

Effect of biochars, activated carbon and multiwalled carbon nanotubes on phytotoxicity of sediment contaminated by inorganic and organic pollutants



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ABSTRACT

To reduce the risk related with the presence of contaminants in sediments, methods based on the use of adsorbents (mainly activated carbon) are applied. Adsorbents neutralise the contaminants by reducing their mobility, bioavailability and toxicity. The objective of this study was to determine the toxicity of sediment contaminated with organic compounds and heavy metals with and without the addition of selected adsorbents. In the study three carbonaceous materials (CM) potentially useful in remediation were applied: activated carbon (AC), biochars (BC1, BC2), and multi-walled carbon nanotubes (CNTs). The effect of the dose, particle diameter and time of contact between sediment and CM on the effectiveness of the detoxification were estimated. Ecotoxicological assessment was made based on the Phytotoxkit F™ test, using *Lepidium sativum* as the test plant. The materials tested reduced the negative effect of sediment on *L. sativum*. The highest effectiveness was achieved after the application of AC (70% reduction of seed germination inhibition, 27.5% reduction of root growth inhibition). The reduction of phytotoxicity of the sediment as a result of addition of BC1, BC2 and CNT varied within the range from 30 to 40% (reduction of seed germination inhibition) and from 17.7 to 28.9% (reduction of root growth inhibition). The reduction of sediment toxicity decreased with decreasing diameter of the biochars applied. Probably because of increasing fouling extension of the time of contact between CM and sediment had an unfavourable effect on the reduction of root growth inhibition in the case of all materials tested.

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1. Introduction

To reduce the risk related with the presence of contaminants in sediments, actions are undertaken with the aims of elimination or minimisation of the toxicity of contaminants occurring in sediments.

In view of the expense related with the measures commonly applied (e.g. dredging), the aim of which is the removal of contaminants, there appears the need for a search for more cost-effective solutions (Ghosh et al., 2011). The application of treatments aimed at reducing the bioavailability of contaminants can be considered

as one of such solutions (Hilber and Bucheli, 2010; Rakowska et al., 2012; Tang et al., 2007). In this method various carbon-based adsorbents have been used. Adsorbents most frequently used for this purpose include activated carbon (AC). Among other materials that could find a potential application in remediation of sediments, biochars (BC) (Cao et al., 2011) have attracted an increasing interest in recent years. Research shows that BC can be successfully applied in soil for the purpose of its detoxification as well as because of N and P content biochars may play the role of a fertiliser (Park et al., 2011). An additional advantage of BC is low production cost and diversity of biomass from which they can be produced (Beesley et al., 2011). Therefore BC, next to AC, may also constitute a promising solution in the remediation of sediments (Major et al., 2010; Park et al., 2011; Ren et al., 2011). Another advantage of BC is its ability of CO₂ sequestration in soil

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(Sohi, 2012). The last of the materials tested that can find potential application in remediation is CNTs. In spite of the favourable properties of those materials for the sorption of contaminants (Yang and Xing, 2010), so far CNTs have not found any more extensive application. The low interest in this respect may result from the still high cost of those materials, and from the still insufficient level of knowledge on their eco-toxicological properties. Studies on the utilisation of CNTs should be conducted, as their production costs go down, which may result in their more common application in environmental protection (Shan et al., 2009).

In spite of the abundance of information on the reduction of bioavailability of contaminants by carbonaceous materials (CM), this is not always converted into a positive biological response (Rakowska et al., 2012). Therefore, biological tests should be an inseparable element in the estimation of applicability of CM for the detoxification of sediments. Kupryianchuk et al. (2011) observed an increase in the survival rate of *Gammarus pulex* and *Asseles aquaticus* after the application of AC to sediments contaminated with PAHs. Other studies carried out with clean sediments, on the other hand, indicate a negative response of organisms to the application of CM. In an earlier study (Cornelissen et al., 2011), a toxic effect of AC on the richness and abundance of benthic fauna was observed. Also Jonker et al. (2009) found a reduction of lipid content in *Lumbriculus variegatus* in the presence of sediments containing AC. In contrast, there is less data available on the effect of BC on the toxicity of contaminated sediments (Shen et al., 2012). Studies by Lou et al. (2011) demonstrated an increase in the germination rate and root length of wheat subjected to the effect of extracts of pentachlorophenol-polluted sediment amended with rice-straw derived biochar. However, there is a lack of information on the effect of CNTs on the reduction of toxicity of sediments. In spite of the distinct advantages of those materials, resulting from their high affinity to contaminants, there is a lack of information on the possibilities of their utilisation in the process of remediation. Studies conducted so far show, however, that the presence of CNTs may cause a significant reduction of the bioavailability of organic contaminants (Xia et al., 2012), which potentially creates a possibility of their application in remediation.

Studies conducted so far on the eco-toxicological effects resulting from the application of CM in sediments did not involve plants as test organisms. Studies on the phytotoxicity of sediments constitute one of the significant elements of estimation of the toxicity of sediments. The use of phytotests follows from the sensitivity of plants to contaminants accumulated in sediments, thanks to which those tests permit the estimation of effectiveness of actions undertaken for the purpose of detoxification of contaminated sediments (Czerniawska-Kusza et al., 2006).

The objective of the study presented herein was the determination of the effect of various CM (AC, BC, CNTs) on the phytotoxicity of sediment contaminated with both inorganic (heavy metals) and organic compounds (PAHs, organotin compounds). The effect of CM dose, particle sizes and time of contact between CM and sediment on the inhibition of seed germination and root growth of *Lepidium sativum* was determined.

2. Methods and materials

2.1. Sediments, activated carbon, biochars and carbon nanotubes

Sediments from Bergen Harbour (Norway) were air-dried, and then sieved through a 1-mm sieve for chemical and ecotoxicological analysis. Six different carbonaceous materials were applied in presented study as follows: activated carbon (AC), biochar obtained from corn stover (BC1), biochar obtained from straw (BC2) and

three multiwalled carbon nanotubes with different outer diameter (<10 nm–CNT10, 20–40 nm–CNT40, >100 nm–CNT100). AC from Jacobi Carbon 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. BC1 (Musgrave experimental farm, Ithaca, NY, USA) was produced from corn stover residues *Zea mays* L. at 600 °C using a slow pyrolysis (Daisy Reactor, Best Energies, Inc., Cashton, WI, USA) method in a continuous unit with a residence time of 20 min. BC2 was produced from straw via a slow pyrolysis without a catalyst on a fluidised bed (700 °C). CNTs were purchased from Shenzhen Nanotech Co., China. The CNTs were synthesised by chemical vapor deposition from the CH₄/H₂ mixture at 700 °C using Ni as a catalyst. The synthesised CNTs were purified by mixed HNO₃ and H₂SO₄ solution for reducing the content of metal catalyst and amorphous carbon. The properties of CM are presented in Table 1.

2.2. Preparation of samples

The sediment caused total inhibition of seed germination and root growth of *L. sativum*. For the estimation of phytotoxicity by the Phytotoxkit FTM test, the sediment was mixed with a standard OECD soil (1984) at the dose of 10%, which reduced its toxicity – the inhibition of seed germination and root growth of *L. sativum* was 70 and 64%, respectively.

Fig. S1 (Supporting Information) presents a chart of the experiment. For the estimation of the materials with regard to the reduction of sediment toxicity, the sediment was mixed with CM (1–10%, details of the doses applied are presented below), and then added to OECD soil at the dose of 10%. Immediately after mixing, sediment in OECD soil was placed into Phytotoxkit FTM test plate.

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To determine the effect of CM dose on the level of toxicity of the sediment, the adsorbents (AC, BC1, BC2 and CNT40) were mixed with sediment at the dose of 1, 5 or 10% (w/w). Samples were mixed with a glass spatula and rolled end over end for 30 days in the dark. The sediment with CM was then mixed with soil OECD (30 min) and immediately afterwards analysed with the Phytotoxkit FTM test.

In the experiment involving the influence of the particle diameter of biochar on *L. sativum* phytotoxicity, BC1 was divided on three fractions regarding to diameter of <300 µm (BC300), 300–500 µm (BC300–500) and >500 µm (BC500). In the experiment with an effect of particle size of CNTs on the reduction of sediment phytotoxicity, CNTs with three different diameter were used: <10 nm (CNT10), 20–40 nm (CNT40) and 60–100 nm (CNT100). Then the materials (BC, CNTs) were mixed with sediment at the dose of 5% according to the procedure described above.

In the ageing experiment the sediment was mixed with AC, biochars and CNT40 (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

Sediments, CM and their mixtures toxicity was assessed with the commercial toxicity bioassay – PhytotoxkitTM test (Phytotoxkit, 2004). The phytotoxkit microbiotest measures the decrease (or the absence) of seed germination and of the growth of the young roots after 3 days of exposure of seeds to contaminated matrix in comparison to the controls in a reference soil. Ten plant seeds were positioned at equal distance near the middle ridge of the test plate on a filter paper placed on top of the hydrated soil. After closing the test plates were placed vertically in a holder and incubated at 25 °C for 3 days. At the end of the incubation period a digital picture

Table 1
Elemental composition and physico-chemical properties of carbonaceous materials (CM) used for sediment detoxication.

Carbon materials	Elemental composition (%)				H/C	O/C	pH	CEC (mmol/kg)	S _{BET} (m ² /g)
	C	H	N	O					
AC	91.78	0.70	0.40	7.09	0.008	0.077	9.6	9.0	1158
BC1	41.57	1.50	0.42	8.05	0.036	0.194	8.7	384.0	6.3
BC300	39.33	1.82	0.56	n.d.	0.046	–	8.6	n.d.	3.9
BC300-500	15.81	1.83	0.6	n.d.	0.116	–	8.5	n.d.	7.3
BC500	7.91	1.64	0.71	n.d.	0.207	–	8.6	n.d.	10
BC2	53.85	2.00	0.92	6.14	0.037	0.114	9.9	641.2	8.6
CNT10	96.41	0.42	–	0.20	0.004	0.002	n.d.	n.d.	357
CNT40	98.15	0.19	–	0.02	0.002	0.00002	n.d.	n.d.	86
CNT100	98.01	0.11	–	–	0.001	–	n.d.	n.d.	58

AC – activated carbon, BC1 and BC2 – biochars, CNT – multiwalled carbon nanotubes. BC300, BC300-500, BC500 – BC1 divided in three fractions with diameters of <300 μm, 300–500 μm and >500 μm, respectively. C, H, N, O – carbon, hydrogen, nitrogen and oxygen respectively, pH in KCl, CEC – cation exchange capacity, S_{BET} – surface area determined by BET method.

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 percent inhibition of seed germination (SG) and root growth inhibition (RI) were calculated with the formula:

$$SG \text{ or } RI = \left(\frac{A - B}{A} \right) \times 100$$

where, *A* – mean seed germination and root length in the control OECD soil; *B* – mean seed germination and root length in sediment or CM-amended sediment.

2.4. Chemical analysis

The chemical properties of sediments and CM studied were determined by standard methods. The pH was measured potentiometrically in 1 M KCl after 24 h in the liquid/soil ratio of 10. The cation exchange capacity (CEC) in ammonium acetate and available potassium, phosphorus and magnesium were determined according to procedures for soil analysis (van Reeuwijk, 2002). Total organic carbon (TOC) was determined by TOC-VCSH (SHIMADZU) with Solid Sample Module SSM-5000. The total nitrogen (Nt) was determined by the Kjeldahl's method (van Reeuwijk, 2002) without the application of Dewarda's alloy (Cu–Al–Zn alloy-reducer of nitrites and nitrates).

Native PAHs were exhaustively extracted from the wet sediments (*n* = 12) by heptane (40 ml)–acetone (10 ml) reflux (6 h) as described in Cornelissen and Gustafsson (2004). Heptane extracts were shaken overnight with activated Cu, passed through a silica column, and dried with Na₂SO₄. The quantification of 14 PAHs was done on a gas chromatograph coupled to a mass spectrometer (GC–MS; Agilent (Santa Clara, CA, USA) 6850 GC coupled to 5973 MS in electron impact mode).

Heavy metals were extracted by acid reflux extraction (1 M HCl) followed by quantification on ICP–MS.

The elemental C, N and O contents were determined through catalytic combustion elemental analysis at 1030 °C (Carlo Erba model 1106). 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 H₂O using an infrared method.

The microporous surface area (SA) was determined using a Quantachrome Autosorb I with CO₂ as the probe gas according. This method determines the specific SA of pores with diameters as

small as 0.2 nm. Approximately 100 mg of AC for N₂–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 N₂ at 77 K were performed using a Quantachrome Autosorb-3.

3. Results

3.1. Characteristics of the tested materials

The properties of the CM studied are presented in Table 1. The C contents in the adsorbents varied in relation to the material tested. The highest C content was characteristic of AC and CNTs (above 90%). The level of C in BC1 and BC2 was nearly half compared to the values observed for AC and CNTs. The CM differed from one another also in their contents of the remaining elements: H, N and O (Table 1). Molar ratios of elements were determined to estimate the aromaticity (H/C ratio) and polarity (O/C ratio) of CM (Table 1). Both BC1 and BC2 were characterised by a very low H/C ratio confirming a high level of carbonization and aromatisation of these materials (Chen et al., 2008). The O/C ratios of 0.194 for BC1 and 0.114 for BC2 indicate BC1 has more surface polar functional groups than BC2. The H/C ratio of AC and CNTs (0.007 and 0.001–0.004) was notably lower than in the case of BC, which indicates greater aromaticity of those materials relative to BC. AC and CNTs were also characterised by lower polarity compared to BC, which is evidenced by the low values of the O/C ratio (0.07 and below 0.002, respectively) (Chen et al., 2008). The degree of polarity of the CM was as follows: CNT100 < CNT40 < CNT10 < AC < BC2 < BC1, while that of aromaticity: BC2 < BC1 < AC < CNT10 < CNT40 < CNT10. The materials differed notably from one another also in terms of their surface area (S_{BET}). Among the CM under study, AC was characterised by the highest specific surface area (1158 m²/g). The CNTs had distinctly smaller specific surface area S_{BET} than that of the AC; in the case of CNTs, S_{BET} was negatively correlated with outer diameter and varied from 58 m²/g to 357 m²/g. The lowest values of S_{BET} were noted in relation to BC1 and BC2 (6.3 and 8.3 m²/g).

The pH of AC, BC1 and BC2 was alkaline and did not vary notably among them. Whereas, the materials displayed notable differences in the values of CEC. The highest CEC value was characteristic of BC2 (641 mmol/kg), that value being nearly twice as high as that for BC1 (384 mmol/kg) and over 70-fold greater than that for AC (9 mmol/kg).

3.2. Contaminants content in sediment

Table 2 presents the content of contaminants in the sediment studied. The total of sum of 16 PAHs was at the level of 17 mg/kg.

Table 2

Total contaminants content and standard deviation in triplicate in sediment used in the experiment.

Compound	Content
<i>Oils (mg/kg)</i>	
oil >C10–C12	54.3 ± 12.1
oil >C12–C16	276.7 ± 30.55
oil >C16–C35	4466.7 ± 404.15
<i>Polycyclic aromatic hydrocarbons (mg/kg)</i>	
Naphthalene	0.1 ± 0.03
Acenaphthalene	0.1 ± 0.02
Acenaphthene	0.2 ± 0.04
Fluorene	0.2 ± 0.04
Phenanthrene	1.4 ± 0.34
Anthracene	0.5 ± 0.12
Fluoranthene	2.3 ± 0.49
Pyrene	2.5 ± 0.55
Benzo[a]anthracene	1.4 ± 0.34
Chryzene	1.6 ± 0.4
Benzo[b]fluoranthene	1.6 ± 0.38
Benzo[k]fluoranthene	1.5 ± 0.32
Benzo[a]pyrene	2.0 ± 0.5
Dibenz[a,h]anthracene	0.3 ± 0.06
Benzo[ghi]perylene	1.2 ± 0.27
Indeno[1,2,3-cd]pyrene	1.2 ± 0.28
Sum PAH-16	17.7 ± 4.0
<i>Organotin compounds (µg/kg)</i>	
MBT	59.7 ± 14.19
DBT	220 ± 34.64
TBT	980 ± 280
TeBT	26.3 ± 9.5
<i>Heavy metals (mg/kg)</i>	
As	19.3 ± 0.58
Pb	526.7 ± 30.55
Cd	2.6 ± 0.12
Cu	403.3 ± 15.28
Cr	83.3 ± 3.21
Hg	9.5 ± 0.4
Ni	23.7 ± 1.15
Zn	973.3 ± 25.17

The highest concentrations in the sediment were characteristic of pyrene (2.5 mg/kg), fluoranthene (2.3 mg/kg) and benzo[a]pyrene (2 mg/kg). The contents of oils and organotin compounds were 4797.7 µg/kg and 1286 µg/kg, respectively. The highest concentration was recorded in the case of oil >C16–C35 (4466.7 mg/kg). Among the organotin compounds the highest content was observed for TBT whose concentration was at the level of 980 µg/kg. Among heavy metals, dominant in the sediment were Zn, Pb and Cu, the contents of which were 973.3, 526.7 and 403.3 mg/kg, respectively.

3.3. Effect of activated carbon, biochars and CNTs dose on the phytotoxicity

The degree of reduction of sediment toxicity after the application of the particular materials clearly depended on the CM dose applied and on the parameters tested (Fig. 1). In no case an increase in adsorbent dose was accompanied by a proportional increase in the reduction of toxicity. Only after the application of CNT40 a reverse relation was observed, where an increase in the dose of CNT40 resulted in a decrease of the effectiveness of toxicity reduction (Fig. 1D). The particular CM varied in their effectiveness of reduction of toxicity in relation to the doses applied. In the case of seed germination at the lowest dose (1%), the highest effectiveness was characteristic of CNT40 which reduced the inhibition of seed germination by 60%. AC and BC2 applied at the dose of 1% caused a reduction of the inhibition of germination by 30 and 40%, respectively. Relatively the weakest effect was obtained in the case of BC1, for which the reduction of toxicity was only 10%. Increase of the dose of CM added to the sediment at rates of 5 and 10% changed

the effectiveness of the particular materials. Application rates of AC at the level of 5% caused an elimination of sediment toxicity with regard to seed germination of *L. sativum* (Fig. 1A). The other materials caused a considerably smaller reduction of the negative effect of the sediment compared to AC. BC2 and CNT40 at the dose of 5% reduced the toxicity of the sediment by 20 and 40%, respectively, in relation to sediment with no content of adsorbents. Whereas, BC1 (5%) did not affect the degree of seed germination inhibition. The highest of the AC doses applied (10%) still had a positive effect on the reduction of sediment toxicity with relation to *L. sativum* (Fig. 1A), while the other CM (BC1, BC2, CNT40) applied at the dose of 10% reduced the toxicity at a similar level of 10%.

A notably lower variation among the particular materials was observed in the case of estimation of inhibition of root growth of *L. sativum*. In the case of this parameter, BC1, BC2 and CNT40 applied to the sediment at the dose of 1% caused a reduction of its toxicity at a fairly similar level, within the range from 9.7 to 15.8% (Fig. 1B–D). Whereas, AC applied at the dose of 1% did not cause any significant change in root growth of *L. sativum* (Fig. 1A). As in the case of seed germination, an increase of the dose of CM resulted in differences among the particular materials in the reduction of inhibition of root growth of *L. sativum*. The strongest reducing effect on root growth inhibition at the dose of 5% was noted for AC and BC2 (reduction of toxicity by 19.5 and 11%). In contrast, BC1 and CNT40 (at dose of 5%) reduced the toxicity of the sediment to a lesser degree than BC2 and AC (reduction of root growth inhibition by 6%). Decrease of toxicity at a similar level (15.2–19.4%) was observed after the application of AC, BC1, BC2 at the dose of 10%, while CNT40 applied at the dose of 10% did not cause any decrease in the level of toxicity of the sediment.

3.4. Effect of particle diameter on phytotoxicity

The particular fractions of BC1 had a varied effect on the reduction of toxicity of the sediment studied (Fig. 2). The BC1 fraction with the smallest diameter (BC300) had no significant effect on the reduction of inhibition of seed germination and root growth of *L. sativum* in relation to the sediment with no additives (Fig. 2). Fractions of BC1 with larger diameters, i.e. BC300–500 and BC500, significantly reduced the inhibition of seed germination of *L. sativum* in relation to the sediment with no adsorbents. The addition of fraction BC300–500 to the sediment caused total elimination of the toxic effect, while fraction BC500 reduced the toxic effect by 60%. The particle size of BC also had a significant effect on the inhibition of root growth of *L. sativum*. A distinct relationship was observed between the BC particle size and the inhibition of root growth of *L. sativum* (Fig. 2). In the case of the smallest fraction applied, BC1, no effect on root growth inhibition was observed in relation to the sediment with no content of that biochar. It was only BC1 fractions with diameters of BC300–500 and BC500 that significantly reduced the toxic effect of the sediment on *L. sativum*. However, the effect observed was not as remarkable as in the case of seed germination. Root growth inhibition was lower by 11.1 and 15.4% after the application of BC300–500 and BC500 than in the sediment with no additives (Fig. 2).

As in the case of BC1, also the diameter of CNTs played a significant role in the reduction of toxicity of sediment. A significant correlation was observed between the diameter of CNTs and seed inhibition (Fig. 3). The greatest reduction of the inhibition of both seed germination and root growth was noted in the case of CNT10, when reduction of the inhibition of seed germination at the level of 60% was observed in relation to the sediment with no additives. CNTs with larger diameters, i.e. CNT40 and CNT100, caused lesser reduction of seed germination inhibition, by 20 and 10%, respectively, compared to that observed for CNT10 (Fig. 3). What may

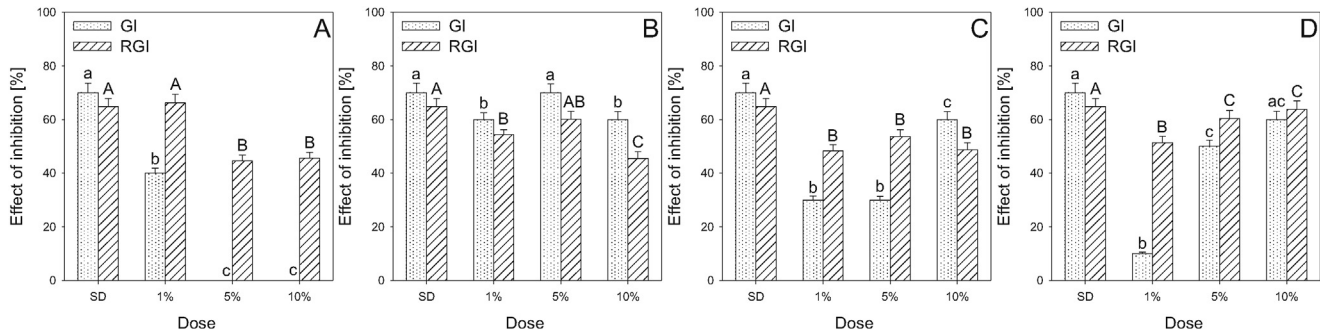


Fig. 1. Effect of dose of AC (A), BC1 (B), BC2 (C), CNT40 (D) on toxicity of sediments. SD – raw sediments, GI – growth inhibition, RGI – root growth inhibition. Different letters means statistically significant differences ($P \geq 0.05$) between bars.

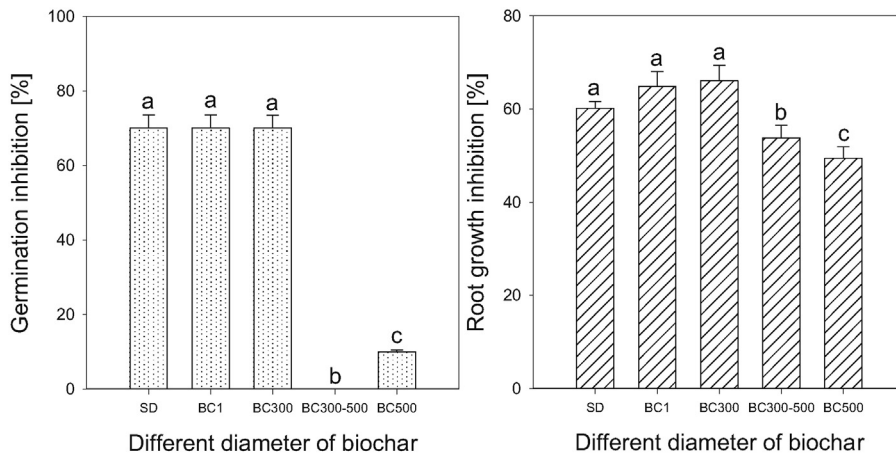


Fig. 2. Effect of biochar BC1 size on toxicity (seed germination and root growth inhibition of *L. sativum*) of raw sediment (SD) and sediment with biochars (BC1, BC1 < 300, BC1300-500, BC1 > 500). Different letters means statistically significant differences ($P \geq 0.05$) between bars.

be related with stronger fouling and pore blockage in CNT40 and CNT100 than in CNT10. In the case of inhibition of root growth of *L. sativum* no relationship was noted between CNT diameter and effect. The most significant reduction of root growth inhibition was observed for CNT10 and CNT100, at 24.3 and 17.8%, respectively. Whereas, the application of CNT40 had no significant effect on the growth of roots of *L. sativum* compared to sediment with no addition of CNTs.

3.5. Influence of the contact time between adsorbents and sediment on phytotoxicity

The contact time between CM and the sediment had a distinct effect on the range of effectiveness of the materials tested in terms of the reduction of toxicity of the sediment studied. The changes in the level of toxicity were varied (Fig. 4) and depended both on the kind of material applied and on the duration of the time

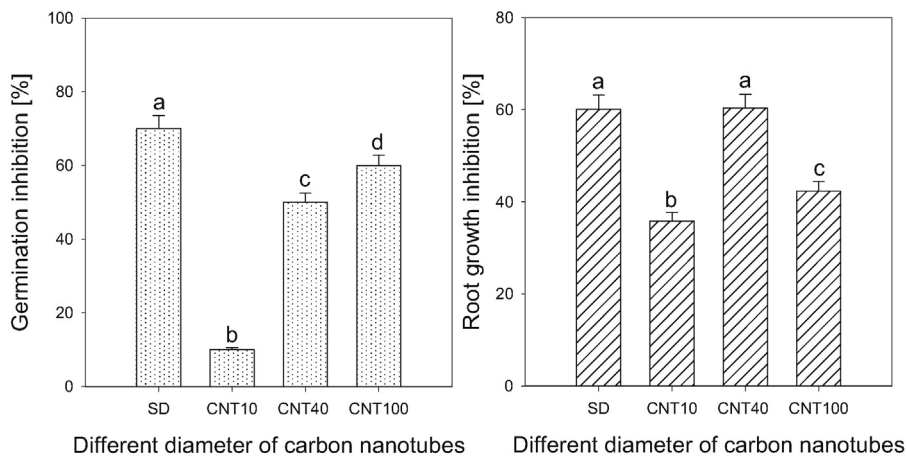


Fig. 3. Effect of CNT size on toxicity (seed germination and root growth inhibition of *L. sativum*) of raw sediment and sediment with CNTs. Different letters means statistically significant differences ($P \geq 0.05$) between bars.

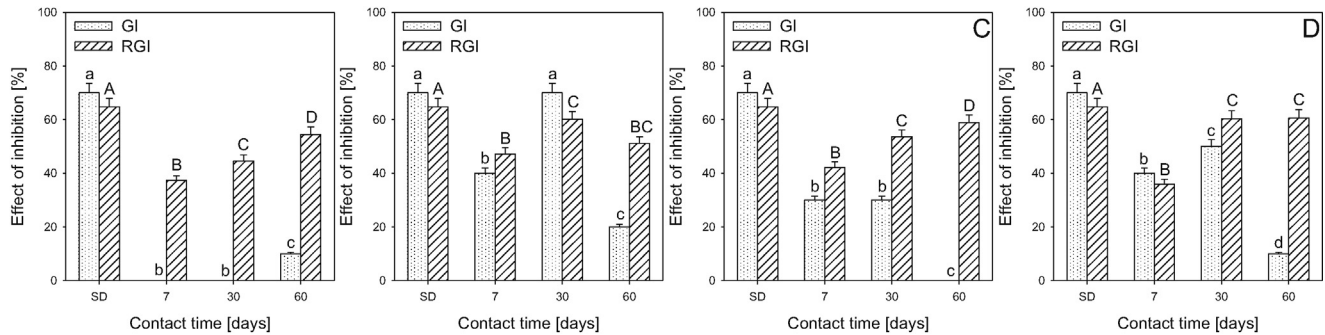


Fig. 4. Influence of ageing on toxicity of sediments spiked with AC (A), BC1 (B), BC2 (C) and CNT40 (D). SD – sediments, GI – seed germination inhibition, RGI – root growth inhibition. Different letters means statistically significant differences ($P \geq 0.05$) between bars.

of contact. The reduction of seed germination inhibition after the application of AC was at a similar level after 7 and 30 days of contact (Fig. 4A). During those periods of incubation 100% germination of *L. sativum* was observed (no seed germination inhibition). After 60 days of incubation of AC with the sediment, the germination capacity of *L. sativum* was slightly reduced. Extension of the contact time between AC and the sediment had a more pronounced effect on the reduction of inhibition of root growth of *L. sativum*. A significant negative correlation was obtained between the time of contact and the toxicity reduction observed. The greatest effectiveness in the reduction of toxicity was noted for AC after 7 days of incubation with the sediment, reducing the root growth inhibition by 26.7%. Extension of the time of contact to 30 and 60 days reduced the toxic effect by only 19.5 and 9.6%, respectively, in relation to sediment with no addition of AC (Fig. 4A).

The contact time between BC1 and the sediment had a varied effect on the toxicity of the sediment, and totally different than in the case on AC (Fig. 4B). The highest effectiveness of reduction of the negative effect of the sediment on the seed germination capacity was observed after 60 days (reduction by 50%). The reduction of seed germination inhibition after 7 days of incubation was 30%, while after 30 days the inhibition of germination was at the same level as in sediment without any content of BC1. In the case of root growth inhibition, the weakest effect was also observed for the 30-day period of incubation. No significant differences were noted between root growth inhibition in sediments with and without an addition of BC1. After 7 and 60-days periods of incubation the reduction of toxicity was at a similar level, at 12.9 and 16.9%, respectively.

The effect of the contact time between BC2 and the sediment displayed similar behaviour as in the case of AC in terms of root growth inhibition, but in the case of seed germination it had a different characteristic. After 7 and 30 days of incubation, BC2 caused a 40% reduction of germination inhibition compared to the sediment without addition of BC2. Extension of the time of contact of BC2 with the sediments to 60 days eliminated the toxic effect, resulting in 100% germination. The longer the period of incubation of the materials tested, the lower was the reduction of root growth inhibition (Fig. 4C). After 7 days of incubation, BC2 caused a reduction of inhibition of root growth of *L. sativum* by 21.9%, whereas after 30 days the reduction was 10.4% and after 60 days only 5.9%. However, it was still statistically significantly different in comparison to the sediment with no addition of BC2.

In the case of CNT40, the greatest degree of reduction of inhibition of seed germination was observed for the 60-day period of incubation, when the reduction of toxicity amounted to as much as 60%. Notably less pronounced effects of CNT40 on the sediments were observed after 7 and 30 days on incubation, when the reduction of toxicity was 30% and 20%, respectively (Fig. 4D). As it was

observed for AC and BC2, the extension of the time of contact between CNT40 and the sediment had an unfavourable effect on root growth of *L. sativum*. After the 30 and 60-day periods of incubation no significant differences in root growth inhibition were observed between the sediments with and without an addition of CNT40. In contrast, after the 7-day period of incubation CNT40 reduced the toxic effect by 28.1%.

4. Discussion

Sediments can be the place of deposition of various contaminants (Rakowska et al., 2012), which may create a threat to living organisms. The application of selected materials with high affinity to contaminants, that reduce their bioavailability and indirectly also their toxicity, may be a promising solution to that problem. Numerous studies demonstrate considerable reduction of pore-water concentration of such contaminants as PAHs, PCBs, DDT and TBT in the presence of AC (Brandli et al., 2009; Vasilyeva et al., 2010; Zimmerman et al., 2004). Research shows that BC, which in recent years enjoys a growing interest and potentially can be considered as a substitute to AC, has the additional ability of binding heavy metals (Ghosh et al., 2011; Tomaszewski et al., 2008). So far BC has been successfully applied in the remediation of soils (Major et al., 2010) and at present attempts are undertaken at its application for contaminated sediments (Ghosh et al., 2011). CNTs – due to their strong sorptive properties – are also in interesting materials in this respect. So far, however, that solution is extremely expensive, which precludes the application of CNTs at any large scale (Ren et al., 2011). Nevertheless, the rapidly developing nanotechnology may cause a reduction of the prices of CNTs, which will permit their industrial-scale application in remediation.

4.1. Effect of different CM on phytotoxicity

The materials used in the experiment varied in their effectiveness in the reduction of the toxicity of the sediment studied. The differences observed between the particular materials may result from the origin of the initial raw material and from the method of production, determining the sorptive properties of those materials (Beesley et al., 2011). Sorption capacity, as the primary factor responsible for the reduction of toxicity of sediments, is determined mainly by: surface area, content of organic carbon, and rate of carbonisation (Beesley et al., 2011; Ghosh et al., 2011; Hale et al., 2010). In the case of the materials applied, AC and CNT were characterised by the highest carbon content, but the strength of their effect on the toxicity of the sediments was different. AC was distinctly more effective in the reduction of toxicity than CNT40 in spite of their similar C content. This was particularly observable in the case of the highest application rates (5 and 10%). Most probably

Table 3
Chemical characteristics of mixture of activated carbon and biochar.

	SD	SD + AC	SD + BC1	SD + BC300	SD + BC300–500	SD + BC500
<i>30 days</i>						
TOC	6.6	9.1	7.3	8.1	7.8	7.0
Nt	0.6	0.5	0.5	0.5	0.4	0.5
TOC/Nt	11.7	19.9	14.2	17.2	18.0	15.1
<i>60 days</i>						
TOC	6.6	10.4	7.5	7.7	7.1	7.8
Nt	0.6	0.4	0.5	0.5	0.5	0.5
TOC/Nt	11.7	23.6	14.7	14.9	15.1	15.3
<i>30 days</i>						
P ₂ O	380	400	395	425	425	465
K ₂ O	1367	1667	2167	2667	2165	1467
Mg	1910	1000	1044	1022	1010	1044

SD – sediment without additives, TOC – total organic carbon content (%), Nt – total nitrogen content (%), P₂O, K₂O, Mg – content of available forms of phosphorous, potassium and magnesium, respectively (mg/kg).

No significant changes between 7 and 30 days of ageing for TOC, Nt and TOC/Nt ratio.

No significant changes between 7, 30 and 60 days of ageing for available forms of P₂O, K₂O and Mg.

the differences were determined by the specific surface area of the materials tested (the surface area of AC was 10-fold larger than that of CNT40), which in this case may play a greater role in the binding of contaminants than carbon content (Oleszczuk et al., 2012a). Although BC were characterised by notably smaller surface area and carbon content than AC and CNT, the differences in reduction of root growth inhibition were not significant (especially after the application of BC2, but also BC1 at doses of 1 and 10%). In this case the fertiliser function played by BC may be of importance (Beesley et al., 2011). As demonstrated in our experiment (Table 3) the application of BC1 to the sediment enriched it by 800 mg/kg in available K₂O. Potassium plays an important role in the metabolism of plants, e.g. by activating numerous enzymes (Maathuis, 2009). BC compensates its lower effectiveness in adsorption with a greater effect on properties that improve plant growth at the same time. In addition, BC1 reduced the available water retention (AWC) to a lesser degree than AC (Fig. 5).

4.2. Effect of CM dose on phytotoxicity

The effectiveness of various CM in the reduction of toxicity of sediments can be determined by the dose, size of particles and contact time between sediment and adsorbents (Jakob et al., 2012; Rakowska et al., 2012). Studies conducted so far show the relations between the dose of CM and the effect, both in the context of reduction of concentration of contaminants (Cho et al., 2012; Ghosh et al., 2011; Zimmerman et al., 2005) and in that of the reduction of toxicity (Fagervold et al., 2010; Jonker et al., 2009). Studies by Fagervold et al. (2010) demonstrated that higher dose of AC (5%) caused greater reduction (91%) of the toxicity of equivalent of polychlorinated dibenzo-p-dioxins/dibenzofurans in earthworms compared to a do 2% dose of AC (78%). In an earlier study (Oleszczuk et al., 2012b), the reduction of phytotoxicity of sewage sludge caused by the presence of AC and BC was correlated with the dose of the CM only to the level of 5%, while an increase of the dose (to 10%) did not cause any further reduction of toxicity. This study also demonstrated that an increase in the dose of AC caused greater reduction of toxicity also only to a certain level. The lack of further reduction of toxicity with increasing doses could have been caused e.g. by the clogging of pores (Oleszczuk et al., 2012b). Fewer available surfaces of the adsorbent mean that a smaller amount of contaminants can be bound, which increases the risk of exposure of the contaminants to living organisms. The reduction of the toxic effect after the application of a larger dose of adsorbent may also result from the occurrence of other factors responsible for the toxic effect. In the case of CNTs it was observed that an increase of their concentration in the sediment caused a lower effectiveness in the reduction of toxicity. One of the probable explanations for this phenomenon could have been a direct negative effect of CNTs on the growth of test plants. The presence of CNTs may cause their adsorption on the surface of roots, which inhibits the transport of water and nutrients into the plant (Canas et al., 2008). In addition, as indicated by studies by Wild and Jones (2009), CNTs may increase the accumulation of organic contaminants by plants, which also could have caused an increase of toxicity at higher doses of CNTs.

4.3. Effect of particle size on phytotoxicity

The sorptive properties may be significantly affected by the particle size of the adsorbent (Canas et al., 2008; Ghosh et al., 2011; Shan et al., 2009), which indirectly determines its effectiveness in the reduction of toxicity. Studies concerning AC showed that decreasing particle sizes increase its effectiveness in reduction of pore-water concentration of PCBs and PAHs (Zimmerman et al.,

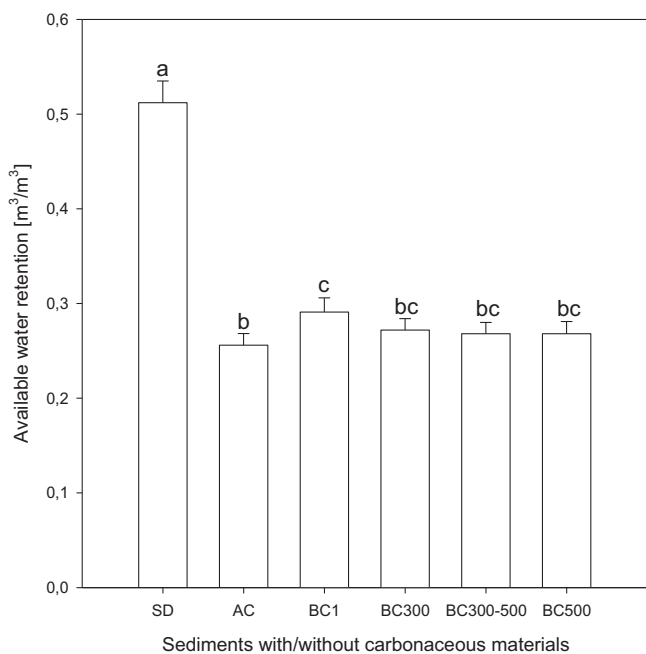


Fig. 5. The influence of activated carbon (AC), biochar (BC1) and biochar BC1 divided on different fraction (BC < 300, BC300–500, BC > 500) on limiting available water retention. Different letters means statistically significant differences ($P \geq 0.05$) between bars.

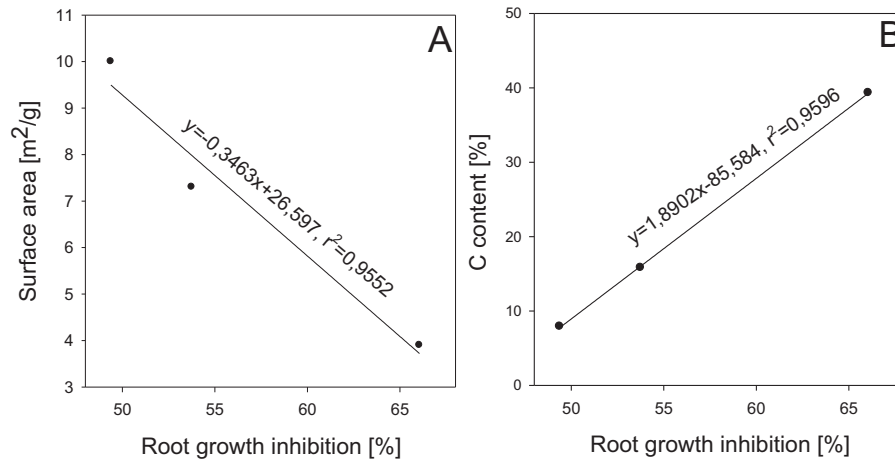


Fig. 6. The relationship between surface area and C content in BC1 fractions and root growth inhibition of *L. sativum*.

2005). However, in research involving the use of living organisms a different tendency was observed. Jakob et al. (2012) found that powdered AC had a negative effect on the growth and development of both earthworms and plants, while granulated AC caused only positive effects. In the case of two materials applied in this study (CNT and BC), only in the case of BC a significant relation was noted between particle size and reduction of toxicity. BC particles characterised by larger size were more effective in reducing the negative effect of sediments than particles of smaller size (Fig. 2). Sorption of contaminants is one of the primary mechanisms of detoxification of sediments by CM. As mentioned earlier, the primary role in that process is that of the specific surface area of the adsorbent (Ghosh et al., 2011; Park et al., 2011). The separation of BC into particular fractions diversified in them both the content of C and the surface area (Table 1). At the same time a reverse relation was observed between carbon content and surface area, which is contrary to research results conducted hitherto. Usually, an increase in carbon content is accompanied by an increase of surface area (Park et al., 2011). Larger particles of biochars were characterised by greater surface area than that of smaller diameter particles (Table 1). It shows that larger particles are better in contaminants binding than smaller one. The results obtained show that surface area dominates in the process of reduction of toxicity (Fig. 6A), while carbon content has an opposite effect (Fig. 6B). Apart from those parameters (C content, surface area), the effect of size of BC1 may be related to a change in the availability of nutrients and water, and with a change in bulk density (Jakob et al., 2012) as well as the TOC/N_t ratio (Gaskin et al., 2010). The addition of the particular fractions of BC1 had no effect on the content of P₂O₅ and Mg in the sediment. Only the concentration of K₂O varied with relation to the BC1 fraction applied. The concentration of K₂O in the sediment decreased with increase in the size of the BC1 fraction (Table 3), while the reduction of root growth inhibition was correlated with the size of BC1. This cannot be taken to imply a toxic effect of K₂O on plant growth, as the sediment without and with an addition of BC500 had a similar level of K₂O. This excludes the availability of nutrients as a factor playing a significant role in the differential effectiveness of detoxification of sediments by the particular fractions of BC1. The availability of water may be another cause of potential differences among the fractions of BC (Jakob et al., 2012). In this case, however, no distinct differences were noted among the particular fractions of BC1 in reducing the available water retention (AWC). Yet it was observed that the adsorption of water (unavailable for plants) constituted a larger share in sediment containing fraction BC300 than in sediment with BC300-500 and BC500 (Table S1),

which could have been one of the causes of lower effectiveness in the reduction of toxicity after the application of BC300. Jakob et al. (2012) claim also that powdered AC could clog soil pores, and thus cause an increase of bulk density (BD), which could have inhibited the growth of plant roots. In the study presented here all the fractions reduced the bulk density by ca. 12% (Table S1) in comparison to sediment without BC. In this respect no significant differences were noted both within the particular fractions and also between the particular fraction and BC not separated into fractions. Another possible cause for the differences in the reduction of phytotoxicity among the particular fractions could be a change in the TOC/N_t ratio by the BC addition (Rondon et al., 2007). Rondon et al. (2007) observed that an increase in the TOC/N_t ratio causes a reduction of plant uptake of N, which has an unfavourable effect on plant growth. In this study, the ratio of TOC/N_t was the highest for the smallest fraction (BC300) which did not reduce the toxicity of the sediment (Fig. 2). Fraction BC500 was characterised by the lowest TOC/N_t ratio, which may indicate better conditions for plant growth (greater availability of N). In the case of CNTs, a relation was observed between diameter and germination inhibition, while the level of root growth inhibition was not dependent on the diameter of the CNTs.

4.4. Effect of contact time between CM and sediment on phytotoxicity

An important aspect of the field application of CM is the maintenance of positive effects for as long a period of time as possible. Research shows that with longer exposure time the effectiveness of sorption of contaminants in AC-amended sediments may be reduced (Hale et al., 2009). In turn, Cho et al. (2012) observed that sorption of certain contaminants (e.g. PCBs) may persist at a constant level for as long as 5 years. Whereas, little data are available on the effect of the time of sediment – CM contact on the level of reduction of sediment toxicity. In the context of environmental influence, the effect of ageing was studied primarily on the basis of the level of bioaccumulation of contaminants originating from sediments containing CM. The studies showed a reduction of the level of accumulation of contaminants with time (Gaskin et al., 2010; Jonker et al., 2009). In our study, however, we found a negative effect of the time of contact between the sediment and CM on phytotoxicity. That effect was particularly observable in the estimation of root growth inhibition. One of the possible explanations for the phenomenon observed may be the reduction, over time, of the availability of nutrients due to their binding by the CM

(Millward et al., 2005). Another potential cause of the decrease in the effectiveness in the detoxification of the sediments could have been a reduction of the availability of water (Jakob et al., 2012). Fouling mentioned above may also be an important factor which affects increase of root growth inhibition of *L. sativum* over time. Oxidation of BC can also reduce adsorption of hydrophobic contaminants by making the surfaces more hydrophilic (Cheng and Lehmann, 2009). Still another factors determining the negative effect of the time of contact on the effectiveness of CM can be the immobilisation of N, caused by an increase in the concentration of C (TOC/N_T) (Gaskin et al., 2010). In the case of AC application to the sediments, the TOC/N_T ratio increased over time (Table 3). The application of BC1 to the sediments also increased the proportion of TOC relative to N_T, but that had no effect on the TOC/N_T ratio (Table 3). Nevertheless, the effectiveness of BC1 in the reduction of toxicity of the sediments in the particular periods displayed differences, which may indicate another factor determining the process of reduction of toxicity in the case of BC1. There is a possibility that several factors act simultaneously in reducing the toxic effect of sediments by the addition of CM.

5. Conclusion

This report presents the effect of three different carbonaceous materials on the toxicity of sediments with relation to *L. sativum*. This type of research has not been conducted so far. Following the application of the carbonaceous materials, the reduction of phytotoxicity was not as pronounced as observed reductions in pore-water contaminants concentration and bioaccumulation of contaminants. This, however, does not preclude the effectiveness of the method proposed. The use of plants for the estimation of the effectiveness or sediment remediation treatments with the application of adsorbents may involve certain limitations that require a series of additional experiments. The adsorbents applied may cause a change to the physicochemical properties of sediments, due to which the final effect may turn out to be unsatisfactory (insufficient reduction of toxicity), suggesting low effectiveness of the method. This, however, may result from the fact that the toxicity of sediments with relation to plants after the application of CM is not necessarily related to a limited reduction of bioavailability of the target contaminants (or sediment toxicity), but results from other factors that indirectly inhibit plant growth, e.g. binding of nutrients and water availability for plants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ecoleng.2013.07.064>.

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