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Organic compounds leached from fast pyrolysis mallee leaf and bark biochars

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HIGHLIGHTS

- Quick and simple set-up for identifying leached organics from biochars.
- Phenolics were GC/MS detected after solvent extraction from biochar.
- Large polar multi-fused aromatic rings were water leached.
- Kinetics depended on pyrolysis temperature and leaching time.

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ABSTRACT

Characterization of organic compounds leached from biochars is essential in assessing the possible toxicity of the biochar to the soils' biota. In this study the nature of the leached organic compounds from Mallee biochars, produced from pyrolysis of Mallee leaf and bark in a fluidised-bed pyrolyser at 400 and 580 °C was investigated. Light bio-oil compounds and aromatic organic compounds were investigated. The 'bio-oil like' light compounds from leaf and bark biochars 'surfaces were obtained after leaching the chars with a solvent, suitable to dissolve the respective bio-oils. GC/MS was implemented to investigate the leachates. Phenolics, which are potentially harmful toxins, were detected and their concentration shown to be dependent on the char's origin and the char production temperature. Further, to simulate biochars amendment to soils, the chars were leached with water. The water-leached aromatic compounds from leaf and bark biochars were characterized using UV-fluorescence spectroscopy. Those results suggested that biochars contain leachable compounds of which the nature and amount is dependent on the biomass feedstock, pyrolysis temperature and leaching time.

1. Introduction

Application of biochar to soil is gaining increasing attention because of its potential for soil conditioning, such as improving nutrient retention and water holding capacity (Lehmann and Joseph, 2009; Jeffery et al., 2011; Lehmann et al., 2011; Barrow, 2012). Although biochar is known to be highly recalcitrant in soils, with reported residence times for wood biochar up to 1000s of years (Lehmann and Joseph, 2009), part of the organic matter in biochar may be leachable. During the pyrolysis of biomass, a fraction of bio-oil compounds may condense on the biochar surface (Spokas et al., 2011; Buss and Mašek, 2014). Some of these chemical compounds, e.g. phenols, could be leached when chars are added to soils. In contact with soil, phenolic substances are adsorbed to solid surfaces, where they interfere with ecosystem equilibrium through selective toxicity affecting biogeochemical pathways of organic matter and nutrient recycling (Djokic et al., 2013; Buss and Mašek, 2014). The identification of leached organic matter is essential in assessing the toxicity to the recipient soils and its biota.

In Western Australia, mallee, a type of eucalyptus tree, is currently grown as a soil amendment option to control salinity in wheat growing regions. Because they are a fast growing, coppicing crop, they make a very interesting biomass source for bioenergy production, via e.g. thermochemical conversion (Bell et al., 2001; Bartle et al., 2002; Zohar et al., 2010). During pyrolysis of Mallee trees (wood, bark and leaf) bio-oils are produced and significant amounts of biochars that could be used for soil amendment and enrichment (Lehmann and Joseph, 2009).

At the Fuel and Energy Technology Institute, analysis of mallee bark, leaf and wood in terms of AAEM, S and P results showed that

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these elements are more concentrated in leaves and bark than in the wood fraction of mallee biomass, because these elements prefer to reside in water-rich tissues or are central to chlorophyll (French and Milne, 1994; Barker and Pilbeam, 2007). Hence, the fast pyrolysis of mallee bark or leaves could concentrate these nutrients in the biochar, when the temperature is within a certain range (<600 °C) (Keown et al., 2005; Okuno et al., 2005), making these biochars very interesting as they show potential as a poor soil amendment option. However, apart from the quantification of the amount of organic carbon leached from biochars (Mukherjee and Zimmerman, 2013), no analysis or kinetics of the organic compounds leached from Mallee biochar have been conducted, nor ever assessed whether toxic bio-oil compounds could be leached.

Therefore, the objective of this study was to investigate the kinetics and nature of the leached organic compounds from biochars, produced from the pyrolysis of mallee leaf and bark in a fluidised-bed pyrolyser at 400 and 580 °C. A distinction was made between light bio-oil compounds and aromatic organic compounds. The 'bio-oil like' light compounds from leaf and bark biochars 'surfaces were obtained after leaching with the chars a mixture of methanol/chloroform and methanol, resp. The leachates were identified by GC/MS and were identified as the potential maximal concentrations of bio-oil compounds leached from the chars 'surfaces (bark and leaf). Further, to simulate biochars amendment to soils, the chars were leached with water. At different time intervals leaf and bark biochar water-leachates were obtained and investigated with UV-fluorescence spectroscopy providing information of the nature of the compounds as a function of time.

2. Materials and methods

2.1. Production and characterization of biochar

Since these biochars are considered for soil amendment, we chose biomass which is rich in nutrients, hence leaf and bark biomass were implemented (French and Milne, 1994; Barker and Pilbeam, 2007). Biochars were produced from low and high temperature pyrolysis of mallee leaf and bark (180–425 μm particle size) at 400 and 580 °C in a fluidised-bed pyrolyser. The detailed description of the pyrolyser can be found elsewhere (Garcia-Perez et al., 2008; He et al., 2012). The char used for this experiment were collected in two sequential cyclones before being homogenized for testing. Some char is also accumulated in the fluidized bed but, given the difficulty in easily separating the biochar and the sand, only the char of the cyclones was used. The cyclones themselves were electrically heated at 400 °C for the 400 °C pyrolysis or 420 °C for the 580 °C in order to minimize condensation and/or further reactions of the volatiles.

Ash yield (CEN 14775) and moisture content (CEN 14774) of biochars were determined in an external laboratory according to European standards. Carbon, hydrogen and nitrogen were determined using a Leco Truspec Analyser. Sulphur in the char samples was determined using a Leco sulphur analyzer following AS1038.6.3.3.

The leaf biochars were observed by SEM at Curtin's Electronic Microscopy Centre a Zeiss Evo 40XVP machine, after the samples were carbon-coated.

2.2. Characterization of leachate from washing biochars with organic solvent

The leaf and bark biochars (1.5 g) were washed, in a small batch reactor at room temperature, with 10 g of a mixture of chloroform and methanol (4:1 – HPLC quality of Merck) and 10 g of methanol (LC Chromasolv, HPLC quality of Merck), resp. for 72 h. Methanol and the chloroform/methanol were implemented in the washing procedures, since our experience taught us that these organic solvents were the most adequate to dissolve the bio-oils of mallee leaf and mallee bark. There were no pre-treatments of biochar prior to the leaching of the organics from the biochars' surface. After the stirring time lapsed, the solutions were filtered over a 0.2 μm Supor® membrane filter. The organic solvent leachates of the bark and leaf biochars were further investigated for 'bio-oil like' compounds via GC/MS.

The analysis of the compounds in the biochars washing solutions was carried out using an Agilent GC–MS (6890 series GC with 5973 series MS detector). Biochar leaching samples were analyzed using a 30 m × 0.25 mm i.d HP-Innowax capillary column (0.25 μm cross-linked polyethylene glycol). The analysis consisted of injecting 1 μL of sample under the following conditions: splitless, initial oven temperature of 40 °C held for 3 min, then heated with at a rate of 10 °C min^{-1} to 260 °C and held for 5 min. A solvent delay of 3.6 min was employed. Masses were scanned from 15 to 500 mass units. The identification of the peaks in the chromatogram was based on the comparison with standard spectra of compounds in the NIST library and/or on the retention times of known species injected. Standard solutions of phenol and levoglucosan were used to obtain the calibration curves to calculate the concentrations in the leachates.

2.3. Characterization of leachate from washing biochars with water

At room temperature, leaf and bark biochars were washed with ultrapure water (Millipore 18.2 MΩ) water (0.5 g in 10 ml) in a small batch reactor, and stirred while soaked. Ultrapure water was chosen as leaching agent, because we wanted to exclude the influence of anions, cations and organic matter present in natural environment water, on the leaching. The soaking times were: 1 h, 1 d, 1 week, 2 weeks and 1 month. After the stirring time lapsed, the solutions were filtered over a 0.2 μm Supor® membrane filter. After filtration, biochar leachates were refrigerated (4 °C). The obtained leachates were investigated further with UV-fluorescence spectroscopy.

UV-fluorescence spectroscopy has been widely used (Mourant et al., 2013; Wang et al., 2013; Zhou et al., 2013) to characterize the structural features of bio-oil derived from biomass, giving information about the relative size and concentration of aromatic ring systems in the sample. In this study, the UV-fluorescence spectra of water samples of the chars were recorded using a Perkin–Elmer LS50B spectrometer. The leachates were diluted 20 times with ultrapure water. The synchronous spectra were recorded with a constant energy difference of −2800 cm^{-1}. The slit widths were 2.5 nm and the scan speed was 200 nm min^{-1}. The "wavelength" shown for each spectrum refers to that of the excitation monochromator. Wavelength is a brief indication of the aromatic ring sizes (e.g. <290 nm for mono-ring, 290–340 nm for aromatic ring systems containing 2 fused benzene rings, etc.) although a clear delineation about ring sizes and wavelength ranges is impossible (Li et al., 1994; Wang et al., 2011). At the same concentration, the fluorescence intensity was divided by the carbon content in biochar to express the fluorescence intensity on the basis of "per gram of C".

3. Results and discussion

3.1. Key characteristics of biochars

Table 1 gives the proximate analysis and the ultimate analysis of leaf and bark biochars. The oxygen content was calculated by difference.