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Metal Reactivity in Laboratory Burned Wood from a Watershed Affected by Wildfires

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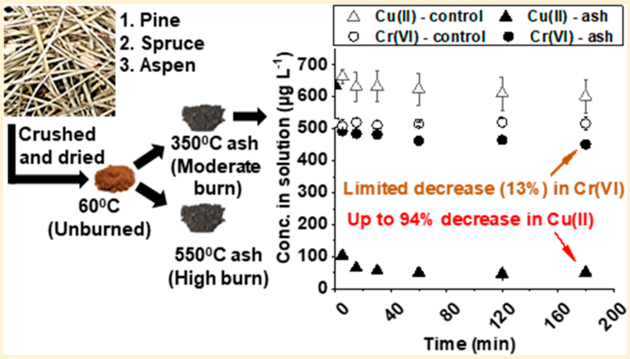
Supporting Information



ABSTRACT: We investigated interfacial processes affecting metal mobility by wood ash under laboratory-controlled conditions using aqueous chemistry, microscopy, and spectroscopy. The Valles Caldera National Preserve in New Mexico experiences catastrophic wildfires of devastating effects. Wood samples of Ponderosa Pine, Colorado Blue Spruce, and Quaking Aspen collected from this site were exposed to temperatures of 60, 350, and 550 °C. The 350 °C Pine ash had the highest content of Cu (4997 ± 262 mg kg^{-1}), Cr (543 ± 124 mg kg^{-1}), and labile dissolved organic carbon (DOC, 11.3 ± 0.28 mg L^{-1}). Sorption experiments were conducted by reacting 350 °C Pine, Spruce, and Aspen ashes separately with 10 μM Cu(II) and Cr(VI) solutions. Up to a 94% decrease in Cu(II) concentration was observed in solution while Cr(VI) concentration showed a limited decrease (up to 13%) after 180 min of reaction. X-ray photoelectron spectroscopy (XPS) analyses detected increased association of Cu(II) on the near surface region of the reacted 350 °C Pine ash from the sorption experiments compared to the unreacted ash. The results suggest that dissolution and sorption processes should be considered to better understand the potential effects of metals transported by wood ash on water quality that have important implications for postfire recovery and response strategies.

INTRODUCTION

Postfire storm events in watersheds can cause the transport of wood ash into nearby streams which has detrimental impacts on water quality. In the United States, the forests in the southwestern regions have seen increased occurrences of large intensity wildfires because of worldwide effects of climate change.[1−3] The Valles Caldera National Preserve (VALL) in north central New Mexico is an example of a site with frequent wildfire activity in recent years.[4] For example, the following two major wildfires have affected the VALL watershed since 2011: (1) the Thompson Ridge wildfire burned 23 965 acres in VALL in 2013,[5] and (2) the catastrophic Las Conchas, one of the largest in New Mexico history, burned over 156 000 acres in the Jemez Mountains in 2011.[6] Postfire runoff of debris and ash in the Rio Grande river, following thunderstorms over the burned area, caused turbidity peaks of over 1000 NTU, sags in dissolved oxygen (DO), and fluctuations in pH (7.5 to 9).[7] Total concentrations of Al and Cu in the Rio Grande following the Las Conchas fire were above the aquatic life criterion for both metals.[8] Additionally, postfire runoff caused transport of organic matter and nutrients (6× background levels for NO_3−

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N and 100× background levels for PO_4) with debris and ash in the VALL, which substantially affected the quality of water supplied to nearby communities.[7,9] Information on the composition and reactivity of metals associated with wood ash is important to better understand the potential impacts on water quality.

While previous studies have characterized metals and organic matter in ash and soil,[10−13] the specific mechanisms controlling postfire metal mobilization remain poorly understood. Elevated concentrations of metals have been observed in sediments and surface water in fire-affected watersheds, for several months after the fire events.[1,14−17] Recent studies have linked water extractable organic matter (WEOM) from burned soil[10,18] and ash[19] to the formation of disinfection byproducts (DBPs).[20,21] Temperature is a particularly important factor that affects the elemental composition and mineralogy of wood ash.[22−24] For example, a previous study from our group identified the presence of Ca, Mg, Al, Fe, and Mn as metal bearing carbonate and oxide phases in wood ash burned at 550 °C.[12] Results from laboratory batch experiments suggested that these metal-bearing phases are readily water-soluble, but the readsorption of these metals to ash can occur in later times of the experiments.[12] Although this study provides valuable insights into the presence of metal bearing phases in ash and their potential effects on metal readsorption, the knowledge on the specific processes affecting metal dissolution and sorption in wood ash is still limited.

More mechanistic investigations have been reported in the literature related to reactivity of biochar, a material similar to wood ash in composition.[25,26] Biochar is a natural sorbent and is increasingly applied in environmental remediation of organic and inorganic contaminants.[27−29] The sorption of Cu(II) to organic functional groups of biochar in water can occur at pH below 7.[30] However, Cu-associated phases like azurite ($Cu_3(CO_3)_2(OH)_2$) and tenorite (CuO) precipitate within the biochar surface at pH higher than 7.[30] Sorption between positively charged ions and negatively charged biochar is an effective mechanism for immobilizing metals in soil.[29,31,32] The immobilization of Cr(VI) through biochar sorption is significantly reduced at pH 5 and above.[33−35] Enhanced mobility of oxyanions like As[36,37] and Sb[38] has been observed in biochar-treated soil. Similar mechanistic studies are necessary to better understand sorption, precipitation, and dissolution reactions facilitated by wood ash that can affect postfire metal mobility.

The main objective of this study is to investigate the interfacial processes affecting wood ash reactions with water by integrating laboratory experiments, spectroscopy, microscopy, and aqueous chemistry methods. Soil and surface water chemistry from burned areas of VALL provide environmental context for the study. The release of metals and dissolved organic carbon (DOC) was assessed in batch experiments reacting laboratory burned wood ash with water. Additional experiments were conducted to investigate sorption processes that affect ash−metal interactions. The focus of this study is to identify interfacial physical−chemical processes that have not been extensively studied in the existing wildfire literature. The results from this investigation have relevant implications for the improvement of postfire response in affected watersheds.

■ MATERIALS AND METHODS

Field Sampling and Ash Preparation. The East Fork Jemez River and the adjacent area were affected by the Las Conchas and Thompson Ridge wildfires in the past. There is a lack of information about metals in soils, water, and wood from the VALL. Water and soil sampling were done to assess the current availability of metals in this fire affected watershed. Wood was collected from an unburned area to experiment with laboratory burn temperatures. Additional details about sampling methods are provided in the Supporting Information. The description and coordinates of the sampling sites in Valles Caldera for wood, water, and soil samples are shown in Figure S1. The vegetation in the VALL is dominated by different species of Pine, Spruce, Aspen, and Oak.[39] Wood samples of Ponderosa Pine, Colorado Blue Spruce, and Quaking Aspen were collected from higher elevation mixed coniferous forest areas which have a fire disturbance history from Las Conchas and other fires.[12,40] This area in VALL is also densely forested which undergoes prescribed burns periodically and account for approximately 25% of the precipitation volume in the Caldera.[41] From this point on, we will call these tree species simply Pine, Spruce, and Aspen. The collected wood samples were crushed using a wood chipper (Sun Joe CJ601E). The crushed samples were ground to fine powders using a Powdertec 3090 sample mill and then oven-dried at 60 °C for 48 h before burning. The ground and dried samples for each tree were mixed in a container to homogenize the samples before burning. The homogenized samples were burned in a laboratory muffle furnace at 350 °C (moderate burn) and at 550 °C (high burn) for 4 h to prepare ash. Table S1 contains data on the mass of samples before and after burning.

Acid Digestion and Solution Chemistry Analyses. Wood samples were acid digested in triplicates ($n = 3$) at 95 °C for 4 h using Aqua Regia [2 mL of HNO_3 (67−70%) + 6 mL of HCl (34−37%), trace metal grade]. Following heating, acid extracts were diluted with 18 MΩ water to 50 mL. Processing of all aqueous samples (water, soil, and wood) for this study was done by filtering through a 0.45 μm filter, acidifying with 2% HNO_3, and refrigerating at 4 °C until further solution chemistry analyses. Inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 5300DV) was used for detection of concentrations of major elements (Ca, Mg, and K). Minor or trace elements were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, PerkinElmer NexION 300D). Both the ICP-OES and ICP-MS analyzed an internal indium standard and were calibrated using a 5-point calibration curve. The quality of the results was ensured with proper quality control and quality assurance standards. The detection limits for the ICP-OES and ICP-MS for specific elements are shown in Table S2. The DOC in these samples was measured using a Tekmar-Dohrmann Phoenix 8000 TOC Analyzer.

Batch Experiments for DOC Concentration and Metal Dissolution. For DOC dissolution experiments, batch reactors were operated in triplicates by reacting a 0.1 g sample of 60, 350, and 550 °C Pine, Spruce, and Aspen with 30 mL of 18 MΩ deionized water. Replicates ($n = 3$) were sampled at 0, 4, 24, and 72 h and were analyzed using a Tekmar-Dohrmann Phoenix 8000 TOC Analyzer, following the 5310-C persulfate-ultraviolet (UV) method.[42] For metal dissolution experiments, 0.1 g samples of 350 and 550 °C Pine ash were reacted with 30 mL of 18 mΩ water. Samples were collected at 5 min, 15 min, 30 min, 1 h, 2 h, and 3 h, centrifuged at 3000 rpm (1660g) for 15 min, and processed for further ICP analyses.

Batch Sorption Experiments of Cu(II) and Cr(VI) onto 350 °C Ash. Batch sorption experiments in triplicates were

Table 1. Elemental Content of Water (Sites 1 to 5) and Soil (Sites V1 to V3) Samples from the East Fork Jemez River within the Valle Grande Area in VALL[a]

				water elemental content ($\mu g\ L^{-1}$)				
site	pH	alkalinity ($mg\ L^{-1}$)	TOC ($mg\ C\ L^{-1}$)	Cu total	Cr total	Fe total	Zn total	Mn total
Site 1	7.17−8.44	30.5−42.0	0.80−2.00	2.81−16.7	BDL[b]−105	289−932	52.2−103	6.90−57.2
Site 2	7.11−8.06	31.0−38.3	1.60−10.8	5.44−37.4	BDL−8.20	465−2650	41.4−335	8.83−146
Site 3	6.55−7.66	24.1−43.8	4.00−10.3	7.93−23.4	BDL−48.4	38.2−677	57.4−352	1.58−39.2
Site 4	6.48−8.01	38.7−43.7	4.60−11.3	5.31−21.7	BDL−16.5	358−757	60.7−241	6.56−22.4
Site 5	6.48−7 0.97	33.8−40.9	3.20−11.0	BDL−25.2	BDL−11.5	331−948	72.8−135	BDL−44.4

soil sampling sites	soil elemental content ($mg\ kg^{-1}$)				
	Cu total	Cr total	Fe total	Zn total	Mn total
Site V1	59.4−86.9	10.9−35.3	7800−9620	13.0−38.5	219−319
Site V2	71.3−89.9	9.25−20.4	4980−9850	10.2−31.4	50.8−194
Site V3	44.2−261	11.0−17.2	5050−7940	14.9−37.9	92.7−139
Site V4 (high burn)	7.16−17.5	5.81−13.3	109−221	19.5−35.2	260−347
Site V5 (low burn)	5.97−18.6	4.96−15.2	86.4−190	22.2−54.2	179−344
Site V6 (unburned)	7.97−13.9	5.31−11.3	102−184	30.8−39.4	217−454

[a] Aqueous and soil elemental content was measured with ICP-OES and ICP-MS. Sites V4 to V6 contain soil samples from the hill slope of the Sierra de Los Valles dome located near the headwaters of the river. Ranges of concentrations (minimum to maximum) for each site are shown. [b] BDL = below detection limit.

conducted to investigate the effect of 350° Pine, Spruce, and Aspen ashes on mobilization of Cu(II) and Cr(VI) in water. We selected Cu(II) and Cr(VI) as examples of a cation that acts as a Lewis Acid (e.g., Cu) and an oxyanion (e.g., CrO_4^{2-}) that could negatively impact surface waters. Additionally, elevated concentrations of these metals were found in surface water following wildfire events near VALL.[8,43] Before the sorption experiments, ash samples were characterized by measuring Brunauer−Emmett−Teller (BET) specific surface area, zeta potential, and C, H, N, and O elemental contents (wt %). Detailed descriptions of these methods are in the Supporting Information. For the sorption experiments, stock solutions (1000 ppm) of Cr(IV) and Cu(II) were prepared by dissolving analytical grade (>99% purity) $K_2Cr_2O_7$ and $CuCl_2\cdot 2H_2O$ in 18 MΩ water. For the experiment, a 0.1 g sample of 350 °C Pine, Spruce, and Aspen ashes was reacted separately with 10 μM of Cu(II) and Cr(VI) stock solutions mixed in 50 mL of 18 MΩ water. The concentrations of Cu(II) and Cr(VI) were chosen to reflect maximum levels measured in water samples collected during storm events after the Cerro Grande fire.[43] The pH was adjusted to 7.0 ± 0.2 using 2% HNO_3. Control experiments were done at pH 7.0 ± 0.2 for Cu(II) and Cr(VI). Samples were collected at 0, 4, 24, and 72 h, centrifuged at 6000 rpm (6640*g*) for 3 min, and processed for further solution chemistry analyses using ICP-MS.

Solid Phase Analyses (SEM/EDX, EPMA, XRD, XPS). Solid phase analyses were performed on the unreacted and reacted 350 °C Pine ash from the batch sorption experiments by applying X-ray photoelectron spectroscopy (XPS), scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM/EDX), electron probe microanalysis (EPMA), and X-ray diffraction (XRD). Additional descriptions of these methods are in the Supporting Information.

Statistical Analysis. Univariate data analyses were performed using the statistical software R.[44] The statistical package in OriginPro[45] was used for principal component analysis (PCA). Due to the non-normality of the data, nonparametric tests for differences in acid extractable metal concentrations ($\log_{10}$ transformed to reduce skewness in distribution) were performed to differentiate among 3 tree species (Pine, Spruce, and Aspen) and among 3 temperatures (60, 350, and 550 °C). The Kruskal−Wallis test was performed to determine if the tree species and the temperatures differ significantly (defined as $p < 0.05$) with respect to metal concentrations ($\log_{10}$ transformed). Wilcoxon rank sum test was used to do pairwise comparisons of all the samples to test for significant differences between tree species and temperatures (defined as $p < 0.05$). PCA was performed to better understand the correlations among ash samples in triplicates with respect to acid extractable metal (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Si, Sr, Zn) concentrations for all tree species.

■ RESULTS AND DISCUSSION

Water Quality and Sediment Data from Valles Caldera. The presence of Cu, Cr, Fe, Zn, and Mn was observed in water from the wildfire affected East Fork Jemez River and in soils exposed to varying burn severities upslope from the East Fork Jemez River headwaters (Table 1). Maximum total concentrations of Cu (37.4 $\mu g\ L^{-1}$) and Fe (2650 $\mu g\ L^{-1}$) in the water samples collected from site 2 and Zn (352 $\mu g\ L^{-1}$) from site 3 were above the USEPA standards for acute or chronic exposure values for aquatic life in freshwater (Tables 1 and S3). Total Cr (105 $\mu g\ L^{-1}$) in the water samples collected from site 1 exceeded the USEPA standards for acute or chronic exposure for both Cr(III) (74 $\mu g\ L^{-1}$) and Cr(VI) (11 $\mu g\ L^{-1}$). In a 2001 study by the New Mexico Environment Department, Al, pH, DO, and turbidity in the East Fork Jemez river were listed as exceeding the Total Maximum Daily Load, while metals, such as Cu, Cr, and Zn, were found to be below the detection limit,[46,47] lower than found in this study. Average concentrations of major and trace elements ($mg\ kg^{-1}$) in nonanthropogenically affected soils in the US estimated by Burt et al.[48] (Table S3) were used to evaluate the metal concentrations in the soil samples collected along the river reaches. Iron (Fe) was the most abundant metal with concentrations ranging from 4980 to 9850 $mg\ kg^{-1}$. Copper (Cu) concentration in the collected soil samples from sites V1, V2, and V3 ranges from 44.2 to 261 $mg\ kg^{-1}$, higher than the average Cu concentration (24.7 $mg\ kg^{-1}$) of nonanthropogenic affected soils in the US (Table S3).

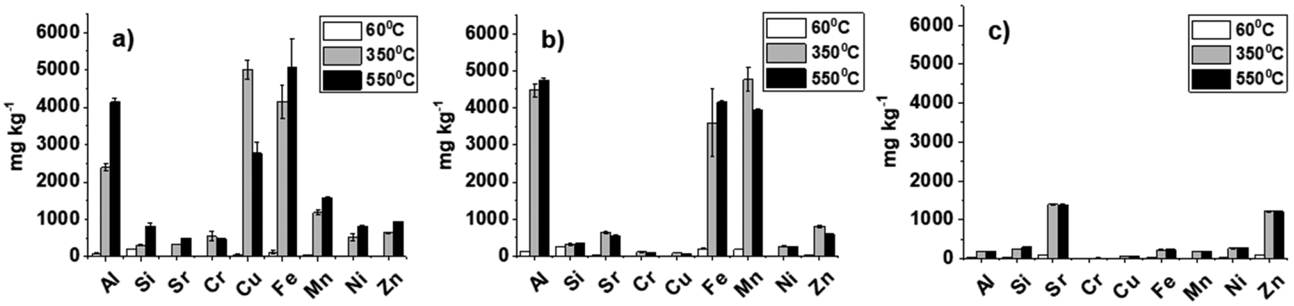


Figure 1. Acid extractable concentrations (mean ± SD) of 9 metals varied across different tree species of (a) Pine, (b) Spruce, and (c) Aspen. The major elements (Ca, Mg, and K) were predominant in all tree species at 60, 350, and 550 °C (Table S2). Ash produced at both 350 °C (moderate burn) and 550 °C (high burn) contained higher metal concentrations than in samples dried at 60 °C (unburned) for all species.

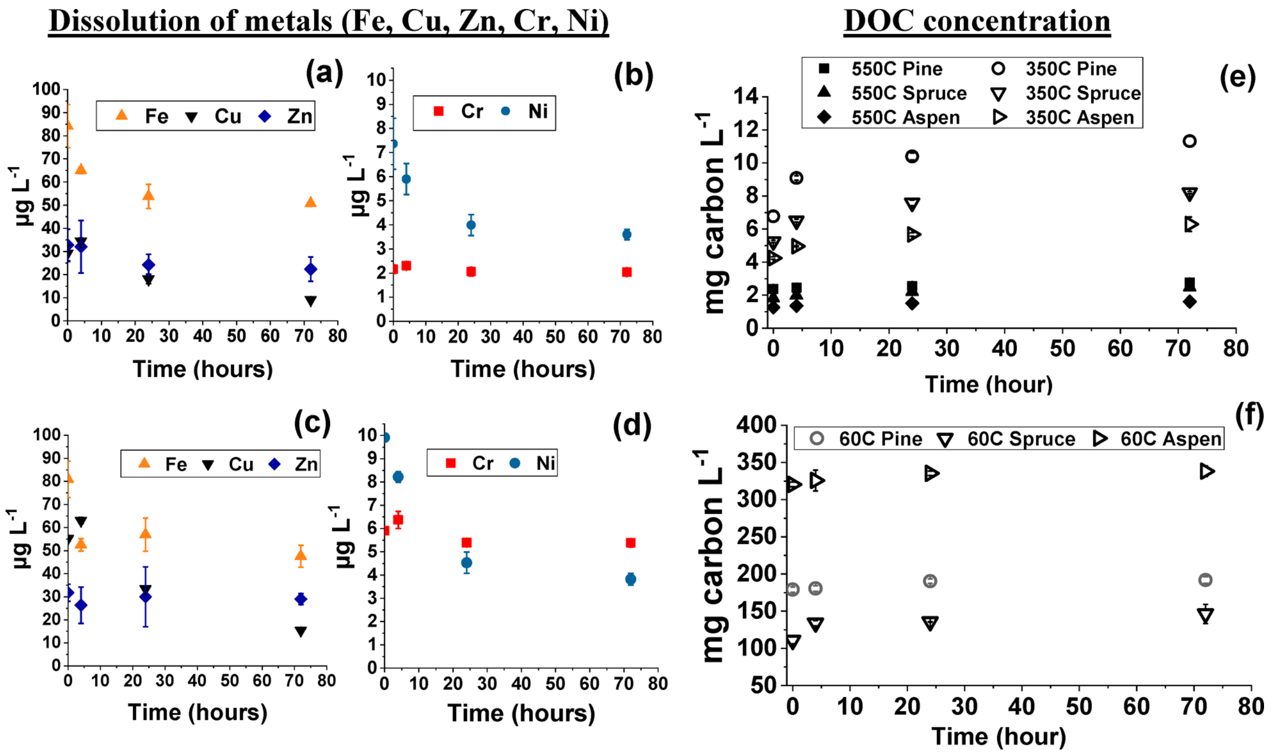


Figure 2. Concentrations of (a) Fe, Cu, and Zn and (b) Cr and Ni at 0, 4, 24, and 72 h in reaction of 550 °C Pine ash with 18 MΩ water. In (c) and (d), metal concentrations are shown for reaction of 350 °C Pine ash with 18 MΩ water. DOC concentration (mg carbon L^{-1}) at 0, 4, 24, and 72 h ($n = 3$) is shown in (e) for 350 and 550 °C ash samples and in (f) for 60 °C crushed wood samples.

Concentrations of Cu, Cr, and Fe were found lower in soils collected from high, low, and unburned sites of V4 to V6 (Table 1) compared to soil in the channel and banks of the East Fork Jemez River. The higher concentrations of metals in water and soil in a river located near a burned watershed, such as the East Fork Jemez, can increase from the addition of ash and debris by stormwater runoff. For example, after the Cerro Grande fire in 2000, elevated concentrations of total Cu (610 μg L^{-1}) and total Cr (510 μg L^{-1}) were measured in postfire runoff water samples collected from the burned watersheds near Guaje Canyon which is close to the Los Alamos National Laboratory.[43] Additional laboratory experiments were done to determine the concentrations of metals in oven-dried wood and ash and assess the reactivity of wood ash upon reaction with 18 MΩ water.

Acid Extractable Metal Content in Wood Exposed to 60, 350, and 550 °C. We compared the acid extractable metal contents in 9 samples (Pine, Spruce, and Aspen at 60, 350, and 550 °C, Figure 1, Table S4). Median metal concentrations at 350 °C (moderate burn) and 550 °C (high burn) for all tree species (e.g., Pine, Spruce, and Aspen) were significantly higher ($p < 0.05$, Tables S5 and S6) compared to oven-dried wood at 60 °C (unburned). The acid extractable metal concentrations for all samples at 60, 350, and 550 °C are shown in Table S4. Pairwise comparisons suggest that metal contents in oven-dried wood at 60 °C for Pine, Spruce, and Aspen were not significantly different from each other ($p > 0.05$, Tables S5 and S6). Among the ash samples at 350 and 550 °C, Pine and Aspen were significantly different ($p < 0.05$, Table S6) from each other with respect to acid extractable metal concentrations. Principal component analysis (PCA, Figure S2) suggests that 350 and 550 °C Pine ash samples were associated with high concentrations of most of the metals (Cu, Cr, Si, Ni, Fe, K, and Mg). High concentrations of Ca, Sr, and Zn were associated with 350 and 550 °C Aspen ash samples, while 350 and 550 °C Spruce

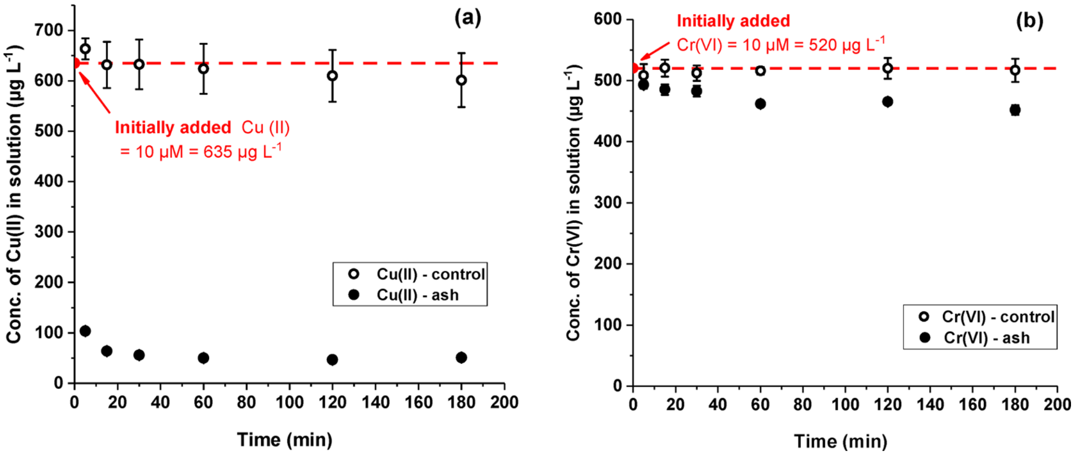


Figure 3. Results from the metal sorption experiments (*n* = 3, sampling interval = 5 min, 15 min, 30 min, 1 h, 2 h, and 3 h) conducted by reacting 10 μM of (a) Cu(II) and (b) Cr(VI) separately in a solution containing 0.1 g of 350 °C Pine ash with 50 mL of 18 MΩ water. Note that the control experiments were conducted by reacting 10 μM of Cu(II) and Cr(VI) in 18 MΩ water without ash.

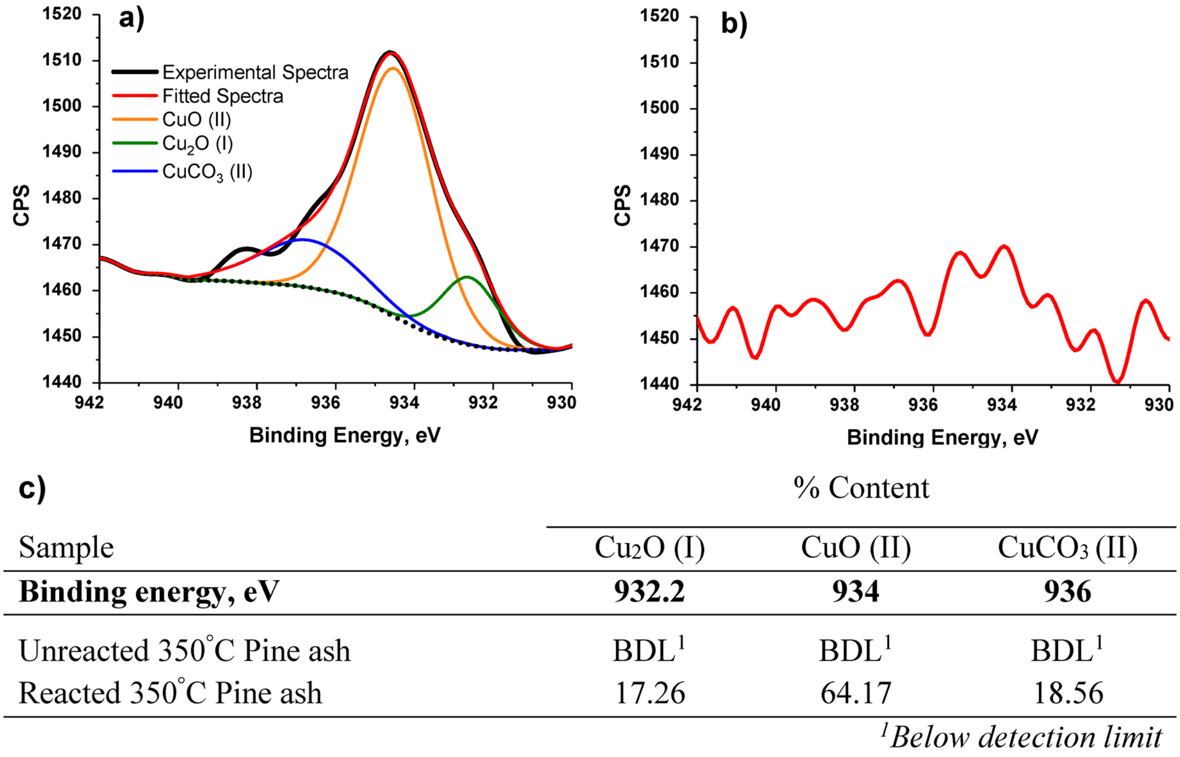
ash samples were associated with high concentrations of Mn, Al, and Fe.

Major elements (Ca, Mg, K) were found to be predominant in oven-dried wood (60 °C) and in ash samples (350 and 550 °C) for all tree species (Table S4), consistent with findings for wood[49] and wood ash[12,50] from previous studies. Pine ash showed higher concentrations with increasing temperatures for major elements (Ca, Mg, and K) and for heavy metals such Al, Fe, Mn, and Ni (Table S4), consistent with findings from a previous study conducted on Lodgepole Pine.[51] The concentration of Cu in Pine ash (4997 ± 262 mg kg^{-1} at 350 °C and 2765 ± 302 mg kg^{-1} at 550 °C) was higher than previously reported values for Pine ash.[12,51] Due to the dominance of Pine tree species in the forests of the western United States, much of the existing literature has focused on the metal and DOC composition of ash produced from different species of Pine (e.g., Ponderosa and Lodgepole).[12,18,52−54] We conducted additional experiments with 350 °C Pine, Spruce, and Aspen ashes to assess the release of dissolved organic carbon and other metals over time.

Metal and DOC Leachates from Ash (350 and 550 °C) Reacted with Water. Metal leaching experiments were conducted to observe the dissolution of selected metals (Cr, Ni, Fe, Cu, and Zn) in reaction with 350 and 550 °C Pine ash in 18 MΩ water (Figure 2a−d). Dissolution of metal bearing phases caused a rapid increase in the pH of water (Figure S3), measured at 10.0 ± 0.5 for the duration of the experiment. Less than 3% by mass [determined in acid extractable analysis (Table S4)] of Cr, Ni, Fe, Cu, and Zn was released in solution after 72 h of reaction. Metals like Cu, Fe, Zn, and Ni showed an initial release followed by a decrease in metal concentration over time for both the 350 and 550 °C ash samples (Figure 2a−d). Limited fluctuations in the concentration of Cr released in solution were observed over time (Figure 2b,d). The high pH and alkalinity in these experiments (Figure S3) are likely due to the dissolution of metal bearing carbonate and oxide phases, such as calcite, quartz, and whewellite [$Ca(C_2O_4)\cdot H_2O$], which were identified by XRD analysis in the unreacted 350 °C Pine ash (Figure S4). A previous study from our group also identified the presence of calcite and other metal bearing phases in ash burned at 550 °C.[12]

The DOC concentration decreased with increasing temperature in reaction of 60, 350, and 550 °C samples with 18 MΩ water. The 60 °C (unburned) samples released higher DOC concentrations (110.7 to 338 mg carbon L^{-1}) compared to 350 °C (4.25 to 11.3 mg carbon L^{-1}) and 550 °C ash samples (1.27 to 2.77 mg carbon L^{-1}) (Figure 2e,f). In this study, different sections (i.e., leaves, twigs, needles) of the collected tree species were crushed and ground to powders and homogenized before conducting the experiments. This process could have contributed to the high DOC release from the unburned samples. Additionally, a variable release of DOC could result from contributions from different tree sections, obtaining DOC concentrations that are higher than the ones reported in this study.[55,56] The decrease in DOC concentration from 350 to 550 °C ash suggests that a greater loss of organic matter occurs at a higher burning temperature, consistent with findings from previous studies.[10,12] The range of DOC concentrations (1.27 to 11.3 mg carbon L^{-1}) measured for 350 and 550 °C ash samples in this study are consistent with those reported in previous studies from field[15,18] and laboratory studies.[10] Previously. Wang et al.[54] observed decreased reactivity of the ash in forming DBPs such as trihalomethane (THM) and chloral hydrate (CHD) with increasing temperature from 50 to 400 °C. The DOC loss at higher temperatures for ash in this study is comparable to that observed in laboratory heated soil by Cawley et al.[10] Thus, the temperature dependent variability for both ash and soil can have implications in terms of variable loading of DOM and DBP precursors from different burn conditions associated with wildfires and prescribed fires, as suggested by others.[10,54]

Sorption to 350 °C Ash. We further explored the sorption of Cu(II) (a cationic metal) and Cr(VI) (an oxyanion) to 350 °C ash at pH 7.0 ± 0.2 in batch sorption experiments. Zeta potential measurements for the 350 °C Pine ash showed increasingly negative surface charge with increasing solution pH (Figure S5), similar to another carbon-based material like biochar.[57,58] The surface area of Pine ash increased from 36.9 m^2/g at 350 °C to 294.4 m^2/g at 550 °C (Table S7). Previously, de Mendonça et al.[57] reported an increase in surface area due to the creation of micropores for biochar burned at 400 and 600 °C. A higher loss of C, H, and O occurred in ash with increasing temperature (Table S8). Lower H/C ratios in 350 and 550 °C can be a measure of a higher degree of aromaticity in the ash samples, as suggested by previous studies on biochar.[58,59] Higher O/C and (O + N)/C



	% Content		
Sample	Cu_2O (I)	CuO (II)	$CuCO_3$ (II)
Binding energy, eV	**932.2**	**934**	**936**
Unreacted 350°C Pine ash	BDL[1]	BDL[1]	BDL[1]
Reacted 350°C Pine ash	17.26	64.17	18.56

[1] *Below detection limit*

Figure 4. Cu 2p high resolution spectra for the (a) reacted 350 °C Pine ash and (b) unreacted 350 °C Pine ash. (c) Percentages of different oxidation states in the Cu 2p spectra for the reacted ash determined by using reference Cu 2p spectra for CuO, $CuCO_3$, Cu_2O, and Cu metal.

ratios, for the 350 and 550 °C ash samples, are indicators of increased hydrophilicity and polarity.[58−60] We observed more than an 80% decrease initially in Cu(II) concentration in the solution reacting with 350 °C Pine ash (Figure 3a), as indicated by measured Cu(II) concentration (103.6 ± 3.1 μg L^{-1}) after 5 min of reaction and up to a 92% decrease after 180 min of reaction. Cu(II) concentration in the control decreased only 5%, to 601.2 ± 53.8 μg L^{-1} after 180 min of reaction from the initially added concentration of 635 μg L^{-1}. In experiments with Cr(VI), a low decrease in Cr(VI) concentration was observed, as the measured concentration after 180 min was 451.7 ± 7.8 μg L^{-1}, representing only a 13% decrease from the initially added Cr(VI) of 520 μg L^{-1} (Figure 3b). Cr(VI) showed a negligible decrease in concentration in the Cr(VI)−control experiment (Figure 3b). Similar results were observed for both Cu(II) and Cr(VI) in the sorption experiments with 350 °C Spruce and Aspen ashes (Figure S6). These results suggest that burning caused similar effects on metal reactivity of all three ashes (Pine, Spruce, and Aspen).

The different response of Cu(II) and Cr(VI) concentration during the sorption experiments suggests that high Cu(II) association to ash occurred due to possible electrostatic attraction of the positively charged Cu(II) to the negatively charged ash surface. The effect of sorption capacity of the carbonate phases in wood ash in reacting with cations such as Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} has been discussed in other studies.[12,13] This is a relevant property of wood ash that should be considered when investigating the persistence of metals such as Cu, Pb, Ni, Fe, and Zn associated with ash and debris in wildfire affected watersheds, as reported in several postfire investigations.[61−63] The low sorption of Cr(VI) observed in this study is consistent with other studies reporting low sorption rates for As(V), Cr(VI), and Se(VI) to carbonaceous materials at pH 5.0 and above.[64−66] For example, a recent study by Alam et al. observed over 90% removal of Cd(II) and below 20% removal for Se(VI) at pH 6.0 and above, using biochar as an adsorbent.[64] At the experimental pH of 7.0 ± 0.2 used in this study, Cr(VI) is expected to exist in the solution as stable oxyanion forms (e.g., CrO_4^{2-}, $HCrO_4^-$).[67] Therefore, the electrostatic repulsion between the negatively charged ash surface and Cr(VI) oxyanions can account for the low decrease in Cr(VI) concentration in solution. The association of Cu(II) in the unreacted and reacted 350 °C Pine ash solids was further analyzed using microscopy and spectroscopy.

Solid Phase Analyses of Unreacted and Reacted 350 °C Pine Ash. SEM analysis detected the presence of Cu on 350 °C Pine ash before and after exposure to batch experiments (Figure S7). For example, EDS spectra of a Cu grain showed 69.51 wt % of Cu for the unreacted ash and 63.55 wt % of Cu for the reacted ash. SEM/EDS results confirmed the high Cu concentration (4997 ± 262 mg kg^{-1}) measured from the acid extraction analyses. Electron microprobe mapping detected a low level of Cu (0.012%) associated with the Ca^{2+} minerals in the reacted ash (Figure S8), while it was below the detection limit for the unreacted ash. The predominant form of the Ca^{2+} mineral is most likely calcite ($CaCO_3$), given the presence of 76−78 wt % of calcite in the reacted sample (Figure S4). Given that Ca is a macronutrient in plants, Ca^{2+} minerals in the form of CaO and $CaCO_3$ are abundant across a variety of plant cells.[68,69] XRD analyses on reacted and unreacted samples indicated presence of quartz and calcite ($CaCO_3$) as predominant mineral phases (Figure S4). While microscopy analyses identified the presence of Cu, it was challenging to obtain specific information about the association of Cu on the reacted ash surface from these analyses. Thus, additional analyses using XPS were done to measure the signal of Cu 2p on the “near-surface” region to identify the possible association of Cu to ash after reaction in batch sorption experiments.

Results from the XPS survey scan revealed that 0.11% Cu 2p was present in the reacted ash, suggesting that Cu is associated at the top 5−10 nm of the ash "near surface" region (Table S9). However, the Cu 2p % for the unreacted ash was below the detection limit (Table S9). Thus, the high resolution Cu 2p peak obtained for the unreacted ash was noisy and could not be used for curve fitting analyses (Figure 4). Curve fitting of high resolution XPS Cu 2p spectra obtained for the reacted sample was conducted using reference spectra for CuO, $CuCO_3$, Cu_2O, and Cu metal as indicated in the Materials and Methods section. Curve fitting analysis suggests that the main species of Cu present on the reacted ash are Cu(II) in the form of CuO (64.2%) and $CuCO_3$ (18.6%) and Cu(I) in the form of Cu_2O (17.3%) (Figure 4). The presence of Cu(I) on the reacted ash surface suggests a possible reduction of some of the Cu(II) to Cu(I), as suggested by a previous study by Bogusz et al.[60]

The association of Cu on the reacted 350 °C Pine ash near surface region suggests a likely surface controlled process involved in the removal of Cu(II) in the sorption experiments. Curve fitting analysis of C 1s high resolution spectra showed an increase in the percentages of $C^*{-}CO_x$, C═O, and C−OH bonds in the reacted ash (Figure S9). The presence of surface functional groups (−C═O, −COOH) in ash can act as negatively charged binding sites for positively charged cations. The increased polarity (higher O/C and (O + N)/C ratios) in the ash samples measured by the C, H, N, and O analyses (Table S8) is consistent with the increase in functional groups, identified by XPS. The removal of cationic metals such as Cu^{2+} and Cd^{2+} through associations with surface functional groups of biochar has been discussed in the literature.[30,60,70] These properties are also relevant to better understand the effect of burned soil and ash on postfire mobilization of heavy metals.

Environmental Implications. The results from this investigation indicate how metal and DOC content associated with ash burned at different temperatures (350 and 550 °C) can differ for Pine, Spruce, and Aspen. This outcome may have relevant implications when considering the wide variation in vegetation across large watersheds when assessing response to wildfire events. Ash burned at 350 °C had higher DOC concentration in water compared to ash burned at 550 °C. This observed increase may have important implications in terms of increased DOC fluxes in postfire watersheds from moderately burned ash and soil reported in previous studies.[15,71] The batch experiments conducted in 18 MΩ water indicate that metals such as Cr, Ni, Fe, Cu, and Zn were dissolved in the initial stages of the experiment, followed by a decrease in concentration over the duration of the experiment. This observation is consistent with a previous study suggesting that metal (Ca, Mg, Al, Fe, and Mn) dissolution occurred in initial stages of the batch experiments conducted with ash from Pine, Aspen, and Spruce trees from the Caldera, followed by reassociation of these metals to ash over time.[12] However, a new finding was obtained from the sorption experiments conducted in this study which indicate that up to 94% of Cu is removed from solution after 180 min of reaction due to association of this metal in the 350 °C Pine ash surface. A similar behavior is expected for other positive cations such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Fe^{2+}, Cd^{2+}, and Pb^{2+} among others, as suggested in other studies related to wood ash[12,13] and biochar[29,72] reactivity. The integration of results from the metal dissolution and sorption experiments in this study provide novel insights about postfire mobilization of cationic metals in burned watersheds. However, oxyanions such as Cr(VI) are expected to have limited association to ash in natural pH conditions and are likely to have higher mobility in watersheds affected by wildfires. Future experiments are necessary to study metal reactivity in wood ash in dynamic flow conditions which allow interactions between ash and sediments in water. This study provides relevant insights on water quality that could be considered for postfire response and recovery strategies by local authorities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00530.

> Additional materials and methods; mass of wood samples; detection limits for analyses; maximum contaminant level and different standards for exposure limits; acid extractable elemental content for wood samples; Kruskal Wallis test; Wilcoxon rank sum test; specific surface areas and elemental composition and ratios of samples; atomic content of Pine ash; map of sampling locations; principal component analysis; pH and alkalinity; XRD patterns; zeta potential measurements; results from the metal and batch sorption experiments; microprobe mapping; XPS high resolution C 1s spectra and percent compositions; XPS high-resolution Cu 2p spectra and binding energies (PDF)

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