

Krzysztof GONDEK 1* , Monika MIERZWA-HERSZTEK 1,2 , Michał KOPEĆ 1 and Iwona SPAŁEK 1

COMPOST PRODUCED WITH ADDITION OF SEWAGE SLUDGE AS A SOURCE OF Fe AND Mn FOR PLANTS

Abstract: Direct application of sewage sludge to soil is controversial due to, among others, its highly variable composition, odour, and risks for health. The obtained composts with the addition of sewage sludge were tested for the contents and availability of manganese and iron. Once composts were applied to the soil, their effect on the content and availability of Mn and Fe in soil and bioaccumulation in the plant were determined. The addition of sewage sludge enriched composts with manganese and iron, but did not increase the content of water-extracted forms of Mn and Fe. The composts with addition of biochar had more organic matter-bound forms of Mn and Fe. Composts amended with sewage sludge had lower effect on the amount of *Poa pratensis* L. biomass than maize straw compost. The content of Mn and Fe in *Poa pratensis* L. was in the range permissible for biomass used as fodder. Smaller addition of all composts to the soil significantly increased the content of mobile manganese forms; however, neither the type nor the dose had effect on the content of iron mobile forms. There was no significant differences in the content of organic matter-bound forms of Mn and Fe in soil after the application of composts.

Keywords: iron, manganese, bioavailability, compost, soil, plant

Introduction

The need to improve methods of managing waste such as sewage sludge is dictated by the systematic increase in their quantity and the growing threat to the environment [1]. Methods of sewage sludge management usually depend on the level of economic development of a given country. According to estimated data, the amount of sewage sludge generated in Europe will increase by 2020 and significantly exceed 10 million Mg [2]. In Poland, the problem of sewage sludge management is even more serious, because of changes in regulations of 2013, which introduced significant restrictions on the storage of these wastes [3].

In this situation, it is necessary to apply alternative solutions to allow the safe use of sewage sludge. Given the nutrient resources accumulated in sewage sludge, its use in the environment is one of the possible directions to solve the problem. However, direct application of this material is controversial due to, among others, its highly variable composition, odour, and risks for health [4, 5].

¹ Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31-120 Kraków, Poland, phone +48 12 662 43 46, fax +48 12 662 43 41, email: krzysztof.gondek@urk.edu.pl, rrgondek@cyf-kr.edu.pl ² Department of Mineralogy, Petrography and Geochemistry, AGH University of Science and Technology,

² Department of Mineralogy, Petrography and Geochemistry, AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Kraków, Poland

^{*} Corresponding author: krzysztof.gondek@urk.edu.pl, rrgondek@cyf-kr.edu.pl

In view of the problems of sewage sludge management in the environment, many countries adopted thermal conversion of sewage sludge as the main method. Thermal treatment of sewage sludge reduces its mass and results in the formation of residues, which are most often intended for storage. This method of sewage sludge transformation generates a significant load of volatiles released to the atmosphere [6]. Composting of sewage sludge in combination with other materials rich in organic matter can be an alternative solution for some types of this material [7].

Composting of organic waste is the aerobic process resulting in mineralisation and humification of organic matter [8]. Disposal of organic matter waste in the composting process is generally considered environmentally safe, which means that there are no emission risks [9, 10]. The selection of components affects the intensity of processes occurring during composting, including gas emissions. Therefore, proper composition and adequate standards of the process are a key factor determining its environmental and economic effects [11, 12]. The use of proper components is also crucial for the content and mobility of trace elements [7]. This is a very important aspect of the compost quality assessment, the more that the organic matter content is significantly reduced during the composting process as a result of microbiological degradation, and the originally bound forms of trace elements may be activated [13]. Degradation of organic compounds and synthesis of new connections can significantly alter relations between not only C and N, the content of humic and fulvic acids, but also between total and available forms of trace elements in the composted material. He et al. [14] and Martinho et al. [15] concluded that the content and speciation of trace elements in composted sewage sludge is a major cause for the negative impact of this material on the environment and health of living organisms.

The composting conditions can be improved by adding biochar, which will result in better aeration, less odour, and lower mobility of trace elements. Biochar is a solid product of thermal transformation of organic materials, which aroues considerable interest, because, under limited air access, it counteracts many problems related to environmental protection, such as worsening quality of soil, greenhouse gas emissions, increasing concentration of carbon dioxide (CO₂) in the atmosphere, contamination of soils and waters, and organic waste dumping [16, 17]. The universality of biochar, which translates into its multi-directional application, depends on its properties: large specific surface area, organic carbon content, many different functional groups, and optimum pore volume. What is more, biochar strongly resembles organic and inorganic contaminants [16].

Manganese and iron are biophilic elements necessary for the proper functioning of living organisms due to their participation in metabolic processes. In soil environment, manganese and iron form many compounds, and their bioavailability is conditioned by soil properties, mainly redox potential, pH, as well as organic matter content [18-20]. Currently, deficiencies of these elements are more and more common due to the intensified cultivation of soils in Poland. Waste, including sewage sludge can be a cheap source of manganese and iron. The content of available forms of manganese and iron in sewage sludge is relatively low. However, it should be remembered that the treatment of sewage sludge aimed at improving its physical and chemical properties and eliminating health risks leads to changes in the total content iron and manganese, as well as changes in the bioavailability of both these elements.

The following hypotheses were formulated: the addition of sewage sludge to composted materials affects the content and availability of Mn and Fe in composts; the application of such composts amended with sewage sludge to the soil increases the content and availability of both manganese and iron in the soil and results in the accumulation of Mn and Fe in the plant.

Materials and methods

Feedstocks and conditions of the composting process

Organic materials were composted for 140 days (from mid-May to the end of September 2015) in $1.2 \times 1.0 \times 0.8$ m bioreactors. The active aeration of the composted biomass was possible thanks to the perforated bottom of bioreactors. Bioreactors were sheltered to ensure heat exchange and protection against precipitations.

The experimental scheme included the following treatments: control - shredded maize straw (Compost-MS), shredded maize straw mixed with municipal sewage sludge (Compost-MS+SS), and shredded maize straw mixed with sewage sludge and willow biochar (Compost-MS+SS+B). Maize straw had the same chemical composition and structure as grass and wood chips (commonly used in industrial composting). The study was conducted with the use of an oxygen-stabilised sewage sludge (the aeration process in separate open chambers was carried out for 5 days) from mechanical and biological municipal wastewater treatment plant located in the Malopolskie Province (Southern Poland). Biochar was obtained by thermal conversion of willow, conducted by Fluid S.A. (Sedziszow, Poland) under a limited supply of air (1-2 %) [21]. Organic material was converted into biochar at 350 °C. Chemical composition of materials used in the composting process are shown in Table 1.

Determination	Maize straw (MS)	Sewage sludge (SS)	Biochar (B)	
Dry matter [g/kg]	978 ±10	219 ±3	923 ±9	
Ash [g/kg d.m.]	124 ±1	496 ±5	142 ±2	
Nitrogen [g/kg d.m.]	10.8 ±0.5	35.9 ±0.2	8.9 ±0.9	
Carbon [g/kg d.m.]	422 ±1	259 ±2	682 ± 37	
Sulphur [g/kg d.m.]	1.43 ±0.11	12.57 ±0.12	0.88 ± 0.18	
Hydrogen [g/kg d.m.]	65.3 ±0.8	45.4 ±0.4	26.2 ± 1.5	
Oxygen [g/kg d.m.]	447 ±1	232 ±2	199 ±38	
Mntot [mg/kg d.m.]	47 ±1	416 ±2	160 ±1	
Fe _{tot} [mg/kg d.m.]	832 ±17	25627 ±364	5448 ±514	

Selected properties of organic materials

Each value represents the mean of three replicates \pm SD (standard deviation), d.m. - dry matter

The amounts of organic materials used in composting depended on the humidity and physical properties of the material. The ratios of feedstocks used in individual treatments were, by weight of the dry matter: MS : SS - 1 (29.3 kg d.m.) : 0.15 (4.40 kg d.m.); MS : SS : B - 1 (29.3 kg d.m.) : 0.15 (4.40 kg d.m.) : 0.095 (2.78 kg d.m.). Once feedstocks were mixed, their humidity was maintained at 60 %. The exchange of air in the reactor was carried out in cycles, 6 times a day; air was flowing through the reactor at the rate of 15 dm³ per minute for 60 minutes. For better aeration, the biomass was removed from the reactor and manually shifted every 10 days. The outside temperature and temperature of the composed biomass (at half height of the composted matter) were recorded every 30 minutes using DT-171 data loggers.

Table 1

Chemical composition of feedstocks and composts

Electrical conductivity (material : water = 1 : 5) of composts was determined using a conductivity meter (Conductivity/Oxygen meter CCO - 501) as well as their pH (material : water = 1 : 5) electrochemically using a pH meter (pH-meter CP - 505) [22]. Feedstocks and composts were dried at 105 °C for 12 hours [23], 1 mm ground in a laboratory mill and subjected to further analyses. The ash content [24] and elemental composition (C, H, N, S) were determined in the prepared material using a CHNS analyser (Vario El Cube Elementar, GmbH Germany) [25]. Content of oxygen [% w/w] was derived by subtraction according to DIN 51733 [21] method as follows:

$$Oxygen = 100 - (ash + carbon + nitrogen + hydrogen + sulphur)$$
(1)

The content of extracted carbon was determined in composts after 24-hour extraction with cold water (compost : water = 1 : 10). The total manganese and iron were determined after mineralization the material in Multiwave PRO microwave reaction system, manufactured by Paar [7]. The mobile forms of Fe and Mn were determined after 12-hour extraction with distilled water (sample : solution = 1 : 10). The content of organic matter-bound forms of Mn and Fe was determined according to the sequential chemical extraction described by Zeien and Brummer [26], in which organic matter-bound forms of Mn and Fe were extracted with 0.025 M solution of $C_{10}H_{22}N_4O_8$, pH = 4.6 (compost : solution = 1 : 25) for 90 minutes. The Mn and Fe contents in the obtained solutions and extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7300 DV) [27].

Specific surface area (S_{BET}) of composts, as well as pore volume and diameter were determined using multifunction accelerated surface area and porosimetry analyser ASAP 2010 manufactured by Micromeritics [28].

Growing experiment

The growing experiment was carried out on loamy sand collected from 0-20 cm layer in southern Poland. The soil had a natural content of Mn and Fe; its other properties are shown in Table 2.

Table 2

Determination	Unit	Value		
pH H ₂ O	[-]	5.79 ±0.07		
pH KCl	[-]	4.60 ±0.01		
Electrical conductivity, EC	[µS/cm]	21.0 ±9.0		
C _{tot}	[g/kg d.m.]	4.20 ±0.10		
$\mathbf{N}_{\mathrm{tot}}$	[g/kg d.m.]	0.87 ±0.04		
Mn _{tot}	[mg/kg d.m.]	137 ± 10		
Fe _{tot}	[mg/kg d.m.]	1500 ± 120		
Sand	[g/kg d.m.]	870 ± 56		
Silt	[g/kg d.m.]	80 ±6		
Clay	[g/kg d.m.]	50 ±4		

Selected chemical and physical properties of soil

Each value represents the mean of three replicates $\pm SD$ (standard deviation), d.m. - dry matter

The experiment was carried out in containers filled with 500 g of dry soil, to which 0.5 and 1.0 % (w/w) of the following composts were added: Compost-MS,

Compost-MS+SS, Compost-MS+SS+B. Soil without compost was the control treatment. After mixing composts with soil, the material was moistened with distilled water. After 24 hours, *Poa pratensis* L. seeds of Bariris variety were sown. During the experiment, the moisture of soil in the container was maintained at 50 % of soil water capacity. The experiment was carried out for 100 days. After the experiment, the aboveground parts of plants were collected and their roots were separated from the soil. The roots were washed in distilled water. The biomass was dried at 105 °C and then, its amount was determined.

Analysis of plant material

The plant material was mineralised in a chamber furnace at 450 °C. The residue was dissolved in dilute nitric acid (1 : 2), and the Mn and Fe contents were determined in the obtained solutions by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7300 DV) [27]. In the presented studies, the Mn and Fe contents were presented as the weighted arithmetic mean (Metal: Mn-content [mg/kg d.m.], Fe-content [mg/kg d.m.], respectively) for aboveground parts and roots of *Poa pratensis* L. (2):

$$M_{\rm c} = [M_{\rm ap} \cdot B_{\rm ap}) + (M_{\rm r} \cdot B_{\rm r})] / (B_{\rm ap} + B_{\rm r})$$
⁽²⁾

where: M_c - metal content [mg/kg d.m.], M_{ap} - metal content in aboveground parts [mg/kg d.m.], M_r - metal content in the roots [mg/kg d.m.], B_{ap} - biomass of aboveground parts [g d.m./pot], B_r - biomass of roots [g d.m./pot].

Amounts of taken up manganese and iron (Mn-uptake, Fe-uptake [mg/pot]) were calculated on the basis of the amount of biomass (aboveground parts and roots) of *Poa pratensis* L and the Mn and Fe contents in biomass (3):

$$M_{\rm u} = (B_{\rm Y} \cdot M_{\rm c}) \,/\, 1000 \tag{3}$$

where: M_u - metal uptake [mg/pot], B_Y - biomass yield [g d.m./pot], M_c - metal content in biomass [mg d.m./kg].

Selected chemical properties of soil

The following parameters were determined in dried and 2 mm sieved soil samples: total carbon on the CHNS analyser [25], pH - electrochemically in the suspension of soil and 1 M solution of KCl (soil/solution ratio 1 : 2.5), and electrical conductivity of soil (soil/solution ratio 1 : 2.5) (Conductivity/Oxygen meter CCO - 501) [7]. Total manganese and iron contents (Mn_{tot} , Fe_{tot}) were determined after ashing the sample in chamber furnace at 550 °C for 12 hours and mineralising its residues in a mixture of concentrated nitric and perchloric acids (3 : 2) (v/v). Mobile forms of Mn and Fe were extracted from soil with 1 M solution of NH_4NO_3 [29]. The content of analysed metals mixed with organic matter was determined according to the sequential chemical extraction described by Zeien and Brummer [26]. The analysed elements in the resulting extracts were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 7300 DV).

Statistical analysis

The experiment involving composting of organic materials was conducted in two replicates, whereas vegetation experiment in three replicates. The obtained data were compiled with the use of STATISTICA 12 (StatSoft Inc.). The mean values of analysed

properties were compared using Duncan's multiple range test at $p \le 0.05$. Variations in the treatments were determined by calculating the standard deviation ($\pm SD$).

Results and discussion

Selected chemical and physical properties of composts

Dry matter content in composts was influenced by the feedstock used (Table 3). Compared to Compost-MS, higher ash content was determined in Compost-MS+SS and Compost-MS+SS+B. Results of the study show that the greatest load of mineral substances was introduced with sewage sludge [30].

Table 3

Determination	Compost-MS	Compost-MS+SS	Compost-MS+SS+B	
Dry matter [g/kg]	705 ±9	745 ±10	642 ±7	
Ash [g/kg d.m.]	209 ±2	296 ±3	288 ±4	
pH H ₂ O	7.89 ±0.79	7.96 ±0.80	7.60 ±0.76	
Electrical conductivity, EC [µS/cm]	6.78 ±0.70	4.86 ±0.49	4.64 ±0.46	
C _{tot} [g/kg d.m.]	406 ±3	365 ±4	382 ±32	
Cextracted [g/kg d.m.]	24.4 ± 1.4	18.2 ±2.1	9.8 ±0.8	
N _{tot} [g/kg d.m.]	31.8 ±0.7	39.4 ±1.9	33.2 ±2.8	
Stot [g/kg d.m.]	3.72 ±0.17	6.86 ±0.10	6.16 ±0.47	
Specific surface area (S_{BET}) [m ² /g]	0.54 ±0.05	0.72 ±0.03	1.07 ±0.09	
Pore volume [cm ³ /g]	0.0021 ± 0.0001	0.0029 ±0.0002	0.0036 ±0.0003	
Pore diameter [nm]	17 ±2	18 ±2	15 ±1	

Selected chemical and physical properties of composts

Each value represents the mean of three replicates \pm SD (standard deviation), d.m. - dry matter

The pH values of the obtained composts ranged from 7.60 to 7.96; however, higher values were determined for Compost-MS and Compost-MS+SS (Table 3). The addition of sewage sludge had alkalising effect. This was probably due to the introduction of alkalising substances with sewage sludge or degradation of organic (mainly protein) compounds, which, in consequence, lead to the release of ammonia [31]. Reduced pH of Compost-MS+SS+B could result from metabolic processes carried out by microorganisms and fungi, whose effect was the release of CO₂ and organic acids [31]. Oxidation of carboxyl groups can be the possible cause of the reduced pH of the compost amended with biochar.

According to Liu et al. [32], an excessive content of soluble salts can be the main factor restricting natural use of composts, as it leads to disturbances in the ionic balance of the soil solution and may adversely affect the plants. The highest electrical conductivity, *EC*, was determined for Compost-MS (Table 3). Lower *EC* values, by 28 and 31 %, respectively, were determined in Compost-MS+SS and Compost-MS+SS+B. The highest value of electrical conductivity determined in maize straw compost can be attributable to the mineralisation of organic material, resulting in the release of nutrients, probably to a much greater extent than in the other two composts (Compost-MS+SS, Compost-MS+SS+B). Sewage sludge has a low content of readily available ions. On the other hand, biochar has sorption capacity, which caused the reduction of *EC* values in both composts amended with that material.

Total carbon and extracted carbon contents were lower in Compost-MS+SS and Compost-MS+SS+B than in Compost-MS (Table 3). It should be emphasised that a 40 % reduction in the extracted carbon content determined in Compost-MS+SS+B compared to Compost-MS may, on the one hand, limit the ability of microorganisms to use this source of carbon after introducing compost into the soil, and, on the other hand, lead to a longer time of retention of carbon compounds in the soil.

The study revealed higher contents of nitrogen and sulphur in Compost-MS+SS than in Compost-MS; however, Compost-MS+SS+B was characterised by a light dilution of both components.

In the case of Compost-MS+SS and Compost-MS+SS+B, the values of S_{BET} were by 33 and 98 %, respectively, higher and pore volume by 38 and 71 %, respectively, higher than these determined for Compost-MS [33]. The pore diameter slightly increased in Compost-MS+SS compared to Compost-MS, but in Compost-MS+SS+B, it decreased.

Content of total, mobile and organic matter-bound Mn and Fe in composts

The study revealed over 100 % higher Mn content in Compost-MS+SS and over 80 % Mn content in Compost-MS+SS+B compared to Compost-MS (Table 4). Differences in the total Mn content in the obtained composts were reflected in the content of Mn extracted with water. Compared to Compost-MS, significantly lower Mn_{H2O} contents were determined in Compost-MS+SS and Compost-MS+SS+B. The highest Mn_{org} value was determined in Compost-MS+SS+B. The share of Mn_{org} in total Mn (Mn_{tot}) was over 80 %. A comparable share of Mn_{org} in Mn_{tot} was determined in both remaining composts and it was lower than 50 %.

Determination	Compost-MS	Compost-MS+SS	Compost-MS+SS+B	
Mntot [mg/kg d.m.]	141 ±7	289 ±6	260 ±3	
Mn _{H2O} [mg/kg d.m.]	0.18 ±0.02 0.07 ±0.01		0.12 ±0.02	
Share of Mn _{H2O} in Mn _{tot} [%]	0.13	0.02	0.05	
Mn _{org} bound to organic matter [mg/kg d.m.]	69 ±1	140 ±2	219 ±6	
Share of Mnorg in Mntot [%]	49	48	84	
Fetot [mg/kg d.m.]	1365 ±9	9798 ±366	8405 ±328	
Fe _{H2O} [mg/kg d.m.]	1.61 ±0.11	3.48 ±0.23	1.99 ±0.16	
Share of Fe _{H2O} in Fe _{tot} [%]	0.12	0.03	0.02	
Fe _{org} bound to organic matter [mg/kg d.m.]	211 ±10	2402 ±143	4229 ±12	
Share of Fe _{org} in Fe _{tot} [%]	15	25	50	

Contents of Mn and Fe in composts

Table 4

Each value represents the mean of three replicates $\pm SD$ (standard deviation), d.m. - dry matter

Total iron content in Compost-MS+SS and Compost-MS+SS+B was similar (Table 4). Considerable load of Fe introduced to the composted biomass with sewage sludge increased the Fe_{H2O} content in Compost-MS+SS. However, this did not translate into the share of water extracted Fe forms in the Fe total content, as the Fe_{tot} content significantly increased compared to the value determined in Compost-MS. The content of organic matter-bound Fe was the lowest in Compost-MS (211 mg/kg d.m.). An increase in the organic matter-bound form of Fe was determined in other composts, which resulted from the increased content of

Fe_{tot}. A significantly higher share of Fe_{org} in Fe_{tot} was determined in Compost-MS+SS and Compost-MS+SS+B. The share of Fe_{org} in Fe_{tot} in Compost-MS+SS+B was 50 %.

The content of trace elements in the final product may increase due to the loss of organic matter during the composting process. Our study revealed a significantly smaller share of water extracted forms of Mn and Fe in Compost-MS+SS and Compost-MS+SS+B compared to Compost-MS. Despite the increase in the total Mn and Fe contents in both composts, this indicates a reduced mobility of the two tested elements. Reduced mobility of these elements may be due to the formation of connections with organic matter, which is confirmed by our results. The formation of hardly soluble complexes may be a process that also affects iron mobility. Hua et al. [34] analysed the effect of the addition of biochar to the composted biomass and showed a decrease in the content of ions of DTPA-extracted trace elements. Also our study revealed that the addition of biochar to composted materials reduced the content of water-extracted iron, which was probably due to the adsorption of Fe on the biochar surface. According to Hiller and Brummer [35], charcoal particles tend to accumulate trace elements.

Biomass, content, and amounts of Mn and Fe taken up by Poa pratensis L.

The amount of biomass (aboveground parts and roots) of *Poa pratensis* L. was significantly the highest after the application of Compost-MS, regardless of the dose (Table 5).

Table 5

Parameter	Soil	Soil with addition of 0.5 %			Soil with addition of 1.0 %		
	control	MS	MS+SS	MS+SS+B	MS	MS+SS	MS+SS+B
Amount of biomass [g d.m./pot]	$\begin{array}{c} 0.68^{ab} \\ \pm 0.04 \end{array}$	$\begin{array}{c} 0.82^{de} \\ \pm 0.05 \end{array}$	0.62ª ±0.06	$0.69^{ab} \pm 0.04$	0.86 ^e ±0.03	$0.74^{bc} \pm 0.02$	0.77 ^c ±0.03
Mn-content [mg/kg d.m.]	267 ^b ±72	146 ^a ±12	171 ^a ±19	155 ^a ±5	129 ^a ±13	143 ^a ±15	143 ^a ±22
Mn-uptake [mg/pot]	0.18 ^b ±0.05	0.12 ^a ±0.02	0.11ª ±0.02	0.11 ^a ±0.00	0.11 ^a ±0.01	0.11 ^a ±0.01	0.11ª ±0.02
Fe-content [mg/kg d.m.]	1216 ^b ±30	648 ^a ±29	1066 ^b ±19	841 ^{ab} ±52	814 ^{ab} ±21	$936^{ab} \pm 28$	$875^{ab} \\ \pm 80$
Fe-uptake [mg/pot]	0.83 ^a ±0.22	0.54 ^a ±0.27	0.67ª ±0.17	0.58 ^a ±0.06	0.70 ^a ±0.20	0.69ª ±0.20	$0.68^{a} \pm 0.08$

Total (aboveground parts and roots) amount of *Poa pratensis* L. biomass and weighted mean (aboveground parts and roots) content of Mn and Fe and total uptake of these elements with biomass

Each value represents the mean of three replicates $\pm SD$ (standard deviation), d.m. - dry matter. The different letters within a line indicate a significant difference at $p \le 0.05$ according to Duncan's multiple range tests

Compared to the control, lower or similar *Poa pratensis* L. biomass amounts were determined in treatments where 0.5 % additions of Compost-MS+SS and Compost-MS+SS+B were applied. A 1% addition of these composts increased the amount of plant biomass, although a statistically significant difference in relation to control soil concerned the treatment with Compost-MS+SS+B (Table 5).

According to Vandecasteele et al. [36], the introduction of biochar to the composted biomass has no great effect on the compost fertilising value. However, biochar can significantly reduce the availability of some nutrients. The direct application of biochar or compost amended with this material is not in parallel with a significant increase in the amount of cultivated plant biomass. As stated by Gaskin et al. [37] and Major et al. [38], one should take into account the lack of significant differences in plant yield, and even a negative effect of biochar on crop yield in the first year after its application to the soil. Also Schmidt et al. [39] indicated only a small and economically unimportant effect of biochar-compost treatments in viticulture in the three-year period.

The weighted average content of manganese and iron in *Poa pratensis* L. biomass (Mn-content, Fe-content) and the amounts of both elements taken up (Mn-uptake, Fe-uptake) are shown in Table 5. Significant ($p \le 0.05$) decrease in the manganese content in plant biomass was noted in all treatments compared to the control. More Mn was determined in *Poa pratensis* L. when a lower dose of composts (regardless of the type) was applied.

The greatest (by over 30 % on average) Mn-uptake was determined in the control treatment. The type of the compost applied and its dose had no significant effect on the Mn-uptake. The iron content (Fe-content) in *Poa pratensis* L. did not differ significantly in terms of the compost applied and its dose. However, the results for Fe-content were similar to these for content of Mn. The greatest amounts of iron (Fe-uptake) was determined in the control treatment. The use of a higher dose of composts did not significantly diversified Fe-uptake.

The use of composts as a source of plant nutrients may be a viable alternative in global agriculture. The amount and quality of biomass depend on many factors, and the amount and availability of nutrients play a key role here. There are limited data on the effect of composts on the amount and, in particular, the content of Fe and Mn in plant biomass. According to Saha et al. [40], fertilisation with organic materials, including composts, increases the iron content in rice compared to an inorganic fertilisation. In our study, the use of composts produced with sewage sludge and biochar did not significantly change the content of Fe in the biomass of Poa pratensis L. This was dictated by both the low availability of Fe in the tested composts and a significant reduction in soil acidification, which could undoubtedly decrease the content of mobile Fe forms [41]. The study of Demir et al. [42] showed that the use of organic materials as fertilisers has no effect on the content of, inter alia, iron in the plant biomass. Also Hernandez et al. [43] proved that the fertilisation with vermicompost is better for the Fe content than compost. On the other hand, the authors demonstrated a positive effect of organic fertilisation on the Mn content in lettuce. Our study did not reveal the increased content of Mn in *Poa pratensis* L. after the application of composts produced with sewage sludge.

The pH value and electrical conductivity of soil

Both the type and amount of compost added to the soil had a significant effect on pH values determined in the suspension of soil and KCl solution. Compared to the control soil, a significant deacidification effect was identified regardless of the type and dose of compost. Increased pH in soils fertilised with composts is confirmed by the results of, among others, Castillo et al. [44] and Buttler and Muir [45]. The pH values already determined in composts had an alkaline nature.

A number of biochemical processes occurring in the composted biomass causes that the proportions between organic and mineral connections change [8]. It should be noted that there is an increase not only in the number of mineral connections, but also the content of active forms of some elements that easily migrate into the soil solution. The deacidification capacity of composts can be different, given the material from which the compost has been produced. In our study, the pH values of the tested materials were greater than 7.00, regardless of components used to produce composts. One should also remember that a significant load of organic matter introduced into the soil with composts will affect the stabilisation of soil properties by improving the buffer properties [46]. Our results allowed to discover a better deacidifying effect of higher doses of composts (Fig. 1).

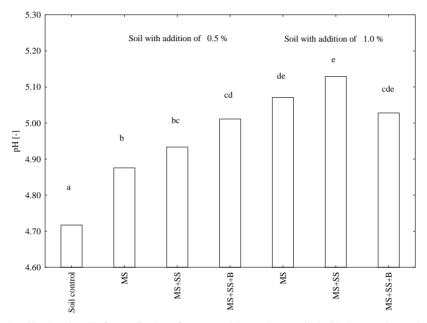


Fig. 1. pH values in soil after application of composts. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

Higher values of electrical conductivity, EC, were determined in soil with 1.0 % addition of composts (Fig. 2). The type of compost was not relevant in this regard. Carmo et al. [47] discovered increased EC value after applying various organic materials, including composts, but the EC increase was conditioned by the soil type.

The carbon content significantly increased in the soil of all treatments into which composts were introduced (Fig. 3). Generally, the adopted doses of composts had no significant effect on the carbon content. Our results correspond to the results of Bouajila and Sanaa [48].

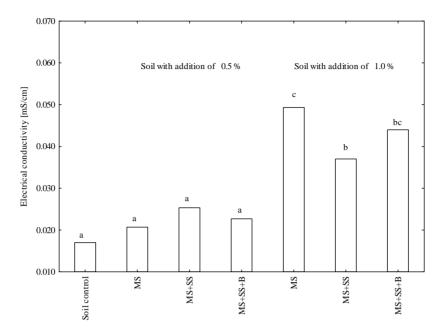


Fig. 2. Electrical conductivity, *EC*, values in soil after application of composts. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

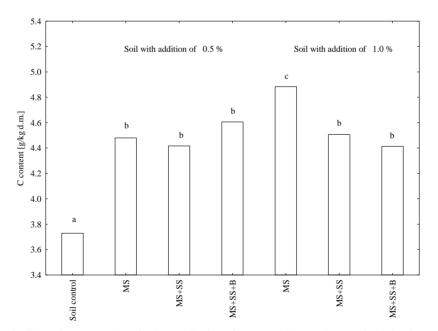


Fig. 3. The carbon content in soil after application of composts. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

Content of Mn and Fe in total and mobile forms and in forms bound to soil organic matter

The application of Compost-MS+SS and Compost-MS+SS+B caused no significant changes in the total content of manganese and iron in soil compared to the treatment amended with Compost-MS and to the control soil (Fig. 4). The addition of all composts at a lower dose (0.5 %) to the soil significantly increased the content of mobile manganese forms; however, neither the type nor the dose had effect on the content of iron mobile forms (Fig. 5). The study also revealed a very low share of mobile manganese (usually below 2 %) and iron (usually below 0.02 %) forms in their total contents.

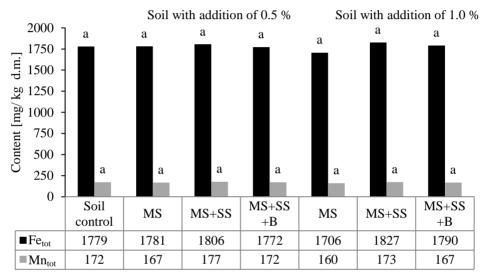


Fig. 4. The content of Fe_{tot} and Mn_{tot} in soil. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

Organic matter-bound forms of iron and manganese are presented in Figure 6. Our results show that, regardless of the type and dose of compost, the share of organic matter-bound forms of manganese in its total content ranged from 9.70 to 11.27 %. The share of organic matter-bound forms of iron was lower and ranged from 1.46 to 3.31 %. It should be noted that neither the type of compost nor its dose had a significant effect on the content of organic matter-bound forms of both elements in the soil.

Reaction, sorbent nature, presence and concentration of organic and inorganic ligands (humic and fulvic acids, root exudates, and nutrients) are of great importance for the mobility of trace elements. Additionally, biotic and abiotic redox reactions play a key role in controlling the oxidation and thereby, the mobility and toxicity of many elements. Redox reactions can both mobilise or immobilise metals, and it depends on individual metal types and microenvironments [49].

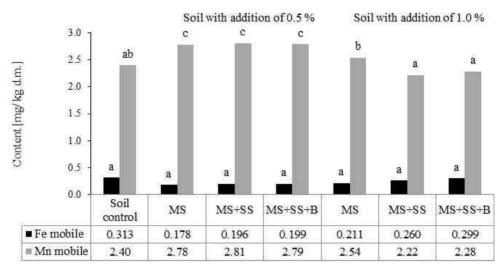


Fig. 5. The content of mobile forms Fe and Mn in soil. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

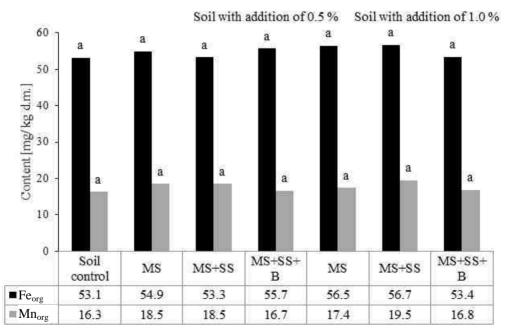


Fig. 6. The content of bound to organic matter of Fe and Mn in soil. Mean values marked with the same letters do not differ significantly according to the Duncan's multiple range test at $p \le 0.05$

Introduction of organic matter into the soil and its liming may immobilise trace elements and transform their readily available forms into more stable ones. Consequently, their mobility and bioavailability are lower [16]. In our study, only the content of mobile manganese forms increased after the application of a lower dose of composts. Also lower soil pH was determined in these treatments compared to the ones amended with higher doses of composts. In an earlier study Gondek [50] showed that after the application of organic materials, the content of mobile manganese was significantly lower than the one determined in treatments fertilised with mineral salts, regardless of soil grain size composition. As stated by Hsu and Lo [51], the availability of manganese from organic materials after their application to the soil, depends on the rate of mineralisation of organic matter in which the manganese content is significant. In our study, the total iron content in the soil was much higher than that of manganese, regardless of the compost used, and its mobility was relatively lower. The mobility of this element in soil is conditioned by, among others, pH and the organic matter content [20]. According to Maqued et al. [52], the application of plant compost and the elimination of synthetic fertilisers increase Fe and Mn extractability compared to inorganically fertilised soil which is prone to have long-term fertility benefits.

Conclusion

- 1. The addition of sewage sludge to composted feedstocks increased total content of Mn and Fe, but does not increased the mobility of these elements in composts.
- 2. The organic matter of composts she was an important role in the binding of Mn and Fe.
- 3. Fertilisation of *Poa pratensis* L. with composts amended with sewage sludge did not increase the bioaccumulation of Mn and Fe.
- 4. The introduction of composts amended with sewage sludge into the soil in dose 0.5 % and 1.0 % does did not increased the total content of Mn and Fe, but increases the content of mobile forms of these elements.

Acknowledgements

The research was financed by the Ministry of Science and Higher Education of the Republic of Poland.

References

- Latośińska J, Kowalik R, Gawdzik J. Risk assessment of soil contamination with heavy metals from municipal sewage sludge. Appl Sci. 2021;11:548. DOI: 10.3390/app11020548.
- [2] Environmental, economic and social impacts of the use of sewage sludge on land. Final Report, part I: Overview Report prepared by Milieu Ltd, WRcand RPA for the European Commission; 2008. Available from: https://ec.europa.eu/environment/archives/waste/sludge/pdf/part_i_report.pdf.
- [3] Błaszczyk K, Krzyśko-Łupicka T. Microbiological and physico-chemical composition of sewage sludge derived from the food industry. Chem Didact Ecol Metrol. 2013;18(1-2):89-95. DOI: 10.2478/cdem-2013-0021.
- [4] Ding A, Zhang R, Ngo HH, He X, Ma J, Nan J, et al. Life cycle assessment of sewage sludge treatment and disposal based on nutrient and energy recovery: A review. Sci Tot Environ. 2021;15:14451. DOI: 10.1016/j.scitotenv.2020.144451.
- [5] Miller U, Grzelka A, Romanik E, Kuriata M. Analysis of the application of selected physico-chemical methods in eliminating odor nuisance of municipal facilities. E3S Web of Conferences 28, 01023, Air Protection in Theory and Practice. 2018. DOI: 10.1051/e3sconf/20182801023.
- [6] Werle S. Nitrogen oxides emission reduction using sewage sludge gasification gas Reburning process. Ecol Chem Eng S. 2015;22(1):83-94. DOI: 10.1515/eces-2015-0005.

- [7] Golbaz S, Zamanzadeh MZ, Pasalari H, Farzadkia M. Assessment of co-composting of sewage sludge, woodchips, and sawdust: feedstock quality and design and compilation of computational model. Environ Sci Pollut Res Int. 2021;28:12414-27. DOI: 10.1007/s11356-020-11237-6.
- [8] Bernal MP, Alburquerque JA, Moral R. Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresour Technol. 2009;100(22):5444-53. DOI: 10.1016/j.biortech.2008.11.027.
- [9] Amon B, Kryvoruchko V, Amon T, Zechmeister-Boltenstern S. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric Ecosyst Environ. 2006;112(2-3):153-62. DOI: 10.1016/j.agee.2005.08.030.
- [10] Godlewska P, Schmidt HP, Ok YS, Oleszczuk P. Biochar for composting improvement and contaminants reduction. A review. Bioresour Technol. 2017;246:193-202. DOI: 10.1016/j.biortech.2017.07.095.
- [11] Czekała W, Malińska K, Cáceres R, Janczak D, Dach J, Lewicki A. Co-composting of poultry manure mixtures amended with biochar-The effect of biochar on temperature and C-CO₂ emission. Bioresour Technol. 2016;200:921-27. DOI: 10.1016/j.biortech.2015.11.019.
- [12] Kopeć M, Gondek K, Mierzwa-Hersztek M, Zaleski T. Effect of the composting process on physical and energetic changes in compost. Acta Agroph. 2015;23(4):607-19. Available from: http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.agro-15a994a0-dca4-429e-87cf-b4845a3a0619.
- [13] Kopeć M, Baran A, Mierzwa-Hersztek M, Gondek K. Chmiel MJ. Effect of the addition of biochar and coffee grounds on the biological properties and ecotoxicity of compost. Waste Biom Val. 2018;9:1389-98. DOI: 10.1007/s12649-017-9916-y.
- [14] He MM, Tian GM, Liang XQ. Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge. J Hazard Mater. 2009;163(2):671-7. DOI: 10.1016/j.jhazmat.2008.07.013.
- [15] Martinho J, Campos B, Brás I, Silva E. The role of compost properties in sorption of heavy metals. Environ Prot Eng. 2015;41:57-65. DOI: 10.5277/epe150205.
- [16] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, et al. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere. 2014;99:19-33. DOI: 10.1016/j.chemosphere.2013.10.071.
- [17] Papageorgiou A, Azzi ES, Enell A, Sundberg C. Biochar produced from wood waste for soil remediation in Sweden: Carbon sequestration and other environmental impacts. Sci Tot Environ. 2021;776:145953. DOI: 10.1016/j.scitotenv.2021.145953.
- [18] Jansen B, Nierop KGJ, Verstraten JM. Mechanisms controlling the mobility of dissolved organic matter, aluminium and iron in podzol B horizons. Europ J Soil Sci. 2005;56(4):537-50. DOI: 10.1111/j.1365-2389.2004.00686.x.
- [19] Xue N, Seip HM, Guo J, Liao B, Zeng Q. Distribution of Al, Fe, Mn pools and their correlation in soils from two acid deposition small catchments in Hunan, China. Chemosphere. 2006; 65(11):2468-76. DOI: 10.1016/j.chemosphere.2006.04.045.
- [20] Gruba P. The solubility of iron in forest soil. Electr J Pol Agric Univ. 2010;13(4). Available from: http://www.ejpau.media.pl/volume13/issue4/art-23.html.
- [21] European Biochar Certificate EBC, 2012. Guidelines for a Sustainable Production of Biochar. Version 6.1 of 19th June 2015. European Biochar Foundation (EBC), Arbaz, Switzerland. DOI: 10.13140/RG.2.1.4658.7043. Available from: http://www.europeanbiochar.org/en/download.
- [22] Meier S, Curaqueo G, Khan N, Bolan N, Rilling J, Vidal C, et al. Effect of biochar on copper immobilization and soil microbial communities in a metal-contaminated soil. J Soil Sedim. 2017;17(5):1237-50. DOI: 10.1007/s11368-015-1224-1.
- [23] Jindo K, Suto K, Matsumoto K, Garcia C, Sonoki T, Sanchez-Monedero MA. Chemical and biochemical chracterisation of biochar-blended composts prepared from poultry manure. Bioresour Technol. 2012;110:396-404. DOI: 10.1016/j.biortech.2012.01.120
- [24] Agrafioti E, Bouras G, Kalderis D, Diamadopulos E. Biochar production by sewage sludge pyrolysis. J Anal Appl Pyrol. 2013;101:72-8. DOI: 10.1016/j.jaap.2013.02.010.
- [25] Elementar Analysensysteme GmbH. Operating instructions vario MAX cube. 2013; 407. www.elementar.com/en/products/organic-elemental-analyzers/vario-max-cube.
- [26] Zeien H, Brümmer GW. Chemische extraction zur bestimung vin schwermetallbindungsformen in böden. Mitteilg. Dtsch. Bodenkundl. Gesellsch. 1989;59:505-10.
- [27] Oleszczuk N, Castro JT, da Silva MM, Korn Md, Welz B, Vale MG. Method development for the determination of manganese, cobalt and copper in green coffee comparing direct solid sampling electrothermal atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry. Talanta. 2007;73(5):862-9. DOI: 10.1016/j.talanta.2007.05.005.

- [28] Barret EP, Joyner LG, Halenda PH. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J Amer Chem Soc. 1951;73(1):373-80. DOI: 10.1021/ja01145a126.
- [29] Park JH, Choppala GK, Bolan NS, Chung JW, Chusavathi T. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil. 2011;348:439-51. DOI: 10.1007/s11104-011-0948-y.
- [30] Monzó J, Paya J, Borrachero MV, Córcoles A. Use of sewage sludge ash (SSA)-cement admixtures in mortars. Cem Conc Res. 1996;26(9):1389-98. DOI: 10.1016/0008-8846(96)00119-6.
- [31] Singh J, Kalamdhad AS. Bioavailability and leachability of heavy metals during water hyacinth composting. Chem Spec Bioavailab. 2013;25(1):1-14. DOI: 10.3184/095422913X13584520294651.
- [32] Liu HT, Gao D, Chen TB, Cai H, Zheng GD. Improvement of salinity in sewage sludge compost prior to its utilization as nursery substrate. J Air Waste Manage Assoc. 2014;64(5):546-51. DOI: 10.1080/10962247.2013.872710.
- [33] Tennant MF, Mazyck DW. The role of surface acidity and pore size distribution in the adsorption of 2-methylisoborneol via powdered activated carbon. Carbon. 2007;45:858-64. DOI: 10.1016/j.carbon.2006.11.009.
- [34] Hua L, Wu W, Liu Y, McBride MB, Chen Y. Reduction of nitrogen loss and Cu and Zn mobility during sludge composting with bamboo charcoal amendment. Environ Sci Pollut Res. 2009;16(1):1-9. DOI: 10.1007/s11356-008-0041-0.
- [35] Hiller DA, Brümmer GW. Electron microprobe studies on soil samples with varying heavy metal contamination: Part 2. Contents of heavy metals and other elements in aggregations of humic substances, litter residues, and charcoal particles. Z Pflanzenernähr Bodenkd. 1997;160:47-55. DOI: 10.1002/jpln.19951580204.
- [36] Vandecasteele B, Sinicco T, D'Hose T, Nest TV, Mondini C. Biochar amendment before or after composting affects compost quality and N losses, but not P plant uptake. J Environ Manage. 2016;168:200-9. DOI: 10.1016/j.jenvman.2015.11.045.
- [37] Gaskin JW, Speir RA, Harris K, Das KC, Lee RD, Morris LA, et al. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agron J. 2010;102:623-33. DOI: 10.2134/agronj2009.0083.
- [38] Major J, Rondon M, Molina D, Riha SJ, Lehmann J. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil. 2010;333:117-28. DOI: 10.1007/s11104-010-0327-0.
- [39] Schmidt HP, Kammann C, Niggli C, Evangelou MWH, Mackie KA, Abiven S. Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. Agricult Ecosyst Environ. 2014;191:117-23. DOI: 10.1016/j.agee.2014.04.001.
- [40] Saha S, Pondey AK, Gopinath KA, Bhattacharaya R, Kundu S, Gupta HS. Nutritional quality of organic rice grown on organic composts. Agron Sustain Dev. 2007;27(3):223-9. DOI: 10.1051/agro:2007002.
- [41] Hashemimajd K, Mohamadi Farani T, Jamaati-e-Somarin S. Effect of elemental sulphur and compost on pH, electric al conductivity and phosphorus availability of one clay soil. Afr J Biotechnol. 2012;11(6):1425-32. DOI: 10.5897/AJB11.2800.
- [42] Demir K, Sahin O, Kadioglu YK, Pilbeam DJ, Gunes A. Essential and non-essential element composition of tomato plants fertilized with poultry manure. Sci Hort. 2010;127(1):16-22. DOI: 10.1016/j.scienta.2010.08.009.
- [43] Hernández A, Castillo H, Ojeda D, Arras A, López J, Sánchez E. Effect of vermicompost and compost on lettuce production. Chil J Agric Res. 2010;70(4):583-9. Available from: https://www.semanticscholar.org/paper/Effect-of-Vermicompost-and-Compost-on-Lettuce-Hern%C3%A1ndez-Castillo/33ca48adf783f53e0ad5497eea187514b31a265e.
- [44] Castillo C, Rubio R, Contreras A, Borie F. Hongos micorrizógenos arbusculares en un Ultisol de la IX Región fertilizado orgánicamente (Effect of compost addition on arbuscular mycorrhizal propagules in a southern Chilean volcanic soil). Rev Cienc Suelo Nutr. 2004;4(2):39-47. Available from: https://scielo.conicyt.cl/pdf/rcsuelo/v6n3/art03.pdf.
- [45] Buttler TJ, Muir PM. Dairy manure compost improves soil and increase tall wheatgrass yield. Agron J. 2006;98:1090-6. DOI: 10.2134/agronj2005.0348.
- [46] Leifeld J, Siebert S, Kögel-Knabner I. Changes in the chemical composition of soil organic matter after application of compost. Eur J Soil Sci. 2002;53:299-309. DOI: 10.1046/j.1351-0754.2002.00453.x.
- [47] Carmo DL, de Lima LB, Silva CA. Soil fertility and electrical conductivity affected by organic waste rates and nutrient inputs. Rev Bras Cienc Solo. 2016;40:1-17. DOI: 10.1590/18069657rbcs20150152.
- [48] Bouajila K, Sanaa M. Effect of organic amendments on soil physic-chemical and biological properties. J Mater Environ Sci. 2011;2:485-90. Available from: https://www.jmaterenvironsci.com/Document/vol2/ vol2_S1/12-GSO-S1-01-Bouajila%20kkedija.pdf.

- [49] Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M. Mobility and bioavailability of heavy metals and metalloids in soil environments. J Soil Sci Plant Nutr. 2010;10(3):268-92. DOI: 10.4067/S0718-95162010000100005.
- [50] Gondek K. Contents of manganese in maize and soil fertilized with organic materials. Ecol Chem Eng A. 2008;15(10):1057-66.
- [51] Hsu J-H, Lo S-L. Characterization and extractability of copper, manganese, and zinc in swine manure compost. J Environ Qual. 2000;29(2):447-53. DOI: 10.2134/jeq2000.00472425002900020012x.
- [52] Maqueda C, Herencja JF, Ruiz JC, Hidalgo MF. Organic and inorganic fertilization effects on DTPA-extractable Fe, Cu, Mn and Zn, and their concentration in the edible portion of crops. J Agric Sci. 2011;149(4):461-72. DOI: 10.1017/S0021859610001085.