

UC Davis

UC Davis Previously Published Works

Title

Wildfire Burn Intensity Affects the Quantity and Speciation of Polycyclic Aromatic Hydrocarbons in Soils

Permalink

<https://escholarship.org/uc/item/7bg6228z>

Journal

ACS Earth and Space Chemistry, 2(12)

ISSN

2472-3452

Authors

Chen, Huan
Chow, Alex T
Li, Xiu-Wen
[et al.](#)

Publication Date

2018-12-20

DOI

10.1021/acsearthspacechem.8b00101

Peer reviewed

Wildfire Burn Intensity Affects the Quantity and Speciation of Polycyclic Aromatic Hydrocarbons in Soils

Huan Chen,[†] Alex T. Chow,[†] Xiu-Wen Li,[§] Hong-Gang Ni,[§] Randy A. Dahlgren,^{||} Hui Zeng,^{*,§} and Jun-Jian Wang^{*,†,‡,#}

[†]Biogeochemistry & Environmental Quality Research Group, Clemson University, Clemson, South Carolina 29442, United States

[§]Shenzhen Key Laboratory of Circular Economy, Shenzhen Graduate School, Peking University, Shenzhen 518055, China

^{||}Land, Air and Water Resources, University of California—Davis, Davis, California 95616, United States

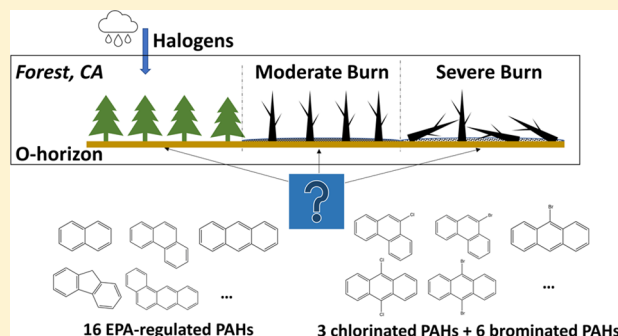
[‡]Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

[#]State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

Supporting Information

ABSTRACT: Wildfire-altered soil may be an important source of polycyclic aromatic hydrocarbons (PAHs) in the environment. With projected increase of wildfire frequency and intensity due to changing global climate, understanding the quantity and speciation of PAHs, including halogenated PAHs (XPAHs), resulting from different burn intensities has important ramifications for environmental quality concerns and global soil carbon dynamics. Here, we quantified levels of 16 U.S. Environmental Protection Agency regulated PAHs, 3 chlorinated PAHs, and 6 brominated PAHs in nonburned forest soils and burned ash/soil samples covered with black ash (B-Ash; moderate burn intensity) or white ash (W-Ash; severe burn intensity) from the 2013 Rim Fire (1,041 km²) in California. The $\sum_{16}\text{PAH}$ concentrations follow (mean \pm standard deviation; $\mu\text{g}/\text{kg}$) B-Ash (893 ± 285) > W-Ash (515 ± 333) \approx nonburned soils (247 ± 58). Moreover, the $\sum_{16}\text{PAH}$ profiles were altered by both moderate and severe burn conditions with the size of aromatic structures following B-Ash > W-Ash > nonburned soils. Neither chlorinated nor brominated PAH concentration was significantly elevated by moderate or severe wildfire. Overall, fire intensity is critical in regulating soil PAH concentrations and profiles. Given the high erodibility of wildfire ash, these PAHs can be easily transported to rivers and reservoirs where they could impact the aquatic food web and drinking source water.

KEYWORDS: Wildfire combustion processes, Climate change, Temperate forests, Water quality, Parent polycyclic aromatic hydrocarbons, Naphthalene, California



1. INTRODUCTION

Under the context of climate change,¹ forest wildfires are occurring with increasing frequency, intensity, and burned area in the western United States,² and throughout arid/semiarid regions of the world.³ Among many fire-induced consequences,^{4–6} the formation of polycyclic aromatic hydrocarbons (PAHs) in soils⁷ is a major concern because of their high toxicity (i.e., carcinogenicity, mutagenicity, and reproductive toxicity), persistence, and bioaccumulation.^{7,8} Wildfire as a significant PAH source has been previously shown by measuring the increase of soil PAH concentrations immediately after fires.^{7,9} For example, Kim and co-workers¹⁰ reported that $\sum_{16}\text{PAH}$ concentrations ranged from 153 to 1570 $\mu\text{g}/(\text{kg}$ of soil) one month after a forest fire in South Korea, which were 4–24 times higher than those of nonburned soils. Choi¹¹ found an ~ 20 -fold increase in average $\sum_{16}\text{PAH}$ concentrations in the O-horizon after a forest fire in South Korea. It was

estimated that PAH production by wildfire sources amount to 13.6% of the global PAH budget,¹² and their production in fire-prone regions is expected to increase under a drier and warmer future climate for several global regions.

During wildfires, a heterogeneous fire/burn intensity occurs across the landscape because forest fires do not burn uniformly owing to differences such as fuel load and moisture content.¹³ Depending on burn intensity, black and white ash can be generated from the incomplete (moderate burning; commonly 200–500 °C) and near-complete (high intensity burning; commonly >510 °C) combustion, respectively.^{14–16} A study in southern California estimated that $\sim 25\%$ of the land surface

Received: August 3, 2018

Revised: October 21, 2018

Accepted: October 29, 2018

Published: October 29, 2018

was covered by white ash, due to high temperature combustion of large fuel loads.¹⁷ Compared to black ash, white ash generally contains more mineral materials and less pyrogenic/charred organic matter.^{18,19} Our previous study¹⁶ showed that white ash had a higher aromaticity in the water extractable organic matter fraction compared to black ash and nonburned detritus. It suggested that organic matter in white ash was more aromatic and hydrophilic than for black ash. Although several studies have examined PAH production from wildfires, they generally evaluated soil or water samples without consideration of burn intensity.^{10,11} Therefore, investigation of the abundance and profiles of PAHs in black and white ash is important to better understand the role of burn intensity on the resulting PAHs in burned soils. There is also a strong potential for transporting PAHs in the wildfire ash to aquatic environments given the susceptibility of wildfire ash to postfire erosion processes due to the lack of soil cover and the loose consistency of the ash materials.

Halogenated PAHs (XPAHs), including chlorinated PAHs (Cl-PAHs) and brominated PAHs (Br-PAHs), are a class of PAH derivatives having elevated health concern. They are generated by attachment of one or more halogens to the aromatic rings of their corresponding parent PAHs (PPAHs),²⁰ and they have appreciably higher carcinogenic and mutagenic toxicity than their PPAHs.²¹ The source of XPAHs is related to the simultaneous presence of halogens and aromatic precursors.²² Combustion processes including engine combustion and waste incineration are considered major emission sources of XPAHs.^{22,23} For example, Tu and co-workers²⁴ reported elevated concentrations of 160–220 $\mu\text{g}/\text{kg}$ for $\sum_{20}\text{Cl-PAH}$ and 19–46 $\mu\text{g}/\text{kg}$ for $\sum_5\text{Br-PAH}$ in open e-waste burning areas, compared to those in control areas which were less than the limits of detection (0.02–0.08 $\mu\text{g}/\text{kg}$). Horii et al.²² found a significant correlation between concentrations of Cl-PAH and PAH and suggested chlorination of PPAHs as the main pathway for formation of Cl-PAHs during waste incineration. The chlorination of PPAHs was also suggested by Ma and co-workers²⁵ as the dominant pathway for Cl-PAH formation during e-waste recycling operations. California forest ecosystems may have high chlorine and bromine inputs from atmospheric deposition given their close proximity to the ocean.²⁶ In addition, widespread use of brominated flame retardants by firefighters is another possible source of halogens during wildfires.²⁷ Therefore, the litter and duff materials could be a potential source of XPAHs following combustion processes during California wildfires. To date, studies on the occurrence and profiles of Cl- and Br-PAHs in soils after forest wildfires are lacking, compared to investigations of PPAHs, though one study²⁸ identified XPAHs in soils after a fire that involved combustion of poly(vinyl chloride).

The Rim Fire in 2013 was the third largest wildfire in California history and burned 1,041 km^2 of the Stanislaus National Forest in the Sierra Nevada Mountains.¹⁶ This event attracted a high level of attention from both government resource agencies and the public because the wildfire occurred within the watershed that supplies drinking water to 2.6 million residents in/around San Francisco and the environmental/health consequences of wildfires remain largely unknown. In the present study, we collected the surface soil materials (0–5 cm) from five burned sites (both black [moderately burned] and white [severely burned] ash) within the Rim Fire perimeter and two nonburned sites outside the burned perimeter. The main goal of this study was to assess whether

the burn intensity affected the occurrence, profiles, and potential toxicity of PAHs and XPAHs in wildfire-altered soils. The results of this study are important for informing land restoration and water quality management decisions following large wildfires in watersheds serving as a drinking water source.

2. MATERIALS AND METHODS

2.1. Soil Sampling. Detailed site and soil sampling information were described in our previous studies.^{16,29} Briefly, we selected a 13 km transect spanning the north–south axis of the Rim Fire, which contained all the representative vegetation types for the burned area (Figure 1). The postfire soil samples

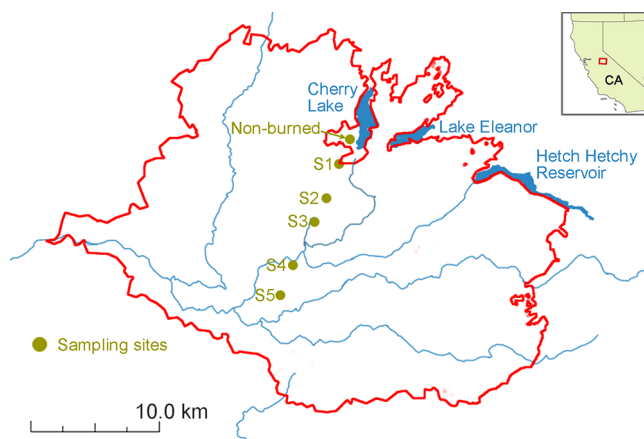


Figure 1. Soil and ash/soil materials were collected in October 2013 from five sites within the Rim Fire area (red line). Soils from nonburned sites were collected from a forest located about 2 km north of the northern-most burned-area sampling site (site 1) near Cherry Lake. Adapted with permission from ref 16 (Supporting Information). Copyright 2015 American Chemical Society.

were collected from 5 sites along this transect on Oct. 2, 2013 (fire ignition on Aug. 17, 2013 and full containment on Oct. 24, 2013) prior to any rainfall events. The sites were dominated by ponderosa pine (*Pinus ponderosa* Dougl.) forest (site 1), mixed conifer forest (sites 2 and 3), mixed oak woodland (site 4), and chaparral (site 5).¹⁶ All vegetation was killed and the O-horizon (litter layer) was completely consumed at all five burned sites. Wildfire ash color is a field indicator and diagnostic feature of burn intensity.³⁰ Based on ash color, two relative burn intensities were selected for analysis at each site: black ash (200–500 °C) indicative of moderate intensity fire and white ash (>510 °C) characteristic of a high intensity fire.³¹ Estimates of landscape-level burn intensity based on field observation of white vs black ash distribution were 8–10% high intensity and 90–92% moderate intensity at sites 2–5 and 3% high intensity and 97% moderate intensity at site 1. We used a 7.6 cm diameter \times 5.0 cm depth stainless steel coring device to randomly collect three composite ash/soil samples with surface deposits of white ash (W-Ash) or black ash (B-Ash) along a 50 m transect at each site. At least three subsamples were collected within a 10 m radius to make up one composite sample that weighed more than 1.5 kg. The 5 cm depth increment was dominated by the surface ash layer (typically 3–4 cm) with a thin layer of charred soil material typically not exceeding 2 cm in thickness. It should be noted that B-Ash and W-Ash characterization represents the dominant materials visually identified in the field, but they should not be considered pure end-members, as

there is tremendous short-range spatial variability in both the horizontal and vertical dimensions of the ash layer. Nonburned ponderosa pine and white fir *Abies concolor* forest sites located about 2 km north of site 1 near Cherry Lake were selected as reference sites. At these reference sites, the 0–5 cm surface soils were collected after removing the litter materials and designated as “nonburned”. All soil samples were freeze-dried, passed through a 2 mm sieve, and further ground to a fine powder before further chemical analyses.

2.2. Chemical Analyses. A 10 g amount of ground soil/ash sample was mixed with recovery standards (naphthalene- d_8 , ace-naphthylene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) and 2.0 g of copper (for sulfur removal) and then Soxhlet-extracted for 24 h with a 200 mL mixture of hexane and dichloromethane (1:3, v:v). The soil extract was concentrated to 4 mL using a rotary evaporator and then purified with a silica gel and alumina column (2:1, v:v; 30 cm height \times 10 mm i.d.). Each column containing the target PAHs was eluted with 70 mL of hexane and dichloromethane mixture (7:3, v:v), concentrated to 0.5 mL with a gentle N_2 stream, and spiked with internal standards (2-fluorobiphenyl and *p*-terphenyl- d_{14}) before instrumental analysis. Concentrations of PAHs and XPAHs in the eluted solution were determined by gas chromatography–mass spectrometry (GC-MS; Agilent 7890A GC equipped with 5975C MSD, Agilent Technologies, Foster City, CA, USA) using a 30 m DB-SMS fused silica capillary column (0.25 mm i.d., 0.25 mm film thickness, J&W Scientific, Folsom, CA, USA) and helium (1 mL/min) as the carrier gas. The column oven temperature was ramped from 60 to 200 °C (10 °C/min), to 214 °C (2 °C/min), to 254 °C (5 °C/min), and finally to 290 °C (18 °C/min). The temperature was held for 2 min at 254 °C and 17 min at 290 °C. We detected 16 PAHs ($\sum_{16}\text{PAH}$), 3 Cl-PAHs ($\sum_3\text{Cl-PAH}$), and 6 Br-PAHs ($\sum_6\text{Br-PAH}$) (Table 1). Procedural and spiked blanks were included with each batch of 10 samples for quality assurance/quality control. Recoveries of spiked standards in samples were $101 \pm 21\%$ for naphthalene- d_8 , $87 \pm 14\%$ for acenaphthene- d_{10} , $91 \pm 16\%$ for phenanthrene- d_{10} , $97 \pm 13\%$ for chrysene- d_{12} , and $82 \pm 19\%$ for perylene- d_{12} . We did not add isotope-labeled standards of XPAHs to samples because they were not commercially available. Detection limits for all target PAHs and XPAHs were in the range of 0.25–5.1 $\mu\text{g}/\text{kg}$. All glassware was cleaned successively with sulfuric acid, tap water, and Milli-Q water (18.2 $\text{M}\Omega/\text{cm}$) at least three times and then baked for >24 h at 450 °C.

2.3. Toxic Equivalency Quotients. Toxic equivalency quotients (TEQs) are considered an index for potential toxicity.³² TEQs of XPAHs and PAHs were calculated by eq 1 and eq 2, respectively.^{32–34}

$$\text{TEQ}_{\text{XPAHs}} = \sum C_i \times \text{REP}_{\text{BaP},i} \quad (1)$$

$$\text{TEQ}_{\text{PAHs}} = \sum C_j \times \text{TEF}_{\text{BaP},j} \quad (2)$$

where TEQ is the toxic equivalency quotients of XPAHs or PAHs, in $\mu\text{g}/\text{kg}$; i is an individual XPAH; j is an individual PAH; C is the concentration in $\mu\text{g}/\text{kg}$; $\text{REP}_{\text{BaP},i}$ is the toxic potency value of i relative to that of benzo[*a*]pyrene (BaP), unitless (Table S1); and $\text{TEF}_{\text{BaP},j}$ is the toxic equivalency factor for j relative to BaP, unitless (Table S1).

2.4. Statistical Analyses. Similar to our previous studies,^{16,35} preliminary data analysis showed that burn severity was the dominant factor compared to sampling site effects

Table 1. List of Polycyclic Aromatic Hydrocarbons (PAHs) and Halogenated Polycyclic Aromatic Hydrocarbons (XPAHs) in This Study

target analytes	abbreviations
PAHs	
naphthalene	Nap
acenaphthylene	Acy
acenaphthene	Ace
fluorene	Fle
phenanthrene	Phe
anthracene	Ant
fluoranthene	Flu
pyrene	Pyr
benzo[<i>a</i>]anthracene	BaA
chrysene	Chr
benzo[<i>b</i>]fluoranthene	BbF
benzo[<i>k</i>]fluoranthene	BkF
benzo[<i>a</i>]pyrene	BaP
indeno[1,2,3- <i>c,d</i>]pyrene	IcdP
dibenzo[<i>a,h</i>]anthracene	DahA
benzo[<i>g,h,i</i>]perylene	BghiP
XPAHs	
2-bromofluorene	2-BrFle
9-chlorophenanthrene	9-ClPhe
2-chloroanthracene	2-ClAnt
9-bromophenanthrene	9-BrPhe
9-bromoanthracene	9-BrAnt
9,10-dichloroanthracene	9,10-Cl ₂ Ant
9,10-dibromoanthracene	9,10-Br ₂ Ant
1-bromopyrene	1-BrPyr
7-bromobenz[<i>a</i>]anthracene	7-BrBaA

incorporating differences in the chemical properties of the detritus from contrasting vegetation sources. Therefore, with the aim of testing how burn intensity alters the concentrations and profiles of PAHs and XPAHs in ash/soil samples, we focused on differences across nonburned soils, B-Ash, and W-Ash in this study. Analyses of variance (ANOVA) followed by posthoc Tukey HSD (honestly significant difference) were used to assess differences among the three sample types (nonburned, B-Ash, and W-Ash) for PAH or XPAH characteristics. Shapiro–Wilk normality test was conducted using the *shapiro.test* function in the *stats* package to assess normality. For non-normal data, the *boxcox* function in the *MASS* package was used to perform a Box-Cox transformation. When data could not be transformed to a normal distribution by Box-Cox transformation, the *kruskal.test* function in the *stats* package was used to conduct the nonparametric Kruskal–Wallis test, followed by Dunn’s posthoc multiple comparison with a Bonferroni correction, using the *dunnTest* function in the *FSA* package. The level of significance for all statistical tests was set at $p \leq 0.05$. Correlation coefficients between XPAH and their PPAH were calculated with the *cor* function in the *stats* package, whereas the p -value was calculated by the *cor.test* function in the *stats* package.

3. RESULTS AND DISCUSSION

3.1. Levels of PAHs and XPAHs. The $\sum_{16}\text{PAH}$ concentrations (mean \pm standard deviation) were 247 ± 58 $\mu\text{g}/\text{kg}$ in the nonburned soils, 893 ± 285 $\mu\text{g}/\text{kg}$ in B-Ash, and 515 ± 333 $\mu\text{g}/\text{kg}$ in W-Ash, respectively (Figure 2a). The $\sum_{16}\text{PAH}$ concentrations in B-Ash were significantly higher

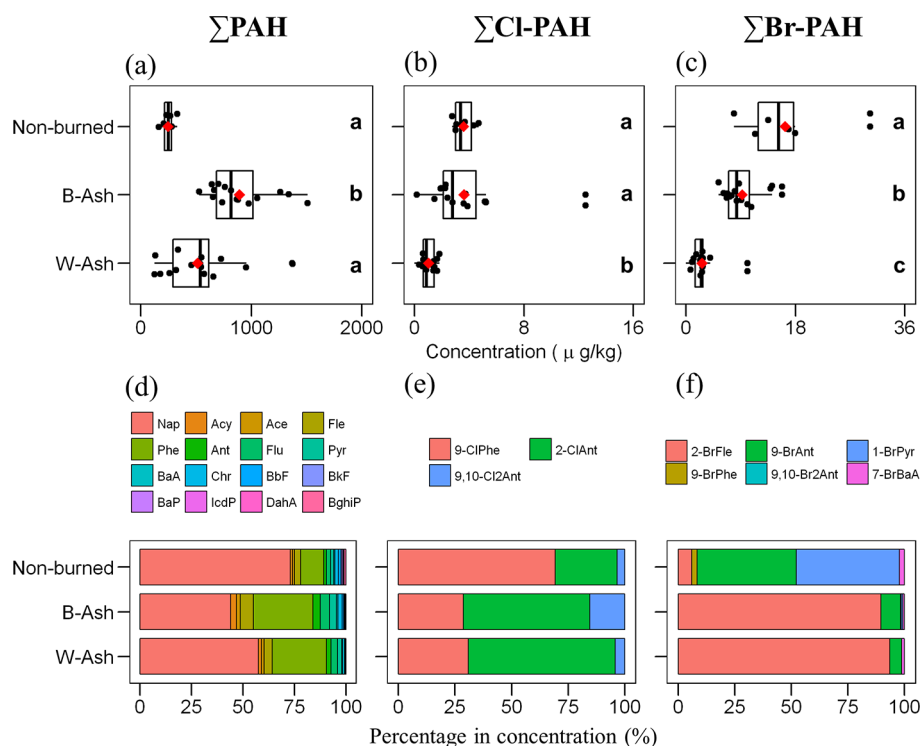


Figure 2. Concentrations (mean \pm standard deviation) and profiles of (a, d) \sum_{16} PAH, (b, e) \sum_3 Cl-PAH, and (c, f) \sum_6 Br-PAH in the nonburned soils, black ash (B-Ash), and white ash (W-Ash) at sites 1–5. In panels a–c, the mean value in each box is labeled as the red diamond. Boxes with the different lower-case letters indicate significant difference ($p \leq 0.05$) among materials. Abbreviations for PAHs are available in Table 1.

than those in nonburned soils ($p < 0.001$), consistent with previous studies that showed elevated PAH levels in burned forest soils (Table S2).^{10,11,36,37} For example, Kim et al.¹⁰ reported \sum_{16} PAH concentrations ranging from 153 to 1570 $\mu\text{g}/(\text{kg}$ of soil) one month after a forest fire. PAHs are posited to form via unimolecular cyclization, dehydrogenation, dealkylation, and aromatization of ligneous and cellulosic plant biopolymers as well as lipids during the charring process.^{38,39} Clearly, the results of the present and previous studies consistently indicate that forest fires can be a significant source of soil PAHs.

Our study showed that \sum_{16} PAH concentrations in W-Ash were significantly lower than B-Ash ($p = 0.001$). This suggests that W-Ash formed from more severe burning (i.e., higher temperatures) does not contribute to soil PAHs compared to background soil levels, which is probably due to a high degree of organic matter pyromineralization. A similar phenomenon has been found in municipal solid waste incineration, where low temperature burning caused elevated PAH formation but high temperature burning with sufficient O_2 reduced PAH formation.⁴⁰ Additionally, decreased PAH emissions to the atmosphere were reported for high temperature burning in laboratory combustion studies.^{41,42} Zhang et al.⁴¹ also found lower \sum_{16} PAH emissions during combustion of agricultural crop residues at higher burn intensities. Similarly, Molto et al.⁴² found decreased \sum_{16} PAH yields from pine needles and cones when the burn temperature increased from 550 to 850 $^\circ\text{C}$. Although \sum_{16} PAH concentrations showed no significant difference ($p = 0.06$) between W-Ash and the nonburned soils in this study, the average \sum_{16} PAH concentration in W-Ash was about two times higher than the nonburned soils with a p -value (0.06) approaching our significance threshold ($p \leq 0.05$). Further investigations are necessary to elucidate the specific

roles of temperature thresholds, oxygen levels, and fuel characteristics in controlling PAH production during wildfire.

The \sum_{16} PAH levels in our nonburned soils ($247 \pm 58 \mu\text{g}/\text{kg}$) were relatively higher than those from other nonburned forests previously reported, such as 6.27–52.2 $\mu\text{g}/\text{kg}$ for nonburned soils from a Korean pine forest¹¹ and 1–36 $\mu\text{g}/\text{kg}$ for nonburned soils in Costa Rica (more comparison in Table S2).⁴³ High PAH levels in forest soils have been attributed to anthropogenic disturbance^{44,45} and/or natural sources,^{10,11,36} such as previous wildfires (Table S2). For example, Xiao and co-workers⁴⁵ found \sum_{16} PAH concentrations were 71.28–515.34, 39.85–201.01, and 18.90–75.17 $\mu\text{g}/\text{kg}$ in forest soils from urban, suburban, and rural areas, implicating the influence of anthropogenic activities. However, the high \sum_{16} PAH concentrations in our nonburned samples were less likely from anthropogenic activities because the sites are in a remote forest area far from urban and industrial centers. The potential for PAH accumulation from historic wildfires in this fire-prone region could be a major reason for the high background soil PAH levels as the fire return frequency for these Sierra Nevada forest is <35 years.

The \sum_3 Cl-PAH and \sum_6 Br-PAH levels did not show the same variations across sample types as \sum_{16} PAH concentrations. The \sum_3 Cl-PAH concentrations followed B-Ash ($3.63 \pm 2.86 \mu\text{g}/\text{kg}$) \approx nonburned soils ($3.58 \pm 0.78 \mu\text{g}/\text{kg}$) $>$ W-Ash ($1.03 \pm 0.54 \mu\text{g}/\text{kg}$) (Figure 2b). Thus, moderate burning did not affect \sum_3 Cl-PAH concentrations in soils, while higher temperature burning decreased \sum_3 Cl-PAH concentrations. In contrast, \sum_6 Br-PAH concentrations were significantly lower in both B-Ash ($9.26 \pm 3.14 \mu\text{g}/\text{kg}$) and W-Ash ($2.66 \pm 2.30 \mu\text{g}/\text{kg}$) compared to nonburned soils ($16.33 \pm 7.76 \mu\text{g}/\text{kg}$; Figure 2c). Despite higher PAH occurrence in burned soils, there was no significant increase in \sum_3 Cl-PAH or \sum_6 Br-PAH concen-

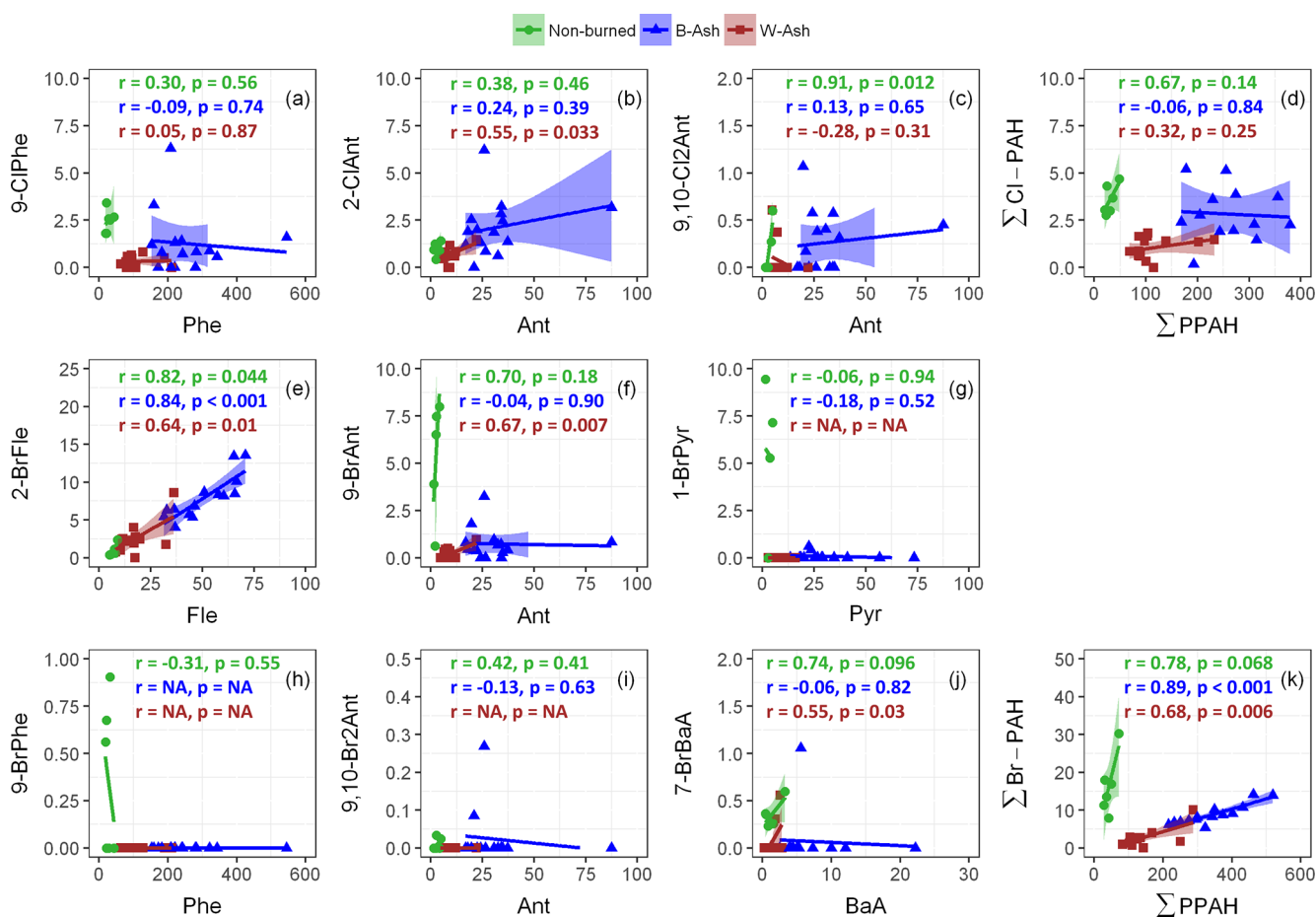


Figure 3. Correlations between halogenated polycyclic aromatic hydrocarbons (XPAHs) and their parent polycyclic aromatic hydrocarbons (PPAHs): (a) 9-ClPhe vs Phe; (b) 2-ClAnt vs Ant; (c) 9,10-Cl₂Ant vs Ant; (d) \sum_3 Cl-PAH vs \sum_2 PPAH; (e) 2-BrFle vs Fle; (f) 9-BrAnt vs Ant; (g) 1-BrPyr vs Pyr; (h) 9-BrPhe vs Phe; (i) 9,10-Br₂Ant vs Ant; (j) 7-BrBaA vs BaA; and (k) \sum_6 Br-PAH vs \sum_5 PPAH. Plotted using the *ggscatter* in the *ggpubr* package. The “Pearson” correlation coefficient was computed using the *stat_cor* function. The fitted linear equations between paired XPAH and PPAH are shown in Table S3.

trations indicating that wildfire is not a significant source of soil XPAHs. Compared to nonburned soils and B-Ash, W-Ash had consistently lower \sum_3 Cl-PAH and \sum_6 Br-PAH levels indicating that wildfires with high burn severity may result in the loss of XPAHs from soils.

The \sum PPAH concentration correlated with \sum_6 Br-PAH content but not with \sum_3 Cl-PAH content (Figure 3). For individual compounds, we only observed significant correlations ($p \leq 0.05$) for anthracene (Ant) vs 2-chloroanthracene (2-ClAnt) (W-Ash; Figure 3b), 9,10-dichloroanthracene (9,10-Cl₂Ant) vs Ant (nonburned; Figure 3c), and 2-bromofluorene (2-BrFle) vs fluorene (Fle) (nonburned, B-Ash, and W-Ash; Figure 3e). Only these XPAHs appear to have potential linkage to their respective PPAHs. Direct chlorination of PAHs was previously hypothesized as the major pathway for Cl-PAH formation, and several studies have observed significant correlations between PAHs and Cl-PAH levels in urban particulate matter⁴⁶ and fly ash samples.^{20,22} In contrast, the lack of significant correlations for PPAHs-Cl-PAH relationships in this study suggests that the formation or degradation of most Cl-PAHs differ from their PPAHs during forest fires. Several studies^{20,22,46} have reported decoupled PAH and Br-PAH relationships despite significant correlations between PPAH and Cl-PAH levels. However, our study does support the possibility that Br-PAHs were closely related to their

PPAHs for nonburned ($r = 0.78, p = 0.068$), B-Ash ($r = 0.89, p < 0.001$), and W-Ash ($r = 0.68, p = 0.006$). Notably, the slope between \sum_6 Br-PAH and \sum_5 PPAH, indicating the amount of \sum_6 Br-PAH formed per unit increase in \sum_5 PPAH, followed B-Ash < W-Ash < nonburned (Table S3). We noted that soil extractable bromide concentration increased with increasing burn intensity (nonburned < B-Ash < W-Ash) in our previous study,¹⁶ which supports that the mineralization of organobromine compounds might partially explain the loss of Br-PAHs in both B-Ash and W-Ash. Additionally, burning-induced halogen volatilization may reduce the Cl and Br availability for XPAH formation in ash.^{47,48} For waste incineration, Kakimoto et al.⁴⁹ found that the ratio of Cl-PAHs to PPAHs was affected by the type of waste incinerator,²² furnace temperature,^{21,50} and combusted materials.⁵⁰ It is still unclear why waste incineration yields considerable amounts of XPAHs but forest wildfire did not. Laboratory burning experiments under controlled conditions are needed to better characterize critical factors controlling halogenated PAH dynamics during wildfires.

3.2. Profiles of PAHs and XPAHs. Wildfire altered the profiles of \sum_{16} PAH, although \sum_{16} PAH in all the samples were dominated by naphthalene (Nap), followed by phenanthrene (Phe) (Figure 2d). The percentage of Nap in the \sum_{16} PAH content of nonburned soils ($72.8 \pm 8.9\%$) was significantly

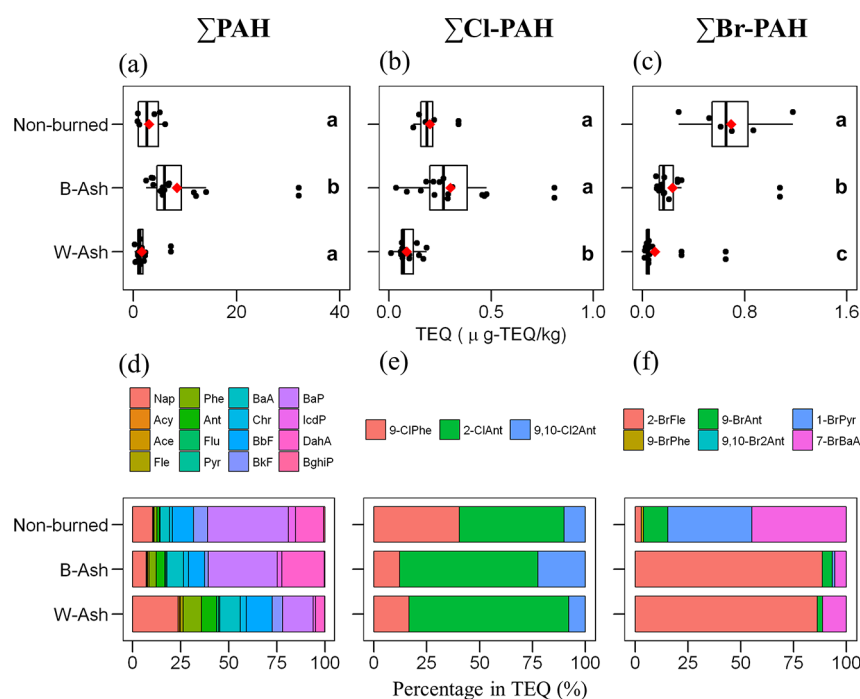


Figure 4. Toxic equivalency quotient (TEQ, in μg of TEQ/kg, mean \pm standard deviation) and percentage contributions (%) of different compounds to the toxic equivalency quotients (TEQs) of (a, d) $\Sigma_{16}\text{PAH}$, (b, e) $\Sigma_3\text{Cl-PAH}$, and (c, f) $\Sigma_6\text{Br-PAH}$ in nonburned soils, black ash (B-Ash), and white ash (W-Ash) samples at sites 1–5. In panels a–c, the mean value at each box is labeled as the red diamond and different letters in each subfigure indicate significant difference with $p \leq 0.05$. Abbreviations for PAHs are available in Table 1.

higher than B-Ash ($43.9 \pm 15.9\%$; $p = 0.006$), but did not differ with W-Ash ($57.4 \pm 21.8\%$; $p = 0.19$) (Figure 2d and Table S4). According to the Estimation Programs Interface (EPI Suite, U.S. Environmental Protection Agency (EPA)),⁵¹ the water solubility at 25 °C is 142.1 mg/L for Nap, which is 50 times higher than the other 15 regulated PAHs (Table S1). We detected its existence in both the water extractions of ash (including both B-Ash and W-Ash) and natural river waters of the burned watershed following the Rim Fire (Tables S5–S6). Phe accounted for $11.4 \pm 3.6\%$ of $\Sigma_{16}\text{PAH}$ in nonburned soils, and this percentage was significantly lower ($p < 0.001$) than those in B-Ash ($28.8 \pm 7.8\%$) and W-Ash ($26.4 \pm 14.9\%$). This indicates that the size of the aromatic structure for PAHs followed B-Ash > W-Ash > nonburned soils. The $\Sigma_{16}\text{PAH}$ concentrations in both nonburned and burned samples were dominated by low-molecular-weight (LMW) PAHs (<4 rings) (Figure S1). The molar ratio of LMW PAHs to $\Sigma_{16}\text{PAH}$ was 0.95 ± 0.03 , 0.94 ± 0.03 , and 0.97 ± 0.02 for nonburned soils, B-Ash and W-Ash, respectively. This is consistent with previous studies^{10,11} reporting the domination of LMW PAHs, particularly naphthalene, in burned soil and wildfire ash. For example, Choi¹¹ reported that the $\Sigma_{16}\text{PAH}$ concentration in burned pine bark and litter samples was dominated by Nap (76% and 44%, respectively), followed by Phe and fluoranthene (Flu). It is notable that soils after wildfire contained a high percentage of LMW PAHs, which are expected to be lost via volatilization during the wildfire. Choi¹¹ attributed the high percentage of LMW PAHs after wildfire to the charcoal structure of the burned detritus/ash, which can capture the gaseous and particulate phases of PAHs. The high LMW PAH concentrations in the nonburned soils may result from historic PAH accumulation associated with past wildfires in this fire-prone region.

Similar to $\Sigma_{16}\text{PAH}$, the profiles of both $\Sigma_3\text{Cl-PAH}$ and $\Sigma_6\text{Br-PAH}$ were altered by wildfire. After wildfire, the dominance of $\Sigma_3\text{Cl-PAH}$ shifted from 9-chlorophenanthrene (9-ClPhe) to 2-ClAnt (Figure 2e). Specifically, 9-ClPhe accounted for $69.2 \pm 11.2\%$ of $\Sigma_3\text{Cl-PAH}$ in nonburned soils and significantly decreased to $28.6 \pm 21.4\%$ in B-Ash ($p = 0.004$) and $31.0 \pm 27.3\%$ in W-Ash ($p = 0.004$). Nonburned soils contained $27.4 \pm 9.5\%$ 2-ClAnt in the $\Sigma_3\text{Cl-PAH}$ fraction, and this percentage increased to $56.0 \pm 20.4\%$ for B-Ash ($p = 0.05$) and $64.8 \pm 29.9\%$ for W-Ash ($p = 0.007$). Regarding Br-PAHs, the percentages of 9-BrAnt and 1-BrPyr decreased ($p \leq 0.002$) while the percentage of 2-BrFle increased ($p \leq 0.002$) after wildfire (Table S4). Specifically, nonburned soils were dominated by 9-bromoanthracene (9-BrAnt; $43.9 \pm 27.0\%$) and 1-bromopyrene (1-BrPyr; $45.5 \pm 28.8\%$) (Figure 2f). However, the dominant Br-PAH in the burned soils was 2-BrFle, accounting for $89.7 \pm 12.4\%$ of $\Sigma_6\text{Br-PAHs}$ in B-Ash and $93.6 \pm 7.9\%$ in W-Ash. The percentages of these three Br-PAHs showed no significant difference ($p = 0.44$ for 9-BrAnt; $p = 0.45$ for 1-BrPyr; $p = 0.40$ for 2-BrFle) between B-Ash and W-Ash, indicating a negligible effect of burn intensity. Previous studies attributed equilibrium between soil and gas phases to explain the profiles of XPAHs.^{23,52} Jin et al.⁵² investigated emissions from copper smelters and found that Cl-PAHs and Br-PAHs with higher molecular weights and lower vapor pressures had a higher abundance in soils than in stack gases. Wang et al.²³ reported 9-ClPhe and 9-BrPh were dominant in the gaseous phase while 1-ClPyr and 1-BrPyr were present in both the gaseous and particulate phases generated from waste incineration. However, the distribution of XPAH congeners in soils before and after wildfire in this study cannot be explained by this equilibrium mechanism. While the gas–solid phase equilibrium process may be involved, it appears that formation and/or degradation

processes are also involved in regulating XPAH dynamics during wildfires.

3.3. TEQs of PAHs and XPAHs. The TEQ variations of PAHs and XPAHs among sample types were similar to their concentration variations. A moderate degree of burning (B-Ash) increased the toxicity of PAHs in soils, but the high degree of burning (W-Ash) did not cause increased toxicity. The TEQs of $\sum_{16}\text{PAH}$ were $3.1 \pm 2.3 \mu\text{g/kg}$ in nonburned samples, $8.5 \pm 7.3 \mu\text{g/kg}$ in B-Ash, and $1.7 \pm 1.7 \mu\text{g/kg}$ in W-Ash (Figure 4a). The average TEQs for B-Ash were significantly higher than for nonburned soils ($p = 0.006$) and W-Ash ($p < 0.001$), while the difference between W-Ash and nonburned soils was not significant ($p = 0.22$). High intensity burning favored a decrease of $\sum_3\text{Cl-PAH}$ TEQs in soils, whereas moderate intensity burning did not change the toxicity significantly. The $\sum_3\text{Cl-PAH}$ TEQs were significantly lower in W-Ash ($0.09 \pm 0.05 \mu\text{g/kg}$) compared to both nonburned samples ($0.20 \pm 0.08 \mu\text{g/kg}$; $p = 0.02$) and B-Ash ($0.30 \pm 0.19 \mu\text{g/kg}$; $p < 0.001$) (Figure 4b). In addition, the $\sum_3\text{Cl-PAH}$ TEQs were not significantly different between nonburned soils and B-Ash ($p = 0.54$). Horii et al.²² estimated that the TEQs from Cl-PAHs were <0.0003 to $104 \mu\text{g/kg}$ in fly ash and <0.00003 to $0.7 \mu\text{g/kg}$ in bottom ash from waste incinerators in South Korea. In contrast to $\sum_3\text{Cl-PAH}$ TEQs, both moderate and high intensity burning significantly reduced the toxicity of Br-PAHs in burned soils. The $\sum_6\text{Br-PAH}$ TEQs were lower in W-Ash ($0.10 \pm 0.17 \mu\text{g/kg}$) compared with nonburned soils ($0.69 \pm 0.31 \mu\text{g/kg}$; $p < 0.001$) and B-Ash ($0.24 \pm 0.24 \mu\text{g/kg}$; $p = 0.005$) (Figure 4c). In addition, the $\sum_6\text{Br-PAH}$ TEQs was lower in B-Ash compared with nonburned soils ($p = 0.04$). The TEQs for XPAHs were lower compared with values reported from waste incinerations. Wang et al.²³ reported TEQs for XPAHs were 0.0541 – $101 \mu\text{g/kg}$ in fly ash and 0.000914 – $2.00 \mu\text{g/kg}$ in bottom ash from waste incinerators in Japan. Our study shows XPAHs were not a major contributor to the TEQ compared with PAHs.²⁴

The major contributor to the $\sum_{16}\text{PAH}$ TEQs was BaP (with 5 rings), followed with dibenzo[*a,h*]anthracene (DahA; with 5 rings). BaP is considered as carcinogenic to humans (Group 1) based on strong and consistent evidence in both humans and animals.⁵³ It contributed to $42.0 \pm 11.8\%$ of the $\sum_{16}\text{PAHs}$ TEQs in nonburned samples, $35.8 \pm 6.9\%$ in B-Ash, and $15.9 \pm 15.3\%$ in W-Ash (Figure 4d). Both nonburned soils ($p < 0.001$) and B-Ash ($p < 0.001$) had a higher BaP percentage than W-Ash, while this percentage was not significantly different between nonburned soils and W-Ash ($p = 0.53$) (Table S6). DahA is considered as probably carcinogenic to humans (Group 2A) because of evidence from animals; no data for humans are available.⁵³ It accounted for $14.4 \pm 22.3\%$ of the $\sum_{16}\text{PAH}$ TEQs in nonburned soils, $21.9 \pm 16.1\%$ for B-Ash, and $4.6 \pm 17.7\%$ for W-Ash. B-Ash had a significantly higher percentage of DahA TEQ compared to W-Ash ($p = 0.004$).

High-molecular-weight (HMW) PAHs were the major contributor to the $\sum_{16}\text{PAH}$ TEQs, although $\sum_{16}\text{PAHs}$ were dominated by low-molecular-weight (LMW) PAHs (Figures S1–2). Considering the number of aromatic rings, the 5-ring PAHs contributed to $60.2 \pm 15.7\%$ of the $\sum_{16}\text{PAH}$ TEQs in nonburned soils compared to $60.2 \pm 11.4\%$ in B-Ash and $21.8 \pm 23.1\%$ in W-Ash, while the percentages by 4-ring PAHs were $24.7 \pm 8.1\%$, $21.9 \pm 5.0\%$, and $33.2 \pm 14.0\%$, respectively (Figure S2). This is consistent with previous studies.^{33,54} For example, Blomqvist et al.⁵⁴ found HMW PAHs, especially BaP

and DahA, were the major contributors to toxicity of $\sum_{16}\text{PAH}$, although LMW PAHs were dominant in the $\sum_{16}\text{PAH}$ following fire. Ding et al.³³ concluded that 94% of the $\sum_{16}\text{PAH}$ TEQs in rice was from eight HMW PAHs accounting for less than 4% of the $\sum_{16}\text{PAH}$ concentration. The PAHs with 4–5 rings are likely more toxic than those with 2–3 rings and thus more concern should be placed on highly toxic PAH congeners from an environmental–human health perspective.

The major contributor to $\sum_3\text{Cl-PAH}$ TEQs was 2-ClAnt (with 3 rings) in all three sample types in this study. The highest contribution to $\sum_3\text{Cl-PAH}$ TEQs in nonburned samples was $49.6 \pm 13.7\%$ from 2-ClAnt followed by $40.4 \pm 15.3\%$ from 9-ClPhe (Figure 4e). The TEQ percentage of 2-ClAnt increased to $65.4 \pm 22.2\%$ in B-Ash ($p = 0.11$) and to $75.6 \pm 30.7\%$ in W-Ash ($p = 0.01$), while the TEQ percentage of 9-ClPhe decreased to $12.1 \pm 10.9\%$ in B-Ash ($p = 0.005$) and $16.6 \pm 25.5\%$ in W-Ash ($p = 0.004$). In addition, 9-ClPhe and 2-ClAnt TEQs showed no significant difference in TEQ percentage contribution between B-Ash and W-Ash ($p = 0.54$). The dominant Br-PAH in the $\sum_6\text{Br-PAH}$ TEQs shifted from 7-bromobenz[*a*]anthracene (7-BrBaA; with 4 rings) to 2-BrFle (with 2 rings) following wildfire. Among the six identified Br-PAHs, 7-BrBaA was the major contributor to the $\sum_6\text{Br-PAH}$ TEQs in nonburned samples ($44.7 \pm 12.4\%$). However, the major contributor to $\sum_6\text{Br-PAH}$ TEQs was 2-BrFle in burned samples, accounting for $88.5 \pm 21.9\%$ in B-Ash and $86.3 \pm 28.0\%$ in W-Ash (Figure 4f). That is, after wildfire, the percentage contributions in the $\sum_6\text{Br-PAH}$ TEQs were reduced for 7-BrBaA ($p \leq 0.001$) but increased for 2-BrFle ($p \leq 0.01$). These TEQs showed no significant difference between B-Ash and W-Ash ($p > 0.50$).

4. CONCLUSIONS

Wildfire has been considered as an important PAH source, and increased soil PAH concentrations were frequently reported immediately after wildfires.^{7,9} However, the uneven burn intensity across the landscape could affect the soil PAH concentrations immediately after wildfires. Evaluating soil PAH concentrations as a function of fire intensity is important because PAHs in soils can be readily transported by runoff/erosion into aquatic environments and thus affect drinking water safety. Our study demonstrated that both the occurrence and profiles of PAHs and XPAHs were altered by burn intensity. Specifically, the $\sum_{16}\text{PAH}$ concentrations in moderately burned soils were significantly higher than those in nonburned soils and severely burned soils. By implication, although soil PAH concentration increases immediately after wildfires, we can expect much higher concentrations and potential toxicity in moderately burned soils compared with more severely burned soils. Therefore, burn intensity should be evaluated as an important factor when considering potential aquatic ecosystem/drinking water contamination by soil PAH concentrations after wildfires. In addition to wildfires, this study provides important information for prescribed fire practices, which are currently being employed as a fuel reduction practice worldwide to reduce fuel loads and the intensity of future wildfires. The $\sum_3\text{Cl-PAH}$ and $\sum_6\text{Br-PAH}$ concentrations were not elevated after wildfire at either moderate or severe burning intensities, indicating that wildfire is not a significant source of soil XPAHs. Furthermore, inconsistent correlation results among XPAHs and PPAHs and changes of XPAHs after thermal treatments suggest that the mechanisms for XPAH generation require further investiga-

tion. Future studies examining controlling factors and mechanisms are required to better understand and potentially reduce XPAH formation.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.8b00101.

Percentages of the concentration and TEQ of PAHs with different aromatic rings; properties of the studied PAHs and XPAHs; PAH concentrations in nonburned and burned forest samples reported in previous studies; linear relationship between XPAHs and PPAHs; percentage differences in concentration and TEQ of PAHs and XPAHs among nonburned soils, B-ash, and W-ash; PAH levels in the 1:5 (w/v) water extracts and natural river waters (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*(H.Z.) E-mail: zengh@pkusz.edu.cn.

*(J.-J.W.) E-mail: wangjj@sustc.edu.cn.

ORCID

Huan Chen: 0000-0001-9998-1205

Alex T. Chow: 0000-0001-7441-8934

Jun-Jian Wang: 0000-0002-3040-0924

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The project described in this work was supported by the National Institute of Food and Agriculture, United States Department of Agriculture (Grant SCN-2013-02784). Additional supports were provided by the Natural Sciences Foundation of China (Grant 41807360), Southern University of Science and Technology (Grant G01296001), and Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control (Grant 2017B030301012).

■ REFERENCES

- (1) Westerling, A. L.; Hidalgo, H. G.; Cayan, D. R.; Swetnam, T. W. Warming and earlier spring increase western US forest wildfire activity. *Science* **2006**, *313* (5789), 940–943.
- (2) Westerling, A. L. Increasing western US forest wildfire activity: Sensitivity to changes in the timing of spring. *Philos. Trans. R. Soc., B* **2016**, *371* (1696), 20150178.
- (3) Scholze, M.; Knorr, W.; Arnell, N. W.; Prentice, I. C. A climate-change risk analysis for world ecosystems. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (35), 13116–13120.
- (4) O’Laughlin, J. Conceptual model for comparative ecological risk assessment of wildfire effects on fish, with and without hazardous fuel treatment. *For. Ecol. Manage.* **2005**, *211* (1–2), 59–72.
- (5) Thompson, M. P.; Calkin, D. E.; Finney, M. A.; Ager, A. A.; Gilbertson-Day, J. W. Integrated national-scale assessment of wildfire risk to human and ecological values. *Stoch Env Res. Risk A* **2011**, *25* (6), 761–780.
- (6) Miller, C.; Ager, A. A. A review of recent advances in risk analysis for wildfire management. *Int. J. Wildland Fire* **2013**, *22* (1), 1–14.
- (7) Simon, E.; Choi, S. D.; Park, M. K. Understanding the fate of polycyclic aromatic hydrocarbons at a forest fire site using a conceptual model based on field monitoring. *J. Hazard. Mater.* **2016**, *317*, 632–639.
- (8) Placha, D.; Raclavska, H.; Matysek, D.; Rummeli, M. H. The polycyclic aromatic hydrocarbon concentrations in soils in the Region of Valasske Mezirici, the Czech Republic. *Geochem. Trans.* **2009**, *10*, 12.
- (9) Vergnoux, A.; Malleret, L.; Asia, L.; Doumenq, P.; Theraulaz, F. Impact of forest fires on PAH level and distribution in soils. *Environ. Res.* **2011**, *111* (2), 193–198.
- (10) Kim, E. J.; Choi, S. D.; Chang, Y. S. Levels and patterns of polycyclic aromatic hydrocarbons (PAHs) in soils after forest fires in South Korea. *Environ. Sci. Pollut. Res.* **2011**, *18* (9), 1508–1517.
- (11) Choi, S.-D. Time trends in the levels and patterns of polycyclic aromatic hydrocarbons (PAHs) in pine bark, litter, and soil after a forest fire. *Sci. Total Environ.* **2014**, *470-471*, 1441–1449.
- (12) Shen, H. Z.; Huang, Y.; Wang, R.; Zhu, D.; Li, W.; Shen, G. F.; Wang, B.; Zhang, Y. Y.; Chen, Y. C.; Lu, Y.; Chen, H.; Li, T. C.; Sun, K.; Li, B. G.; Liu, W. X.; Liu, J. F.; Tao, S. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ. Sci. Technol.* **2013**, *47* (12), 6415–6424.
- (13) Carlson, D. J.; Reich, P. B.; Frelich, L. E. Fine-scale heterogeneity in overstory composition contributes to heterogeneity of wildfire severity in southern boreal forest. *J. For. Res.* **2011**, *16* (3), 203–214.
- (14) Smith, A. M. S.; Hudak, A. T. Estimating combustion of large downed woody debris from residual white ash. *Int. J. Wildland Fire* **2005**, *14* (3), 245–248.
- (15) Hudak, A. T.; Ottmar, R. D.; Vihnanek, R. E.; Brewer, N. W.; Smith, A. M. S.; Morgan, P. The relationship of post-fire white ash cover to surface fuel consumption. *Int. J. Wildland Fire* **2013**, *22* (6), 780–785.
- (16) Wang, J. J.; Dahlgren, R. A.; Ersan, M. S.; Karanfil, T.; Chow, A. T. Wildfire altering terrestrial precursors of disinfection byproducts in forest detritus. *Environ. Sci. Technol.* **2015**, *49* (10), 5921–5929.
- (17) Goforth, B. R.; Graham, R. C.; Hubbert, K. R.; Zanner, C. W.; Minnich, R. A. Spatial distribution and properties of ash and thermally altered soils after high-severity forest fire, southern California. *Int. J. Wildland Fire* **2005**, *14* (4), 343–354.
- (18) Bodi, M. B.; Mataix-Solera, J.; Doerr, S. H.; Cerda, A. The wettability of ash from burned vegetation and its relationship to Mediterranean plant species type, burn severity and total organic carbon content. *Geoderma* **2011**, *160* (3–4), 599–607.
- (19) Woods, S. W.; Balfour, V. N. The effect of ash on runoff and erosion after a severe forest wildfire, Montana, USA. *Int. J. Wildland Fire* **2008**, *17* (5), 535–548.
- (20) Sun, J. L.; Zeng, H.; Ni, H. G. Halogenated polycyclic aromatic hydrocarbons in the environment. *Chemosphere* **2013**, *90* (6), 1751–1759.
- (21) Wang, D. L.; Xu, X. B.; Chu, S. G.; Zhang, D. Analysis and structure prediction of chlorinated polycyclic aromatic hydrocarbons released from combustion of polyvinylchloride. *Chemosphere* **2003**, *53* (5), 495–503.
- (22) Horii, Y.; Ok, G.; Ohura, T.; Kannan, K. Occurrence and profiles of chlorinated and brominated polycyclic aromatic hydrocarbons in waste incinerators. *Environ. Sci. Technol.* **2008**, *42* (6), 1904–1909.
- (23) Wang, Q.; Miyake, Y.; Tokumura, M.; Amagai, T.; Horii, Y.; Nojiri, K.; Ohtsuka, N. Effects of characteristics of waste incinerator on emission rate of halogenated polycyclic aromatic hydrocarbon into environments. *Sci. Total Environ.* **2018**, *625*, 633–639.
- (24) Tue, N. M.; Goto, A.; Takahashi, S.; Itai, T.; Asante, K. A.; Nomiyama, K.; Tanabe, S.; Kunisue, T. Soil contamination by halogenated polycyclic aromatic hydrocarbons from open burning of e-waste in Agbogbloshie (Accra, Ghana). *J. Mater. Cycles Waste Manage.* **2017**, *19* (4), 1324–1332.
- (25) Ma, J.; Horii, Y.; Cheng, J. P.; Wang, W. H.; Wu, Q.; Ohura, T.; Kannan, K. Chlorinated and parent polycyclic aromatic hydrocarbons in environmental samples from an electronic waste recycling facility and a chemical industrial complex in China. *Environ. Sci. Technol.* **2009**, *43* (3), 643–649.

- (26) Knipping, E. M.; Dabdub, D. Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environ. Sci. Technol.* **2003**, *37* (2), 275–284.
- (27) Zhang, M. M.; Buekens, A.; Li, X. D. Brominated flame retardants and the formation of dioxins and furans in fires and combustion. *J. Hazard. Mater.* **2016**, *304*, 26–39.
- (28) Fernando, S.; Jobst, K. J.; Taguchi, V. Y.; Helm, P. A.; Reiner, E. J.; McCarry, B. E. Identification of the halogenated compounds resulting from the 1997 Plastimet Inc. Fire in Hamilton, Ontario, using comprehensive two-dimensional gas chromatography and (ultra)high resolution mass spectrometry. *Environ. Sci. Technol.* **2014**, *48* (18), 10656–10663.
- (29) Wang, J. J.; Dahlgren, R. A.; Ersan, M. S.; Karanfil, T.; Chow, A. T. Temporal variations of disinfection byproduct precursors in wildfire detritus. *Water Res.* **2016**, *99*, 66–73.
- (30) Bodi, M. B.; Martin, D. A.; Balfour, V. N.; Santin, C.; Doerr, S. H.; Pereira, P.; Cerda, A.; Mataix-Solera, J. Wild land fire ash: Production, composition and eco-hydro-geomorphic effects. *Earth-Sci. Rev.* **2014**, *130*, 103–127.
- (31) Cilimburg, A. C.; Short, K. C. Rating the severity of fire in forest soils. *Forest fire in the U. S. Northern Rockies: A primer*, <http://www.northernrockiesfire.org/effects/soilrate.htm>, 2005.
- (32) Ni, H. G.; Guo, J. Y. Parent and halogenated polycyclic aromatic hydrocarbons in seafood from south China and implications for human exposure. *J. Agric. Food Chem.* **2013**, *61* (8), 2013–2018.
- (33) Ding, C.; Ni, H. G.; Zeng, H. Parent and halogenated polycyclic aromatic hydrocarbons in rice and implications for human health in China. *Environ. Pollut.* **2012**, *168*, 80–86.
- (34) Sun, J. L.; Wang, Y. B.; Zeng, H.; Ni, H. G. Parent and halogenated polycyclic aromatic hydrocarbons in farmed cockroaches and implications for human exposure. *Ecotoxicol. Environ. Saf.* **2015**, *111*, 256–262.
- (35) Wang, J. J.; Dahlgren, R. A.; Chow, A. T. Controlled burning of forest detritus altering spectroscopic characteristics and chlorine reactivity of dissolved organic matter: Effects of temperature and oxygen availability. *Environ. Sci. Technol.* **2015**, *49* (24), 14019–14027.
- (36) Campo, J.; Lorenzo, M.; Cammeraat, E. L. H.; Pico, Y.; Andreu, V. Emerging contaminants related to the occurrence of forest fires in the Spanish Mediterranean. *Sci. Total Environ.* **2017**, *603-604*, 330–339.
- (37) Majidzadeh, H.; Wang, J. J.; Chow, A. T., Prescribed fire alters dissolved organic matter and disinfection by-product precursors in forested watersheds - Part I. A controlled laboratory study. *Recent Advances in Disinfection By-Products*; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2015; Vol. 1190, pp 271–292, DOI: 10.1021/bk-2015-1190.ch015.
- (38) Simoneit, B. R. Biomarker PAHs in the environment. *PAHs and Related Compounds*, Part I; The Handbook of Environmental Chemistry, Vol. 3; Springer-Verlag: Berlin, 1998; pp 175–221.
- (39) Keiluweit, M.; Kleber, M.; Sparrow, M. A.; Simoneit, B. R. T.; Prah, F. G. Solvent-extractable polycyclic aromatic hydrocarbons in biochar: Influence of pyrolysis temperature and feedstock. *Environ. Sci. Technol.* **2012**, *46* (17), 9333–9341.
- (40) Watanabe, M.; Noma, Y. Influence of combustion temperature on formation of nitro-PAHs and decomposition and removal behaviors in pilot-scale waste incinerator. *Environ. Sci. Technol.* **2009**, *43* (7), 2512–2518.
- (41) Zhang, H. F.; Hu, D. W.; Chen, J. M.; Ye, X. N.; Wang, S. X.; Hao, J. M.; Wang, L.; Zhang, R. Y.; An, Z. S. Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning. *Environ. Sci. Technol.* **2011**, *45* (13), 5477–5482.
- (42) Molto, J.; Font, R.; Galvez, A.; Munoz, M.; Pequenin, A. Emissions of polychlorodibenzodioxin/furans (PCDD/Fs), dioxin-like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and volatile compounds produced in the combustion of pine needles and cones. *Energy Fuels* **2010**, *24* (2), 1030–1036.
- (43) Menzie, C. A.; Potocki, B. B.; Santodonato, J. Exposure to carcinogenic PAHs in the environment. *Environ. Sci. Technol.* **1992**, *26* (7), 1278–1284.
- (44) Falay, E. O.; Altio, A.; Kara, M.; Dumanoglu, Y.; Bayram, A.; Tolunay, D.; Elbir, T.; Odabasi, M. Spatial variation of polycyclic aromatic hydrocarbons (PAHs) in air, soil and tree components in Iskenderun industrial region, Turkey. *Int. J. Chem., Environ. Biol. Sci. (IJCEBS)* **2013**, *1*, 263–267.
- (45) Xiao, Y. H.; Tong, F. C.; Kuang, Y. W.; Chen, B. F. Distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in forest soils from urban to rural areas in the Pearl River Delta of southern China. *Int. J. Environ. Res. Public Health* **2014**, *11* (3), 2642–2656.
- (46) Ohura, T.; Sawada, K. I.; Amagai, T.; Shinomiya, M. Discovery of novel halogenated polycyclic aromatic hydrocarbons in urban particulate matters: Occurrence, photostability, and AhR activity. *Environ. Sci. Technol.* **2009**, *43* (7), 2269–2275.
- (47) Lobert, J. M.; Keene, W. C.; Logan, J. A.; Yevich, R. Global chlorine emissions from biomass burning: Reactive chlorine emissions inventory. *J. Geophys. Res.-Atmos* **1999**, *104* (D7), 8373–8389.
- (48) Burling, I. R.; Yokelson, R. J.; Griffith, D. W. T.; Johnson, T. J.; Veres, P.; Roberts, J. M.; Warneke, C.; Urbanski, S. P.; Reardon, J.; Weise, D. R.; Hao, W. M.; de Gouw, J. Laboratory measurements of trace gas emissions from biomass burning of fuel types from the southeastern and southwestern United States. *Atmos. Chem. Phys.* **2010**, *10* (22), 11115–11130.
- (49) Kakimoto, K.; Nagayoshi, H.; Konishi, Y.; Kajimura, K.; Ohura, T.; Hayakawa, K.; Toriba, A. Atmospheric chlorinated polycyclic aromatic hydrocarbons in East Asia. *Chemosphere* **2014**, *111*, 40–46.
- (50) Takasuga, T.; Umetsu, N.; Makino, T.; Tsubota, K.; Sajwan, K. S.; Kumar, K. S. Role of temperature and hydrochloric acid on the formation of chlorinated hydrocarbons and polycyclic aromatic hydrocarbons during combustion of paraffin powder, polymers, and newspaper. *Arch. Environ. Contam. Toxicol.* **2007**, *53* (1), 8–21.
- (51) U.S. EPA. *Estimation Programs Interface Suite for Microsoft Windows*, v 4.11; United States Environmental Protection Agency: Washington, DC, USA, 2015.
- (52) Jin, R.; Liu, G. R.; Zheng, M. H.; Jiang, X. X.; Zhao, Y. Y.; Yang, L. L.; Wu, X. L.; Xu, Y. Secondary copper smelters as sources of chlorinated and brominated polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2017**, *51* (14), 7945–7953.
- (53) EPA. *Integrated risk information system (IRIS)*; Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, United States Environmental Protection Agency: Cincinnati, OH, USA, 1995.
- (54) Blomqvist, P.; McNamee, M. S.; Andersson, P.; Lonnermark, A. Polycyclic aromatic hydrocarbons (PAHs) quantified in large-scale fire experiments. *Fire Technol.* **2012**, *48* (2), 513–528.