Qualitative analysis of volatile organic compounds on biochar

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ABSTRACT

Qualitative identification of sorbed volatile organic compounds (VOCs) on biochar was conducted by headspace thermal desorption coupled to capillary gas chromatographic-mass spectrometry. VOCs may have a mechanistic role influencing plant and microbial responses to biochar amendments, since VOCs can directly inhibit/stimulate microbial and plant processes. Over 70 biochars encompassing a variety of parent feedstocks and manufacturing processes were evaluated and were observed to possess diverse sorbed VOC composition. There were over 140 individual chemical compounds thermally desorbed from some biochars, with hydrothermal carbonization (HTC) and fast pyrolysis biochars typically possessing the greatest number of sorbed volatiles. In contrast, gasification, thermal or chemical processed biochars, soil kiln mound, and open pit biochars possessed low to non-detectable levels of VOCs. Slow pyrolysis biochars were highly variable in terms of their sorbed VOC content. There were no clear feedstock dependencies to the sorbed VOC composition, suggesting a stronger linkage with biochar production conditions coupled to post-production handling and processing. Lower pyrolytic temperatures ($\leqslant$350 °C) produced biochars with sorbed VOCs consisting of short carbon chain aldehydes, furans and ketones; elevated temperature biochars (>350 °C) typically were dominated by sorbed aromatic compounds and longer carbon chain hydrocarbons. The presence of oxygen during pyrolysis also reduced sorbed VOCs. These compositional results suggest that sorbed VOCs are highly variable and that their chemical dissimilarity could play a role in the wide variety of plant and soil microbial responses to biochar soil amendment noted in the literature. This variability in VOC composition may argue for VOC characterization before land application to predict possible agroecosystem effects.

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1. Introduction

The presence of individual volatile organic compounds (VOCs) in the soil system can have mechanistic effects by triggering various plant and microbial responses or "*soil volatilomics*" (Insam and Seewald, 2010). VOCs produced in the rhizosphere can regulate plant growth (Simms and Rausher, 1987; Ryu et al., 2003; Kloepper et al., 2004; Baldwin et al., 2006; Zhang et al., 2007) as well as microbial processes (Klinke et al., 2004; Almeida et al., 2009; Graber et al., 2010). These studies have shown that even low VOC concentrations ($\mu g\ m^{-3}$) can have a significant impact on the well-being of plants, impacting seed germination, herbivore resistance, invasive plant responses, and nutrient uptake. VOCs also control the ability of soil micro- and macro-organisms to participate in abiotic and biotic reactions known to influence soil quality (Insam and Seewald, 2010).

During biochar production, VOCs are produced regardless of the process used (Olsson et al., 2003, 2004; Chouchene et al., 2010; Mun and Ku, 2010; Song and Peng, 2010). These VOCs are formed during pyrolysis by the breakdown or rearrangement of the original biomass chemical structures (Demirbas, 2000; Zeng et al., in press). Pyrazines, pyridines, pyrroles and furans were the typical classes of volatile compounds observed during the pyrolysis of chitosan (Zeng et al., in press) and glucosamine (Chen and Ho, 1998). Volatile compounds are typically trapped and condensed into the liquid fraction (bio-oil) product (Boateng et al., 2007; Yu et al., 2007). In bio-oil, the most frequent compounds observed include: methanol, acetic acid, acetone, methyl acetone, acetaldehyde, furan, furfural, and volatile organic acids (Mullen et al., 2010; Tiilikkala et al., 2010). Other studies have confirmed the presence of these compounds in wood vinegar (condensates of wood smoke from pyrolysis), which historically is used for its herbicide and pesticide properties (Orihashi et al.,

2001; Yatagai et al., 2002). During the pyrolysis process, VOCs re-condensed as liquids are known to cause mixed impacts on plant growth as a function of production conditions and application amount (Mu et al., 2004, 2006). In particular, phenols present in these liquid distillates are speculated to be responsible for noted negative plant-growth impacts (Mun and Ku, 2010).

Although VOCs from biochar have the potential to mediate profound changes in the soil gas atmosphere, very few studies have examined the chemical nature of VOCs associated with biochar. Previous chemical characterizations of biochar have primarily used pyrolysis with generated vapors swept into a GC/MS (Py-GC/MS) to monitor the degree of solid alteration (Galipo et al., 1998). However, since high temperatures (550–800 °C) are used, this analytical technique further thermally alters the sample (Kaal and Rumpel, 2009). Therefore, it is difficult to distinguish whether the compounds observed are break-down products due to the analytical pyrolysis conditions or sorbed originally to the material, which complicates the quantitative nature of this technique (Kaal et al., 2008; Kaal and Rumpel, 2009). Despite these limitations, Py-GC/MS has confirmed the presence of polyaromatic hydrocarbons (PAHs) on biochar (Rumpel et al., 2007).

Some of the VOCs released from biochar potentially can either stimulate or reduce both plant productivity (Deenik et al., 2010) and microbial processes (Graber et al., 2010; Khodadad et al., 2011), due to biochar's sorbed organic chemical composition. Clough et al. (2010) observed acetaldehyde, α-pinene, β-pinene, and trans-pinocarveol using an automated headspace solid-phase micro-extraction (SPME) gas chromatography-mass spectrometry (GC/MS) analysis of a slow pyrolysis wood biochar. Graber et al. (2010) hypothesized that sorbed VOCs were capable of disease suppression in pepper and tomato plants in soilless media treated with biochar. Spokas (2010) quantified varying ethylene production rates originating from different biochars. The authors speculated that this ethylene could be involved in both the plant (fine root hair development) and soil microbial responses observed from biochar additions. Furthermore, both ethylene (McCarty and Bremner, 1991) and α-pinene (Clough et al., 2010) can act as nitrification inhibitors. Sorbed VOCs on biochar have also been implicated with reduced plant germination and growth (Vantsis and Bond, 1950; Turner, 1955; Kadota and Niimi, 2004; Deenik et al., 2010; Free et al., 2010). Even though these studies focused on different VOC compounds and soil processes, the overall conclusions following biochar amendments suggest a mixed role of VOCs in the plant-soil system; albeit, individual compounds can serve as inhibitors or stimulants to biological systems.

It has been well established that biochar chemistry and yields varies considerably with production process conditions (Novak et al., 2009; Keiluweit et al., 2010; Lee et al., 2010) and surface oxidation (i.e., activation, aging, weathering) (Boehm, 1994; Yao et al., 2010). The yield of biochar is particularly influenced by the feedstock's initial moisture content, ash content, and elemental composition (Gray et al., 1985). Previously, attention to VOC contents has been focused on the bio-oil because of its influence on marketability and post-collection processing (Bridgwater et al., 1999; Mohan et al., 2006; Boateng et al., 2010; Shuping et al., 2010).

The linkage between VOC associated with biochar to microbial and plant responses is agriculturally and environmentally important. Unfortunately, there is limited information on the impact of various feedstocks, production conditions and different pyrolysis technologies on the chemical characteristics of sorbed VOCs associated with these biochars. Moreover, this could be an important consequence when selecting biochar to improve soil quality (Lehmann, 2007; Laird, 2008; Novak and Busscher, in press). Therefore, our objectives were to evaluate the effects of feedstock, pyrolysis technology, and pyrolysis temperatures on the qualitative properties of sorbed VOCs on biochar.

2. Material and methods

2.1. Biochar production processes

Biochars were obtained from a variety of commercial and research sources[1] because it was postulated that VOC profiles associated with the biochars would correspondingly be diverse. The biochars were manufactured under an array of production levels, including homemade, laboratory, and pilot scale pyrolysis equipment. Exact production parameters were not known for all biochars, due to the fact that some of the biochars were created in pyrolysis units lacking industrial process monitoring equipment. Nevertheless, these biochars were included among the employed suite to capture irregularity in the types of biochar currently available. There were a total of 77 different biochars evaluated in this study (Table 1). All biochars were evaluated as received from the various suppliers. Each supplier, or pyrolysis unit, is designated in the unit column, with similar labels designating the same pyrolysis unit. To produce the biochars, an assortment of conversion technologies were used, including; fast pyrolysis (3), slow pyrolysis (46), traditional methods (4), gasification (5), wood fired boilers (6), microwave assisted pyrolysis (4), hydrothermal carbonization (4), and activated carbons (5), with the number in parentheses indicating the respective number of biochars from that technique. The two types of traditional pyrolysis (fast and slow) biochars were both created in some type of engineered unit, typically under anaerobic conditions by an inert gas purge. These biochars were further divided based on the residence time of the material in the reactor chamber, with fast designating less than 15 min and slow greater than 15 min (Table 1). Traditional soil kiln methods were biochars that were created in the absence of an engineered unit, such as a soil mound or soil pit. Gasifier biochars were those produced under elevated temperatures with no efforts to exclude oxygen from the reaction chamber (i.e., no inert gas purge). Wood boiler biochars were considered a special sub-set of gasifier biochars, since these were all created in wood fired boilers, which were common in the paper and pulp industry (Etiégni and Campbell, 1991). Microwave assisted pyrolysis biochars were those created with microwave energy for pyrolysis heating (Wan et al., 2009). Hydrothermal carbonization (HTC) biochars were produced under lower temperatures (200–250 °C) and elevated steam/water pressures to carbonize the biomass material (Cao et al., 2011; Libra et al., 2011). Selected activated carbons were included as examples of biochar that underwent further chemical and/or thermal processing after production (Azargohar and Dalai, 2006; Ippolito et al., in preparation).

Biochar pH was determined in a 1:5 (1 g biochar to 5 mL distilled water) slurry. Proximate (ASTM D121/D5142/D7582) and ultimate analyses (ASTM D5373/D3176) were performed by Hazen Research (Golden, CO) and N_2 BET surface area (Brunauer et al., 1938) analyses were performed by the USGS (D. Rutherford, Boulder, CO) and Material Synergy (Oxnard, CA), if equivalent data was not available for the particular biochar. Not all biochars were fully characterized due to lack of material needed for these assessments.

2.2. Headspace thermal desorption–gas chromatographic–mass spectrometer system

The use of headspace instrumentation is common for the analysis of sorbed compounds on charcoal sample tubes (Canela and Muehleisen, 1986; Gan et al., 1994; Risholm-Sundman et al., 1998; Kusch and Knupp, 2004). Therefore, headspace instrumentation would be an ideal tool for the analysis of sorbed VOCs on bio-

Table 1
List of biochars examined in this study and accompanying characterization and production parameters that were known. Units with the same designations were made on the same pyrolysis unit.

						(% dry weight)						
BC#	Parent material	Unit	PT (°C)	pH	SA ($m^2\,g^{-1}$)	C	N	O	H	H_2O	VM	Ash
Fast pyrolysis biochar												
1	Macadamia shells	F1	n/a	6.2	6.9	84.3	0.6	1.5	2.3	9.5	15.2	1.7
2	Oak hardwood sawdust	F2	500	8.0	46	61.8	0.21	2.3	0.6	80.7	5.0	15.8
3	Macadamia shells	F3	650	6.9	0.45	71.0	0.88	1.2	2.5	5.0	19.5	20.4
Slow pyrolysis biochar												
4	Corn stover	SP1	515	9.5	4.4	45.0	0.5	1.0	1.7	11.5	30.9	55.0
5	Pine wood chip	SP2	465	6.8	0.1	75.0	0.3	9.0	3.4	55.0	34.9	6.0
6	Peanut hulls	SP2	481	8.0	1.0	59.0	2.7	12.0	2.3	72.0	5.3	15.0
7	Corn stover	SP3	500	8.9	4.2	25.0	0.6	5.0	1.1	9.1	41.3	69.0
8	Corn stover	SP2	410	n/a	2.2	42.0	1.0	11.0	1.8	4.1	n/a	54.0
9	Pine wood chip	SP2	465	6.8	0.2	71.0	0.2	11.0	3.3	12.0	72.3	9.0
10	Peanut hulls	SP2	481	5.1	286	60.0	0.9	10	1.1	5.2	n/a	15.0
11	Corn stover	SP4	505	10.0	17.3	46.0	1.2	4.0	1.5	28.0	13.8	54.0
12	Coconut shell	SP1	550	8.9	15.1	80.1	0.5	2.5	n/a	12.4	8.7	n/a
13	Distillers grain	SP5	350	6.8	0.3	67.4	7.4	6.5	4.7	1.8	43.9	11.3
14	Distillers grain	SP5	400	6.9	0.3	68.1	7.3	5.9	4.2	2.0	36.9	11.7
15	Corn cob	SP5	350	8.7	<0.1	76.5	0.7	12.9	4.2	2.9	32.2	2.8
16	Corn cob	SP5	400	9.0	<0.1	80.1	0.6	8.8	3.7	3.1	24	3.7
17	Wood waste	SP6	400	6.9	3.5	76.9	0.8	11.5	3.6	3.7	25.8	3.5
18	Wood waste	SP6	450	8.4	26.8	77.9	0.7	11	3.1	3.6	22.8	3.6
19	Wood waste + composting	SP7	465	8.6	63.5	43.0	2.2	n/a	n/a	11.4	32.3	n/a
20	Wood chip (pellet)	SP8	650	9.8	177.2	69.3	0.2	17.7	1.2	5.6	11.7	6.0
21	Oak hardwood	SP9	538	9.8	33.7	53.4	0.4	9.8	2.6	6.3	32.5	27.1
22	Wood waste	SP10	500	5.0	66.3	68.7	0.1	19.9	3.3	3.3	33.6	4.6
23	Oak hardwood	SP11	540	6.6	n/a	73.3	0.3	n/a	n/a	1.7	n/a	2.4
24	Oak hardwood	SP12	n/a	8.5	106.3	90.1	0.3	4.5	2.8	1.3	15	1.0
25	Pine wood chip	SP13	500	7.2	n/a	87.2	0.43	6.44	3.6	3.24	45.8	2.3
26	Sugar cane bagasse	SP15	350	5.0	n/a	75.2	0.66	15.8	4.6	3.42	39.2	3.6
27	Pine wood chip	SP15	350	4.6	n/a	74.7	0.45	18.4	5.0	2.74	45.2	1.5
28	Swine manure	SP15	350	8.1	0.92	50.8	3.74	6.64	5.0	2.31	46.2	32.3
29	Switchgrass	SP15	250	6.2	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
30	Poultry litter	SP16	400	10.3	n/a	42.3	4.2	n/a	n/a	n/a	n/a	n/a
31	Pine chips	SP16	500	7.3	n/a	73.3	0.2	n/a	n/a	n/a	n/a	n/a
32	Wood wastes	SP17	n/a	8.4	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
33	Wood waste	SP18	n/a	9.1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
34	Wood pellets	SP19	n/a	5.5	78.3	77.3	0.4	3.9	1.6	6.8	14.1	10.1
35	Wood pellets	SP19	n/a	10.8	4	73.9	0.4	10.8	2.8	4.8	26.3	7.3
36	Wood pellets	SP19	n/a	6.7	n/a	76.4	0.4	11.7	2.7	5.1	27.3	3.7
37	Wood pellets	SP19	n/a	6.8	1.7	77.2	0.3	12.5	2.9	5.1	28.6	1.9
38	Wood ash + fertilizer	SP20	n/a	8.3	n/a	68.0	1.53	n/a	n/a	58.1	n/a	8.1
39	Oak hardwood	SP20	n/a	10.2	n/a	59.8	0.6	n/a	n/a	n/a	n/a	n/a
40	Mixed hardwood	SP20	n/a	8.8	n/a	76.9	0.5	n/a	n/a	2.2	n/a	11.6
41	Mixed wood	SP21	n/a	4.7	n/a	60.8	0.44	n/a	n/a	6.8	n/a	n/a
42	Oak hardwood	SP22	550	10.2	134.8	52.0	0.2	3.9	0.6	n/a	4.3	43.4
43	Oak hardwood	SP22	550	10.5	116.8	56.0	0.2	0.7	0.9	n/a	4.4	42.2
44	Cottonseed hull	SP23	200	3.7	n/a	48.2	5.6	37.7	5.6	5.3	69.3	3.1
45	Cottonseed hull	SP23	350	6.6	4.7	71.5	4.2	14.6	4.2	6.8	34.9	5.7
46	Cottonseed hull	SP23	500	8.5	<0.1	78.7	2.5	6.9	2.5	6.5	18.6	7.9
47	Cottonseed hull	SP23	650	8.6	34	84.4	1.2	5.5	1.2	8.2	13.3	8.3
48	Cottonseed hull	SP23	800	7.7	322	84.3	0.6	6.6	0.6	9.9	11.4	9.2
49	Coal + wood pellets	SP24	900	5.5	5.0	6.8	0.2	n/a	0.10	1	1.8	86.4
Traditional kiln biochar (e.g. soil mound, pits)												
50	Oak hardwood	K1	400–600	8.9	n/a	72.4	0.4	n/a	n/a	n/a	n/a	n/a
51	Oak hardwood (possible?)	K2	n/a	6.5	n/a	83.8	0.3	n/a	n/a	0.8	n/a	1.7
52	Hardwood	K3	n/a	6.8	19.2	69.0	0.7	9	2.4	10.0	69.9	14
53	Hardwood	K4	n/a	7.4	n/a	77.4	0.3	n/a	n/a	n/a	n/a	n/a
Gasifier biochar (e.g. ashes)												
54	Oak Hardwood	G1	n/a	11.2	33.5	31.5	0.3	n/a	0.6	0.6	20.3	66.6
55	Mixed waste wood	G2	>600 °C	11.8	144.0	27.2	0.3	n/a	0.3	0.9	18.8	72.2
56	Turkey manure and wood chips	G3	850	10.9	4.8	1.0	0.1	3	0.5	5.0	22.2	89
57	Wood ash	G4	n/a	11.8	n/a	<0.1	0.01	n/a	n/a	16.5	0.6	82.9
58	Corn stover	G5	815	10.1	9.9	31.0	1	0	0.9	14.0	33.0	74
Wood fire boiler biochar (wood ash)												
59	Wood ash	WB1	n/a	9.1	176.7	16.0	0.2	2.1	0.1	32.3	6.8	49.3
60	Wood ash	WB2	n/a	8.4	193.5	15.9	0.2	2.5	0.1	41.9	9	39.3
61	Wood ash	WB3	n/a	8.7	57	4.6	0.09	1.3	0.04	41.7	5.2	52.1
62	Wood ash	WB4	n/a	8.6	335.9	20.9	0.1	1.5	0.2	67.3	4	10
63	Wood ash	WB5	n/a	5.8	63.1	10.1	0.1	1.7	0.4	65.6	3.1	22.1

Table 1 (*continued*)

BC#	Parent material	Unit	PT (°C)	pH	SA (m² g⁻¹)	(% dry weight)						
						C	N	O	H	H₂O	VM	Ash
64	Wood ash	WB6	n/a	10.3	n/a	89.6	1.01	<0.01	n/a	0.1	5.8	5.2
Activated charcoals												
65	Coconut shells (activated)	AC1	500 °C steam activated 900 °C	7.6	1200	83.1	0.4	<0.01	0.06	5.5	1.7	12.3
66	Coconut shells (activated)	AC2	900 °C activation (steam)	6.8	922	90.2	1.72	3.08	0.38	3	0.5	15
67	Hardwood	AC3	n/a	5.8	1661	89.4	0.4	0.6	2.1	3.4	7.8	4.1
68	Bituminous coal	AC4	Activated at 800 °C	9.4	988	94.9	1.27	2.49	0.7	1.6	1.8	0.3
69	Hardwood	AC5	Phosphorus acid activated 600 °C	3.8	877	95.8	0.2	1.0	0.6	5.0	0.5	0.2
Hydrothermal biochars												
70	Algae	HT1	250	3.3	0.1	48.9	7.9	16.5	9.1	10.2	n/a	0.2
71	Swine manure + sugar beet	HT2	200–250	4.4	2.5	50.7	2.3	25.4	5.0	4.1	63.2	12.2
72	Swine manure + pine bark	HT3	200–250	4.0	6.5	56.0	0.7	23.7	4.4	5.6	55.2	29.7
73	Algae	HT4	200	3.9	<0.1	66.3	7.3	18.0	7.9	9.2	n/a	0.3
Microwave assisted pyrolysis biochar												
74	Chicken feathers	MAP1	Not measured (n/a)	9.2	n/a	33.6	3.1	n/a	n/a	n/a	n/a	n/a
75	Swine manure + bedding	MAP2	Not measured (n/a)	9.8	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
76	Distiller grain	MAP3	Not measured (n/a)	10.1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
77	Corn stover	MAP4	600	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Notes compositional values are weight percentages related to dry mass; VM = volatile matter; SA = surface area; PT = pyrolysis temperature; H₂O = moisture content; and n/a = data not available.

char, and has been used in one existing study (Bernardo et al., 2010).

To analyze the chemical composition of sorbed VOCs associated with biochars, a headspace sampler (HP-7694; Agilent, Santa Clara, CA) was modified through the use of a 10-port diaphragm valve (DV22-2110; Valco Instruments Co., Inc.; Houston, TX) to allow the introduction of two simultaneous gas samples from a single headspace venting to two different analytical GC columns. The effluent from one of the columns [RTX-624 (60 m × 0.32 mm ID), Restek Corp.; Bellefonte, PA] was directed to a mass spectrometer (MS) detector (Clarus P600; Perkin–Elmer; Waltham, MA) and the other column's effluent [Porapak Q (6.4 mm × 1.8 m); Restek Corp.; Bellefonte, PA] was connected directly to a thermal conductivity detector (TCD), which was in series with a flame ionization detector (FID). The GC and MS instruments were controlled through TurboMass software (Perkin–Elmer; Waltham, MA), and the TCD and FID signals were collected via a interface box (Perkin–Elmer 900; Perkin–Elmer, Waltham, MA) using TotalChrom software (ver. 2.2; Perkin–Elmer; Waltham, MA). In this fashion, the carbon dioxide (CO_2) evolved during heating and the corresponding light weight volatiles (C_1–C_4 compounds) could be quantified that would otherwise be lost in the air/water peak on the MS. The VOCs analyzed in this study were desorbed thermally from the biochars, we did not use any solvents on the biochars to extract VOCs. The overall settings and conditions of the system are provided in Table S1 (Supplementary material).

Typically, 0.5 g biochar samples were placed into a 10 mL headspace vial (#5182-0838, Agilent, Santa Clara, CA) and sealed with Teflon-lined high-temperature silicone septa (#22831, Restek Corp.; Bellefonte, PA). For headspace methods, vial temperature and equilibration time are the most vital for method development (Friant and Suffet, 1979; Penton, 1992). For the analysis here, biochar samples were thermally heated to 150 °C for 10 min in a sealed headspace vial prior to injection. These conditions were selected based on preliminary experiments across several biochars. However, there was no single optimum desorption temperature for all biochars. To collect data that would be universal across all biochars (i.e., compounds that were thermally desorbed under set conditions), a fixed thermal desorption temperature of 150 °C was selected, which is similar to other studies using headspace methods for charcoal desorption (e.g., Markelov and Bershevits, 2001; Candole et al., 2007). Furthermore, a desorption time of 10 min was used to minimize the pressure build up in the vial resulting from the variable water content of the biochars, which

is a significant difficulty in headspace analyses (Novotny et al., 1974; Bicchi et al., 2008).

Qualitative peak identification was conducted by comparing the collected ion spectra to the reference spectral library (NIST; Perkin–Elmer; Waltham, MA). Peak retention times and library spectral identification was confirmed with external liquid standards (AccuStandard; New Haven, CT), which were injected as a liquid (<5 μL) into a sealed headspace vial and analyzed under the same conditions (Table S1, Supplementary material). Only qualitative analyses were conducted, due to the high number of identified peaks that lead to overlapping and co-eluting interferences. In addition, extraction efficiency of VOCs from charcoal (biochar) was known to be a function of the compound and biochar (Raguso and Pellmyr, 1998), which leads to dissimilar extraction efficiencies for various biochars. Therefore, further refinement in the analytical technique is needed before accurate quantification can be accomplished by headspace methodology. An 85% level of certainty in the spectral match criteria was used as a cut-off for spectral identification.

Samples vials were run with corresponding air blank vials to avoid cross-contamination and establish laboratory VOC baselines. If the biochar's integrated compound area was significantly greater than the corresponding compound in the air blank sample, the resulting identified peak was retained in the table. On the other hand, if the integrated area was not significantly different than the air blank control, these compounds were flagged as not-detected. In this fashion, potential VOCs present in the laboratory air or septa contamination were accounted for.

Chemical data were averaged across biochar production styles. These means were compared utilizing a one-way analysis of variance (InStat, GraphPad Software) to determine if statistical ($P < 0.05$) differences existed in chemical properties as a function of pyrolysis production technique.

3. Results

3.1. Chemical and physical biochar analyses

The biochars possessed a range of 1–95% total carbon, 0.5–43.9% volatile matter content, 0.3–96% ash, 0.1–7.4% nitrogen, <0.1–1661 m² g⁻¹ BET surface areas, 0–63% moisture, and a range of pyrolysis temperatures from 200 to >800 °C (Table 1). Overall, pH values ranged from 3.3 to 10, with significant differences among production styles ($P < 0.05$). Gasifier biochars were typically

alkaline, hydrothermal biochars were acidic, fast pyrolysis biochars were near neutral pH values, and the slow pyrolysis biochars ranged from acidic to alkaline (pH 4–10) (Table 1). There were also significant differences in the total residual carbon as a function of the type of pyrolysis ($P < 0.05$). Biochars produced through gasification had low carbon contents, which would indicate oxygen presence during the heating allowing for combustion to CO_2. As expected, the activated carbons consistently possessed the highest total carbon contents ($90.7 ± 5.1\%$) and surface areas ($1130 ± 360 \, m^2 \, g^{-1}$). The most common technique used to produce the biochars in Table 1 was slow pyrolysis, which also was the technique with the highest variability in all assessments, resulting in no clear distinction in chemical characteristics for the slow pyrolysis biochars.

3.2. Biochar headspace desorption VOC profiles

We observed differences in VOC profiles from biochars created from different pyrolysis production units with equivalent feedstock and pyrolysis temperatures. There were 77 compounds positively identified in this study (Table S2, Supplementary material), with the remainder of the chromatographic peaks insufficiently characterized through a mass spectral match to positively identify the target compounds. Fig. 1 illustrates the differences in the GC/MS thermal desorption total ion chromatograms (TIC) obtained from a similar feedstock (oak hardwood) across five pyrolysis production platforms, ranging from slow (BC21; 538 °C; Fig. 1A), slow (BC42; 550 °C; Fig. 1B), fast (BC2; 500 °C; Fig. 1C), limited oxygen supply gasifier (BC54; unknown; Fig. 1D) and traditional soil mound (BC50; 400–600 °C; Fig. 1E). The corresponding retention times (RT) of the identified compounds are listed in Table S2 (Supplemental material). Even though quantitative analysis was not conducted, the differences in the peak height would be proportional to thermally desorbed concentrations for equivalent compounds. Samples BC21 (Fig. 1A) and BC2 (Fig. 1C) possessed a high number of sorbed VOCs of differing amounts. Both of these pyrolysis units utilized an inert gas stream purging the reaction chamber during production and equivalent final production temperatures (540–550 °C). For BC21, the most prevalent VOC identified was acetone (9.7 min), followed by methyl ethyl ketone (14.2 min; Fig. 1A); whereas for sample BC2, methyl acetate (10.8 min) occurred in the highest abundance followed by acetone (9.7 min; Fig. 1C). On the other hand, samples BC42 (Fig. 1B), BC54 (Fig. 1D), and BC50 (Fig. 1E) had significantly lower sorbed volatiles than the fast (Fig. 1C) and other slow pyrolysis unit (Fig. 1A). The most prevalent VOCs in samples BC54 and BC50 were acetone (9.7 min) and benzene (16.3 min). Both benzene (16.3 min) and trichloroethene (17.9 min) were most abundant in BC42, with all compounds being significantly lower than BC21 and BC2 (Fig. 1). Due to the unknown production temperature (lack of process monitoring equipment), the differences observed in BC54 and BC50 could be attributed to pyrolysis temperature differences rather than solely residence time. However, these results do suggest that feedstock is probably not the primary determining factor for sorbed VOCs profiles in this dataset.

The only regularly identified contaminant on the GC/MS scans was 1,1,1,5,5,5-hexamethyl-3-(trimethylsilyl) trisiloxane, which originated from the septa (silicone). This peak showed up in all samples in varying amounts (retention time = 28.3 min). Atmospheric methane was also a contaminant in all samples due to its presence in laboratory air. However, the value for methane in the control laboratory air blanks was subtracted from the biochar area to correct for its interference. Occasional peaks for ethanol, methanol, and dichloromethane (solvents in use in the laboratory building) were identified in the air samples. However, no correction was required, since the focus was on qualitative detection, with

detected biochar compounds typically exceeding these background levels by an order of magnitude.

The presence of oxygen in the pyrolysis unit appears to be a controlling factor in the number and amount of sorbed volatiles. Increasing oxygen presence during pyrolysis (B21, B2; both with inert gas purging) to gasification (B54; greater oxygen presence) resulted in a decrease in sorbed VOCs (Fig. 1). The oxygen level similarly influenced the sorbed VOCs characteristics for slow pyrolysis biochars compared to the traditional soil kiln biochar (produced for a period of time in oxygen presence, prior to burial). However, detailed data on the oxygen content during pyrolysis was not directly collected during the production of the various biochars used in Fig. 1.

Despite equivalent feedstock and pyrolysis conditions, we observed substantially different biochar sorbed VOCs from the diverse pyrolysis facilities. Fig. 2 illustrates the differences in sorbed volatiles on corn stover biochar from four different slow pyrolysis facilities (BC 4, 7, 8, and 11), produced at nearly equivalent temperatures (410–515 °C). These four corn stover biochars possessed drastically different concentration and distribution of sorbed VOCs as a function of the pyrolysis facility, which was similar to the observations for the two slow pyrolysis biochars of oak hardwood (Fig. 1A and B). These differences exist despite the fact that pyrolysis conditions were similar for these biochars (Table 1). Sample BC4, produced at the highest temperature (515 °C), contained the most abundant sorbed volatiles (Fig. 2A), dominated by furan (8.8 min), acetone (9.7 min), and methyl acetate (10.8 min). In contrast, sample BC7 was lower in total sorbed species (Fig. 2B), with benzene (16.3 min), toluene (21.1 min), and acetone (9.7 min) being the most prevalent. Likewise, sample BC8 (Fig. 2C) had acetone (9.7 min) in the greatest abundance followed by 1-dodecane (36.1 min). BC11 had extremely low VOC levels, which were characterized by benzene (16.3 min) and methyl acetate (10.8 min) being the largest peaks (Fig. 2D). These results illustrate the striking dissimilarity in VOC compositional chemistry among the four biochars made from the same feedstock and slow pyrolysis technique.

There was also substantial variability in VOC profiles between pyrolysis temperatures using a single feedstock on the same pyrolysis unit. Fig. 3 illustrates the TIC for waste cottonseed hull (containing both hull and cottonseed) pyrolyzed at 800, 650, 500, 350, and 200 °C for 4 h under a nitrogen flow (BC44–48), on the same slow pyrolysis unit. The biochar with the highest sorbed content of VOCs was the biochar produced at the lowest temperature (BC44; 200 °C; Fig. 3E). This biochar was characterized by high proportions of short-chain aldehydes and furans, with the three most dominant compounds being 2-propanal (9.2 min), ethyl acetate (12.5 min), and 2-hexenal (26.5 min). The next temperature step (350 °C; BC45) showed overall decreases in the amount of longer (6–7 carbon) chain aldehydes to shorter chain aldehydes and ketones, with propanal (9.4 min), acetone (9.7 min), and methyl ethyl ketone (14.2 min) comprising the most dominant peaks. At 500 °C (BC46), the three most abundant compounds were dodecane (36.1 min), toluene (21.1 min), and benzylaldehyde (31.2 min). At 650 °C (BC47) the overall quantities of sorbed volatiles decreased due to the reduced peak magnitude observed in the TIC (Fig. 3B). The largest three peaks in this temperature regime were unidentifiable compounds. Background spectra subtraction did not aid in their identification, suggesting co-eluting compounds impacting the spectral comparisons. At 800 °C (BC48), the biochar had very low quantities of sorbed volatiles, as indicated by reduced peak magnitudes (Fig. 3A). The three VOCs with the greatest peak areas were toluene (21.1 min), octanal (31.6 min), and potentially 4-methyloctane ($R^2 = 78\%$; 34 min).

Although there were substantial variability between pyrolysis units and feedstock (Figs. 1 and 2), there were some trends in
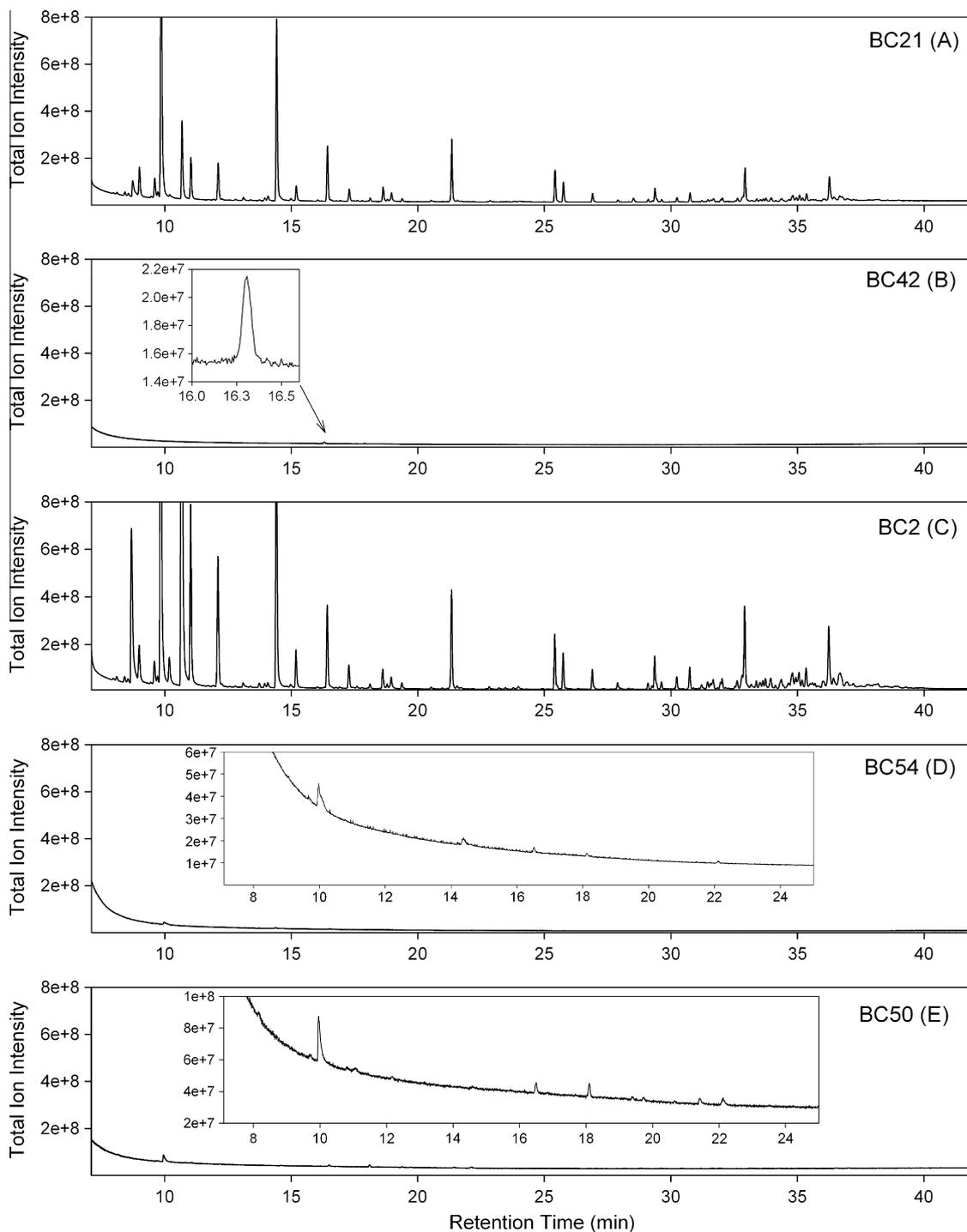
Fig. 1. Images of the total ion chromatograms from the thermal desorption GC/MS analysis of five different oak hardwood biochars: (A) Slow pyrolysis (BC21), (B) Slow pyrolysis (BC42), (C) Fast pyrolysis (BC2), (D) Gasifier (BC54), and (E) Tradition soil mound kiln (BC50) production methods. All chromatograms are scaled equally, with the inset chromatograms showing the rescaled chromatogram. All pyrolysis techniques had nearly equivalent production temperatures.

sorbed VOC compounds as a function of production temperature from the same feedstock with the same pyrolysis unit. Fig. 4 illustrates the abundance trends (relative TIC peak areas) for a few selected compounds for cottonseed hull (containing both hull and cottonseed) pyrolyzed at 200, 350, 500, 650, and 800 °C. The abundance of sorbed toluene (21.1 min) (Fig. 4A) was maximum at the lowest temperature (BC44; 200 °C), and decreased with increasing temperature to 800 °C (BC48). However, not all VOCs followed this decreasing trend as a function of production temperature. For instance, the initial detection of benzene (16.3 min) on these biochars was not at 200 °C but those made at 350 °C (BC45), and then

the quantity of sorbed benzene decreased with increasing production temperature, with the highest amount of sorbed benzene being present on the 350 °C biochar (Fig 4B). The amount of sorbed ethylene/acetylene (Fig. 4C), methane (Fig. 4D), and ethanol (Fig. 4E) also peaked with the observed benzene maximum (BC45; 350 °C). All of these shorter chain hydrocarbons decreased with further increases in pyrolysis temperature from 350–800 °C. Ethanol, ethylene, and methane were still detectable even at the highest temperatures (BC48; 800 °C). These trends can be seen visually on the TIC, with the shift in the appearance of the peaks from earlier eluting times (Fig. 3E) (typically short carbon chain
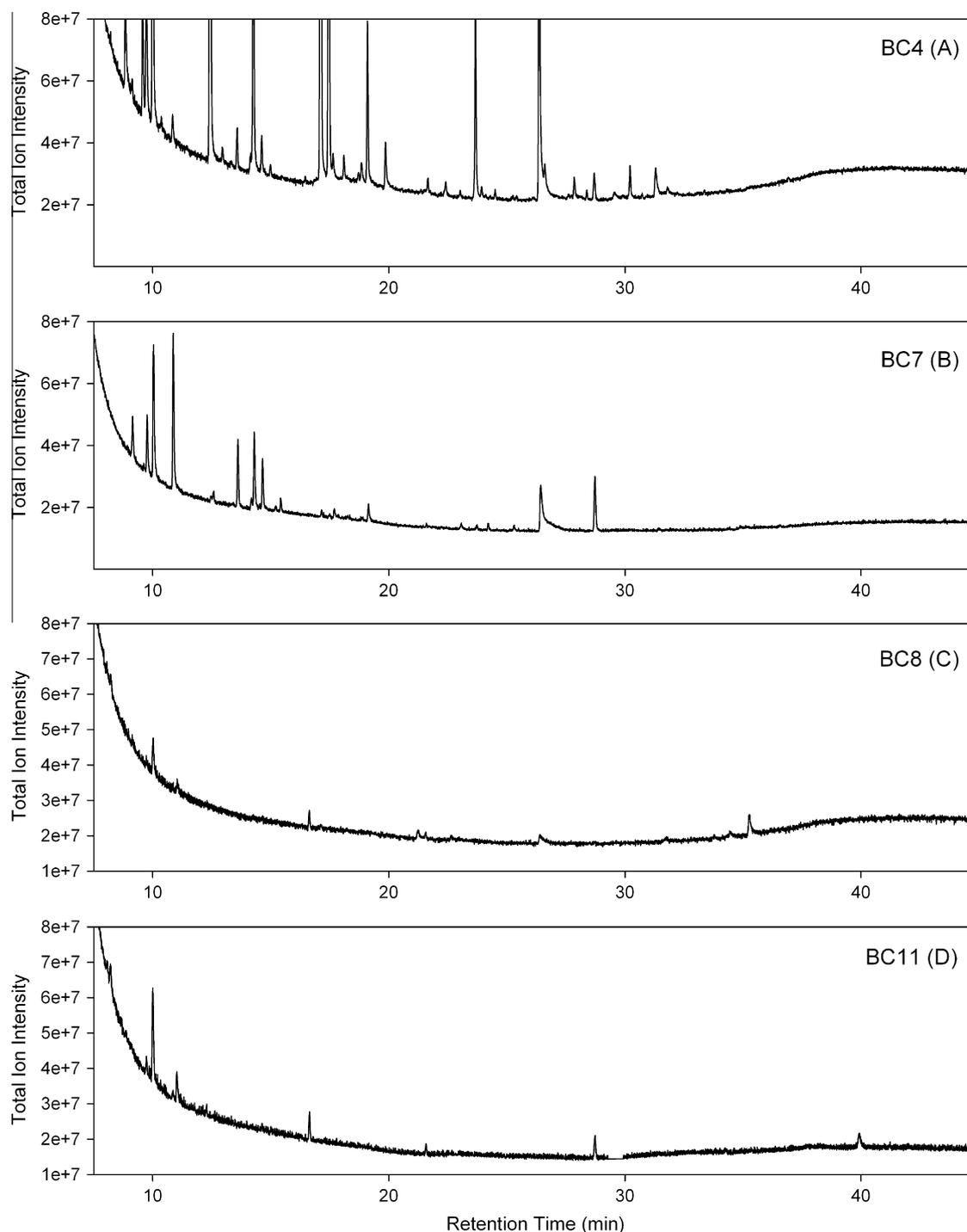
Fig. 2. Illustrations of the headspace thermal desorption GC/MS total ion chromatograms for corn stover biochar produced by four different slow pyrolysis units: (A) BC4, (B) BC7, (C) BC8, and (D) BC11. All chromatograms are scaled equally and had nearly equivalent production temperatures.

compounds) to higher molecular weight compounds, typically possessing a benzene ring that appear at later elution times (typically after 20 min; Fig. 3A). There was a general decrease in the magnitude of the aldehyde, furan and ketone peaks with increasing production temperature (Fig. 3). Furthermore, aromatic species (e.g., benzene, toluene, phenol, etc.) and longer branched species became the more dominant compound class sorbed, even though the total concentrations of sorbed species were lower at elevated temperatures (Fig. 3).

The sum of all detected peaks from the GC/MS for each biochar is presented in Figure S1 (Supplementary material). The conservative estimate was that the ranges of sorbed volatiles on biochar

spanned at least six orders of magnitude (from ng kg^{-1} to mg kg^{-1} levels), although this was not confirmed in this study. Despite the graphical appearance, there was no significant relationship between total TIC peak area and production temperature (Fig. S2, Supplementary material; $R^2 = 0.23$) or volatile matter content ($R^2 < 0.1$).

The frequencies of VOC identification on biochar by GC/MS are given in Table 2 and for the FID/TCD in Table 3. The top ten most frequently observed compounds by GC/MS in this collection of biochar samples were: acetone, benzene, methylethyl ketone, toluene, methyl acetate, propanal, octanal, 2,3-butadiene, pentanal, and 3-methylbutanal (Table 2). From the TCD/FID data, carbon dioxide,
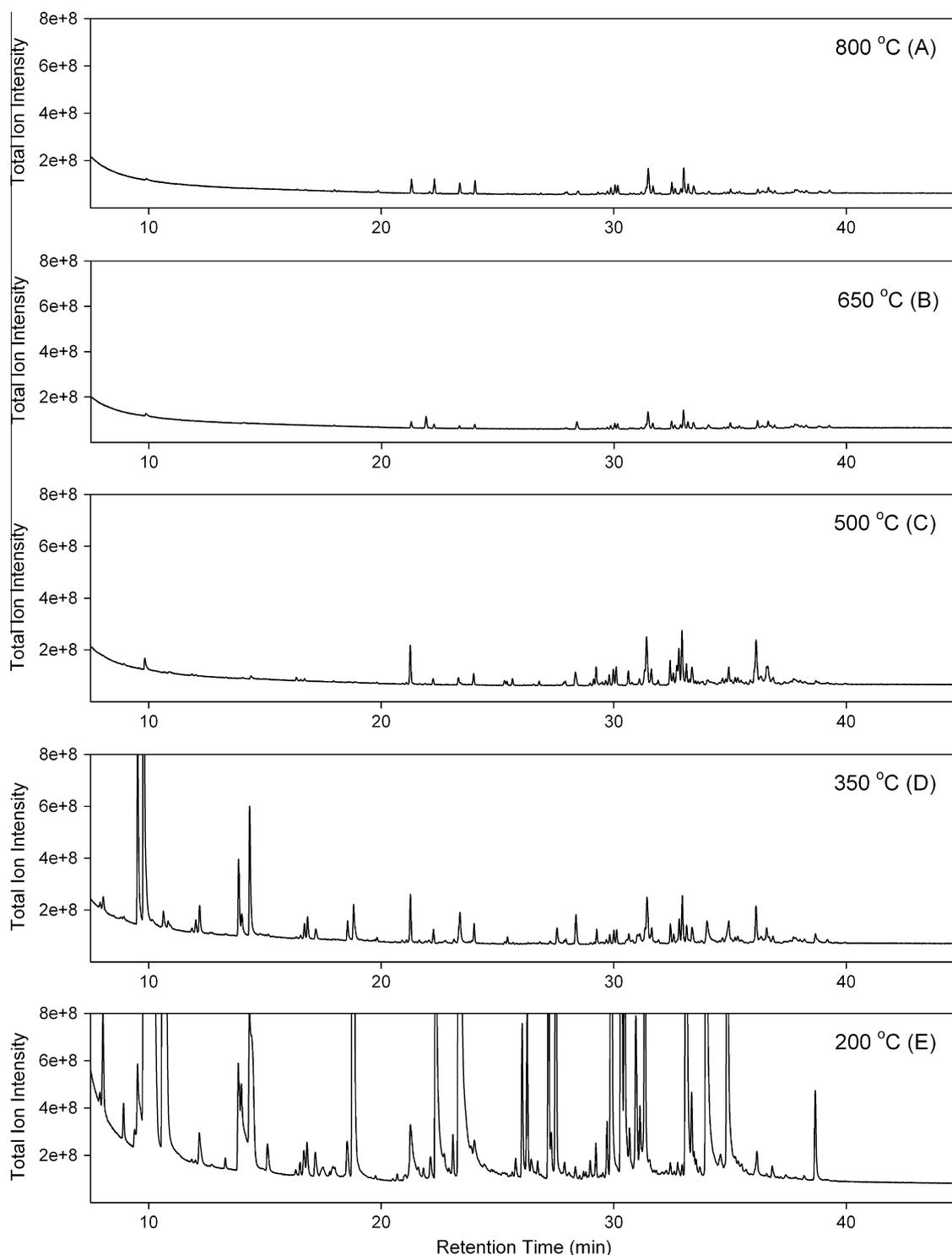
Fig. 3. Total ion chromatograms for the analysis of cottonseed hull biochar pyrolyzed at (A) 800, (B) 650, (C) 500, (D) 350, and (E) 200 °C for 4 h under 1600 mL min^{-1} N$_2$ flow. All chromatograms are scaled equally.

methane, ethylene/acetylene, and ethanol were detected in all of the sampled biochars (Table 3).

4. Discussion

4.1. Implications of feedstock, pyrolysis unit, and pyrolysis type

There were over 140 individual VOCs identified that were sorbed to biochars, not to mention the semi-volatiles and non-vol-atiles that still require investigation. Semi-volatiles (e.g., naptha-lene) and non-volatile organic compounds are not adequately quantified with thermal headspace desorption (Kolb and Ettre, 1997). There was a visual grouping of the total sorbed VOCs on bio-char by some pyrolysis techniques (Fig. S2, Supplementary mate-rial). Biochars made using hydrothermal carbonization, fast pyrolysis and gasification clustered in the regions shown, on the other hand, slow pyrolysis biochars were highly scattered indicat-ing no clear clustering (Fig. S2, Supplementary material). However,
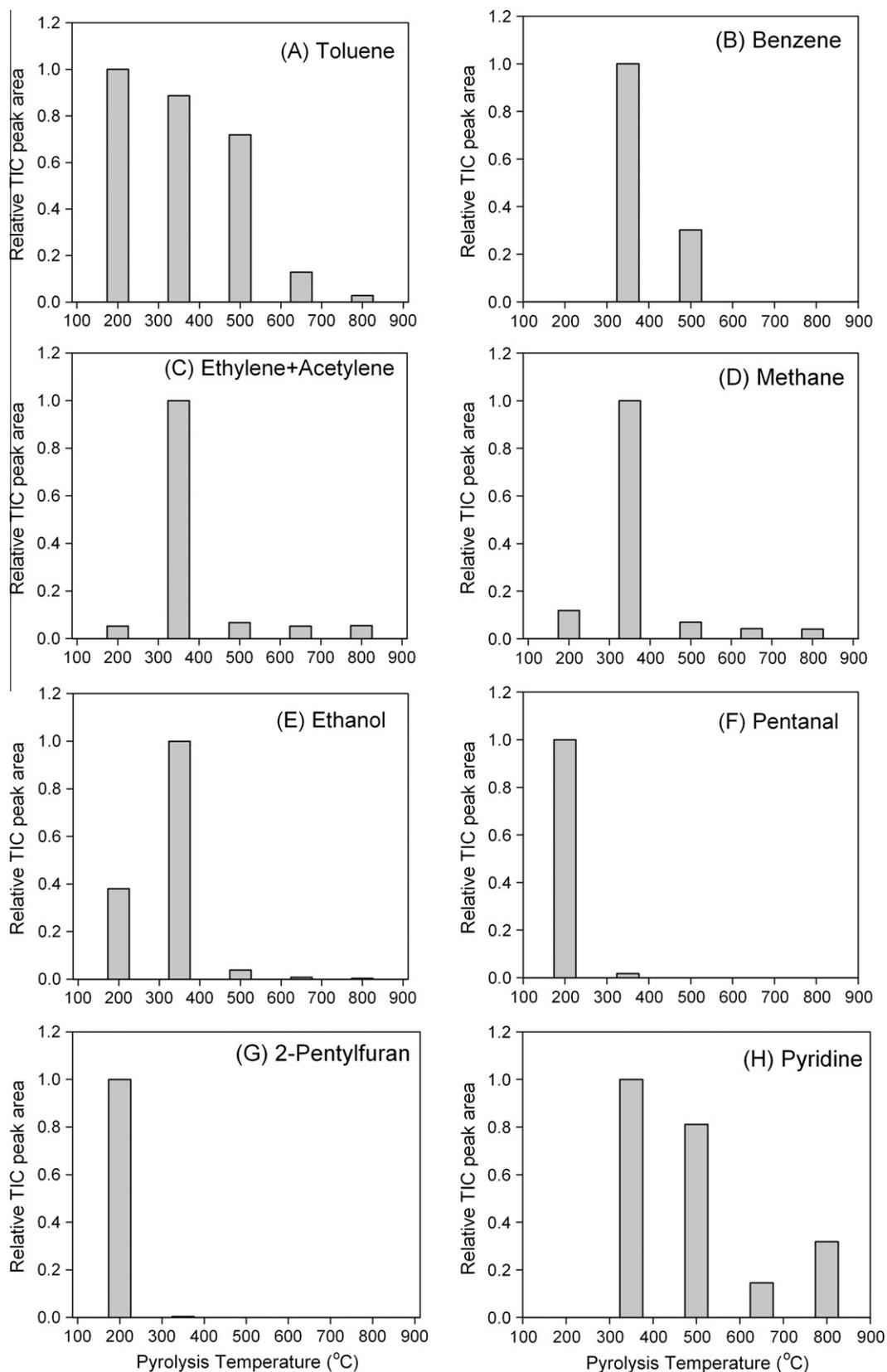
Fig. 4. Illustration of trends in relative peak areas for (A) toluene, (B) benzene, (C) ethylene-acetylene, (D) methane, (E) ethanol, (F) pentanal, (G) 2-pentylfuran, and (H) pyridine detected in cottonseed hull biochars as a function of pyrolysis temperature.

these relationships could also be an artifact of our uneven sample size of production techniques, with 46 biochars from slow pyrolysis and only 3 biochars from fast pyrolysis, 4 from hydrothermal carbonization, and 11 from gasification methods (Table 1). In addition, since thermal desorption only analyzed those compounds that were volatilized and not the total sorbed organic

concentrations, further elucidation of chemical relationship with the production styles needs to wait for the total sorbed concentrations to be known.

These results are in agreement with past literature on identified compounds present in wood smoke (gases) and wood vinegars (liquids) (Asita and Campbell, 1990; Guillén and Manzanos, 2002; Olsson et al., 2004; Blake et al., 2009; Estrellan and Iino, 2010; Mun and Ku, 2010). Woody materials have low ash contents (<1%) and contain variable amounts of other organic compounds, e.g., terpenes, phenols, quinones, and tannins (Umezawa and Higuchi, 1991). The VOCs desorbed from non-charred wood samples typically contain acetaldehyde, methanol, 2-pentylfuran, acetic acid and hexanal for deciduous trees and α-pinene, 3-carene, hexanal, and other terpenes for conifer species as the major components (Risholm-Sundman et al., 1998). Some of these compounds were still observed in the wood biochar (Table 2).

The observed pyrolysis temperature dependence in desorbed VOCs (Figs. 3 and 4) was in agreement with the greatest changes in VM content (Table 1), BET surface area (Keiluweit et al., 2010), aromatic peaks using solid-state ^{13}C NMR (Sharma et al., 2002), and Fourier transform infrared (FTIR) spectra (Uchimiya et al., 2011) of various plant-derived slow pyrolysis biochars produced at 300–500 °C. It should be noted that the lighter weight volatiles (C_1–C_4) were more frequently observed than heavier VOC compounds using GC/MS. For instance, acetone was the most prevalent VOC identified by GC/MS, which only had a 67% frequency compared to over 80% detection frequencies for the lighter weight compounds by TCD/FID (Tables 2 and 3). The atmospheric air and water vapor peaks from the biochar headspace gas sample

interfered with the detection of these earlier eluding VOC peaks on the GC/MS.

Elemental composition of the feedstock appeared to influence some of the VOC species identified in our biochar sample pool. The relatively high chlorine content of agricultural biomass lowers burn efficiencies by forming scales and causing other corrosion issues in gasifiers (Hansen et al., 1998; Spliethoff and Hein, 1998). Obernberger et al. (2006) attributed these corrosion problems to the high concentrations of chlorine, nitrogen, and sulfur in straws, cereals, grasses, grains and fruit residues relative to other biomass sources. Furthermore, Vierle et al. (1999) observed chlorinated VOCs from burning biomass derived pellets. The variable chlorine levels in biomass sources could explain the presence of some chlorinated species sorbed to the biochars analyzed in this study (Table 2). However, there was no clear feedstock type dependence

Table 3
Frequency of detection of various compounds sorbed to biochars by TCD-FID analyses.

Compound	% of biochars containing
Carbon dioxide	100
Methane	100
Ethylene/acetylene[a]	97
Ethane	95
Propylene	99
Propane	95
Butane	93
Methanol	81
Ethanol	100

[a] Ethylene and acetylene co-elute on the packed Porapak Q column.

Table 2
Frequency of detection of VOCs sorbed to various biochars by GC/MS.

Compound	% of biochars containing	Compound	% of biochars containing
Acetone	67	1,4 Dimethyl benzene	17
Benzene	65	1,3 Dimethyl benzene	17
Methyl ethyl ketone	60	Cyclohexane	16
Toluene	60	3 Pentanone	14
Methyl acetate	52	2-Hexenal	12
Propanal	50	Ethanol	11
Octanal	48	2 Methoxy 2 methyl propane	11
2,3 butanedione	45	Dichloromethane	10
Pentanal	45	Carbon tetrachloride	9
3-Methyl-butanal	43	2-Butanol	7
Ethylbenzene	43	Methylcyclohexane	7
1-Dodecane	42	1,2 Dichloroethene (z)	6
Tetrachloroethene	40	1,2,4 Trichlorobenzene	5
Butanal	39	1,2,3-Trichlorobenzene	4
Cyclo pentanone	38	1,1 Dichloroethane	3
Furan	37	Trichloromethane	3
Heptanal	37	1,2-Dibromo 3-chloropropane	3
2-Pentanone	35	1,1,2 Trichloro 1,2,2 –trifluoro ethane	2
Hexanal	35	1,1 Dichloroethene	2
Hexane	34	ethyl Acetate	2
Benzaldehyde	34	Trimethyl ester boric acid	2
1,2,3-Trimethylbenzene	34	Trans 1,2 dichloroethene	2
Methyl propanal	31	1,1,1 Trichloroethane	2
Hexene	31	1,2 Dichloroethane	2
Carbon disulfide	30	1,2 Dichloropropane	2
2-Hexanone 5-methyl	28	Bromodichloromethane	2
Trichloroethene	27	1,3 Dichloropropene (z)	2
Furfural	27	1,3 Dichloropropene (e)	2
1 Methylethyl benzene	26	1,1,2 Trichloroethane	2
2-Propenal	25	Dibromochlormethane	2
2-Heptanone	25	1,2 Dibromoethane	2
2-Methyl-2-cyclopenten-1-one	22	Chlorobenzene	2
2 Methyl furan	20	Tribromomethane	2
Naphthalene	20	1,1,2,2-Tetrachloroethane	2
Styrene	18	1,3-Dichlorobenzene	2
Pentane 2-methyl	17	1,4-Dichlorobenzene	2
1,2 Dimethylbenzene	17	1,2-Dichlorobenzene	2
Siloxanes (unidentified)	17		

on detectable chlorinated species, e.g., tetrachlorethylene was observed in a variety of feedstocks including hardwood, manure, corn stover, pine, and macadamia nut shells across a variety of pyrolysis types and conditions (Table 2). Plants in the *Cyperaceae* (e.g., switch grass) and *Poaceae* (e.g., sugarcane) families are known to possess relatively high amounts of silica in their plant tissues (Hodson and Evans, 1995), which correspondingly could be the source for the unidentified siloxane compounds in the switch grass and sugar cane biochars. Sulfur contents of feedstock and pyrolysis products are similar, often at lower concentrations in biomass feedstocks (Di Blasi et al., 1999). Other studies on pyrolysis oils and gases have observed various nitrogen compounds (ammonia, aliphatic amines; pyridine; aniline; pyrroles; indoles; quinolines and benzothiazoles), which were predominately observed from feedstocks with high nitrogen contents (Mirmiran et al., 1992; Hansson et al., 2004). However, the chemical complexity of the resulting isomers and possible ring substitutions from biomass require improvements in the mass spectral database and up-front analytical separation to improve compound identification (Overton and Manura, 1995; McLafferty et al., 1999).

The elevated sorbed volatiles on HTC biochar could potentially be due to contact with the liquid phase, which includes products of hydrolysis during biochar production (Kruse and Gawlik, 2002; Funke and Ziegler, 2010). This condition could result in higher concentrations of sorbed volatiles, unless the biochar is washed or otherwise post-processed (Hoekman et al., in press; Libra et al., 2011). For instance, if biochar was activated (i.e., steam, acid, or base chemical activation) (Lima and Marshall, 2005; Langley and Fairbrother, 2007), this process removed sorbed surface volatiles, and a corresponding increase in the effective surface area was typically observed (Azargohar and Dalai, 2006, 2008). Bernardo et al. (2010) observed over a 2–3 order reduction in the concentration of various organic compounds in leachates from chars following dichloromethane rinsing. This was also seen in the activated carbons possessing lowest total sorbed VOCs of the suite of biochars analyzed here (Figs. S1–S2, Supplementary material). This condition implied that the elapsed time from production and post-production processing of the biochar would impact the distribution of sorbed volatiles. Thereby, one can conceptualize how different concentrations can be sorbed to the biochar as a function of the pyrolysis conditions as well as the cooling rate of the biochar, and whether it was in contact with the pyrolysis gases or liquids, water, and oxygen during cooling. Our results have shown that post-production processing reduced the amount of sorbed VOCs on biochar (Fig. S1, Supplementary material).

Despite individual compound differences, the overall trend associated with an increase in pyrolysis temperature within the same unit was a net decrease in total sorbed VOCs with an increasing proportion of aromatic compounds (Fig. 3). These temperature relationships were not observed when biochar was sampled across different pyrolysis units, despite the similarities in design and production parameters (Fig. 2). The lack of clear relationships with production temperature and feedstock indicated that the production method and post production handling and storage of the biochar could be dominant factors controlling the variability in the sorbed VOC profile. In this study, not only were differences observed as a function of pyrolysis unit, feedstock, and temperature; but there were also differences imposed by the post-production processing (activation) of the biochar (Fig. S1, Supplementary material).

Lastly, biochars that possessed the lowest levels of sorbed volatiles were produced under partial aerobic conditions (i.e., hog fuel boilers, fire pits or soil kilns; pyrolysis processes without an inert gas purge or temperature regulation) or that underwent secondary activation (treatments). Incidentally, wood ash from aerobic gasifiers has been shown to be low in sorbed VOC content (Someshwar,

1996). These data suggested that the presence of oxygen during the pyrolysis reaction reduced the amounts of sorbed volatiles, potentially through oxidation or allowing more complete combustion (Jenkins et al., 1998; Simoneit, 2002), which could be a desired biochar characteristic for soil fertility improvements (Brewer et al., in press). However, a surplus of oxygen during pyrolysis results in gasification, producing a low carbon and high ash residual (Table 1), which is not optimal for C sequestration.

4.2. Sorbed VOC implications

Historically, both positive and negative effects on plant and microbial systems of soil applied charcoal have been attributed to specific compounds entrained within or emitted from the charcoal (Vantsis and Bond, 1950; Nutman, 1952; Turner, 1955). Benzene and ethylene are the dominate products of oxidative pyrolysis during glowing combustion of charcoal (Olsson et al., 2003, 2004) and can inhibit microbial responses in soils (Smith, 1976; Prosen et al., 1993; Nunes-Halldorson et al., 2004).

Methoxyphenols and phenols have been observed as a product of pyrolysis of hemicelluloses and lignin (Faix et al., 1991; McDonald et al., 2000; Lingens et al., 2005). These compounds, along with carboxylic acids, ketones, and furans are also known microbial inhibitors (Klinke et al., 2004; Mu et al., 2006; Mun and Ku, 2010). Moreover, these compounds even possess nematicidal qualities (Ali et al., 2002). The presence of these inhibitory compounds on biochar could be optimized for pathogenic control (Graber et al., 2010).

In addition to suppressing microbial activity, polyphenols have been observed to shift the dominant pathway of N-cycling from mineral to organic N-forms (Palm and Sanchez, 1990; Northup et al., 1998; Tian et al., 2001). These microbial responses are already known to vary as a function of ecosystem (Shneour, 1966; Spokas and Reicosky, 2009). Additionally, polyphenols are known to be effective in repelling other soil fauna and anthropods (Bottimer, 1929). Therefore, given the fact that some of the biochar analyzed here possess these components (Table 2), these VOCs released from biochar could trigger an array of microbial, animal, and plant responses (Ryu et al., 2003). Incidentally, a possible explanation for the historical observations of biochar losing its agronomic benefit with storage could be if these beneficial VOCs were lost with time following production (e.g., Lefroy, 1883). More importantly, we corroborate that sorbed VOCs can be removed from biochar by further post-production treatment, such as chemical, thermal, or microbial (composting). The conditions and duration of these post-production treatments still require investigation.

Biochars will sorb not only pyrolysis gases generated during production (Olsson et al., 2003, 2004; Chouchene et al., 2010; Mun and Ku, 2010; Song and Peng, 2010), but they could also absorb other volatile compounds directly from the environment (Masclet et al., 1987). These sorbed volatiles could influence sorption behavior of other inorganic species (Uchimiya et al., 2011) as well as organic contaminants such as naphthalene, nitrobenzenene (Cheng et al., 2008), and benzene (Chun et al., 2004) possessing structural similarity to VOCs and other volatile components of biochars.

Since the analysis here was solely volatile headspace gases, semi-volatile compounds were not adequately assessed (Wei and Jen, 2003). However, the observation of naphthalene in 20% of the biochars evaluated here does confirm polyaromatic hydrocarbon presence on some biochars, as reported by others (e.g., Rey-Salgueiro et al., 2004; Rumpel et al., 2007). However, the frequency and potential impacts of these polyaromatic compounds require additional studies, with particular attention devoted to the quantification of all sorbed compounds.

5. Conclusions

The diverse range of sorbed VOCs moieties between individual biochars could be partially responsible for the noted variance in soil and plant responses after biochar additions. Differences in the chemical composition of the sorbed VOCs from the same pyrolysis type, temperature, and feedstock suggested that even biochars created under similar pyrolysis conditions and equivalent feedstocks can result in biochars with sorbed VOCs that are chemically diverse. Clear influences of production conditions, especially the presence of O_2, pyrolysis temperature, post-production conditions and activation were observed, but with very little consistent effect of feedstock. The post-production handling of the biochar controls the quantities of sorbed volatiles that remain on the biochar, with further thermal and chemical processing virtually removing all sorbed VOCs. Variability in the sorbed VOC profiles could be linked to other structural features of biochar, but these were not examined here. The complexity and distribution of VOCs on biochar still warrants supplementary investigation, which will require further analytical method improvements, in order to adequately compare biochar impacts across various studies. However, these results indicated that the VOC composition of biochar contained within this study have been linked by others with both stimulative or inhibitive effects in plant and microbial systems. It is important that the presence of individual VOC compounds and the combined effects of these compounds be elucidated because their presence may cause diverse responses from biochar additions to soils or other growth media.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.06.108.

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