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Characteristics of soil organic matter 14 years after a wildfire: A pyrolysis-gas-chromatography mass spectrometry (Py-GC-MS) study

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ABSTRACT

Severe wildfires combust most above ground vegetation and detritus layers, altering the content and chemical composition of soil organic matter (SOM). To evaluate the lasting effects of wildfire on SOM and the recovery of burned soils, we sampled surface (Oa horizon) and mineral soils (0–5 and 5–15 cm depths) in unburned areas and areas burned at moderate and high severity 14 years after the 2002 Hayman Fire, in Colorado, USA. We characterized SOM using Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC–MS) and identified 106 pyrolysates within eight chemical classes [aromatic hydrocarbon (ArH), carbohydrate (Carb), lignin compound (LgC), nitrogen containing compound (Ntg), polyaromatic hydrocarbon (PAH), phenol compound (PhC), saturated hydrocarbon (SaH), and unsaturated hydrocarbon (UnSaH)]. Burned soils had greater total quantified peak areas (TQPA) for the pyrogenic C indicator (PyC) benzene, compared to unburned soils; however, other common PyC markers were not abundant in burned relative to unburned soils. Factor analysis on the individual pyrolysates suggests that factors 1 and 2 correlated with pyrolysate aromaticity and hydrophobicity, respectively. Sample factor scores potentially suggest that SOM aromaticity increases with fire severity, though difference between moderate and high severity was slight. Factor analysis also indicates that the ratio of [ArH + Ntg] / [PhC + LgC] may serve as index of PyC content in SOM. This study shows that wildfire effects on SOM character may persist for more than a decade of ecosystem recovery and that Py-GC–MS coupled with factor analysis has utility for evaluating how disturbance alters SOM and PyC in complex environments.

1. Introduction

The number of severe wildfires has increased worldwide during the last two decades [1,2]. Not only do severe wildfires combust most vegetation, they also alter the thickness, extent and composition of soil organic layers [3,4]. A significant portion of combusted biomass is lost to the atmosphere as CO_2 and volatile organic carbon, but large amounts of partly burned residues and pyrogenic organic carbon (PyC) are also integrated into the forest floor [5,6], where it may play an important role in regional and global C cycles. Since PyC is not completely inert, abiotic and biotic oxidation processes alter its structure and chemical properties [7,8]. Fine, charred organic particles are common in upper mineral soil layers (0–3 cm). However, oxidized PyC is relatively polar and easily transported as dissolved black carbon (DBC) both within soil horizons and downslope [7,9,10]. Through there has been considerable effort to characterize PyC distribution and composition shortly after wildfires [11,12], few studies have evaluated the long-term fate and vertical movement of PyC (e.g., > 1 decade after wildfire) within soil profiles. In fire-affected mineral soils, PyC is comprised of both labile (i.e., ~ 0.03 yr mean resident time), and slowly degraded fractions (i.e, ~ 40 yr mean resident time) [13]. The signal intensities of pyrolyzed materials including aromatic hydrocarbons (i.e., benzene and toluene) and polyaromatic hydrocarbons (i.e., pyrene) increase across a range of charcoal ages and demonstrate changes with time since burning [14–16].

Pyrolysis gas chromatography - mass spectrometry (Py-GC–MS) is a versatile analytical technique with wide utility for natural organic matter characterization. The approach has been used to study foliar litter decomposition [17] and determine the chemical composition of pyrogenic organic matter in biochar and charcoal [14,18,19]. Specifically, total quantified peak areas (TQPA) of the pyrolysates benzene, naphthalene and benzonitrile increase with pyrolysis temperature and have been used as indices of thermal alteration [14]. The abundance of three and four benzene ring polyaromatic hydrocarbons has been

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suggested as an indicator of the presence of charred or burnt materials [15]. Almendros, et al. [20] reported accumulations of condensed polyaromatic and lignin-derived, phenolic compounds following high- and moderate-intensity fires, respectively. Recently, the van Krevelen (VK) diagram, commonly used to visualize Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS) data [21–23], has been used to classify pyrolysates quantified by Py-GC–MS [16,20]. However, the classification is based on two dimensions of O/C and H/C atom ratios and without appropriate optimization and justification may lead to inconclusive and/or confounding results [22]. Most previous Py-GC–MS studies have been conducted under laboratory conditions or shortly (< 2 years) after wildfire, and few have examined the long-term effects of wildfire on soil PyC. Therefore, the effectiveness of the approach to evaluate changes as ecosystems recover from wildfire remains unknown. A recent statistical approach (i.e., ANOVA and factor analysis) was used to increase analysis efficiency, sensitivity and data throughout for tens of Py-GC–MS peaks [24]. In this study, we will compare different data analysis approaches to identify the best Py-GC–MS method for tracking PyC in natural environments.

The 2002 Hayman Fire was the largest fire (558 km^2) in recent Colorado history [25]. A century of fire suppression increased fuel loads in these and many Colorado forests and a severe drought in 2002 created conditions that results in high severity wildfire across large areas of the burn. Post-fire forest vegetation recovery following the Hayman Fire has been extremely slow [26] and stream nutrients and carbon has remained elevated relative to unburned watersheds [27,28]. We hypothesis that the influence of the 2002 Hayman Fire on soil organic composition especially PyC is still evident 14 years after the fire. To study the long-term fate of PyC in 2016, we collected soil across fire severity gradient within and adjacent to the Hayman Fire (Fig S1) from three depths and analyzed them using Py-GC–MS, to: (1) evaluate the effect of fire on soil C and N content 14 years after fire; (2) examine the effectiveness of PyC markers as indicators of fire 14 years after fire; and (3) characterize the fire burned SOM using factor analysis on pyrolysates.

2. Materials and methods

2.1. Soil sampling

The Hayman Fire burned ponderosa pine (*Pinus ponderosa* Dougl. ex Laws) and Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] forests of the lower montane elevation zone (1980–2750 m) [29]. The majority of the fire was underlain by Pikes Peak batholith, a coarse-grained biotite, and hornblende-biotite granite [30] that weathers to form weakly developed, excessively drained, coarse sandy loams (*Typic Ustorthents*) [31]. Soils were sampled in 2015 across a severity gradient that includes unburned areas, moderate-severity areas where organic soil horizons were partially combusted, and high-severity areas where vegetation and surface organic matter were completely combusted (Fig S1), with five replicates. Burn severity was mapped according to standard US Forest Service approaches [28], using remotely sensed pre- and post-burn vegetation reflectance and validated by on-site assessment [32,33]. In general, the consumption of biomass during fire forms black ash under moderate severity (200−500 ℃) and white ash under high severity (>510 ℃) [34]. At each sampling plot, needle litter (Oi layer) was carefully removed where it existed, and well-decomposed O-horizon material (Oa layer), along with 0−5 and 5−15 cm mineral soil depths were collected. All soil samples were oven-dried at 65 ℃ for ≥ 48 h, passed through a 2-mm sieve, and ground to a fine powder before further analysis.

2.2. Soil C and N characterizations

We analyzed total soil C and N contents by Dumas dry combustion (LECO CHN 2000; St. Joseph, MI). Soil organic matter was characterized by a Py-GC–MS instrument with a pyrolysis injector (CDS 5000, CDS Analytical Inc., Oxford, PA) interfaced directly with an Agilent GC7980 gas chromatograph (GC) combined with a 220-ion trap mass spectrometer (Agilent, Santa Clara, USA) at Clemson University was used. Each subsample was heated from 50 to 700 ℃ at 5 ℃/ms and held for 10 s under a helium carrier gas with 1 mL/min flow rate to flush pyrolytic compounds into a DB-5MS column (30 m ×0.32 mm ID, 0.25 mm film thickness, J&W Scientific Inc.). The GC injector was operated in split mode (10:1) with an inlet temperature of 250 ℃. The column temperature was held at 35 ℃ for 5 min, and then increased at 3 ℃/min to 300 □, and held at this temperature for 10 min.

An automated pyrolysate identification and quantification pipeline based on the National Institute of Standards and Technology (NIST) Mass Spectral Library (2008) through NIST Mass Spectral Search 2.0 was developed [24] for efficiently extracting information from the Py-GC–MS data. A total of 113 peaks were assigned from the 45 soil samples. Pyrolysates were semi-quantified using the percentage of total peak area comprised by all identified individual peaks within each pyrochromatgram [35]; major pyrolysate peaks (Table S1) were obtained from the NIST Mass Spectral Library (2008). One hundred and six (106) pyrolysates (out of 113) were categorized into the following classes: aromatic hydrocarbon (ArH), carbohydrate (Carb), lignin compound (LgC), nitrogen containing compound (Ntg), polyaromatic hydrocarbon (PAH), phenol compound (PhC), saturated hydrocarbon (SaH), and unsaturated hydrocarbon (UnSaH). Additionally, seven pyrolysates (7 of 113) were not commonly observed or reported in previous studies and classified as unknown compounds (Unk). In addition, we determined a modified aromatic index [AI_{mod}; calculated by (1 + C–0.5O–S–0..5 H)/(C-0.5O-S-N-P)] [36], water solubility, and the octanol-water partition coefficient (K_{ow}) of each pyrolysate. Pyrolysates with $AI_{mod} \leq 0.5$ are aliphatic and olefinic or non-aromatic compounds, those with $0.5 < AI_{mod} \leq 0.67$ are aromatic compounds, and $AI_{mod} > 0.67$ are condensed aromatic compounds [37,38]. Water solubility (mg/L) and K_{ow} were obtained using Fragment Methodology (v1.01 est) and KOWWIN v1.68, coupled with an Estimation programs interface (EPI Suite™, US EPA) [39].

2.3. Statistical analysis

We used factor analysis to quantify variability among pyrolysates within burn severity classes (RStudio Desktop V. 1.0.44; Boston, MA, USA). Factor analysis is a statistical method used to describe variability among observed, correlated variables in terms of a potentially lower number of unobserved variables called factors. We used one-way analysis of variance and Tukey's HSD means comparisons to identify differences among burn severity classes within soil layers, after checking assumptions of normality (Shapiro-Wilk) and homogeneity of variance (Bartlett's). Box-Cox transformations were implemented to normalize data. Where transformations failed to normalize data, we used the non-parametric Kruskal-Wallis test and Dunn's post-hoc multiple comparison with a Bonferroni correction. Significant effects are indicated for $p \leq 0.05$.

3. Results and discussions

3.1. Total soil C and N content

The effect of the Hayman Fire remained evident 14 years after the fire with significantly lower C content ($p < 0.05$) in the O-horizon of area burned at high (13.7 ± 6.2 %) and moderate (18.4 ± 4.9 %) severity compared to unburned soils (28.6 ± 5.0 %). There was also a decreasing trend of soil N (1.04 ± 0.15, 0.95 ± 0.33 to 0.70 ± 0.30 %) in O-horizon for unburned, moderate, and high severity wildfire areas, though differences were not statistically significant. The O-horizon C/N ratio followed the same pattern as soil C content with the lowest ratio at high severity (19.2 ± 1.0), following with moderate severity (19.7 ± 1.7) and unburned (27.5 ± 2.0) soils, respectively. The persistent effect of the fire

on C and N contents was the net effect of combustion losses from vegetation and detritus and extremely slow post-fire vegetation recovery [26,27]. The fire had no lasting effect on C or N content in the mineral soil layers.

3.2. TQPA and ratios of pyrolysates

Aromatic and phenolic pyrolysates including benzene and toluene and ratios of pyrolysates (i.e., benzene/phenol, benzene/toluene) have been considered as pyrogenic carbon (PyC) markers of wildfire occurrence or severity because total quantified peak areas (TQPA) of these pyrolysates change with heating temperature [14,40]. However, in this study, few of the proposed PyC markers responded as expected. Toluene (Ar2) had the highest TQPA in Hayman soils (Figs. 1 and 2 a) but did not respond to wildfire severity or soil depth. In fact, only 35 of the 113 pyrolysates we identified differed statistically among severity classes or soil depths (Tables S1 & S2). The sum of those pyrolysates accounted for $<$ 20 % of TQPA in each chromatogram. We also compared each pyrolysate (113 in total) between fire severity (i.e., unburn vs moderate severity, unburn vs high severity, and moderate vs high severity) and soil depth (i.e., O-horizon vs 0−5 cm, O-horizon vs 5−15 cm, 0−5 cm vs 5−15 cm) pairs; only 58 out of 1017 pairs (3 depths $\times$ 3 fire severity classes $\times$ 113 pyrolysates) differed statistically (Table S2). The chemical composition of SOM was generally uniform across a wildfire severity gradient 14 years after the Hayman Fire. Both microbial degradation and photo-oxidation alter the PyC created by wildfire [7,41] and the slow recovering vegetation adds fresh organic matter both above and belowground to burned soils.

Few of the proposed PyC markers were useful as indicators of the Hayman Fire more than a decade after it occurred. The percentage of benzene was elevated in moderate and high severity burned soils in all depths (Fig. 2d), and its TQPA generally increased with soil depth. For example, benzene accounted for 1.4, 2.5 and 3.5 % of TQPA in the O horizon of unburned, moderate and high severity soils. In moderate severity soils, benzene accounted for 2.5, 4.9 and 4.9 % in the O-horizon, 0−5 and 5−15 cm depths. Though the abundance of benzene increases with pyrolysis temperature [14], aromatic compounds such as benzene can also be produced by the microbial degradation of aromatic-ring-containing compounds, such as lignin, polysaccharides, and proteins [35]. The appearance of benzene with similar average TQPA in unburned and burned samples indicates that benzene is not a good indicator for the Hayman Fire. Conversely, *p*-vinylguaiacol was lower in burned soils, and the TQPA of this lignin compound decreased with depth (Fig. 2j). On average, benzene to phenol and benzene to toluene ratios of burned soils were generally higher than those of unburned soils, and these ratios generally increased with soil depth (Fig. 2k and l). Although these PyC markers remained altered a decade after wildfire, none of them accounted for more than 5% TQPA of each pyrochromatogram and most of the observed trends were not statistically significant.

3.3. Chemical classes of pyrolysates

Grouping pyrolysates into chemical classes with similar functional moieties is a common approach for evaluating chemical composition of organic matter [24,42,43]. Of the chemical classes we observed (Fig. 3), ArH was the most abundant (mean: 27 % of TQPA; range: 20−32% of TQPA) followed by Carb (mean: 21 %; range: 18–23 %) and PhC (mean: 21 %; range: 17–22 %). These three classes comprised 59–74 % of TQPA. The ArH class was generally higher in burned soils though the fire effect was only statistically significant for moderate severity wildfire in the 0−5 cm layer (Fig. 3b). This pattern was consistent with previous wildfire studies that found increases in aromatic compounds during charcoal formation [42,44,45]. The Ntg class was also higher in all burned soil layers which agrees with observations of higher streamwater N export from catchments burned by the Hayman Fire [46]. Pyrrole-derived compounds were sensitive indicators of burning more than a decade after the Hayman Fire (e.g., Nt3, Nt4 and Nt7 in Fig. 2 and Table 1). For example, benzonitrile (Nt7) accounted for 0, 0.7 and 0.6 % in unburned, moderate and high severity O-horizon soils (Table S3). Burned soils had few LgC and PhC compounds, indicating a post-fire decline in lignin, the likely result of demethoxylation of lignin macromolecules during heating or reduced litter inputs associated with slow vegetation recovery. We observed a low abundance of compounds in the PAH class and though this class have been considered a fire surrogate [15,20] these compounds did not respond clearly to either soil depth or fire severity in our study. For example, the PAH class represented 0.6 %, 0.7 % and 1.0 % of TQPA in the O horizon of unburned, moderate and

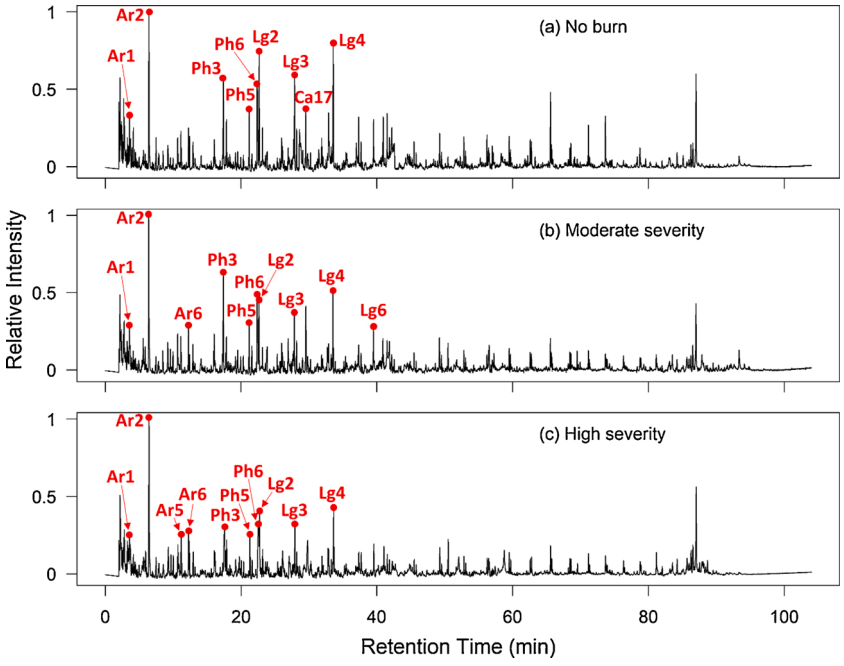

Fig. 1. Pyrograms of O-horizon from (a) no burn, (b) moderate severity and (c) high severity.

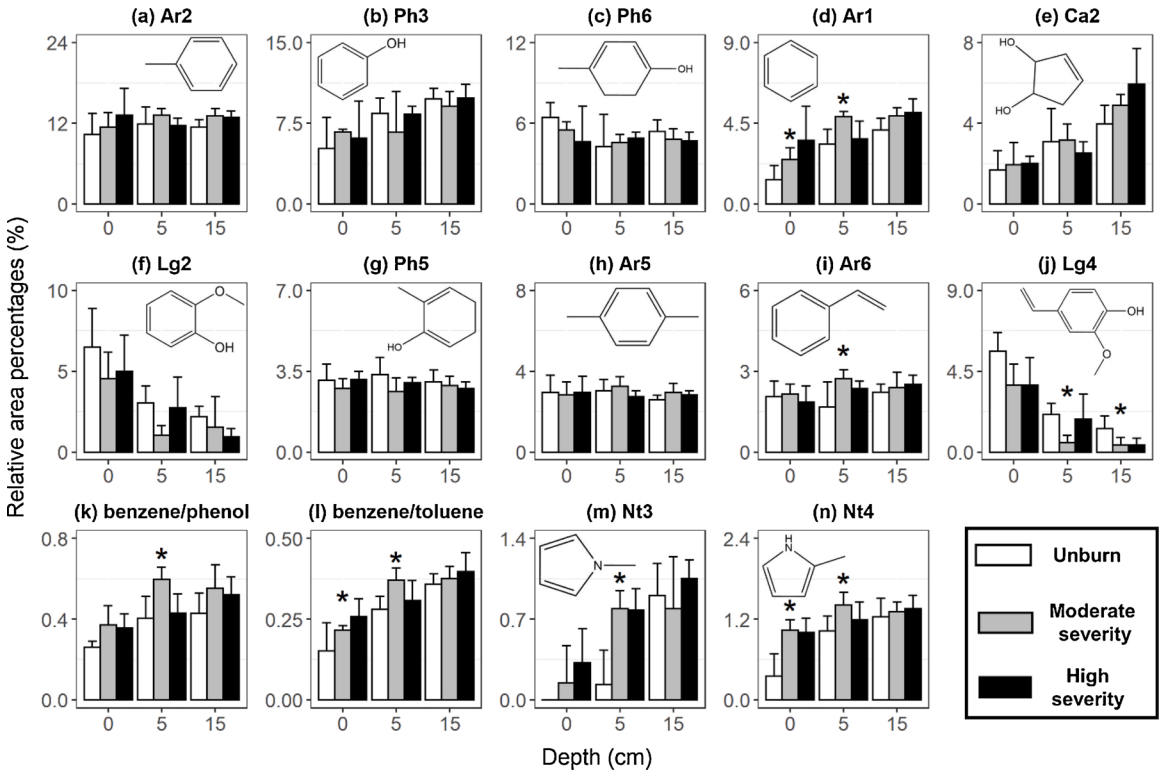

Fig. 2. The 10 most abundant pyrolysates by TQPA percentage (panels a-j), ratios of relative area percentages of representative pyrolysates (panels k-l), and pyrrole-type N containing pyrolysates (panels m-n) in three different depths across the burn severity gradient (mean ± standard errors, n = 5). Asterisks indicate statistical differences within a specific soil depth ($p \leq 0.05$).

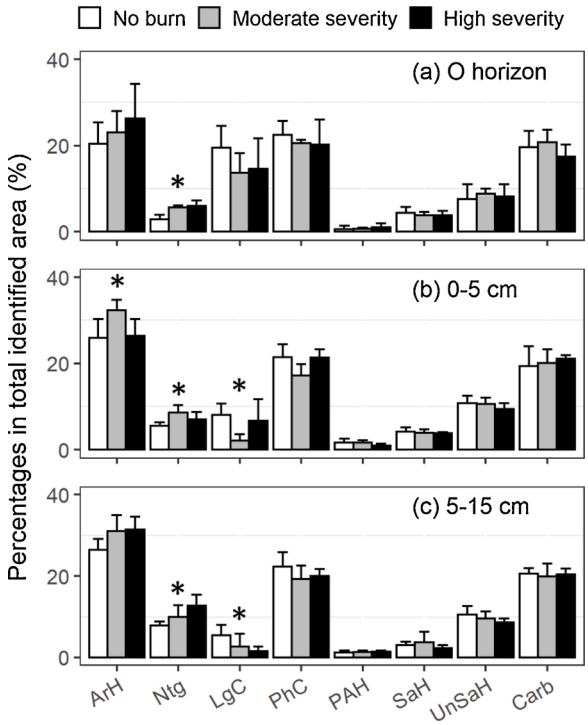

Fig. 3. Relative area percentage (mean ± standard error, n = 5) of chemical classes in (a) O horizon; (b) 0-5 cm; and (3) 5-15 cm mineral soils between wildfire severity classes. Asterisks indicate statistical differences. Chemical class labels as follows: aromatic hydrocarbons (ArH), carbohydrates (Carb), lignin compounds (LgC), nitrogen-containing compound (Ntg), polyaromatic hydrocarbons (PAH), phenolic compounds (PhC), saturated hydrocarbons (SaH), and unsaturated hydrocarbons (UnSaH).

high severity soils. In high severity soils, PAH class accounted for 1.0, 1.0 and 1.4 % in the O-horizon, 0–5 and 5–15 cm depths. Moreover, the number of aromatic rings was 2 for the pyrolysates in PAH class.

3.4. Factor analysis

The first two components (F1 and F2) of the factor analysis explained 35 % of the total variance (Fig. 4). The F1 factor axis separated aromatic hydrocarbons from lignin and phenolic compounds (Fig. 4a). F1 loading is strongly positive with ArH and PAH classes having an aromatic index (AI_{mod}) ≥ 0.5 for benzene (Ar1), benzonitrile (Nt7), and naphthalene (PA1). Conversely, F1 loading is strongly negative with LgC and PhC classes having AI_{mod} < 0.5 for creosol (Lg3) and *p*-xylenol (Ph9). We interpret F2 as an index of hydrophobicity since it was positively correlated with water solubility [Log_{10}(water solubility in mg/L) = 1.16 × F2 loading + 2.72; p-value = 0.03] and negatively correlated with the octanol-water partition coefficient (K_{ow}) [$Log(K_{OW})$ = -1.08 × F2 loading + 2.75; p-value = 0.02] for individual pyrolysates (Figs S2a and S2b).

From the factor analyses we observe general patterns of aromaticity with fire severity, from unburned, moderately severity, to high severity along the F1 loading axis and the difference between moderate and high severity was slight (Fig. 4b). Regrouping samples by soil depth (Fig. 4c) indicates greater SOM aromatic (PAH and ArH) and N content (Ntg) in deeper soil layers, the net result of downward movement of PyC. It has been estimated that forest vegetation will require an 20–50 more years to return to pre-fire conditions at the Hayman Fire [46,47]. As seen elsewhere, the greater SOM aromatic and N content we observed in deeper soil layers may have resulted from downward post-fire movement of PyC [7,41]. The post-fire transport and fate of PyC was well summarized by Santin, et al. [6]. After fire, soil erosion is enhanced due to the loss of vegetation cover and increased soil water repellency, so a large portion of the PyC created during litter and vegetation combustion

Table 1
The 113 pyrolysates identified during this study. Total quantified peak areas (TQPA) percentage of highlighted compounds differ significantly ($p \leq 0.05$) between unburned soils and those burned by moderate or high severity wildfire. Light grey indicates that differences in burn severity occurred in O-horizon. Dark grey indicates that differences only occurred in mineral soil layers (either 0-5 or 5-15 cm soil). The products with bold fonts are the 10 top-ranked products in % TQPA.

Labels	Compounds	Groups	Labels	Compounds	Groups
Ar1	**Benzene**	**ArH**	Nt1	Methanamine, N-hydroxy-N-methyl-	Ntg
Ar2	**Toluene**	**ArH**	Nt2	Acetic acid, cyano-, methyl ester	Ntg
Ar3	1-cyclobutylcyclobutene	ArH	Nt3	1H-Pyrrole, 1-methyl-	Ntg
Ar4	Ethylbenzene	ArH	Nt4	1H-Pyrrole, 2-methyl-	Ntg
Ar5	***p*-Xylene**	**ArH**	Nt5	1H-Pyrrole, 3-methyl-	Ntg
Ar6	**Styrene**	**ArH**	Nt6	2-Pyrroline, 1,2-dimethyl-	Ntg
Ar7	Benzene, 1-ethyl-2-methyl-	ArH	Nt7	Benzonitrile	Ntg
Ar8	Benzene, 1-ethyl-3-methyl-	ArH	Nt8	Benzene, 1-isocyano-2-methyl-	Ntg
Ar9	Benzene, 1-ethyl-4-methyl-	ArH	Nt9	Benzoxazole, 2-methyl-	Ntg
Ar10	Benzene, 1-propynyl-	ArH	Nt10	Indolizine	Ntg
Ar11	Benzene, 1,2,3-trimethyl-	ArH	Nt11	Benzenepropanoic acid, π(hydroxyimino)-	Ntg
Ar12	Benzene, 2-propenyl-	ArH	Nt12	Ethyl 3-(3-pyridyl)propenoate	Ntg
Ar13	Benzene, propyl-	ArH	Nt13	Hydroxylamine, O-decyl-	Ntg
Ca1	2-Cyclopenten-1-one	Carb	Nt14	4-(2,5-Dihydro-3-methoxyphenyl)butylamine	Ntg
Ca2	**3-Cyclopentene-1,2-diol, cis-**	**Carb**	PA1	Naphthalene	PAH
Ca3	1,4-Butanediol, 2,3-bis(methylene)-	Carb	PA2	Naphthalene, 1,2-dihydro-3-methyl-	PAH
Ca4	3-Hexen-1-ol, (E)-	Carb	PA3	Naphthalene, 1,3-dimethyl-	PAH
Ca5	4-Penten-1-ol, 2-methyl-	Carb	PA4	Naphthalene, 1,6,7-trimethyl-	PAH
Ca6	Furan, 2,5-dimethyl-	Carb	Ph1	1,2-Benzenediol	PhC
Ca7	2-Cyclopenten-1-one, 2,3-dimethyl-	Carb	Ph2	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	PhC
Ca8	2,4-Dimethylcyclopentanol	Carb	**Ph3**	**Phenol**	**PhC**
Ca9	5-Methyl-5-hexen-3-yn-2-ol	Carb	Ph4	1,2-Benzenediol, 4-methyl-	PhC
Ca10	cis-3-Methylcyclohexanol	Carb	**Ph5**	**Phenol, 2-methyl-**	**PhC**
Ca11	Cyclopentaneacetic acid	Carb	**Ph6**	**Phenol, 4-methyl-**	**PhC**
Ca12	1,2-Dioxaspiro[4.4]nonan-3-one, 4-methylene-	Carb	Ph7	Phenol, 2-ethyl-	PhC
Ca13	3-Hexen-1-ol, acetate, (E)-	Carb	Ph8	Phenol, 2,3-dimethyl-	PhC
Ca14	4-Octyn-2-ol	Carb	Ph9	Phenol, 2,5-dimethyl-	PhC
Ca15	5-Octyn-3-ol	Carb	Ph10	Phenol, 3-ethyl-	PhC
Ca16	Benzeneacetaldehyde	Carb	Ph11	Cyclopentanol, 3,3,4-trimethyl-4-p-tolyl-, (R,R)-(+)-	PhC
Ca17	Benzofuran, 2,3-dihydro-	Carb	Sa1	Cyclopentane, 1,2-dimethyl-, cis-	SaH
Ca18	Cyclohexanol, 2,4-dimethyl-	Carb	Sa2	Cyclopentane, 1-ethyl-2-methyl-, cis-	SaH
Ca19	1-Propanone, 1-phenyl-	Carb	Sa3	Pentane, 2-cyclopropyl-	SaH
Ca20	1,2-Dioxaspiro[4.5]decan-3-one, 4-methylene-	Carb	Un1	2-Butene	UnSaH
Ca21	Benzofuran, 2-methyl-	Carb	Un2	Bicyclo[2.1.0]pentane	UnSaH
Ca22	1,4-Dimethoxy-2,3-dimethylbenzene	Carb	Un3	Cyclopentene	UnSaH
Ca23	1,8-Nonanediol, 8-methyl-	Carb	Un4	1,4-Cyclohexadiene	UnSaH
Ca24	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-, cis-	Carb	Un5	2,4-Hexadiene, (Z,Z)-	UnSaH
Ca25	Benzofuran, 4,7-dimethyl-	Carb	Un6	1-Ethylcyclopentene	UnSaH
Ca26	Bicyclo[3.1.1]hept-3-en-2-ol, 4,6,6-trimethyl-	Carb	Un7	1,2-Heptadiene	UnSaH
Ca27	10-Oxatricyclo[4.2.1.1(3,9)]dec-4-ene, 9-ethenyl-	Carb	Un8	1,3,5-Heptatriene, (E,E)-	UnSaH
Ca28	5-Hepten-3-yn-2-ol, 6-methyl-5-(1-methylethyl)-	Carb	Un9	1,4-Cyclohexadiene, 1-methyl-	UnSaH
Ca29	[1,1'-Bicyclohexyl]-2-one	Carb	Un10	1,4-Hexadiene, 2,3-dimethyl-	UnSaH
Ca30	4,7-Methano-1H-inden-1-ol, 3a,4,7,7a-tetrahydro-, acetate	Carb	Un11	1-Nonene	UnSaH
Ca31	8-Decen-2-one, 9-methyl-5-methylene-	Carb	Un12	1,2-Cyclononadiene	UnSaH
Ca32	Cyclopentadecanone, 2-hydroxy-	Carb	Un13	3a,6-Methano-3aH-indene, 2,3,6,7-tetrahydro-	UnSaH
Ca33	9-Heptadecene-4,6-diyn-8-ol, (Z)-	Carb	Un14	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-	UnSaH
Ca34	10-Heptadecen-8-ynoic acid, methyl ester, (E)-	Carb	Un15	Dihydromyrcene	UnSaH
Ca35	2,5-Octadecadiynoic acid, methyl ester	Carb	Un16	E-1,5,9-Decatriene	UnSaH
Ca36	Hydrocinnamic acid, o-[(1,2,3,4-tetrahydro-2-naphthyl)methyl]-	Carb	Un17	1,12-Tridecadiene	UnSaH
Ca37	Octadecane, 1-(ethenyloxy)-	Carb	Uk1	Borazine, 1-methyl-	Unk
Lg1	Maltol	LgC	Uk2	Dicyclopropyl carbinol	Unk
Lg2	**Phenol, 2-methoxy-**	**LgC**	Uk3	1(4H)-Naphthalenone, 4a,5,8, 8a-tetrahydro-4-hydroxy-, (4π4aπ8aπ-	Unk
Lg3	Phenol, 2-methoxy-4-methyl-	LgC	Uk4	Tetracyclo[5.3.0.0<2,6>.0<3,10>]deca-4,8-diene	Unk
Lg4	**2-Methoxy-4-vinylphenol**	**LgC**	Uk5	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	Unk
Lg5	Phenol, 4-ethyl-2-methoxy-	LgC	Uk6	Acetohydrazide, 2-(3-indolyl)-N2-[3-(2-furyl)-2-methylprop-2-enylideno]-	Unk
Lg6	Phenol, 2-methoxy-4-(1-propenyl)-	LgC	Uk7	2-Myristynoyl pantetheine	Unk
Lg7	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	LgC			

Chemical class labels as follows: aromatic hydrocarbons (ArH), carbohydrates (Carb), lignin compounds (LgC), nitrogen-containing compound (Ntg), polyaromatic hydrocarbons (PAH), phenolic compounds (PhC), saturated hydrocarbons (SaH), unsaturated hydrocarbons (UnSaH), and unknown compounds (Unk).

is mobilized [6]. In addition to lateral transport, PyC can move vertically through the soil profile [48]. A greater vertical mobility was found for biochar (as PyC particles) with smaller sizes and lower surface charges [49]. Lopez-Martin, et al. [50] reported the decrease of the aryl-C from 46 % to 23 % of organic C in A horizon seven years after the fire, possibly due to lateral and/or vertical movement or microbial degradation. The labile aliphatic fraction of PyC is degraded fast [51], while microbial degradation of aromatic PyC portion results in the increase of O-containing functional groups (e.g., carboxyl C) in PyC [52]. It is notable that degradation processes transform PyC into various forms, but that only its transformation to CO_2 represents a net ecosystem loss [6]. With the improvement in water solubility, the formerly hydrophobic PyC can be transported into deeper soil layers with soil solution and rainfall [7]. This regrouping (Fig. 4c) also shows that SOM hydrophobicity declines with soil depth.

3.5. A proposed surrogate for pyrogenic carbon

In the years since the Hayman Fire, microbial degradation and photo-oxidation of PyC and organic inputs from regenerating vegetation may have altered the chemical composition of SOM and reduced the sensitivity of specific PyC markers [7,41]. Instead of individual pyrolysate or chemical classes, our findings suggest that a ratio of chemical classes may be a better indicator of the PyC proportion in SOM and fire severity. The numerator [ArH + Ntg + PAH], the TQPA sum of pyrolysates, represents pyrogenic organic matter, and the denominator [PhC + LgC], the TQPA sum of lignin and phenolic containing pyrolysates, is associated with fresh litter and unburned vegetation. There is considerable evidence that burning transforms vegetation and litter materials with high lignin content to charred residues comprising aromatic carbon and nitrogen. Using Py-GC–MS, the TQPA of benzene, benzonitrile and naphthalene as pyrolysates increased with pyrolysis temperature [14], while condensed, polyaromatic hydrocarbons were abundant in charred or burnt materials after high-intensity fire [15]. Jimenez-Gonzalez, et al. [48] used both Py-GC–MS and ^{13}C NMR to determine that aromatic compounds increased in burned topsoils. Using GC–MS, researchers [53,54] identified wildfire as a significant source of 16 US EPA regulated PAHs in topsoil and ash. Black nitrogen, primarily comprised of N-containing heterocyclic aromatic structures, is an important fraction of pyrogenic organic matter [55]. Recently, Torres-Rojas, et al. [56] found the significant increase of aromatic C = N in 6-membered (oxygenated) rings and quaternary aromatic N with pyrolysis temperature from 350 to 700 °C, by using N (1 s) K near edge X-ray adsorption fine structure (NEXAFS) spectroscopy.

Factor analysis showed strong positive F1 loadings for ArH, Ntg, and PAH and strong negative loadings for PhC and LgC. We excluded PAH from the ratio, since it comprised only 0.6 % TQPA. Unlike earlier PyC markers based on individual pyrolysates (i.e., benzene to phenol and benzene to toluene) that comprise < 20 % of TQPA, our proposed ratio [ArH + Ntg] / [PhC + LgC] includes 48 of 113 pyrolysates and

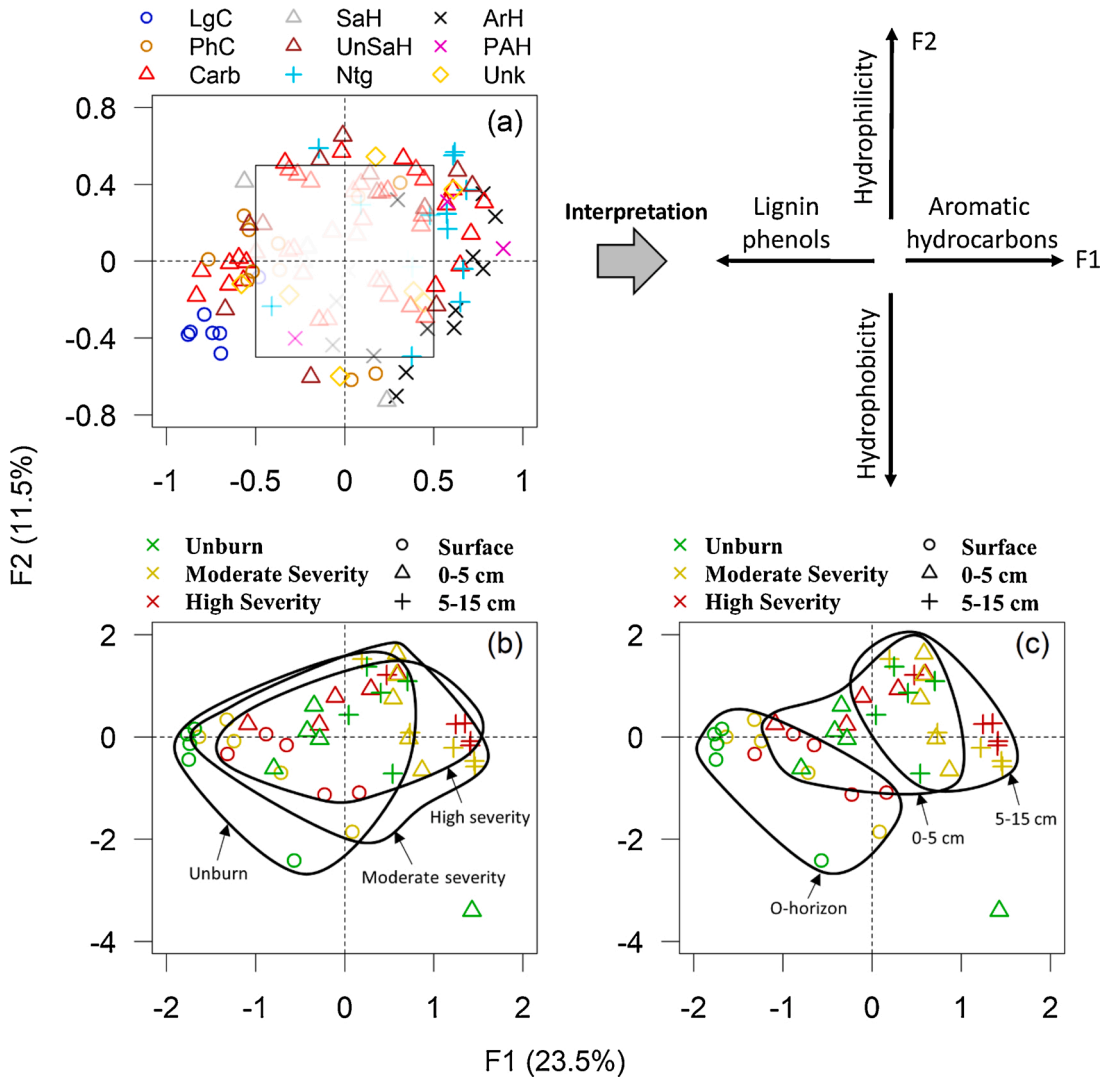

Fig. 4. Factor analysis loadings (a) and scores (b, c) on the relative area percentages of 113 pyrolysis products identified in 45 soil samples. Semi-transparent symbols in Fig. 4a represent weak (i.e., -0.5 < loading value < 0.5) correlations for both F1 and F2 loading. Chemical class labels as follows: aromatic hydrocarbons (ArH), carbohydrates (Carb), lignin compounds (LgC), nitrogen-containing compound (Ntg), polyaromatic hydrocarbons (PAH), phenolic compounds (PhC), saturated hydrocarbons (SaH), unsaturated hydrocarbons (UnSaH), and unknown compounds (Unk).

represents > 60 % of TQPA in each chromatogram. The ratios in our O-horizon samples were 0.6 ± 0.1, 0.9 ± 0.3, and 1.1 ± 0.5 for unburned, moderate severity, and high severity wildfires, respectively. The corresponding ratios for the 0−5 cm mineral soil layer were 1.1 ± 0.3, 2.3 ± 0.6, 1.3 ± 0.5, and 5−15 cm depth were 1.3 ± 0.4, 2.0 ± 0.6, 2.1 ± 0.4. The ratios were consistently higher in burned soils, though were statistically insignificant due to the small sample size (n = 5) of this study. The ratio also increased with depth, which agrees with observations that PyC moves downward over time [7,41]. Additional field samples from different burning conditions are needed to verify the usefulness of this surrogate.

4. Conclusion

Soil C declined after the Hayman Fire and the changes in SOM quantity and chemical characteristics have persisted for 14 years. However, due to vegetation recovery, litter inputs and decomposition during that period, traditional PyC markers were no longer sensitive to post-fire changes in SOM composition. Some individual pyrolysates (i.e., benzene and *p*-vinylguaiacol) and chemical classes (i.e., ArH) had utility as wildfire indicators but provided little information about fire severity or SOM composition. We applied factor analysis to link the chemical properties of individual pyrolysates to better characterize the properties of fire-impacted SOM. Of the 113 pyrolysates recorded in our samples, those in the ArH and Ntg classes had strong positive F1 loadings, whereas those in the PhC and LgC classes had strong negative F1 loadings. We propose that a ratio of these classes (i.e., [ArH + Ntg] / [PhC + LgC]) can serve as an indicator of the long-term influence of wildfire severity on SOM composition of the proportion of PyC in post-fire SOM. The F1 and F2 loadings were well correlated with pyrolysate aromaticity and hydrophobicity. Our results show a potential increase in SOM aromaticity with increasing fire severity and depth in burned soils. This study illustrates that the long-term influence of wildfire on SOM can be tracked using Py-GC–MS chemical analysis coupled with a data management pipeline and statistical approach developed to characterize large numbers of chemical compounds. A potential next step would be to evaluate Py-GC–MS data from multiple fires to verify the changes in SOM character we report across fire severity gradients at the Hayman Fire.

Author statements

Dr. Huan Chen was the first author of the manuscript. He was in charge of the data analysis and manuscript preparation, including peak assignment on the mass spectrometry, statistical analysis on the collected data, as well as the layouts of figures and tables.

Dr. Charles Rhoades was the co-author of the manuscript. He was in charge on the field sampling design and sampling collection. He reviewed and assisted manuscript preparation. He was the principal investigator of the Joint Fire Science Project (14-1-06-11), which provided financial support of this study.

Dr. Alex Chow was the corresponding author of the manuscript. He proposed this pyrolysis study and coordinated the field and laboratory experiments (14-1-06-11). He prepared and reviewed the manuscript. He was also the co-principal investigator of the Joint Fire Science Project, which provided financial support of this study.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jaap.2020.104922.

References

[1] A.L. Westerling, H.G. Hidalgo, D.R. Cayan, T.W. Swetnam, Warming and earlier spring increase western US forest wildfire activity, Science 313 (5789) (2006) 940–943.
[2] T. Schoennagel, J.K. Balch, H. Brenkert-Smith, P.E. Dennison, B.J. Harvey, M. A. Krawchuk, N. Mietkiewicz, P. Morgan, M.A. Moritz, R. Rasker, M.G. Turner, C. Whitlock, Adapt to more wildfire in western North American forests as climate changes, Proc. Natl. Acad. Sci. U. S. A. 114 (18) (2017) 4582–4590.
[3] A. Lombao, A. Barreiro, T. Carballas, M.T. Fonturbel, A. Martin, J.A. Vega, C. Fernandez, M. Diaz-Ravina, Changes in soil properties after a wildfire in Fragas do Eume Natural Park (Galicia, NW Spain), Catena 135 (2015) 409–418.
[4] G. Certini, C. Nocentini, H. Knicker, P. Arfaioli, C. Rumpel, Wildfire effects on soil organic matter quantity and quality in two fire-prone Mediterranean pine forests, Geoderma 167-68 (2011) 148–155.
[5] M.I. Bird, J.G. Wynn, G. Saiz, C.M. Wurster, A. McBeath, The pyrogenic carbon cycle, Annu. Rev. Earth. Pl. Sc. 43 (2015) 273–298.
[6] C. Santin, S.H. Doerr, E.S. Kane, C.A. Masiello, M. Ohlson, J.M. de la Rosa, C. M. Preston, T. Dittmar, Towards a global assessment of pyrogenic carbon from vegetation fires, Global Change. Biol. 22 (1) (2016) 76–91.
[7] M. Velasco-Molina, A.E. Berns, F. Macias, H. Knicker, Biochemically altered charcoal residues as an important source of soil organic matter in subsoils of fire-affected subtropical regions, Geoderma 262 (2016) 62–70.
[8] C.P. Ward, R.L. Sleighter, P.G. Hatcher, R.M. Cory, Insights into the complete and partial photooxidation of black carbon in surface waters, Environ. Sci-Proc. Imp. 16 (4) (2014) 721–731.
[9] R.B. Abney, T.J. Kuhn, A. Chow, W. Hockaday, M.L. Fogel, A.A. Berhe, Pyrogenic carbon erosion after the Rim Fire, Yosemite National Park: the role of burn severity and slope, J. Geophys. Res-Biogeo. 124 (2) (2019) 432–449.
[10] T. Dittmar, C.E. de Rezende, M. Manecki, J. Niggemann, A.R.C. Ovalle, A. Stubbins, M.C. Bernardes, Continuous flux of dissolved black carbon from a vanished tropical forest biome, Nat. Geosci. 5 (9) (2012) 618–622.
[11] C. Santin, S.H. Doerr, C.M. Preston, G. Gonzalez-Rodriguez, Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle, Glob. Change Biol. Bioenergy 21 (4) (2015) 1621–1633.
[12] M.F. Cotrufo, C.M. Boot, S. Kampf, P.A. Nelson, D.J. Brogan, T. Covino, M. L. Haddix, L.H. MacDonald, S. Rathburn, S. Ryan-Bukett, S. Schmeer, E. Hall, Redistribution of pyrogenic carbon from hillslopes to stream corridors following a large montane wildfire, Global Biogeochem. Cy. 30 (9) (2016) 1348–1355.
[13] H. Knicker, F.J. Gonzalez-Vila, R. Gonzalez-Vazquez, Biodegradability of organic matter in fire-affected mineral soils of Southern Spain, Soil Biol. Biochem. 56 (2013) 31–39.
[14] J. Kaal, C. Rumpel, Can pyrolysis-GC/MS be used to estimate the degree of thermal alteration of black carbon? Org. Geochem. 40 (12) (2009) 1179–1187.
[15] J.A. Gonzalez-Perez, G. Almendros, J.M. De la Rosa, F.J. Gonzalez-Vila, Appraisal of polycyclic aromatic hydrocarbons (PAHs) in environmental matrices by analytical pyrolysis (Py-GC/MS), J. Anal. Appl. Pyrol. 109 (2014) 1–8.
[16] A.Z. Miller, J.M. De la Rosa, N.T. Jimenez-Morillo, M.F.C. Pereira, J.A. Gonzalez-Perez, H. Knicker, C. Saiz-Jimenez, Impact of wildfires on subsurface volcanic environments: new insights into speleothem chemistry, Sci. Total Environ. 698 (2020).
[17] Y. Huang, B.A. Stankiewicz, G. Eglinton, C.E. Snape, B. Evans, P.M. Latter, P. Ineson, Monitoring biomacromolecular degradation of *Calluna vulgaris* in a 23 year field experiment using solid state ^{13}C NMR and pyrolysis-GC/MS, Soil Biol. Biochem. 30 (12) (1998) 1517–1528.
[18] F.J. Gonzalez-Vila, P. Tinoco, G. Almendros, F. Martin, Pyrolysis-GC-MS analysis of the formation and degradation stages of charred residues from lignocellulosic biomass, J. Agric. Food. Chem. 49 (3) (2001) 1128–1131.
[19] J. Kaal, A.M. Cortizas, K.G.J. Nierop, Characterisation of aged charcoal using a coil probe pyrolysis-GC/MS method optimised for black carbon, J. Anal. Appl. Pyrol. 85 (1-2) (2009) 408–416.
[20] G. Almendros, P. Tinoco, J.M. De la Rosa, H. Knicker, J.A. Gonzalez-Perez, F. J. Gonzalez-Vila, Selective effects of forest fires on the structural domains of soil humic acids as shown by dipolar dephasing ^{13}C NMR and graphical-statistical analysis of pyrolysis compounds, J. Soil Sediment 18 (4) (2018) 1303–1313.
[21] E.C. Minor, M.M. Swenson, B.M. Mattson, A.R. Oyler, Structural characterization of dissolved organic matter: a review of current techniques for isolation and analysis, Environ. Sci-Proc. Imp. 16 (9) (2014) 2064–2079.
[22] A. Rivas-Ubach, Y.N. Liu, T.S. Bianchi, N. Tolic, C. Jansson, L. Pasa-Tolic, Moving beyond the van Krevelen diagram: a new stoichiometric approach for compound classification in organisms, Anal. Chem. 90 (10) (2018) 6152–6160.
[23] X.Q. Wu, L.Y. Wu, Y. Liu, P. Zhang, Q.H. Li, J.Z. Zhou, N.J. Hess, T.C. Hazen, W. L. Yang, R. Chakraborty, Microbial interactions with dissolved organic matter drive carbon dynamics and community succession, Front. Microbiol. 9 (2018).
[24] H. Chen, G.D. Blosser, H. Majidzadeh, X.J. Liu, W.H. Conner, A.T. Chow, Integration of an automated identification-quantification pipeline and statistical techniques for pyrolysis GC/MS tracking of the molecular fingerprints of natural organic matter, J. Anal. Appl. Pyrol. 134 (2018) 371–380.
[25] R.T. Graham, Hayman Fire Case Study, General Technical Report RMRS-GTR-114, USDA Forest Service, Rocky Mountain Research Station, Fort Collins, CO, US, 2003.
[26] S.L. Malone, P.J. Fornwalt, M.A. Battaglia, M.E. Chambers, J.M. Iniguez, C.H. Sieg, Mixed-severity fire fosters heterogeneous spatial patterns of conifer regeneration in a dry conifer forest, Forests 9 (1) (2018).
[27] C.C. Rhoades, K.A. Pelz, P.J. Fornwalt, B.H. Wolk, A.S. Cheng, Overlapping bark beetle outbreaks, salvage logging and wildfire restructure a lodgepole pine ecosystem, Forests 9 (3) (2018).
[28] A.T. Chow, K.P. Tsai, T.S. Fegel, D.N. Pierson, C.C. Rhoades, Lasting effects of wildfire on disinfection by-product formation in forest catchments, J. Environ. Qual. 48 (6) (2019) 1826–1834.
[29] R.T. Graham, Hayman Fire Case Study. Gen. Tech. Rep. RMRS-GTR-114, USDA Forest Service, Rocky Mountain Research Station, Ogden, UT, 2003, p. 396.
[30] B. Bryant, L.W. McGrew, R.A. Wobus, Geologic Map of the Denver 1 Degree by 2 Degrees Quadrangle, North-central Colorado, IMAP, 1981.
[31] J.E. Cipra, E.F. Kelly, L. Macdonald, J. Norman, Soil Properties, Erosion, and Implications for Rehabilitation and Aquatic Ecosystems, USDA, Forest Service, Rocky Mountain Research Station, 2003, pp. 204–219.
[32] J.E. Keeley, Fire intensity, fire severity and burn severity: a brief review and suggested usage, Int. J. Wildland Fire 18 (1) (2009) 116–126.
[33] A. Parsons, P.R. Robichaud, S.A. Lewis, C. Napper, J.T. Clark, Field Guide for Mapping Post-fire Soil Burn Severity, USDA, Forest Service, Rocky Mountain Research Station, 2010, p. 49.
[34] J.J. Wang, R.A. Dahlgren, A.T. Chow, Controlled burning of forest detritus altering spectroscopic characteristics and chlorine reactivity of dissolved organic matter: effects of temperature and oxygen availability, Environ. Sci. Technol. 49 (24) (2015) 14019–14027.
[35] J. Schellekens, T. Almeida-Santos, R.S. Macedo, P. Buurman, T.W. Kuyper, P. Vidal-Torrado, Molecular composition of several soil organic matter fractions from anthropogenic black soils (Terra Preta de Indio) in Amazonia - a pyrolysis-GC/MS study, Geoderma 288 (2017) 154–165.
[36] B.P. Koch, T. Dittmar, From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter, Rapid Commun. Mass Spectrom. 20 (5) (2006) 926–932.
[37] A. Nebbioso, A. Piccolo, Molecular characterization of dissolved organic matter (DOM): a critical review, Anal. Bioanal. Chem. 405 (1) (2013) 109–124.
[38] J.W.T. Blackburn, W. Kew, M.C. Graham, D. Uhrin, Laser desorption/Ionization coupled to FTICR mass spectrometry for studies of natural organic matter, Anal. Chem. 89 (8) (2017) 4382–4386.
[39] U.S. EPA, Estimation Programs Interface Suite™ for Microsoft® Windows, V 4.11, United States Environmental Protection Agency, Washington, DC, USA, 2015.
[40] J. Campo, K.G.J. Nierop, E. Cammeraat, V. Andreu, J.L. Rubio, Application of pyrolysis-gas chromatography/mass spectrometry to study changes in the organic matter of macro- and microaggregates of a Mediterranean soil upon heating, J. Chromatogr. A 1218 (30) (2011) 4817–4827.

[41] K. Nathe, D.F. Levia, M. Steffens, B. Michalzik, Solid-state ^{13}C NMR characterization of surface fire effects on the composition of organic matter in both soil and soil solution from a coniferous forest, Geoderma 305 (2017) 394–406.
[42] J.A. Gonzalez-Perez, F.J. Gonzalez-Vila, G. Almendros, H. Knicker, The effect of fire on soil organic matter - a review, Environ. Int. 30 (6) (2004) 855–870.
[43] J. Schellekens, P. Buurman, K. Kalbitz, A. van Zomeren, P. Vidal-Torrado, C. Cerli, R.N.J. Comans, Molecular features of humic acids and fulvic acids from contrasting environments, Environ. Sci. Technol. 51 (3) (2017) 1330–1339.
[44] S.R. Faria, J.M. De la Rosa, H. Knicker, J.A. Gonzalez-Perez, J.J. Keizer, Molecular characterization of wildfire impacts on organic matter in eroded sediments and topsoil in Mediterranean eucalypt stands, Catena 135 (2015) 29–37.
[45] J.M. De la Rosa, J.A. Gonzalez-Perez, R. Gonzalez-Vazquez, H. Knicker, E. Lopez-Capel, D.A.C. Manning, F.J. Gonzalez-Vila, Use of pyrolysis/GC-MS combined with thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest, Catena 74 (3) (2008) 296–303.
[46] C.C. Rhoades, A.T. Chow, T.P. Covino, T.S. Fegel, D.N. Pierson, A.E. Rhea, The legacy of a severe wildfire on stream nitrogen and carbon in headwater catchments, Ecosystems 22 (3) (2019) 643–657.
[47] J.M. Wang, X.Y. Zhang, Impacts of wildfires on interannual trends in land surface phenology: an investigation of the Hayman Fire, Environ. Res. Lett. 12 (5) (2017).
[48] M.A. Jimenez-Gonzalez, J.M. De la Rosa, N.T. Jimenez-Morillo, G. Almendros, J. A. Gonzalez-Perez, H. Knicker, Post-fire recovery of soil organic matter in a Cambisol from typical Mediterranean forest in Southwestern Spain, Sci. Total Environ. 572 (2016) 1414–1421.
[49] D.J. Wang, W. Zhang, X.Z. Hao, D.M. Zhou, Transport of biochar particles in saturated granular media: effects of pyrolysis temperature and particle size, Environ. Sci. Technol. 47 (2) (2013) 821–828.
[50] M. Lopez-Martin, F.J. Gonzalez-Vila, H. Knicker, Distribution of black carbon and black nitrogen in physical soil fractions from soils seven years after an intense forest fire and their role as C sink, Sci. Total Environ. 637 (2018) 1187–1196.
[51] F.N.D. Mukome, A.L.D. Kilcoyne, S.J. Parikh, Alteration of biochar carbon chemistry during soil incubations: SR-FTIR and NEXAFS investigation, Soil Sci. Soc. Am. J. 78 (5) (2014) 1632–1640.
[52] A. Hilscher, H. Knicker, Carbon and nitrogen degradation on molecular scale of grass-derived pyrogenic organic material during 28 months of incubation in soil, Soil Biol. Biochem. 43 (2) (2011) 261–270.
[53] H. Chen, A.T. Chow, X.W. Li, H.G. Ni, R.A. Dahlgren, H. Zeng, J.J. Wang, Wildfire burn intensity affects the quantity and speciation of polycyclic aromatic hydrocarbons in soils, ACS Earth Space Chem. 2 (12) (2018) 1262–1270.
[54] I. Campos, N. Abrantes, P. Pereira, A.C. Micaelo, C. Vale, J.J. Keizer, Forest fires as potential triggers for production and mobilization of polycyclic aromatic hydrocarbons to the terrestrial ecosystem, Land. Degrad. Dev. 30 (18) (2019) 2360–2370.
[55] H. Knicker, "Black nitrogen" - an important fraction in determining the recalcitrance of charcoal, Org. Geochem. 41 (9) (2010) 947–950.
[56] D. Torres-Rojas, R. Hestrin, D. Solomon, A.W. Gillespie, J.J. Dynes, T.Z. Regier, J. Lehmann, Nitrogen speciation and transformations in fire-derived organic matter, Geochim. Cosmochim. Acta 276 (2020) 170–185.