High-VOC biochar—effectiveness of post-treatment measures and potential health risks related to handling and storage

High-VOC biochar – Effectiveness of post-treatment measures and potential health risks related to handling and storage

Wolfram Buss[a], Ondřej Mašek[a]*

[a] UK Biochar Research Centre, School of Geosciences, University of Edinburgh, Crew Building, Alexander Crum Brown Road, Edinburgh, EH9 3FF, UK

*Correspondence: Ondřej Mašek, tel. 0131 6505095, fax +44 131 662 0478, e-mail: ondrej.masek@ed.ac.uk

Abstract

Biochar can contain volatile organic compounds (VOCs), formed and introduced during the pyrolysis process. In some pyrolysis units or under specific conditions during production, pyrolysis vapours can deposit on biochar in significant amounts. In this study, it was tested to which extent VOCs are released from such high-VOC biochars when openly stored, which post-treatment measures are most effective in reducing phytotoxic potential and whether the VOC emissions could exceed human health-related threshold values. It was shown that the initial VOC release of high-VOC biochars can exceed occupational exposure limit values and even after 2 months the biochar still emitted VOCs exceeding air quality guideline values. Consequently, the investigated high-VOC biochars pose health risks when handled or stored openly. Simple open-air storage turned out not to be sufficient for VOC-removal. Low temperature treatment on the other hand removed VOCs from the high-VOC biochar effectively and alleviated any human health risks and phytotoxic effects. The low-VOC biochar not only did not emit any VOCs, but was even able to sorb VOCs from the VOC-rich biochar to a certain extent. Thermal treatment and blending with low-VOC biochar are methods which could be used in practise to treat high-VOC biochar to reduce VOC emissions.

Keywords

biochar; VOC; post-treatment; human health; phytotoxicity; PAH

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Abbreviations

VOC, volatile organic compound; PAH, polycyclic aromatic hydrocarbon; GC biochar, gas contaminated biochar; LC biochar, liquid contaminated biochar; NC biochar, non-contaminated biochar; LMW, low-molecular weight

1 Introduction

Pyrolysis, which is thermal treatment of biomass at temperature of 350-750°C under oxygen limited condition, alters the physical and chemical characteristics of the processed material significantly (Brown et al. 2015). The solid product is a carbon-rich material, which, when intended for soil application, is called biochar (Sohi et al. 2010). Biochar has shown to possess a range of beneficial properties which make it suitable for various purposes, e.g. carbon storage, soil remediation, soil improvement and wastewater treatment (Lehmann and Joseph 2015).

However, in some studies, biochar has shown to cause adverse effects on plants and soil organisms (Deenik et al. 2010; Gell et al. 2011; Rogovska et al. 2012; Rajkovich et al. 2012; Smith et al. 2013; Oleszczuk et al. 2013; Jones and Quilliam 2014; Buss and Mašek 2014; Domene et al. 2015). High salinity and nitrogen immobilization after biochar application have been suggested to be two of the factors that led to inhibitions of plant growth (Deenik et al. 2010; Gell et al. 2011; Rajkovich et al. 2012; Domene et al. 2015), yet, the majority of studies identified contaminants to be responsible for observed phytotoxicity (Gell et al. 2011; Smith et al. 2013; Oleszczuk et al. 2013; Jones and Quilliam 2014; Buss et al. 2015). For application of biochar to soil, as well as for general handling of biochar, it needs to be ensured that biochar does not pose any excessive risk to plants, humans and the ecosystem. Consequently, conducting phytotoxicity tests and analysing contaminants in biochar is essential and different groups of contaminants have been found; inorganics, as well as organics.

Potentially toxic elements (PTEs) in biochar most often originate from the feedstock but sometimes also from materials used for construction of the processing equipment (Buss et al. 2016b). Organic contaminants in biochar are a more complex issue, as these are formed in elaborate reactions during the high-temperature treatment in pyrolysis units; the relevant groups are volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and dioxins (Bucheli et al. 2015; Buss et al. 2015; Buss et al. 2016a). It has been shown that, while total concentrations of dioxins are typically below threshold values for soils (Hale et al. 2012; Bucheli et al. 2015), concentrations of PAHs can, in some cases, exceed

values recommended in current legislation (Hilber et al. 2012; Hale et al. 2012; Buss et al. 2016a). However, concentrations of available dioxins were below the detection limit of analytical equipment and available PAH levels were lower than clean urban sediments (Hale et al. 2012). The third category, i.e. VOCs, on the other hand, are not studied very well in biochar, but the studies that exist indicate that a wide selection of VOCs are present with considerable potential for negative or positive impact on plants and soil due to their high mobility (Elad et al. 2011; Spokas et al. 2011; Buss et al. 2015). Consequently, phytotoxicity tests were conducted investigating the effect of vapours from VOC-rich biochars and indeed strong inhibitions were observed (Buss and Mašek 2014). Post-treatment measures showed only partly to be successful in alleviating negative effects and there is a need for understanding the VOC-removal mechanisms and developing more effective methods for post-treating biochars.

VOCs are defined as organic compounds that have boiling points of ≤ 250°C and due to their volatility are often considered contaminants that can threaten air quality (Directive 2004/42/CE of the European parliament and of the council 2004). During handling or storage of VOC-rich biochars, people involved could be exposed to VOCs which could be a health and safety hazard. Depending on the use of biochars, different threshold values for human health would apply. When used at a work place, occupational exposure limit values regulate the VOC concentration thresholds, which exist in most countries (EU Commission Directive 91/322/ECC 1991; Aussschuss für Gefahrstoffe 2006; US Department of Health and Human Services 2007). When biochar is used privately e.g. in growing media, VOCs released from biochar would have to be evaluated differently. E.g. in Germany, guideline values for indoor air pollution in private and public buildings were introduced to assess the toxicological risk for long-term exposure to VOCs (Arbeitsgemeinschaft Ökologischer Forschungsintitute 2013) or to regulate the maximum permissible VOC release for construction products which was also partially implemented in EU legislation (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten 2012; European Union Joint Research Centre 2013). To our knowledge, compliance of biochar with existing VOC threshold values has not been tested before which could be highly relevant for human health and safety.

This study focused on the release mechanisms of VOCs from biochar to understand the effects of vapours from VOC-rich biochars on plant growth and the way post-processing affects VOC-release. Furthermore, the potential impact of VOCs from biochar on humans during biochar handling and storage was assessed by comparing VOC concentrations with threshold values for human health. The release of VOCs from two types of biochar during open storage was investigated: a) biochar contaminated during production with pyrolysis vapours (high-VOC) and b) comparable biochar (same feedstock and pyrolysis conditions) with low concentration of VOCs (low-VOC). Mass change of the biochars during open storage was measured to see if it is possible to use this easy-to-perform method to assess the volatile carbon fraction that is already emitted at room temperature and if this can be correlated with VOC concentration in the head-space of the samples measured with a VOC analyser. Furthermore, potential mitigation measures, such as sorption of VOCs onto low-VOC biochar and low-temperature oxidation were tested. The objective of this research was to assess the release dynamics of VOCs from contaminated biochars and to develop effective post-treatment measures for reducing VOC concentrations.

2 Materials and Methods

An overview of all the experiments that were conducted in this study can be found in Figure 1.

2.1 Biochars

Three biochars, produced in the same pyrolysis unit (rotary kiln), under identical process conditions (550°C highest treatment temperature, 20 min mean residence time) and from the same feedstock (softwood pellets) were investigated in this study. The only difference between the biochars was the fact that two of these were contaminated due to condensation of pyrolysis vapours in the chamber where biochar was separated from pyrolysis gases (discharge chamber). As a result, the two contaminated biochars had high content of VOCs (high-VOC) and henceforth, will be referred to as gas contaminated (GC) and liquid contaminated (LC) biochar, to reflect the different mechanisms of contamination. The third biochar is a low-VOC biochar, produced under standard operating conditions and will be referred to as non-contaminated (NC) biochar. Although the extent of contamination of GC and LC biochar with pyrolysis vapours in this study was unusual for the investigated pyrolysis unit (Buss and Mašek 2014), a study testing several commercial biochars found similar phytotoxic effects and PAH concentrations as observed for the tested biochars (Buss et al. 2015; Kołtowski and Oleszczuk 2015), showing that such contamination can occur.

2.2 VOC measurements

For the VOC measurements, a miniRAE lite VOC analyser (RAE Systems, Inc, San Jose, California) with a photoionisation detector and a 10.6 eV gas-discharge lamp was used. The instrument has a flow rate of around 0.5 L min^{-1} and detects VOCs with a resolution of 0.1 ppm. A two-point calibration using fresh air (0 ppm) and isobutylene standard reference gas (100 ppm) was performed. As control, the air in the lab was sampled for each measurement.

2.3 VOC emissions of fresh biochar samples

To analyse the initial VOC release of the three biochars, 10 g of ‘fresh’ (stored in a sealed container after production) NC, GC and LC biochar pellets were added into 125 mL glass jars and the VOC concentration in the head-space above the biochar

samples was measured. The biochars were not ground prior to analysis to be able to measure the VOC concentration released from the undisturbed samples (the same for thermally treated samples in 2.3). The concentration in the head-space of the biochar samples was measured for 10 s and the peak VOC concentration within this time period was reported. Triplicate analysis were performed by measuring the VOC concentration in the head-space of the container after 5 min sealed storage (open container, measure for ~10 s, close container for 5 min, open container and measure for ~10s, repeat all).

2.4 Time series measurements of VOC release dynamics

Three different experiments were performed to investigate the VOC release dynamics by high- and low-VOC biochars when openly stored (exposed to air), after storage in sealed containers since the day of production. The VOC concentration in the head-space above the samples, the change of mass of the samples and the change of pH of a water reservoir surrounding the samples was determined (grey underlined experiments in Figure 1). For the following time series of VOC measurements during open storage, the samples were ground using pestle and mortar. 2 g of ground NC, GC and LC biochar were filled in 125 mL glass vials, respectively.

2.4.1 VOC measurement in the head-space of biochar

Prior to the first VOC measurement, the samples were stored openly for 5 min because the VOC concentrations of the freshly ground samples fluctuated significantly. To investigate the release of VOCs during open storage, the VOC concentration in the head-space of the biochar samples were measured every 30 min over the course of 50 h using the miniRAE lite VOC analyser as described. To eliminate short-term fluctuations, instead of taking one measurement every 30 min, at each stage the concentration was measured four times within 40 s and an average was reported. Cross-contamination was avoided by conducting the experiments with the different biochars individually, at different days. The temperature was kept at ~17±1°C. Afterwards, the samples were stored openly in the lab for 2 month (17-22°C) before the VOC concentration in the head-space was measured again.

2.4.2 Change of mass of biochar sample

To determine the change in biochar mass as a result of VOC release, ~2 g of each of NC, GC and LC biochar was added to pre-weighed aluminium foil cups (25 mm height, 70 mm diameter at the top, 40 mm at the bottom) and the mass was measured over 50 h. Variations of relative humidity in the lab led to significant fluctuations of the mass of the samples and to account for this, the same experiment was performed with samples that were stored in the lab for several weeks prior to the experiment (no net change of mass). The change in mass of these samples was subtracted from the fresh samples for the different points in time. The analyses were performed in triplicates.

2.4.3 Change of pH of water reservoir affected by biochar vapours

To investigate the acidity of the vapours released, the change of pH of a water reservoir surrounding, but not in direct contact with the biochar samples, was measured. Again 2 g of ground NC, GC and LC biochar was added to aluminium cups and placed into plastic jars on an elevated platform above 100 mL of a 0.1 mol L^{-1} KCl solution. The KCl was added because resistance errors can occur measuring the pH of distilled water and the resulting value can differ significantly (Youmans 1972). The pH was measured with a pH meter (Mettler Toledo FE 30) over the course of 50 h. The change in H^+ concentration was calculated from the pH. The analyses were performed in triplicates.

2.5 Blending of low-VOC and high-VOC biochars

To evaluate if low-VOC biochar had the ability to sorb measurable amounts of VOCs from high-VOC biochar, fresh samples of LC biochar were mixed in ratios of 1 g : 9 g and 2 g : 8 g with NC biochar (same ratio as used in the germination test in Buss and Mašek (2014)). The biochars were ground, mixed together and 10 g of the mixture was placed into a 125 mL glass jar. In the following, the blends will be referred to as LCB 1:9 and LCB 2:8. The VOC concentration in the head-space was measured (section 2.2). The experiment was not performed for 50 h as for the experiment with the unblended biochars, but for 60 h as the VOC concentration was still changing after 50 h.

2.6 Thermal post-treatment

Samples of all three uncrushed biochars (NC, GC and LC biochar) were spread in aluminium trays in one layer and exposed to air at 200°C for 20 h in a laboratory oven. 10 g of each of the thermally treated biochars was placed in a 125 mL glass jar and the VOC concentration in the head-space was measured as described in 2.2. The treated samples were used for germination tests (section 2.7) and parts were stored openly for 14 days and the VOC emission was measured again.

2.7 Germination tests

'Volatiles only' and 'all exposure routes' cress seed germination tests (Buss and Mašek 2014) were performed using 1, 2 and 5 g of ground NC, GC and LC biochar treated at 200°C for 20 h (for 'volatiles only' test) and 1, 2 and 5% of the three biochars in sand (for 'all exposure routes' test). In the 'volatiles only' germination test, seeds were not directly exposed to the biochar but only to its vapours. In the 'all exposure routes' germination test, seeds were either only exposed to the vapours from a biochar-sand mixture, exposed to the vapours and leachate from the mixture or were in direct contact with biochar. For the 'volatiles only' germination test, length of shoots and roots were determined, while in the 'all exposure routes' germination test the roots were categorized in three fractions (roots < 15 mm, roots between 15-60 mm and roots > 60 mm). More details can be found in Buss and Mašek (2014). The tests were performed in triplicates.

2.8 PAH analysis

Concentrations of total and water extractable PAHs were determined using 36 h toluene extraction and shaking of biochar in DI water with a ratio of 1:10, respectively. PAH analyses were performed by Northumbrian Water Scientific Services (Newcastle, United Kingdom), laboratories accredited by United Kingdom Accreditation Service (UKAS). More details can be found in Buss et al (2015).

2.9 Data analysis

Freundlich-langmuir sorption isotherms were fitted to the data for VOC release and change of H^+ concentration according to a best fit model. R^2 was used to show the deviation of the data from this fit. For the evaluation of the germination tests the

difference to the control was determined using one-way ANOVAs in SigmaPlot 12.5 (Systat Software Inc).

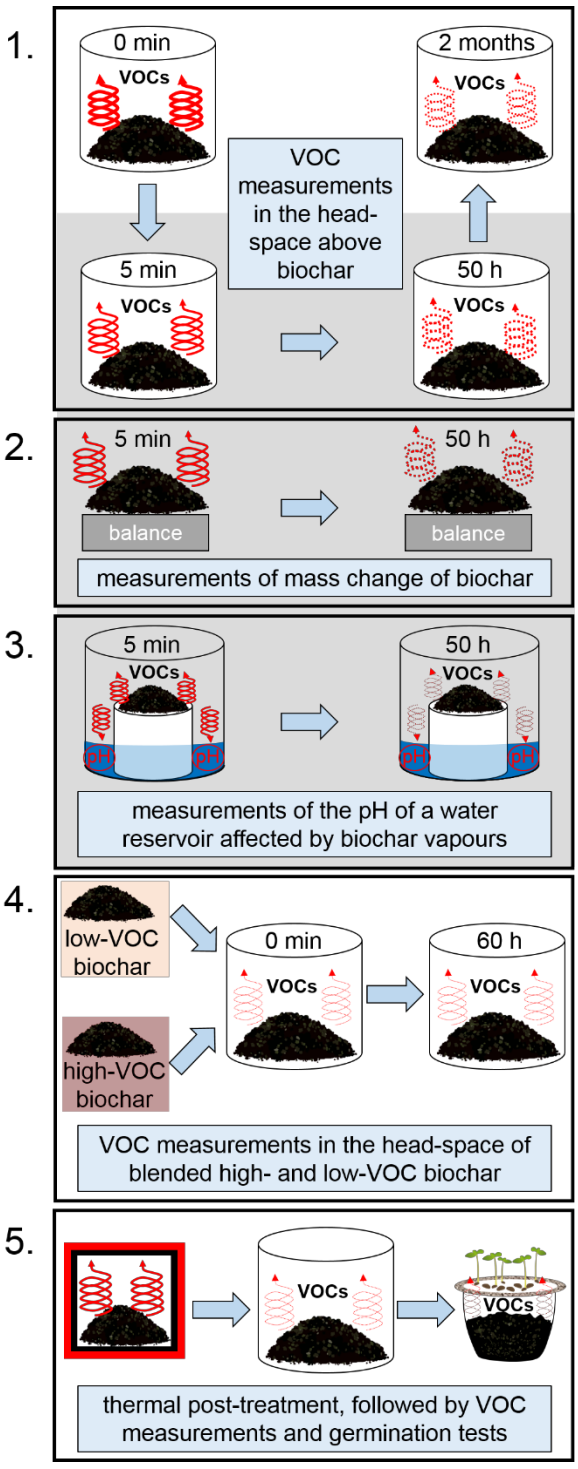

Figure 1 Schematic of the experiments conducted in this project. The low-VOC biochar and the two high-VOC biochars were tested in all five tests. Results for experiment 1 can be found in Table 1, the results for the grey underlined experiments which were all performed on the same time scale are depicted in Figure 2, the results of experiment 4 are shown in Figure 3 and results of experiment 5 can be found in Table 1 and in the SI. More details about the experiments can be found in materials and methods

3 Results and discussion

3.1 VOC release of fresh and stored biochars and implications for plant growth

To investigate the VOC release of biochars, two high- and one low-VOC biochar were tested in three times series experiments conducted over 50 h. The experimental set-ups can be found in Figure 1 (grey underlined area). VOC release characteristics of GC, LC and NC biochars were investigated by measuring the head-space VOC concentration, the change of mass of the biochars and the change of the pH of a water reservoir surrounding the samples (measured as change of H^+ concentration). The combined results are shown in Figure 2.

The low-VOC, NC biochar increased in mass rapidly within the first 5-6 h of open storage, saturation was reached at around 6% with barely any additional weight change until the end of the experiment (freundlich-langmuir sorption isotherm, R^2 = 0.999). The mass gain can be attributed to uptake of moisture from the air which is typical for hygroscopic, porous carbons (Li et al. 2008). Measurement of concentrations of VOCs in the head-space showed that the NC biochar did not release any detectable levels of VOCs and there was also no noticeable change in the pH of the water reservoir surrounding it (Figure 2).

Unlike the NC, both the GC and LC biochar released considerable amount of VOCs. The head-space concentrations of VOCs for fresh (crushed) samples were 2.9 ppm for GC and 8.5 ppm for LC biochar (Table 1) which reduced dramatically with exposure to air, dropping to 1 ppm after 10 h open storage and then to 0.4 ppm until the end of the experiment (50 h) for GC biochar (Figure 2). For LC biochar the concentration declined to 1.8 ppm after 10 h exposure to air and in the following 40 h it decreased slowly to 0.7 ppm. During the 50 h VOC release period under ambient conditions, the GC biochar sample increased in mass by around 2% while the mass of LC biochar remained constant. This could mean that LC, in contrast to NC biochar, did not take up any moisture and the mass of the VOCs released was too small to be captured with the balance. However, in Buss and Mašek (2014), using thermogravimetric analysis, it was shown that, when heated to 110°C for 15 min, there was an extra mass loss of ~5% in the LC biochar sample compared to the NC biochar, indicating that measurable amount of VOCs were released. This 5% extra

loss of mass of the LC biochar matches the 6% mass uptake of the NC biochar very closely, suggesting that VOC release and moisture uptake happened simultaneously and to a similar extent in LC biochar, overall, resulting in no change in mass. In addition, the mass gain curve (moisture uptake) of the NC sample and the VOC release curve of the LC sample are inversely correlated (Figure 2), which means the moisture uptake and VOC release dynamics and rate were similar. Overall, the simultaneous release of VOCs and uptake of moisture resulted in constant weight of the LC biochar confirming that moisture uptake masked the release of VOCs. This highlights an issue with using gravimetric methods for simple assessment of VOC release in biochar.

Furthermore, the high-VOC biochars (GC, LC) increased the H^+-concentration in the water reservoir surrounding the samples (this corresponds to a pH decrease) (Figure 2). The VOC release and change of H^+-concentration were inversely correlated, which, in addition to high concentrations of LMW aliphatic acid detected in the samples in Buss et al. (2015), strongly indicates that the pH change indeed originated from VOCs emitted by biochar. The change of the pH of the water reservoir was very similar for both high-VOC biochars (~$6*10^{-6}$ mol L^{-1}) which showed to have the same pH (3.64) and very similar amounts of volatile, LMW, aliphatic acids (~1600 mg kg^{-1}) (Buss and Mašek 2014; Buss et al. 2015) (the higher amounts of phenols detected in LC biochar is the likely cause of the difference in head-space VOC concentrations). The starting pH in the tests varied slightly, nevertheless, change of H^+ concentration of $6*10^{-6}$ mol L^{-1} corresponds to a pH decrease of 1.8 units when starting at a pH of 7. Here it was shown that VOCs emitted by biochar indeed have the ability to change the pH of a water reservoir to a significant extent which means emissions of VOC from biochars could lead to corrosion of metal containers or metal structures close to the area these biochars are stored.

Overall, after 50 h of storage in open air and even after open storage for 2 months in the lab, still, VOC emissions from GC and LC biochars were at detectable levels (Table 1). It shows the ineffectiveness of simple, open storage as post-treatment for removing VOCs from these specific biochars. In Busch et al. (2012), on the contrary, storage of char from hydrothermal carbonization for 2 weeks showed to reduce VOC emissions successfully and cress seeds were able to grow unhampered. The

phenomenon of constant release of VOCs shown by the two highly contaminated biochars, even after long-term storage could be a hazard for application of such biochar to soil. However, previously, it was shown that incorporation of biochars into wet sand or washing of biochar alleviated phytotoxic effects of VOCs to a large extent (Bargmann et al. 2013; Buss and Mašek 2014). Consequently, under natural conditions, biochar will be exposed to natural weathering and precipitation/irrigation which will reduce effects of VOCs significantly.

Table 1 VOC concentrations (ppm) in the head-space of low-VOC (NC) and two high-VOC (GC and LC) biochars treated in different ways

		low-VOC		high-VOC			
		NC biochar		GC biochar		LC biochar	
treatment	unit	AV	SD	AV	SD	AV	SD
* fresh (0 min)	ppm	0.0	0.0	7.3	0.9	13.7	2.2
# crushed and stored for 5 min	ppm	0.0	0.0	2.9	0.2	8.5	0.7
# open storage for 50 h	ppm	0.0	0.0	0.4	0.0	0.7	0.0
# open storage for 2 months	ppm	0.0	0.0	0.2	0.1	0.3	0.1
* 200°C for 20 h from fresh	ppm	0.0	0.0	0.0	0.0	0.7	0.2
* + 14 days of storage	ppm	0.0	0.0	0.0	0.0	0.0	0.0

* 10 g of uncrushed biochar were measured in 125 mL vials in triplicates

2 g of crushed biochar was measured in 125 mL vials in quadruplicates

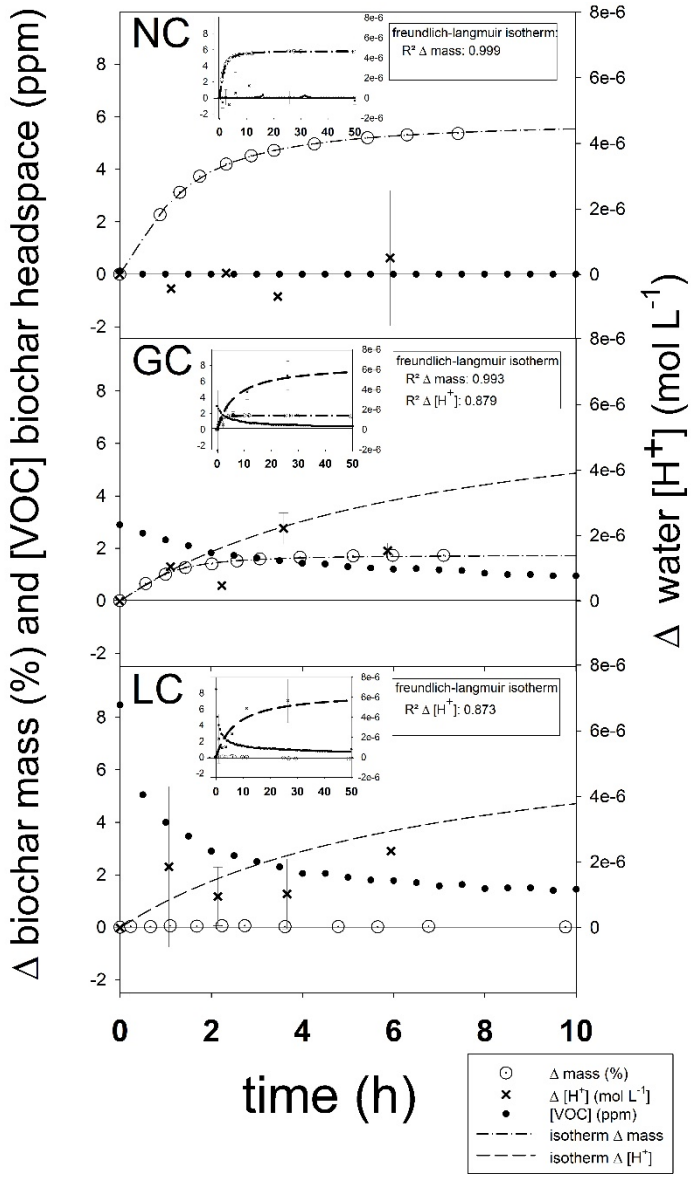

Figure 2 Mass change (%), VOC concentration in the head-space (ppm) (both left axis) of non-contaminated (NC), gas contaminated (GC) and liquid contaminated (LC) biochar when exposed to air and the change of H^+ concentration (mol L^{-1}) of a water reservoir surrounding the samples is shown (right axis). H^+ concentration and mass change are given with standard deviation (n = 3). R^2 are depicted where freundlich-langmuir sorption isotherms were fitted to the data. The small graphs in each figure show the same data over the whole duration of the experiment, i.e. 50 h

3.2 Blending of low-VOC and high-VOC biochars as a measure for mitigation risk for plant growth

In this experiment, it was tested, whether low-VOC biochar can sorb measureable amounts of VOCs from high-VOC biochar. The initial (0 h) VOC concentration in the head-space above LC biochar samples amended with low-VOC (NC) biochar was 0 ppm for both blends (LCB 1:9 and LCB 2:8) (Figure 3). Compared to the initial concentration of VOCs above the pure 2 g LC sample (8.5 ppm, added in Figure 3), it shows that blending with NC was effective and that NC biochar was able to sorb most, if not all, of the VOCs released by LC biochar. However, after a few hours the VOC concentration in the head-space of LCB 2:8 increased and a peak concentration of 0.9 ppm after around 14 h was detected. Consequently, it seems that NC biochar reached its maximum sorption capacity and could not take up more of the VOCs. Subsequently, the VOC concentration slowly decreased until it reached 0.1 ppm after 52 h. The situation was different for the LCB 1:9, which showed no detectable VOC release for the duration of the experiment, confirming NC biochar's ability to prevent VOC release from the LC sample at lower concentrations (Figure 3).

In the case of activated carbon, the VOC sorption capacity in two studies was tested with gaseous benzene and different activated carbons were able to take up around 0.4 g benzene/g on average (Chiang et al. 2001; Rodríguez-Mirasol et al. 2005). Our biochars clearly did not have the capacity to sorb an amount as high. Still, blending high-VOC and low-VOC biochars could be used to help controlling the desorption rate of VOCs, providing more time for their degradation in soil or for deliberate release of small amounts of VOCs to trigger positive effects on plant growth as observed in several studies (Keeley and Pizzorno 1986; Kwapinski et al. 2010; Elad et al. 2011).

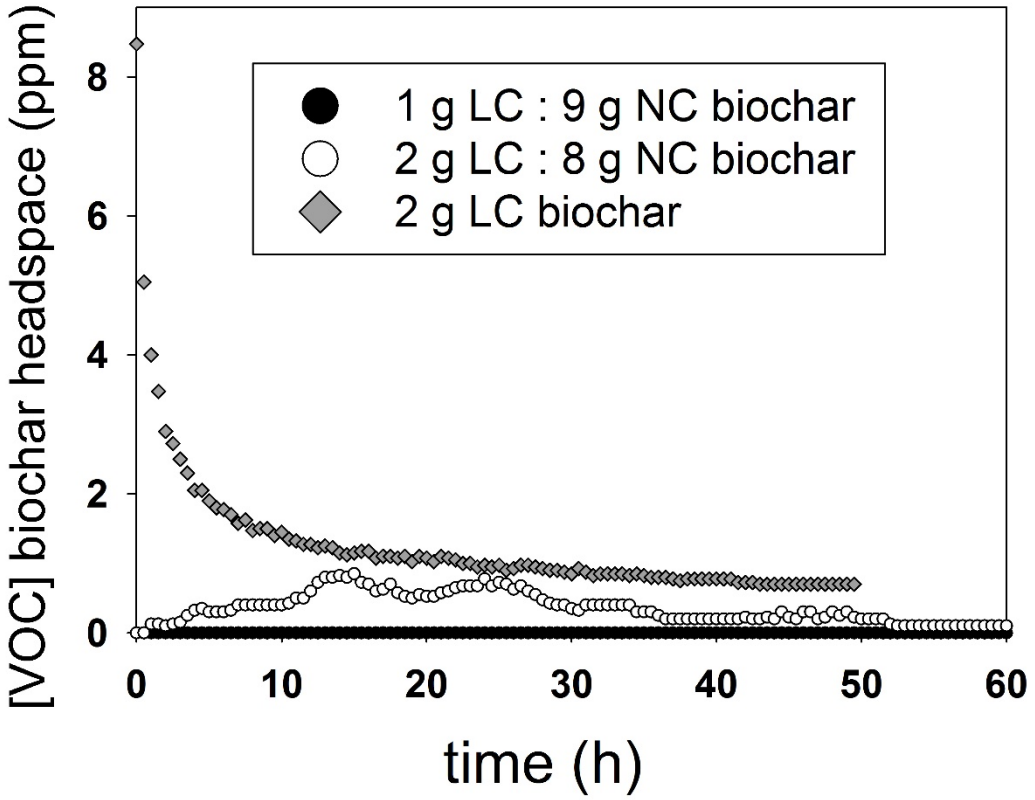

Figure 3 VOC concentration (ppm) in the head-space of LC biochar samples blended in different ratios when exposed to air for 60 h. 1 g of LC biochar was mixed with 9 g of NC biochar (LCB 1:9) and 2 g LC mixed with 8 g NC biochar (LCB 2:8). For comparison the VOC concentration in the head-space of 2 g LC biochar as in Figure 2 is shown (measured for 50 h)

3.3 Thermal post-treatment for VOC-removal and alleviation of phytotoxic effects

As long-term open-storage did not show to be promising in terms of VOC release mitigation and blending was effective only at relatively low concentrations of contaminated biochar, we investigated low-temperature oxidation/devolatilisation (200°C for 20 h) as another method for VOC content management. Thermal treatment reduced the VOC content in the head-space in GC biochar to 0 ppm and in LC biochar to 0.7 ppm (Table 1). In combination with open-air storage for 14 days, the VOC concentration in the head-space of LC biochar also dropped to 0 ppm in the LC biochar sample.

In Kołtowski and Oleszczuk (2015), a similar thermal treatment approach was tested for removal of PAHs in biochars with similar PAH concentrations (3.5, 20 and 40 mg kg^{-1}) as determined in the biochars investigated in this study (6, 28 and 53 mg kg^{-1}) (analysed in Buss et al. (2015)). As in Kołtowski and Oleszczuk (2015), thermal treatment effectively reduced the total concentrations of PAHs to 1.79 mg kg^{-1} for NC, 2.79 mg kg^{-1} for GC and 1.21 mg kg^{-1} for LC biochar and the water-extractable concentrations to below 0.001 mg kg^{-1} (SI Table 1) (fresh GC biochar contained 1.6 and LC 2 mg kg^{-1} water extractable PAHs (Buss et al. 2015)). This shows that 200°C treatment for 20 h can remove VOCs as well as PAHs from biochar.

The thermally treated biochars were tested in 1, 2 and 5 g in ‘volatiles only’ cress seed germination tests and where vapours from fresh and 4 week-stored biochars resulted in 100% germination inhibition (Buss and Mašek 2014), low-temperature thermal treatment alleviated all toxic effects (SI Figure 1) (100% germination rate was observed in all treatments and the shoot and root growth did not differ statistically from the control). Analysing all three biochars in ‘all exposure routes’ seed germination tests revealed the same, seeds affected by vapours, seeds affected by the leachate from biochar-sand and seeds in direct contact with biochar-sand showed no inhibition of germination rate and early seedling growth compared to the control (SI Figure 2). In Kołtowski and Oleszczuk (2015), thermal treatment did remove PAHs, however, the thermally treated biochars showed inconclusive effects (positive and negative) on growth of shoots and roots in the same plant species as

tested here, suggesting that other than VOC or PAH effects were responsible for the toxicity.

Overall, in the current study, thermal treatment showed to be effective in reducing PAHs and VOCs in both contaminated biochars (GC and LC biochar) and in alleviating previously observed phytotoxicity.

Table 2 Threshold values for individual VOCs based on German, EU and US guidelines and legislations

	occupational exposure limits				indoor air quality	
	short-term		40 h-week		GV II	LCI
	[1]EU	[2]NIOSH	[1]EU/[3]TRGS	[2]NIOSH	[4]AGÖF 2013	[5]AgBB 2012
	ppm	ppm	ppm	ppm	ppm	ppm
phenol	4	[+]15.6	2	5	0.052	
cresol				2.3	*0.011	
naphthalene		15	0.1	10	0.006	0.0001
formic acid			5	5		0.66
acetic acid		15	10	10		0.13
propionic acid	20	15	10	10		0.12
$TVOC_3$						2.6
$TVOC_{28}$						0.26

* sum of three cresols

[+] ceiling value: should not be exceeded at any time

[1] EU Commission Directive 2000/39/EC, 2000; EU Commission Directive 2006/15/EC, 2006; EU Commission Directive 2009/161/EU, 2009; EU Commission Directive 91/322/ECC, 1991

[2] US Department of Health and Human Services, 2007, "Pocket Guide to Chemical Hazards".

[3] Aussschuss für Gefahrstoffe, 2006 (Germany), "Technische Regeln für Gefahrenstoffe, Arbeitsplatzgrenzwerte".

[4] Arbeitsgemeinschaft Ökologischer Forschungsintitute, 2013 (Germany), "Guidance Values for Volatile Organic Compounds in Indoor Air". GV II, reference value, for indoor air quality of private and public homes, based on toxicological studies, when exceeded countermeasures to be taken.

[5] Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten, 2012 (Germany), "Health-related evaluation procedure for volatile organic compounds emissions (VOC and SVOC) from building products". LCI, lowest concentration of interest, threshold value emitted by construction products in a test chamber after 28 days. $TVOC_3$, total VOCs after 3 days. $TVOC_{28}$, total VOCs after 28 days.

[123] Occupational exposure limits based on weighted-averages in a 40 h work-week and short-term (15 min) exposure limits.

[13] lower of the EU/German occupational limit value depicted.

[45] Values of GV II and LCI in µg m^{-3} were converted into ppm based on 25°C and 1 bar pressure, for $TVOC_3$ and $TVOC_{28}$ in addition the molecular weight of phenol was used.

3.4 Potential human health and safety risks associated with VOC release from fresh and treated biochars

During handling and storage of contaminated biochar, such as GC and LC used in this study, relatively high amounts of VOCs can be released, leading to risk of exposure for anyone working with these materials, particularly in enclosed areas with poor ventilation. Fresh LC and GC biochar resulted in head-space concentrations of VOCs of up to 13.7 ppm (LC) and 7.3 ppm (GC) directly after removing from closed containers. In a previous study, the individual composition of LMW-hydrocarbons in GC and LC biochar was analysed. Although measured in water extracts from the samples, a very similar composition can be assumed in the head-space above the biochars as the identified compounds are typical VOCs which partially vaporize at room temperature (Buss et al. 2015). Methanol, phenol, cresols and LMW aliphatic acids were the compounds in the highest concentrations; naphthalene was also present but in comparably low concentrations (Buss et al. 2015).

According to EU and US legislation, short-term occupational exposure limits for workers for the described VOCs are in the range of 4-20 ppm (Table 2). The exposure to phenol should not exceed 4 ppm for 15 min and 15.6 ppm should never be exceeded. Naphthalene, acetic and propionic acid short-term exposure threshold values, as defined by the US National Institute for Occupational Safety and Health, were set to 15 ppm (US Department of Health and Human Services 2007). Based on results obtained in this study, 13.7 and 7.3 ppm release of a mixture of VOCs by high-VOC biochar, it seems feasible for short-term exposure values for certain VOC constituents to be exceeded, under certain conditions, especially during handling. Risks related to long-term exposure can also be foreseen, as limits in this case are much lower than for short-term exposure, e.g. phenol should not exceed 2-5 ppm, acetic acid 5 ppm and cresol 2.3 ppm (Table 2). Overall, long-term exposure could be an issue where, for example, VOC-contaminated biochar would be stored openly next to a work place. Considering that biochars stored for 50 h showed head-space concentrations of VOCs of 0.4 ppm (GC) and 0.7 ppm (LC) (Table 1), it seems rather improbable that threshold values would be exceeded. Furthermore, low-VOC biochar, e.g. NC biochar in this study, did not emit any detectable concentrations of VOCs and would definitely comply with occupational exposure limits.

In addition to risks to workers handling contaminated biochar, public and private indoor air quality could also become an issue for use of high-VOC biochar. This could be the case, for example, if such contaminated biochar was used in growing media used for potted plants in residential or commercial buildings. VOC-rich biochars stored for 2 months still emitted measurable amounts of VOCs (0.2, 0.3 ppm) (Table 1) which could exceed the toxicological reference values for phenol (0.052 ppm), sum of the three cresols (0.011) and naphthalene (0.006) of indoor air quality guidelines in Germany (Table 2). Another concept for monitoring indoor air quality which could apply for biochar, is VOC testing of building products in a ventilated test chamber after 3 and 28 days (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten 2012). As an example, in Germany the total values of VOCs emitted by construction products (materials used in buildings and furniture) as well as so-called “lowest concentration of interest (LCI)” for individual VOCs were established and were partially incorporated into EU legislation (Ausschuss zur Gesundheitlichen Bewertung von Bauprodukten 2012; European Union Joint Research Centre 2013). In this study, high-VOC biochar openly stored for 50 h (0.4, 0.7 ppm) did not exceed the total VOC threshold value for 3 days (2.6 ppm) but biochars stored for 2 months (0.2, 0.3 ppm) exceeded the value for 28 days (0.26 ppm). Again, the low-VOC biochar did not show any VOC emissions, therefore, did not exceed any of the threshold values for VOC exposure and in fact can act as a sorbent for VOCs, subsequently, improving indoor air quality.

Overall, it shows that handling of high-VOC biochar, as well as the use in closed spaces can pose hazards to human health and where handling of contaminated biochar cannot be avoided, appropriate measures need to be implemented. Further processing of such high-VOC biochar is highly recommended to allow safe handling and use, such as, blending with low-VOC biochar or thermal post-treatment.

4 Conclusions

In this study, the VOC release dynamics from biochars contaminated by deposition of pyrolysis vapours during biochar production was investigated and the effectiveness of potential post-treatment measures aimed at reducing VOC contamination were assessed. It was shown that simply measuring the mass change of biochar sample when openly stored is not a sufficient indicator for assessing changes in VOC content due to the simultaneous uptake of water vapour. From three measures for reducing VOC content in contaminated biochar reported in this study, open air storage proved to be the least effective. Blending of contaminated biochar with clean biochar yielded promising results and showed biochar's ability to take up VOCs from its surroundings, however, for the biochar studied, this method was effective only at relatively low concentrations of contaminated biochar (1 g high-VOC biochar in 9 g of low-VOC biochar). The most effective post-treatment method was thermal treatment at relatively low temperature (200°C), as such treatment removed VOCs and previously observed phytotoxic effects. Furthermore, it was shown that under certain circumstances, high-VOC biochars can pose a risk to human health. However, this is limited only to extreme cases and in general most biochars are likely to sorb VOCs from the environment rather than to release them.

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