

Nitrogen Enrichment during Soil Organic Matter Burning and Molecular Evidence of Maillard Reactions

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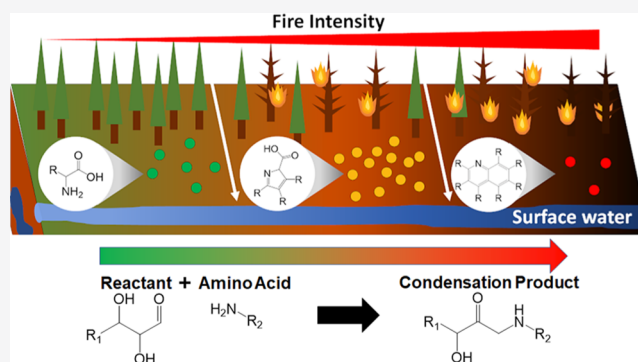
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ABSTRACT: Wildfires in forested watersheds dramatically alter stored and labile soil organic matter (SOM) pools and the export of dissolved organic matter (DOM). Ecosystem recovery after wildfires depends on soil microbial communities and revegetation and therefore is limited by the availability of nutrients, such as nitrogen-containing and labile, water-soluble compounds. However, SOM byproducts produced at different wildfire intensities are poorly understood, leading to difficulties in assessing wildfire severity and predicting ecosystem recovery. In this work, water-extractable organic matter (WEOM) from laboratory microcosms of soil burned at discrete temperatures was characterized by ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry to study the impacts of fire temperature on SOM and DOM composition. The molecular composition derived from different burn temperatures indicated that nitrogen-containing byproducts were enriched with heating and composed of a wide range of aromatic features and oxidation states. Mass difference-based analysis also suggested that products formed during heating could be modeled using transformations along the Maillard reaction pathway. The enrichment of N-containing SOM and DOM at different soil burning intensities has important implications for ecosystem recovery and downstream water quality.

KEYWORDS: nitrogen, FT-ICR MS, soil organic matter, pyrogenic organic matter



INTRODUCTION

The 2020 wildfire season was the worst wildfire season to date for many regions around the world, including the western United States, which burned approximately 10 million acres,^{1,2} and Australia, which was devastated with over 40 million acres burned.³ Wildfires are predicted to increase globally,^{4–7} threatening forested watersheds responsible for supplying drinking water^{8–10} to 180 million people in the western United States¹¹ and many more abroad.^{12–14} Alteration of the soil organic matter (SOM) present will adversely affect both water quality downstream and soil properties for years after the fire has subsided.^{9,15–20} Therefore, understanding how wildfires alter SOM composition following fires is of great interest.

The extent of thermal transformation and loss of SOM, known as burn severity, is commonly assessed by comparing bulk prefire SOM, vegetation, and soil properties to postfire features, including soil microbial communities.²¹ Importantly, recovery and revegetation depend on the presence of labile, water-soluble nutrients, such as nitrogen.²² Nitrogen is a limiting reactant for soil microbial productivity,²³ and soil carbon-to-nitrogen (C/N) ratios inversely correlate with SOM reactivity during microbial metabolism.^{24,25} Above 200 °C, wildfires can volatilize, transform, and mobilize organic

nitrogen,²⁶ which then leaches from the organic soil layer as water passes through the soil as dissolved organic nitrogen.^{27,28} Charred particulate and water-soluble organic matter will be transported downstream from fire-affected watersheds,²⁹ negatively impacting water quality and even producing toxic effects.³⁰ Furthermore, the increased formation of toxic nitrogen-containing disinfection byproducts (DBPs) has been observed during drinking water treatment downstream of burned areas.^{31–33} Therefore, the molecular composition of charred, water-soluble nitrogen species formed during wildfires is of great interest for the recovery of fire-affected watersheds and water quality studies.

Several reviews summarize the effects of fire intensity on SOM quantity and quality under both laboratory and field conditions, defining fire intensity as a “specific heating temperature over a fixed interval of time below the soil

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surface”.³⁴ In brief, heating between 200 and 250 °C results in the transformation of biomolecules with concurrent formation of aliphatic, alcohol, carbonyl, and aromatic functionalities, as reported by nuclear magnetic resonance (NMR) spectroscopy.^{35–39} Carbonization toward more graphitic structures has been observed around 300 °C, followed by the near total consumption of SOM and formation of a highly condensed aromatic material, often discussed as “dissolved black carbon” when referring to the water-soluble fraction.^{36,40,41} Recent models suggest that thermally altered SOM species contain considerable substitution of aromatic rings with nitrogen (including “dissolved black nitrogen”),⁴² oxygen, and sulfur species.⁴³

Targeted methods have also been applied to study specific constituents that comprise fire-affected SOM. Residues released by biomolecular components and known pyrolysis products of biomolecules, known as biomass burning markers,⁴⁴ have been previously studied using pyrolysis^{19,45–49} and derivatization^{50–52} prior to gas chromatography mass spectrometry, and using liquid chromatography–mass spectrometry.^{53,54} The precise identity of many charred residues remains elusive, including nitrogen-containing heterocyclic residues (e.g., pyridines, pyrazines, and pyrrole structures). These residues can resemble melanoidins^{42,55,56} which typically form through a cascade of reactions associated with the heating of polysaccharides and proteins, referred to as the Maillard reaction pathway.⁵⁷ Melanoidin and intermediate Maillard reaction products (MRPs) are frequently discussed as a pathway for both carbon and nitrogen sequestration following heating in soils^{36,58–61} and may therefore describe nutrient sources in postwildfire ecosystems.^{62,63} Direct measurement of this pathway has not yet been conducted in charred SOM and would require ultrahigh resolution to probe changes to individual residues associated with the transformation of SOM.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) routinely achieves the ultrahigh mass resolving power sufficient to separate and accurately assign elemental compositions to ionized components of highly complex mixtures.^{64–68} This includes SOM and dissolved organic matter (DOM),^{69–86} solid and water-soluble char residues,^{61,87–94} and petroleum,^{95–100} where the m/z differences can be as small as the mass of an electron.¹⁰¹ The characterization of both field-^{61,87} and laboratory^{87,89}-produced char have provided insight into molecular-level changes to different organic matter substrates induced by heating; however, limited information connects compositional changes in charring SOM to changes throughout progressive fire intensity gradients and the enhanced mobility of water-soluble organic nitrogen following a fire.

The soil samples selected for this study originate from Boulder County, CO, USA, to simulate SOM from forested watersheds, similar to those affected by the High Park fire in 2012 and Cameron Peak fire in 2020 (northern Colorado).¹⁰² While DOM does exhibit unique characteristics that can be used to distinguish different sources,⁸³ many of its features are remarkably consistent.¹⁰³ Dissolved pyrogenic organic matter also has common characteristics that can be observed at numerous sites and locations.^{40,88,104} Therefore, these samples were considered representative of soil from similar sites in the western United States and Canada, where forest fires and their effects on ecosystems and watersheds currently generate tremendous interest and concern. Organic carbon quantifica-

tion^{105,106} and solid-state ¹³C NMR¹⁰⁶ have been previously reported for these samples. Additionally, benzene polycarboxylic acids (BPCAs) and pyridinic analogues were identified by quadrupole time-of-flight mass spectrometry as biomass burning markers (>150 °C).¹⁰⁶ These findings only address a fraction of the molecules present during heating, suggesting that ultrahigh-resolution mass spectrometry is required to develop a more complete picture of the compositional changes that occur during heating.

Here, we present a compositional comparison of water-extractable, acidic SOM species produced at discrete temperatures (i.e., 150, 250, 350, and 450 °C) by negative ESI FT-ICR MS. This study focuses on nitrogen-containing residues due to their enrichment during the previous analysis¹⁰⁵ of the samples studied here and importance in ecosystem recovery following fires. We compare and catalog molecular transformations of nitrogen species in heated SOM at discrete temperatures by FT-ICR MS. Mass difference-based analysis is performed to identify potential reaction products formed during heating and suggest potential pathways in heated SOM as a function of temperature.

■ MATERIALS AND METHODS

Site Description and Sample Processing. Soil samples were collected from the south of the Gross Reservoir in Boulder County at 2222 m above the sea level during the summer of 2016 and correspond to site H samples in the reports of Thurman et al.¹⁰⁶ In brief, triplicate soil samples were collected within 10 m of each other in 1 m² transects with a shovel at a depth of 1–5 cm after visible litter and vegetation debris were removed. The surrounding overhead vegetation was composed of four main coniferous tree species varying in density: ponderosa pine (*Pinus ponderosa*), lodgepole pine (*Pinus contorta*), limber pine (*Pinus flexilis*), and Douglas fir (*Pseudotsuga menziesii*). Understory vegetation for the sampling area included a mix of grasses, forbs, and shrubs, largely dominated by cheatgrass (*Bromus* spp.) and Canada thistle (*Cirsium arvense*). Following sampling, the soils were distributed on metal trays 1 cm deep and oven-dried at 100 °C for 2 h to eliminate moisture and to suppress the survival of microbial communities present in the soil¹⁰⁷ that may compromise sample integrity during storage. The soil was passed through a 2 mm (no. 10) stainless-steel sieve to remove large rocks and through a 0.841 mm (no. 20) sieve to remove smaller plant matter before storage.

Simulated Laboratory Heating and Leachate Preparation. Soils were heated in an electric muffle furnace at the temperatures of 150, 250, 350, and 450 °C in 90 mL porcelain dish crucibles using a Lindberg/Blue Box Furnace model BF51442C with a Lindberg Furnace Power Supply Controller model 59344. To ensure uniformity in soil heating, each soil sample was separated into 10 g per crucible (approximately 0.5 cm high) and heated in batches of 10 crucibles for a total of 100 g of the soil sample at each temperature. Batches were held at each temperature under atmospheric conditions for 2 h, cooled to room temperature, and then stored in 40 mL amber glass vials at –5 °C until used. The furnaced samples were then leached for 24 h in deionized water at 5 g of soil per liter. The leachates were decanted and filtered using a 0.45 μm glass fiber syringe filter. A portion of the leachates were freeze-dried and used in organic carbon and nitrogen analysis on the solid soil and leachates and have been described elsewhere.¹⁰⁶ Section

S2 in the [Supporting Information](#) contains additional information on this method to simulate the effects of a wildfire.

The aqueous leachates were fractionated using hydrophobic and hydrophilic resins, as previously described.¹⁰⁶ In brief, aqueous leachates were fractionated into hydrophobic (XAD-8) and hydrophilic (XAD-4) fractions to facilitate better separation and identification of SOM features and their properties.^{27,64} Section S3 in the [Supporting Information](#) provides a full description of the fractionation procedure.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Resin extracts were resolubilized in methanol (HPLC grade, Sigma-Aldrich Chemical Co., St. Louis, MO) at 50 ppm carbon concentrations prior to analysis. Each sample solution was infused via a microelectrospray ionization (ESI) source operated in the negative mode.¹⁰⁸ DOM extracts were analyzed with a custom-built 9.4 T FT-ICR mass spectrometer and absorption mode mass spectra calibrated and assigned as previously described.^{109,110} Section S4 of the [Supporting Information](#) provides a full description of the FT-ICR MS operating conditions and data processing procedure. Formulas containing carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) were assigned using the experimentally measured masses and converted from the International Union of Pure and Applied Chemistry mass scale to the Kendrick mass scale¹¹¹ for the rapid identification of homologous series for each heteroatom class (i.e., KMD_{CH_2} for species differing only by degree of alkylation)¹¹² using PetroOrg software.^{64,113–115} Molecular formula assignments with an error >0.5 ppm were discarded, and only heteroatom ($\text{N}_x\text{O}_y\text{S}_z$) classes with a combined relative abundance of $\geq 0.15\%$ of the total were considered. Formulas were used to calculate ring-plus-double-bond (to carbon) equivalents ($\text{RDBE} = 1 + c - h/2 + n/2$),^{114,115} where c , h , n , o , and s refer to the stoichiometric carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively. Formulas were also used to calculate modified aromaticity indices (AI_{Mod}),^{116,117} which estimate the density of unsaturated carbon after assuming that a portion of the RDBE is not attributable to carbon-carbon bonds (e.g., carbonyl or carboxyl functional groups).

RESULTS AND DISCUSSION

Bulk Heating Effects on Organic Carbon and Nitrogen. The organic carbon and nitrogen content has been previously reported for these samples^{105,106} and will be used here to support compositional analysis by FT-ICR MS. [Table S1](#) shows the total organic carbon (TOC), total organic nitrogen (TON), water-extractable organic carbon (WEOC), and water-extractable organic nitrogen (WEON), and also inorganic nitrogen measurements ($\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, and $\text{NH}_4\text{-N}$). In brief, the TOC and TON decreased continuously from the control (46.303 ± 0.000 mg TOC/g soil, 2.179 ± 0.004 mg TON/g soil) to 450°C (1.435 ± 0.001 mg TOC/g soil, 0.315 ± 0.000 mg TON/g soil) with increased rates of removal at temperatures $>150^\circ\text{C}$. The WEOC and WEON changed from the control (0.485 ± 0.004 mg WEOC/g soil, 0.032 ± 0.004 mg WEON/g soil) during heating, reaching a maximum at 250°C (2.247 ± 0.036 mg WEOC/g soil, 0.211 ± 0.002 mg WEON/g soil) and minimum at 450°C (0.065 ± 0.002 mg WEOC/g soil, 0.008 ± 0.002 mg WEON/g soil). The difference in magnitude of the water-extractable fraction and total SOM content suggests that most of the SOM was

mineralized during heating and thus did not partition into water at any temperature.

[Table S2](#) shows the C/N ratios of the total (TOC/TON) and water-extractable (WEOC/WEON) fractions. Both decrease from the control (total: 21.24, water-extractable: 15.16) to 250°C (total: 14.77, water-extractable: 10.63) and further by 450°C (total: 4.56, water-extractable: 8.10). Nitrogen is enriched in both the solid and water-extractable fractions at temperatures $\geq 250^\circ\text{C}$. Additionally, the WEOC/WEON does not lower to the same extent as the TOC/TON at 350 and 450°C , which may indicate that a larger proportion of carbonaceous residues are mineralized directly from the solid phase, as opposed to undergoing a reaction that would increase water solubility.

Solid-State ^{13}C NMR Spectroscopy. Solid-state CP/MAS and DP/MAS ^{13}C NMR spectra of the hydrophobic acid (XAD-8) and hydrophilic acid (XAD-4) samples were described in detail previously.¹⁰⁶ The CP/MAS spectra are reproduced in [Figures S1 and S2](#) and the integrations in [Table S3](#). In brief, the spectrum of the hydrophobic acid sample at 150°C shows a relative increase in the proportion of the C-alkyl carbon peak ($0\text{--}60$ ppm) above the control. From 150 to 450°C , there are successive decreases in the C-alkyl carbon, O-alkyl carbon ($60\text{--}90$ ppm), aromatic/acetal carbon ($90\text{--}110$ ppm), and ketone/quinone carbon ($190\text{--}230$ ppm) peaks and a narrowing of the aromatic carbon ($110\text{--}190$ ppm) and carboxyl/amide ($160\text{--}190$ ppm) carbon peaks. Peptide amides are assumed to have been destroyed by 350°C . The residual aromatic carbon peaks at 131 ppm and carboxylic acid peaks at 172 ppm in the 350 and 450°C spectra are consistent with the benzene and pyridine carboxylic acids as previously reported¹⁰⁶ among other constituents. The spectra of the hydrophilic acid samples follow a similar pattern from control to 350°C , with the exception that the latter spectrum shows residual C-alkyl and O-alkyl carbon peaks at 30 and 65 ppm, respectively. Comparison of the control hydrophobic and hydrophilic acid spectra shows that water-extractable soil carbohydrates preferentially isolate on the XAD-4 resin, indicated by the carbohydrate peaks at 72 and 102 ppm in the hydrophilic acid spectrum. These peaks are significantly reduced in the hydrophilic acid spectra from the 250 and 350°C samples, confirming destruction of the carbohydrate material in the soil at these temperatures.

The quantities of hydrophobic and hydrophilic acid samples isolated ($\sim 10\text{--}90$ mg) were insufficient for the analysis of naturally abundant nitrogen by solid-state ^{15}N CP/MAS NMR, within reasonable spectrometer accumulation times. However, losses or transformation of nitrogen functionalities with temperature can be inferred from the ^{13}C NMR spectra and are listed in [Table S4](#). The forms of nitrogen in SOM, not impacted by fire or heat, may include amines (terminal amino groups of amino acids, amino sugars, primary amines of purine and pyrimidine bases, and primary and secondary amino-quinones), peptides, N-acetylated sugars, the imide and lactam nitrogens of nucleotide bases, and heterocyclic nitrogens such as pyrrole, indole, and imidazole. Carbons alpha to the amine group of amino acids in peptides have ^{13}C chemical shifts in the range from 40 to 65 ppm, while ring carbons bonded to the amine group in amino sugars have chemical shifts in the approximate range from 50 to 60 ppm. These are in the range of sp^3 -hybridized carbons that decrease in the ^{13}C NMR spectra of the hydrophobic acid (XAD-8) fractions from 150 to 250°C and have disappeared from 350 to 450°C ([Figures S1](#)

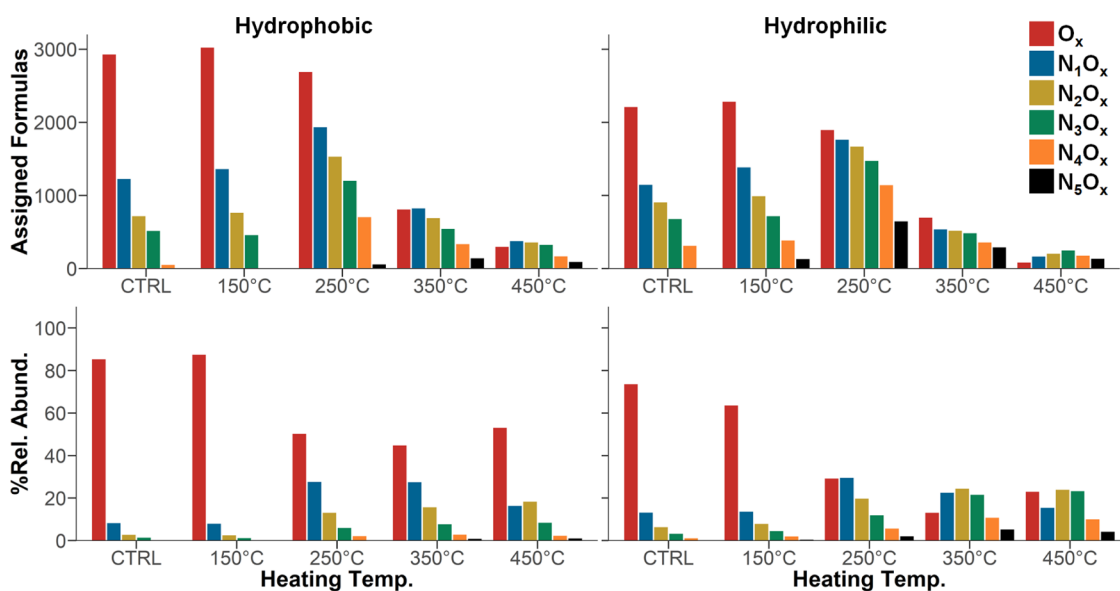


Figure 1. Number of assigned molecular formulas (top) and percent relative abundance (bottom) of the CHO and CHNO heteroatom classes at each temperature measured by the 9.4 T FT-ICR MS using negative ESI. CHNO classes are distinguished by the nitrogen content ($N_{1-5}O_x$).

CHNO Assignments

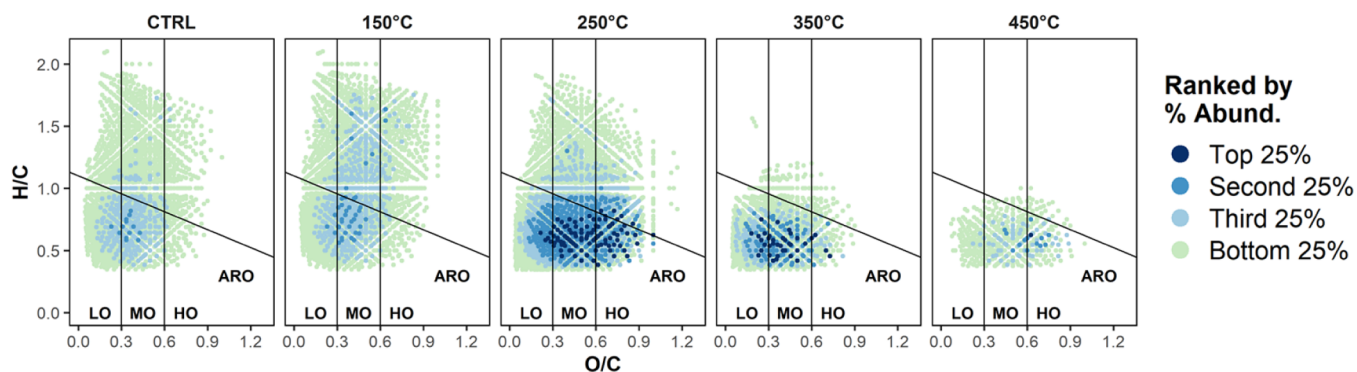


Figure 2. Abundance-weighted VK plots of the N_xO_x species derived from negative-ion ESI FT-ICR MS spectra for the unburnt control (CTRL) and heated soil leachates isolated on the hydrophilic resin. Lines were added to each plot to indicate regions where aromatic features predominate ($AI_{Mod} \geq 0.5$, indicated by the ARO line), and relative oxygen density: “LO” = low oxygen density, $O/C \leq 0.3$; “MO” = mid-oxygen density, $0.3 < O/C \leq 0.6$; “HO” = high oxygen density, $O/C > 0.6$. The plotted formulas were grouped using their abundances, where the “top 25%” (dark-blue points) are 25% of the sample’s cumulative abundance comprising the most abundant formulas, the “second 25%” are the next 25% comprising the next most abundant formulas, and so on.

and S2). Therefore, removal or transformation of amino acid, peptide, and amino sugar structures in the soil to leachable aromatic nitrogen compounds or volatile degradation products, including nitrogen gases, is a reasonable inference from these ^{13}C NMR spectra. Nitrogen-containing functionalities encompassed within the 100–190 ppm chemical shift region of the residual peaks between the 350 and 450 °C spectra would be limited to nonpeptide amide and aromatic heterocyclic structures. Of the water-extractable organic matter (WEOM) that sorbs to the XAD-4 resin, the ^{13}C NMR spectra also indicate a decrease, but not total destruction, of amino acid, peptide, and amino sugar structures from 150 to 350 °C (Figure S2).

WEOM: Proliferation of Nitrogen-Containing Heteroatom Classes. Broadband negative ion ESI FT-ICR mass spectra for hydrophobic and hydrophilic fractions as a function of temperature are shown in Figures S3 and S4, respectively. All samples spanned a similar molecular weight range between

m/z 150–600 with an achieved resolving power $>1,500,000$ at m/z 400. Figure 1 shows the number of assigned formula and percent relative abundance of the CHO (O_x) and CHNO heteroatom classes separated by the nitrogen content ($N_{1-5}O_x$). Counts for each class can be found in Table S5, alongside the abundance-weighted average C/N ratios and m/z , discussed below. The CHO and CHNO assigned molecular formulae from the control (hydrophilic: 5518 and hydrophobic: 5846) increased slightly at 150 °C (hydrophilic: 6149 and hydrophobic: 5960) and the most at 250 °C (hydrophilic: 8770 and hydrophobic: 8554). Assignments decreased at 350 °C (hydrophilic: 2948 and hydrophobic: 3584) and reached a minimum at 450 °C (hydrophilic: 1035, hydrophobic: 1734).

Importantly, only the CHNO assignments contributed to the increased formulae at 250 °C and remained the largest class, containing over 70% of the formulae assigned at intensities ≥ 250 °C in both fractions (Figure 1, top). The percent relative abundance of the heteroatom classes followed



Figure 3. Percent relative abundance of CHNO classes in the unburnt (CTRL) and heated (150–450 °C) hydrophilic samples separated by the nitrogen and oxygen ($N_{1-4}O_{2-15}$) content. The $N_{5}O_{2-15}$ and assignments from the hydrophobic fraction can be found in Figures S8 and S9, respectively.

a similar trend: class abundances changed slightly below 250 °C, after which the CHNO classes in the hydrophilic fraction increased to ~75% and the hydrophobic fraction up to ~50% of the total abundance at temperatures ≥ 250 °C (Figure 1, bottom). Of the CHNO assignments, the $N_{2-5}O_x$ classes appeared to increase the most in assignments at 250 °C. At higher temperatures, the $N_{2-5}O_x$ assignments generally decreased less than the N_1O_x assignments. The increase in relative abundances for $N_{2-5}O_x$ is also reflected by the average weighted C/N ratio (Table S5) that decreased from 250 to 450 °C (hydrophilic: 9.61 to 5.46 and hydrophobic: 12.31 to 8.03).

Despite a similar trend between fractions of increased CHNO assignments and abundance above 150 °C, in the hydrophobic fraction, the CHO class retained ~50% of the relative abundance at 350 and 450 °C but was composed of fewer, highly abundant peaks. These assignments included BPCAs that were previously measured in these samples from 250 to 450 °C and were found to be concentrated in the hydrophobic fraction.¹⁰⁶ Other CHO assignments that are only abundant in the hydrophobic fraction at 350 and 450 °C also appeared to be related by carboxylic acid groups, some matching formulas tentatively identified by Ferrer et al.¹¹⁸ Pyridinic analogues to BPCAs were also tentatively identified at low concentration in the hydrophilic fraction only¹⁰⁶ but only corresponded to two assignments in the current study. Interestingly, numerous other CHNO assignments were assigned at higher abundance throughout the temperature gradient in the hydrophilic fraction and to a lesser extent in the hydrophobic fraction. These are explored below.

Speciation of the Water-Extractable Nitrogen-Containing Residues. The hydrophilic fraction was the focus throughout the rest of this study based on the increase in WEON and corresponding increase in CHNO formula assignments that appeared better isolated in the hydrophilic fraction. While generally similar, differences will be noted for

the hydrophobic fraction and analogous figures can be found in the Supporting Information.

Figure 2 displays the van Krevelen (VK) plots of the CHNO assignments, which can be used to infer changes to saturation and oxygen content throughout the temperature gradient in the hydrophilic fraction (Figure S5 for the hydrophobic fraction). Unique and common assignments between fractions are illustrated in Figure S6. In the control (CTRL), the CHNO assignments before heating (bottom, third, and second 25% bins) displayed coverage over a large range of H/C (~0.4 to 2.0) and O/C (~0.1 to 1.0) values, typical of a heterogeneous WEOM mixture.^{27,77,119,120} At 150 °C, peaks encompass similar regions to the CTRL and also include additional assignments at H/C > 1, above the ARO line. These midsaturated and aliphatic CHNO species at 150 °C may result from the release of plant, root, and microbial residues that can occur at this temperature.^{17,121} At 250 °C, CHNO assignments in the aromatic plot region (below the ARO line) increased in abundance and midsaturated and aliphatic features decreased.

The enriched aromatic regions were more pronounced at 350 and 450 °C, with high abundance peaks encompassing a narrower range and fewer assignments. The changes in saturation are also reflected by the RDBE, which is visualized in Figure S7 by the nitrogen content ($N_{1-5}O_x$). While the hydrophilic and hydrophobic fractions were generally similar, high RDBE peaks (relative to the control) at 350 and 450 °C were only attributed to $N_{2-5}O_x$ formulas in the hydrophilic fraction. The nitrogen dense assignments exhibited increased abundance and aromaticity during heating, which is in good agreement with the ¹³C NMR.

The most abundant O/C regions also appeared to shift during heating. At 250 °C, aromatic plot regions were enriched across all O/C but enriched most in mid- and high-oxygen aromatic plot regions. The most abundant aromatic plot region shifted at 350 °C to lower O/C, encompassing the low- and mid-oxygen density regions. Finally, at 450 °C, abundant peaks

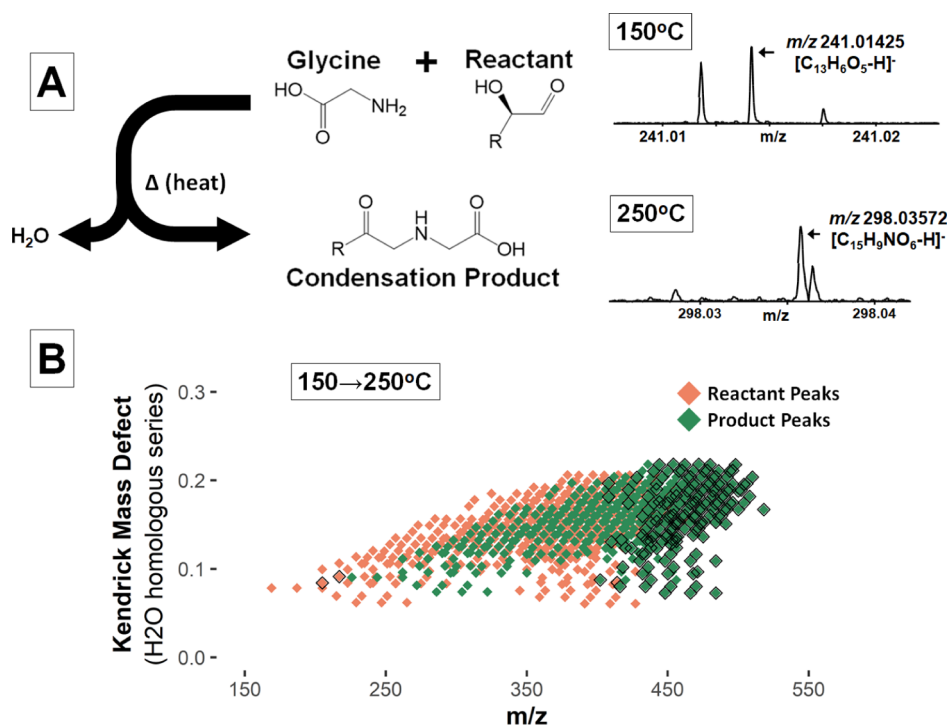


Figure 4. Scheme and visualization of the Maillard reactant–product pairs that were identified throughout the temperature transitions that correspond with a Gly condensation. (A) Simplified scheme of a glycine condensation reaction using a generic reactant and product, where the exact mass difference is 57.02146 Da. Single peaks are shown and labeled that match a Gly condensation mass difference across the 150 → 250 °C transition and are present in a $\text{KMD}_{\text{H}_2\text{O}}$ series of ≥ 3 peaks and (B) plot of the $\text{KMD}_{\text{H}_2\text{O}}$ series matching the Gly condensation in the 150–250 °C transition. Data was truncated for ease of visualization. Reactants (orange) and products (green) were outlined if they were unique to 150 or 250 °C, respectively.

were in high-oxygen density regions and in mid-oxygen regions to a lesser extent, although fewer peaks were present to indicate a trend.

To explore the shift in oxygen content further, Figure 3 displays the percent relative abundance of the CHNO classes separated by nitrogen and oxygen ($\text{N}_{1-4}\text{O}_{2-15}$) (hydrophilic $\text{N}_5\text{O}_{2-15}$ and hydrophobic fraction in Figures S8 and S9, respectively). Features were similar between the control and 150 °C sample, where nitrogen classes were centered around $\text{N}_{1-4}\text{O}_{5-6}$ or were too low in abundance to detect (i.e., N_5O_x). At 250 °C, the N heteroatom classes increased both in abundance and oxygen number, and several new CHNO classes ($\text{N}_1\text{O}_{13-15}$, $\text{N}_{2-4}\text{O}_{11-14}$, and $\text{N}_5\text{O}_{3-10}$) were assigned. This could indicate multiple oxidation reactions by N- and O-containing species or condensation reactions among SOM species.

At 350 °C, the abundances of $\text{N}_x\text{O}_{10-15}$ species decreased greatly or disappeared entirely, and the oxygen numbers of the most abundant N heteroatom classes decreased, now centering around N_1O_{4-5} and N_{2-5}O_4 . The abundance-weighted average m/z and C/N of the detected peaks also changed more between 250 and 350 °C than at any other temperature transition, decreasing from 315.15 to 266.11 m/z and 9.61 to 7.01 C/N (Table S5). This could indicate the loss of O-containing species through dehydration, decarboxylation, or other fragmentation reactions. At 450 °C, the most abundant heteroatom classes rose in oxygen number from 350 °C; however, each of the class distributions became less uniform. Specific classes appeared enriched at 450 °C (e.g., N_2O_6 and N_2O_8), potentially corresponding to specific char products.

While the most abundant N_xO_x class at each temperature differed depending on the amount of nitrogen assigned, the increase and decrease in the oxygen content between 150 and 350 °C appeared to occur consistently across every nitrogen class. The trend observed here might suggest the presence of distinct transformations and features in each of the classes, dependent on temperature. In such complex samples, it is difficult to discern whether nitrogen-containing species are persistent once formed, formed continuously as new by-products through heating, or a combination of both. Similarly, it is difficult to determine if decreasing or disappearing peaks are attributable to new or enriched peaks upon heating or mineralization. Nevertheless, formation mechanisms that contribute to the observable nitrogen enrichment can be studied if known transformations throughout the temperature gradient can be modeled.

Modeling Maillard Reaction Processes. The Maillard reaction involves the condensation of reducing sugars with amino acids, followed by many more reactions, and is well known in the context of cooking and preparing food.⁵⁷ In fact, many Maillard reaction intermediates and fragments, referred to here as Maillard Reaction Products (MRPs), have been well described and characterized in food chemistry using simple systems.^{122–125} Hemmler et al.¹²⁶ studied MRPs by heating equimolar mixtures of ribose and glycine at 100 °C for up to 10 h. They reported several findings consistent with the behavior of WEOM in this study, including the enrichment of aromatic nitrogen and increased N_2O_x assignments following heating longer than 4 h and the presence of several reaction pathways that dominated the MRPs within 6 h. These factors

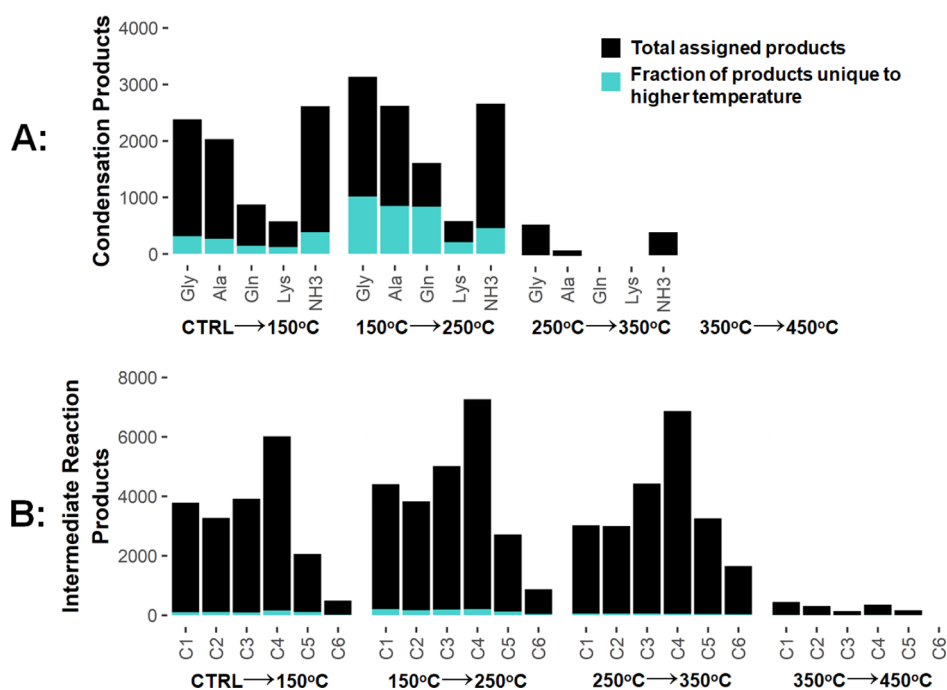


Figure 5. Number of product assignment matching reactions with predicted mass differences along the Maillard reaction pathway at each temperature transition from the hydrophilic sample fractions. Blue bars within each plot indicate the number of products that were newly assigned at the higher temperature only. (A) Counts for product peaks matching amino acid condensations or ammonia additions. (B) Intermediate reaction products were separated by the carbon number (C#) of the fragment lost, ranging from C1 (e.g., formic acid) to C6 (e.g., glucosone). For a complete list of all the amino acid condensation and C# fragment compositions, see Table S6.

motivated the exploration of Maillard reaction pathways in the current study.

Potential MRPs were identified using a mass difference-based analysis that is depicted in Figure 4. Mass differences were computed between peaks based on known Maillard reactions, where potential Maillard “precursor” and “product” peaks were identified going from lower to higher temperatures, respectively, when they differed by the expected mass difference, using the theoretical masses of the assigned formulas (Table S6). For instance, a peak at 150 °C needed to differ from a peak at 250 °C by the exact mass of the reaction of interest to be considered a potential MRP. In a complex biogeochemical mixture such as SOM, it is possible that some of the expected mass differences will occur by chance or due to the presence of common structures in SOM molecules. For this reason, the best evidence of potential MRPs comes from (i) product peaks that were not detected at the lower temperature or (ii) product peaks that were present at both temperatures but whose abundances increased relative to the corresponding precursor peaks at the higher temperature.

The temperature transitions studied here were CTRL → 150 °C, 150 → 250 °C, 250 → 350 °C, and 350 → 450 °C. The reactions modeled included amino acid condensations, where glycine (Gly), alanine (Ala), glutamine (Gln), and lysine (Lys) were chosen based on their presence in soil¹²⁷ and the contributions of peptidoglycan and other microbial biomass to SOM.^{128–131} Hemmler et al.¹²⁶ reported that the initial condensation reaction was followed by an extended series of dehydration reactions, leading to MRPs with greater degrees of unsaturation and aromaticity, so tentative MRPs were only considered when they occurred in “dehydration series” associated with successive water losses ($n \geq 3$). These were

identified in these samples using a modified Kendrick mass defect analysis (KMD_{H_2O}) based on the accurate mass of water (IUPAC mass $\times 18/18.01057$)^{123,126,132} and can be visualized in Figure S10, which plots a subset of dehydration series for N_3O_x assignments.

Ammonia (NH_3) addition was studied as an alternative pathway for nitrogen enrichment because ammonia was retained here (Table S1) and is retained in soil after fires,^{133,134} and fire-derived organic matter has been reported to retain ammonia through covalent bond formation.¹³³ Peaks were also examined for the loss of byproducts specific to the Maillard reaction pathway (Table S6), which are referred to here as intermediate reaction products. The intermediate reaction products are identified by the size of the carbon fragment (C#) lost, ranging from C1 (e.g., formic acid) to C6 (e.g., glucosone).^{123,126,135} These C# include carbonyl-containing species (e.g., α -hydroketones and α -hydroxyaldehydes) that can react further to form heterocyclic nitrogen.¹³⁵ The reactions studied here were not intended to include every possible reaction but to investigate whether some of the changes in WEOM composition during soil burning could be modeled with time-resolved Maillard reactions previously observed in simpler systems.

Molecular Evidence of Maillard Reactions and Ammonia Additions. Figure 4 displays the product counts for each of the potential condensation and intermediate reaction pairs. Condensation products and ammonia additions were observed in the CTRL → 150 °C (8473 total), 150 → 250 °C (10 595 total), and 250 → 350 °C (3363 total) temperature transitions (Figure 4A). Intermediate reaction products were also found at each of the transitions and were also highest in the 150 → 250 °C transition (24 081 total) (Figure 5B). The hydrophobic fraction exhibited similar trends

but at lower counts and can be seen in Figure S11. It is worth noting that in the hydrophilic fraction, the average m/z of the assigned formulae increased the most at 250 °C and decreased the most at 350 °C (Table S5).

The condensation and ammonia addition reaction pairs shared some of the same product peaks and are shown numerically in Venn diagrams in Figure S12. This is most prominently observed in the 150 → 250 °C transition with the Gly and Ala condensation reactions that shared 2065 of their total product peaks (Gly: 3132 and Ala: 2619) with each other and ammonia addition pairs. This could indicate that different reactions create product peaks with identical elemental compositions, which is certainly possible in such a complex mixture, but it also highlights the difficulty of evidencing specific reactions in a complex mixture. Importantly, the condensation product peaks also included assignments that were unique to the higher temperature and to only one modeled reaction (Figures 5 and S11). These product peaks present the clearest evidence of specific Maillard reactions in the burned soil systems. They are not dispositive, but they are numerous and consistent with previous observations from much simpler systems.¹²⁶ These findings are also supported when considering the loss of carbohydrate signatures by 350 °C in the ¹³C NMR that coincided with the decrease in assigned MRPs. Similarly, the evidence of unique ammonia additions is not dispositive, but they are numerous and their occurrence is consistent with previous reports.¹³³

In comparison, many of the intermediate reaction products were common to at least one of the other C# reaction pairs or peaks assigned at lower temperatures and are shown numerically in Venn diagrams in Figure S12. It seems likely that the high relatedness between the intermediate reaction products and assignments at lower temperatures is due to SOM complexity and the multitude of pathways occurring to individual compounds during heating. Studies^{126,136} have reported an exponential increase in MRPs when nitrogen was present during the heating of simple systems, so it seems reasonable that numerous transformations can occur for a single residue. Still, the presence of intermediate reaction products from 250 → 350 °C and the absence of condensation products does correspond to the decreased N_xO_{10-15} and increased N_xO_{3-6} class abundances and lower average m/z .

The presence of shared and uniquely assigned product peaks suggests that products appear to be forming as a function of specific amino acid reactions and also inorganic nitrogen additions. It should be noted that in a study measuring ribose-amino acid products formed during heating at 100 °C, Hemmler et al.¹³⁶ indicated that reactions with Lys produced the most products and had the highest reactivity, and Gly had the lowest, up to N_4O_x . In our study, the order was Gly (3132) > Ala (2619) > Gln (1606) > Lys (580). The discrepancy might originate from differences in source materials and the higher temperatures used, or it might result from confounding mass differences in such a complex material. Ammonia appeared to contribute to the products through inorganic nitrogen addition, but other pathways such as nitration may also be valid for inorganic nitrogen enrichment of WEOM. Finally, reactions between the MRPs formed may contribute to the relative increase of $N_{3-5}O_x$ classes in SOM at above 250 °C, but the investigation of these reactions or persistent products would require a more precise understanding of the specific MRPs formed during heating.

Environmental Implications. While the experimental design of this study was a proxy for soil heating in the field, the temperatures used here are reflective of temperatures in the organic soil horizon in mineral soils during wildfires. Low-severity heating (e.g., fast-moving, prescribed fires) can produce temperatures as low as 50 °C at 5 cm depths, and high-severity heating (e.g., slow-moving, smoldering fires) can reach temperatures of >250 °C at up to 10 cm depths with potential to last from minutes to several days.²⁶ Patterns in the molecular formulae identified here were not observed up to 450 °C, which corresponds to the near total consumption of SOM and WEOM at 450 °C in this study and elsewhere.^{26,38} Most residues were removed completely when heating to this temperature; therefore, residues from 150 to 350 °C will predominate when studying fire-affected field sites, despite the heterogeneity in wildfire intensities. This implies that SOM at specific soil depths within this temperature range will be responsible for what is being leached from soils.

The apparent solubility of the charred organic matter is somewhat contrary to the formation of hydrophobic features¹⁰⁴ and has numerous implications for postfire watershed and water quality conditions. The mobility of these residues not only removes an organic carbon and nitrogen source at the site of the burn, but the absence of plants and plant nutrient uptake following fires will increase the subsurface transport of the WEOM.¹³⁷ This removal is associated with an initial pulse of nutrients during the fire and long-term leaching that will influence stream biota metabolism^{138,139} and could correspond to the changes in the microbial community structure observed following fires with implications regarding C storage in fire-affected ecosystems.¹⁴⁰ Interestingly, the enriched aromatic CHNO observed here is not considered a reactive precursor for DBP formation during water treatment.¹⁴¹⁻¹⁴³ It is possible that the CHNO fractions containing alkylated amine precursors are not well represented in the samples studied here as the ionization mode used for mass spectrometry was not amenable to basic nitrogen moieties;^{144,145} however, these groups are often transformed during even moderate heating.¹⁴⁶

This study employed a laboratory-based heating method to exert the most control over the experimental conditions. The general trend in aromaticity was consistent with other laboratory-⁸⁷ and field-based^{61,88} SOM chars analyzed by FT-ICR MS. The enriched nitrogen observed here is also common to chars with proteinaceous biomass, such as grasses.^{42,89,93,147} While the results of this study focus on a laboratory-simulated microcosm that represents transformations that occur with heating in the field, the observed changes in aromaticity, changes in nitrogen density relative to the oxygen content, and mass-difference analysis provide evidence for SOM-specific transformations such as Maillard reactions that have been reported in simpler systems. The occurrence of MRPs here is not the definitive evidence of Maillard reactions due to the qualitative analysis by FT-ICR MS but does support the existence of Maillard reactions when considering the existing knowledge of Maillard reactions,^{36,60,126,136} the well-known presence of amino acid and carbohydrate functionalities in SOM,¹²⁷⁻¹³¹ and the observed enrichment of N-containing compounds in SOM during heating here and elsewhere.^{42,55,58,59}

Without knowledge of the precise precursors present in the SOM, a comprehensive understanding of how the Maillard reaction applies to transformations in heated SOM remains

uncertain. However, the evidence presented here suggests that the Maillard reaction pathway can in part describe transformations in heated SOM. Interestingly, the potential MRPs and their reactions appeared to be specific to heat intensity, such that the trends and unique peaks might contribute new N-containing biomass burning markers specific to fire intensity. The introduction of known precursor materials, such as specific amino acids, to SOM during controlled heating could more clearly identify product residues that are associated with Maillard reaction pathways.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c06745>.

Measured quantities of carbon and nitrogen; ^{13}C NMR, FT-ICR MS spectra, and analogous figures of the hydrophobic fraction presented here; explanation for the use of muffle furnaces for the soil heating experiments; description of the resin-based fractionation; and description of the FT-ICR MS settings and protocol (PDF)

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Notes

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