Article

Utilization of Sewage Sludge-Derived Pyrogenic Material as a Promising Soil Amendment

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Abstract: The use of advanced treatment technologies such as pyrolysis and carbonization of bio-waste materials has the promise to develop coupled solutions for organic C and P problems in the future of food processing. Sewage sludge-derived pyrogenic materials that are applied to the soil system contain notable levels of P (1–20%). However, only a small portion of total phosphorus is available for plants. Therefore, our study assessed the pretreatment of sewage sludge with Na_2CO_3 and subsequent pyrolysis at 400 °C and 500 °C for the production of MPCM400 and MPCM500 as potential alternatives for inorganic P fertilizers. Non-pretreated sewage sludge-derived pyrogenic carbonaceous materials (PCM400 and PCM500) were produced as controls. The derived materials obtained by slow pyrolysis at a residence time of 120 min and pyrolysis temperatures of 400 °C and 500 °C, were analyzed by determination of electrical conductivity (EC), pH, elemental analysis of total C, H, N, scanning electron microscopy (SEM) and total concentrations of P, Cd, Fe, Pb and Zn. PCM400, PCM500, MPCM400 and MPCM500 were characterized by analysis of total 16 US-EPA (U.S. Environmental Protection Agency) PAHs by a toluene extraction procedure. Additionally, PCM400, PCM500, MPCM400 and MPCM500 were tested by a germination test with cress seeds (*Lepidium sativum* L.) and a short-term rye seedling test. Total C concentrations were raised in the order: MPCM500 < MPCM400 < PCM500 < PCM500. Concentration of Σ16 US-EPA PAHs was almost five times higher at PCM500 (21.87 mg/kg) compared to PCM400 (4.38 mg/kg) and three times higher at MPCM500 (23.12 mg/kg) compared to MPCM400 (7.55 mg/kg) with a dominant role of two and three-ring aromatic structures. Total P-concentrations in rye biomass increased in the order for the controls: (2.43 ± 0.95 mg/g) < PCM400 (3.57 ± 0.27 mg/g) < PCM500 (4.04 ± 0.24 mg/g) < MPCM400 (5.23 ± 0.09 mg/g) < MPCM500 (5.57 ± 0.70 mg/g) < IF (7.53 ± 2.65 mg/g). Obtained results showed that pyrolysis materials produced from sewage sludge represent a potential alternative of conventional P inorganic fertilizers and organic C suppliers.

Keywords: sewage sludge; pyrolysis; phosphorus; Na_2CO_3; feedstock pretreatment

1. Introduction

Intensification of industrial activities and subsequent anthropogenic emissions of greenhouse gases will bring increases in global mean temperatures and climate changes. A full understanding of how soil organic matter will respond to these changes in the climate system is crucial. This is because organic matter is a multi-functional component of soil that provides vital ecosystem services, including support of primary production [1]. Furthermore, soil organic matter provides one of the Earth's richest C reservoirs, holding more than

three-fold the amount of C that is currently in the atmosphere as CO_2 and has implications for the mitigation or exacerbation of climate change. Recently the international initiative "4 per 1000" emphasised the importance in not only deceleration of climate changes but mainly carbon stabilization in soil by promoting of agro-environmental techniques that increase the amount of organic matter in soils and meet the 4% per year target [2]. Farmland around the world is threatened by the loss of organic carbon due to intensive tillage and inappropriate cropping practices. Approximately 45% of all mineral soils in Europe have poor organic C content (0–2%) [3]. This enhances their vulnerability to biodiversity loss, soil erosion, compaction, reduced fertility and low water retention capacity. The relevance of soil organic C stems from its function as the primary component of soil organic matter, which has a stable moiety known as humus. Furthermore, sustainable soil fertility is not feasible without an adequate flow of nutrients to vegetation. Among the principal elements required for vegetation growth, P is one of the most important macronutrients. Inorganic P is extracted from rock phosphate and constitutes a limited resource that is believed to become exhausted during the current or next century and that is characterized by a very patchy geographical spreading [4]. The quality of the remaining rock phosphate resources is continuously decreasing because the concentrations of undesirable companion elements, such as cadmium and uranium, are increasing. Therefore, recycling of phosphorus-rich materials, such as sewage sludge, is a necessary strategy to alleviate the pressures on the residual resources and to improve the efficiency of current phosphorus input. Although the reduction of phosphorus use, the improvement of bioavailability and support for mycorrhizal activity in the soil are necessary, supplementary strategies to conserve the remaining phosphate resource, innovative recycling strategies for phosphorus recovery from wastes will be a main pillar of the future phosphorus economy. Existing phosphorus precipitation processes in wastewater treatment plants require significant amounts of input chemicals, such as $MgCl_2$, $FeCl_3$, $FeSO_4$ or Al-salts, but the use of the resulting precipitates or sewage sludge as direct fertilizers is tightly regulated and frequently not legal. However, large amounts of sewage sludge are burnt or deposited in landfills where phosphates are withdrawn from any further use. Besides, residual phosphate concentrations in wastewater treatment plant effluents contribute to the eutrophication of surface waters.

The use of advanced treatment technologies such as pyrolysis and carbonization of bio-waste materials has the capacity to provide coupled solutions for organic C and P problems in the future of food processing. Pyrolysis refers to a carbonization technique in which biomass or other organic materials are thermochemically transformed into essentially stable, recalcitrant organic C compounds, with the process requiring an oxygen-poor or oxygen-free inert atmosphere, pyrolysis temperatures of 300–1000 °C and residence time ranging from a few seconds to a few hours [5]. Pyrolysis materials produced have increased (two to three times) content of total C and other elements (P, Zn and Ca) compared to the input feedstock. Sewage sludge composition is highly heterogenous. Sludge is mainly derived in the sewage network of cities by a combination of sewage, rainwater with sand particles, industrial and municipal wastewaters. Therefore, the characteristics of the sludge itself are a combination of the properties of these components. In an applied material such as sewage sludge potential ecotoxicity based on heavy metal (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) mobility and organic pollutants (polycyclic aromatic hydrocarbons, pharmaceuticals, per- and polyfluoroalkyl substances), availability must be closely monitored [6]. Therefore, the effect of thermochemical processes on phosphorus bioavailability, carbon content and potential hazardous substances concentrations is crucial and will be mediated by pyrolysis optimization, the pretreatment of feedstock or the preparation of combined feedstock.

Producing a fertilizer product that considers both the nutrients' demand of crops and soil organic carbon gap will be a highly effective soil amendment with characteristics that cannot readily be imitated by traditional organic or mineral fertilizers. The deployment of such innovative materials demands feedstock-specific pyrolysis steps that will alter the labile C of wastes and residues into stable organic C compounds with mean soil residence times ranging from decades to centuries [7]. On the one hand, these amendments allow

for a long-term carbon sequestration in soil as a component of climate change mitigation strategies; on the other hand, positive side effects on physicochemical soil characteristics will be entrained. Thus, the usage of carbonization products as soil amendments or fertilizers is highly efficient in terms of resources (multi-purpose use of organic residues or wastes) and energy (exothermic carbonization process for production).

Sewage sludge-derived pyrogenic materials that are applied to the soil system contain notable levels of P (1–20%). However only a small portion of total phosphorus is available for plants [8]. Transformation of apatite phosphorus (mainly Ca/Mg bound P) to non-apatite forms of inorganic phosphorus during thermochemical treatment of sewage sludge has been reported by several authors [9–11]. The bioavailability of this form of P in sludge-derived pyrogenic materials has shown lower intensity compared to feedstock materials and variability based on sludge type. This kind of slow phosphorus-releasing fertilizer represents an important step in P-loss mitigation and subsequent environmental problems. On the other hand, better availability of P in pyrogenic materials is often a limiting factor for pyrolysis application in sewage sludge treatment [12]. Therefore, suitable sludge modification or pretreatment and co-pyrolysis represent options on how to improve nutrient bioavailability. There have been several studies on sewage sludge pretreatment with CaO [13], $MgCl_2$ [14], NaCl [14], $CaCl_2$ [14], KCl [15] and K_2SO_4 [15], but only limited information on Na_2CO_3 effects.

Based on these scenarios, the main research objective of this study was to investigate the effect of Na_2CO_3 as an additive agent on P solubility and bioavailability in sewage sludge-derived pyrogenic carbonaceous material. We attempted to characterize modified and unmodified pyrogenic carbonaceous materials produced by slow pyrolysis of municipal sewage sludge at 400 °C and 500 °C as potential soil additives for agriculture (i.e., industrial crops) and green infrastructure (i.e., green roofs, green walls)

2. Materials and Methods

2.1. Simulation Experiment

For the assessment of the Na_2CO_3 pretreatment effect on P bioavailability, a simulation experiment was conducted based on the work by Wzorek et al. [16]. Briefly, the iron and aluminium phosphates, as main forms of P in municipal sewage sludge ($FePO_4 \cdot 2H_2O$ and $Al(H_2PO_4)_3$, Sigma-Aldrich, Taufkirchen, Germany), were mixed with Na_2CO_3 (Sigma-Aldrich, Germany) in molar ratios of 1:1 and 1:2. After homogenization (2 h, lab-shaker), 10 g of each mixture was weighed into a container and pyrolyzed at 400 °C and 500 °C by a modified lab-scale pyrolysis reactor for 120 min under N_2 atmosphere (heating rate 25–30 °C/min, N_2 gas flow 2 L/min). As a control, the pure forms of chemicals were pyrolyzed under the same conditions. For P availability evaluation, prepared products were homogenized and the obtained representative sample was extracted by deionized water (0.04 μS/cm) in ratio 1/20 (*w/w*) on a laboratory shaker at 225 rpm, 120 min and 22 °C. Obtained extracts were filtered using syringe filters (pore size 0.45 μm) and analyzed for total P content by traditional colorimetric vanadate/molybdate method (yellow method) at λ = 430 nm by spectrophotometry (UV-VIS Shimadzu, 160A, Shimadzu, Kyoto, Japan) [17]. The filters were tested for P retention before each application.

2.2. Sewage Sludge Pretreatment and Pyrolysis Treatment

Sewage sludge (BSS) was obtained from municipal WWTP in Seibersdorf (Austria). After, the collection of BSS was dewatered and oven-dried at 60 °C for 96 h. For the Na_2CO_3 pretreatment study, the one part of sludge was modified with Na_2CO_3 ($w_{sludge}/w_{Na2CO3} = 100/1$) and the suspension was oven-dried at 60 °C for 96 h. Prepared pretreated and non-pretreated feedstock BSS was pyrolyzed at 400 °C and 500 °C by a modified lab-scale pyrolysis unit for 120 min under N_2 atmosphere (heating rate 25–30 °C/min, N_2 gas flow 2 L/min, thermal heating). The produced Na_2CO_3-modified pyrogenic carbonaceous material (MPCM400 and MPCM500) and unmodified pyrogenic carbonaceous

material (PCM400 and PCM500) were ground and sieved to obtain uniform fractions of 0.5–1 mm for characterization and cultivation experiments.

2.3. Physicochemical Characterization

Prior to each analysis, PCM400, PCM500, MPCM400 and MPCM500 were thoroughly mixed in a laboratory stirrer. Characterization analyses were performed for each studied material in three replicates. The pH values of the samples were determined by pH meter (inoLab pH level 2P, Weilheim, Germany) after mixing the samples with a solution of 0.01 mol/L $CaCl_2$ (ratio 1:10 m/v) for 1 h and 1 h of equilibration. The electrical conductivities (EC) of the samples were determined by conductivity meter (inoLab pH level 2P, Weilheim, Germany) in deionized water (1:10 m/v) after 24 h of stirring. The total C, H and N contents of the samples were quantified by an elemental analyzer (CHNS-O EA 1108, Carlo Erba Instruments, Milan, Italy). The morphological structures of PCM and MPCM were recorded by scanning electron microscopy (SEM) using JEOL JSM7500F scanning electron microscope (Tokyo, Japan). The method described in our previous work [18] was used to determine ash content. Total Cd, Fe, P, Pb and Zn concentrations were determined in PCM and MPCM samples by ICP-MS (Perkin Elmer, Elan DRCe 9000, Shelton, CT, USA) and ET-AAS (PerkinElmer, AA 400, Shelton, CT, USA) methods after previous digestion of the samples using the modified HNO_3 method [19]. The limits of detection (LOD) for selected analytes were defined by 3σ criterion. The total content of 16 PAHs classified by the U.S. Federal Environmental Federal Environmental Protection Agency (US-EPA) were determined in PCM400, PCM500, MPCM400 and MPCM500 by HPLC (Agilent 1100 with column GRACE/Vydac C18 polymeric reversed-phase, 4.6×250 mm, 5 μm; and GRACE/Vydac C18 guard column, 4.6×7.5 mm, 5 μm, Santa Clara, CA, USA) after previous Soxhlet extraction by toluene as an extraction agent (solid/liquid: 1/15, 36 h, 110 °C). Detection was conducted using a diode array HPLC detector DAD ($\lambda = 310$ nm) and fluorescence detector FLD (Ex = 260 nm, Em = 350 nm, 420 nm, 440 nm and 500 nm). The extraction procedure and analytical quantification of 16 PAHs were carried out as reported by [20,21].

2.4. Germination Test

The germination test with cress seeds (*Lepidium sativum* L.) was performed according to the scheme developed by Buss and Mašek [22]. The advantage of this test variant is that the germination of cress can be investigated in three different ways in one pot. Briefly, the experimental pot was divided into three levels in order to determine the different influences of contaminants in the three different forms (gaseous, dissolved and attached to PCM400, PCM500, MPCM400 and MPCM500) on cress seed germination. Therefore, three levels of seed contact system were prepared. On the first level, the effect of volatile compounds: PCM400, PCM500, MPCM400 and MPCM500 only was tested. The second level was focused on the combined effect of volatile and leachable (dissolved) compounds (in water): PCM400, PCM500, MPCM400 and MPCM500. The last level was targeted on volatile compounds, leachable compounds and direct contact with PCM400, PCM500, MPCM400 and MPCM500. Crushed samples of PCM and MPCM were mixed with quartz sand to ensure total P content equal to 40 mg P/40 mg sand in each aluminium container. There were 30 cress seeds per level, but only the third level had direct contact with the coals. The whole pot was covered with cling foil for 96 h in order to promote germination. Figure 1 shows the experimental design with the three levels. After 96 h, the number of geminated seeds was counted for each level separately. A germination test was conducted in triplicates for each tested material and control samples (non-amended sand). For the statistical evaluation, the normality and Tukey's post-hoc tests were used (Statistica 8, StatSoft 2007, Tulsa, OK, USA).
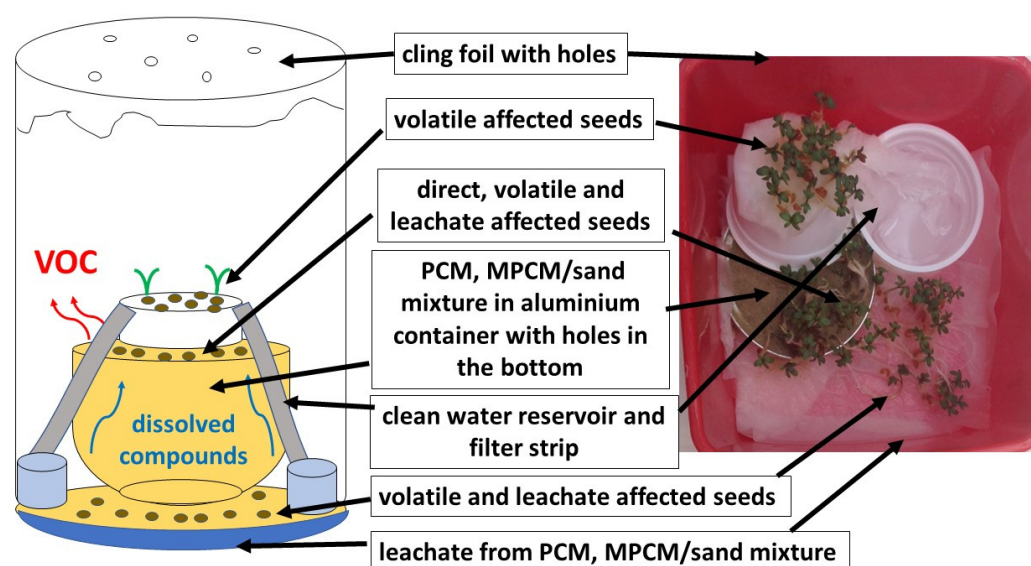
Figure 1. Experimental design for the germination test for assessing the effect of direct contact, released volatile and dissolved compounds in water.

2.5. Neubauer Test

A Neubauer test [23] as a standard rye seedling test to determine plant-available phosphorus fraction from PCM and MPCM was used. The seedling test lasted 17 days and was carried out in greenhouse conditions (12 h light/12 h dark, constant humidity, 25 °C). Rye seeds (*Secale cereale* L.) were treated in a 70% ethanol solution for about 5 s and then washed thoroughly with deionized water. Experimental pots were fulfilled with fine silica sand (washed 3 times with solution 0.01 mol/L HCl and deionized water (electrical conductivity EC < 0.04 μS/cm)) and PCM400, PCM500, MPCM400 and MPCM500, and a commercial inorganic P fertilizer (IF, 42% P_2O_5, Glatz, Vienna, Austria) in a ratio to achieve per pot total amount of 40 mg P/400 g sand. Non-amended sand was used as a control. In each experimental pot, exactly 100 rye seeds in 0.5–1 cm department were positioned. To accelerate germination and growth, the pots were covered with a plastic film during the first three days. Pots were irrigated with Hoagland's solution without P, including all other nutrients, to maintain water holding capacity at a constant value over the experimental period. The experiment was arranged in 4 blocks to keep the scattering of results due to external influences (light, heat). The location of replicate samples within each experimental block was randomized. The harvesting of leaves and roots was carried out after 17 days of cultivation. The plant materials were washed in deionized water, separated from sand and PCM and MPCM particles, and oven-dried for 4 days at 60 °C. Subsequently, dried leaves and roots were ground and digested with $HNO_3/HClO_4$ (*v/v* 5:1) for P, Cd, Fe, Pb and Zn concentration by ICP-MS (Perkin Elmer, Elan DRCe 9000, Shelton, CT, USA) and ET-AAS (PerkinElmer, AA 400, Shelton, CT, USA). For the statistical evaluation, the normality and Tukey's post-hoc tests were used (Statistica 8, StatSoft 2007, Tulsa, OK, USA).

3. Results

3.1. Chemicals Pyrolysis

A high number of wastewater treatment plants in Europe still use precipitation with $Fe_2(SO_4)_3$-$FeCl_3$ (sometimes, but rarely, $FeSO_4$), $Al_2(SO_4)_3$-$14H_2O$ and Ca as lime milk to remove phosphorus from wastewater [16,24]. After this type of chemical precipitation, phosphorus is present in sludge in the form of poorly soluble and weak bioavailable compounds. Subsequently, when sewage sludge is used as a feedstock for pyrolysis treatment, a sintering process occurs, which completes the chemical stability and relatively low bioavailability of phosphorus. The use of multiple additions and the use of copyrolysis of materials has proven to be an effective option in several cases [13–15]. Our experiment aimed at

performing a simulation of an Na_2CO_3 effect on P-extractability from products obtained by the pyrolysis of soda ash with $FePO_4$ or $Al(H_2PO_4)_3$ and finding the optimal molar ratio of Na_2CO_3 and $FePO_4$ or $Al(H_2PO_4)_3$. The influence of Na_2CO_3 on the extractable phosphorus content in the various tests is shown in Table 1. In all experiments, it was found that higher extractable phosphorus contents can be achieved at a pyrolysis temperature of 500 °C. At combination of Na_2CO_3 and $FePO_4 \cdot 2H_2O$ with a molar ratio 1:1, at a pyrolysis temperature of 500 °C, the highest phosphorus yield was 58.670 mg/g. The second highest extractable phosphorus concentration of 31.881 mg/g was achieved by a combination of Na_2CO_3 and $FePO_4 \cdot 2H_2O$ with a 2:1 molar ratio followed by a combination of Na_2CO_3 and $Al(H_2PO_4)_3$ with a 2:1 molar ratio and a concentration of 26.242 mg/g. The work by Wzorek et al. [16] showed that in thermochemical processes, phosphorus availability can be increased by adding Na_2CO_3 to chemicals. The authors demonstrated that the addition of soda ash significantly increased the availability of phosphorus compounds in $Na_2CO_3/FePO_4 \cdot 2H_2O$ with a molar ratio range from 1 to 5. The importance of the molar ratio in the mean crystalline phase type formation was emphasized. The shift to the hematite formation during thermochemical conversion and more mobile P form synthesis was discussed. Our results confirmed a positive effect of Na_2CO_3 addition on P availability in both ratios compared to the control (pyrolyzed pure $FePO_4$ or $Al(H_2PO_4)_3$). Additionally, obtained results were used to predict the amount of Na_2CO_3 required for sewage sludge modification based on the Fe content.

Table 1. Chemical constitution and phosphorus extractability of tested samples.

Sample	Pyrolysis Temperature (°C)	Molar Ratio	$P_{extractable}$ (mg/g)
$FePO_4 \cdot 2H_2O$ + Na_2CO_3	400	1 mol/1 mol	9.078 ± 0.05 [e]
$FePO_4 \cdot 2H_2O$ + Na_2CO_3	500	1 mol/1 mol	58.670 ± 0.81 [a]
$Al(H_2PO_4)_3$ + Na_2CO_3	400	1 mol/1 mol	4.406 ± 0.15 [g]
$Al(H_2PO_4)_3$ + Na_2CO_3	500	1 mol/1 mol	5.585 ± 0.15 [fg]
$FePO_4 \cdot 2H_2O$	400	1 mol/1 mol	0.073 ± 0.01 [i]
$FePO_4 \cdot 2H_2O$	500	1 mol/1 mol	0.167 ± 0.01 [i]
$Al(H_2PO_4)_3$	400	1 mol/1 mol	0.960 ± 0.03 [h]
$Al(H_2PO_4)_3$	500	1 mol/1 mol	<LOD
$FePO_4 \cdot 2H_2O$ + Na_2CO_3	400	1 mol/2 mol	5.763 ± 0.06 [fg]
$FePO_4 \cdot 2H_2O$ + Na_2CO_3	500	1 mol/2 mol	31.881 ± 0.37 [b]
$Al(H_2PO_4)_3$ + Na_2CO_3	400	1 mol/2 mol	13.791 ± 0.15 [d]
$Al(H_2PO_4)_3$ + Na_2CO_3	500	1 mol/2 mol	26.242 ± 0.84 [c]

P LOD = 0.05 µg/L. $P_{extractale}$ is given as average value with standard deviation. Different letters mean statistically significant difference ($p < 0.05$).

3.2. PCM and MPCM Characterization

The sewage sludge suspension contained 82% water after sampling in WWTP, which was eliminated to a minimum value (<0.01%) during the drying process. Subsequent feedstock modification and pyrolysis of both modified (MPCM) and unmodified (PCM) sludge resulted in products with 38–48% yield (Table 2). The yield values were higher for both PCM400 and MPCM400 compared to their analogues produced at a pyrolysis temperature of 500 °C. The effect of Na_2CO_3 modification was evidently reflected in several physicochemical characteristics of the studied materials. The pH value was higher for the MPCM materials compared to the PCM and the same for the materials produced at 500 °C. The effect of soil amendments with higher pH values can be crucial, mainly for acidic soils with extensive nutrients losses. As can be seen in Table 2, both PCM and MPCM represent materials with relatively high ash content (38–45%). Determination of total C content confirmed higher values for PCM400 (33.37%) compared to PCM500 (30.94%). On the other hand, MPCM400 showed a total C content of 29.92% compared to MPCM500 at 27.64%. Based on the values found, we can confirm that both PCM and MPCM represent pyrogenic carbonaceous material (C content less than 50%) according to the EBC (European Biochar Certificate) [25]. The EBC also strictly defines the input biomasses that can be used

for production. As a feedstock, sewage sludge remains in the group of potential materials that could be used in the future. Determination of total P showed increasing values in the order: MPCM400 (51.7 mg/kg) < PCM400 (55.5 mg/kg) < MPCM500 (56.1 mg/kg) < PCM500 (58.7 mg/kg). Determination of total concentration of selected heavy metals showed Cd levels of 0.19 mg/kg for both PCM400 and MPCM400 and 0.10 mg/kg for both PCM500 and MPCM500. The values of total Pb concentration were below the LOD for the given determination (0.22 μg/L) for all four materials. In case of total Fe, concentrations were higher for PCM500 (23.06 mg/kg) than for PCM400 (20.55 mg/kg). The MPCM400 and MPCM500 materials had total Fe as well as Zn concentrations statistically similar to each other.

Table 2. Physico-chemical characteristics of PCM400, PCM500, MPCM400 and MPCM500 (average value ± SD).

Sample	Yield (%)	pH	EC (mS/cm)	Ash Content (%)	C_{tot} (%)	N_{tot} (%)	H_{tot} (%)	Cd (mg/kg)	Fe (mg/kg)	P (mg/g)	Pb (mg/kg)	Zn (mg/g)
PCM400	45.1	8.81 ± 0.15	0.29 ± 0.05	38.7 ± 0.50	33.37 *	4.19 *	2.14 *	0.19 ± 0.01	20.55 ± 0.67	55.5 ± 0.5	<LOD	0.34 ± 0.01
PCM500	38.5	9.58 ± 0.10	0.19 ± 0.02	43.9 ± 0.70	30.94 *	3.07 *	1.85 *	0.10 ± 0.01	23.06 ± 0.07	58.7 ± 1.9	<LOD	0.37 ± 0.01
MPCM400	48.1	10.38 ± 0.15	0.54 ± 0.05	39.8 ± 0.30	29.92 *	2.93 *	2.54 *	0.19 ± 0.01	21.34 ± 0.74	51.7 ± 2.5	<LOD	0.32 ± 0.01
MPCM500	46.3	10.52 ± 0.12	0.57 ± 0.01	44.5 ± 0.60	27.64 *	2.04 *	2.06 *	0.10 ± 0.01	20.82 ± 0.30	56.1 ± 0.8	<LOD	0.34 ± 0.02

Pb LOD = 0.22 μg/L, * single measurement of analytically representative sample.

Obtained results of physicochemical characteristics suggest substantial differences between modified and unmodified pyrolysis materials produced at 400 °C and 500 °C. The formation of new structures or disappearance of original polycyclic aromatic hydrocarbons during the pyrolysis process of sewage sludge at 400 °C and 500 °C were characterized by 16 US-EPA PAHs determination using the toluene extraction protocol in Soxhlet extraction unit (Table 3). Total concentrations of extractable naphthalene represent >50% for PCM400, >42% for PCM500, >88% for MPCM400 and >40% for MPCM500 of total Σ16 US-EPA PAHs. The effect of thermochemical conversion on raised total concentration of PAHs in PCM and MPCM was confirmed. Especially, pyrolysis at a higher temperature conditioned the formation of two and three-ring aromatic structures in sewage sludge. The main substrates for their formation can be dead biomass of microorganisms, free organic matter or hardly degradable polymers [26]. Bucheli et al. [27] showed pyrosynthesis as a crucial process of gaseous hydrocarbon radicals' generation by organic matter cracking at a temperature < 500 °C. Zielinska and Olesczuk [28] showed correlation between pyrolysis temperature and individual PAHs structure formation during the pyrolysis of sewage sludge. They confirmed an increased trend of low molecular weight compounds' formation with increasing temperature. A similar effect of thermochemical conversion on PAHs concentration in sewage sludge-derived pyrogenic carbonaceous material has been found by several scientific works [29–31]. The effect of carbonates on PAHs concentration has been studied in detail by Kwon et al. [32]. The authors confirmed a positive effect of calcium carbonate on the reduction of PAHs concentrations in sewage sludge-derived pyrolysis products produced at a temperature > 650 °C.

The surface structure and morphology of PCM and MPCM obtained by scanning microscopy (Figure 2) showed amorphous particles with combined character. The original smooth surfaces of sewage sludge feedstock were transformed into rough and partly porous structures. The mineral character was more pronounced in the MPCM sample compared to the PCM. Similar structures were characterized in our previous study [33].

Table 3. Total concentrations (mean ± SD) of naphthalene, acenaphtene, acenaphthylene, phenanthrene, fluorene, anthracene, benz[*a*]anthracene, chrysene, pyrene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and dibenz[*ah*]anthracene in PCM400, PCM500, MPCM400 and MPCM500 determined by Soxhlet extraction with toluene (solid/liquid: 1/15, 36 h, 110 °C).

| Polycyclic Aromatic Hydrocarbon (PAH)	PCM400 (mg/kg)	PCM500 (mg/kg)	MPCM400 (mg/kg)	MPCM500 (mg/kg)
Naphthalene	2.27 ± 0.16	9.40 ± 0.05	6.71 ± 0.31	9.29 ± 0.41
Acenaphtene	ND	ND	ND	ND
Acenaphthylene	0.72 ± 0.03	4.41 ± 0.2	0.43 ± 0.02	5.81 ± 0.2
Phenanthrene	0.37 ± 0.02	1.05 ± 0.05	0.14 ± 0.01	1.06 ± 0.47
Fluorene	ND	2.59 ± 0.11	ND	1.85 ± 0.06
Anthracene	0.49 ± 0.01	2.08 ± 0.2	0.27 ± 0.01	2.06 ± 0.2
Benz[*a*]anthracene	ND	0.52 ± 0.01	ND	0.65 ± 0.01
Chrysene	ND	0.82 ± 0.01	ND	1.14 ± 0.05
Pyrene	ND	0.36 ± 0.02	ND	0.33 ± 0.02
Fluoranthene	0.53 ± 0.02	0.25 ± 0.01	ND	0.37 ± 0.01
Benzo[*b*]fluoranthene	ND	0.23 ± 0.01	ND	0.26 ± 0.01
Benzo[*k*]fluoranthene	ND	ND	ND	ND
Benzo[*a*]pyrene	ND	0.16 ± 0.01	ND	0.30 ± 0.01
Indeno[1,2,3-*cd*]pyrene	ND	ND	ND	ND
Benzo[*ghi*]perylene	ND	ND	ND	ND
Dibenz[*ah*]anthracene	ND	ND	ND	ND
$\sum$16 PAHs	4.38	21.87	7.55	23.12

ND = non-detected, <LOD evaluated from the concentration of PAHs required to give at least a signal-to-noise ratio of 3.
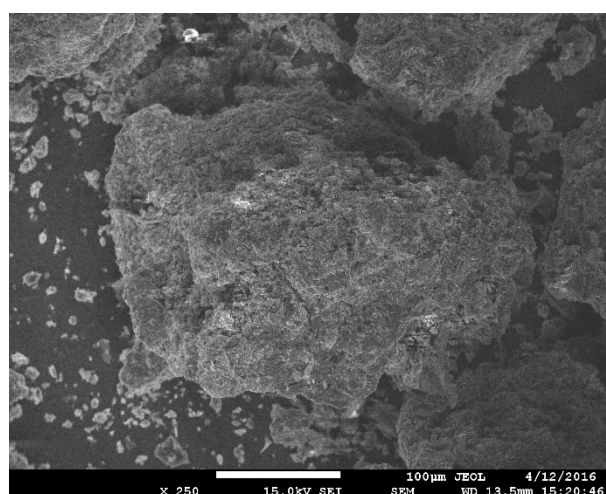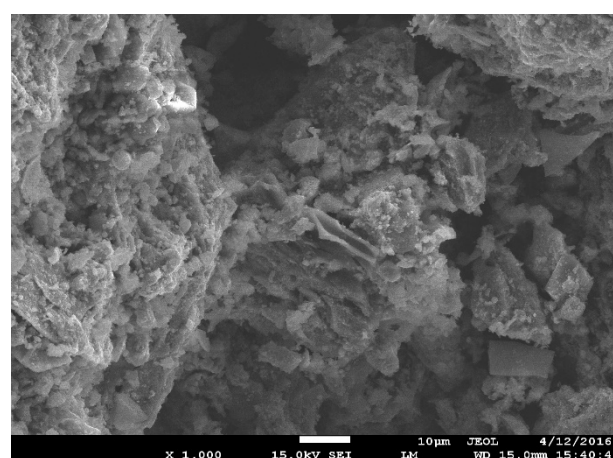

(**a**)
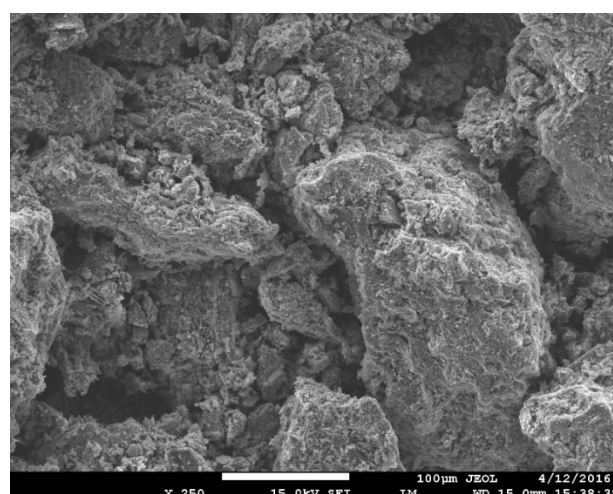
(**b**)
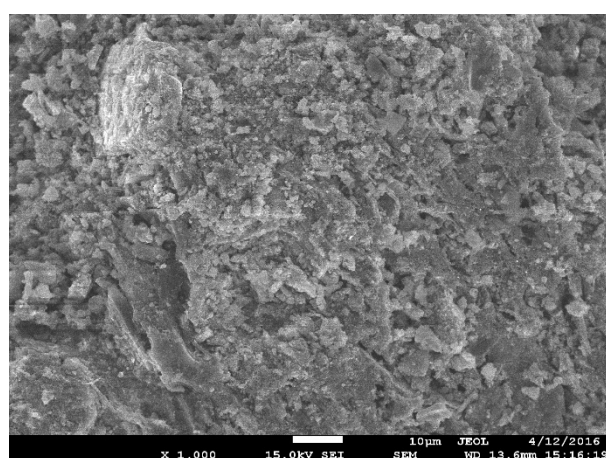
(**c**)

(**d**)

Figure 2. Microimages of PCM (**a**,**c**) and MPCM (**b**,**d**) obtained by scanning electron microscopy at 250× (**a**,**b**) and 1000× (**c**,**d**).

3.3. Assessment of Phytotoxicity

The rate of cress seed germination in the test for volatile compounds only, leachable and volatile compounds, leachable, volatile compounds and direct contact with PCM400, PCM500, MPCM400 and MPCM500 can be seen in Figure 3. The volatile compounds (I) release from all tested pyrolysis products showed no statistically significant effect on seed germination compared to the control. The difference between pyrolysis materials produced at 400 °C and 500 °C was negligible. Buss and Masek [22] showed that biochar produced at higher pyrolysis temperatures possess lower volatile matter concentrations compared to low-temperature biochars. Ronsse et al. [34] confirmed less or no toxic effects of high-temperature biochars on seed germination.
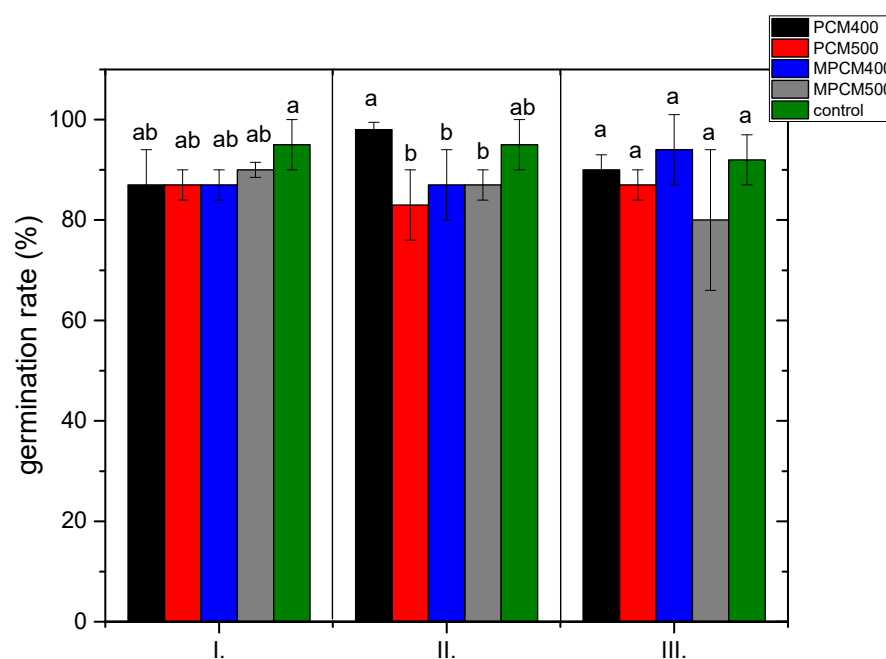

Figure 3. Germination rate (%) of cress seeds tested in volatile compounds only (I), leachable and volatile compounds (II), leachable, volatile compounds and direct contact with pyrolysis products (III). Germination rate is given as average value with standard deviation. Different letters mean statistically significant difference ($p < 0.05$) of germination rate between treatments in each environment.

The germination test of cress seeds in the environment of leachable and volatile compounds (II) of PCM400, PCM500, MPCM400 and MPCM500 showed a difference between PCM400 and PCM500, MPCM400 and MPCM500. However, the reduction in germination rate of PCM500, MPCM400 and MPCM500 samples was not statistically significant compared to the control. Water soluble compounds from the studied materials cannot cause seed toxicity and have negligible effects on germination. In the last level (III), cress seeds were in direct contact with PCM400, PCM500, MPCM400 and MPCM500 and were exposed to released volatile and dissolved compounds. It can be clearly seen (Figure 3) that exposure to all routes of toxicity did not demonstrate a significant difference in germination rate between the control and sand amended by the studied PCM400, PCM500, MPCM400 and MPCM500. Produced pyrolysis materials confirmed very low and negligible phytotoxicity.

3.4. P Bioavailability

The evaluation of PCM400, PCM500, MPCM400 and MPCM500 as potential soil amendments and mainly P fertilizers, was performed by the application of a rye seedling cultivation test. After the cultivation period of 16 days, biomass production of rye (d.w.) increased in the order: control = PCM400 = PCM500 $\leq$ inorganic fertilizer (IF) $\leq$ MPCM500 $\leq$ MPCM400 (Figure 4a). Differences between the control and MPCM400 and MPCM500 were statistically significant ($p < 0.05$). On the other hand, the total concentration of P in the

produced biomass showed a significant increase in all treatments in comparison to the control (Figure 4b). The positive trend in total phosphorus in the aboveground part followed very closely the trend of total phosphorus in the belowground part of rye plants. Total phosphorus content in rye biomass increased in the order: control < PCM400 = PCM500 < MPCM400 = MPCM500 = IF. It is obvious from the determined P concentrations that Na_2CO_3-modified sewage sludge-derived pyrogenic carbonaceous material (MPCM) provides a higher concentration of available phosphorus for the plant compared to unmodified pyrolyzed sewage sludge.
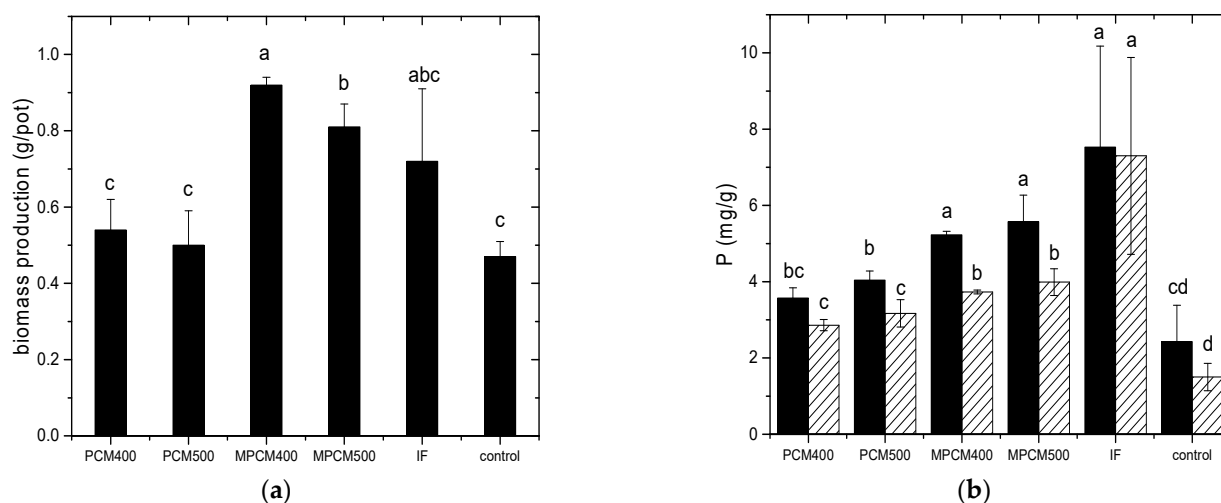

Figure 4. Biomass production (**a**) of rye (d.w.) and total concentrations of P (**b**) measured in rye tissues (solid fill) and roots (hatched fill) obtained from pots (mean ± SD) amended by PCM400, PCM500, MPCM400, MPCM500, inorganic fertilizer (IF) and non-amended soil (control). Conditions of digestion procedure: method $HNO_3 + HClO_4$, digestion block—temperature program 80 °C/60 min, 120 °C/40 min, 160 °C/40 min, 180 °C/60 min, 210 °C/60 min) diluted in 61–62% HNO_3 and quantification by ICP-MS. Different letters mean statistically significant difference ($p < 0.05$).

Pyrolysis treatment can convert sewage sludge to pyrogenic material with multiple concentrations of several nutrients, such as P, K and Zn [6]. A major part of the phosphorus present in the sludge is transferred to the inorganic fraction during the pyrolysis process. Phosphorus incorporated into organic constituents tends to disappear and forms amorphous, semi-crystalline and crystalline constituents. Crystallinity of P species will increase with increasing pyrolysis temperature [35]. As reported by Liu et al. [13], decomposition of organic matter in BSS equally results in the release of intracellular phosphorus from the cells of microorganisms with its subsequent interaction with inherent metals in the production of PCM. Similarly, thermochemical conversion of sludge entails the transition of a non-apatite form of phosphorus to apatite form with increasing temperature [9,10]. Orthophosphates (PO_4^{3-}) represent the main P species observed in pyrolysis products from manures and sludge at temperatures > 500 °C. Pyrophosphates ($P_2O_7^{4-}$) can be found in biochars produced mainly from plant residues by pyrolysis at >650 °C [36]. The main P minerals present in sewage sludge-derived pyrogenic carbonaceous materials represent whitlockite (($Ca,Mg)_3(PO_4)_2$, dehydrated struvite (NH_4MgPO_4) nad hydroxyapatite ($Ca_5(PO_4)_3(OH)$). The stabilization mechanisms of P during pyrolysis have been shown to become impaired when adding Na_2CO_3 to the feedstock [37]. The authors showed a positive effect of soda on P solubility in a canola cake biochar. Our results confirmed the hypothesis that the Na_2CO_3 addition to sludge improves P bioavailability from produced pyrogenic materials. We assumed that during the pyrolysis process, Na_2CO_3 as an agent digests organic forms of P and converts them to $CaNaPO_4$ or Na_3PO_4 that are better available for plants.

The application of PCM400, PCM500, MPCM400 and MPCM500 as a soil amendment in the rye seedling test showed negligible changes in total concentrations of Pb and Zn in

plant tissues compared to the control or IF (Table 4). Obtained concentrations of Pb were under LOD (0.22 µg/L). Determination of Zn in plant digests confirmed concentrations of 0.020 ± 0.003 mg/kg for all amendments. The PCM400 and PCM500 caused a reduction in Cd uptake by rye. The Cd content in the plant biomass obtained from pots amended by MPCM400 and MPCM500 showed comparable values to the control unamended sample (0.027 ± 0.002 mg/kg). On the other hand, application of MPCM400 and MPCM500 led to a statistically significant increase in total Fe content in rye tissues. PCM400 and PCM500 did not affect the Fe uptake by rye. Similar results were obtained in our previous studies where pyrolysis materials based on sewage sludge caused no-significant increase in concentrations of heavy metals [6,20].

Table 4. Total concentration of Cd, Fe, Pb and Zn in rye tissues obtained from pots (mean $\pm$ SD) amended by PCM400, PCM500, MPCM400, MPCM500, inorganic fertilizer (IF) and non-amended soil (control).

	Cd (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
PCM400	<LOD	0.041 ± 0.003 [c]	<LOD	0.020 ± 0.003 [a]
PCM500	<LOD	<LOD	<LOD	0.020 ± 0.003 [a]
MPCM400	0.027 ± 0.002 [b]	0.050 ± 0.002 [b]	<LOD	0.020 ± 0.002 [a]
MPCM500	0.026 ± 0.002 [b]	0.060 ± 0.003 [a]	<LOD	0.022 ± 0.003 [a]
IF	0.050 ± 0.008 [a]	0.040 ± 0.002 [c]	<LOD	0.025 ± 0.004 [a]
CONTROL	0.031 ± 0.011 [ab]	0.040 ± 0.005 [c]	<LOD	0.020 ± 0.002 [a]

Conditions of digestion procedure: method $HNO_3 + HClO_4$, digestion block—temperature program 80 °C/60 min, 120 °C/40 min, 160 °C/40 min, 180 °C/60 min, 210 °C/60 min) diluted in 61–62% HNO_3 and quantification by ICP-MS and ET-AAS. Cd LOD = 0.19 µg/L, Pb LOD = 0.22 µg/L, Fe LOD = 0.04 µg/L. Different letters mean statistically significant difference ($p < 0.05$).

4. Conclusions

The obtained results in this study showed that pyrogenic carbonaceous materials produced from sewage sludge represent a potential alternative for conventional P inorganic fertilizers and organic C suppliers. Total carbon concentrations were raised in the order of MPCM500 < MPCM400 < PCM500 < PCM500. Concentration of Σ16 US-EPA PAHs was almost five times higher at PCM500 (21.87 mg/kg) compared to PCM400 (4.38 mg/kg) and three times higher at MPCM500 (23.12 mg/kg) compared to MPCM400 (7.55 mg/kg) with a dominant role of two and three-ring aromatic structures. An ecotoxicological test with cress seeds (*Lepidium sativum* L.) studied in an environment of volatile compounds only, leachable and volatile compounds, leachable, volatile compounds and direct contact with PCM400, PCM500, MPCM400 and MPCM500 showed no-statistical significance in germination rates between tested materials and the control (pure sand). The effect of the application of Na_2CO_3-modified MPCM resulted in increased phosphorus availability and hence higher concentrations of total phosphorus present in rye tissues. P concentrations in rye biomass increased in order: control (2.43 ± 0.95 mg/g) < PCM400 (3.57 ± 0.27 mg/g) < PCM500 (4.04 ± 0.24 mg/g) < MPCM400 (5.23 ± 0.09 mg/g) < MPCM500 (5.57 ± 0.70 mg/g) < IF (7.53 ± 2.65 mg/g). This trend in total phosphorus was followed very closely by the trend in total phosphorus in the roots of rye plants. Depending on the metals studied, we can conclude that application of both PCM and MPCM materials does not have a significant effect on Zn and Pb uptake by rye plants. Furthermore, we did not observe a significant increase in Cd concentration in plant samples. Fe content was higher in the case of MPCM400 as well as MPCM500 compared to the control. Results obtained from short-term experiments demand comparison with the results of longer-term experiments aimed at monitoring the stability of MPCM products in the soil matrix under real conditions and kinetic of P releasing.

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