Bioresource Technology 111 (2012) 84–91

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge

Patryk Oleszczuk [a,b,*], Sarah E. Hale [a], Johannes Lehmann [c], Gerard Cornelissen [a,d,e]

[a] Department of Environmental Engineering, Norwegian Geotechnical Institute NGI, Oslo, Norway
[b] Institute of Soil Sciences and Environmental Management, University of Life Sciences, Lublin, Poland
[c] Department of Crop and Soil Sciences, Cornell University, Ithaca, USA
[d] Department of Applied Environmental Sciences (ITM), Stockholm University, Stockholm, Sweden
[e] Institute for Plant and Environmental Sciences, University of Life Sciences (UMB), Ås, Norway

ARTICLE INFO

Article history:
Received 14 December 2011
Accepted 3 February 2012
Available online 12 February 2012

Keywords:
Biochar
Activated carbon
Polycyclic aromatic hydrocarbons
Bioavailability
Sewage sludge

ABSTRACT

The aim of the research was to determine the influence of biochar and activated carbon (AC) on the freely dissolved concentration of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. Two different biochars (MSB and PMW) and two ACs (CP1 and BP2) were used in the present experiment. Addition of AC/biochar to sewage sludge caused significant decrease of freely dissolved PAHs concentration. Depending on the dose, the reduction of freely dissolved PAHs ranged from 56% to 95% (ACs) and from 0% to 57% (biochars). Only for the biochars was there a significant difference between short 7-d and long 30/60-d mixing time. It is concluded that both AC and biochar are effective at reducing PAH pore-water concentrations, the more expensive and non-carbon negative AC having the greatest effect.

1. Introduction

Sewage sludge is an abundant organic waste or by-product generated in wastewater treatment plants (WWTP) after primary and secondary treatment processes. In Europe, dry weight per capita production of sewage sludge resulting from primary and secondary treatment is on average 90 g per person per day. Wastewater treatment plants in the USA alone produced over 6.2 million metric tons of dry sludge every year (Fytili and Zabaniotou, 2008). It is estimated that in the future this number will steadily increase due to increasing urbanization and industrialization. Sewage sludge contains a number of valuable substances which have a positive influence on soil properties. However, due to the presence of contaminants in digested sewage sludges (Smith, 2009) their use as a soil fertilizer is becoming more frequently scrutinized. Incineration, which is one way of sewage sludge disposal, is very expensive and meets opposition from the public. Composting, which may be an interesting alternative to incineration, does not always lead to the elimination of all threats associated with the presence of contaminants. Due to these difficulties it is frequently necessary to landfill sewage sludge in the area of a sewage treatment plant. Such sewage sludge management may lead to contaminant leaching and consequent environmental risk.

Apart from heavy metals, which may disqualify the agricultural use of sewage sludge from a legal point of view, organic contaminants are also ubiquitous in sewage sludge (Smith, 2009). PAHs are a group of organic pollutants often found in sewage sludges. Most of them are characterized by highly toxic, mutagenic and carcinogenic properties; and due to their high persistence in the environment, they belong to the group of persistent organic pollutants (POPs). After sewage sludge deposition or application into the soil, organic contaminants including PAHs may be taken up by organisms or migrate to water basins. Methods that limit the leaching of contaminants from sewage sludge (during their deposition or agricultural use) may be an interesting solution to this environmental problem. However economically effective and efficient methods of limiting organic contaminant mobility in sewage sludge have not been tested yet.

A method of sediment amendment using materials characterised by high sorption capacity in order to reduce organic contaminants bioavailability and mobility was proposed by Luthy and co-workers (Zimmerman et al., 2004; McLeod et al., 2004; Millward et al., 2005). The effectiveness and acceptability of this method has been confirmed by other studies (Brandli et al., 2008, 2009; Ghosh et al., 2011). The use of activated carbons (AC) reduced the bioavailability of hydrophobic contaminants such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs),

* Corresponding author at: Institute of Soil Sciences and Environmental Management, University of Life Sciences, Lublin, ul Leszczyńskiego 7, 20-069 Lublin, Poland. Tel.: +48 81 5248160; fax: +48 81 5248150.
E-mail address: patryk.oleszczuk@up.lublin.pl (P. Oleszczuk).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2012.02.030

polychlorinated dibenzo-*p*-dioxins/dibenzofurans and tributyltin (Brandli et al., 2009, 2008; McLeod et al., 2004; Millward et al., 2005; Zimmerman et al., 2004). A mass transfer of pollutants occurs from the soil/sediment matrix to the amended adsorbent, which reduces pore-water concentrations and contaminant bioavailability. The method of stabilizing organic compounds with adsorbents seems interesting, simple, cost-effective and besides contaminated soils and sediments, might be also used in case of sewage sludge. Application of biochar or activated carbon to sewage sludge would be, to the best of our knowledge, the first such attempt, especially with regards to the organic contaminants' content.

Although the costs of the AC application in the context of remediation is not high compared to other remediation technologies (Ghosh et al., 2011), new and cheaper adsorbents are attractive. It has been shown in the literature that biochars are characterized by high affinity for organic contaminants (Cao et al., 2009; Kookana, 2010; Wang et al., 2010; Sun et al., 2011a,b), thus these materials potentially may be an alternative for AC. In addition, application of biochar to soil has recently been considered as having great potential to sequester carbon and reduce greenhouse gas emissions (Lehmann and Joseph, 2009). Addition of biochar to sewage sludge in a similar manner as AC is used, should decrease the bioavailability, toxicity and mobility of organic pollutants (Kookana, 2010). An additional advantage of using biochars as sewage sludge additive may be the immobilization of heavy metals (Beesley and Marmiroli, 2011; Beesley et al., 2010).

The aim of the present research was to test both AC and biochar with regard to their effectiveness in reducing risk-relevant freely dissolved PAHs concentrations in sewage sludge. PAHs are common contaminants of sewage sludge. Both bitumen and organic waste-based AC qualities were tested at various mixing/aging times, and state-of-the-art passive samplers were deployed to determine freely dissolved concentrations.

2. Methods

2.1. Chemicals

Heptane, acetone, methanol and hexane (all supra solv quality), dimethylformamid (DMF), silica gel 100 (0.063–0.200 mm), sodium sulphate (pro analysis) and sodium azide (NaN_3) were purchased from VWR International AS (Kalbakken, Norway). AlphaQ-water purification system was from Millipore SA (Molsheim, France). External PAH standard (PAH Mix 2) was from Supelco (Belleforte, PA, USA) and internal standard containing deuterated phenanthrene, fluoranthene, pyrene, benzo[a]pyrene and benzo[ghi]perylene from Cambridge Isotope Laboratories Inc. Polyoxymethylene (POM) was purchased in 1 kg cylinder-shaped blocks from Astrup AS (Oslo, Norway) and cut in 1.5 cm wide and 55 μm thick slices with a lathe equipped with a high-precision razor blade (Cornelissen et al., 2008).

2.2. Materials

Sewage sludge was collected during summer 2010 from municipal sewage treatment plant localized in southeastern part of Poland (Zamość). The sludge sample (about 50 kg) was collected at the end point, after the sewage sludge digestion process. A few representative subsamples (5 × 100 g) were taken for the present experiments. Samples were mixed, dried in air (about 25 °C for two weeks) in the dark, ground and passed through a 2 mm sieve.

Two different biochars called MSB and PMW were used in the present research. Maize stover biochar (MSB) was produced from corn stover residues Zea mays L. at 600 °C using a slow pyrolysis (Best Reactor, Australia) method in a continuous unit with a residence time of 20 min. PMW was produced from paper mill waste which was collected from Mohawk Paper Company (Waterford, NY, USA). The water was removed from the pulp waste with a coagulant and flocculent before fibres were collected. The PMW was charred via a slow pyrolysis batch system at 600 °C (Daisy reactor, Best Energies, Inc., Cashton, WI, USA). Before the experiment with sewage sludge, biochars were passed through a 2 mm mesh size sieve.

The two activated carbon (AC) qualities from Jacobi Carbon were one bitumen-based material (BP2) and one coconut shell-based material (CP1). 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 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. 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.

2.3. Sewage sludge-AC/biochar mixture preparation

Aging was carried out in the laboratory in the batch experiment. Samples (sewage sludge, biochar, activated carbon) were added to 50 mL glass flasks with glass lids. The sewage sludge (2 g) and AC/biochar (depending on the dose used) were thoroughly mixed with a glass spatula and rolled end over end for 30 days (in the dark, room temperature) at 10 rpm. Sewage sludge was spiked with AC or biochar at the dose of 0.5%, 2%, 5% and 10% (w/w). In the aging experiment the sewage sludge was mixed with AC or biochar at the dose of 5% and rolled end over end in the dark for 7, 30 and 60 days.

2.4. Freely dissolved PAHs extraction and quantification

The freely dissolved concentration of PAH in soil/water suspensions was determined as described in (Cornelissen et al., 2008). Shortly, sewage sludge (2 g, dry weight) with and without AC/Biochar were shaken in 50 mL glass flasks with glass lids end over end with 200 mg POM and 40 mL AlphaQ-water. The system was sterilized with 0.2% NaN_3. After 6 weeks, POM strips were taken out, wiped off with a paper tissue and extracted in 20 mL heptane:acetone mixture (8:2, v/v) by horizontal shaking (48 h). A shaking time of six weeks was considered sufficient since equilibration time of powdered AC-sediment systems was less than 31 d (Cornelissen et al., 2008). Deuterated PAHs in heptane were added before extraction as internal standard (100 ng). An aliquot of 20 mL of the organic phase (after POM extraction) was evaporated to 0.5 mL and subjected to partitioning between DMF/hexane for clean-up as described in Brandli et al. (2006). Further clean-up was performed on a microcolumn filled with silica gel (deactivated with 10% AlphaQ-water) and sodium sulphate. Samples were reduced to 0.8 mL before analysis.

Determination of the total PAHs content included extraction of samples via a soxhlet method with toluene (90 ml) for 6 h at

160 °C, followed by the cleaning up of the concentrated extracts by DMF/hexane and microcolumn filled with silica gel as described above.

POM–water distribution ratios (K_{POM}) from Cornelissen et al. (2008) were used to calculate the freely dissolved PAH concentration in the water from the PAH concentration measured in the POM. PAH mass balances in the used closed solid phase/water systems were found to be satisfactory in an earlier study for sediments (Cornelissen et al., 2004) and consequently only POM was analyzed in the present study.

2.5. PAH quantification

PAH were separated on a Agilent 6850 Gas Chromatograph equipped with a Agilent DB-XLB Column (length 30 m, 0.25 mm id and 0.1 lm film thickness, TeknoLab, Kolbotn, Norway) with a flow of 1 mL/min and the following temperature programme: 2 min at 50 °C, to 150 °C at 10 °C/min, to 280 °C at 5 °C/min, 9 min at 280 °C, to 310°C with 40 °C/min, at 310 °C for 8 min. PAHs detection.

Detection was performed with an Agilent 5973 mass spectrometer in the electron impact mode with a 70 eV ionisation energy and a dwelling time of 25 ms. Identification of the PAH was assured by using two compound-specific ions: a quantifier ion corresponding to the respective molecular weight (m/z = M+) and a qualifier ion ([M-2H]+ for analytes and [M-2D]+ for internal standards) with a mass ratio similar to the one determined in the calibration. Four external calibration standards (1–1000 μg/mL of analyte) containing constant amounts of internal standards (100 μg/mL) were run before each series.

Detection limits were 0.02 μg/kg per single PAH in sewage sludge and around 50 pg PAH, i.e. 0.2 ng/g in POM. Absolute recoveries from a POM spiking experiment were 80–95% for all 10 PAHs (spike levels: 1–10 ng individual PAH). Blanks were run with each series and levels were below detection limits in all POM experiments and below 5% in soil analysis.

2.6. TOC-water distribution coefficient calculation

To check the effect of AC/biochar-sewage sludge amendment on TOC-water distribution coefficients (K_{TOC}), The organic carbon–water partitioning coefficient is the ratio of the mass of a chemical that is adsorbed in the matrix (soil/sediment/sewage sludge) per unit mass of organic carbon in the matrix per the equilibrium chemical concentration in solution. K_{TOC} was calculated by the following equation:

$$K_{TOC} = C_S/(f_{TOC} \times C_{W,free}) \quad (1)$$

where C_S is the PAH concentration in sewage sludge (μg/kg$_{dw}$), f_{TOC} the fraction of organic carbon in the sewage sludge and $C_{W,free}$ the freely dissolved concentration in the water (μg/L).

3. Results and discussion

3.1. Sewage sludge and biochar characteristic

Sewage sludge was characterised by a weakly acidic reaction (pH 6.1). The content of the total organic carbon and organic nitrogen was at the level of 188.2 and 40.6 g/kg, respectively. The sewage sludge was characterized by a high content of available phosphorus (272.0 mg/kg) and very low content of potassium (34.0 mg/kg). The cation exchange capacity (CEC) and total exchangeable bases (TEB), which demonstrate the richness of sorption complex, were at high levels of 1404 and 1440 mmol/kg, respectively. In sorption complex Ca^{2+} (408.8 mmol/kg) and Mg^{2+} (367.1 mmol/kg) cations were predominant. The total content of Pb, Cd, Cr, Cu, Cd, Ni and Zn were 12.1, 1.28, 25.4, 97.2, 26.4 and 1170 mg/kg, respectively. EU standards were not exceeded for any contaminant (Communities, 1986). This indicates that sewage sludge used in the experiment can be applied in agriculture and for the purpose of soil re-cultivation for agricultural purposes.

The elemental composition and chemical properties of biochars used in the experiment are listed in Table 1. Both of biochars were highly alkaline pH (pH = 10). This value is typical for most biochars generated at high temperature (Lehmann and Joseph, 2009). The carbon content of MSB was about 50% higher than that of PMW biochar. The carbon content, particularly in PMW, was low but within the range noted by other authors (Lehmann and Joseph, 2009). Molar ratios of elements were determined to estimate the aromaticity (H/C ratio) and polarity (O/C ratio) of biochars (Table 1). Both MSB and PMW biochars were characterised by a very low H/C ratio (Table 1) confirming a high level of carbonization and aromatization of these materials (Chen et al., 2008). The O/C ratios of 0.19 for MSB and 1.12 for PMW indicate PMW biochar has more surface polar functional groups than MSB biochar (Chen et al., 2008). The AC qualities had similar specific surface areas (1199 and 1158 m^2/g, respectively). The SAs of the biochars were much smaller than those of the ACs. The biochars mainly had nanoporosity, as exemplified by the far higher CO_2-based SA values than the N_2-based ones. The ACs were observed to have higher C contents (80–90%) than the biochars (20–40%). Both ACs were fine powders, with 80% smaller than 45 μm and an average particle size of 20 μm.

3.2. Total PAH contents in sewage sludge

The total content of PAHs in the sewage sludge was at the level of 5.9 ± 0.1 mg/kg. Such a concentration of PAHs is typical for sewage sludges from municipal sewage treatment plants with similar load. Sewage sludge fulfilled the European Union standards (UE, 2000). The concentration of 10 PAHs included in EU norms was at the level of 4.7 ± 0.1 mg/kg. Fig. 1A shows the distribution of individual PAHs in sewage sludge. 4-ring PAHs were predominant in the sewage sludge and constituted over half (51%) of all determined compounds.

3.3. Freely dissolved concentration of PAHs in sewage sludge

Freely dissolved concentration of PAHs sum in sewage sludge was 13.2 ng/L. The profile of the individual freely dissolved PAHs (Fig. 1B) was clearly different from the total content of these compounds (Fig. 1A). Phenanthrene (25.6%), fluoranthene (22.7%) and pyrene (17.9%) were characterized by the highest concentration as well as contribution in freely dissolved fraction. The 5- and 6-ring compounds, which constituted over 30% of the total PAHs content, did not exceed 3% in case of freely dissolved PAHs (Fig. 1B). This is understandable because light PAHs (2–3 rings) are more mobile and their transfer between phases is faster than for compounds with higher number of rings, i.e. 5 and 6-rings PAHs (Xing and Pignatello, 1996). TOC-water distribution ratios for individual PAHs in the sludge will be presented in Section 3.6.

3.4. Effect of ACs on PAHs pore-water concentration

Addition of ACs to sewage sludge significantly decreased freely dissolved PAHs concentrations (Fig. 2A). The freely dissolved PAHs concentration at the lowest dose of AC was reduced from 13.2 ng/L to 5.3 ng/L (BP2) to 5.8 ng/L (CP1). An increase of AC dose from 0.5% to 2% caused a further twofold decrease of freely dissolved concentration of PAHs in investigated sewage sludge (Fig. 2A). Regardless of AC type, an increase of BP2 and CP1 dose to 5% caused a further

Table 1
Elemental composition and pH values of biochars and ACs used in the experiment.

Biochar/AC	C	N	H	O	C/N	H/C	O/C	(O + N)/C	pH_{KCl}	SA (BET-N_2)	SA (CO_2)
PMW	19.22	0.08	0.11	21.54	240.25	0.0057	1.12	1.12	11.60	13.3	n.d.
MSB	41.57	0.42	1.54	8.05	98.98	0.0370	0.19	0.20	9.91	6.3	178
BP2	81.18	0.22	0.03	8.44	369.00	0.0004	0.10	0.11	9.61	1199	726
CP1	91.78	0.73	0.40	7.09	125.73	0.0044	0.08	0.09	9.73	1158	977

Elemental composition (CNHO) in %, SA – surface area (m^2/g).

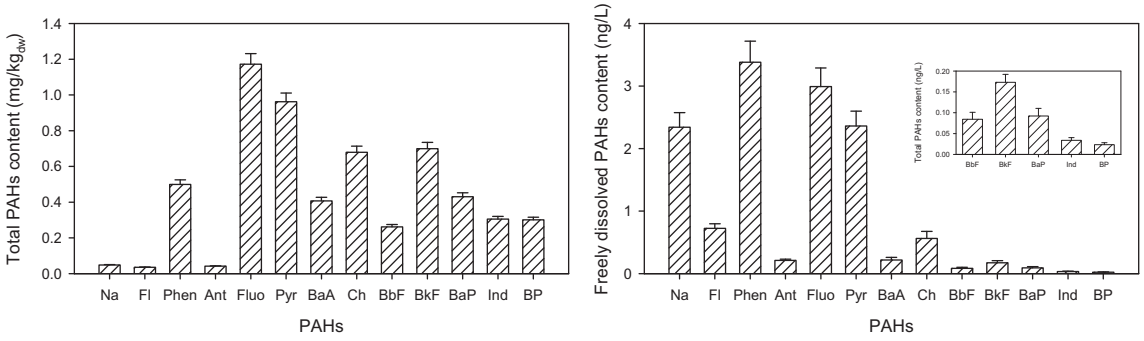

Fig. 1. Total (mg/kg) and freely dissolved (ng/L) PAHs concentration in sewage sludge used in the experiment. Error bars represents standard deviation error ($n = 3$ extractions). Na – naphthalene, Fl – fluorene, Phen – phenanthrene, Ant – anthracene, Fln – fluoranthene, Pyr – pyrene, BaA – benzo[a]anthracene, Ch – chryzene, BbF – benzo[b]fluoranthene, BkF – benzo[k]fluoranthene, BaP – benzo[a]pyrene, Ind – indeno[1,2,3-cd]pyrene, BP – benzo[ghi]perylene.

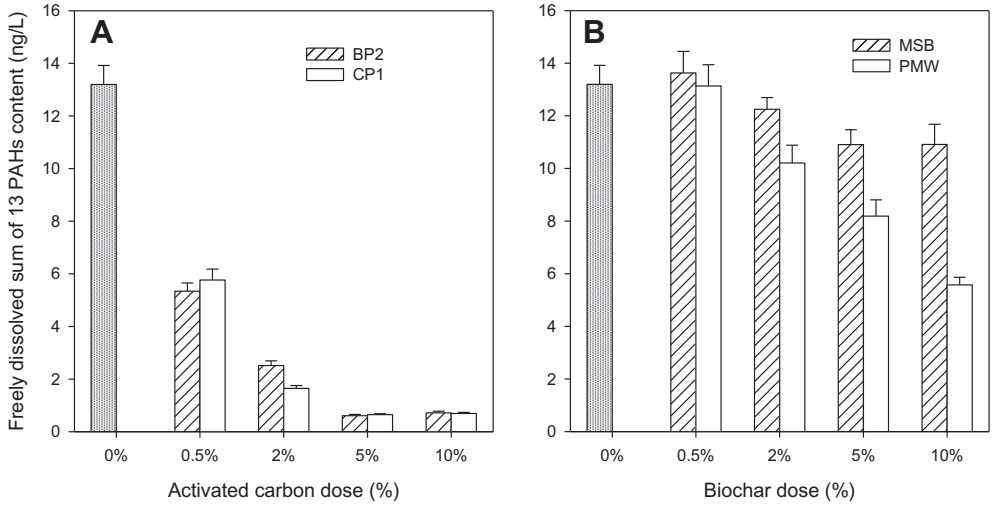

Fig. 2. The freely dissolved PAHs (sum of 13 compounds) concentration in sewage sludge and activated carbon or biochar-amended sewage sludge. (A) activated carbon-amended sewage sludge, (B) biochar-amended sewage sludge. Error bars represents standard deviation ($n = 3$ determinations).

decrease of freely dissolved PAHs to 95% (compared to control without ACs). Upon increasing the AC dose from 5% to 10%, no significant further changes in freely dissolved PAH concentration were observed (Fig. 2A).

Fig. 3 presents the influence of ACs addition on the freely dissolved concentration of different PAHs groups. In the reduction of freely dissolved fraction after the addition of AC important differences both between different groups of PAH as well as between the applied ACs were observed for the lowest doses of the adsorbent (0.5% and 2%) (Fig. 3). Increasing of the AC doses resulted in an increased reduction of freely dissolved concentration for all groups of PAHs. There were no significant differences in the reduction of the different groups of PAHs between ACs dose at the level of 5% and 10%. Naphthalene was characterised by the weakest reduction of freely dissolved concentration.

The reduction of freely dissolved PAHs concentration in AC-amended sewage sludge obtained in the present study ranged from 56.3% to 95.4% in case of PAHs sum, and from 16.2% to 99% in case of individual PAHs. For PAHs and PCBs it was shown that amendment of a contaminated harbor sediment with 3.4% 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). In previous research a 92% reduction of freely dissolved PAHs concentration after soil amending with 2% of AC was observed (Cornelissen et al., 2011). In the present study only application of AC at the highest doses (5% and 10%) resulted in comparable to the soil or sediment reductions of freely dissolved PAHs concentration. There are two possible factors influencing

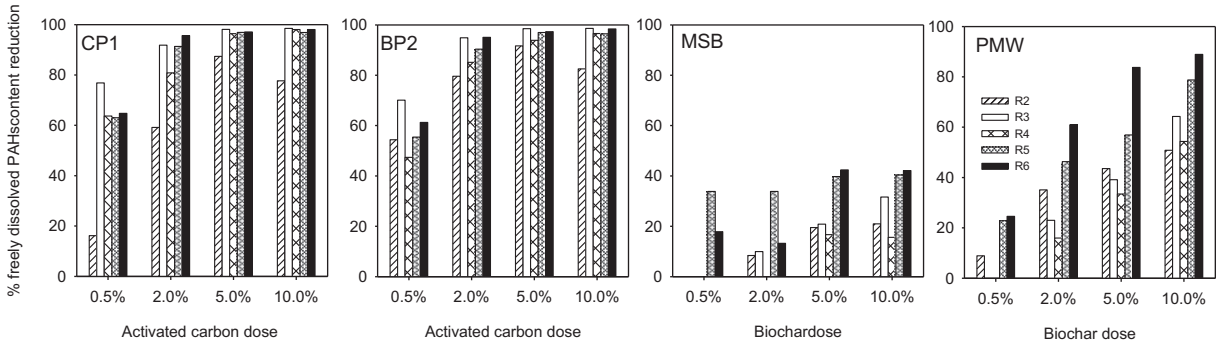

Fig. 3. The reduction of freely dissolved PAHs content depending on number of PAH rings (R2-R6).

the observed differences between sewage sludge, soil and sediments. First, relatively high organic carbon content in sewage sludge (about 200 g/kg) compared to soil or sediments seems to have a significant influence on the reduction of PAHs binding by AC (e.g. as a result of AC pores blocking). Research showed (Pignatello et al., 2006) that strong organic pollutant sorptivity of AC in clean water is reduced when sediment is added to the system as AC can be fouled by organic matter, resulting in attenuation of the target contaminants' access to AC sorption sites (Pignatello et al., 2006). Second, the observed differences between soil/sediments and sewage sludge in contaminants binding by AC could be due to the presence of other substances/compounds in the sewage sludge that may cause fouling of AC by direct site competition (Brandli et al., 2008). Sewage sludge contains metal ions such as K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+} and Na^+ as well as, ammonium ions, acetate ions, bicarbonate, fatty acids and lipids. Besides pore blocking and direct site competition all of these compounds and components may influence the distribution behavior of the PAHs between the solid and the aqueous part of the sewage sludge (Oleszczuk, 2009).

3.5. Effect of biochar on the freely dissolved PAHs content

Biochars were characterised by a lower influence on freely dissolved PAHs content than ACs (Fig. 2). At the lowest dose of biochars, freely dissolved PAHs concentration were 13.6 and 12.5 ng/L for MSB and PMW, respectively (Fig. 2B). These values were not statistically ($P \leqslant 0.05$) different from the values noted for the sewage sludge without biochar (13.2 ng/L). However gradual increase of biochar dose in sewage sludge caused a statistically significant ($P \leqslant 0.05$) decrease of freely dissolved PAHs concentration for both MSB and PWM. The observed changes, however, were not as notable for ACs. A more significant influence on the reduction of freely dissolved PAHs concentration was observed for PMW than for MSB (Fig. 2B). The increase of biochar dose by 4 (from 0.5% to 2%) and 10-fold (from 0.5% to 5%) in the sewage sludge caused the reduction of freely dissolved PAHs content by 5.2 (dose 2%) and 19.3% (dose 5%) for MSB and 22.6 (dose 2%) and 37.9% (dose 5%) for PMW. Further increase of biochar dose (up to 10%) only had an influence on freely dissolved PAHs concentration for PMW, without statistically significant influence on MSB biochar (Fig. 2B). The content of freely dissolved PAHs in sewage sludge with the highest dose of biochars was 10.2 (MSB) and 5.6 ng/L (PMW), which corresponds to the reduction of this fraction of contaminants at the level of 31.6% and 57.7% respectively, compared to the sewage sludge without biochar.

The influence of biochars on freely dissolved concentration of individual PAH groups was different depending on the tested material (Fig. 3). However for these two tested biochars, the largest reduction of freely dissolved PAHs content was observed for 5- and 6-ring PAHs, whereas, 2- and 4-ring PAHs were characterised in most cases by a relatively small reduction (Fig. 3). In the case of PMW, a clear relationship between the dose of biochar and the reduction of freely dissolved content for all PAH groups was noted.

There are very few studies evaluating the influence of biochar on the content of the freely dissolved concentrations of organic contaminants in soils or sediments (Beesley et al., 2010; Cao et al., 2011; Gomez-Eyles et al., 2011). Cao et al. (2011) observed that after 210 days, soils treated with the highest rate of 5% biochar showed more than 66% reduction in atrazine concentration in 0.01 M $CaCl_2$. In the case of PAHs, Beesley et al. (2010) noted that after 60 days of soil-biochar contact time, there was a 50% reduction of PAHs fraction extracted with cyclodextrin. Similarly to the presented study, higher efficiency of contaminants binding was observed for 5- and 6-ring PAHs than for 2–4-ring compounds (Beesley et al., 2010). These results are particularly encouraging in the context of sewage sludge stabilization. Our research shows that in spite of different properties between sewage sludge and soil/sediment, the obtained reduction of freely dissolved PAHs content in biochar-amended sewage sludge is still at a reasonable level. It should be emphasised that the type of biochar used had a significant influence on the reduction of freely dissolved PAHs content (Figs. 2 and 3). Previous research has shown (Chen et al., 2008; Kookana, 2010) that the affinity of organic contaminants to biochar may be vary depending on feedstock material and pyrolysis conditions, mainly temperature. These parameters have a direct impact on the elemental composition and SA of biochar, which determines the contaminant binding by biochar (Cao et al., 2009). Elemental composition and structural characteristics of biochars possibly play a dominant function in their sorption behavior. In spite of lower content of carbon (by 53%), PMW had lower H/C ratio than MSB (Table 1), which indicates a higher level of carbonization and aromaticity. It can be conclude possible explanation for the higher sorption capacity of PMW compared to MSB is that the aro-

Table 2
Correlation coefficients between surface area of AC/biochar and range of PAHs reduction in amended sewage sludge depending on AC/biochar dose.

PAHs	AC/biochar dose							
	0.5%		2%		5%		10%	
	CC	Sig	CC	Sig	CC	Sig	CC	Sig
Sum	0.999*	0.001	0.982*	0.018	0.982*	0.019	0.911	0.089
2-rings	0.730	0.270	0.890	0.111	0.958*	0.042	0.900	0.100
3-rings	0.999*	0.001	0.992*	0.008	0.983*	0.017	0.911	0.089
4-rings	0.986*	0.014	0.986*	0.014	0.987*	0.013	0.918	0.083
5-rings	0.959*	0.041	0.986*	0.014	0.971*	0.029	0.810	0.190
6-rings	0.994*	0.007	0.868	0.133	0.762	0.238	0.706	0.294

CC – correlation coefficient.
Sig. – significant at.
* Significant at $P \leqslant 0.05$.

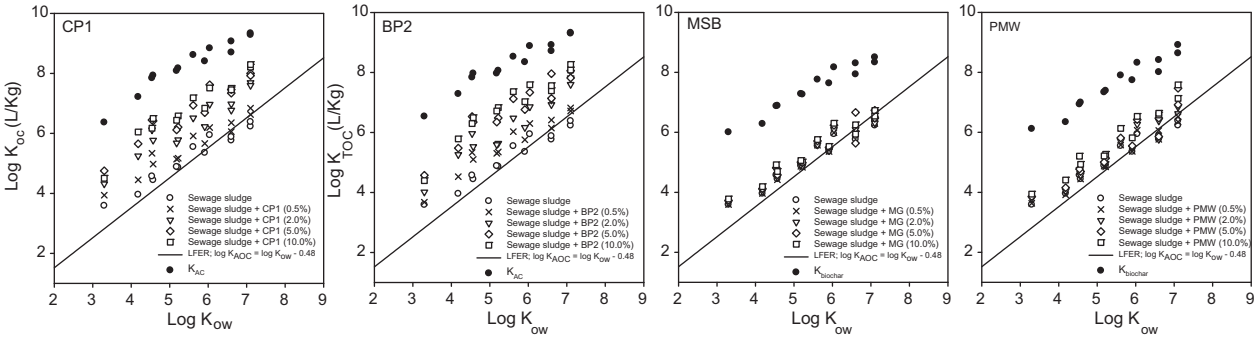

Fig. 4. Kow vs KTOC for sewage sludge with different concentration of activated carbon (CP1, BP2) and biochars (MG, PMW).

matic moieties of PMW biochar. Moreover, PMW had twice as much higher specific surface area than MSB, which is probably the main reason for better PAHs reduction after PMW addition comparing to MSB. Significantly higher efficiency in reduction of freely dissolved PAHs content in AC containing sewage sludge than in biochar with sewage sludge is not surprising. Similar dependence was observed in previous research concerning soil (Cao et al., 2011). Biochars have smaller area than AC (~50–300 m^2/g for biochar (Cao et al., 2009; Chen et al., 2008) as compared to 1000–1500 m^2/g for AC (Cao et al., 2011)), thus their ability to bind contaminants is lower. There was observed a high correlation between specific surface area of AC/biochar and range of PAHs reduction in amended sewage sludge (Table 2). However statistically significant values were mainly observed (apart from a few exceptions) for AC/biochar doses in the range of 0.5–5% and for 3–5 rings PAHs. In the case of other compounds and highest adsorbent dose probably another factor than specific surface is important.

3.6. Total organic carbon–water, AC-water and biochar-water distribution ratios of native PAH

The observed $\log K_{TOC}$ were compared with the $\log K_{oc}$ predicted from the equilibrium partition model based on a correlation with $\log K_{ow}$. The results are illustrated in Fig. 4. K_{TOC} values calculated for individual PAHs were very close to the values for amorphous organic carbon (AOC) obtained by a frequently used Linear-Free-Energy Relationship (LFER; $\log K_{AOC} = \log K_{ow} - 0.48$) (Seth et al., 1999). To our knowledge, this is the first time that K_{TOC} for PAHs in sewage sludge has been determined. This indicates that the sewage sludge organic matter is somewhat similar to the average sediment AOC, in contrast to many black-carbon impacted soils and sediments showing much higher K_{TOC} values (Brandli et al., 2008).

The addition of AC significantly increased the K_{TOC}. With the increase of AC dose, moving K_{TOC} above LFER (Fig. 4A) was observed. Previous research showed that the presence of soot or charcoal (material similar to AC) in soil or sediment influences the relations between K_{TOC} and K_{ow} in a similar way (Seth et al., 1999). This effect has not been so distinct in case of biochars (Fig. 4B and C).

Sorption to ACs or biochars in an AC/biochar-amended sediment was calculated with a nonlinear Freundlich isotherm according to the equation proposed by Oen et al. (in press) (details in Supporting information). The calculated values were presented in Fig. 4 and Tables S1 and S2 (Supporting information). K_{AC} values were 2–3 order higher than those for nonamended sewage sludge TOC. Similarly to K_{AC}, $K_{biochar}$ values were 1–2 orders higher than in those for sewage sludge TOC.

3.7. Effect of aging on pore-water PAHs concentration

The reduction of freely dissolved PAH contents as a result of aging of AC/biochar with sewage sludge depended on the type of material used (Fig. 5). A 7-day period was apparently long enough for a maximum reduction of most groups of freely dissolved PAHs in case of the two tested ACs. Statistically significant differences were noted only for 5- and 6-ring PAHs (Fig. 5). For these compounds 30 days were needed to obtain complete equilibrium, due to slower sludge-to-AC mass transfer for these less water-soluble compounds. This relation was observed in the case of both ACs. This confirms the necessity of a prolonged contact time between sewage sludge and AC in order to reduce the risks related to the presence of heavier PAHs.

The aging had a statistically significant ($P \leqslant 0.05$) influence on both the sum and all PAHs groups in sewage sludge with addition of biochars (Fig. 5). Increasing of the contact time between sewage sludge and biochars caused an increase of PAHs reduction in all cases (except for 2-rings PAHs for MSB and PMW as well as 5-ring PAHs for PMW) (Fig. 5). It should be emphasized that the period of first 30 days was crucial in reducting of freely dissolved PAHs for

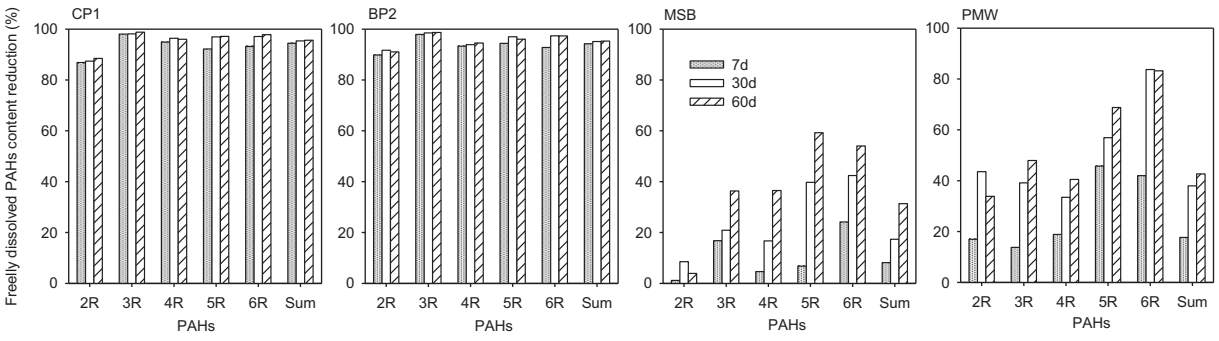

Fig. 5. Influence of AC/BC aging with sewage sludge during 7, 30 and 60 days on the freely dissolved PAHs concentration.

PMW biochar. In that time over 80% total reduction occured. In later period (i.e. from 30 to 60 day) the increase of reduction of freely dissolved PAHs in the case of PMW was statistically significant but the reduction was not as large as in the first 30 days (Fig. 5). For MSB biochar, reduction of freely dissolved fraction of PAHs was more constant. In the period from 7 to 30 and from 30 to 60 day, significant reduction of their freely dissolved concentration was observed for all PAHs. These results show that the transfer of contaminants was faster in case of PMW than MSB.

The research shows that AC/biochar-soil/sediment matrix contact time is one of the main parameters that determine the binding of contaminants by ACs or biochars (Ghosh et al., 2011; Hilber and Bucheli, 2010). The mass transfer of pollutants from matrix to AC or biochar particles can be conceptualised as a three step process where first the pollutant is desorbed from the matrix, then the pollutant diffuses through the water to the AC/biochar particle and finally the pollutant is sequestered by the AC/biochar particle (Werner et al., 2006). In the present research PAHs transfer from sewage sludge to AC was clearly faster than it was noted by other authors (Zimmerman et al., 2004). Probably, it is related to the fact that PAHs are bound by sewage sludge more weakly than to soil or sediment. This is confirmed by lower values of K_{TOC} for PAHs in sewage sludge comparing to K_{TOC} calculated for PAHs in soils or sediments (Cornelissen et al., 2008; Seth et al., 1999). Moreover, sewage sludge may contain surfactants (Smith, 2009), which increase solubility or desorption of hydrophobic organic contaminants from environmental matrices (Zhu and Aitken, 2010).

The reduction of freely dissolved PAHs content required longer contact time for biochars than for ACs (Fig. 5). Previously it was hypothesized (Cao et al., 2009; Kookana, 2010; Pignatello et al., 2006) that pore filling is the main mechanism of contaminants binding by biochars. We have mentioned above that contaminants access to pores is restricted by the organic matter from sewage sludge. However over time, contaminants may diffuse through the humic layer, albeit retarded and more tortuously, and occupy biochar micropores (Pignatello et al., 2006). Such a slow diffusion is probably related to aging effect in the case of biochars. By increasing the dose or reducing the particle size (e.g. application of AC) it is possible that the effect of any organic matter per outer surface area of the grain is reduced (Hale et al., 2009). This may explain lack of this effect in case of ACs, which are characterized by larger specific surface areas and smaller diameter of grains than biochars.

3.8. Environmental implications

This study showed that the addition of AC or biochar to sewage sludge was effective in reducing freely dissolved, risk-relevant PAH contents. Freely dissolved concentration is probably the most appropriate chemical indicator of the bioavailable fraction of contaminants in ecosystems. PAH binding by ACs or biochars in sewage sludge reduces the transfer of contaminants to water and their bioaccumulation, and this expands the possibilities of potential use of sewage sludge. Dosing of AC at the level of 5% was enough to bind 90% of PAHs. Such a strong effect was not observed in the case of biochars. However it was observed that longer contact time between biochar and sewage sludge leads to a further decrease of freely dissolved PAH concentrations. The additional advantages of biochar are carbon sequestration, neutralization of acidity, reduction of green house gasses emissions and reducing nutrient leaching (Lehmann and Joseph, 2009). It is also worth mentioning that the price of biochar is significantly lower compared to activated carbon. It was estimated that biochar is about 10 times cheaper than activated carbon (2 USD/kg). This makes biochar very interesting material with actual use in practice, even though longer equilibration times are needed (Fig. 5).

4. Conclusion

The main conclusion from the present study is that biomass-based AC (the CP1 quality used) might be the optimal amendment for sewage sludge, since it combined a relatively high pollutant binding effect (comparable to bitumen-based AC and much higher than unactivated biochars) with carbon sequestration, although some of the carbon sequestration effect goes lost in the energy-intensive activation process. A previous study comprising a complete life-cycle assessment of sediment remediation by several amendments as well a natural recovery also indicated that coconut-based AC was the optimal material in a global perspective (Sparrevik et al., 2011).

Acknowledgement

The work was funded by the Norwegian Research Council, in the frames of Grant no. 202734 (personal stipend to PO in the Yggdrasil Program) as well as project 203901/H30 in the NorGlobal program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.02.030.

References

Beesley, L., Marmiroli, M., 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environ. Pollut. 159, 474–480.
Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ. Pollut. 158, 2282–2287.
Brandli, R.C., Breedveld, G.D., Cornelissen, G., 2009. Tributyltin sorption to marine sedimentary black carbon and to amended activated carbon. Environ. Toxicol. Chem. 28, 503–508.
Brandli, R.C., Bucheli, T.D., Kupper, T., Stadelmann, F.X., Tarradellas, J., 2006. Optimised accelerated solvent extraction of PCBs and PAHs from compost. Int. J. Environ. Anal. Chem. 86, 505–525.
Brandli, R.C., Hartnik, T., Henriksen, T., Cornelissen, G., 2008. Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere 73, 1805–1810.
Cao, X., Ma, L., Gao, B., Harris, W., 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 43, 3285–3291.
Cao, X., Ma, L., Liang, Y., Gao, B., Harris, W., 2011. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. Environ. Sci. Technol. 45, 4884–4889.
Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by ciochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137–5143.
Communities, C.C.O.T.E., 1986. Directive of 12 June 1986 on the protection of the environment and in particular of the soil, when sewage slude is used in soil, Brussels.
Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., Gustafsson, O., 2004. Relations between environmental black carbon sorption and geochemical sorbent characteristics. Environ. Sci. Technol. 38, 3632–3640.
Cornelissen, G., Okkenhaug, G., Amstatter, K., Bue, H.L., Hale, S.E., Jakob, L., Gocht, T., Hartnik, T., Meynet, P., Werner, D., Jensen, J., 2011. Active materials for the in-situ stabilization of contaminated soil. Norwegian Geotechnical Institute, Oslo.
Cornelissen, G., Pettersen, A., Broman, D., Mayer, P., Breedveld, G.D., 2008. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbons concentrations. Environ. Toxicol. Chem. 27, 490–508.
Fytili, D., Zabaniotou, A., 2008. Utilization of sewage sludge in EU application of old and new methods – A review. Renew. Sust. Energ. Rev. 12, 116–140.
Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: a new direction in contaminated sediment management. Environ. Sci. Technol. 45, 1163–1168.
Gomez-Eyles, J.L., Sizmur, T., Collins, C.D., Hodson, M.E., 2011. Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements. Environ. Pollut. 159, 616–622.
Hale, S.E., Tomaszewski, J.E., Luthy, R.G., Werner, D., 2009. Sorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites by activated carbon in clean water and sediment slurries. Water Res. 43, 4336–4346.
Hilber, I., Bucheli, T.D., 2010. Activated carbon amendment to remediate contaminated sediments and soils: a review. Global NEST J. 12, 305–317.

Kookana, R.S., 2010. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Aust. J. Soil Res. 48, 627–637.

Lehmann, J., Joseph, S., 2009. Biochar for environmental management. Earthscan Publishers.

McLeod, P.B., Van Den Heuvel-Greve, M.J., Allen-King, R.M., Luoma, S.N., Luthy, R.G., 2004. Effects of particulate carbonaceous matter on the bioavailability of benzo[a]pyrene and 2,2′,5,5′-tetrachlorobiphenyl to the clam, *Macoma balthica*. Environ. Sci. Technol. 38, 4549–4556.

Millward, R.N., Bridges, T.S., Ghosh, U., Zimmerman, J.R., Luthy, R.G., 2005. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). Environ. Sci. Technol. 39, 2880–2887.

Oen, A.M.P., Elmquist-Kruså, M., Beckingham, B., Ghosh, U., Luthy, R.G., Hartnik, T., Henriksen, T., Cornelissen, G., (in press). Sorption of organic compounds to fresh and field-aged activated carbons in soils and sediments. Environ. Sci. Technol.

Oleszczuk, P., 2009. Sorption of phenanthrene by sewage sludge during composting in relation to potentially bioavailable contaminant content. J. Hazard. Mat. 161, 1330–1337.

Pignatello, J.J., Kwon, S., Lu, Y., 2006. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. Environ. Sci. Technol. 40, 7757–7763.

Seth, R., Mackay, D., Muncke, J., 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. Environ. Sci. Technol. 33, 2390–2394.

Smith, S.R., 2009. Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling. Philos. T. Roy. Soc. A 367, 4005–4041.

Sparrevik, M., Saloranta, T., Cornelissen, G., Eek, E., Fet, A.M., Breedveld, G.D., Linkov, I., 2011. Use of life cycle assessments to evaluate the environmental footprint of contaminated sediment remediation. Environ. Sci. Technol. 45, 4235–4241.

Sun, K., Keiluweit, M., Kleber, M., Pan, Z., Xing, B., 2011a. Sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. Bioresour. Tech. 102, 9897–9903.

Sun, K., Ro, K., Guo, M., Novak, J., Mashayekhi, H., Xing, B., 2011b. Sorption of bisphenol A, 17a-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars. Bioresour. Tech. 102, 5757–5763.

UE, 2000. European Union Draft directive on sewage sludge, Brussels, pp. 1–20.

Wang, H., Lin, K., Hou, Z., Richardson, B., Gan, J., 2010. Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. J. Soils Sediments 10, 283–289.

Werner, D., Ghosh, U., Luthy, R.G., 2006. Modeling polychlorinated biphenyl mass transfer after amendment of contaminated sediment with activated carbon. Environ. Sci. Technol. 40, 4211–4218.

Xing, B., Pignatello, J.J., 1996. Mechanisms of slow sorption of organic chemicals to natural particles. Environ. Sci. Technol. 30, 1–11.

Zhu, H., Aitken, M.D., 2010. Surfactant-enhanced desorption and biodegradation of polycyclic aromatic hydrocarbons in contaminated soil. Environ. Sci. Technol. 44, 7260–7265.

Zimmerman, J.R., Ghosh, U., Millward, R.N., Bridges, T.S., Luthy, R.G., 2004. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physicochemical tests. Environ. Sci. Technol. 38, 5458–5464.