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Hydrothermally carbonized plant materials: Patterns of volatile organic compounds detected by gas chromatography

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HIGHLIGHTS

- Digestate, straw and various wood feedstock are carbonized between 190 and 270 °C.
- Volatile organic compounds are determined using head space gas chromatography.
- Relative amount and composition of volatiles from different feedstock are compared.
- Benzenes, phenols, furans, ketones and aldehydes increase with process temperature.
- Monitoring of VOC is an option to optimize hydrochars for environmental application.

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ABSTRACT

The nature and concentrations of volatile organic compounds (VOCs) in chars generated by hydrothermal carbonization (HTC) is of concern considering their application as soil amendment. Therefore, the presence of VOCs in solid HTC products obtained from wheat straw, biogas digestate and four woody materials was investigated using headspace gas chromatography. A variety of potentially harmful benzenic, phenolic and furanic volatiles along with various aldehydes and ketones were identified in feedstock- and temperature-specific patterns. The total amount of VOCs observed after equilibration between headspace and char samples produced at 270 °C ranged between 2000 and 16,000 μg/g (0.2–1.6 wt.%). Depending on feedstock 50–9000 μg/g of benzenes and 300–1800 μg/g of phenols were observed. Substances potentially harmful to soil ecology such as benzofurans (200–800 μg/g) and *p*-cymene (up to 6000 μg/g in pine wood char) exhibited concentrations that suggest restrained application of fresh hydrochar as soil amendment or for water purification.

1. Introduction

Solid carbonaceous products termed hydrochars have been suggested for various applications such as soil amendment and carbon sequestration (Titirici et al., 2007; Sevilla et al., 2011). They are obtained from biomass by means of hydrothermal carbonization (HTC), typically at 180–250 °C, 2–10 MPa and in the presence of liquid water. In comparison with chars obtained from pyrolysis, hydrochars show a lower carbon content, less aromatic structure, and less biological stability, but HTC allows a higher char yield as well as a higher overall energy efficiency for wet feedstock (Libra et al., 2011). The option to use wet organic waste such as biogas digestate (Mumme et al., 2011) makes HTC specifically interesting compared to pyrolysis, which requires dry feedstocks. The use of hydrochars for soil amendment promises various benefits such as improved water holding capacity and long-term storage of carbon branched off the biomass cycle that may lead to an overall negative greenhouse gas balance. Furthermore, chars are chemically related to black carbon components in soil, which have been discussed as a sink for persistent pollutants (Koelmanns et al., 2006).

However, the experimental application of hydrochars from various sources to soils in laboratory and field trials revealed various proven or potentially detrimental effects on seed germination (Busch et al., 2011), microbial activity (Steinbeiss et al., 2009), and mycorrhiza growth (Rillig et al., 2010), and gene repression in soil nematodes (Chakrabarti et al., 2011). Phytotoxic behavior is not an exclusive effect of hydrochars but has also been reported for chars obtained from the pyrolysis of bioenergy residues such as digestates (Gell et al., 2011). The adverse effects of fresh hydrochars may partly be attributable to volatile organic compounds (VOCs) (Busch et al., 2011). As a consequence, the VOC content is

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