABATA-PENDIAS 1995). Lead was the only heavy metal whose content (48.9 mg kg^{-1} soil) somewhat exceeded the "0" contamination level for very light soils after the application of 37.5 g SS per kg of soil. Similar Pb levels were also noted in soil fertilized with the highest dose of SSA. In the above treatments, the increase in soil Pb levels also resulted from the relatively high initial content of Pb in the experimental soil. In treatments fertilized with 12.5 g and 25.0 g of SS per kg of soil, the concentrations of Fe, Mn, Pb and Cd in soil were even lower than in the control treatment, which could be associated with higher uptake of these metals by plants. Sewage sludge ash promoted a higher increase in the Mn, Zn, Cu and Fe content of soil than SS.

The results of this study indicate that safe heavy metal levels ("0" class of pollution) were not exceeded in soil fertilized with SS and SSA. The only exception was Pb, whose concentration only slightly exceeded the reference range ("0" class of pollution) for very light soils after the application of high doses of SS and SSA.

CONCLUSIONS

Dried municipal SS and SSA from the incineration plant in Olsztyn were characterized by a high concentration of plant-available P, Mg and low concentrations of toxic trace elements, such as Cd, Pb, Ni, Cr and Hg. Fertilization with SS and SSA exerted a significant yield-forming effect. Sewage sludge ash and SS were very good sources of P and Mg for maize plants. The tested waste products significantly increased P and Mg uptake by plants and the content of available P in soil. They did not contribute to a significant increase in the heavy metal content of soil or plants.

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