

PROCEEDINGS OF THE TWENTY-EIGHTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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Students: KAITLYN SUAREZ, Union College, WILLIAM GRIMM, Carleton College, RANIER LEMPERT, Amherst College, ELAINE YOUNG, Ohio Wesleyan University, FRANK MOLINEK, Carleton College, EILEEN ALEJOS, Union College

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Students: BRIANNA BERG, University of Montana, AMAR MUKUNDA, Amherst College, REBECCA BLAND, Mt. Holyoke College, JACOB HUGHES, Western Kentucky University, LUIS RODRIGUEZ, Universidad de Puerto Rico-Mayaguez, MARIAH ARMENTA, University of Arizona, CLEMENTINE HAMELIN, Smith College

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ANTARCTIC PLIOCENE AND LOWER PLEISTOCENE (GELASIAN) PALEOCLIMATE RECONSTRUCTED FROM OCEAN DRILLING PROGRAM WEDDELL SEA CORES:

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Students: LYDIA LOOPESKO, Whitman College, ANNE FULTON, Pomona College, THOMAS BARTLETT, Colgate University

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FIRE AND CATASTROPHIC FLOODING, FOURMILE CATCHMENT, FRONT RANGE, COLORADO:

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Short Contributions— Fire and Catastrophic Flooding, CO Project

FIRE AND CATASTROPHIC FLOODING, FOURMILE CATCHMENT, FRONT RANGE, COLORADO:

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WILLIAM. B. OUMET, University of Connecticut
WILLIAM KASTE, The College of William and Mary

INVESTIGATING THE USE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AS PROXIES FOR HOLOCENE FOREST FIRES ON THE COLORADO FRONT RANGE

GREGORY HARRIS, University of Connecticut
Research Advisors: Michael Hren, University of Connecticut, Will Ouimet, University of Connecticut

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WILL WICHERSKI, Williams College Department of Geosciences
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INVESTIGATING THE USE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AS PROXIES FOR HOLOCENE FOREST FIRES ON THE COLORADO FRONT RANGE

GREGORY HARRIS, University of Connecticut

Research Advisors: Michael Hren; Will Ouimet

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds composed of carbon and hydrogen atoms fused into two or more aromatic ring structures (Kim et al., 2011). PAHs are ubiquitous in the environment, and are generated mainly as byproducts of the incomplete combustion of hydrocarbon material. The high temperatures associated with combustion cause organic materials to break down into extremely reactive free radicals, which are converted into more chemically stable PAHs (Hwang et al., 2003). PAHs are characterized by the number of rings which correlate to burn temperature (Kim et al., 2011). Light molecular weight (LMW) PAHs consist of fewer than four rings and are typically formed by lower intensity combustion; high molecular weight (HMW) compounds of four or more rings are formed by greater temperatures (Kim et al., 2011). Sources for environmental PAHs are primarily petrolytic, derived from anthropogenic combustion of fossil fuel materials (Foan et al., 2013). Natural, pyrolytic events, namely forest fires and volcanic eruptions, also release PAHs, but these sources constitute a lower average percentage of those found in the environment (Foan et al., 2013). Furthermore, a recent study by Vergnoux et al. (2011) demonstrated that specific patterns of PAH compounds are indicative of human or natural origins.

Once released into the atmosphere, PAHs are transported and dispersed as aerosols, capable of both proximal and distal deposition (Kim et al., 2011, Choi et al., 2007, Ding et al., 2007, Su et al., 2006). Deposition pathways occur directly through wet and dry scavenging, as well as indirectly through fluvial transportation of PAHs attached to particles in the

suspended load or in runoff (Mai et al., 2003). Due to their hydrophobic nature, PAHs mainly exist adsorbed to clays and organic materials in the soil matrix, and concentrations are largely functions of fire intensity and location relative to the source, frequency of emission, climatic conditions following deposition-wind erosion, rain frequency- and mobilization of the critical zone (Vergnoux et al., 2011). PAHs are highly resistant to biodegradation and photooxidation, and thus have the potential to persist in the soil (Kim et al., 2011).

The goal of this research was to study the influence of forest fire events on the concentrations of PAHs in burned and unburned soils, and evaluate the viability of these compounds as proxies for reconstructing forest fire occurrences along the Colorado Front Range and within the Boulder Creek Critical Zone Observatory (BcCZO). The semi-arid climate of this region has led to many forest fires throughout the Holocene. This study includes analysis of soil and sediment samples within the BcCZO from Gordon Gulch, Betasso Gulch, and Fourmile Canyon, which in 2010 experienced an intense, 16.5 km² forest fire on moderate to steep slopes (Fig 1), as well as severe flooding in 2013.

MATERIALS AND METHODS

Sites and Field Sampling Methods

Soils and colluvial deposits were sampled at several sites of recent or historic Holocene forest fire events in Fourmile Canyon. Soil samples from hillslopes affected by the 2010 forest fires were collected utilizing a variation of the method described in

Vergnoux et al. 2010; three layers- the surface litter, 0-5 cm from surface, and 5-10 cm- were sampled at three soil pits along a 10 meter transect perpendicular to downslope with consistent aspect and ecology. The intention of this method was to assess whether translocation of PAHs occurs and/or causes a concentration variation with depth from the surface. High resolution topographic data (LiDAR) and a map of fire-intensity were used to select transects with varying burn intensity (moderate, severe, etc.). The second sample from the 2010 Fourmile fire (WO-F-1 series) was collected by Will Ouimet and Keck students in 2012. The sample location lay within the burned area, and was covered with a tarp soon after the fire to prevent erosion, vegetation growth and addition/loss by wind and preserve ash for sampling at a later time. Four soil layers were collected- at 1 cm, 5 cm, 10 cm, and 20 cm intervals- to similarly account for analysis of concentration variation with depth.

Samples related to historic forest fires were collected at various outcrops within the BcCZO. Flooding along Fourmile Creek in September 2013 exposed outcrops of layered stratigraphy containing distinct

dark, organic-rich layers interlayed with colluvium or flood deposits. The connection of these outcrops to forest fires was based on the presence of charcoal and ash fragments within the dark layers. Based on the properties of PAHs, it was assumed that the dark, organic lenses corresponded to the fire events and would have the highest PAH concentrations. Therefore, samples were collected in three layers corresponding to the darker lenses at each outcrop: each lens, the layer directly below it, and the layer between that lens and the one above it. The first series of samples was collected from a colluvial toe slope deposit downstream from homeowner Robert Beebee's house (CO-BB). Another series was collected at Wood Mine (CO-WM) from a colluvial outcrop which interfingered with fluvial deposits at depth. At both CO-BB and CO-WM, dark layers near the top of the outcrop contained coal and were presumed to be associated with area's railroad and mining history (and hence younger than 1870 AD). Samples at depth from CO-BB and CO-WM did not contain coal, and ^{14}C ages for 3 layers at each site presented by fellow Keck student Maneh Kotikan confirm them as Holocene in age (500 – 3200 yrs BP).

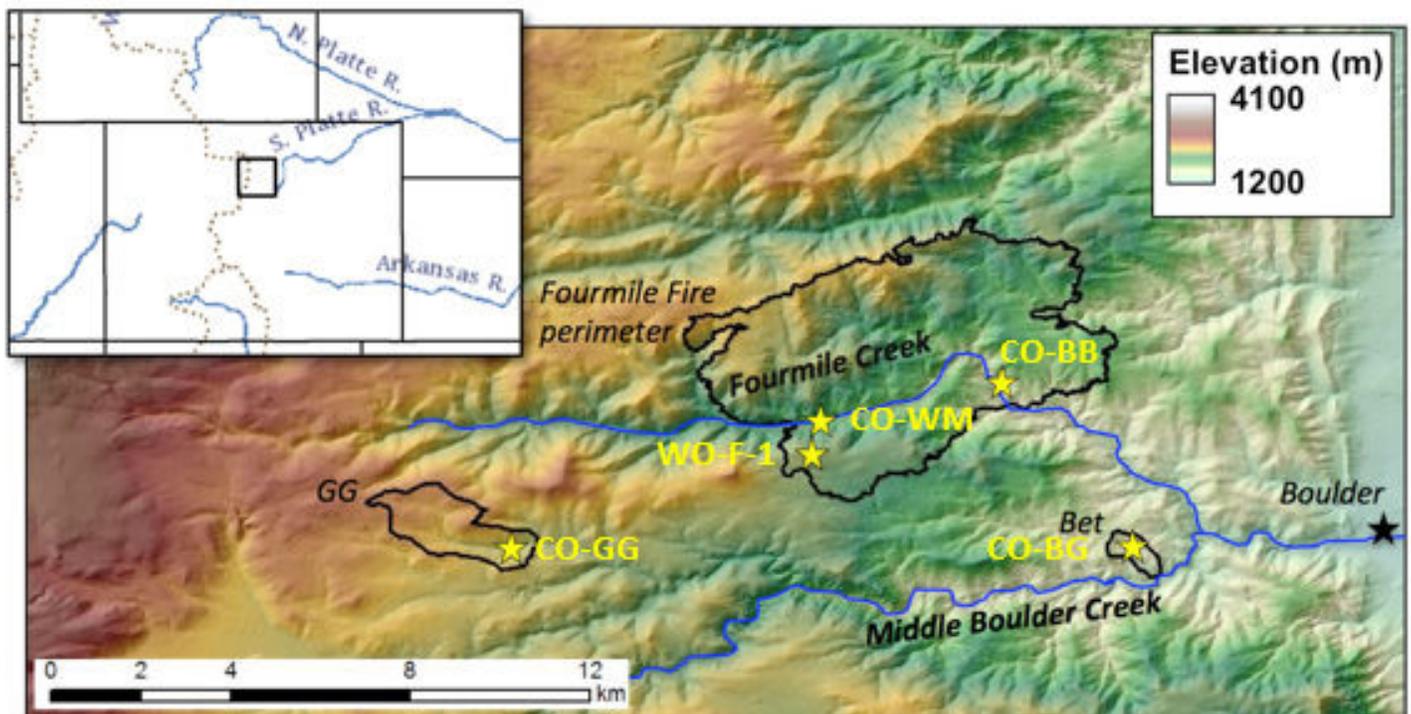


Figure 1. A map displaying the sample locations for CO-BB, CO-WM, and WO-F-1 within Fourmile Canyon, CO-BG in Betasso Gulch, and CO-GG in Gordon Gulch.

Away from Fourmile Canyon, additional sites analyzed include: an outcrop of layered colluvium in Betasso Gulch (CO-BG) that contains a darker colluvium layer at depth previously dated and discussed in Leopold et al. 2011; an alluvial fan exposure collected in 2011 in Gordon Gulch by Will Ouimet (CO-GG) that had no distinct organic lenses but contained three Holocene ^{14}C dates. CO-GG consists of colluvial/alluvial fan deposits transitioning to fluvial deposits at depth, and provides a profile whose direct connection to forest fire has not been established.

Laboratory and Analytical Methods

Samples were freeze-dried using a Labconco FreezeZone® 4.5 freeze dryer at -55°C and ≤ 0.133 mbar pressure for the minimum time necessary to remove moisture, while minimizing the loss of the more volatile PAHs. All samples were run on soxhlet extractors for 48 hours using 400ml of dichloromethane to remove the organic-soluble, aromatic compounds. Extraction thimbles were filled up to 2 cm below the rim with a representative sample, and the dried mass of each was recorded prior

to extraction. Column chromatography using a 2:1 mixture of activated silica gel and aluminum was used to separate the PAHs from the total extracted organic material based on polarity. Vials containing the total organic extract were rinsed three times with 1 ml of hexane to elute the saturated aliphatic hydrocarbons, and then three times with 1 ml of 70:30 hexane:dichloromethane to collect the PAHs. The fractions containing the PAHs were evaporated under a gentle stream of N_2 , transferred to 2 ml vials, and diluted in 1 ml of hexane before being run on a GC-FID (TraceGC Ultra) equipped with a DB-1 column (60m x 0.32mm x 0.25 μm).

PAHs contained in the samples were identified by retention time relative to a calibration standard containing the 16 EPA priority PAHs. Peaks were manually identified using the Chromeleon 7 software, and the areas of each were calculated and correlated to the specific compounds. To obtain the compound-specific regression equations needed to calculate the PAH concentrations in the samples, the PAH calibration standard was run on the GC at two concentrations: 1:250 μl and 1:1000 μl . The

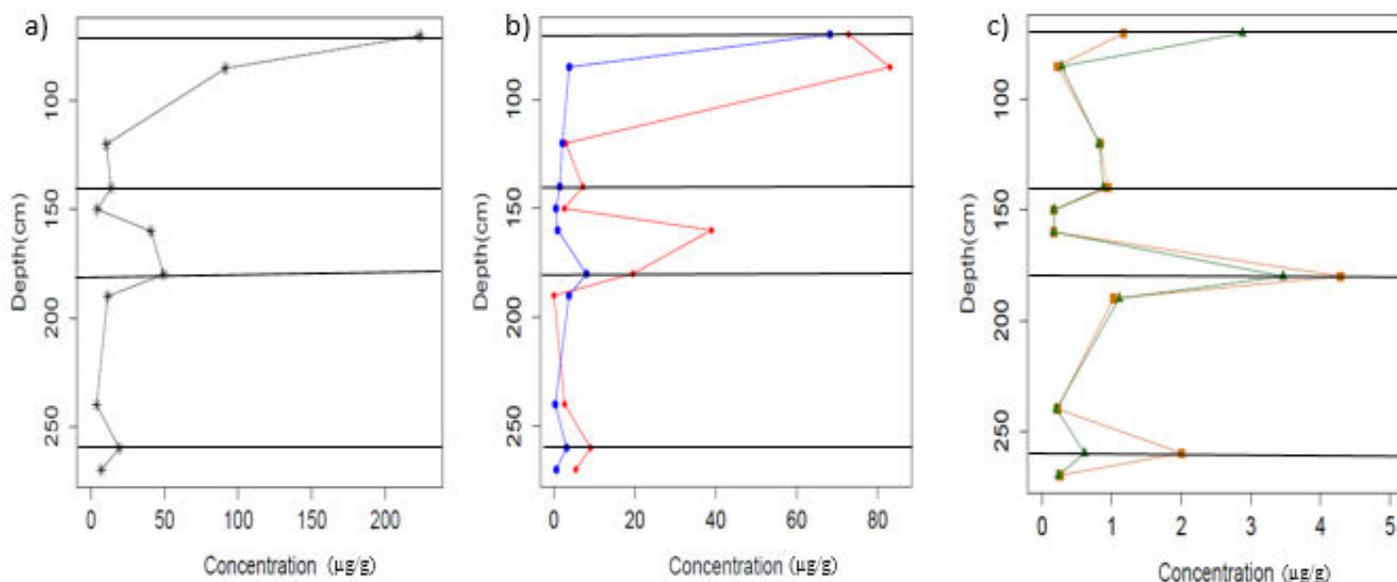


Figure 2. PAH concentrations in μg per g of soil as a function of depth, with the burned layers denoted by solid black lines and PAH concentrations by a color code: total PAH concentrations (black), LMW PAHs phenanthrene (red), and anthracene (blue), HMW PAHs benzo[ghi]perylene (orange), and dibenzo[a,h]anthracene (green). (a) The figure displays total PAH concentrations, with the highest total concentrations occurring relative to respective burn layers. (b) The concentrations of two LMW PAHs (phenanthrene, anthracene) at each sampled layer display a slightly different trend from the Figure 2a, with several instances of peak concentrations occurring separate from the burned layers. (c) The concentrations of two HMW PAHs (benzo[ghi]perylene, dibenzo anthracene[a,h]anthracene) display a similar trend to the total PAH profile, and occur in the lowest concentrations.

concentration of the standard at each dilution was calculated by dividing the initial concentration of the standard (200 ng/ml) by the volumes run on the GC. The areas of each EPA priority PAH peak were manually selected at both dilutions, and plotted against the above concentrations to provide a linear equation for each compound. The areas of the peaks corresponding to the 16 PAHs in each sample were inputted into these equations to solve for the sample concentrations. The data was then divided by the dilution each sample was run with on the GC (either 200 μ l or 1000 μ l), and then by the total dry mass of the sample extracted. This provided the masses for each of the PAHs per mass of sample (in μ g/g).

RESULTS

CO-BB

The incremental samples taken above, of, and below the burned or ashy soil layers at CO-BB display increases in total PAH concentrations corresponding to individual burn layers (Fig. 2). Total PAH concentration was found by computing the sum of all individual PAH concentrations measured in each sample. Total PAH concentrations in burned layers at depths of 260, 180, 140, and 70cm were calculated as 19.35, 49.40, 13.81, 223.44 μ g/g respectively. In all instances the total PAH signal is lower beneath and above the respective burned layers (Fig 2a).

Trends in PAH profiles differ at CO-BB when compound-specific PAH concentrations are analyzed for each sample (Fig. 2b and 2c). Phenanthrene and anthracene provide the clearest signal of the LMW PAHs, but have slightly different spikes regarding the same sample than those for total PAHs (Figure 2b). Phenanthrene occurs in the highest concentrations of all PAHs at this site, yet concentrations at the highest (70 cm depth) and second lowest (180 cm) layers were greater below and above the burned layer, respectively. Anthracene provides the second greatest signal of present PAHs, and similarly differs at the 180 cm burned layer, where peak concentrations occur in the sample taken slightly above the burn layer. Of the HMW PAHs, benzo[ghi]perylene and dibenzo[a,h]anthracene occur in lower concentrations than both the

LWM compounds, yet display a trend which follows more consistently with one another, as well as with the total PAH profile (Fig 2c).

WO-F-1 Soil Profile

The soil profile collected at incremental depths after the 2010 Fourmile Canyon fire displays a peak in both the total and measured LMW PAH concentrations at 5 cm below the surface. This is followed by a decreasing trend with increasing depth, yet concentrations do not decrease to near zero values within the top 20cm of the soil. Of note, surface concentrations taken at a depth of 1 cm are generally lower than those at 5 cm for these trends. HMW PAHs do not display as discernable a trend with depth, however. Benzo[b]fluoroanthene concentrations were calculated as

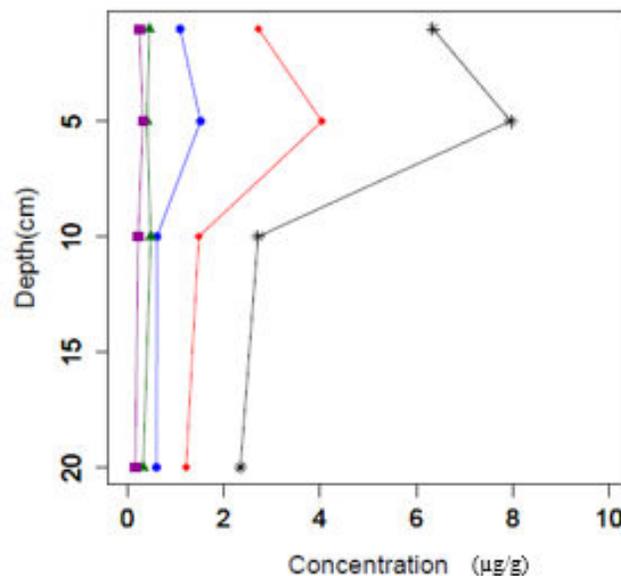


Figure 3. PAH concentrations as a function of depth below the surface taken from a site after the 2010 Fourmile Canyon fire, displayed by a color code: total PAH concentrations (black), LMW PAHs phenanthrene (red), and anthracene (blue), HMW PAHs benzo[b]fluoroanthene (purple), and dibenzo[a,h]anthracene (green). LMW PAHs (phenanthrene, anthracene) and the total PAH concentrations display a trend similar trend, with greatest concentrations occurring at the 5 cm depth, and decreasing thereafter with increasing depth. HMW PAH concentrations (dibenzo[a,h]anthracene, benzo[b]fluoroanthene) are not in agreement with this trend, which suggests that LMW compounds are better proxies than HMW regarding recent fires.

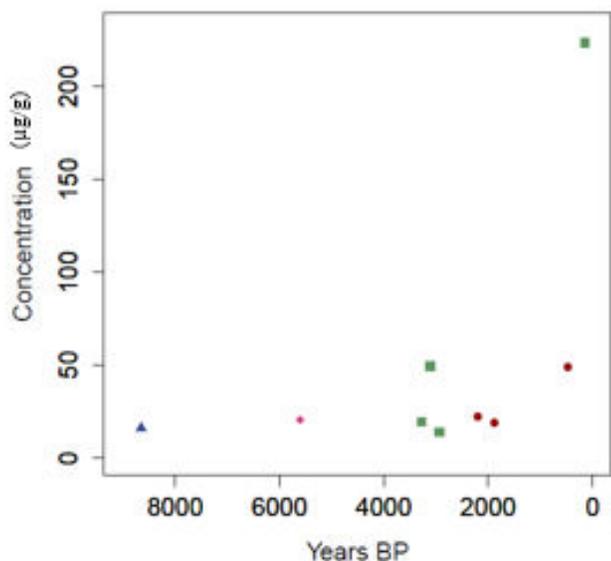


Figure 4. Total PAH concentrations for select burned or buried ash layers at CO-BB, CO-GG, CO-WM, and CO-BG sites correlated with radiocarbon dates. Each site is represented by a color code: CO-BG (blue triangle), CO-GG (pink dot), CO-BB (green square), and CO-WM (red circle). Measurable PAH quantities were recorded in all samples, with highest concentrations occurring in younger samples, yet sampling resolutions are not clear enough to suggest a definitive trend.

0.252785, 0.3236, 0.225562, 0.168005 µg/g for depths of 1, 5, 10, and 20 cm, respectively, while the profile for dibenzo[a,h]anthracene, among the highest weighted of the preserved PAHs, displays concentrations of 0.459525, 0.409228, 0.485093, and 0.330848 µg/g corresponding to depths of 1, 5, 10, and 20 cm, respectively. Both HMW values differ from one another as well as from the trend established by the other measurements.

PAH Concentration with Age at CO-BB, CO-BG, CO-GG, and CO-WM

Total PAH concentrations taken from burned or ashy buried layers at CO-BB, CO-BG, CO-GG and CO-WM were correlated with new and existing ^{14}C dates (Fig 4) (Leopold et al. 2011; Shea et al., in review; Kotikan, this volume). The presumed historic (~150 year old) sample at CO-BB, which contained visible coal grains, stands out as the highest concentration of total PAHs measured and is likely of anthropogenic origin as opposed to a related fire. Among the forest fire samples, the data display discernable, non-zero total PAH concentrations, but there are no clear trends or spikes with age: the oldest sample of 8649

years (CO-BG) had concentrations of 16.04 µg/g, and the youngest, non-mining-legacy sample (from CO-WM) was recorded at 22.40 µg/g. Younger samples in general appear to have the greatest total concentrations, yet there is still significant variation between samples of similar ages

DISCUSSION

Deposits at CO-BB highlight the creation and preservation of PAHs from several Holocene forest fires. Total PAH concentrations within the layered colluvial sediment at CO-BB display an increase in concentration corresponding to each burned and/or ashy buried layer relative to samples gathered above or directly below (Fig 2). This site was interpreted as a depositional area of material mobilized off the hill slope, with the bottom three charcoal lenses related to three separate Holocene forest fire events occurring in Fourmile Canyon, and the uppermost layer believed to be associated with the mining legacy of the canyon due to the observed coal fragments in the layer.

Some discrepancy is apparent given that the concentrations of each burned and/or ashy layer differ from the other burned layers, as well as in the disparity between surrounding samples without discernable burned materials gathered for each sequence. Among the older Holocene fires, the highest and lowest total PAH concentrations are 49.40 and 13.81 µg/g, respectively. A potential explanation for relative significant variation of 35.60 µg/g could be attributed to the higher concentration of charcoal pieces in the sample; apart from the relationship between charcoal and the direct deposition of PAHs during forest fires, charcoal has a large quantity of surface area for the compounds to adsorb to, and therefore higher concentrations of PAHs could be expected whenever there are relatively higher amounts of charcoal in the soil. The variation in quantity of charcoal or ash per each burned layer could be a function of fire intensity, given that a more intense forest fire is expected to produce greater quantities of both charcoal and PAHs, including a higher ratio HMW PAHs. The mobilization of forest fire progeny material on the landscape before deposition according to geomorphic stability phases could also be a factor; if the organics were transported from a further source before deposition, there would be a higher likelihood for PAH volatilization

and erosion, as well as an increase in mixing with colluvium or alluvium and a dilution of the burned materials. This indeed may be the case, given that the above sample with the PAH concentration of 13.81 $\mu\text{g/g}$ had a higher composition of sand. It appears that PAH degradation due to the passing of time, while likely a factor, is not the only variable responsible for this discrepancy between sites; the burned layer with the highest concentration was ascribed a radiocarbon date older than the lower concentrated layer (Fig. 4). The age difference between these sites is around 175 years, which is marginal when the near 3000 year old ages are considered. As expected, the historic (~150 years old) coal layer associated with railroad deposition had the highest total concentration of PAHs, as well as the highest concentrations of the HMW PAHs; both factors are likely attributed to the petrolytic origin and recent deposition. Therefore, it is vital to make a distinction between source materials within a site before comparison.

To understand the viability of PAHs as biomarkers, it is important to distinguish compound-specific PAH profiles for each sample at depth. Given information regarding the formation and physical properties of each PAH, a certain relationship can be expected between the compounds- namely those of HMW- which would be more resistant to degradation over time versus those more quantitatively generated by forest fires. Regarding the CO-BB site, the vast majority of PAHs were of LMW. However, the HMW PAHs display a trend which agrees more closely with one another, as well as with the total concentration trend. The HMW profile corresponds the highest compound-specific concentrations with the organic layers, and shows relatively lower concentrations for the layers above and below which were devoid of clear fire indications when sampling. These measurements could be similarly explained by differences in fire intensity and remobilization, but it appears from this study that the HMW PAHs provide a truer correspondence with the older Holocene fire-associated layers.

Regarding the soil profile at WO-F-1, the greatest total PAH concentrations occur at a depth of 5 cm (Fig. 3). It was originally expected that the uppermost cm of the surface would provide the largest PAH signal due to the increased direct deposition from the

2010 Fourmile fire. Possible explanations for this result include higher than expected volatilization rates for PAHs exposed on the surface as well as an increase in mobilization of the surface ash and adsorbed PAHs away from the sample site due to the alteration of the surface ecology and stability. Furthermore, peak concentrations at the 5 cm interval and non-zero concentrations at the 20 cm depth suggest the following: the compounds are undergoing translocation through the soil column, there has been some degree of mixing near the surface, or some combination of the above. The compound-specific trend for the LMW signals of phenanthrene and anthracene occur in the greatest concentrations and reflect a similar pattern as the total PAH profile. We presume that this is attributed to preferential formation of the LMW compounds under the temperatures of the 2010 fire. The while benzo[b]fluoroanthene displays a similar, albeit muted, trend with depth, the HMW PAHs in general at this site occur in considerably lower concentrations, and disagree generally with the results of the total and LMW profiles. This suggests, contrary to the results of CO-BB, that the LMW PAHs provide a more accurate signal relative to the total PAH trend for recent fires.

The concentrations at the WO-F-1 site, despite coming from direct deposition and a recent fire, occur in much lower total concentrations than those recorded from CO-BB. This is likely a factor of the physical differences in the samples; the WO-F-1 series was composed of dusty ash and sand, while the samples from CO-BB contained discernable charcoal fragments. These observations suggest that the presence of charcoal fragments is a more important factor in determining forest fire related PAH concentrations than the time elapsed since the fire. Following a similar trend, PAH concentrations of the burned organic layers, when correlated with radiocarbon dates, suggest the presence of measurable PAHs 8649 years before present. Therefore, PAHs appear to have the capability to act as proxies for studying ancient fires within burned layers. There appears to be a general trend of increasing total PAH concentration as fire age decreases, but some significant variation does occur between samples of similar age.

CONCLUSION

This is among several pioneering studies assessing the viability of PAHs as proxies for reconstructing recent and historic forest fire occurrence and intensity from terrestrial sediments. It is apparent from this study that measurable quantities of PAHs are preserved on timescales of several thousand years. Compound-specific PAH analysis of burned and unburned layers offers an anomalous profile of peak total PAH concentrations corresponding to the occurrence of buried, organic rich layers. On longer timescales, it appears that HMW PAHs, though occurring in smaller concentrations than LMW PAHs, offer a more accurate proxy for reconstructing fire occurrence. Regarding samples corresponding to recent fires (2010), we see an opposite trend, wherein LMW PAHs profiles fall in closer agreement with the total PAH trend, as well as display an increase in concentration from 1 to 5 cm depths, followed by a more rapid decrease to 10 and 20 cm depths. Moreover, the results of this study indicate that the material collected for sampling carries possibly more significant weight in the reconstruction of PAH concentration than does time elapsed since the forest fire. Samples from recent fires were comprised mainly of dusty ash, but produced lower signals than samples collected from fires ranging several hundred to near 8000 years ago containing discernable charcoal fragments. Future work will aim at conducting LOI to normalize the percentage of organic matter in soils extracted for PAHs, as well as conducting carbon isotope measurements of the PAHs to look for a potential relation to fire intensity.

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