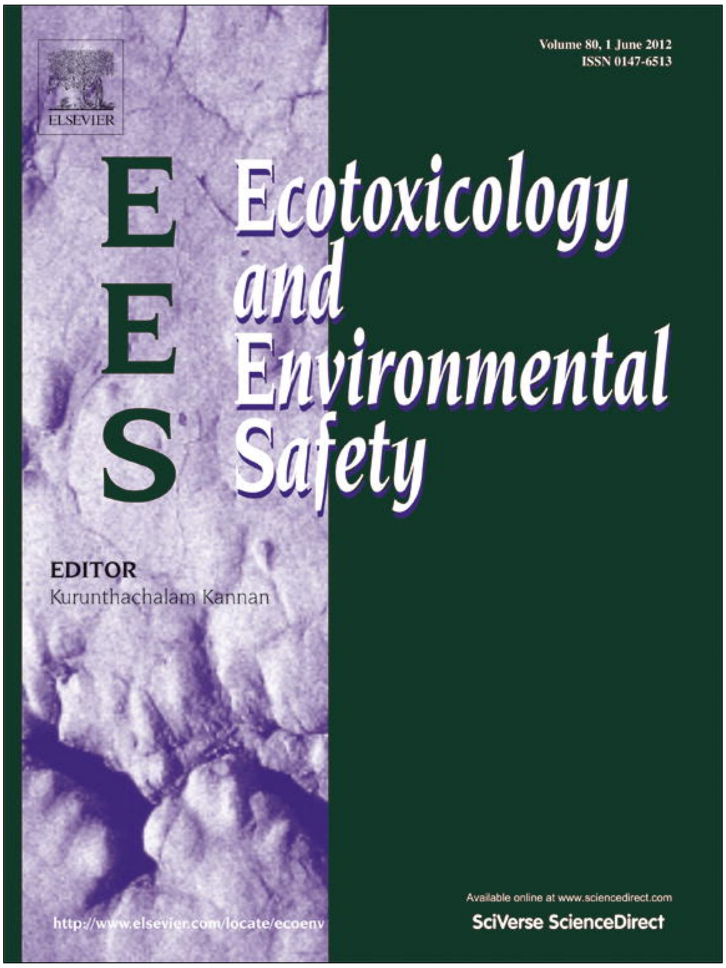
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Influence of activated carbon and biochar on phytotoxicity of air-dried sewage sludges to *Lepidium sativum*

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ABSTRACT

The goal of the research was to determine the phytotoxicity (using *Lepidium sativum*) of two activated carbon/biochar-amended sewage sludges. Apart from the impact of the AC/biochar dose, the influence of biochar particle diameter (<300, 300–500 and >500 μm) and the influence of the contact time (7, 60, 90 days) between AC/biochar and sewage sludges on their phytotoxicity was also assessed. No negative impact of sewage sludges on seed germination was observed ($P>0.05$). The application of AC or biochar to the sludges positively affected root growth by reducing the harmful effect by 7.8 to 42% depending on the material used. Furthermore, the reduction range clearly depended on the type of sewage sludge. No differences were observed in the inhibition of the toxic effect between both biochar types used and the biochar particle size. The extension of the contact time between AC/biochar and sewage sludges had a negative impact on root growth.

1. Introduction

Using materials characterised by a high sorption affinity is becoming a common method for the reclamation of soils and sediments contaminated by organic compounds (Beesley et al., 2011). The adsorption of contaminants by the adsorbent reduces their mobility, leading to lower bioaccessibility and toxicity (Ghosh et al., 2011; Kupryianchyk et al., (in press); Vasilyeva et al., 2010). Of various materials used for this purpose, the most popular are activated carbon (AC) (Fagervold et al., 2010; Millward et al., 2005; Tomaszewski and Luthy, 2008), and recently also biochar (Cao et al., 2011; Fellet et al., 2011). Luthy et al. (McLeod et al., 2004; Millward et al., 2005; Zimmerman et al., 2004), regarded as the pioneers of the application of AC for sediment remediation, demonstrated that the amendment of harbour sediment contaminated by PAHs and PCBs with 3.4 wt% of AC led to reductions of about 1 order of magnitude in aqueous concentrations, uptake by semipermeable membrane devices, fluxes to overlying water (Zimmerman et al., 2004), and bioaccumulation by polychaetes, amphipods (Millward et al., 2005), and clams (McLeod et al., 2004). A less expensive alternative to AC is biochar obtained from the pyrolysis of plant material, waste, etc. Biochar tends to have a lower specific surface area (Ghosh et al., 2011; Lehmann and Joseph, 2009) than AC, which is why its contaminant sorption ability is lower than in the case of AC. However, biochar may have several additional advantages, owing to which it is worth considering as a substitute for AC. Additional advantages of biochar may arise when (Lehmann and Joseph, 2009): (1) biochar reduces the need for fertilizer, resulting in reduced emissions from fertilizer production and reduced nutrient runoff, (2) biochar decomposes more slowly than uncharred biomass, resulting in more carbon storage in soil, (3) biochar reduces emissions of nitrous oxide (a potent greenhouse gas), (4) turning agricultural waste into biochar reduces methane (another potent greenhouse gas) generated by the natural decomposition of the waste in landfills.

Biochar/AC's proven capability to reduce the bioaccessibility of contaminants, combined with the above advantages, allow the use of these materials for other environmental matrices than contaminated soils and sediments. Another interesting solution is to use AC/biochar as materials improving the properties of sewage sludges by limiting the bioaccessibility of contaminants contained in them, and thereby limiting their toxicity. Our most recent research (Oleszczuk et al., 2012) indicated that the application of AC/biochar as an additive to sewage sludge causes a significant (50–98%) reduction of pore-water polycyclic aromatic hydrocarbon (PAHs) concentration. However, there is little research on the influence of AC/biochar on the toxicity of reclaimed soils, sediments, and recently, sewage sludges (Beesley

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et al., 2011; Jonker et al., 2009; Kupryianchyk et al., in press; Vasilyeva et al., 2010). Recent publications concern pore water concentrations and invertebrates, but provide no data on plants. In the case of sewage sludges, determining the phytotoxicity is particularly important due to the potential application of these materials to agricultural soil. Furthermore, the ecotoxicological assessment of the reclamation method using AC/biochar becomes especially significant. It is significant in the case of sewage sludges, which may contain a number of unidentified, and potentially toxic, contaminants.

The aim of the present research was to determine the phytotoxicity of sewage sludges from municipal sewage treatment plants, stabilised with biochar or AC. The research also assessed the influence of biochar/AC application rate, the type of biochar, the biochar particle diameter, and the contact time on germination and root growth inhibition.

2. Materials and methods

2.1. Sewage sludges, activated carbons and biochars

Two municipal sewage sludges from two cities (Dęblin—SL1 and Radom—SL2, south-eastern part of Poland) were collected at the end-point after the sewage sludge digestion process. Sewage treatment plants treat about 2700 (SL1) and 4000 (SL2) m^3/d of domestic wastewater. The collected samples were stored in glass bottles and immediately transported to the laboratory. All sewage sludge samples were air-dried and crushed to obtain representative samples. Sewage sludges were crushed in a mortar and then sieved through a 2 mm sieve for chemical and ecotoxicological analysis.

Two different biochars called CS and MS were used in the present research. Maize stover biochar (CS) was produced from corn stover residues *Zea mays* L. at 600 °C using a slow pyrolysis (Pyrochar 300; Best Energies, Australia) method in a continuous unit with a residence time of 30 min. MS was produced from straw via a slow pyrolysis without a catalyst on a fluidised bed (700 °C). Activated carbon (AC) from Jacobi Carbon (CP1 quality) was fine powder with 80% smaller than 45 μm and an average particle size of 20 μm. AC was obtained from a coconut shell-based material.

2.2. Preparation of the materials

Dried sewage sludges were spiked with AC or biochar at a dose of 0.5%, 2%, 5% and 10% (w/w). The sewage sludge (about 6 g) and AC/biochar (depending on the dose used) were thoroughly mixed with a glass spatula and rolled end over end (REAX 20, Carl Roth GmbH, Germany) for 30 days (in the dark). To determine the phytotoxicity, the obtained sewage sludge-AC/biochar mixture was added to artificial soil prepared according to OECD guidelines (OECD, 1984) at the dose of 5%. OECD soil properties are specified in Table 1.

In the experiment involving the influence of the particle diameter of biochar on *L. sativum* phytotoxicity, biochar CS was sieved with a diameter of <300 μm, 300–500 μm and >500 μm. Then the separated material was mixed with sewage sludge (at the dose of 5%) according to the procedure described above. In the aging experiment the sewage sludges were mixed with AC or biochars (as described above) at the dose of 5% and rolled end over end in the dark for 7, 30 and 60 days.

2.3. Phytotoxicity test

Sewage sludge toxicity was assessed with the commercial toxicity bioassay–Phytotoxkit^{TM} Test (Microbiotests, Nazareth, Belgium) (Phytotoxkit, 2004). In the experiment *Lepidium sativum* (cress) was chosen because of its high sensitivity to sewage sludges (Oleszczuk, 2010). The phytotoxkit measures the decrease (or the absence) of seed germination and of the growth of the young roots after 3 days of exposure of seeds of selected higher plants to contaminated matrix in comparison to the controls in a reference soil. Water saturation is calculated according to the user's manual. The distilled water was spread over the entire surface of the soil in the test plate. Ten seeds of *L. sativum* were positioned at equal distance near the middle ridge of the test plate on a filter paper placed on top of the hydrated soil/sewage sludge/biochar mixture. After closing, the test plates were placed vertically in a holder and incubated at 25 C for (instead of by) 3 days. At the end of the incubation period a digital picture was taken of the test plates with the germinated plants. The analyses and the length measurements were performed using the Image Tool 3.0 for Windows (UTHSCSA, San Antonio, USA). The bioassays were performed in three replicates. The per cent inhibition of seed germination (SG) and root growth inhibition (RI) were calculated with the formula:

$$SG/RI = (A - B/A) \times 100$$

where A means seed germination and root length in the control; B means seed germination and root length in the test.

Table 1
Physico-chemical properties of sewage sludges and OECD soil used in the experiment.

Properties	SL1	SL2	OECD
Clay	–	–	19
Silt	–	–	31
Sand	–	–	50
pH	6.8 ± 0.1	6.8 ± 0.1	6.0 ± 0.1
TOC	207.6 ± 4.7	184.2 ± 3.2	4.0 ± 0.4
N	40.6 ± 3.3	39.2 ± 2.1	0.01 ± 0.01
CEC	398.0 ± 10.7	446.0 ± 14.9	0.7 ± 0.1
K_{av}	3.8 ± 0.7	5.6 ± 0.9	–
P_{av}	31.5 ± 2.1	25.8 ± 1.7	–
EC	5.1 ± 0.1	5.2 ± 0.2	–
Pb	18.5 ± 2.7	16.4 ± 1.9	–
Cd	2.3 ± 0.3	1.8 ± 0.1	–
Cr	40.0 ± 1.8	80.0 ± 3.3	–
Cu	94.1 ± 5.5	88.2 ± 4.8	–
Ni	20.2 ± 2.3	55.5 ± 3.9	–
Zn	1620 ± 33	1100 ± 27	–
16 PAHs	6.32 ± 1.2	9.81 ± 2.1	n.d.

pH = reactivity in KCl, CEC = cation exchange capacity (mmol/kg), TEB = the total of the exchangeable bases (mmol/kg), K_{av} and P_{av} = available potassium and phosphorus (mg/kg), TOC = total organic carbon content (g/kg), N = total nitrogen content (g/kg).

2.4. Chemical analysis

The pH was measured potentiometrically in 1 M KCl after 24 h in the liquid/soil ratio of 10 w/v, the cation exchange capacity (CEC) were determined in the 0.1 N HCl extract (Misztal et al., 1997). The total nitrogen (N_t) was determined by the Kjeldahl's method (van Reeuwijk, 1995) without the application of Dewarda's alloy (Cu–Al–Zn alloy-reducer of nitrites and nitrates). Available potassium and phosphorus were determined according to the method of Egner as cited in Misztal et al. (1997). Total forms of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were determined by Pallman methods in 1 N NH_4Cl (Misztal et al., 1997). To determine heavy metal content sewage sludge samples were mineralised in a PROLABO microwave oven (Microdigest 3.6, France) using a wet method. This method uses a mixture of nitric acid and perchloric acid at the ratio of 1:1. Details of the mineralisation are described in Baran et al. (2000). The total contents of Cd, Cr, Cu, Pb, Ni and Zn were performed using emission spectrometry of the Leeman Labs (PS 950) apparatus with Inductively Coupled Plasma (ICP) induction in argon. For PAHs analysis samples (15 g) were extracted in an ultrasonic bath (Sonic-3, Polsonic, Poland). The extracts were centrifuged, decanted, and evaporated to dryness. The residues were then purified by solid phase extraction (Oleszczuk and Baran, 2004). A qualitative and quantitative analysis of PAHs was performed on the liquid chromatograph with UV detection (TermoSeparation Products). For PAHs separation an analytical Spherisorb S5 PAH (250 3 4.6 mm I.D., 5 lg by Schambeck SFD GmbH, Germany) column was used. Data acquisition and analysis was performed using the Clarity Lite Chromatographic Station (DataApex, Czech Republic).

The elemental C, N and O contents were determined through catalytic combustion elemental analysis at 1030 °C (Carlo Erba model 1106, Italy). Prior to analysis, samples were dried at 110 °C over night and ground to a fine powder. Duplicate samples (2–10 mg) were weighed into silver capsules, treated with 60 μL 1 M hydrochloric acid to remove inorganic carbonates and dried at 60 °C overnight before analysis. The elemental H content was determined at the University of Life Sciences, Ås, Norway, using a Leco CHN 1000 and analysing for H_2O using an infrared method.

The microporous surface area (SA) was determined using a Quantachrome Autosorb I with CO_2 as the probe gas according to Zimmerman (2010). This method determines the specific SA of pores with diameters as small as 0.2 nm. Approximately 100 mg of AC for N_2-BET analysis were weighed in and pretreated for 3 h at 300 °C under vacuum. AC is expected to be stable at those temperatures since it has been charred at higher temperatures. The measurements with N_2 at 77 K were performed using a Quantachrome Autosorb-3.

2.5. Data analysis

The effects of each sludge type on seed germination (SG) and root growth inhibition (RI) were analysed using the Statistica 5.0. One-way ANOVA was performed to compare the means of different treatments; when significant F values were obtained, differences between individual means and control mean were tested using the Dunnett test. Sewage sludge concentrations responsible for 50% inhibition of root growth (EC50) were calculated on the basis of the linear regression best fitting models.

3. Results

3.1. Physico-chemical characteristics of sewage sludges

The basic physico-chemical properties of the sewage sludges used in the experiment are presented in Table 1. Both sewage sludges were characterised by a neutral pH (6.8) and electrical conductivity at the level of 5.1 mS/cm. A similar level of total nitrogen (40 g/kg) was observed in both sewage sludges. The content of total organic carbon and available phosphorus in sewage sludge SL1 was higher than in SL2, by 11% and 18%. However, sewage sludge SL2 was characterised by 47% higher concentration of available potassium, and by 12% higher CEC values compared to sewage sludge SL1.

The heavy metal concentration differed depending on the sewage sludge (Table 1). Only in the case of Cu and Pb no significant differences were observed between the sludges. In SL1 sludge a higher content of Cd (by 21%) and Zn (by 32%) was noted, whilst SL2 had a higher content of Cr (by 100%) and Ni (by 175%). European Union standards were not exceeded for any contaminant (Communities, 1986). This indicates that sewage sludges used in the experiment can be applied in agriculture and for the purpose of soil re-cultivation for agricultural purposes. The content of total polycyclic aromatic hydrocarbons (PAH) in the sludges under research equalled 6.32 mg/kg (SL1) and 9.81 mg/kg (SL2). In both sewage sludges 3- and 4-rings PAH predominated, constituting 36% and 44% in SL1 sludge and 47% and 39% in SL 2 sludge, respectively (data not presented).

3.2. Biochars and activated carbon characteristics

The elemental composition and chemical properties of biochars and AC used in the experiment are listed in Table 2. Both biochars were of a highly alkaline. The carbon content of MS was about 30% higher than that of CS biochar. MS was also characterised by a higher contribution of H and N and lower contribution of O compared to CS. Molar ratios of elements were determined to estimate the aromaticy (H/C ratio) and polarity (O/C ratio) of biochars (Table 2). Both CS and MS biochars were characterised by a very low H/C ratio indicating a high level of carbonization and aromatisation of these material, although their low SA indicate a moderate degree of carbonization (Chen et al., 2008). The O/C ratios of 0.194 for CS and 0.114 for MS indicate CS biochar has more surface polar functional groups than MS biochar (Chen et al., 2008). The CS biochar had a 37% greater specific surface area than CS and almost twice as high cation exchange capacity (Table 2). The AC was observed to have higher C contents (91.8%) than the biochars (41.6 and 53.8%). AC, compared to biochars, had a lower share of H and N. The BET-surface areas of the biochars were much smaller than that of the AC (Table 2).

Table 2
Elemental composition and selected physico-chemical properties of activated carbon and biochars used in the experiment.

Carbon materials	Elemental composition (%)						pHKCl	CEC (mmol/kg)	SA (BET) (m^2/g)
	C	H	N	O	H/C	O/C			
AC	91.78	0.70	0.40	7.09	0.008	0.077	9.6	9.0	1158
CS	41.57	1.50	0.42	8.05	0.036	0.194	8.7	384.0	6.3
MS	53.85	2.00	0.92	6.14	0.037	0.114	9.9	641.2	8.6

Table 3
Phytotoxicity of activated carbon (AC), biochars (CS, MS) and sewage sludges (SL1, SL2) used in the experiment, all mixed into OECD soil at the indicated percentages.

Materials	Inhibiton of seed germination [%]			Root growth inhibition (%)		
	1	5	10	1	5	10
SL1	0	0	0	43.4 ± 5.3	76.9 ± 8.2	98.0 ± 11.3
SL2	0	0	0	39.1 ± 3.4	68.6 ± 4.8	82.7 ± 9.9
AC	10.0 ± 1.0	10.0 ± 0.9	0	13.3 ± 1.4	8.4 ± 0.8	4.0 ± 0.3
CS	0	0	0	9.2 ± 0.7	-4.3 ± 0.3	-9.0 ± 0.1
MS	0	0	0	-0.1 ± 0.01	37.2 ± 3.7	n.d.

Negative values means positive effect of analysed materials on seed germination or root growth.

3.3. Influence of sewage sludges, biochars and activated carbon on root growth of *L. sativum*

Both sewage sludges were toxic to *L. sativum*. Despite the fact that no significant impact on plant germination was observed; the inhibition of root growth was already present at the lowest dose and reached the levels of 43.4 and 39.1% respectively for SL1 and SL2. Increasing the dose of sewage sludge resulted in an immediate increase in the negative influence on *L. sativum*, reaching at the highest dose the level of 98.0% (SL1) and 82.7% (SL2) (Table 3). The EC50 values were 1.6% (SL1) and 2.7% (SL2) respectively. This indicates the significantly higher toxicity of SL1 compared to SL2.

The toxicity assessment of the AC/biochar indicates a positive or neutral influence of AC and CS (Table 3). The lowest applied doses of AC (1 and 5%) resulted in a slight inhibition of *L. sativum* germination. AC applied in the highest dose did not significantly affect germination. Root-growth inhibition ranged from 4.0 to 13.3%, reaching maximum values with the lowest AC dose (Table 3). Increasing AC dosage significantly reduced its negative impact on *L. sativum*. A similar relationship was observed with CS, while applying this biochar in the dose of 5 and 10% significantly augmented root growth in relation to the control OECD soil, evidently showing the positive impact of this material on plant growth. However, the impact of MS on *L. sativum* was different from that of AC and CS. The positive influence of the lowest dosage of MS was minimal (0.1%, statistically insignificant, $P \geq 0.05$). However, the application of this material in a 5% dose considerably reduced root-growth inhibition ($37.3\% \pm 3.7$). Unfortunately, due to the low density of MS (0.16 Mg/m^3), it was not possible to carry out the experiment with 10% dose of biochar. No negative influence on *L. sativum* germination was observed, either in the case of CS or MS.

3.4. Effect of activated carbon on the sewage sludge phytotoxicity

For sewage sludge, as well as for AC/biochar-amended sewage sludge, no inhibition of germination was noted (all seeds germinated). For this reason, this paper will focus on root-growth inhibition. Fig. 1 shows the influence of the application of AC to sewage sludge on the root-growth inhibition of *L. sativum*. In the case of both sewage sludges tested a significant decrease was observed in root growth-inhibition in comparison to non-amended sewage sludge. The reduction in the toxicity of sewage sludges after amending them with AC was more apparent in the case of SL2 than SL1. Adding AC in a dose of 1% to sewage sludges caused a increase in root-growth by 20 and 25% respectively in SL1 and SL2. Increasing AC dosage to 5% had a further positive impact on *L. sativum* root growth with both sludges. However, a stronger effect on phytotoxicity reduction was observed for SL2 sludge than for SL1. In this case the reduction of the negative impact of sewage sludge on *L. sativum* was lower by 33% (SL1) and

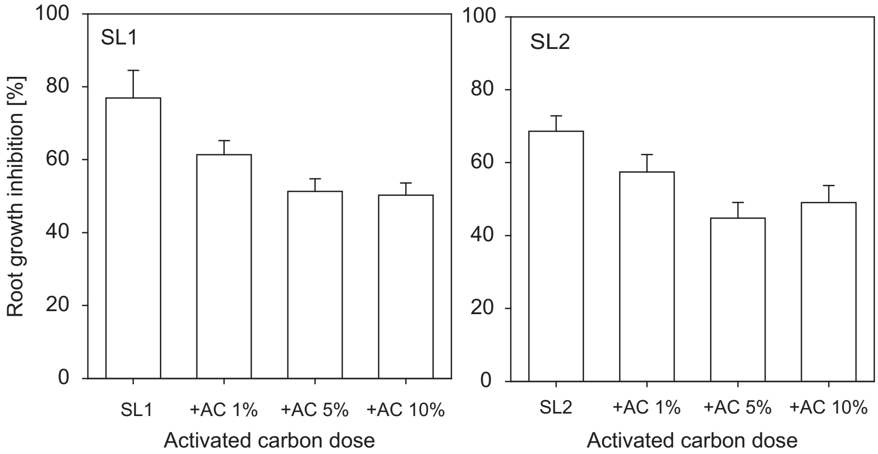

Fig. 1. Effect of activated carbon (AC) dose on root growth inhibition of *L. sativum* in sewage sludges amended to OECD soil at a level of 5%.

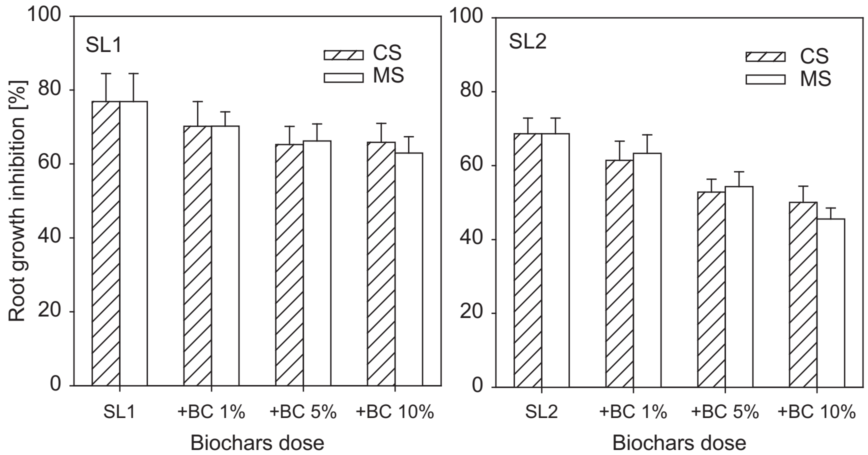

Fig. 2. Influence of biochar dose on root growth inhibition of *L. sativum* in sewage sludges amended to OECD soil at a level of 5%.

42% (SL2) compared to the sludge containing no AC. No significant differences were observed in both sludges between the application of 5 and 10% AC dose (Fig. 1).

3.5. Effect of biochar on the phytotoxicity

The influence of biochar on phytotoxicity towards *L. sativum* varied, depending on the type of sewage sludge (Fig. 2). Similarly to AC, the influence of biochar was more visible in the case of SL2 than SL1. However, no significant differences in phytotoxicity reduction were observed depending on the biochar used. Root-growth inhibition in sewage sludges containing the lowest dose of biochar compared to the sludges with no biochar was lower by 7.8 to 10.5%, depending on the sludge. No significant differences were observed between the respective sludges and biochars used in the experiment. There was also no considerable difference between these values and the values observed for sewage sludge without the application of the materials under study. Increasing biochar application rates significantly decreased the toxicity effect of sludges. However, no significant ($P \leq 0.05$) change was observed between 5 and 10% of biochar dose for SL1 sludge in the case of CS (Fig. 2).

3.6. Effect of biochar outer diameter

Fig. 3 presents the influence of biochar with different particle diameters on the phytotoxicity of the sewage sludges. The inhibition of *L. sativum* root growth in SL1 sludge amended with different fractions of biochar ranged from 65.0 to 67.8%, and in SL2 sludge from 50.0 to 55.5%. There was no substantial difference between these values and the values obtained for undivided biochar (Fig. 3). Similarly to the previous observations, a higher toxicity reduction was obtained for SL2 sludge than for SL1.

3.7. Aging time

The contact time between sewage sludge and AC/biochar had a significant effect both for AC and biochars. However, major differences were observed depending on the material used. Extending the contact time between AC and MS and sewage sludge significantly reduced their positive effect on sewage sludge phytotoxicity. After 30 days of contact between sewage sludge and AC, an over 76% increase in toxic effect was observed compared to a 7-day period. Extending the duration of the contact between these materials to 60 days resulted in the further reduction of AC effectiveness. The root-growth inhibition rate in sewage sludge that was reached 60 days after the AC application was only slightly (however statistically significant, $P \leq 0.05$) lower than the one observed for unamended sewage sludge (Fig. 4). A similar tendency was observed for MS, with root-growth inhibition for this biochar reaching the level of sludge unamended with AC/biochar, 30 days after the application. After 60 days of contact with MS, sewage sludge did not differ significantly ($P \leq 0.05$) from the values obtained after a 30-day period. The only exception concerned CS, for which after a 30-day

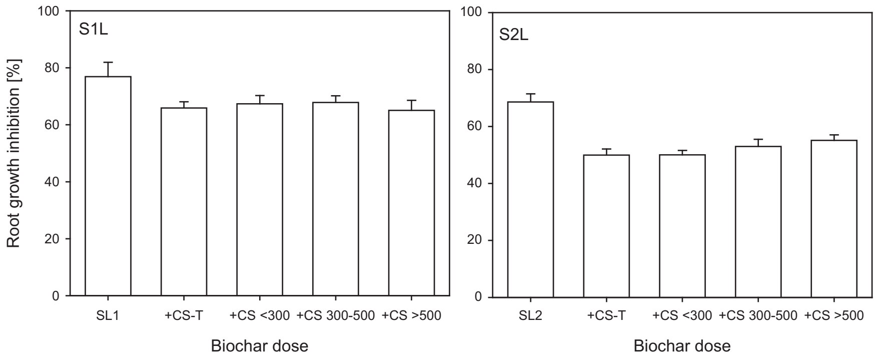

Fig. 3. Effect of biochar particle diameter on root growth inhibition of *L. sativum* in sewage sludge amended to OECD soil at a level of 5%. CS-T—nonsieved biochar CS.

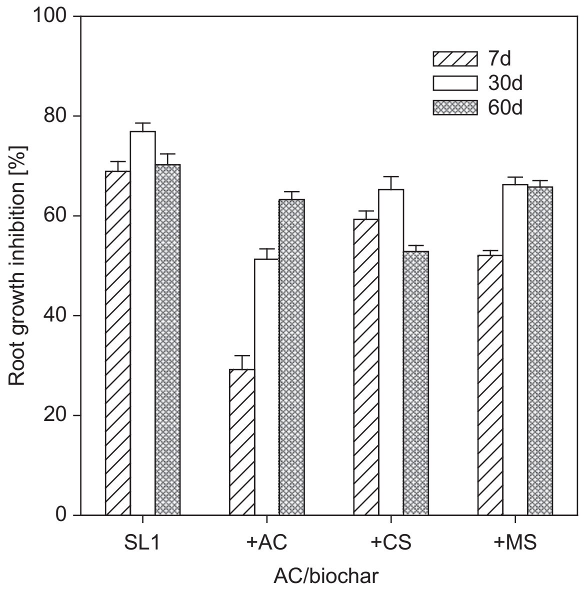

Fig. 4. Root growth inhibition of *L. sativum* in AC/biochar-amended sewage sludge depending on the contact time.

period a slight increase in root growth inhibition was observed, together with a significant reduction in toxic effect (by 11%) compared to a 7-day period.

4. Discussion

The reduction in phytotoxicity after the application of biochar/AC observed in this research is probably explained by (1) binding contaminants by the added adsorbent, and (2) the positive influence of these materials (especially biochar) on the properties of the sewage sludges/OECD soil mixture. In the present research AC showed a stronger reduction of growth inhibition by sewage sludge than biochar. This indicates that the first mechanism is more important than the second one: AC is more effective than BC in reducing contaminant availability (Oleszczuk et al., submitted) whereas BC is more effective in stimulating growth (Glaser et al., 2002; Lehmann and Joseph, 2009). The extent of toxic-effect reduction depended on the type of sewage sludge. A stronger impact of AC/biochar was observed for SL2 than SL1 (Figs. 1 and 2). It may be assumed that the contaminants present in SL2 had a stronger influence on its toxicity, which explains the phytotoxicity reduction being higher in SL2 than in SL1. The higher PAHs content in SL2 sludge than in sewage sludge SL1 (Table 1) may be the cause for this. The higher PAHs content in SL2 sludge may also suggest a higher content of other anthropogenic contaminants compared to SL1, which could affect the phytotoxicity of the sewage sludge.

Increasing the AC/biochar dosage caused a gradual reduction in the toxic effect (Figs. 1 and 2). This was not observed in the full range of the applied doses in the case of AC. The application of AC at the dose of 10% did not cause any significant changes in phytotoxicity compared to 5% AC dose. In the case of biochar, as opposed to AC, increasing the dosage resulted in reducing phytotoxicity in the full range of applied doses (Fig. 2). As mentioned above biochar was characterised by a lower specific surface area than AC (Table 2). Due to the relatively low surface area, this requires applying biochar in higher quantities than AC in order to achieve a comparable effect.

None of the cases, however, indicated a reduction in toxic effect down to the level observed in control soil (OECD) (Figs. 1 and 2). Assuming that AC/biochar removes most of the toxic chemicals from the pore-water, one should assume that the toxic effect connected with these contaminants constitutes only about 15–20% of the total toxicity caused by sewage sludge (the difference between the phytotoxicity of sludge not containing and containing AC/biochar). The remaining phytotoxic effect is most probably connected with contaminants not bound by AC and biochar such as some heavy metals such as Cd and Ni and/or other factors unrelated to the presence of contaminants, e.g. electrical conductivity (Table 1). Electrical conductivity in both sludges exceeded 3 mS/cm^{-1}, above which plant growth and development may be inhibited (Wang et al., 2002).

The second factor potentially contributing to the observed reduction of sewage sludge phytotoxicity following the application of AC/biochar, may be the fertilising properties of these materials, especially biochar. The application of biochar to soils can increase their pH as well as their cation exchange capacity (Beesley et al., 2011) which can increase seed germination, plant growth and crop yields (Glaser et al., 2002). The data presented in Table 4, concerning pH and CEC change after the application of a 10% AC/biochar dose to sewage sludge, indicate that the change in these properties, depending on the type of sludge and AC/biochar, ranged from 1.5 to 8% for CEC and from 2.9 to 5.9% for pH. Novak et al. (2009) reported a decrease in Zn concentrations in leachate after 2% pecan-shell biochar addition to an acidic agricultural soil, possibly related to an increase in pH. Fellet et al. (2011) amended mine tailings with 0–10% orchard prune derived biochar, finding that, as well as increasing pH and CEC, biochar reduced bioavailable concentrations of Cd, Pb and Zn. Fellet et al. (2011) showed that the pH change by 0.5 of a unit (similar to the one observed in this research) resulted in a significant reduction in bioavailable Pb, by about 20%. However, it is not to assume that applying AC/biochar in the amount used in this research and the observed change has such considerable influence on the improvement of

Table 4
Changes of pH (in KCl) and CEC (mmol/kg) after sewage sludge-amendment with AC or biochar at the dose of 10%.

Mixture	CEC	pH
SL1	398	6.8
SL1+CS	404	7.1
SL1+MS	430	7.2
SL1+AC	390	6.9
SL2	446	6.8
SL2+CS	454	7.0
SL2+MS	462	7.0
SL2+AC	458	6.9

sludge properties and the reduction in its phytotoxicity. The observed reduction in sewage sludge phytotoxicity on applying AC/biochar is probably a product of many processes, among which the immobilisation of contaminants plays a major role, whether by surface sorption or a change in matrix properties (e.g. pH), which consequently reduce their mobility.

A surprising phenomenon is the reduction in the positive impact of AC/MS resulting from extending the duration of contact between these materials and sewage sludges. On one hand, the increase in phytotoxicity over time may be related to the changes that occur within sewage sludges. The mineralisation of organic matter may result in the release of strongly-bound contaminants (Oleszczuk, 2009), which are not bound quickly enough by the added adsorbent. On the other hand, numerous works have proven (Glaser et al., 2002) that biochar, and probably AC as well, can bind nutrients present in soil, limiting their accessibility for plants, which considerably inhibits plant growth and development. Another explanation of the increasing of phytotoxicity with time is the effect of both AC and biochars on pH and indirectly on heavy metal availability. Over time, the AC and biochar will be oxidised, the bases neutralised and the sludge adds more acid functional groups and CO_2 through decomposition, all leading to pH drops. Thus a question arises: why there was no similar phenomenon observed in the case of CS? At the current stage of research we cannot yet explain this discrepancy.

5. Conclusion

Applying AC and biochar reduces the phytotoxicity of sewage sludges. Better effects were achieved for AC than for biochar. The positive impact of AC and biochar was particularly apparent during the first day after the application of the adsorbents. However, as time progressed, the effectiveness of this method significantly decreased, reaching after 60 days of contact in some cases the level of phytotoxicity comparable to that of the sewage sludge not containing AC/biochar. Despite these disadvantages, the application of AC/biochar as an additive to sewage sludge in order to reduce its toxicity is a solution worth considering.

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