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Trace Metals and Dissolved Organic Carbon in Biochar Varying with Feedstock Type and Pyrolysis Temperature

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Dedication

This one, with gratitude, is for

Franca, Patrizia, Franco, Lola, Olga

Abstract

The content of carbon in labile forms (e.g. dissolved organic carbon (DOC)) and potentially hazardous inorganic substances (e.g. trace metals) in biochar (BC) may limit or prevent the utilization of BC for environmental remediation purposes. BCs were produced from slow pyrolysis at different temperatures (i.e. 300, 450 and 700 °C) from different types of feedstock (i.e. wood chips (WC), lignin (LG), digested sewage sludge (DSS), and pine bark (PB)). Total trace metal (Cd, Cr, Cu, Ni, Pb, and Zn) concentration, leachability, and bioavailability were investigated in BCs from WC (BCWC), LG (BCLG), and DSS (BCDSS). DOC leachability from BCs was investigated via up-flow percolation test method. The most suitable pyrolysis temperature (450 or 700 °C) for reducing trace metal leachability and bioavailability depends on the trace metal considered. The temperature of 450 °C was effective in stabilizing Cr and Ni in the analyzed BCs as these trace metals were not prone to leaching or present in bioavailable forms. In the tested BCs, an increase in pyrolysis temperature made trace metals such as Zn and Cu more stable in the char matrix, decreasing in the bioavailable fractions, hindering leachability of Zn, and decreasing leachability of Cu to <1 % of the total Cu concentration. Trace metals such as Cd and Pb did not show a clear temperature trend, increasing or decreasing in the bioavailable or leachable fractions depending on the feedstock. Analysis of the up-flow percolation test showed the same temperature related trend in DOC leachability from BCWC and BCLG, with high temperature (700 °C) BCs releasing lower cumulative amounts of DOC compared with low temperature (450 °C) BCs, which were in the range 0.02–0.07 % and 0.06–0.09 % of total carbon (TC) content, respectively. DOC leaching from BCPB varied with pyrolysis temperatures and types of leachant (i.e. urban storm-water runoff (USWR)). For all the adopted pyrolysis temperature, BCPB released cumulative amount of DOC up to 0.01 % of the TC content with pathway USWR. High temperature (i.e. 700 °C) BCPB released lower cumulative amount of DOC (up to 0.02 % of the TC content) with roof USWR. It is likely that the leachant (i.e. pathway USWR) with relatively higher pH and DOC concentration limited the release of DOC from the BC matrix, whereas the types of leachant (i.e. deionized water, and roof USWR) with relatively lower pH and DOC concentrations enhanced the release of DOC from the BC matrix.

Notations

Symbols

C – carbon;
Cd – cadmium;
Cr – chromium;
Cu – copper;
H – hydrogen;
M – molarity;
N – nitrogen;
Ni – nichel;
O – oxygen;
Pb – lead;
S – sulfur;
Zn – zinc.

Abbreviations

BC – biochar;
BCDSS – biochar from digested sewage sludge;
BCDSS450 – biochar from digested sewage sludge at the pyrolysis temperature of 450 ºC;
BCDSS700 – biochar from digested sewage sludge at the pyrolysis temperature of 700 ºC;
BCLG – biochar from lignin;
BCLG450 – biochar from lignin at the pyrolysis temperature of 450 ºC;
BCLG700 – biochar from lignin at the pyrolysis temperature of 700 ºC;
BCPB – biochar from pine bark;
BCPB300 – biochar from pine bark at the pyrolysis temperature of 300 ºC;
BCPB450 – biochar from pine bark at the pyrolysis temperature of 450 ºC;
BCPB700 – biochar from pine bark at the pyrolysis temperature of 700 ºC;
BCWC – biochar from wood chips;
BCWC450 – biochar from wood chips at the pyrolysis temperature of 450 ºC;
BCWC700 – biochar from wood chips at the pyrolysis temperature of 700 ºC;
DOC – dissolved organic carbon;
DSS – digested sewage sludge;
DW – dry weight;
EBC – European Biochar Certificate;
EC – electrical conductivity;
EU – European Union;
FAAS – flame atomic absorption spectrophotometry;
GFAAS – graphite furnace atomic absorption spectrophotometry;
LG – lignin;
PB – pine bark;
TC – total carbon;
TOC – total organic carbon;

WC – wood chips;
WWTP – wastewater treatment plant.

Chemical compounds

$CaCl_2$ – calcium chloride;
CH_4 – methane;
CO – carbon monoxide;
CO_2 – carbon dioxide;
HCl – hydrochloric acid;
HCN – hydrogen cyanide;
HNO_3 – nitric acid;
KCl – potassium chloride.

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Mutter, ich bin dumm

Ascribed to F. M. Nietzsche

Introduction

Problem formulation

Biochar may contain potentially hazardous inorganic substances that may limit or prevent the utilization of biochar for environmental remediation purposes. Biochar contains carbon in labile forms that are prone to be leached as dissolved organic carbon. Physical and chemical characteristics of biochar vary over a wide range depending on the types of feedstock and the production conditions (e.g. pyrolysis temperature). To avoid potential drawbacks when utilizing biochar both in soil and water system application, it is necessary to evaluate biochar trace metal and dissolved organic carbon content and leachability.

Topicality of work

Biochar technology embraces several environmental issues (e.g. soil improvement, waste management, climate change mitigation, energy production, and remediation of contaminated sites) that are at the forefront of the scientific community. Biochar, as a novel technique, is neither regulated nor standardized. Before testing biochar for environmental remediation purposes, physical and chemical characteristics are to be assessed. The content and the extent to which trace metal and dissolved organic carbon are released from biochar limit or prevent the application of biochar for environmental management.

Research object

Trace metal and dissolved organic carbon content and leachability from biochar varying with types of feedstock and pyrolysis temperatures.

Aim of work

The aim of the work was to investigate variability of trace metal and dissolved organic carbon content and leachability of biochars produced for environmental application in soil or water systems.

Tasks of work

1. To assess the influence of feedstock selection and changes in pyrolysis conditions (i.e. pyrolysis temperature) on total trace metal (Cd, Cr, Cu, Ni, Pb, and Zn) concentration, leachability, and bioavailability in biochars from potentially contaminated feedstock;

2. To investigate the influence of the type of feedstock and the production temperature on dissolved organic carbon content of biochar from slow pyrolysis, based on data gathered from the literature;
3. To investigate the influence of the type of feedstock and production temperature on the dissolved organic carbon content and leachability of biochar from slow pyrolysis.

Methodology of the research

A metadata analysis was performed for collecting data related to dissolved organic carbon content of biochar from the literature. Biochar was produced from slow pyrolysis at different temperatures from different types of feedstock. Based on methodologies reported in the literature, physical and chemical properties of biochars were investigated. Up-flow percolation tests were performed based on standard or specific methodology for analyzing trace metal and dissolved organic carbon leachability of biochars.

Scientific novelty of the research

Based on data gathered from the literature, a linear regression of the values of dissolved organic carbon content of biochar from slow pyrolysis was calculated. Physical and chemical characteristics of biochar from different types of feedstock at different pyrolysis temperatures were evaluated. Dissolved organic carbon content and leachability of biochar from several types of feedstock at different pyrolysis temperatures were investigated. Trace metal content, leachability, and bioavailability in biochar from several types of feedstock at different pyrolysis temperatures were assessed. Potential environmental applications were considered for the tested biochars.

Practical value of the results

Understanding the parameters (i.e. feedstock type and pyrolysis temperature) that affect the amount of dissolved organic carbon released by biochar could be an effective tool for designing ad hoc biochar production and application. If pyrolysis can reduce trace metal leachability and availability in biochars from potentially contaminated feedstock, it may also reduce some of the environmental concerns associated with biochar water system application or land application.

1 Trace metals and dissolved organic carbon in biochar review

1.1 Biochar from slow pyrolysis

Biochar (BC) as a filtering media has been reported to be a promising remediating tool for a variety of potential hazardous organic and inorganic substances both in soil and water systems.

The European Biochar Certificate (EBC European Biochar Certificate 2015) specifies that ‘‘Biochar is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralization to CO_2 and may eventually become a soil amendment’’.

BC used for environmental remediation (Zheng et al. 2015) purposes has received considerable attention in recent years both as a filtering media (Chen et al. 2011; Baltrėnas et al. 2015; Komkienė and Baltrėnaitė 2015) and as a soil amendment for releasing nutrients (Mukherjee and Zimmerman 2013), sequestering carbon, enhancing soil quality and sequestering a variety of contaminants, such as trace metals (Karami et al. 2011; Park et al. 2011). As a low-cost sorbent (Ahmad et al. 2014), BC has attracted increasing attention for applications in treating multi-element polluted water such as landfill leachate (Chemerys and Baltrėnaitė 2017) and urban storm-water runoff (USWR) (Beck et al. 2011; Reddy et al. 2014; Tian et al. 2014; Shimabuku et al. 2016; Kuoppamäki et al. 2016).

BC from slow pyrolysis encompasses BC produced in the range of 350–1000 °C in a low-oxygen thermal process (EBC European Biochar Certificate 2015) characterized by a low heating rate (up to 100 °C/s) and a residence time of hours (Spokas et al. 2011).

Feedstock for BC production is subjected to physical and chemical alterations during the pyrolysis process, thereby affecting the properties of the resulting BC matrix (Rehrah et al. 2014). At temperatures below 450 °C, cellulose and hemicellulose decompose into light molecular weight compounds, tending to form pyrolytic vapors (Lee et al. 2013). In the work by Yang et al. (2007), hemicellulose and cellulose were quickly pyrolyzed, with the main weight loss occurring in the range of 220–315 and 315–400 °C, respectively. According to Zhao et al. (2014), a part of the cellulose content of the feedstock does not volatize and contribute to the lignin pool of the biochar produced through pyrolysis process. Lignin decomposes over a wide range of temperature (150–900 °C) (Yang et al. 2007), being the main responsible for BC formation (Lee et al. 2013). Furthermore, the higher is the lignin/cellulose content of the feedstock, the lower/the faster the reaction rate, respectively

(Gani and Naruse 2007). However, researches based on comparisons between thermochemical behavior of single biomass components (i.e. cellulose, lignin and hemicelluloses) may overlook complex interactions occurring during pyrolysis of raw biomass (Liu et al. 2017).

As far as the influence of pyrolysis temperature on the physico-chemical properties of BC is concerned, several authors have reported a shift to higher pH (Jindo et al. 2014; Yuan et al. 2015), higher electrical conductivity (EC) (Al- Wabel et al. 2013; Rehraha et al. 2014), higher ash and total carbon (TC) content (Gundale and De Luca 2006; Cross and Sohi 2011; Aller 2016) with the increase in pyrolysis temperature. Furthermore, increases in pyrolysis temperature result in biochars with higher C content and lower N, H and O contents due to losses of H-and O-containing functional groups and volatile compounds (Novak et al. 2009; Wu et al. 2011; Crombie et al. 2012) and concurrent formation of aromatic C (Rutherford et al. 2012).

1.2 European policies and regulations related to biochar

BC production is a cross-cutting technology addressing issues covered by several European Union (EU) policy areas such as waste management, agricultural policy, climate change, and energy policy (Montanarella and Lugato 2013). At present, no EU regulation or directive expressly refers to BC (Hammond 2016). As regards the use of BC for soil amendment purposes, it is likely that the regulation of BC application to soil could resemble soil amendment guidance relating to sewage sludge and composts (Freddo et al. 2012). The Circular Economy Package (EC 2016) listed BC, as an inorganic soil improver, among the products to be included in the annexes to the new EU fertilizer regulation that is currently under revision. These annexes are expected to set the end-of-waste criteria regarding BC adoption for soil amendment purposes. According to Meyer et al. (2017), once the carbonaceous material obtained through thermochemical treatments (e.g. pyrolysis) of waste biomass ceases to be considered waste because of achieved safety and quality levels and labelled as BC, it might be registered under the REACH directive (EC 2006).

As to meeting feedstock sustainability criteria (EBC European Biochar Certificate 2015), biomass waste with minor or no use are generally selected for BC production. To this respect, BC technology is intimately linked to policy drivers such as sustainable and smart use of resources (EC 2016) that are at the forefront of the European Union.

1.3 Types of feedstock for biochar production

A large variety of feedstock types has been utilized for BC production (Aller 2016). Both pristine feedstock (e.g. forestry residue), that is produced in large quantities with minor or no use, and potentially contaminated feedstock (e.g. phytoremediation biomass, wood processing waste, and sewage sludge) are of particular interest to meet sustainability criteria and add value to biochar production. Although, the European Biochar Certificate (EBC European Biochar Certificate 2015) set a list of materials that are suitable for producing BC with minor or no risks of unintended contamination resulting from BC application to soil or water.

In the present dissertation, forestry residue and biodegradable by-products of industrial processes were considered as feedstocks suitable for biochar production in Lithuania. From the waste management point of view, the pyrolysis of sewage sludge is an interesting technique since it leads to both a reduction in the waste volume and the stabilization of the organic matter (Hossain et al. 2011). In Lithuania, in 2012 the production and disposal of sewage sludge from urban wastewater accounted for 45 thousand tons in dry substance with about 14 % used for agricultural purposes and 26 % utilized for composting and other applications (Eurostat 2015). Between 2001 and 2009 a 78 % decrease in sludge landfilling and a 23 % increase in the agricultural use of sludge was recorded in Lithuania (Kelessidis et al. 2012). Lignin is a massive by-product of biorefinery industries (Li et al. 2014). Almost all of the bagasse obtained from sugar processing is utilized as fuel for boilers by the sugar mill itself. Other processes and products that traditionally rely on it as a raw material are electricity generation, pulp and paper production, and products based on fermentation (Pandey et al. 2000). BCs produced from lignin at moderate temperature are seldom reported even though lignin is used for producing activated carbon through a pyrolysis process (Li et al. 2014). According to Katinas et al. (2007), the total amount of wood and wood waste for bioenergy production is estimated as 4.55 million m^3 solid volume, per year in Lithuania. Pine bark is a biomass waste produced with a great amount per year with minor use (e.g. bark mulch, and energy production), thus it has been investigated for application in bio-filters as a low-cost bio-sorbent (Luo and Lindsey 2006; Dalahmeh et al. 2012). Lithuania produces about 2.5 million m^3 of forest cutting waste per year for potential use in BC production (Baltrėnaitė et al. 2016).

1.4 Trace metals in biochar

BC itself may contain potentially hazardous inorganic substances (Hilber et al. 2017) that may limit or prevent the utilization of BC for environmental remediation purposes. The presence of metals is likely to depend on contaminated feedstock or on the use of processing conditions that may favor their accumulation in BC (Hossain et al. 2011; Lu et al. 2011; Bernardo et al. 2014).

The extent to which trace metals volatize during the pyrolysis process depends on concurrent factors such as the pyrolysis temperature, the concentration of trace metal in the feedstock, and the chemical composition of the feedstock (Buss et al. 2016; Huang et al. 2017). Except for some trace metals (e.g. Cd) that easily volatilize during pyrolysis, trace metals which are initially present in the parent material generally remain and become concentrated in the BCs (Lievens et al. 2008; Yuan et al. 2015; Liu et al. 2017; Roberts et al. 2017). Applying low heating rates and low temperatures (<450 °C) enhances the extent to which Ni is retained in BC during pyrolysis of biomass (Liu et al. 2017). Lu et al. (2015), analyzing the behavior of trace metals in BC produced from sewage sludge at pyrolysis temperatures in the range of 300–700 °C, found that BC retained 90.4–98.3 % of Pb, 96.4–99.5 % of Zn, 92.5–99.3 % of Ni, 85.8–98.5 % of Cd, 81.5–94.5 % of Cu and 70.0–87.5 % of Cr. The thermo-stable behavior of the trace metals during pyrolysis was explained as the result of the transformation of the studied trace metals from mineral salts and hydroxide into oxide and sulphide forms. In the work by Méndez et al. (2012), BC from sewage sludge pyrolyzed at 500 °C had a higher content of Cu (31 %), and Pb (30 %), as well as about 28 % more Ni, Cd and Zn than the feedstock.

Several studies have reported a decrease in metal availability and leachability from BC as a result of physical and chemical alterations occurring during pyrolysis of waste biomass (Lin et al. 2012; Devi and Saroha 2014; Yargicoglu et al. 2015; Roberts et al. 2017). An investigation of plant available trace element concentrations in BC from digested waste water sludge pyrolyzed over a range of temperatures from 300 up to 700 °C, demonstrated that the concentrations of Cd, Cu, and Zn in the diethylene triamine pentaacetic acid extract of BC were lower than those in the feedstock (Hossain et al. 2011). In the study by Lu et al. (2011), sewage sludge from a wastewater treatment plant (WWTP) was pyrolyzed for 2 h at 550 °C. The amount of trace metals such as Zn (1400 mg/kg), Cu (536 mg/kg), Pb (107 mg/kg) and Ni (76.5 mg/kg) detected in the resulting BC posed negligible concern for metal leaching because of their undetectable level (<0.01 mg/l) in the standard toxicity characteristic leaching procedure extract.

Although the concentration, the leachability, and the bioavailability of trace metals in BC have been becoming one of the main focuses of research on the production and characterization of BC, it is still unclear which factors (e.g. pyrolysis temperature and type of feedstock) determine trace metal behavior during pyrolysis process (Evangelou et al. 2014), trace metal concentration and composition in BC (Tan et al. 2015), and leachability from BC (Wu et al. 2016).

1.5 Dissolved organic carbon in biochar

The content and the forms of C in BC varies depending on the types of feedstock (e.g. lignin- or cellulose-rich feedstocks) and the processing conditions (e.g. pyrolysis temperature) (Aller 2016). BC contains C in labile forms that are prone to be leached as DOC. Several studies have reported an influence of feedstock selection and pyrolysis conditions (i.e. heating rate, residence time and temperature) on the content and the extent to which DOC is released from BC (Lin et al. 2012; Mukherjee and Zimmerman 2013; Alburquerque et al. 2014; Graber et al. 2014).

To investigate the influence of the type of feedstock and the production temperature on the DOC content of BC from slow pyrolysis, data were collected from the literature to conduct a metadata analysis. However, when comparing results of DOC analysis it should be considered that the amount of DOC released from BCs assessed via batch tests has been reported to depend on various parameters such as the ratio of the solvent to solute (Mukherjee and Zimmerman 2013), temperature and pH of the extraction solution (Li et al. 2017).

BC has been produced from a large variety of types of feedstock. BC classification depending on the feedstock was adapted from Aller (2016), as follow:

– BC from lignin-rich feedstock (e.g. lignin, tree part, wood, sawdust, almond and cacao shells, and olive stones);

– BC from cellulose-rich feedstock (e.g. cellulose, grasses, straws, grains, stalks, peanut hulls and shells, sugarcane leaves and bagasse, and maize silage);

– BC from manure and waste (e.g. manures, bio-solids, green waste (e.g. mushroom residue, greenhouse waste, and olive pomace)).

With the aim of collecting data related to the present review, the search platform Engineering Village^{TM} (Elsevier, Netherlands) was used. The search criteria were adopted following Gurwick et al. (2013):

– articles published in peer reviewed journals in the period from 2007 to 2016, including relevant articles cited by recent studies or published in the afore mentioned time span;

– articles published in languages other than English were discarded;

– if either the pyrolysis parameters (e.g. temperature, heating rate or residence time) or the type of thermochemical process (e.g. slow pyrolysis) for producing BC were not clearly reported, data were not considered for calculations;

– for the search query the following terms were entered: “biochar”, “dissolved organic carbon”, “water soluble organic carbon”, “water extractable organic carbon”;

– for determining DOC content of BC, we considered only data referring to samples obtained through one-step extraction or stirring methods filtered through a filter with pore size ≤ 0.45-μm.

As for DOC analysis of BC via batch test method, if the measured concentration of DOC in the samples were reported as mg/l, the DOC content (g/kg) of BC was calculated considering the mass of BC and the volume of extractant (Jamieson et al. 2014). To evaluate the temperature-related trend of DOC content of BC, DOC contents of BC were plotted versus the respective pyrolysis temperatures and a relation was determined by step-wise linear regression with slope and intercept considered significant at $p \leq 0.05$.

Figure 1a shows a linear relation between DOC content of BC from slow pyrolysis and the temperatures in the range of 350–790 °C. Lower temperatures (< 350 °C) were not considered as it would have resulted in a strong degree of scatter (data not shown).

The linear relation in Figure 1a does not fit for temperatures higher than 790 °C, as the BC produced at these temperatures would be associated to negative DOC content. There was a weak correlation ($r^2 = 0.1$) of the data with the linear model with intercept (4.1) and slope (–0.005) significant at $p < 0.001$, with a sufficient degree of scatter at temperatures in the range of 350–450 °C (Fig. 1b). The observed weak correlation suggests that not only the peak temperature but also other parameters (e.g. heating rate, residence time, and pressure) of the thermochemical process concur in determining the DOC content of BC. Jamieson et al. (2014) suggested that pyrolysis conditions such as fast heating rates and low residence times may lead to produce BCs that are more prone to leaching DOC. Increasing pyrolysis temperature has been generally reported to result in a decrease in DOC content of BC (Zhang et al. 2015; Smith et al. 2016). However, rising pyrolysis temperatures in the range 350–450 °C have resulted in BC with higher DOC content in the works by Graber et al. (2014) and Luo et al. (2015).

As for the influence of the type of feedstock on DOC content as well as the extent to which it is prone to leaching from BC, several authors have reported that BCs from wood and woody biomass generally release less DOC compared to non-wood biomass (e.g., agricultural residue and animal wastes) (Mukherjee and Zimmerman 2013; Graber et al. 2014).

Alburquerque et al. (2014) observed that the influence of feedstock selection for BC production on the measured DOC concentrations was highest for BC at lower temperatures (i.e. 350 and 450 °C) compared with higher temperature (i.e. 600 °C). According to data retrieved from the literature grouped depending on the type of feedstock and pyrolysis temperature (Fig. 2), mean DOC content of BC from manure and waste (Fig. 2c) was the highest (2.24–5.35 g/kg) in the temperature range of 350–450 °C.

Mean DOC content of BC from cellulose-rich feedstock (Fig. 2a) was the highest (0.69–1.31 g/kg) in the temperature range of 500–650 °C. Mean DOC content of BC from lignin-rich feedstock (Fig. 2b) was the lowest in the temperature range of 350–550 °C (0.12–2.50 g/kg) as well as at 700 °C (0.52±0.35 g/kg).

The extent of DOC leaching from BC and the parent feedstock likely depends on factors such as chemical forms, physical association, and location (bulk or surface) of C (Wu et al. 2011; Mukherjee and Zimmerman 2013).

As for the mechanism that leads to the release of DOC from BC, Jones et al. (2011) suggested that DOC is released at first from the surface and later from the BC matrix following a

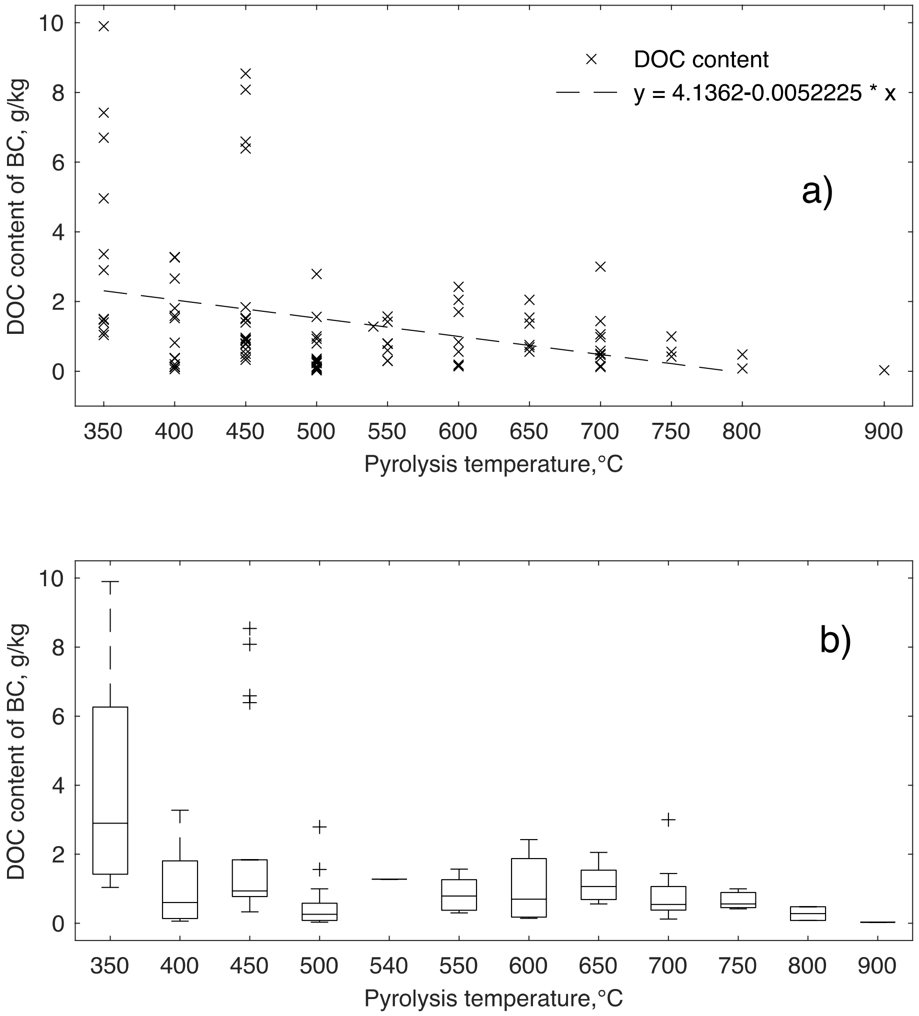

Fig. 1 Scatter plot (a) and box-and-whisker plot (b) for dissolved organic carbon (DOC) content of biochar (BC) from slow pyrolysis. n = 102

Linear regression (a) for the values of DOC content of BC in the temperature range 350–790 °C. Box-and-whisker plots (b) show median (i.e. central line), upper (25%) and lower (75%) quantile (i.e. lower and upper bounds of the box, respectively) of the data, maximum and minimum values outside the central box that are not outliers (vertical lines), and outliers (cross symbols). Adapted from Mancinelli et al (2017a)

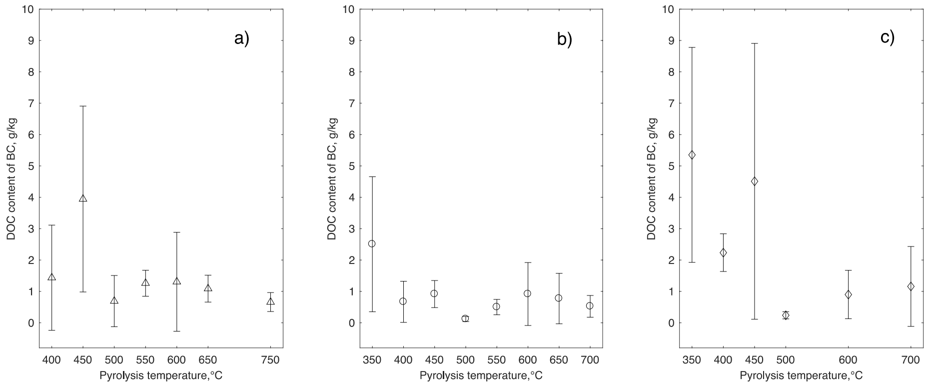

Fig. 2 Mean dissolved organic carbon (DOC) content of biochar (BC) from slow pyrolysis of cellulose-rich feedstock (a), of lignin-rich feedstock (b), and of manure and waste (c). Error bars show standard deviation. n = 33 (a). n = 42 (b). n = 22 (c). Retrieved from Mancinelli et al. (2017a)

diffusion-limited mechanism. Micropores carry the portion of DOC in BC that is more prone to leaching with increasing temperature and pH of the leachant (Li et al. 2017). In column leaching tests performed by Beesley and Marmiroli (2011) and Iqbal et al. (2015), DOC was observed to be rapidly released from biochar with no substantial amount of DOC recorded after a few eluate samples.

1.6 Environmental implications related to trace metals and dissolved organic carbon in biochar

Trace metals in a water-soluble form may represent an environmental issue when they are bioavailable or when they mobilize through soil or water media. In water systems, DOC interacts with dissolved trace metal affecting their mobility and bioavailability through the formation of DOC–metal complexes.

As regards environmental risk caused by metal species within BC, the safe level of BC application to soil depends on the metal content of the biomass feedstock and the pyrolysis conditions (McHenry 2009; Shackley et al. 2010). Trace metals such as Cd and Pb are non-essential elements, having no definite biological function in organism and plant (Bolan et al. 2013). Therefore, introducing trace amount of bioavailable Cd and Pb in soil through BC land application is highly undesirable (Wu et al. 2016).

BC-borne DOC may represent a source of impairment of aquatic environment containing organic species producing an inhibitory effect on the growth of aquatic micro-organisms (Smith et al. 2012), increasing metal mobility through complexation, and altering redox reactions and speciation of metals (Qu et al. 2016). Uchimiya et al. (2013) observed that DOC released by BCs in the temperature ranging 350–500 °C was enriched with carboxyl and poly(phenolic) functionalities that are able to affect metal mobilization via complexation with metal ions.

Formation of DOC metal complexes competing with the adsorption capacity of BC (Iqbal et al. 2015) and fouling of BC surface (Ulrich et al. 2015) have been reported as potential negative effect of DOC on the BC effectiveness in filtering polluted water.

Furthermore, BC-borne DOC may reduce BC effectiveness in carbon sequestration (Wu et al. 2011; Liu et al. 2016). Having lower aromaticity and less fused aromatic structures than bulk biochar, DOC is expected to have lower environmental recalcitrance (Qu et al. 2016). Regarding the recalcitrance of BC-borne DOC in water media (i.e. river water), Norwood et al. (2013) has reported a half-life of 30–40 days for DOC from biochar at 250 °C.

BC may be subject to post production treatment (e.g. rinsing) to limit the release of DOC (Ngueleu et al. 2014). Although, from a sustainable point of view, producing BC with no need for treatments that may be water demanding or energy consuming should be the first choice. Hence, to limit the content of DOC in BC, Smith et al. (2016) has suggested to adopt pyrolysis temperatures above 400 °C.

However, the environmental implications of biochar-derived DOC have not been well elucidated, and further studies are on demand (Luo et al. 2015).

2 Materials and methods

2.1 Feedstock and biochar production

Four types of biodegradable materials were selected as feedstock for BC production. As to be representative of widely available types of feedstock in Lithuania, materials for producing biochar were selected as follow:

– as potentially contaminated feedstock, three types of bio-degradable by-products of industrial processes were chosen (i.e. wood chips (WC), lignin (LG), and digested sewage sludge (DSS);

– as pristine feedstock, pine bark (PB).

DSS was collected from an urban waste water treatment plant in Klaipėda which is the third largest city in Lithuania, with a population of about 159 thousand people in 2013. Sewage sludge production in Klaipėda county has been calculated as 47 thousand tonnes per year (Havukainen et al. 2011). Sewage sludge was subjected to digestion, dewatering and low-temperature drying treatment.

WC were provided by a sawmill in Kaliningrad, Russian Federation. In 2006, 21 % (362 thousand tonnes) of the total wood waste imported to the European Union came from Russia (Villanueva et al. 2010).

LG was produced as a by-product of a sugar refining industry based in Lithuania.

PB was collected from the stem of Scots pines (*Pinus silvestris L.*) in the forest stands located in the premises of Vilnius Gediminas Technical University in Vilnius, Lithuania. Samples were collected from the external surface of stem bark at a height of about 1.5 m above ground. The bark samples were considered representative of a relatively clean suburban area as the sampling area was subjected to no point neither linear (distance from roads >100 m) sources of air pollution. Scots pine was selected as it is a widespread tree species in several European areas and it is abundant in Lithuania. Of the total area covered by forests (about 2 million ha) in Lithuania, about 35.5 % (721 thousand ha) consists of Scots pine forests (Krakau et al. 2013). Of the 8.97 million m^3 trees that are annually felled in Lithuania, Scots pine represents the most felled (29.3 %) tree species with about 2.6 million m^3 (Kuliešis et al. 2016).

The physico-chemical properties of the four types of feedstock are listed in Table 1. The quantity of air-dried feedstock used for pyrolysis at 450 °C was 1070 g WC, 430 g LG, 1750 g PB, and 830 g DSS whereas the amount used at the pyrolysis temperature of 700 °C was 1400 g WC, 1050 g LG, 2750 g PB, and 1330 g DSS.

The pyrolysis of the raw materials was carried out according to the procedure described elsewhere (Komkiene and Baltrenaite 2016). Air dried feedstock was weighed and wrapped in aluminium foil in order to create an oxygen-limited environment. Slow pyrolysis was

Table 1 Electrical conductivity (EC), pH, ash and moisture content of the feedstock

	pH	EC (μS/cm)	Moisture content, %	Ash content, %
WC	N. D.	124.3	15.08	1.31
LG	5.40	928.4	7.70	23.34
PB	3.45 ±0.02	66.4 ±4.8	15.23 ±0.05	1.75 ±0.05
DSS	6.92	5487.3	6.54	33.03

Values are shown as the mean value of two observations (n = 2) for the samples from WC, LG, and DSS. Values are shown as the mean value of three observations (n = 3) ± standard deviation for the samples from PB. N. D. – not determined

performed in a E5CK-T muffle furnace with a heating rate of about 10 °C/min, under oxygen-limited conditions, and under atmospheric pressure. Pyrolysis was performed at the peak temperatures of 300, 450 and 700 ± 5 ºC.

The peak temperatures were chosen to be representative of charring stages occurring during biochar formation (i.e. the temperature of 300 °C for amorphous char (200–350 °C), temperature of 450 °C for composite char (350–500 °C), and the temperature of 700 °C for turbostratic char (>500 °C)) (Keiluweit et al. 2010; Zhao et al. 2014). Biochar is produced at temperatures ≥350 °C (EBC European Biochar Certificate 2015). However, different studies labelled as biochar the carbonaceous solid product of pyrolysis process at temperatures in the range 250–300 °C (Liu et al. 2016; Zhang et al. 2015; Smith et al. 2016; Yue et al. 2016).

The holding time at the desired peak temperatures was of 2 h. Each of the production combinations (the four types of feedstock at two different pyrolysis temperatures) was repeated three times. At the end of the production process, the samples were left to cool in the muffle furnace overnight. In order to determine the yield of BC, the obtained BC samples were weighed at the end of the production process.

The obtained BCs were assigned the following codes:

– BCWC450 and BCWC700 for BC from wood chips (BCWC) at the pyrolysis temperatures of 450 and 700 °C, respectively;

– BCLG450 and BCLG700 for BC from lignin (BCLG) at the pyrolysis temperatures of 450 and 700 °C, respectively;

– BCPB300, BCPB450 and BCPB700 for BC from pine bark (BCPB) at the pyrolysis temperatures of 300, 450 and 700 °C, respectively;
– BCDSS450 and BCDSS700 for BC from digested sewage sludge (BCDSS) at the pyrolysis temperatures of 450 and 700 °C, respectively.

2.2 Physical analysis of the feedstock

The present dissertation is based on the results of research activities performed at the laboratories of the Institute of Environmental Protection and the Department of Environmental Protection of Vilnius Gediminas Technical University during two visits under the Erasmus Programme. Therefore, the methods followed slightly differed depending on the aims of the performed researches as well as on time and resource constraints.

Feedstock for BC production is subjected to physical and chemical alterations (e.g. attrition, cracking, micro-structural rearrangement) during the pyrolysis process, thereby affecting the properties of the resulting BC matrix (Rehrah et al. 2014). Therefore, the methods adopted to determine the physico-chemical characteristics of the BC and the feedstock are often dissimilar. Whenever possible, in the present dissertation, the same methods were adopted for the analysis of both the BCs and the feedstock in order to facilitate the comparison of the results.

As regards the moisture content of the feedstock, samples were put in crucibles, weighed and heated in an oven to a temperature of 105 °C for 2 h according to *ISO 18134-2:2015 – Solid biofuels - Determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method*. The crucibles were allowed to cool down at room temperature in a desiccator, then weighed again. This process was repeated, heating the samples for 1 h until the weight was stabilised.

In order to determine the ash content of WC, LG, and DSS, the samples were put in crucibles, weighed and heated to a temperature of 450 °C for 150 min in an E5CK-T muffle furnace (Pundytė et al. 2011). The samples were left to cool in the muffle furnace overnight then weighed in order to determine the mass loss. This process was repeated until the weight of the residue was stabilised. To determine the ash content of PB, the samples were put in crucibles, weighed, and heated to a temperature of 550 °C for 1 h in an E5CK-T muffle furnace according to the guidelines of EBC (EBC European Biochar Certificate 2015). An analytical balance (Kern 770, Germany) with a sensitivity of 0.0001 g was used.

The EC of PB was measured with a conductivity metre (inoLab Cond 740 WTW) using a water extract with a mass ratio of 1:10 (weight/volume) after shaking (RS12 Rotoshake, Gerhardt, Germany) for 1 h at 20 rpm and filtering through high-quality filter paper (KA2, pore size 10–25 μm, Czech Republic) according to the guidelines of EBC (EBC European Biochar Certificate 2015). The EC of WC, DSS and LG was measured with a conductivity meter (inoLab Cond 740 WTW) using a water extract with a mass ratio of 1:5 (water/dry solid) after shaking (RS12 Rotoshake, Gerhardt) for 20 minutes at 20 rpm and filtering through high quality filter paper (KA2, pore size 10–25 µm) (Thompson et al. 2002 cited in Johnsson et al. 2005).

2.3 Physical analysis of the biochars

The moisture content of the BCs was measured according to the method mentioned in *ASTM D1762−84: The Standard Test Method for Chemical Analysis of Wood Charcoal*. In order to determine the moisture content, 1g BC samples were weighed and then heated at 105 °C in an open crucible until the weight was stabilised. An analytical balance (Kern 770) was used.
The ash content of BCWC, BCLG, and BCDSS were measured according to the method mentioned in *ASTM D1762−84: The Standard Test Method for Chemical Analysis of Wood Charcoal*. The samples were heated in an E5CK-T muffle furnace to a temperature of 750 °C for 6 h. To determine the ash content of BCPB, the samples were put in crucibles, weighed, and heated to a temperature of 550 °C for 1 h in an E5CK-T muffle furnace according to the guidelines of EBC (EBC European Biochar Certificate 2015). For weighting the samples, an analytical balance (Kern 770) was used.

EC measurements of BCWC, BCLG, and BCDSS were performed in 1% (w/w) solution of BC in deionised water with a conductivity meter (inoLab Cond 740 WTW) after stirring for 20 min at laboratory temperature (Ahmedna et al. 1997 cited in Reharaha et al. 2014). The EC of BCPB was measured with a conductivity meter (inoLab Cond 740 WTW) using a water extract with a mass ratio of 1:10 (weight/volume) after shaking (RS12 Rotoshake, Gerhardt) for 1 h at 20 rpm and filtering through high-quality filter paper (KA2, pore size 10–25 µm) according to the guidelines of EBC (EBC European Biochar Certificate 2015).

2.4 Chemical analysis of the biochars and the feedstock

The pH value of DSS and LG was determined in a 1:5 volume ratio 1 M KCl (Merck, Germany) according to the method mentioned in *ISO 10390 2005: Soil quality Determination of pH*. Ten ml of LG or DSS were added to 50 ml of potassium chlorate, then shaken (RS12 Rotoshake, Gerhardt) for 60 min at 20 rpm. The suspension was allowed to stand for 60 min before measuring the pH with an electronic glass electrode (SevenMulti ion/pH/ORP module Mettler Toledo, Switzerland). The pH value of PB was determined in a 1:5 volume ratio 0.01 M $CaCl_2$ according to the method mentioned in the guidelines of EBC (EBC European Biochar Certificate 2015).

Before measuring the pH, the pH-meter was calibrated with buffer solutions at pH 4, 7, and 10 and the resulting calibration curve was determined using a linear regression analysis.

The pH value of BCWC, BCLG, and BCDSS was measured in 1:20 w/v ratio 1 M KCl (Merck) solution, according to a method described in Carrier et al. (2012). Three grams of BC were added to 60 ml of potassium chlorate, then shaken (RS12 Rotoshake, Gerhardt) for 30 minutes at 20 rpm. The pH value of BCPB was determined in a 1:5 volume ratio 0.01 M $CaCl_2$ according to the method mentioned in the guidelines of EBC (EBC European Biochar Certificate 2015). Before measuring the pH, the pH-meter was calibrated as described above for the pH determination of the feedstock.

Aliquots of about 1–3 mg dried (105 °C) ground PB and BCPB were tested for C, H, N, S, and O with a CHNS-O elemental analyser (EuroVector EuroEA3000 series, Italy). For C, H, N, and S determination, samples were placed in tin capsules and the elemental analyser was run in combustion mode. Analysis of oxygen was performed separately from CHNS analysis. Samples were placed in silver capsules and the elemental analyser was run in pyrolysis mode.

DOC concentration in the BCs was determined via a batch test method. Water extracts were prepared using a 1:20 (w:v) suspension after shaking (RS12 Rotoshake, Gerhardt) for 180 min according to a method described in Dias et al. (2010). Samples of BCWC, BCLG, and BCDSS were filtered through a syringe (pore size 0.45 µm, Pall Corporation, USA). Samples of BCPB were filtered through cellulose acetate 0.45 µm pore size filter paper (Prat-Dumas, France). DOC was determined by a Total Organic Carbon (TOC) analyser (Shimadzu-V CSN, Japan). Samples were stored at 4 ºC in the dark till DOC analysis was accomplished.

Total carbon (TC) in the BCs was determined according to Vaitkutė et al. (2010), with slight modifications. The fraction of BC samples passing through a 900 µm sieve (Retsch) was selected for TC determinations, and no further grinding was done. TC content was measured on aliquots of 0.025–0.028 mg using a Total Organic Carbon Analyzer TOC-V Shimadzu equipped with a solid sample module SSM-5000 (Shimadzu) via dry combustion at 900 °C.

Total trace metal (Cd, Cr, Cu, Pb, Ni, and Zn) content was determined for both the potentially contaminated feedstocks (i.e. WC, LG, and DSS) and the resulting BCs (i.e. BCWC, BCLG, and BCDSS). Prior to digestion, the samples of the feedstock and the BCs were reduced to ash following the steps described in Pundytė et al. (2011). Prior to FAAS or GFAAS analysis, a 0.5-g ash sample was mixed with an aqua regia solution (3 ml HNO_3 (65 %) and 9 ml of HCl (37 %)) then heated in an Ethos 900 Milestone Microwave digestion system for 52 min. In order to eliminate any solids remaining after the digestion process, samples were filtered through high-quality filter paper (KA2, pore size 10–25 µm). The resulting sample was poured into a 50-ml flask, and the volume was made up to 50 ml with deionised water (Butkus and Baltrenaitė 2007). The concentration in solution was measured using flame atomic absorption spectrophotometry (FAAS) (210VGP atomic absorption spectrophotometer Buck Scientific, USA). When the concentration of trace metals such as Cd, Cu, and Pb was too low to be accurately detected by FAAS, a graphite furnace (GFAAS) was used. The detection limits of Cu, Cr, Ni, and Zn were 0.1, 0.2, 0.2, and 0.04 mg/l using FAAS. The GFAAS detection limits of Cd, Cu, and Pb were 0.0001, 0.001, and 0.002 mg/l, respectively. All the procedures were carried out in accordance with the methods mentioned in *CEN/TS 16188:2012: Sludge, treated biowaste and soil—Determination of elements in aqua regia and nitric acid digests—Flame atomic absorption spectrometry method (FAAS).*

Bioavailable trace metal (Cd, Cr, Cu, Ni, Pb, and Zn) concentrations in BCs (i.e. BCWC, BCLG, and BCDSS) were determined according to Carrier et al. (2012). A wet digestion in 1 % citric acid (>99.5 % purity, AVSISTA, Lithuania) was carried out by adding warmed (80 °C) 1% citric acid (50 ml) to weighed BC samples (2.5 g) in 250-ml test tubes. The solutions were heated (DK 20 Heating Digester VELP SCIENTIFICA, Italy) to 80 °C for 10 min and shaken. This procedure was repeated three times. The resulting sample was filtered through high-quality filter paper (KA2, pore size 10–25 μm) and poured into a 50-ml flask. The concentration in solution was measured using the FAAS method. When the concentration of trace metals such as Cd, Cu, and Pb was too low to be accurately detected by FAAS, the GFAAS method was adopted.

2.5 Trace metal and dissolved organic carbon leachability via up-flow percolation test

Up-flow percolation tests were performed in order to assess trace metal and DOC leachability from biochars. Figure 3 shows the apparatus that was employed for the up-flow percolation test.

Leaching behavior of Cd, Cr, Cu, Ni, Pb, and Zn from BCWC, BCLG, and BCDSS was investigated according to the methodology described in *CSN P CEN/TS 14405: Characterisation of waste—Leaching behavior tests—Up-flow percolation test (under specified conditions).* Each column with a diameter of 5.5 cm was packed with BCWC, BCLG, and BCDSS to a height of 27.4±0.5 cm. The leachant (i.e. deionized water) was forced through each column from the bottom to the top at approximately 12 ml/h, and the eluate was collected in glass bottles by means of plastic tubes. The leachant was circulated upward in order to displace air from pores and to minimize preferential flow in the packed material (Mohanty and Boehm 2015).

For FAAS or GFAAS analysis, about 50 ml of the eluate from the collected sample was filtered through sterile Acrodisc syringe filters with a Supor (hydrophilic polyethersulfone) membrane and pore size 0.45 μm (Pall Corporation). Trace metals (Cd, Cr, Cu, Ni, Pb, and Zn) were determined by FAAS or GFAAS analysis. All the procedures were carried out in accordance with the methods mentioned in *ISO 8288: Water quality—Determination of cobalt, nickel, copper, zinc, cadmium and lead—Flame atomic absorption spectrometric*

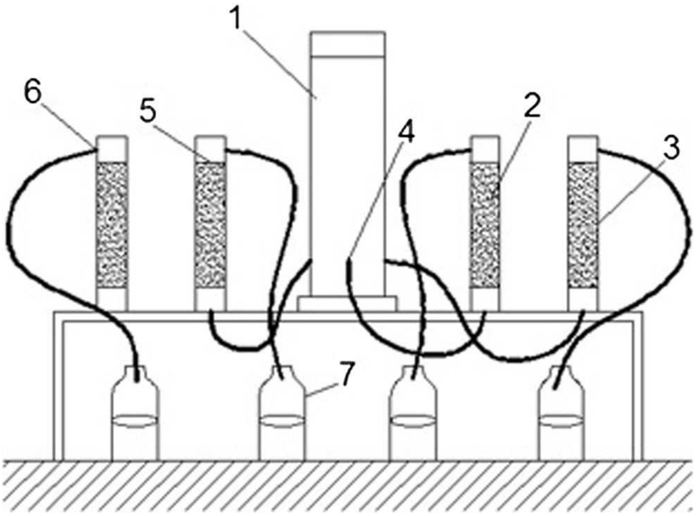

Fig. 3 The setup of the up-flow percolation test. 1—column containing the leachant; 2—material to test; 3—column; 4—leachant inlet; 5—top layer of material to test; 6—leachate outflow; 7—bottles for collecting the eluate. Retrieved from Mancinelli et al. (2016)

methods; ISO 9174: Water quality—Determination of chromium—Atomic absorption spectrometric methods.

The eluate collected during the up-flow percolation test of BCWC and BCLG at liquid to solid (L/S) ratios equal to 1, 3, and 5 l/kg dry weight (DW) was analyzed for EC, pH and DOC measurements. DOC measurements were taken only in the eluates collected from the up-flow percolation test performed on BCWC450, BCWC700, BCLG450, and BCLG700. These BCs were selected for testing DOC leaching behaviour because of the TC analysis results that are discussed in the results section.

The first volume of eluate equal to a cumulative L/S ratio of 1 l/kg DW (i.e. 0.137, 0.131, 0.210, 0.317 litres of eluate from BCWC450, BCWC700, BCLG450, and BCLG700, respectively) was not analysed for DOC. At the beginning of the column leaching test (i.e. until L/S ratios of 0.1 or 0.5 l/kg DW), labile species may be rapidly released by the tested material with the resulting elution curve showing a first flush behaviour (Van der Sloot and Dijkstra 2004). DOC measurements were taken for the eluate collected at L/S ratios equal to 1, 3, and 5 l/kg DW, thus not considering the fraction of DOC in BCLG and BCWC that is subject to rapid washout.

For DOC analysis, samples of about 40 ml volume were taken from the eluate collected during the up-flow percolation test. After filtering the samples through a syringe (pore size

0.45 µm, Pall Corporation), DOC was determined by employing a total organic carbon (TOC) analyzer (Shimadzu–V CSN).

EC and pH were measured immediately after sampling on the whole water sample. EC was measured with a conductivity meter (inoLab Cond 740 WTW) in accordance with the methodology of *ISO 7888: Water quality – Determination of electrical conductivity*. pH was measured with an electronic glass electrode (SevenMulti ion/pH/ORP module Mettler Toledo) after calibrating the pH-meter as described above for the pH determination of the feedstock. pH measurements were carried out in accordance with the methodology described in *ISO 10523: Water quality – Determination of pH.*

Changes in DOC levels of USWR after up-flow percolation tests with PB and BCPB were investigated by the means of the apparatus shown in Figure 3.

Two impervious surfaces were selected to represent an urban environment and to deliver USWR samples supposed to be characterized by different chemical parameters because of differences in material composition and usage (Göbel et al. 2007). The two impervious surfaces were in the premises of Vilnius Gediminas Technical University, in Saulėtekio Street, Vilnius, Lithuania. USWR samples were collected from the downspouts of a roof of a building located along Saulėtekio Street (54° 43′ 27.70″ N, 25° 20′ 03.70″ E). The gutters, the downspouts, and the roofing material are all made of galvanized metal. USWR samples were collected from a ditch along a pathway in a pedestrian zone (54° 43′ 15.56″ N, 25° 20′ 15.35″ E). The ditch drains the USWR coming from a meadow and a pathway surface. Both the ditch and the pathway are made of concrete.

USWR samples were collected during two storm events on 29 May and 7 June 2017. The characteristics of the monitored rainfall events, the flow-rate measured during the sampling of USWR, and the measured chemical parameters are shown in Table 2.

The meteorological data were provided by the meteorological station of Vilnius University located in Vilnius (54° 40′ 58.39″ N, 25° 15′ 38.23″ E), being about 6 km far from the sampling sites. USWR samples were collected manually by taking grab samples directly from the drainage flow. Sequential sampling was performed collecting multiple samples (about 5 l each) in pre-cleaned polyethylene bottles till the cumulative volume of 25 l was reached for each site. Measurements of the flow-rate of the runoff water were done at the time of sampling according to Spurlock (1999).

Each column was packed with 100 g DW of PB, BCPB300, BCPB450, and BCPB700 (Fig. 3). The whole water samples (i.e. USWR samples from the roof and pathway surface) were utilized as leachant for up-flow percolation tests. Up-flow percolation tests were performed in duplicate for each type of leachant for each type of material. Eluates were collected at L/S ratios equal to 0.5, 1, 2, 3, and 5 l/kg DW equivalent to the volume of 50, 100, 200, 300, and

Table 2 Rainfall conditions, flow-rate and chemical parameters measured in the urban storm-water (USWR) runoff samples collected during two storm events on 29 May and 7 June 2017

Type of surface	Date	Antecedent dry period (days)	Daily precipitation (mm)	Flow-rate of USWR (l/s)	Chemical parameters of USWR		
					pH	EC, µS/cm	DOC, mg/l
Roof	29–5	2	0.25	0.04 ±0.01	6.76 ±0.19	41.8 ±13.0	19.1 ±5.9
Pathway	7–6	1	7.87	0.07 ±0.01	8.07 ±0.1	81.7 ±14.4	25.7 ±4.4

Flow-rates and chemical parameters are shown as the mean value (n = 5) ± standard deviation. EC – electrical conductivity; DOC – dissolved organic carbon

500 ml, respectively. The leachant was circulated upward to assure thorough contact between the DOC in the leachant and the surface of BC (Iqbal et al. 2015).

The USWR samples and the eluates from PB and BCPB were characterized for water chemical parameters (i.e. pH, EC, and DOC concentrations). EC and pH were determined immediately after sampling on the whole water sample (i.e. samples of USWR and the eluates). For determination of EC and pH in USWR samples, an aliquot of 100 ml was retrieved from each sub sample of about 5 l each. EC was measured with a conductivity meter (inoLab Cond 740 WTW) in accordance with the methodology of *ISO 7888: Water quality – Determination of electrical conductivity*. pH was measured with an electronic glass electrode (SevenMulti ion/pH/ORP module Mettler Toledo) after calibrating the pH-meter with buffer solutions as previously described for pH analysis of the feedstock. pH measurements were carried out in accordance with the methodology described in *ISO 10523: Water quality – Determination of pH.* After EC and pH determinations, the USWR and the eluate samples were vacuum filtered, 0.45-µm pore size cellulose acetate filter (Prat-Dumas), and stored in the dark at 4 °C till DOC analysis. DOC was determined by employing a TOC analyzer (Shimadzu–V CSN).

2.6 Quality assurance

For quality assurance, measurements were repeated three times. If not specified, samples from BCWC, BCLG, and BCDSS were prepared in duplicate. If not specified, samples from

BCPB were prepared in triplicate. Standard solutions of Cd, Cr, Cu, Ni, Pb and Zn (1000 ppm) (Buck Scientific, USA) were used for FAAS or GFAAS calibration. All the chemicals used in this study were of analytical grade and the solutions were prepared with deionised water. Concentrated nitric (65 %) and hydrochloric (35 %) acid was employed for the digestion of the samples. For GFAAS and FAAS analysis, in order to monitor for possible contaminations deriving from the sample preparation procedure, for every three samples a reagent blank was prepared following the entire sequence of steps as described above for total trace metal determination in DW. For citric acid extractable trace metal determination using the FAAS and GFAAS methods, a reagent blank was prepared following the entire sequence of steps as previously described for trace metal analysis in citric acid extraction. For pH analysis in KCl extract, a blank sample was prepared following the entire sequence of steps as described for pH analysis. For the up-flow percolation test, two blanks were collected from a column filled with the leachant (i.e. deionised water) following the steps described in *CSN P CEN/TS 14405*.

For DOC determination in BCWC, BCLG, and BCDSS, two blank samples were prepared following the entire sequence of steps, as described for DOC analysis.

To check for any possible DOC contamination during field sampling and travel to the laboratory, on each sampling site a container for collecting USWR was filled with deionized water and transferred to the laboratories for DOC analysis. Aliquots of field blanks were subsequently utilized for testing possible additional contamination of DOC from laboratory equipment, filling an empty column of the up-flow percolation test apparatus with aliquots of field blanks and preparing two blank samples following the entire sequence of steps as described for the up-flow percolation test. In each sample the coefficient of variance of the measurements of DOC was under 2 %.

2.7 Calculation and statistical analysis of experimental data

Statistical analysis was carried out using Excel (Microsoft, USA) and MATLAB R2016b (Mathworks, USA). The descriptive statistics of the data were defined by calculating the mean and standard deviation (St. Dev.) values for the observations with $n \geq 3$.

Analysis of variance (ANOVA) was used to test differences between the data obtained in the present research study. Two-way ANOVA was performed to evaluate significant differences between the physical and chemical parameters (i.e. measurement value) grouped depending on the types of feedstock (i.e. WC, LG, and DSS) or the pyrolysis temperatures (i.e. 450, and 700 °C). Comparisons between the physical and chemical parameters and the types of material (i.e. PB, BCPB300, BCPB450, and BCPB700) were carried out suing two-way ANOVA. Differences were reported as significant ($p < 0.05$) or non-significant ($p > 0.05$).

When the Bartlett test rejected the null hypothesis that the data come from normal distribution with equal variance, Welch's t-tests were evaluated for the null hypothesis that two groups have equal means at 5 % significance level.

To evaluate possible relations among the water chemical parameters (i.e. pH, EC, and DOC concentrations) measured in the eluate samples of the up-flow percolation tests with USWR, relations were determined by step-wise linear regression with slope and intercept considered significant at $p \leq 0.05$.

The analysis of the blank samples showed that elements such as Cd (0.0003 mg/l), Cr (0.2 mg/l), and Pb (0.0317 mg/l) had a mean concentration above the detection limit. Therefore, for the computation of the concentration C (mg/kg DW) of metals in DW, a correction was applied by subtracting the mean concentration detected in the blank analysis B (mg/l) from that obtained in the analysis of the digested ashes A (mg/l), as follows:

$$C = \frac{(A - B) \times D \times V}{m} \tag{1}$$

where D is the dilution factor equal to 10 applied for the determination of Zn using the FAAS method and Cd using the GFAAS method both for the analyzed types of feedstock and for the biochar; V is the final volume, ml; m is the dry weight mass of the sample, g.

BC yield (Y) was calculated according to Lu et al. (2015), as follows:

$$Y, \% = \frac{W_2}{W_1} \times 100 \tag{2}$$

where W_1 is the dry weight mass of the feedstock (g); and W_2 is the dry weight mass of biochar (g).

In order to assess the ability of the pyrolysis process to concentrate the trace metals in the produced BCs (i.e. BCWC, BCLG, and BCDSS), the retention rate (RR) of trace metals in BCs was calculated as the ratio of trace metal concentration in BCs (C_2, mg/kg DW) and the respective feedstock (C_1, mg/kg DW) (Lu et al. 2015), according to the following equation:

$$RR = Retention\ rate, \% = \frac{C_2}{C_1} \times \frac{W_2}{W_1} \times 100 \tag{3}$$

where: W_1 – dry weight mass of the feedstock, g; W_2 – dry weight mass of biochar, g.

As far as the up-flow leaching test is concerned, for each set L/S ratio, the cumulatively released quantity ($\sum U_i$) of an element, mg/kg DW, were calculated for analysis in the eluate fraction as described below:

$$\sum U_i = \frac{\sum(V_i \times C_i)}{m_0} \tag{4}$$

where: V_i – volume of the eluate fraction, *l*; *i* – index of the eluate fraction from 1 to 7; C_i – concentration of the analysed element in the eluate fraction mg/l; m_o – dry mass of the test portion in the column, kg.

When the concentration of a studied element in an eluate fraction was below the detection limit the values were displayed as the upper limit (i.e. U_i is calculated considering C_i equal to the detection limit) and the lower limit (i.e. U_i is calculated considering C_i equal to zero) (CSN P CEN/TS 14405).

Carbon loss (C_{loss}, %) (i.e. the content of carbon of the feedstock that is not retained in the biochar during pyrolysis) resulting from pyrolysis of PB at different peak temperatures was calculated using the equation adapted from Zhao et al. (2014), as follow:

$$C_{loss} = \left[1 - \left(\frac{W_1 \times Y \times TC_2}{W_1 \times TC_1}\right)\right] \times 100 \tag{5}$$

where W_1 is the dry weight mass of the feedstock, g; TC_1 and TC_2 is the total carbon content of the feedstock and the biochar, respectively, %; Y is the BC yield defined in equation (2), %.

The dissolved organic carbon (DOC; g/kg) contents of BCs and PB were calculated using the following equation adapted from Jamieson et al. (2014):

$$DOC = \frac{V \times C}{M} \tag{6}$$

where V – volume of deionized water utilized as extractant, l; M – dry mass of biochar, g; C – measured concentration of DOC in the sample, mg/l. DOC concentrations measured in the samples prepared from BCWC, BCLG, and BCDSS were corrected by subtracting the mean concentration (20.4 mg/l), as measured in the blank samples.

The cumulative released quantity ($\sum_i DOC_i$) of DOC expressed as a percentage of total carbon content of BCWC and BCLG was calculated as follows:

$$\sum_{i} \frac{DOC_i}{TC} \times 100 = \sum_{i} \frac{V_i \times C_i}{M} \times \frac{1}{TC} \times 100 \tag{7}$$

where DOC_i – dissolved organic carbon content, g/kg; TC – total carbon content of biochar, g/kg; i – index of the eluate fraction from 1 to 3; V_i – volume of deionised water utilised as eluate, l; C_i – measured concentration of DOC in the sample, mg/l; M – dry mass of biochar, g.

Dissolved organic carbon (DOC, mg/l) released by PB and BCPB during up-flow percolation test with urban storm-water runoff was calculated as follow:

$$DOC_i = C_i - C_{USWR} - B_f - B_l \tag{8}$$

where C_i – measured concentration of DOC in the eluates collected during up-flow percolation test, mg/l; C_{USWR} – mean concentration of DOC measured in the samples of urban storm-water runoff, mg/l; B_f – mean concentration of DOC (3.49 mg/l) measured in the field blanks, mg/l; B_l – mean concentration of DOC (8.31 mg/l) measured in the laboratory blanks, mg/l.

The cumulative released quantity ($\sum_i DOC_i$) of DOC expressed as a percentage of TC content of PB and BCPB was calculated as follow:

$$\sum_{i} \frac{DOC_i \times V_i}{M} \times \frac{1}{TC} \times 100 = \sum_{i} \frac{\left[C_i - C_{USWR} - B_f - B_l\right] \times V_i}{M} \times \frac{1}{TC} \times 100 \tag{9}$$

where DOC_i – dissolved organic carbon calculated as in equation (8), mg/l; TC – total carbon content of the tested material, g/kg; i – index of the eluate fraction from 1 to 5; V_i – volume of urban storm-water runoff utilized as leachant, l; C_i – measured concentration of DOC in the eluates collected during up-flow percolation test, mg/l; C_{USWR} – mean concentration of DOC measured in the samples of urban storm-water runoff, mg/l; B_f – mean concentration of DOC (3.49 mg/l) measured in the field blanks, mg/l; B_l – mean concentration of DOC (8.31 mg/l) measured in the laboratory blanks, mg/l; M – dry mass of PB and BCPB, g.

3 Results

3.1 Biochar production

Figure 4 shows the BC yield from each feedstock for the adopted pyrolysis temperatures. Pyrolysis at a temperature of 450 °C resulted in a BC yield from WC, LG, and DSS varying in the range of 23.1–65.5 % (Fig. 4a). The mean yield of BCWC450 was the lowest (27.1 %), being about 1.7, 2.1 and 2.3 times lower than the yield of BCPB450 (46.6 %), BCDSS450 (56.5 %), and BCLG450 (61.7 %), respectively. The mean yield of BC from WC, LG, and DSS varied between 18.4 and 51.4 % for the pyrolysis temperature of 700 °C (Fig. 4a), with the highest being found for BCDSS700 (46.4 %), followed by BCLG700 (45.6 %), which is about twice the yield of BCWC700 (20.2 %). The yield of BCLG was about 2.3 times higher than that of BCWC for both the adopted pyrolysis temperatures. The BC yields from WC, LG, and DSS decreased in the range of 17.9–26.1 % from the pyrolysis temperature of 450 to 700 °C.

Figure 4b shows the biochar yield from PB for the three pyrolysis temperatures adopted. The mean yield of BCPB300 was the highest (68.7 %), being about 1.5 and 2.2 times higher than the yield of BCPB450 (46.6 %) and BCPB700 (31.8 %), respectively. Each BCPB yield obtained at lower temperature was significantly higher than the one obtained at higher temperature.

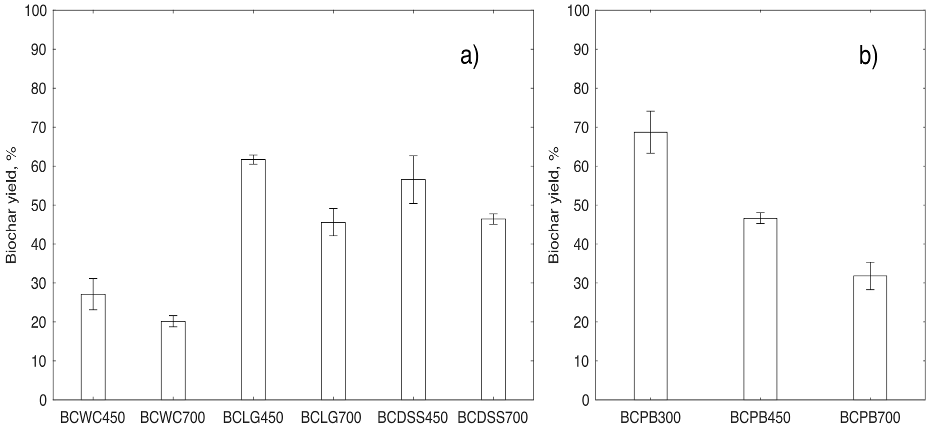

Fig. 4 Mean values of yield of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value (n = 3) ± standard deviation. Figure (a) was adapted from Mancinelli et al. (2016)

For each feedstock, it was observed that the increase in the pyrolysis temperature resulted in a lower BC yield, as commonly reported (Cao and Harris 2010; Rehraha et al. 2014; Jindo et al. 2014). In the work by Yuan et al. (2015), the decrease in BC yield observed in the temperature range 300–700 °C was ascribed to the decomposition of organic material owing to the increase in pyrolysis temperature.

According to McBeath et al. (2015), the conversion of organic material and the destruction of cellulose and hemicellulose during the pyrolysis process are responsible for the decrease in BC yield in the pyrolysis temperature range of 300–450 °C. At temperatures below 450 °C, cellulose and hemicellulose decompose into light molecular weight compounds, tending to form pyrolytic vapors (Lee et al. 2013). According to Zhao et al. (2014), a part of the cellulose content of the feedstock does not volatize and contribute to the lignin pool of the biochar produced through pyrolysis process.

The BCPB yield measured for the pyrolysis temperature of 300 °C was inconsistent with the results reported by Rutherford et al. (2005), who reported a yield of about 53.7 % for pyrolysis of pine bark at 300 °C for 1 h as well as an exponential decrease in yield with increasing holding time. The relatively high BCPB yield obtained at 300 °C suggests that PB was not completely pyrolyzed. In the work by Mukherjee et al. (2011), temperatures below 400 °C yielded slightly charred woody feedstock but no BC. Novak et al. (2009), questioned about considering biochar the carbonaceous product of torrification (i.e. temperatures in the range 200–300 °C, slow heating rate up to 50 °C/min, and under anoxic atmosphere), having low degree of carbonization and chemical properties similar to the feedstock.

Lignin decomposes over a wide range of temperature (150–900 °C) (Yang et al. 2007), being the main responsible for biochar formation (Lee et al. 2013). Comparing the yield of BC from olive husk, corncob, and tea waste, Demirbas (2004) observed that a higher LG content in olive husk gave a higher BC yield. Therefore, the higher yield of BCLG compared to BCDSS and BCWC at the pyrolysis temperature of 450 °C may be attributed to the fact that degradation of LG is not complete at 450 °C.

BCDSS exhibited a lower decrease in BC yield from 450 to 700 °C compared to BCLG and BCWC. This may be attributed to the fact that the cleavage of methyl groups (CH_3) in digested wastewater sludge contributes to the higher mass loss of the resulting BC with pyrolysis temperatures up to 400 °C (Hossain et al. 2011).

3.2 Physico-chemical properties of biochars

Ash content of BCs is shown in Figure 5. The lowest ash content was recorded in BCPB and BCWC for both the pyrolysis temperatures of 450 and 700 °C (Fig. 5). Ash content of BCPB ranged from 2.0 to 4.7 %, which was about 1.1 and 2.7 times higher the ash content of PB (Table 1). Analyzing the ash content as a function of pyrolysis temperature, Mukome et al.

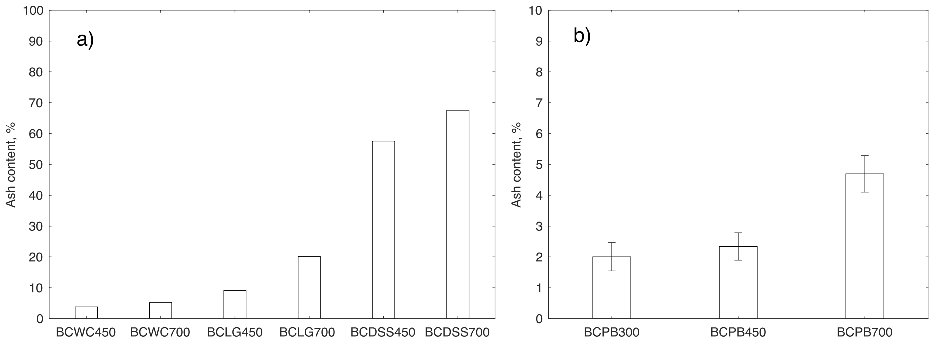

Fig. 5 Mean values of ash content of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

(2013) observed that BCs from woody feedstock had a lower ash content than BCs from different non-woody feedstock (e.g. manure, grass, hull, nutshell), irrespective of the pyrolysis temperature. The ash content of BCDSS700 was 67.5 % which is the same value measured by Méndez et al. (2012), in sewage sludge BC but at a lower temperature (500 °C). A significant increase was observed in BC ash content with increasing pyrolysis temperature for BCDSS, BCLG, and BCWC, whereas the increase in the ash content of BCPB with increasing pyrolysis temperature was not significant. With increases in pyrolysis temperature, BCLG exhibited the highest increase (2.2 times) in the ash content, followed by BCPB (2 times), BCWC (1.4 times), and BCDSS (1.2 times). Kloss et al. (2012) related the increase in ash content of BC with increasing pyrolysis temperature to volatilization and retention of inorganic components. By increasing the pyrolysis temperature, the progressive concentration of minerals and combusted organic matter residues determines an increase in ash content (Cao and Harris 2010).

An increase in ash content is often accompanied with an increase in the EC of biochar as a result of increased concentration of inorganic components with increases in pyrolysis temperature (Aller 2016). Rehraha et al. (2014) related the BC ash content to the increase in the EC of the BC with increasing pyrolysis temperature.

However, in the present research a clear trend about increases in EC and ash content resulting from increases in pyrolysis temperature was observed only for BCDSS with the highest EC as well as the highest ash content at 700 °C. On the contrary, at 450 °C the highest EC was

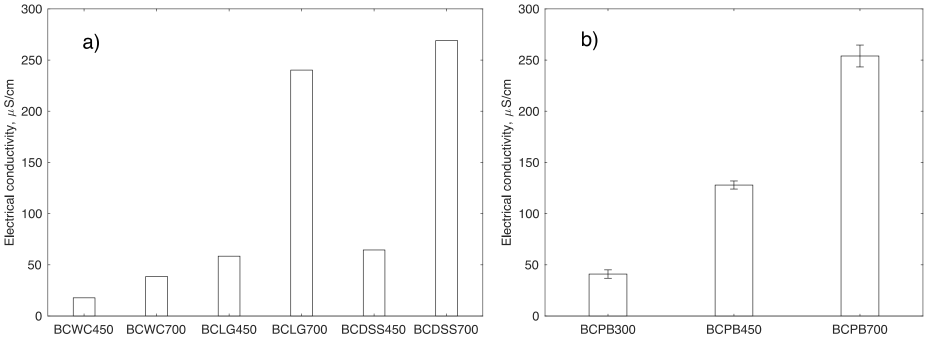

Fig. 6 Mean values of electrical conductivity of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

measured for BC from PB with the lowest ash content. Therefore, the chemical composition of the ash rather than the ash content per se may affect the EC of BC.

Figure 6 shows the EC of the biochars. EC provides information on the salt content of BCs. At the pyrolysis temperature of 450 °C, the highest EC was recorded in BC from PB (127.9 μS/cm), whereas BC from DSS exhibited the highest EC (269 μS/cm) at 700 °C.

For each type of feedstock, the EC of BCs increased significantly with increasing pyrolysis temperature. With increases in pyrolysis temperature, the highest increase in EC was observed for both BCDSS700 and BCLG700 with values being about four times higher than the EC of the respective BC at 450 °C. BCWC700 and BCPB700 showed an increase of about two times compared to the EC of the respective BC at 450 °C. Our results are in agreement with the trend reported in previous studies (Gundale and DeLuca 2006; Al-Wabel et al. 2013; Rehraha et al. 2014), regarding an increase in EC of BC with increases in pyrolysis temperature. However, Aller (2016) observed that the correlation between the adopted peak pyrolysis temperature and the EC of BC is feedstock dependent. Ash residue containing soluble salts accumulates in BCs produced at high temperatures resulting in an increase in EC (Gundale and DeLuca 2006; Rehraha et al. 2014). It is likely that at higher pyrolysis temperature higher quantities of soluble salts precipitated on the surface of the BCs during pyrolysis.

According to Aller (2016), slow pyrolysis at temperatures up to about 475 °C results in BCs with pH values below 7. Although, in the present research of the BC produced at temperatures up to 450 °C only BCPB300 and BCDSS450 exhibited an acidic pH, whereas pH was neutral (7.0) for BCPB450 and basic (up to 8.0) for BCWC450 and BCLG450 (Fig. 7). The pH values of BC from WC and LG produced at 450 °C were almost neutral, whereas

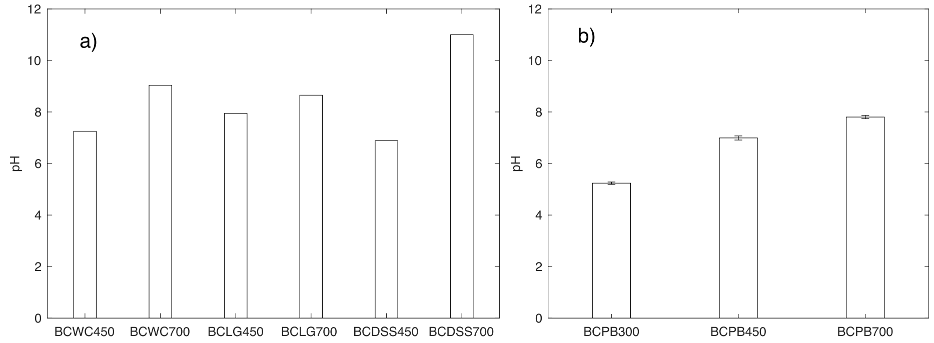

Fig. 7 Mean values of pH of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

at the temperature of 700 °C, BC from WC and LG exhibited an alkaline pH (Fig. 7a). At the pyrolysis temperature of 700 °C, BCDSS700 showed the highest pH (11.0), followed by BCWC700 (9.0), BCLG700 (8.7), and BCPB700 (7.8). Figure 7b shows a change in the pH values from acidic for BCPB300 (5.2), to neutral (7.0) for BCPB450 and to slightly alkaline for BCPB700 (7.8). A significant increase in the pH of BCPB with increasing pyrolysis temperature was observed, being 1.8 and 0.8 units higher with each increase in pyrolysis temperature from 300 to 450 and from 450 to 700 °C, respectively. The pH values of BC from wood feedstock (i.e. WC, and PB) produced at 450 °C were almost neutral, whereas at the temperature of 700 °C, BCWC and BCPB exhibited an alkaline pH. With rising pyrolysis temperature, increases in pH of BC from wood feedstocks are related to losses of acidic surface functional groups (Mukherjee et al. 2011) and increases in concentration of oxides of alkaline metals (Ca, K, and Mg) (Gundale and DeLuca 2006). A shift to an alkaline pH of BC associated with an increase in pyrolysis temperature was also observed in the studies carried out by Hossain et al. (2011) on BC from sewage sludge and by Jindo et al. (2014) on BC from different agricultural residues. Yuan et al. (2015) have suggested that the decomposition of organic acid and carbonate during the sewage sludge pyrolysis process is responsible for a change in pH values from acidic, for the raw material (5.7) and BC produced at 300 °C (6.7), to alkaline, for BCs produced in the range 400–700 °C (7.4–8.4).

Figure 8 shows the results of the TC analysis of BCs. For both the pyrolysis temperatures of 450 and 700 °C, TC content was highest in BC from lignin and wood feedstock. At 450 °C, TC content was the highest in BCPB450 (84.7 %), followed by BCLG450 (83.9 %), BCWC450 (62.9 %), and BCDSS450 (29 %). At 700 °C, TC content was the highest in BCPB700 (90.7 %), followed by BCWC700 (87.7 %), BCLG700 (71.7 %), and BCDSS700

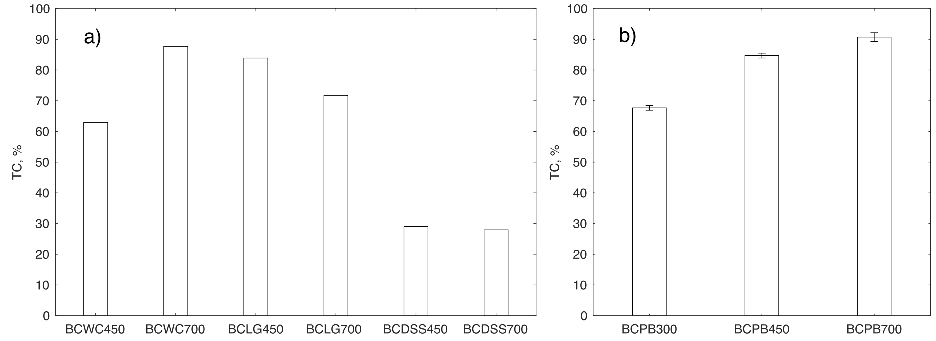

Fig. 8 Mean values of total carbon (TC) of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

(27.9 %). The carbon composition of BCs depends on the feedstock and the pyrolysis parameters adopted for BC production (Chintala et al. 2013).

The TC temperature trend varied depending on the feedstock. TC content of BCPB significantly increased with higher pyrolysis temperature (Fig. 8b). TC content of BCPB was between 1.2 and 1.6 times higher than the TC content of PB (55.6 %). Of the BCs from PB, BCPB700 showed the highest TC content (90.73 %), being about 1.1 and 1.3 times higher than the TC content of BCPB450 and BCPB300, respectively. The observed trend was consistent with the results reported by Liu et al. (2015a), who noted an increase of about 30 % in the TC content of BC from pine bark associated with an increase in temperature from 300 to 600 °C. With an increase in the pyrolysis temperature from 450 to 700 °C, TC in the BCWC and BCPB increased by 39 and 6 %, respectively. Gundale and DeLuca (2006) observed a similar increase in TC content of BCs from wood and bark with an increase in the pyrolysis temperature from 350 to 800 °C.

Conversely, BCLG and BCDSS exhibited a decrease in TC content of about 15 and 4 %, respectively (Fig. 8a). With regard to the temperature trend of TC content of BCDSS, our results were comparable with those reported by Lu et al. (2013) and Yachigo and Sato (2013) regarding a decrease in TC content of BC from sewage sludge with increases in pyrolysis temperatures. In the work by Lu et al. (2013) BCs from sewage sludge pyrolyzed in the temperature range 300–600 °C with a heating rate of 10 °C/min showed TC content in the range 15.2–33.2 %. These authors reported a decrease in TC content associated with each increase in temperature of 100 °C, with the highest decrease (12.7–24.4 %) in TC content for the range 300–400°C, followed by a decrease in the range 2.2–6.1 and 0.9–2.6 % for the

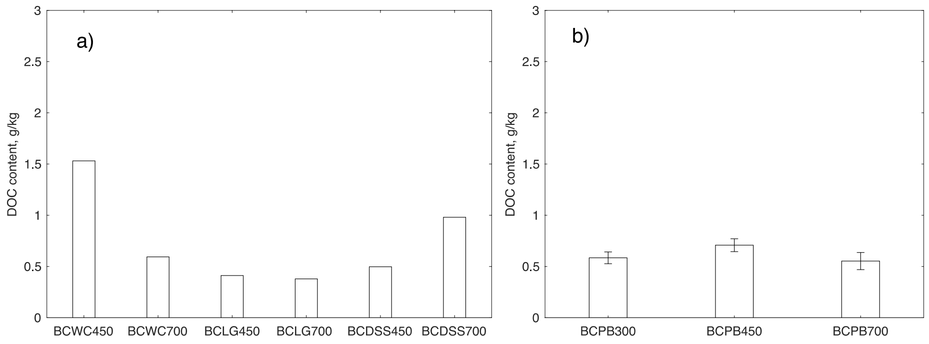

Fig. 9 Dissolved organic carbon (DOC) content in biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b) determined via batch method. Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

temperature range 400–500 °C and 500–600 °C, respectively. In the work by Yachigo and Sato (2013) BC from sewage sludge exhibited a decrease in TC concentration of about 0.7 % from the temperature of 300 to 800 °C.

Figure 9 shows the results of the DOC analysis in the water extract of BCs via the batch test method.

With respect to the values of DOC content of BCWC and BCPB, our findings were comparable to the results reported in the literature about DOC content of BC from wood and woody feedstock at 450 °C (0.33–1.4 g/kg) (Jones et al. 2011; Alburquerque et al. 2014), and at 700 °C (0.12–1.06 g/kg) (Liu et al. 2015a; Baltrenaite et al. 2016). With respect to the values of DOC content of BCDSS at 450 °C (0.5 g/kg) and at 700 °C (0.98 g/kg), our findings were about 2 times lower than the value reported by Baltrenaite et al. (2016) for BC from sewage sludge at 450 °C and up to 7 times higher than the values reported by Zhang et al. (2015) for BC from sewage sludge at 700 °C. However, when comparing results of DOC analysis it should be considered that the amount of DOC released from BCs assessed via batch tests depends on parameters such as the ratio of the solvent to solute (Mukherjee and Zimmerman 2013), and the pH of the extraction solution (Li et al. 2017).

Several studies have observed that wood and woody biomass feedstock tend to release less DOC than non-wood biomass feedstock (Mukherjee and Zimmerman 2013; Alburquerque et al. 2014; Graber et al. 2014). However, at the pyrolysis temperature of 450 °C, BCWC450 showed the highest DOC content which was about 3 and 4 times higher than the DOC contents of BCDSS450 and BCLG450, respectively (Fig. 9). At the pyrolysis temperature of

700 °C, BCDSS700 exhibited the highest DOC content which was about 2 times higher than the DOC contents of both BCWC700 and BCPB700 and about 3 times higher than the DOC content of BCLG700.

The DOC temperature trend varied significantly depending on the feedstock. Applying pyrolysis temperature in the range 300–700 °C resulted in a significant decrease in the range from 70.9–77.3 % of the DOC content of BCPB (Fig. 9b) compared to the DOC content of PB (2.44 g/kg). With an increase in pyrolysis temperature from 450 to 700 °C, BCWC, BCPB, and BCLG showed a decrease in DOC concentration in the water extract by about 61, 22, and 8 %, respectively. A similar trend in a decrease in the amounts of DOC with an increase in pyrolysis temperatures has been reported by several authors over a wide range of biomass feedstock and pyrolysis temperatures (Gaskin et al. 2008; Mukherjee and Zimmerman 2013; Graber et al. 2014; Smith et al. 2016; Domingues et al. 2017). Conversely, the amount of DOC in BCDSS increased by 97 % with the increase in pyrolysis temperature. The observed trend was inconsistent with the results reported by Zhang et al. (2015), who noted a decrease in DOC content associated with each increase in temperature of 100 °C in BC from sewage sludge pyrolyzed in the range 300–900 °C.

In order to analyze the fraction of carbon that is released from BC, the DOC content of BCs was expressed as a percentage of the respective TC content (Fig. 10).

A relatively limited fraction of carbon has been reported to be released from BC as DOC

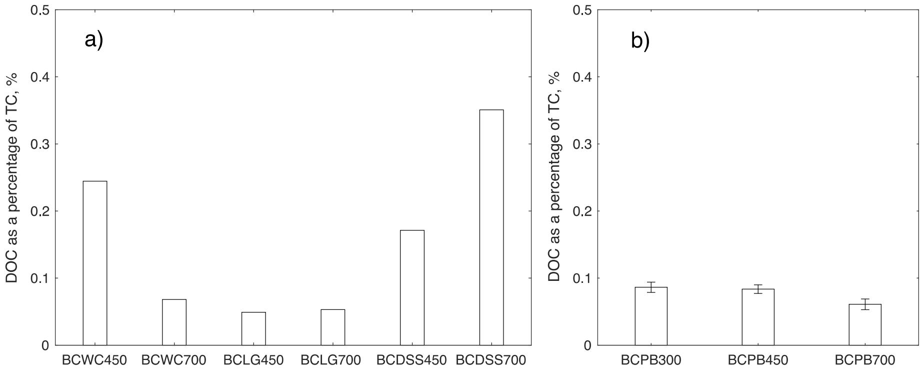

Fig. 10 Dissolved organic carbon (DOC) content expressed as a percentage of total carbon (TC) content of biochars from wood chips, lignin, digested sewage sludge (a), and pine bark (b). Values are shown as the mean value of two observations (n = 2) in (a); values are shown as the mean value of three observations (n = 3) ± standard deviation in (b)

(Mukherjee and Zimmerman 2013; Liu et al. 2016), being about 0.04 % of the TC in BC from mixed hardwood at 450 °C (Jones et al. 2011). We calculated the highest percentage of DOC for BCWC450 (0.24 % TC), followed by BCDSS450 (0.17 % TC), BCPB450 (0.08 % TC), and BCLG450 (0.05 % TC). At the pyrolysis temperature of 700 °C, BCDSS700 exhibited the highest percentage of DOC (0.35 % TC), followed by BCWC700 (0.07 % TC), BCPB700 (0.06 % TC), and BCLG700 (0.05 % TC). Pyrolysis of PB in the range 300–700 °C resulted in a significant decrease from 0.09 to 0.06 % of DOC expressed as a percentage of TC content (Fig. 10b).

According to Alburquerque et al. (2014), the influence of feedstock selection on DOC content of BC decreases with increasing pyrolysis temperatures. In the present dissertation, differences in the DOC content of BC from different types of feedstock decreased with increasing pyrolysis temperature, being up to 0.12 g/kg and 0.3 % of TC at 700 °C and up to 0.6 g/kg and 1.1 % of TC at 450 °C. With regard to the observed differences in DOC content of BC from different types of feedstock, transformations of organic structure into recalcitrant forms (Wu et al. 2011; Domingues et al. 2017) as well as secondary reactions (Lin et al. 2012) occurring during pyrolysis process may have resulted in lowering the content of DOC in the batch extracts of BCWC and BCPB. The observed differences in the DOC temperature trend may be related to differences in molecular weight distribution of DOC between the different types of BC. With increases in pyrolysis temperatures the DOC content of BC decreases because of the decomposition of DOC with a lower molecular weight (Luo et al. 2015), resulting in a lower concentration of DOC in the batch extracts of BC from WC and PB at 700 °C. The observed increase in DOC content of BC from DSS with an increase in pyrolysis temperature may result from the thermo-stable behavior of DOC with higher molecular weight and the concurrent decrease in BC yield (Luo et al. 2015). Furthermore, during pyrolysis process, physical alterations (e.g. formation of larger pores and increases in surface area) occurring in the char matrix (Liaw and Wu 2015) or volatilization of organic volatiles (Zhang et al. 2015) could lead to opening blocked pores, resulting in a higher concentration of DOC in the batch extracts of BCDSS700.

3.3 Carbon loss resulting from pyrolysis of pine bark

Carbon loss related to transformation of PB to biochar occurring during pyrolysis is presented in Figure 11. Carbon loss ranged from 17.86–48.10 %, being lower than the percentage (more than 50 %) of carbon in the feedstock that has been reported to be lost because of decomposition of organic matter during pyrolysis (Zhao et al. 2014). The highest carbon loss was observed with rising pyrolysis temperature from 300 to 450 °C. Zhao et al. (2014) related

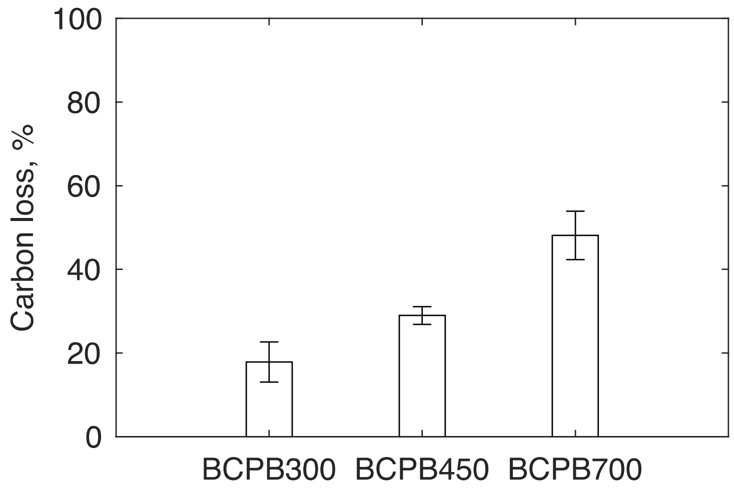

Fig. 11 Carbon loss resulting from pyrolysis of pine bark. Values are shown as the mean value (n = 3) ± standard deviation

carbon loss occurring at temperature <500 °C to a decrease in the organic matter fractions (i.e. hemicellulose and neutral detergent soluble fractions) and loss of cellulose in biochar compared to the feedstock. For pyrolysis at temperatures in the range 300–900 °C, of the carbon content of the feedstock between 20 to 50 % is retained in the resulting biochar whereas the rest volatilizes (Fidel et al. 2017). Depending on the technology of the pyrolyzer, the carbon content of the feedstock that volatilized can be attributed to the carbon content of liquid or gaseous (e.g. CO, CO_2, CH_4, and HCN) co-products or considered lost.

Compared to the calculated carbon loss occurring during pyrolysis of PB, the content of carbon expressed as a percentage of TC that is likely to be lost because of leaching was lower for about two orders of magnitude.

3.4 Elemental analysis of pine bark and biochars from pine bark

Results of the elemental analysis of CHNS and O content of PB and BCPB are shown in Table 3. BCPB showed lower H and O contents as well as higher C contents compared to PB. Furthermore, increasing pyrolysis temperature resulted in BCs from PB with higher C content and lower N, H and O contents, likely due to losses of H-and O-containing functional groups and volatile compounds (Novak et al. 2009; Wu et al. 2011; Crombie et al. 2013) and concurrent formation of aromatic C (Rutherford et al. 2012). Pyrolysis temperature significantly affected the C, N, and O but not the H contents of BCPB.

N tends to decompose at low temperatures during pyrolysis of plant biomass (Liu et al. 2015b). Decreases in N content of BC through volatile matter (e.g. NH_3, HCN) (Crombie et al. 2013) or loss on ignition (Rafiq et al. 2016) have been reported with increasing pyrolysis temperature. However, pyrolysis of lignin- and cellulose-rich biomass generally results in increases in N content of biochar with increases in pyrolysis temperature (Aller 2016).

Elemental analysis results showed no S on the PB and the BCPB. Our findings were consistent with the results reported by Blázquez et al. (2011) regarding S below 0.1 % in pine bark. However, Armolaitis et al. (2013) has measured an average S concentration of 0.52 g/kg in stem bark from Scots pine in Lithuania. The average S content of biochar from plant biomass is about 0.1 % because of the relative low S content in the parent material as well as because of the high tendency of S to volatilize (up to 50 %) during pyrolysis (Aller 2016).

Table 3 Elemental analysis of pine bark (PB) and biochar from PB at 300 °C (BCPB300), 450 °C (BCPB450), and 700 °C (BCPB700)

	%C	%H	%N	%O
PB	56.08 ±15.74	10.60 ±5.68	3.87 ±0.72	45.50 ±2.21
BCPB300	81.24 ±3.24	8.49 ±2.36	2.23 ±0.00	31.98 ±0.59
BCPB450	88.62 ±6.58	6.80 ±4.77	1.71 ±0.17	20.52 ±1.80
BCPB700	98.03 ±0.95	2.23 ±1.12	–	6.43 ±0.61

Values are shown as the mean value (n = 3) ± standard deviation

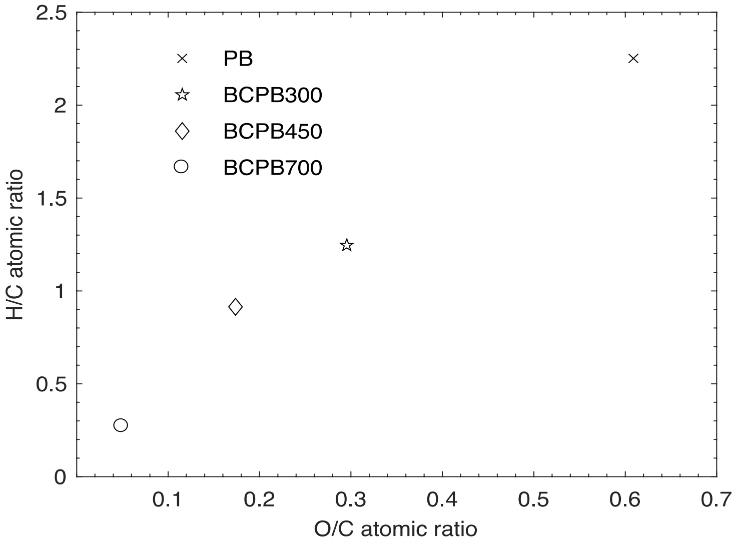

Fig. 12 The van Krevelen plot of the elemental data calculated for pine bark (PB) and biochar (BC) from PB at 300 °C (BCPB300), 450 °C (BCPB450), and 700 °C (BCPB700)

During pyrolysis of biomass organically bound sulphide volatilizes at temperatures below 400 °C whereas inorganic sulfate is retained in the biochar (Liu et al. 2017).

In the Van Krevelen plot (Fig. 12), the biochar H/C atomic ratios decreased versus O/C atomic ratios with increasing pyrolysis temperature as reported in previous studies for biochar from plant biomass (Keiluweit et al. 2010; Kloss et al. 2012). Increasing pyrolysis temperatures in the range 300–700 °C resulted in a decrease in the H/C (from 1.25 to 0.27) and of O/C (from 0.30 to 0.05) atomic ratios of BCPB. Increases in pyrolysis temperatures result in BC with lower H/C and O/C atomic ratios because of dehydration, deoxygenation as well as depolymerization of the cellulose and lignin contents of the biomass (Ahmad et al. 2014). A decrease in the H/C ratio with increasing pyrolysis temperature has been related to higher aromaticity of biochar from several types of feedstock (e.g. plant biomass, manures, and sludge) (Jassal et al. 2015; Xiao et al. 2016). Lower O/C ratio of the biochars are related to higher degree of carbonization (Crombie et al. 2013).

3.5 Trace elements in biochars and feedstock

Table 4 illustrates, in decreasing order, the concentration of total trace metals as detected in the feedstock and the BCs.

For each trace metal, a two-way ANOVA test with replications showed a significant interaction between pyrolysis temperature and feedstock affecting the BC total trace metal concentrations.

Except for some trace metals (e.g. Cd) that tend to volatilize during pyrolysis, trace metals which are initially present in the feedstock generally remain and become concentrated in the BCs (Lievens et al. 2008; Yuan et al. 2015). Zn was the element with the highest concentration in all the types of feedstock analyzed (up to about 848 mg/kg DW) and BCs (up to about 1994 mg/kg DW), apart from LG and BCLG450 that showed Cu as the trace metal with the highest concentration (about 212 and 115 mg/kg DW, respectively). Cd was the trace metal with the lowest concentration in all the analyzed feedstock (between 0.087 and 0.163 mg/kg DW) and BCs (between 0.005 and 0.266 mg/kg DW) (Table 5).

Compared to the limits set in the guidelines of EBC (EBC European Biochar Certificate 2015), BCWC did not exceed the maximum values for all the trace metals analyzed, thereby reflecting the low concentration of trace metals detected in WC. In the present research, the types of feedstock that showed high trace metal concentrations (e.g. Cu, Cr, and Zn in DSS and Cu in LG) originated BCs with trace metal concentrations above the limits set in the guidelines of EBC (EBC European Biochar Certificate 2015). DSS showed high concentrations of Cr, Cu, and Zn exceeding by 1.6–2.6 times the limits indicated in the guidelines of EBC (EBC European Biochar Certificate 2015). Both BCDSS450 and BCDSS700 exceeded the limit set for Cu (100 mg/kg DW), Cr (90 mg/kg DW), and Zn (400

Table 4 Order of trace metal concentration dry weight (DW) as detected in the feedstock and in the produced biochars

WC	$Zn \gg Cu > Cr > Pb > Ni > Cd$
BCWC450	$Zn \gg Cu > Pb > Ni > Cr > Cd$
BCWC700	$Zn \gg Cu > Pb > Ni > Cr \gg Cd$
LG	$Cu > Zn \gg Cr > Ni > Pb \gg Cd$
BCLG450	$Cu > Zn > Cr > Ni > Pb \gg Cd$
BCLG700	$Zn > Cu \gg Cr > Ni > Pb \gg Cd$
DSS	$Zn > Cu > Cr \gg Ni > Pb \gg Cd$
BCDSS450	$Zn > Cu > Cr \gg Ni > Pb \gg Cd$
BCDSS700	$Zn > Cu > Cr > Ni > Pb \gg Cd$

Retrieved from Mancinelli et al. (2016)

Table 5 Total trace metal (Cd, Cr, Cu, Ni, Pb, and Zn) concentrations in feedstock and in biochars

	Cd	Cr	Cu	Ni	Pb	Zn
			(mg kg^{-1} dry weight)			
WC	0.09	0.63	1.20	0.35	0.42	14.04
BCWC450	0.18	0.70	3.51	0.83	1.15	37.56
BCWC700	0.01	0.45	4.69	0.82	1.46	53.80
LG	0.10	39.71	212.27	19.14	8.05	207.15
BCLG450	0.09	32.24	114.75	14.29	6.43	113.56
BCLG700	0.01	12.44	164.98	19.23	8.71	295.47
DSS	0.16	139.83	256.64	23.97	3.72	847.53
BCDSS450	0.27	317.52	459.70	42.23	14.43	1611.38
BCDSS700	0.25	111.03	605.30	49.32	6.68	1994.08
*Maximum value	1.5	90	100	50	150	400

Values are shown as the mean value of two observations (n = 2).
*Maximum values for trace metals in biochar (basic quality grade) (EBC European Biochar Certificate 2015)

mg/kg DW), by 4.6 and 6.1 times, by 3.5 and 1.2 times, and by 4 and 5 times, respectively. The Cu concentration exceeded the limit by 1.1 times in BCLG450 and by 1.6 times in BCLG700, reflecting the initial high concentration of Cu in LG (about twice the set limit). For all the analyzed BCs, Cd and Cr concentrations decreased significantly with increases in the pyrolysis temperature (Table 5). Cantrell et al. (2012) observed a similar temperature trend for Cd concentration in BCs produced from a variety of manure feedstock at pyrolysis temperatures of 350 and 700 °C. Adopting a range of pyrolysis temperatures, Lievens et al. (2008) observed that Cd tended to volatilize with increasing temperature, with about 11 % of Cd retained in the pyrolysis solid product (i.e. char and ash) at a temperature of about 600 °C.

According to Buss et al. (2016), the extent to which trace metals volatize during the pyrolysis process depends on concurrent factors such as the pyrolysis temperature, the concentration of trace metal in the feedstock, and the interaction with various organic and inorganic components. The order of concentration of the analyzed elements in both BCWC450 and BCWC700 was different from the value recorded for the raw material, with the only exception of Cd and Zn exhibiting the smallest and the highest concentrations, respectively (Table 4). The concentration of total trace metals in BCWC450 and BCWC700 decreased in the same order. The total concentration of Cu, Pb, and Zn increased significantly in BCWC, showing a higher tendency to accumulate associated with an increase in the pyrolysis temperature (Table 5). The concentrations of Cd and Cr significantly increased in BCWC produced at 450 °C and significantly decreased at 700 °C. In the work by Evangelou et al. (2014), wood feedstock pyrolyzed for 4 h at 450 and 700 °C resulted in an increase in concentration of trace metals such as Cu and Zn as well as in a decrease in concentration of Cd and Pb in BC at 700 °C. Applying the same increase in the pyrolysis temperature (i.e. from 450 to 700 °C) and a shorter residence time (i.e. 2 h) on a similar feedstock, we observed a similar temperature trend to the one reported by Evangelou et al. (2014) for Cd, Cu, and Zn as well as an opposite trend regarding Pb. It is likely that the extent of the residence time applied in the pyrolysis process has a stronger influence on Pb behavior compared to other trace metals (e.g. Cd, Cu, and Zn) enriching in BC or volatilizing depending on the applied residence time.

Ni showed a different temperature trend, with an increase in concentration in both BCWC450 (136 %) and BCWC700 (135 %) compared to WC but a decrease of about 17 % from 450 to 700 °C (Table 5). All the trace metals in BCWC450 showed a significant increase in concentration compared to the feedstock, with an increase of about 10 % for Cr and an increase in the range 108–191 % for Cd, Cu, Ni, Pb, and Zn. Trace metals such as Cu, Pb, Ni, and Zn showed a significant increase (up to 289 %) in BCWC700 compared to the feedstock (Table 5).

As regards the trace metals in BCLG450 and BCLG700, the concentration of the analyzed elements decreased in the same order, with only Zn and Cu showing a dissimilar order of concentration (Table 4). Zn in BCLG700 showed the highest concentration (295.47 mg/kg DW), being about 44 % higher than Cu (164.97 mg/kg DW) (Table 5). Both LG and BCLG450 showed the same order of concentration of the analyzed elements (Table 4).

Compared to LG, there was a significant decrease in the concentration of all the trace metals, ranging between 11 and 46 % in BCLG450, with Zn (45 %) and Cu (46 %) exhibiting the highest decreases. At the pyrolysis temperature of 700 °C, the trend varied depending on the trace metals: Zn and Pb increased significantly compared to the concentration detected in LG, by 43 and 8 %, respectively. Conversely, Cd, Cr, and Cu showed a significant decrease of about 95, 69, and 22 %, respectively.

The concentration of the trace elements analyzed in DSS, BCDSS450, and BCDSS700 decreased in the same order (Table 4). BCDSS contained the highest concentration of Cd, Cr, Cu, Ni, and Zn as was to be expected from the highest concentration detected in DSS (Table 5). Trace metals originally contained in the wastewater sludge are often reported to be concentrated in the resulting BCs (Lu et al. 2011; Lu et al. 2015; Hossain et al. 2011). According to Lu et al. (2015), during the pyrolysis process, trace metals are transformed from mineral salts and hydroxide into oxide and sulphide forms, resulting in an increase in thermostability.

The total concentration of Cu, Ni, and Zn increased significantly in BCDSS, showing a greater tendency to accumulate in the BCs produced at the higher pyrolysis temperature. Trace metals such as Cd, Cr, Cu, Ni, and Zn were between 39 and 56 % higher in the BCDSS450 compared to the concentrations detected in DSS.

Notably, Cu, Zn, and Ni exhibited an increase of about 135, 136, and 106 %, respectively, in BCDSS700 compared to the raw material.

An increase in trace metal concentrations in BCs compared to the respective feedstock is related to the increase in ash content through the pyrolysis process (Méndez et al. 2012). Cd and Pb showed a different temperature trend, increasing in concentration in both BCDSS450 (63 and 288 %, respectively) and BCDSS700 (53 and 80 %, respectively) compared to DSS but decreasing with the pyrolysis temperatures of 450 to 700 °C by about 6 and 54 %, respectively. Compared to the feedstock, Cr increased by about 127 % at 450 °C and decreased by about 21 % at 700 °C (Table 5). Comparing trace metal (e.g. Ni, Cu, Cr, Pb, and Zn) concentrations in sewage sludge with the values in the resulting BCs, Yuan et al. (2015) reported a tendency for greater trace metal concentrations in BCs associated with the increase in the pyrolysis temperatures in the range 300–700 °C. In the research by Méndez et al. (2012), BC from sewage sludge pyrolyzed at 500 °C had a higher content of Cu (31 %), Pb (30 %), as well as about 28 % more Ni, Cd, and Zn with respect to the feedstock.

In order to prevent the trace elements from once again spreading into the environment, it is important to develop waste treatment technologies that recover trace elements at one end of the chain. One of the aims of the pyrolysis process is to retain trace metals in the solid product (e.g. BC), to avoid their volatilization and to obtain condensable and non-condensable pyrolysis products that are trace metal free (Koppolu et al. 2003; Lievens et al. 2008; Stals et al. 2010). In the present study, in order to assess the ability of the adopted pyrolysis process to concentrate the trace metals in the produced BCs, the RR (Eq. (3)) of trace elements in BCs was calculated (Table 6).

The RR of the investigated trace metals for the produced BCs showed a different temperature trend depending on the trace metal considered. Irrespective of the raw material utilized to produce the BCs, on increasing the pyrolysis temperature, the RR of Cr, Ni, and Cd decreased in the range 52–71 %, 1–26 %, and by as much as 97 %, respectively, whereas the RR of Zn showed an opposite trend, increasing up to 92 %. The temperature trend of the RR for Cu and Pb varied depending on the feedstock. The RR of Cu and Pb decreased in BCs from WC (as much as 5 %) and from DSS (40 and 62 %, respectively) and increased in BC from LG, by 6 and 25 %, respectively. In the work by Lu et al. (2015), almost all of these trace metals remained in the BCs produced from sewage sludge in a range of pyrolysis temperatures (400–700 °C), with the following RRs: Pb 90–97 %, Zn 96.4–99.5 %, Ni 92.5– 97.5 %, Cu 81.5–91.6 %, and Cr 70–87.3 %.

As regards the variations in RR observed with the increase in pyrolysis temperature for the investigated trace metals and different BCs, except for the increase in the RR of Zn in BC from LG (92 %), the observed increase in RR was in the range 2–25 % whereas the observed decrease in RR was in the range 1–71 %, not considering the decrease in the RR of Cd in BC from WC and LG, which was 97 and 96 %, respectively. Therefore, observing the general temperature trend of the RRs for the produced BCs and the investigated trace metals, it may be assumed that increasing the pyrolysis temperature from 450 to 700 °C is not a proper option if the purpose of producing BC is to avoid spreading trace metals in the environment.

Table 6 Retention rate (RR) of the trace metals detected in biochars from wood chips, lignin, and digested sewage sludge. Retrieved from Mancinelli et al. (2016)

RR, %	BCWC450	BCWC700	BCLG450	BCLG700	BCDSS450	BCDSS700
Cd	56.52	1.86	54.98	2.38	91.99	71.07
Cr	67.83	32.41	50.07	14.28	128.33	36.85
Cu	78.99	78.54	33.34	35.42	101.23	61.11
Ni	63.86	47.31	46.05	45.78	99.56	95.48
Pb	75.04	70.92	49.26	61.76	219.11	83.26
Zn	72.55	77.24	33.81	65.00	107.45	109.19

3.6 Trace elements leachability from biochars

The results of the up-flow percolation test are reported as the cumulative released quantity of trace metal detected in the eluate at each cumulative L/S ratio, expressed as a percentage of the respective total trace metal concentration detected in the BCs (Figs. 13, 14, 15, and 16). For all the BCs, the leaching of Cr and Ni was below the detection limit (i.e. 0.2 mg/l) at each L/S ratio. The leaching of Zn was found to be under the detection limit (0.04 mg/l) in the eluate collected from BCWC, BCLG, and BCDSS700 at each L/S ratio. When the concentration of the analyzed trace metals was under the detection limit, the cumulative released quantity (ΣU_i) was calculated as the upper limit calculated for C_i equals to the detection limit and as the lower limit, calculated for C_i equals to zero. The upper limit calculated for the cumulative released quantity of Cr at the final L/S ratio (i.e. $\Sigma L_i/S$ equal to 10) was highest for BCLG700 (16.1 % of the total Cr content), followed by BCLG450 (6.2 % of the total Cr content), BCDSS700 (1.8 % of the total Cr content), and BCDSS450 (0.6 % of the total Cr content). The upper limit calculated for the cumulative released quantity of

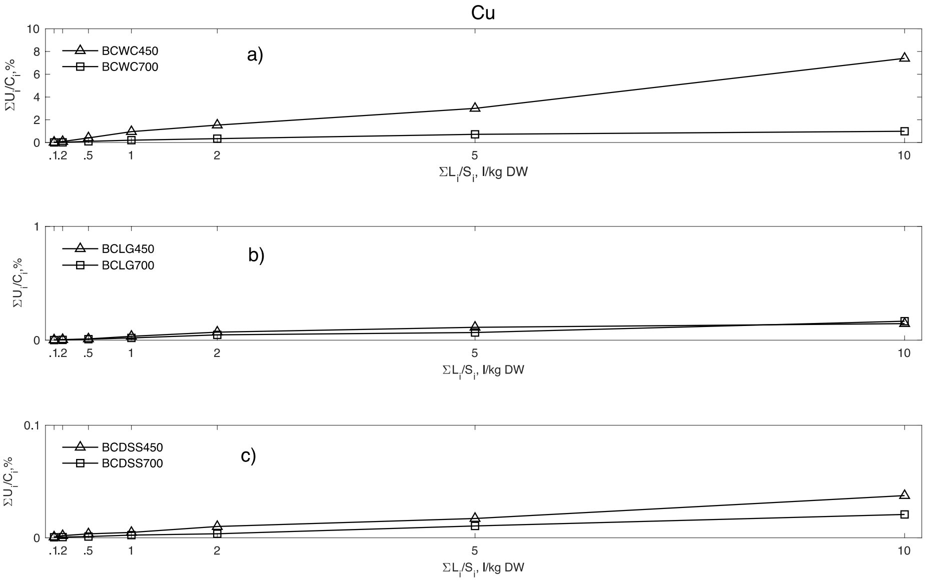

Fig. 13 Cumulative quantity (ΣU_i) of Cu released by biochars (BCs) from wood chips (a), BCs from lignin (b), and BCs from digested sewage sludge (c) at various cumulative liquid to solid ratios ($\Sigma L_i/S$), expressed as percentages of the respective total trace metal concentration (C). (n = 1). *DW* dry weight. Adapted from Mancinelli et al. (2016)

Ni was highest for BCLG450 (about 14 % of the total Ni content), followed by BCLG700 (10.4 % of the total Ni content), BCDSS450 (4.8 % of the total Ni content), and BCDSS700 (4.1 % of the total Ni content). The upper limit calculated for the cumulative released quantity of Zn at the final L/S ratio was highest for BCWC450 (1.1 % of the total Zn content), followed by BCWC700 (0.7 % of the total Zn content), BCLG450 (0.4 % of the total Zn content), BCLG700 (0.1 % of the total Zn content), and BCDSS700 (<0.1 % of the total Zn content).

As regards Cr and Ni leachability from BCWC, the results are not reported since applying the above-mentioned upper limit would lead to a calculated cumulative released quantity at the final L/S ratio, which is about twice the total content of these metals (Table 5).

In the work by Bernardo et al. (2014), Cr was not detected in the eluate from BCs from different mixtures of pine biomass, rubber tire, and plastics pyrolyzed at 420 °C.

Helsen et al. (1997), from the comparison of two leaching procedures to bring charcoal metal content into solution for the quantitative analysis of metals such as Cu and Cr, suggested that there was a stronger bond between Cr and the pyrolysis solid fraction compared to the feedstock (i.e. wood impregnated with copper, chromium, and arsenic salts). In the work by Yargicoglu et al. (2015), no risk of leaching was reported for trace metals such as Cd, Cr, Ni, and Zn from a variety of BC produced from wood waste.

With respect to the trace metals analyzed in the eluate collected from BCWC and BCLG,

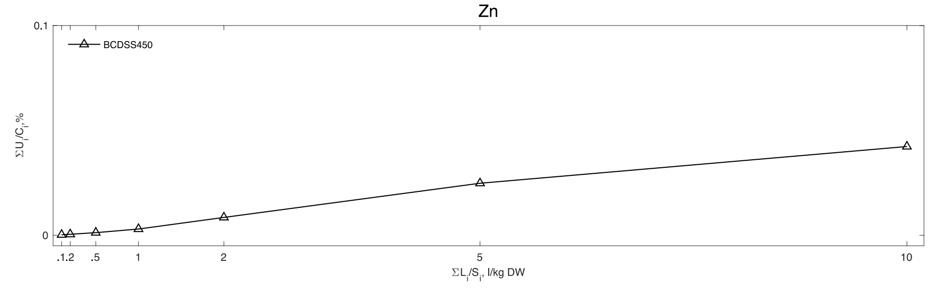

Fig. 14 Cumulative quantity (*ΣU*$_i$) of Zn released by biochar from digested sewage sludge at 450 °C (BCDSS450) at various cumulative liquid to solid ratios (*ΣL*$_i$*/S*), expressed as percentages of the respective total trace metal concentration (*C*). (n = 1). *DW* dry weight. Adapted from Mancinelli et al. (2016)

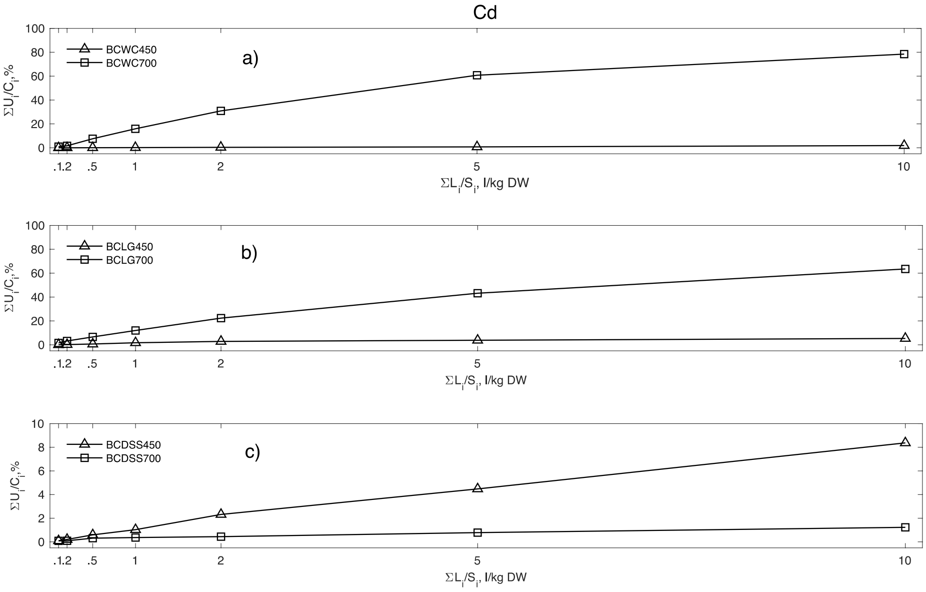

Fig. 15 Cumulative quantity (*ΣU*$_i$) of Cd released by biochars (BCs) from wood chips (a), BCs from lignin (b), and BCs from digested sewage sludge (c) at various cumulative liquid to solid ratios (*ΣL*$_i$*/S*), expressed as percentages of the respective total trace metal concentration (*C*). (n = 1). *DW* dry weight. Adapted from Mancinelli et al. (2016)

the leaching behavior varied depending on the element. Irrespective of the pyrolysis temperature, at the final L/S ratio, Cu was retained in the range 92–99 % in BCWC and BCLG (Fig. 13). The low leached amounts of trace metals such as Cu (Fig. 13) and Zn (Fig. 14) may be related to pH values in the alkaline range that were measured in the eluates collected at L/S ratios equal to 1, 3, and 5 from BCLG and BCWC (Fig. 18). Mellbo et al. (2008), performing an up-flow percolation test on wood ash, reported no leaching of Cu and Zn. These authors suggested that the high pH value (8.8–12.4) of the eluates was responsible for hindering the release of Cu and Zn.

Leaching behavior of Cd in BCLG and BCWC varied with the temperature (Fig. 15). At the final L/S ratio, BCWC450 and BCLG450 retained more than 99 % of the respective total Cd concentration whereas about 20 and 40 % of total Cd concentration were retained in BCWC700 and BCLG700, respectively.

Irrespective of the pyrolysis temperature, at the final L/S ratio, more than 96 % of Pb was retained in BCLG (Fig. 16). Conversely, Pb was calculated to be about four times more likely

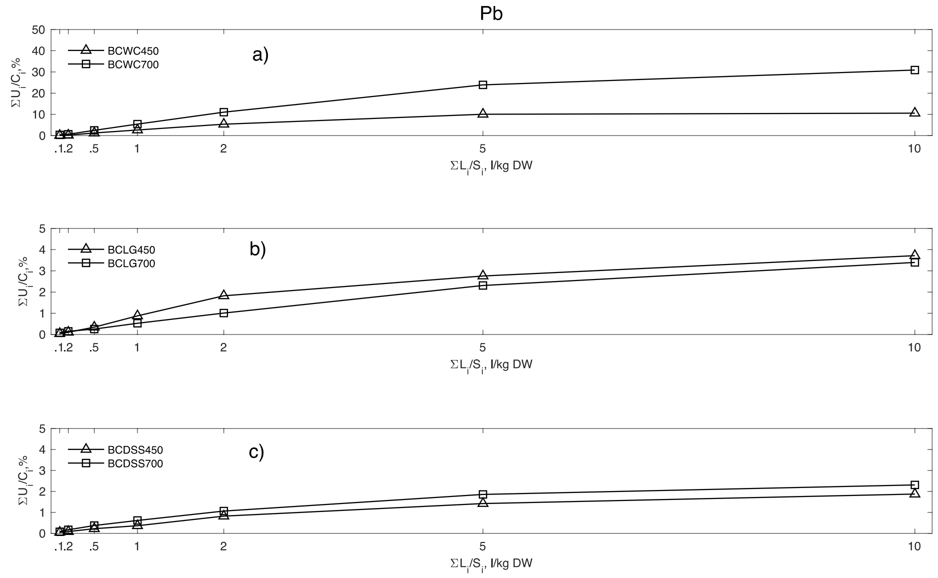

Fig. 16 Cumulative quantity (*ΣU_i*) of Pd released by biochars (BCs) from wood chips (a), BCs from lignin (b), and BCs from digested sewage sludge (c) at various cumulative liquid to solid ratios (*ΣLi/S*), expressed as percentages of the respective total trace metal concentration (*C*). (n = 1). *DW* dry weight. Adapted from Mancinelli et al. (2016)

to be released from BCWC700 compared to BCWC450.

At the final L/S ratio, all the analyzed trace metals were mostly retained in BCDSS, irrespective of the temperature adopted for pyrolysis treatment (Figs. 13, 14, 15, and 16). Trace metals were retained in BCDSS450 in the range of 95.25–99.96 % and in BCDSS700 in the range of 95.94–99.98 %. BCDSS450 exhibited a relatively higher tendency to release trace metals such as Cd (about nine times), Pb, and Zn (about two times) compared to BCDSS700. Roberts et al. (2017) reported negligible risks for Cd, Cu, and Zn leaching from BC from biosolids at high pyrolysis temperatures (i.e. ≥ 600 °C).

The most suitable pyrolysis temperature for reducing trace metal leachability (450 or 700 °C) depends on the feedstock. For BCDSS, it is likely that, with the increase in the pyrolysis temperature, trace metals such as Cd, Cr, Cu, Ni, Pb, and Zn form stronger bonds, thus stabilizing in the char matrix, with BCDSS450 exhibiting a relatively higher tendency to release Cd, Pb, and Zn compared to BCDSS700. Converting WC and LG to BC at 700 °C under the adopted pyrolysis conditions could lead to an increase in the leachability of Cd, with BCWC700 and BCLG700 releasing about 78 and 63 % of their respective total Cd concentration at the final L/S ratio.

In order to avoid potential drawbacks in BC water application (e.g. filtering media) resulting from leaching of potentially harmful trace metals, the results of the up-flow percolation test were compared to the annual average maximum allowable concentrations (AAMACs) for the environment provided by the Order of the Minister of the Environment of Lithuania No. D1–236 of 17 May 2006 on Wastewater Management Regulation. There was no risk of leaching for Cd, Cr, Cu, Pb, and Zn from all the BCs as their cumulative released quantities were under AA-MACs for the environment. The upper limit of the cumulative released concentration of Ni calculated for BCLG and BCDSS equals to the AA-MACs for the environment (Table S1 in supplemental material). Therefore, only BCWC can be considered suitable for water application with no concern for introducing excessive amounts of trace metals in surface water.

3.7 Citric acid extractable trace metals in biochars

Irrespective of the pyrolysis temperature adopted for producing biochars from potentially contaminated feedstock (i.e. WC, LG, and DSS), all the BCs (i.e. BCWC, BCLG, and BCDSS) contained low amounts of bioavailable trace metals such as Cu (0.31–6.13 mg/kg DW) and Zn (4.5–94.27 mg/kg DW), as well as bioavailable potentially toxic elements such as Cd (up to 0.093 mg/kg DW) and Pb (up to 4.33 mg/kg DW) (Fig. 17). The concentration of Cr and Ni was below the detection limit in the citric acid extract of all the analyzed BCs.

Our results were comparable with those reported by Carrier et al. (2012) regarding the analysis of trace metals (e.g. Cd, Pb, and Zn) in the citric acid extract of BC produced from sugarcane bagasse. In the work by Chen et al. (2015), Cr was the metal with the highest fraction converted into more stable and less bioavailable forms in char from dewatered sewage sludge pyrolyzed in the range 400–800 °C. Sewage sludge contains Ni in organic chelated forms, representing a risk of phytotoxicity (Méndez et al. 2012). Therefore, the fact that BCDSS did not contain Ni in a bioavailable form is particularly interesting. Cd and Pb are non-essential elements having no definite biological function in organism and plant (Bolan et al. 2013). Measures such as limiting the Cd content of phosphorous fertilizer have been proposed in order to avoid the accumulation of Cd in agricultural soil (Tóth et al. 2016). Therefore, introducing trace amount of bioavailable Cd and Pb in soil through BC land application is highly undesirable (Wu et al. 2016).

There was no statistically significant variation between bioavailable fractions of Cu at different pyrolysis temperatures. In the work by He et al. (2010), Cu in BC from sewage sludge was mainly bound to organic matter and sulphides, forming more stable and less available complexes at temperatures above 650 °C. With the increase in pyrolysis

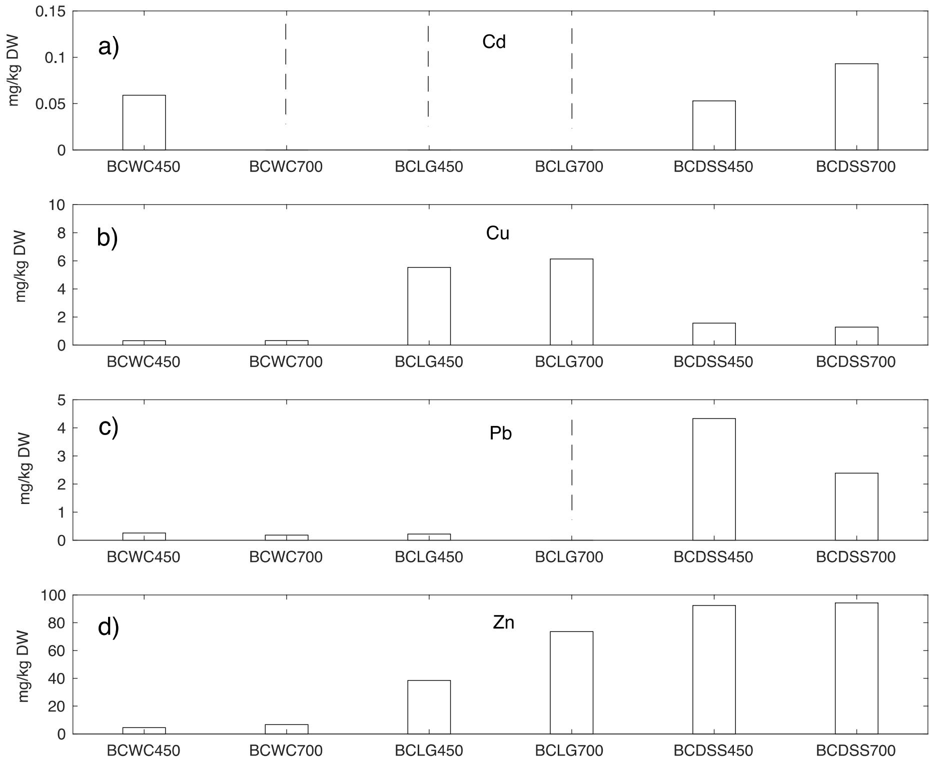

Fig. 17 Biochar bioavailable Cd (a), Cu (b), Pb (c), and Zn (d) concentration in 1 % citric acid extraction. Values are shown as the mean of two observations (n = 2). Dashed lines denote trace metal concentration below the detection limit. *DW* dry weight

temperature, the bioavailable fraction of Zn did not vary in BCWC and decreased significantly in BCLG (9 %) and BCDSS (1 %).

As regards the trace metals (Cr, Cu, and Zn) that were detected in the aqua regia extract above the limits set in EBC (EBC European Biochar Certificate 2015), it should be noted that Cr was not detected in a bioavailable form and that both Cu and Zn showed a decrease in bioavailability with the increase in pyrolysis temperature. As regards the presence of Cd in the citric acid extracts, a different behavior was noted depending on the feedstock. BCLG did not contain Cd in a bioavailable form, as the concentration was below the detection limit. BCWC and BCDSS showed a similar concentration of Cd in the citric acid extract of the respective BCs produced at 450 °C. However, with the increase in the pyrolysis temperature, these BCs showed an opposite trend, with BCWC700 exhibiting a concentration below the detection limit and BCDSS700 showing a slight increase (about 17 %) in the bioavailable fraction.

3.8 Electrical conductivity and pH of eluates

The pH of the eluates collected from BCWC and BCLG up-flow percolation test increased significantly with increases in pyrolysis temperatures (Fig. 18). For each feedstock type (i.e. WC, and LG), pH values of the eluates showed significant differences for L/S ratios and

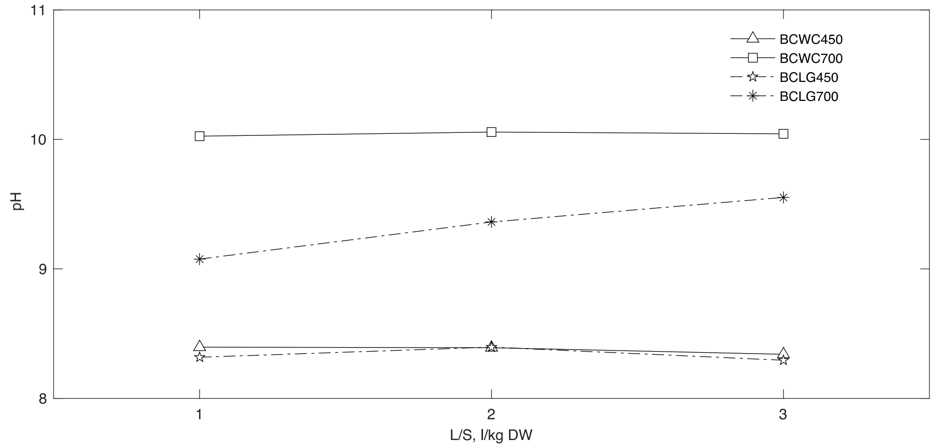

Fig. 18 Mean values of pH of biochar eluates collected at various liquid to solid (L/S) ratios. Values are shown as the mean of two observations (n = 2). *DW* dry weight. Adapted from Mancinelli et al. (2017b)

pyrolysis temperatures. BCWC showed the highest rise in alkalinity, with the pH of eluates from BCWC700 being between 1.6 and 1.7 units higher with each increase in L/S ratio compared to the respective pH levels from BCWC450. The pH levels of the eluate samples from BCLG700 were between 0.8 and 1.3 units higher than the respective levels from BCLG450.

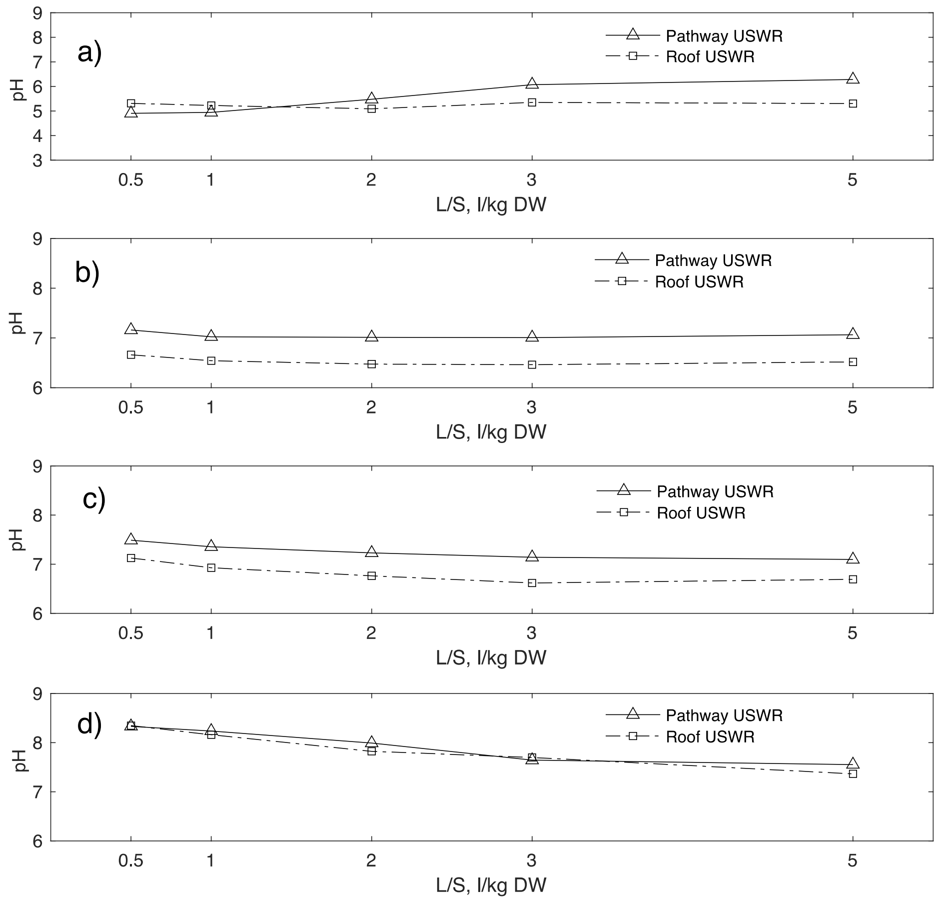

Fig. 19 Mean values of pH of the eluates collected at various liquid to solid (L/S) ratios from roof and pathway urban storm-water runoff (USWR) up-flow percolation tests with pine bark (PB) (a), biochar (BC) from PB at 300 °C (b), 450 °C (c), and 700 °C (d). *DW* dry weight. Values are shown as the mean of two observations (n = 2)

For all the L/S ratios, BCs at 450 °C from WC and LG showed a similar alkaline pH in the range 8.3–8.4.

Figure 19 shows the pH values of the eluates measured after up-flow percolation test with roof and pathway USWR. Statistically significant differences of the values of pH of the eluates collected after filtration of the two types of USWR were observed among the four tested materials (i.e. PB, BCPB300, BCPB450, and BCPB700).

Of all the tested materials (i.e. PB, and BCPB), the highest drop in pH was observed for PB with a decrease for about 1.8–3.2 and 1.4–1.7 units after filtration of pathway and roof USWR, respectively. In the work by Dalahmeh et al. (2012), the release of organic acids from PB was reported as a possible explanation for drops in pH observed after grey water filtration in columns packed with PB. Comparing the pH of the eluates from BCPB after percolations tests with the pH of the respective leachants, BCPB300 and BCPB450 produced the highest decrease (up to 1.1 units) in pH, likely due to a leaching of alkaline ions (Yao et al. 2010). The highest increase (up to 1.6 units) in pH was observed for the percolation test with BCPB700 and roof USWR.

With increasing volume of eluate collected after leaching tests with both types of USWR, the differences among the pH values decreased for PB and BCPB. This may be due to a decrease in buffering capacity of the material with increasing volume of eluate (McLaughlan and Al-Mashaqbeh 2009).

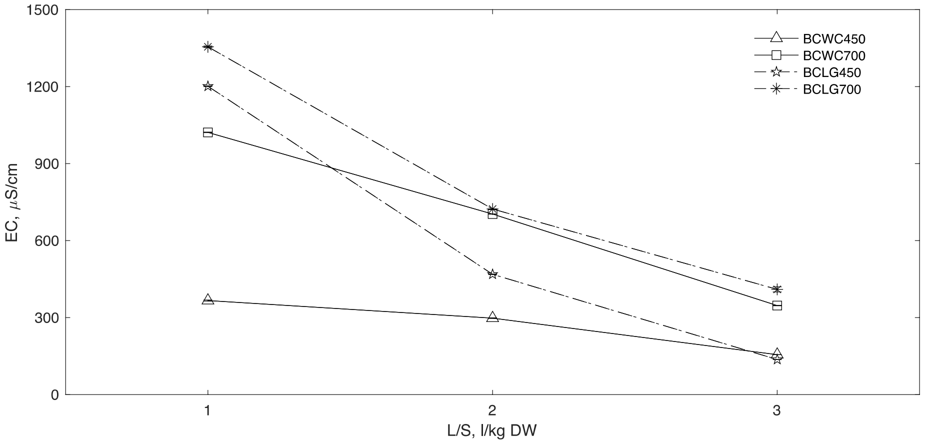

Fig. 20 Mean values of electrical conductivity (EC) of biochar eluates collected at various liquid to solid (L/S) ratios. Values are shown as the mean of two observations (n = 2). *DW* dry weight. Adapted from Mancinelli et al. (2017b)

EC provides information about the presence of total soluble salts in the eluate. For all the types of leachant (i.e. deionized water and USWR) the tested BCs (i.e. BCWC, BCLG, and

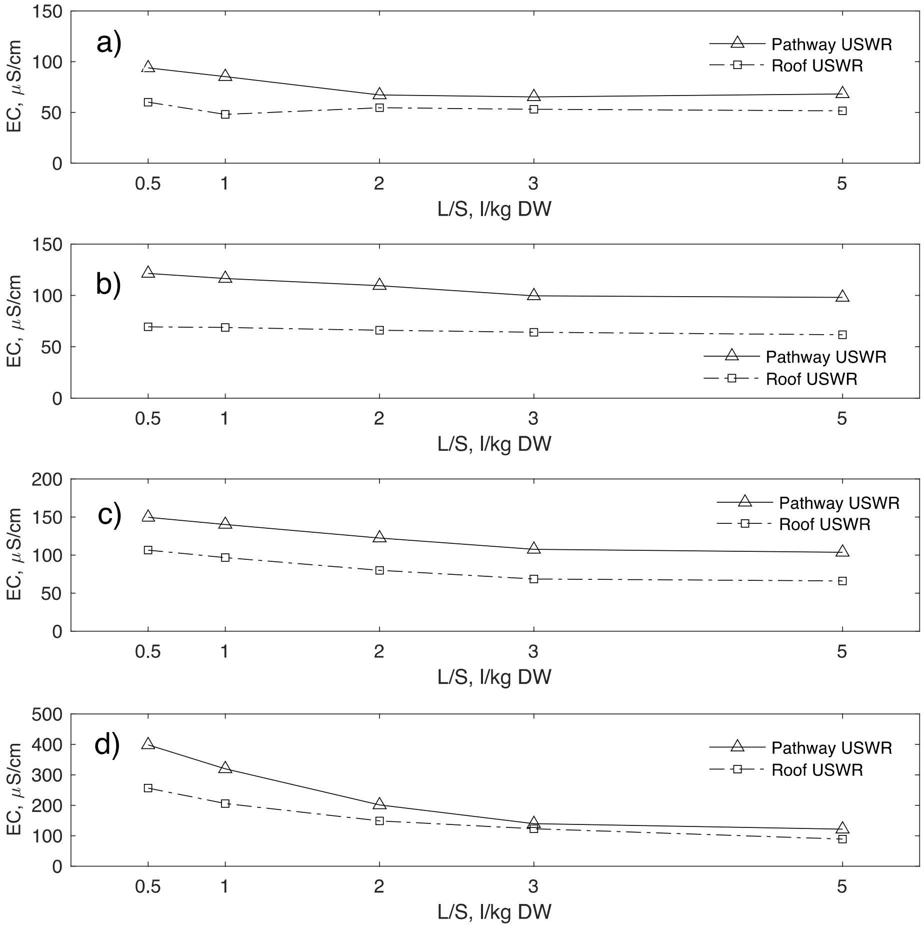

Fig. 21 Mean values of electrical conductivity (EC) of the eluates collected at various liquid to solid (L/S) ratios from roof and pathway urban storm-water runoff (USWR) up-flow percolation tests with pine bark (PB) (a), biochar (BC) from PB at 300 °C (b), 450 °C (c), and 700 °C (d). *DW* dry weight. Values are shown as the mean of two observations (n = 2)

BCPB) released decreasing quantities of soluble salts with increasing volume leached through the columns (Figs. 20, and 21).

The EC of the eluates collected from BCWC and BCLG up-flow percolation test increased significantly with increases in pyrolysis temperatures (Fig. 20). For each feedstock type (i.e. WC, and LG), EC values of the eluates significantly decreased with increases in L/S ratios (Fig. 20).

Statistically significant differences were observed for the values of EC grouped depending on the tested materials (i.e. PB, and BCPB) as well as on the types of leachant (i.e. roof and pathway USWR), but no interaction was observed among the two nominal variables considered (Fig. 21).

The higher the pyrolysis temperature the higher the increase in EC of the eluates compared to the EC of the pathway and roof USWR, with BCPB700 producing an increase in EC up to 388 and 514 %, respectively, followed by BCPB450 (up to 83 and 155 %, respectively) and BCPB300 (up to 49 and 66 %, respectively). The EC of the eluates from BCPB was higher (29–324 %) than the EC of the eluates from PB. The EC of the eluates from PB were from 15–44 % higher than the EC of roof USWR. Apart from an increase (up to 24 %) in the EC of the first two eluates collected from PB, filtering pathway USWR with PB produced a decrease (up 20 %) in the EC.

3.9 Dissolved organic carbon leaching from biochars

Figure 22 shows the DOC concentrations determined in the eluates collected at various L/S ratios in the up–flow percolation test of BCWC and BCLG utilizing deionized water as a leachant. Irrespective of the temperature adopted for pyrolysis treatment, BCWC and BCLG showed a similar release trend characterized by a significant decrease in DOC concentrations of the eluates collected at increasing L/S ratios.

An increase in L/S ratio from 1 to 3 l/kg DW produced the highest decreases in the DOC concentrations of the eluates collected from BCLG700 (50 %) and BCWC450 (49 %), followed by BCLG450 (30 %) and BCWC700 (21 %). A further increase in L/S ratio from 3 to 5 l/kg DW showed a substantial decrease (71 %) in the DOC concentration of the eluate collected from BCLG450, followed by BCWC700 (49 %), BCWC450 (18 %), and BCLG700 with the slightest decrease (1 %). In the works by Beesley and Marmiroli (2011) and Iqbal et al. (2015), DOC was observed to be rapidly released from BC with no substantial amount of DOC recorded after a few eluate samples.

Low temperature (450 °C) BCLG and BCWC significantly released greater amounts of DOC compared with the respective high temperature (700 °C) BC. A decrease in DOC content with an increase in pyrolysis temperature was reported in a previous study on BC leaching trends by Mukherjee and Zimmerman (2013). A decrease in water leachability of organic

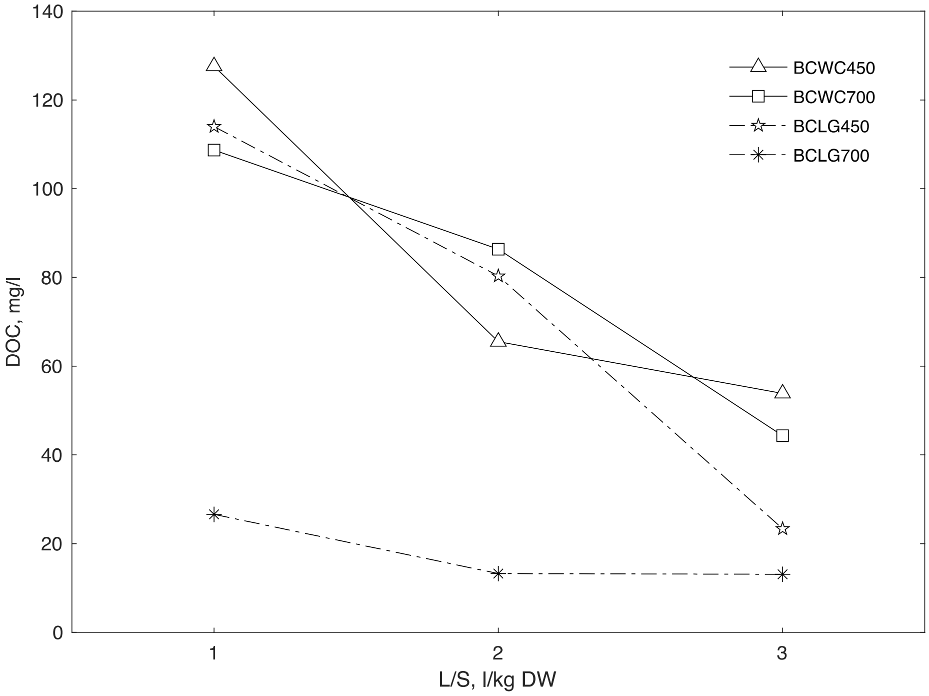

Fig. 22 Mean values of dissolved organic carbon (DOC) of biochar eluates collected at various liquid to solid (L/S) ratios. Values are shown as the mean of two observations (n = 2). *DW* dry weight

matter (quantified as total organic carbon as percentage of TC) in BC is related to the transformation of organic structure into recalcitrant forms occurring during pyrolysis (Wu et al. 2011).

In order to analyze the fraction of carbon that is released from BC, the DOC content of BCs was expressed as a percentage of the respective TC content (Table 7). The calculated cumulative released quantity of DOC at the cumulative L/S ratio of 9 l/kg DW was highest for BCWC450 (0.09 % of the TC content), followed by BCWC700 (0.07 % of the TC content), BCLG450 (0.06 % of the TC content), and BCLG700 (0.02 % of the TC content) (Table 7). As regards the temperature-related trend of the cumulative released quantity of DOC expressed as a percentage of the respective TC content, with an increase in pyrolysis temperature BCWC and BCLG showed a decrease of about 22 and 67 %, respectively.

For both pyrolysis temperatures, BCWC exhibited a higher tendency to release DOC compared with BCLG. The cumulative released quantity of DOC of BCWC expressed as a percentage of TC content was 1.5 times higher at 450 °C and 3.5 times higher at 700 °C than

Table 7 Dissolved organic carbon (DOC) content in biochars from wood chips and lignin determined via up-flow percolation test expressed as a percentage of the respective total carbon (TC) content

	Amount of DOC as a % of TC			Cumulative amount of DOC as a % of TC
	L_1/S	L_2/S	L_3/S	$\Sigma L_i/S$
BCWC450	0.02	0.03	0.04	0.09
BCWC700	0.01	0.03	0.03	0.07
BCLG450	0.01	0.03	0.01	0.06
BCLG700	0.00	0.01	0.01	0.02

DW dry weight. L_i/S – liquid to solid (L/S) ratio equal to 1, 3, and 5 l/kg DW for *i* equal to 1, 2, and 3, respectively. $\Sigma L_i/S$ – cumulative L/S ratio. Values are shown as the mean value (n = 2)

the respective quantity of DOC calculated for BCLG. In the work by Li et al. (2014), BC from wood and lignin pyrolyzed at 400 and 600 °C had different surface properties, with BC from wood exhibiting higher micropore structure (specific surface area, micropore area and volume) compared with BC from lignin at both pyrolysis temperatures. Closed or blocked pores that were formed in BC during pyrolysis open due to the swelling of BC in water (Ahmad et al. 2014). Therefore, organic matter, which was entrapped in the char matrix, may become more accessible to leaching. It is likely that the leaching condition applied in the up-flow percolation test enhanced the swelling of BCWC in water, thus resulting in more DOC as a percentage of TC released with increasing L/S ratios compared with BCLG.

For both the types of leachant (i.e. roof and pathway USWR), PB released higher concentrations of DOC compared to BCPB, with DOC values up to 77.5 mg/l (Fig. 23). DOC concentrations (mg/l) measured in the eluates from BCPB showed significant differences for pyrolysis temperatures and types of leachant. For all the BCPB, the leaching tests with roof USWR showed higher concentrations of DOC (mg/l) compared to those with pathway USWR (Fig. 23). Increases in L/S ratios in the range of 0.5–5 l/kg DW produced the highest decreases in DOC concentrations in the eluates collected from leaching tests of pathway USWR with BCPB700 (78 %), and BCPB300 (77 %). For both the types of leachant, a steady trend was observed for DOC concentrations in the eluates from BCPB450 with values varying within fairly tight ranges for L/S ratios in the range of 0.5–5 l/kg DW.

Table 8 shows the DOC content of PB and BCPB expressed as a percentage of the respective TC content.

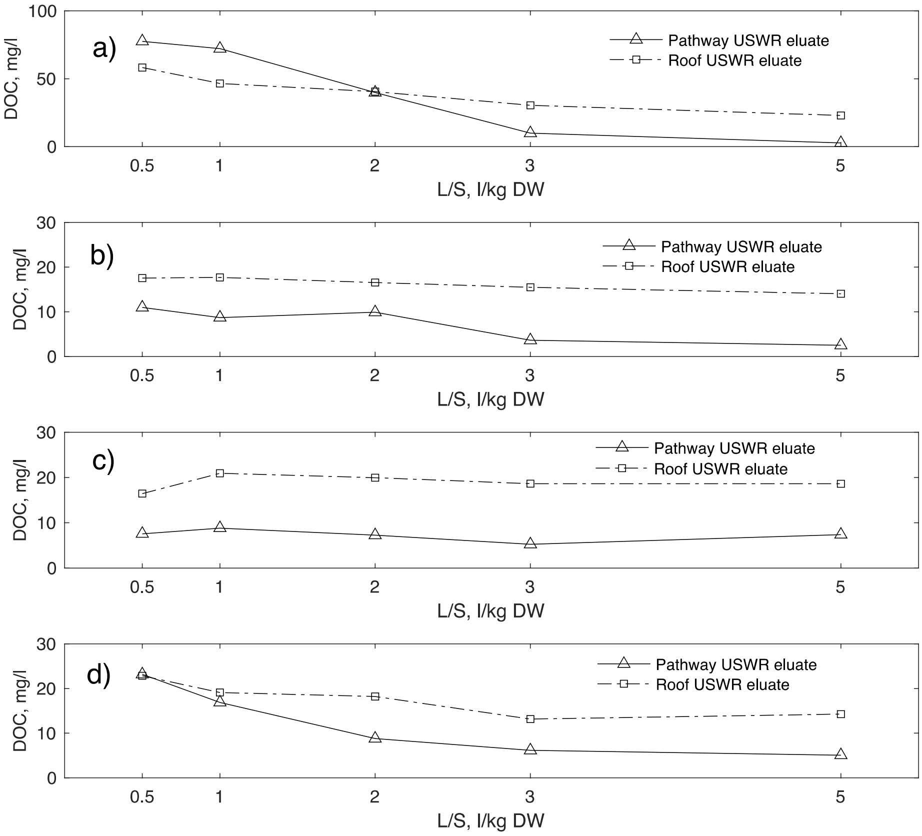

Fig. 23 Mean values of dissolved organic carbon (DOC) released by pine bark (PB) (a), biochar (BC) from PB at 300 °C (b), 450 °C (c), and 700 °C (d) in the eluates collected at various liquid to solid (L/S) ratios from roof and pathway urban storm-water runoff (USWR) up-flow percolation tests. *DW* dry weight. Values are shown as the mean of two observations (n = 2)

In the up-flow percolation test with roof USWR, at the final cumulative volume of eluate (i.e. $\sum L_i/S$ equal to 11.5) BCPB produced at higher temperature released lower cumulative quantities of DOC expressed as a percentage of the respective TC content. For the up-flow percolation test utilizing the pathway USWR as leachant, at the final cumulative volume of eluate the calculated cumulative released quantities of DOC expressed as a percentage of the

Table 8 Dissolved organic carbon (DOC) content in pine bark (PB) and biochars from PB determined via up-flow percolation test with urban storm-water runoff (USWR) expressed as a percentage of the respective total carbon (TC) content

		Amount of DOC as a % of TC					Cumulative amount of DOC as a % of TC
Leachant	Material	L_1/S	L_2/S	L_3/S	L_4/S	L_5/S	$\Sigma L_i/S$
Pathway USWR	PB	0.01	0.01	0.01	0.01	0.00	0.04
	BCPB300	0.00	0.00	0.00	0.00	0.00	0.01
	BCPB450	0.00	0.00	0.00	0.00	0.00	0.01
	BCPB700	0.00	0.00	0.00	0.00	0.00	0.01

		Amount of DOC as a % of TC					Cumulative amount of DOC as a % of TC
Leachant	Material	L_1/S	L_2/S	L_3/S	L_4/S	L_5/S	$\Sigma L_i/S$
Roof USWR	PB	0.01	0.01	0.02	0.02	0.02	0.07
	BCPB300	0.00	0.00	0.01	0.01	0.01	0.03
	BCPB450	0.00	0.00	0.01	0.01	0.01	0.03
	BCPB700	0.00	0.00	0.00	0.01	0.01	0.02

Values are shown as the mean value. (n = 2). L_i/S – liquid to solid (L/S) ratio equal to 0.5, 1, 2, 3, and 5 l/kg dry weight for *i* equal to 1, 2, 3, 4, and 5 respectively. $\Sigma L_i/S$ – cumulative L/S ratio

respective TC content were in the order PB > BCPB700 ≈ BCPB450 ≈ BCPB300, which was in contrast with the results reported by Liu et al. (2015a) and Mukherjee and Zimmerman (2013). These authors observed a decrease in DOC quantities released by BCs with an increase in pyrolysis temperature.

Differences in the DOC leaching behavior of BCPB that were observed for the pyrolysis temperatures and the types of leachant may be explained by differences in pH and DOC concentration of the two types of leachant.

According to Jones et al. 2011, DOC is released at first from the surface and later from the BC matrix following a diffusion-limited mechanism. It is likely that the leachant with lower

DOC concentration (i.e. roof USWR) lead BCPB to release higher quantities of DOC from the BC matrix. Hence, DOC concentrations (mg/l) were highest in the eluate from BCPB after roof USWR up-flow tests compared to those measured in the respective eluates from pathway USWR up-flow tests. Furthermore, the leachant with relatively higher pH and DOC concentration (i.e. pathway USWR) may have limited the release of DOC from the BC matrix. Hence, the similar cumulative released quantity of DOC expressed as a percentage of TC content calculated for BCPB in the pathway USWR up-flow percolation test. For the eluates collected from BCPB700, positive linear correlations were observed for DOC concentrations (mg/l) plotted against EC ($r^2 = 0.99$) and pH ($r^2 = 0.88$) values of the eluates collected from up-flow percolation test with pathway USWR. Blocked pores that were formed in BC during pyrolysis become accessible due to dissolution of inorganic salts coating BC surface (Spokas et al. 2014), thus increasing the accessibility to leaching of the portion of DOC that is carried on the surface of biochar (Jones et al. 2011). Furthermore, the portion of DOC that is carried on the surface of biochar is more susceptible to leaching with increases in pH of the leachant (Li et al. 2017).

4 Conclusions

For each type of feedstock (i.e. wood chips (WC), digested sewage sludge (DSS), lignin (LG), and pine bark (PB)), all the biochars (BCs) showed a similar temperature trend for ash content, BC yield, and physicochemical parameters such as electrical conductivity (EC) and pH, with the BC produced at higher temperature exhibiting lower BC yield and higher values of ash content, pH, and EC. The highest pyrolysis temperature resulted in a lower BC yield with a decrease in the range 18–53.7 %, higher pH (up to 11.0), higher EC (up to 269 μS/cm), and higher ash content (up to 67.5 %).

The temperature trend of dissolved organic carbon (DOC) content in BCs determined via batch test varied depending on the types of feedstock. High temperature (700 °C) BCs from wood feedstock (i.e. WC and PB) exhibited lower amounts of DOC compared with low temperature (450 °C) BCs, which were in the range 0.06–0.07 % and 0.08–0.24 % of total carbon (TC) content, respectively. With an increase in the pyrolysis temperature, the DOC content of BCs from DSS (BCDSS) increased in the range 0.17–0.35 % of TC content.

Analysis of the up-flow percolation test utilizing deionized water as a leachant showed the same temperature related trend in DOC leachability from BCs from wood chips (BCWC) and BCLG, with high temperature (700 °C) BCs releasing lower cumulative amounts of DOC compared with low temperature (450 °C) BCs, which were in the range 0.02–0.07 % and 0.06–0.09 % of TC content, respectively.

The most suitable pyrolysis temperature for limiting DOC leaching from BCPB depends on chemical characteristics (e.g. pH and DOC concentration) of urban storm-water runoff (USWR). For all the adopted pyrolysis temperature, BCPB released cumulative amount of DOC up to 0.01 % of the TC content filtering USWR with pH values in the basic range (8.1± 0.1) and mean DOC concentrations of about 25.7 mg/l. High temperature (i.e. 700 °C) BCPB would be a proper choice for releasing relatively lower cumulative amount of DOC (up to 0.02 % of the TC content) in applications that involve filtration of USWR with slightly acidic pH (6.8± 0.2) and mean DOC concentrations of about 19.1 mg/l.

It is likely that the type of leachant (e.g. pathway USWR) with relatively higher pH and DOC concentration limited the release of DOC from the BC matrix, whereas the types of leachant (e.g. deionized water, and roof USWR) with relatively lower pH and DOC concentrations led BC to release higher quantities of DOC from the BC matrix.

Compared to the quantity of carbon that was not retained in BCPB after pyrolysis (i.e. carbon loss up to 48 %), the quantity of carbon that was prone to be released (i.e. DOC as a percentage of TC content) by BCPB was negligible, being lower about 2 orders of magnitude both for the batch and up-flow percolation tests. Therefore, when considering BC effectiveness in carbon sequestration the quantity of carbon that is not retained in BC because of leaching may be neglected.

At the pyrolysis temperature of 450 °C, all the analyzed trace metals showed the same temperature trend which varied depending on the feedstock, significantly increasing in concentration in BCWC (up to 191 %) and BCDSS (up to 288 %) and significantly decreasing in BCLG (by as much as 46 %). At the pyrolysis temperature of 700 °C, the temperature trend of the trace metals varied depending on the feedstock. In all the tested BCs, trace metals such as Ni (up to 135 %), Pb (up to 248 %), and Zn (up to 283 %) increased significantly whereas total Cr concentrations decreased significantly (by as much as 69 %) compared to the respective feedstock. Trace metals such as Cd and Cu did not show a clear temperature trend, increasing or decreasing in concentration depending on the feedstock.

The most suitable pyrolysis temperature for reducing trace metal leachability and bioavailability (450 or 700 °C) depends on the trace metal considered. Regardless of the pyrolysis temperature, trace metals such as Cr and Ni were not prone to leaching or present in bioavailable forms in BCWC, BCLG, and BCDSS. Thus, the temperature of 450 °C was effective in stabilizing Cr and Ni in the analyzed BCs. In the tested BCs, an increase in pyrolysis temperature made trace metals such as Zn and Cu more stable in the char matrix, decreasing in the bioavailable fractions, hindering leachability of Zn, and decreasing leachability of Cu to less than 1 % of the total Cu concentration. Trace metals such as Cd and Pb did not show a clear temperature trend, increasing or decreasing in the bioavailable or leachable fractions depending on the feedstock. With increases in the pyrolysis temperature, the bioavailable fraction of Cd and Pb decreased whereas the leachable fractions of these trace metals increased in BCWC and BCLG. An opposite trend was observed for Cd and Pb in BCDSS, increasing in the bioavailable fractions and decreasing in leachability with increases in the pyrolysis temperature.

Compared to the limits set in the guidelines of EBC (EBC European Biochar Certificate 2015), the types of feedstock that showed high trace metal concentrations (e.g. Cu, Cr, and Zn in DSS and Cu in LG) originated BCs with trace metal concentrations above the limits (i.e. Cu, Cr, and Zn in BCDSS and Cu in BCLG). Furthermore, there could be a risk for an excessive leaching of Ni from BCLG and BCDSS according to the limits that are enforced in Lithuania. Therefore, only BCWC can be considered for water application or land application with no concern for introducing excessive amounts of trace metals in the environment.

Watchman, what of the night?
Watchman, what of the night?

Isaiah 21:11

5 Recommendations

When designing a pyrolysis treatment for producing BC from biodegradable waste, it should be carefully evaluated the most suitable temperature depending on the targeted trace metals, the type of biodegradable waste, and the purpose of BC production.

If BCs are intended for water application, such as a filter media, the amount of DOC that may be emitted in surface water as a result of BC release should be estimated considering BC production parameters (e.g. pyrolysis temperatures and types of feedstock) and chemical parameters (e.g. pH, and DOC concentration) of the type of water that BC would be exposed to.

As for BC effectiveness in carbon sequestration, the amount of carbon that is not retained in BCs because of leaching as DOC may be considered negligible compared to the carbon loss occurring during pyrolysis of biomass for BC production.

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Supplemental material

Table S1 Cumulative quantity of trace metals released per kg biochar (BC) at the cumulative liquid to solid (L/S) ratio equal to 10 compared to the Lithuanian standards for the limitation of hazardous trace metals discharge to surface water

	AA-MAC to surface water		Cumulative released quantity per kg biochar at the cumulative L/S ratio equal to 10					
			BCWC450	BCWC700	BCLG450	BCLG700	BCDSS450	BCDSS700
Cd (µg/l)	40		0.34	0.63	0.47	0.33	2.23	0.31
Cu (µg/l)	500		25.96	4.63	16.68	27.48	17.25	12.57
Pb (µg/l)	100		12.14	45.10	23.90	29.60	27.03	15.41
Cr (µg/l)	500		<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
		L.L.	0	0	0	0	0	0
		U.L.	—	—	200.0	200.0	200.7	200.3
Ni (µg/l)	200		<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
		L.L.	0	0	0	0	0	0
		U.L.	—	—	**200.0**	**200.0**	**200.0**	**200.0**
Zn (µg/l)	400		<D.L.	<D.L.	<D.L.	<D.L.	68.17	<D.L.
		L.L.	0	0	0	0	—	0
		U.L.	40.0	40.0	40.0	40.0	—	40.1

AA-MAC – maximum allowable concentration expressed as an annual average value. L. L. – lower limit calculated for the concentration equal to zero. U. L. – upper limit calculated for the concentration equal to the limit of detection (D. L.). Retrieved from Mancinelli et al. (2016)

Table S2 Mean values of moisture content of biochars from wood chips, lignin, digested sewage sludge, and pine bark

	Moisture content, %
BCWC450	1.68
BCWC700	1.55
BCLG450	2.19
BCLG700	1.77
BCDSS450	1.45
BCDSS700	0.89
BCPB300	4.34
BCPB450	3.05
BCPB700	1.93

Values are shown as the mean value (n =2)