Ashes from fast pyrolysis bio-oil production of different waste streams may be suited as soil amendment

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Fast pyrolysis bio-oil (FPBO) is a non-fossil fuel produced from renewable, mainly woody biomass. Conserving around 70% of the biomass' initial energy content, FPBO can be a substitute for fossil fuels (Bridgwater et al. 1999), e.g. in residential heating. During fast pyrolysis the biomass is heated to around 500 °C within a few seconds, and, as a result, the biomass is separated into aqueous vapors, pyrolysis gas and charcoal. Rapidly cooled, the vapor condenses into FPBO while gas and charcoal are further used for energy production by combustion. Ashes produced from charcoal combustion (FAs) accumulate in a separate stream. Their characteristics point towards suitability as a soil amendment since they are usually alkaline and contain the majority of minerals and salt present in the initial biomass, such as P, K and Mg as well as Fe, Mn and Zn (Fernández-Delgado Juárez et al. 2016). Consequently, FA addition may provide acid-neutralizing capacity and a variety of nutrients to soil. Limiting their recycling potential, heavy metals, alkali metals and silicon are often present in FAs (James et al. 2012). Thus, if not properly managed, their effect on nutrient leaching from soils might ultimately pose a negative impact on both the soil and the closing of nutrient cycles. For this reason, FAs are usually landfilled or applied in the cement industry. However, the type and composition of FAs vary considerably depending on the original biomass material and the production process (Maresca et al. 2017). For some FAs a positive effect on plant growth and soil characteristics has been reported after soil application (Li et al., 2016; Ochecova et al. 2017; Schiemenz et al. 2011, Schönegger et al. 2018).

In this study, we aimed at evaluating whether FAs generated during combustion downstream of FPBO production from different biomass materials can be applied to soil without harming the environment. Such kind of FA recycling can contribute to improving the environmental integrity of production processes. In order to achieve this goal, we characterized different FAs derived from the fast pyrolysis production regarding their physicochemical characteristics and phytotoxic effect. Selected FAs were applied to grasslands in a field trial and the effect of FA amendment on the soil was analysed.

FPBO was produced from forest residues, wheat straw, bark and *Miscanthus sp.*. The different FAs were characterized amongst other attributes based on their contents of total and total inorganic C, metals and polycyclic aromatic hydrocarbons (PAH) as well as their pH and electrical conductivity (EC). Leachability tests were conducted. The phytotoxicity of the FAs was evaluated by growing garden cress (*Lepidium sativum*) and lettuce (*Lactuca sativa*) in FA leachates' serial dilutions. The plant growth was quantified by the percentage of germinated seeds and root elongation index (RE). FA obtained from FPBO production from Miscanthus sp., bark and forest residues were applied to soil in a grassland field trial (500 kg ha^{-1}). The Cr (IV) content of FA from wheat straw was too high to be used as soil amendment. Plots were amended once, sites without FA amendment served as control. Using a randomized block design on a total area of 160 m^2, all four treatments were set up in quadruplicates. Topsoil samples were collected prior to FAs application (October 2017), before and after the plant growth period. The FAs effect on the soil was evaluated based on soil pH, EC, total C and N, volatile solids, total P and plant-available P, inorganic N and potential nitrification rate. As an estimate of the non-plant biological effect of FA amendment on grassland, soil microbial biomass and basal respiration were determined.

Despite feedstock-dependent characteristics, all FAs investigated in this study had a high nutrient content (averages: 0.6-3%$_{dry\ mass}$ total inorganic C; 1.4-18%$_{dry\ mass}$ total organic C) and an alkaline pH of around 12, indicating that they can be applied as lime substitute in order to reduce soil acidity. The EC (0.5-5 mS cm^{-1}) underlined a high mineral and salt content further supporting the use as soil amendment. For all of the FAs very low PAH levels were detected, emphasizing a good and complete combustion process. The concentrations of Cd, Cu, Pb and Zn were slightly above the Austrian legal limits. Except for *Miscanthus sp.* FA, all FAs exceeded Austrian legal limitations for Ni and Cr. All FAs stabilized properly as indicated by reduced pH. The mobility of

Ni in leaching experiments was low, being 0.7±0.03 mg kg^{-1} for wheat straw and below the detection limit for all the other FAs. For Cr, the mobility was higher compared to Ni (0.9-51 mg kg^{-1}), but not linear to Cr concentrations (1.2-41 mg kg^{-1}). FA leachate dilutions had no toxic effect on *L. sativum* and *L. sativa* germination. However, the root elongation was affected: undiluted leachates impaired (RE close to 1) and 50% diluted FA leachates still moderately reduced elongation (RE around 0.5). Leachates from bark FA had no phytotoxic effect. In agreement with the higher metal concentrations, FA from forest residues and wheat straw had the strongest phytotoxic effect. Nevertheless, this effect was strongly reduced by higher dilution than 25% for all FAs.

The results from the first year of the grassland field trial indicate that the application of *Miscanthus sp.*, bark and forest residue FA did not change soil characteristics compared to the control. Despite the different nutritional contents and metal concentrations, only seasonal changes were detected: ammonium, nitrate, C and EC decreased over time but did not differ between FAs treatments or compared to the control. The soil pH remained constant at around 7 and was unaffected by FA application.

Summarizing, our results underline the potential of some FAs for being used as soil amendment. Although further research investigating long-term effects is necessary, our findings emphasize that not all FAs have to be considered as hazardous wastes. Environmentally friendly treatment options for waste products like FAs might be found by careful assessment and process optimization, this way minimizing the need of landfilling as an ultimate option.

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