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METAL REACTIVITY IN LABORATORY BURNED WOOD FROM A WATERSHED AFFECTED BY WILDFIRES

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**METAL REACTIVITY IN LABORATORY BURNED WOOD
FROM A WATERSHED AFFECTED BY WILDFIRES**

by

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B. Sc. in WATER RESOURCES ENGINEERING

THESIS

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B.Sc. in Water Resources Engineering, 2012

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ABSTRACT

Massive amounts of wood ash are deposited into nearby streams as a result of runoff from storm events after increasing frequency of wildfire events that negatively affect water quality. Ash and debris from burned vegetation can alter the pH, turbidity and dissolved oxygen (DO) in water and can release heavy metals, organic matter, and nutrients. We investigated interfacial processes affecting metal mobility in wood ash burned under laboratory-controlled conditions using aqueous chemistry, microscopy and spectroscopy analyses. Wood was collected from the Valles Caldera National Preserve in New Mexico which has experienced two wildfires since 2011 that have caused devastating effects. Wood samples (e.g. Ponderosa Pine, Quaking Aspen, and Colorado Blue Spruce) collected from this site were exposed to temperatures of 60°C, 350°C and 550°C. Pine ashes burned at 350°C and 550°C were associated with high concentrations of metals (i.e., Cu, Cr, Si, Ni, Fe, K and Mg). Pine ash burned at 350°C had the highest content of Cu ($4997 \pm 262 \text{ mg kg}^{-1}$), Cr ($543 \pm 124 \text{ mg kg}^{-1}$), and labile dissolved organic carbon (DOC, $11.3 \pm 0.28 \text{ mg L}^{-1}$). Metal sorption experiments were conducted by reacting 350°C Pine ash separately with 10 μ M solutions of Cu(II) and Cr(VI), as examples of a cation and an oxyanion found in high concentrations in water following wildfire events near VALL. High decrease in Cu(II) concentration (up to 92%) was observed in solution while Cr(VI) showed limited decrease (up to 13%) in concentration after 180 mins of reaction. X-ray photoelectron spectroscopy (XPS)

analyses detected increased association of Cu(II) on the near surface region of the reacted ash from the sorption experiments compared to the unreacted ash. The results from this investigation suggest that dissolution and sorption processes are essential to understand the transport of metals in water following wildfires. This study provides relevant insights about the potential effects of metals transported by wood ash on water quality that have important implications for post-fire recovery and response strategies

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Chapter 1: Introduction

The thesis has been divided into 3 chapters and an appendix. Chapter 2 provides a summary on the current state of scientific knowledge on the topic, which includes a background on impacts of wildfire ash on water chemistry, mechanisms affecting wood ash reactivity, ending with a review of research gaps and limitations in the proposed field of study. Chapter 3 is the main body of work of the thesis, formatted as a research paper which will be submitted to the peer-reviewed journal *Environmental, Science & Technology*. The main topic covered in Chapter 3 relates to the investigation of metal reactivity in laboratory burned wood from a watershed affected by wildfire. The objective of the study presented in Chapter 3 was to investigate the interfacial processes affecting wood ash reactions with water by integrating laboratory experiments, spectroscopy, microscopy, and aqueous chemistry methods. This chapter also discusses the observed results with discussions providing mechanistic explanations and environmental implications of this study. The Appendix contains supplementary data obtained for the study presented in Chapter 3.

Chapter 2: Background and Literature Review

1. Background and Significance.

Wildfires cause catastrophic damages to natural resources around the world every year. Large scale economic and societal impacts are often observed following a wildfire event. Post-fire adverse impacts on water quality often disrupt the drinking water supply for nearby communities. The effects of wildfires are particularly relevant in semi-arid regions of the world, such as the South-western region of the US, in which the combination of earlier spring snowmelt, decreased winter precipitation and greater vapor-pressure deficit in the warm season results in substantial water limitation stress on forests.¹⁻⁴ Additionally, climate change has contributed to increased drought severity and frequency in the south-western US.⁵ The complex interactions between these factors, combined with uncontrolled urbanization and forest management practices (i.e. fire suppression by forest thinning), have contributed to increased level of wildfire activity.⁶

Wildfires can cause a wide range of effects on the nearby surface water quality. Post-fire storm events in burned watersheds can cause the transport of wood ash, debris and sediments into nearby streams which has detrimental impacts on water quality. Several post fire investigations have reported increased concentration of metals such as Fe, Pb, Ni, Zn, Al, As, Cd, Mn and Cu in the watershed affected by increased loading of ash and sediments.⁷⁻¹⁰ The Valles Caldera National Preserve (VALL) in north central New Mexico is an example of a site with frequent wildfire activity in recent years.¹¹ Two major wildfires have affected the VCNP watershed since 2011: (1) The Thompson Ridge wildfire burned 23,965 acres in VCNP in 2013¹² and (2) The catastrophic Las Conchas, one of the largest in New Mexico history, which burned over 156000 acres of area in the Jemez Mountains in 2011.¹³ Post-fire runoff of debris and ash in the Rio Grande river, following thunderstorms over the burned area caused turbidity peaks of over 1000 NTU and sags

in dissolved oxygen (DO) and pH.¹⁴ The VCNP contains the headwaters of multiple streams including the East Fork Jemez River,¹⁵ a tributary of the Middle Rio Grande which serves as a drinking water source for nearby communities. The load of ash and debris forced temporary shutdowns of local water treatment plants in Albuquerque and Santa Fe. Post fire runoff effects like the one after the Las Conchas fire can cause transport of organic matter, metals and nutrients with debris and ash, which can significantly affect the quality of water supplied to nearby communities and agriculture.^{14,16,17}

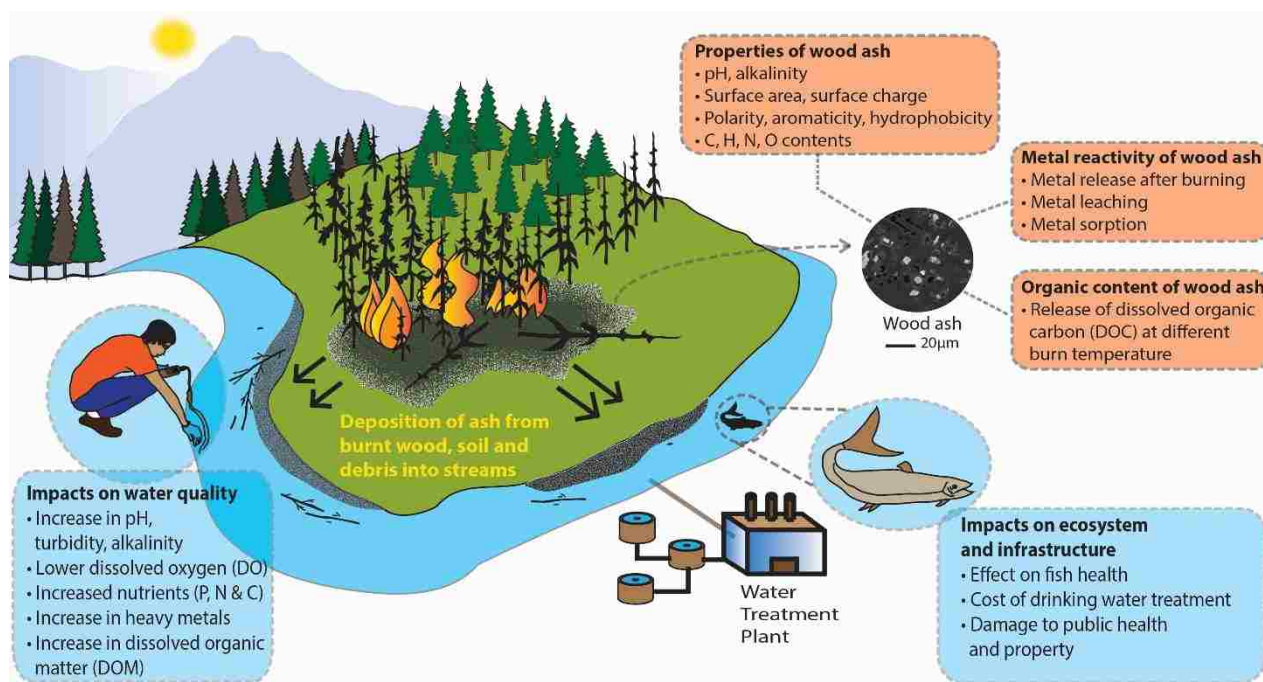


Figure 1: Relevant biogeochemical processes affected by wildfires in a watershed ecosystem.

Information on the composition and reactivity of metals associated with wood ash is important to better understand the potential impacts on water quality caused by wildfires. The following subsections will discuss in more detail, the mineralogy and chemical characteristics of wood ash, the effects of different burning temperatures on wood ash mineralogy and the current literature on reactivity of metals in wood ash and other similar materials like biochar.

2. Wildfire Ash and Water Chemistry.

The current literature on wildfire impacts on water quality is focused heavily on suspended sediment, dissolved organic matter, and nutrients. The knowledge on the impacts of metals associated with ash and debris on water quality is still limited. Wildfire can transform fuel (i.e. biomass, wood, soil organic matter) into ash and other materials of different physical and chemical properties.¹⁸ Wood ash is derived from burned vegetation. Plants contain macro (Ca, K, Mg) and micronutrients (Fe, Mn, Zn, Cu, Ni) essential for their growth.¹⁹ Composition and distribution of the nutrients in plants are mainly controlled by the surrounding soil composition and ecosystem changes.¹⁹⁻²¹ These nutrients become concentrated in the ash produced from burnt vegetation because of wildfire.^{22,23} The nutrients, trace elements and other inorganic and organic constituents in wood ash can accumulate in nearby surface water sources post-fire and impact water quality.

2.1. Release of Metals.

Previous studies have reported elevated concentrations of metals in watersheds due to the transport of ash after wildfire events. After the 2009 station fire in California, total concentrations of As, Pb, Zn and Ni were reported higher in the burned watersheds.¹⁰ Trace elements (e.g., Fe, Mn, Hg) from burned soil and ash were also found in elevated concentrations in nearby streams after the fire.¹⁰ Elevated concentrations of As, Al, Cd, Cr, Fe, Pb, Hg, Ca, Mg, Mn, Ba and K have also been observed in sediments and streamflows in fire-affected watersheds, several months after the fire events.^{7,24-27} A previous study by Ignatavicius et al.²⁸ compared long term environmental data in Lithuanian rivers and correlated the increase of heavy metals such as Cu, Pb and Zn to the occurrences of land fires. In New Mexico, the Cerro Grande fire in May 2000 burned over 7400 acres of mixed conifer forests in the Valles Caldera National Preserve (VALL) area near the Los Alamos National Laboratory (LANL),⁸ resulting in accumulation of ash and debris in the burned

watershed. After the fire, runoff samples were collected from 40 sites and elevated concentrations of trace metals were found in some samples. For example, elevated concentrations of total Cu ($610 \mu\text{g L}^{-1}$) and total Cr ($510 \mu\text{g L}^{-1}$) were measured in post fire runoff water samples collected from the burned watersheds near Guaje Canyon, close to the Los Alamos National Laboratory.⁸ Reports from these post-fire investigations show that concentrations of trace metals in water and soil near a burned watershed can increase from the addition of ash and debris by storm water runoff.

2.2. Release of Nutrients.

Wildfires can release high concentrations of nutrients that can significantly impact the water quality. The primary nutrients of concerns after a wildfire are Phosphorus (P), Nitrogen (N) and Carbon (C). A previous by study by Uldis et. al.²⁹ investigated P availability in post-fire watersheds and found that P concentration were 2 to 13 times higher in burned watersheds than in unburned watersheds. Higher availability of P in burned watersheds can facilitate strong algal productivity and shifts in ecological responses.²⁹ Phosphate, Nitrate and Ammonium concentrations above 5 to 60 fold over background levels were measured in fire affected streams in Glacier National park.³⁰ In New Mexico, post fire runoff caused transport of organic matter and nutrients ($6 \times$ background levels for $\text{NO}_3\text{-N}$ and $100 \times$ background levels for PO_4) with debris and ash in the VALL, which significantly affected the quality of water supplied to nearby communities.^{14,16} Slow recovery of nutrient concentrations leads to long term nutrient availability in the fire affected sites and leaching of nutrients into soil. Another important and widespread water quality issue called eutrophication, is caused by high concentrations of nutrients such as P and N in surface water sources. High P and N in water can lead to the growth of algal blooms, which are toxic and can increase fish kills and reduce water quality.³¹

2.3. Elevated levels of Dissolved Organic Carbon (DOC) and Disinfection Byproducts (DBPs).

After a wildfire event, elevated levels of dissolved organic matter (DOM), generally measured as DOC, in downstream of nearby water sources has been associated to heavy loads of ash and debris by several previous studies.^{18,26,32} Recent studies have linked water extractable organic matter (WEOM) from burned soil^{17,33} and ash³⁴ to the formation of disinfection byproducts (DBPs).^{35,36} DBPs are of particular concern due to their effect on public health, which includes risks of bladder cancer and disruption in cell growth.^{37,38} Two types of DBPs that are of interest are Carbonaceous DBPs (C-DBPs) and Nitrogenous DBPs (N-DBPs). Commonly studied C-DBPs include trihalomethanes (THM) and haloacetic acids (HAA), while N-DBPs such as haloacetonitriles (HAN) and halonitromethanes (e.g., chloropicrin) are also of interest. These species have been observed to form in solution of laboratory burned soil and ash following addition of chlorine.^{33,39}

2.4. Change in water quality parameters (pH, DO, turbidity).

Water quality degradation after a wildfire is a commonly observed phenomenon. A previous study by C. N. Dahm et al.¹⁴ measured continuous water quality data in the middle Rio Grande and found marked changes in pH, dissolved oxygen (DO) and turbidity over a period of two months after the Las Conchas fire. Turbidity peaks of up to 2500 NTU, pH sags (up to 0.75 units) and DO sags (as low as 0 mg L⁻¹) were observed as a result of heavy loadings of ash, debris and sediments.¹⁴ Sherson L. R. et. al.¹⁶ observed similar effects of DO and pH sags in the East Fork Jemez river after the Las Conchas fire. The transport of ash and nutrient often changes the water quality downstream, although it is difficult to quantify the different contributions of ash, sediments and nutrients to the changes in water quality. The change in water quality parameters

caused by ash, sediment and nutrients affects the treatability of source water to be used for drinking purposes and has become a matter of particular concern for many local water authorities.^{17,25}

3. Characteristics of wood ash at different burn intensity and severity.

The terminologies ‘burn intensity’ and ‘burn severity’ has specific usages in literature related to wildfires.⁴⁰ Fire intensity has been related to the energy released during different phases of a fire which is dependent on several factors such as reaction intensity, fireline intensity, temperature, heating duration and radiant energy.⁴⁰ The term ‘burn severity’ is generally associated with the loss of organic matter and conversion of organic matter to ash.⁴⁰ The effects of burn severity and burn severity can have a wide range of impacts on ash properties, specifically on the concentration of nutrients and other major and minor elements present in the ash. These effects can also be used to understand the availability and impacts of wildfire ash on the surrounding soil and water quality post-fire. The following subsections discuss, in detail, the effects of different burn intensity and severity on ash properties.

3.1. Physical and hydrological properties of ash.

The effect of burn severity on ash is evident in different responses observed in physical properties such as color, mass, particle size, hydraulic conductivity and water storage capacity. The color of ash goes from darker shades of brown to lighter shades of gray and white as burning temperature increases.^{18,41} Although the rate of mass loss can vary dependent on the particular tree species being considered, generally the percentage of mass loss increases with higher temperature.⁴¹ In a previous study, Bodi et. al. observed finer ash particle size with increasing temperature between 350°C to 700°C.¹⁸ The hydraulic conductivity and water storage capacity of ash can also vary significantly depending on the burning temperature. Post-fire watersheds are often covered with a layer of ash that affect the infiltration of water after storm events. Several

post-fire investigations have reported increased infiltration and water repellency behavior of ash-covered soil in the burned watersheds.^{18,42,43} However, this behavior is difficult to correlate with properties like hydraulic conductivity and temperature difference due to the highly variable nature of fuel and burning conditions. Further studies linking the hydraulic properties of ash with water repellency behavior is necessary.

3.2. Chemical and mineralogical properties of ash.

Ash can contain both organic and inorganic constituents depending on the combustion temperature. Bodi et. al.¹⁸ has reported previously that at low burning temperature of below 450⁰C, organic constituents are likely to be present in higher amount. Dlapa et. al found that the loss of organic matter in ash with increasing temperature leads to significant decrease of hydrophobic surfaces in ash. The loss of hydrophobicity in ash has important implications in terms of post-fire runoff events. The inorganic constituents consist of a range of macro and micro elements. The macro elements such as Ca, K and Mg are abundant across all tree species.¹⁹ Micro elements include a range of elements such as As, Al, Cd, Cr, Fe, Pb, Hg, Mn, Zn, Si etc. Mineralogical composition of wood ash likely consists of carbonates and oxide phases of different metals.²³ The dissolution of these carbonate and oxide phases in reaction of ash with water can cause rapid pH increase in solution.^{23,44}

3.3. Effects of temperature on ash chemical and mineralogical properties.

Temperature is a particularly important factor that affects the elemental composition of wood ash.^{18,45,46} Wildfires can have a wide temperature range from 200⁰C to 1200⁰C.⁴⁷⁻⁴⁹ Depending on the combustion temperature, ash can contain a range of inorganic minerals, nutrients, heavy metals, trace elements, and organic substances.^{18,22,50} At temperatures lower than 450⁰C^{18,50} ash is likely to contain higher levels of organic substances than at temperatures higher

than 450⁰C, where most of the organic carbon is volatilized.^{18,50} Similar results have been reported in experiments with burned soil samples.³³ The increase in burning temperature has varying effects on the elements present in wood ash. Previously L. Etiégni et. al.⁵¹ observed that K, Na, Zn and CO₃ content decreases with increasing burning temperature from 538⁰C to 1093⁰C but other metals tend to remain constant or increase. The amount of ash yield after burning can also vary depending on the type of tree species and burn temperature. Increase in burn severity can result in the increase of CaCO₃ and pH of ash, as observed in previous field investigations.^{41,52} Increase in the loss of total carbon (TC) and total nitrogen (TN) is observed with increasing burn temperature.⁵² The loss of TC and TN contribute significantly to the total mass loss of ash at higher temperatures.⁴⁶

4. Mechanisms Affecting Wood Ash Reactivity.

Recent studies have linked water extractable organic matter (WEOM) from burned soil^{17,33} and ash³⁴ to the formation of disinfection byproducts (DBPs)^{35,36}. The alteration of DOM with increasing temperature from Ponderosa Pine ash has been studied previously by Wang et al.³⁹ and they observed decreased reactivity of the ash in forming DBPs such as trihalomethane (THM) and chloral hydrate (CHD) with increasing temperature from 50⁰C to 400⁰C. The DOM loss at higher temperatures for ash in this study is comparable to that observed in laboratory heated soil reported in a previous study by Cawley et al³³. 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 previous studies^{33,39}

More insights into the mechanisms of metal mobilization by wood ash can be found from literatures relating metal mobilization to biochar, a material similar to wood ash in composition^{53,54} and is increasingly applied in environmental remediation as a natural sorbent for organic and inorganic contaminants⁵⁵⁻⁵⁷. Previous studies have reported Cu(II) sorption to organic functional

groups of biochar in water at pH 6, while at pH 7 to 9, carbonate phases like azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and oxide phases like tenorite (CuO) precipitated within the biochar⁵⁸. Adsorption between Cu^{2+} and negatively charged biochar was reported as the prevailing mechanism of Cu immobilization in soil^{57,59}. Biochar has also been proven effective in immobilizing positively charged Cd and Zn in water at pH 6 to 8⁶⁰. Conversely, enhanced mobility of oxyanions like As^{61,62} and Sb⁶³ were found in biochar treated soil. The effectiveness of biochar in Cr(VI) immobilization is significantly reduced at pH 5 and above, both in soil⁶⁴ and water^{65,66}.

Carbon-based materials like ash and biochar contain negatively charged surface functional groups that contribute to the sorption of heavy metals. The analysis of light elements such as C, N, O and H and molar ratios of these elements can indicate changes of properties in the material. For example, higher degree of aromaticity and lower degree of hydrophilicity is associated with increasing burn temperatures for biochar.^{67,68} Oxygen containing functional groups (e.g., $-\text{C}=\text{O}$, and $-\text{COOH}$) can act as dominant binding sites. The surface charge of biochar is increasingly negative and the surface area increases with higher burning temperature, suggested by previous studies.^{67,69}

Wood ash, like biochar has applications to agriculture and forestry. The high alkalinity of wood ash is useful for treatment of acidic soil generally found in tropical forests. The application of wood ash to plants can be beneficial for the growth of the plants because of increase in the concentration of macro elements (Ca, K, Mg) and P and decrease in trace metal (Cd, Cu, Cr, Mn, Ni, Pb, Zn) concentration. Previously, Etiegni et al.⁷⁰ observed that, wood ash, if used in levels of 2% or lower, can work as an effective fertilizer and liming agent. However, repeated and long-term application of wood ash can cause leaching of trace metals into soils, as suggested by previous

studies.^{53,71} More studies are necessary to better understand the mechanisms affecting adsorption, precipitation, and dissolution reactions facilitated by wood ash that affect metal mobility.

5. Research Gaps.

While other studies have characterized metals in wood ash,^{22,23,72} the specific mechanisms affecting metal mobilization by ash remain poorly understood. Most of the existing literature on wildfire impacts has focused on the effects of nutrients and dissolved organic carbon on water quality parameters such as pH, turbidity, DO and DBP potential.^{14,17,25,34,73} The release of metals from wood ash and debris has been reported in a number of post-fire investigations.^{7,9,10,74} Previous studies have reported the presence of Ca, Mg, Al, Fe and Mn as metal bearing carbonate and oxide phases in wood ash burned at 550°C.^{23,46} These metal bearing phases are easily dissolvable in reaction of ash with water, resulting in rapid and significant increase in solution pH.^{22,23} However, the adsorptive capacity of the carbonate phases in ash often contribute to the re-adsorption of metals from solution to ash.²³ Burning of organic matter often results in the presence of negatively charged functional groups (i.e. C=O, -COOH) in ash. These functional groups attract positively charged cationic metals, therefore contributing to metal uptake from solution. The ash-metal interaction in solution is also highly dependent on pH. For example, at an environmentally relevant pH range of 6 to 8, metals that act as Lewis acid in solution, such as Cu(II), exhibit positive charge. However, at pH of 6 to 8, metals such as Cr(VI) are known to exist in solution as negatively charged soluble forms of CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. This reversal of charges causes selective adsorption of metal ions from solution by ash. All of these processes play a key role in mobilization of metals by ash after a wildfire. This is why, the investigation of these interfacial processes in reaction of wood ash and water is necessary to facilitate better understanding of post fire metal mobilization. Additionally, the effects of different burn temperatures on the properties and

reactivity of wood ash is necessary to better understand metal and DOC leaching from ash. The investigation presented in this thesis attempts to address these knowledge gaps.

Chapter 3:

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

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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 severe 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°C, 350°C 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 10µM Cu(II) and Cr(VI) solutions. Up to 94% decrease in Cu(II) concentration was observed in solution while Cr(VI) concentration showed limited decrease (up to 13%) after 180 mins 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 post-fire recovery and response strategies.

TOC Art.



Figure 2: TOC figure showing the process from laboratory burning to metal sorption experiments.

1. Introduction

Post-fire 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 south-western regions have seen increased occurrences of large intensity wildfires because of worldwide effects of climate change.^{24,75,76} The Valles Caldera National Preserve (VALL) in north central New Mexico is an example of a site with frequent wildfire activity in recent years.¹¹ 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 2013¹² and (2) The catastrophic Las Conchas, one of the largest in New Mexico history, which burned over 156,000 acres of area in the Jemez Mountains in 2011.¹³ Post-fire 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).¹⁴ Total concentrations of Al and Cu in the Rio Grande following the Las Conchas fire were above aquatic life criterion for both metals.⁷⁷ Additionally, post fire runoff caused transport of organic matter and nutrients ($6 \times$ background levels for $\text{NO}_3\text{-N}$ and $100 \times$ background levels for PO_4) with debris and ash in the VALL, which significantly affected the quality of water supplied to nearby communities.^{14,16} 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,^{22,23,33,72} the specific mechanisms controlling post-fire 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.^{7,24-27} Recent studies have linked water extractable organic matter (WEOM) from burned soil^{17,33} and ash³⁴ to the formation

of disinfection byproducts (DBPs).^{35,36} Temperature is a particularly important factor that affects the elemental composition and mineralogy of wood ash.^{18,45,46} 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.²³ Results from laboratory batch experiments suggested that these metal-bearing phases are readily water soluble, but the re-adsorption of these metals to ash can occur in later times of the experiments.²³ Although this study provides valuable insights into the presence of metal bearing phases in ash and their potential effects on metal re-adsorption, 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.^{53,54} Biochar is a natural sorbent and is increasingly applied in environmental remediation of organic and inorganic contaminants.⁵⁵⁻⁵⁷ The sorption of Cu(II) to organic functional groups of biochar in water can occur at pH below 7.⁵⁸ However, Cu-associated phases like azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and tenorite (CuO) precipitate within the biochar surface at pH higher than 7.⁵⁸ Sorption between positively charged ions and negatively charged biochar is an effective mechanism for immobilizing metals in soil.^{57,59,60} The immobilization of Cr(VI) through biochar sorption is significantly reduced at pH 5 and above.^{64,65,66} Enhanced mobility of oxyanions like As^{61,62} and Sb⁶³ 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 post fire 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 post-fire response in affected watersheds.

2. 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 SI. The description and co-ordinates 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.⁷⁸ 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.^{23,79} 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.⁸⁰ 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 48h before burning. The ground and dried samples for each tree were mixed together 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 hours to prepare ash. Table S1 contains data on 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 hours using Aqua Regia [2 mL HNO₃ (67-70%) + 6 mL HCl (34-37%), trace metal grade]. Following heating, acid extracts were diluted with 18MΩ 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% HNO₃ 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 0.1g sample of 60°C, 350°C and 550°C Pine, Spruce and Aspen samples with 30 mL of 18MΩ deionized water. Replicates ($n=3$) were sampled at 0, 4, 24 and 72 hrs and were analyzed using a Tekmar-Dohrmann Phoenix 8000 TOC Analyzer, following 5310-C persulfate-ultraviolet (UV) method.⁸¹ For metal dissolution experiments, 0.1g samples of 350°C and 550°C Pine ash were reacted with 30 mL of

18 mΩ water. Samples were collected at 0, 4, 24 and 72 hours, centrifuged at 3000 rpm (1660×g) for 15 mins 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 conducted to investigate the effect of 350°C 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., CrO₄²⁻) that could negatively impact surface waters. Additionally, elevated concentrations of these metals were found in surface water following wildfire events near VALL.^{8,77} Before the sorption experiments, ash samples were characterized by measuring Brunauer-Emmett-Teller (BET) specific surface area, zeta potential and C, H, N, O elemental contents (wt %). Detailed descriptions of these methods are in the supporting information (SI). For the sorption experiments, stock solutions (1000 ppm) of Cr(IV) and Cu(II) were prepared by dissolving analytical grade (>99% purity) K₂Cr₂O₇ and CuCl₂·2H₂O in 18MΩ water. For the experiment, 0.1g 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 50mL of 18MΩ 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.⁸ The pH was adjusted to 7.0±0.2 using 2% HCl. 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 hours, centrifuged at 6000 rpm (6640×g) for 3 mins and were 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 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 (SI).

Statistical Analysis. Univariate data analysis were performed using the statistical software R.⁸² The statistical package in OriginPro⁸³ 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, Aspen) and among 3 temperatures (60°C, 350°C and 550°C). 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.

3. 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 $\mu\text{g L}^{-1}$) and Fe (2650 $\mu\text{g L}^{-1}$) in the water samples collected from site 2 and Zn (352 $\mu\text{g L}^{-1}$), 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 $\mu\text{g L}^{-1}$) in the water samples collected from site 1 exceeded the USEPA standards for acute or chronic exposure for both Cr(III) (74 $\mu\text{g L}^{-1}$) and Cr(VI) (11 $\mu\text{g L}^{-1}$). 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 detection limit,^{84,85} lower than found in this study. Average concentrations of major and trace elements (mg kg^{-1}) in non-anthropogenically affected soils in the US estimated by Burt et al.⁸⁶ (Table S3) were used to evaluate the metal concentrations in the soil samples collected along the river ranges. Iron (Fe) was the most abundant metal with concentrations ranging from 4980 mg kg^{-1} to 9850 mg kg^{-1} . Copper (Cu) concentration in the collected soil samples from sites V1, V2 and V3 ranges from 44.2 mg kg^{-1} to 261 mg kg^{-1} , higher than the average Cu concentration (24.7 mg kg^{-1}) of non-anthropogenic affected soils in the US (Table S3). 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 storm water runoff. For example, after the Cerro Grande fire in 2000, elevated concentrations of total Cu (610 $\mu\text{g L}^{-1}$) and total Cr (510 $\mu\text{g L}^{-1}$) were measured in post fire runoff water samples collected from the burned watersheds near Guaje Canyon which is close to the Los Alamos National Laboratory.⁸ 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 18M Ω water.

Acid Extractable Metal Content in Wood Exposed to 60°C, 350°C, and 550°C. We compared the acid extractable metal contents in 9 samples (Pine, Spruce and Aspen at 60°C, 350°C and 550°C, Figure 3, 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 ($p < 0.05$, Table S5, S6) compared to oven dried wood at 60°C (unburned). The acid extractable metal

concentrations for all samples at 60°C, 350°C 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 ($p > 0.05$, Table S5, S6). Among the ash samples at 350°C 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°C 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°C and 550°C Aspen ash samples, while 350°C and 550°C Spruce 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°C and 550°C) for all tree species (Table S4), consistent with findings for wood⁸⁷ and wood ash^{23,88} 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 ($4997 \pm 262 \text{ mg kg}^{-1}$ at 350°C and $2765 \pm 302 \text{ mg kg}^{-1}$ at 550°C) was higher than previously reported values for Pine ash.^{23,51} Due to the dominance of Pine tree species in the forests of 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).^{17,23,39,73,89} 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 Pine Ash (350°C 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°C and 550°C Pine ash in deionized water (Figure 4a to 4d).

Dissolution of metal bearing phases caused 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 were released in solution after 72 hours of reaction. Metals like Cu, Fe, Zn and Ni showed initial release followed by decrease in metal concentration over time for both the 350°C and 550°C Pine ash (Figure 4a to 4d). Limited fluctuations in the concentration of Cr released in solution were observed over time (Figure 4b, 4d). 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 [$\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$], 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.²³

The DOC concentration decreased with increasing temperature in reaction of 60°C, 350°C and 550°C samples with 18 M Ω 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 4e, 4f). 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.^{90,91} The decrease in DOC concentration from 350°C to 550°C ash suggests that a greater loss of organic matter occurs at a higher burning temperature, consistent with findings from previous studies.^{23,33} The range of DOC concentrations (1.27 to 11.3 mg carbon L⁻¹) measured for 350°C and 550°C ash samples in this study are consistent with those reported in

previous studies from field ^{17,25} and laboratory studies.³³ Previously, Wang et al.³⁹ observed decreased reactivity of the ash in forming DBPs such as trihalomethane (THM) and chloral hydrate (CHD) with increasing temperature from 50°C 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.³³ 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.^{33,39}

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.^{67,69} The surface area of Pine ash increased from 36.9 m²/g at 350°C to 294.4 m²/g at 550°C (Table S7). Previously, Mendonça et al.⁶⁹ reported increase in surface area due to creation of micropores for biochar burned at 400°C and 600°C. Higher loss of C, H and O occurred in ash with increasing temperature (Table S8). Lower H/C ratios in 350°C and 550°C can be a measure of higher degree of aromaticity in the ash samples, as suggested by previous studies on biochar.^{67,92} Higher O/C and (O+N)/C ratios, for the 350°C and 550°C ash samples, are indicators of increased hydrophilicity and polarity.^{67,92,93} We observed more than 80% decrease initially in Cu(II) concentration in solution reacting with 350°C Pine ash (Figure 5a), as indicated by measured Cu(II) concentration ($103.6 \pm 3.1 \mu\text{g L}^{-1}$) after 5 mins of reaction and up to 92% decrease after 180 mins of reaction. Cu(II) concentration in the control decreased only 5%, to $601.2 \pm 53.8 \mu\text{g L}^{-1}$ after 180 mins of reaction from the initially added concentration of $635 \mu\text{g L}^{-1}$. In experiments with Cr(VI), low decrease in Cr(VI) concentration was observed, as the measured concentration after 180 mins was 451.7 ± 7.8

$\mu\text{g L}^{-1}$, representing only 13% decrease from the initially added Cr(VI) of $520 \mu\text{g L}^{-1}$ (Figure 5b). Cr(VI) showed negligible decrease in concentration in the Cr(VI)-control experiment (Figure 5b). 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.^{23,72} This is a relevant property of wood ash that should be considered when investigating the persistence of metals such as Cu, Pb, Ni, Fe, Zn associated with ash and debris in wildfire affected watersheds, as reported in several post-fire investigations.^{9,10,74} 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.⁹⁴⁻⁹⁶ 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.⁹⁴ 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^-).⁹⁷ 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 were 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 low level of Cu (0.012%) associated with the Ca⁺² minerals in the reacted ash (Figure S8), while below detection limit for the unreacted ash. The predominant form of the Ca⁺² mineral is most likely calcite (CaCO₃), 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 CaCO₃ are abundant across a variety of plant cells.^{98,99} XRD analyses on reacted and unreacted samples indicated presence of quartz and calcite (CaCO₃) 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 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 detection limit (Table S9). So, the high resolution Cu 2p peak obtained for the unreacted ash was noisy and could not be used for curve fitting analyses (Figure 6). Curve fitting of high resolution XPS Cu 2p spectra obtained for the reacted sample was conducted using reference spectra for CuO, CuCO₃, Cu₂O 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 CuCO₃ (18.6%), and Cu(I) in the form of Cu₂O (17.3%) (Figure 6). The presence of Cu(I) on the reacted

ash surface suggests possible reduction of some of the Cu(II) to Cu(I), as suggested by a previous study by Bogusz et al.⁹³

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, 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.^{58,93,100} These properties are also relevant to better understand the effect of burned soil and ash on post fire mobilization of heavy metals.

4. Environmental Implications

The results from this investigation indicate how metal and DOC content associated with ash burned at different temperatures (350°C 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 post fire watersheds from moderately burned ash and soil reported in previous studies.^{25,101} 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 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 re-association of these metals to ash over time.²³ 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 mins 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} , Pb^{+2} among others, as suggested in other studies related to wood ash^{23,72} and biochar^{57,102} reactivity. The integration of results from the metal dissolution and sorption experiments in this study provide novel insights about post fire 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 post fire response and recovery strategies by local authorities.

5. Acknowledgements

Thanks to Dr. Robert Parmenter for scientific advice and support for this study. Funding for this research was provided by the Oak Ridge Associated Universities (ORAU) Program Ralph E. Powe Jr. Junior Faculty Enhancement Award, the New Mexico Water Resources Research Institute, and the National Science Foundation under New Mexico EPSCoR (Grant Number #IIA-1301346), and CREST (Grant Number 1345169). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Table 1. Elemental content of water (site 1 to 5) and soil (site V1 to V3) samples^a from the East Fork Jemez River within the Valle Grande area in VALL. Site 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 is shown.

Site	pH	Alkalinity (mg L ⁻¹)	TOC (mg C L ⁻¹)	Water elemental content (µg 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 - 7.97	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)				
				59.4 - 86.9	10.9 - 35.3	7800 - 9620	13.0 - 38.5	219 - 319
				71.3 - 89.9	9.25 - 20.4	4980 - 9850	10.2 - 31.4	50.8 - 194
				44.2 - 261	11.0 - 17.2	5050 - 7940	14.9 - 37.9	92.7 - 139
				7.16 - 17.5	5.81 - 13.3	109 - 221	19.5 - 35.2	260 - 347
				5.97 - 18.6	4.96 - 15.2	86.4 - 190	22.2 - 54.2	179 - 344
				7.97 - 13.9	5.31 - 11.3	102 - 184	30.8 - 39.4	217 - 454

^aAqueous and soil elemental content measured with ICP-OES and ICP-MS ^bBDL = Below detection limit

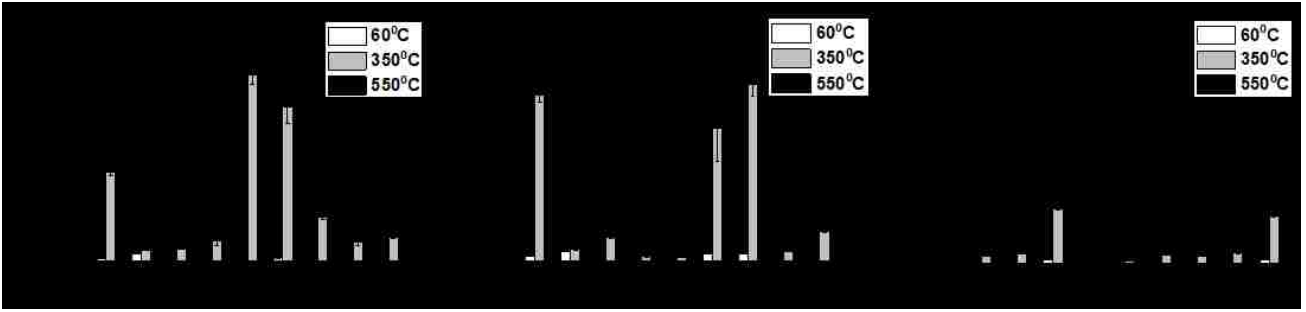


Figure 3. Acid extractable concentrations (mean \pm SD) of 9 metals varied across different tree species of (a) Pine, (b) Spruce and (c) Aspen. The major elements (Ca, Mg and K) were predominant in all tree species at 60°C, 350°C and 550°C (Table S2). Ash produced at both 350°C (moderate burn) and 550°C (high burn) contained higher metal concentrations than in samples dried at 60°C (unburned) for all species.

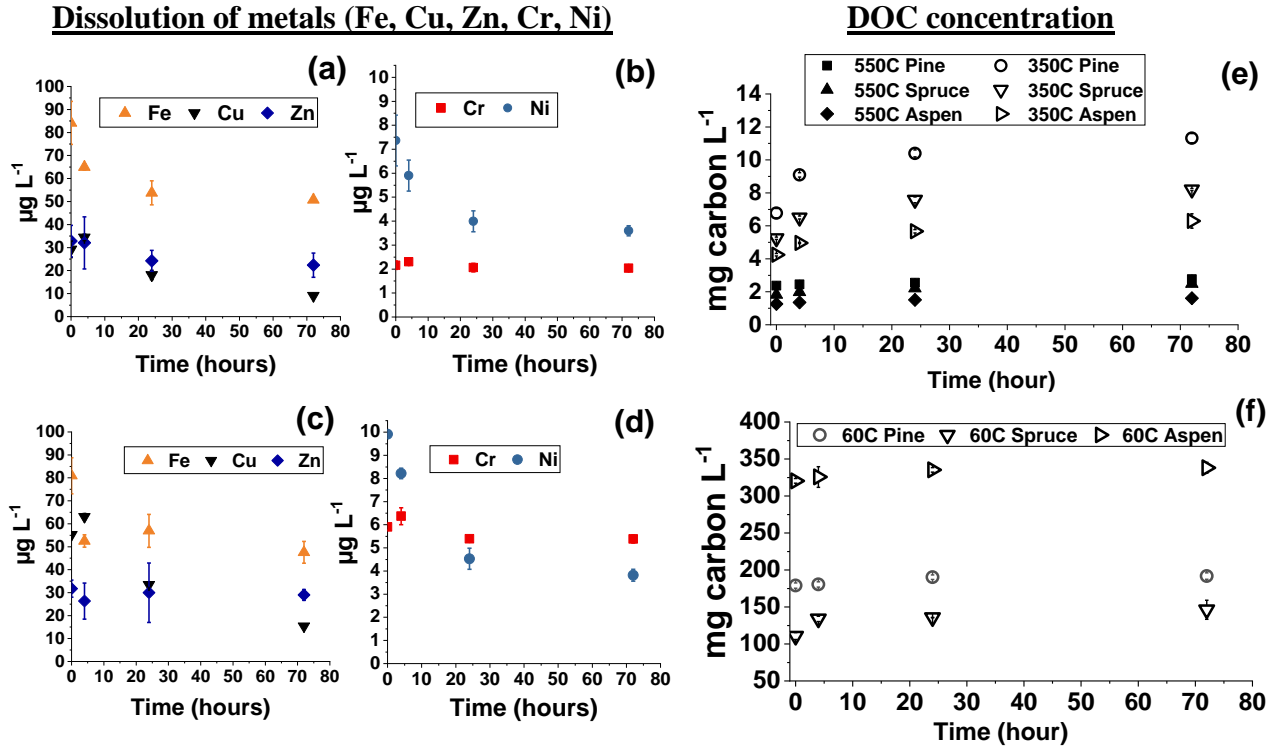


Figure 4. Concentrations of (a) Fe, Cu, Zn and (b) Cr, Ni at 0, 4, 24 and 72 hours in reaction of 550°C Pine ash with 18 MΩ water. In figures (c) and (d), metal concentrations are shown for reaction of 350°C Pine ash with 18 MΩ water. DOC concentration (mg carbon L^{-1}) at 0, 4, 24 and 72 hours ($n=3$)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

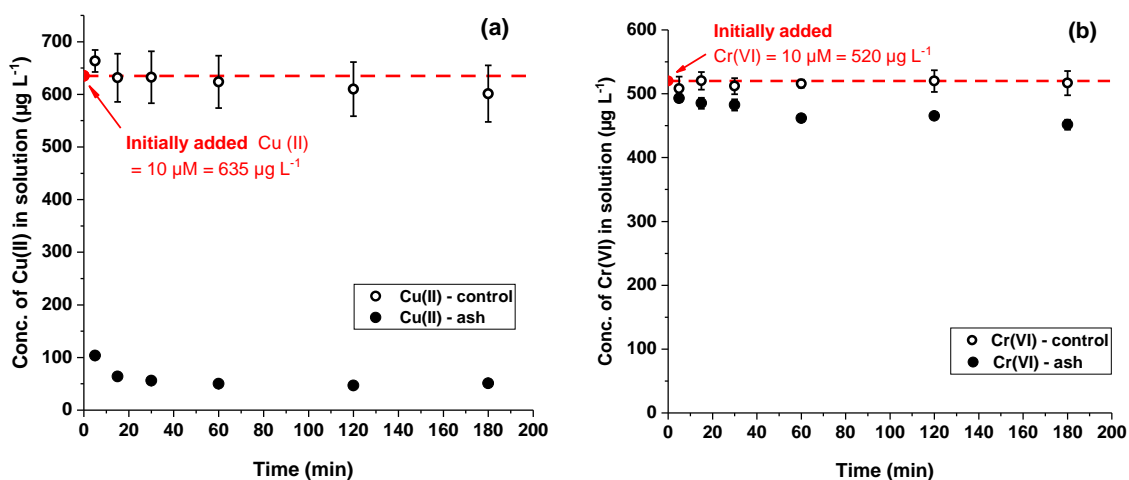
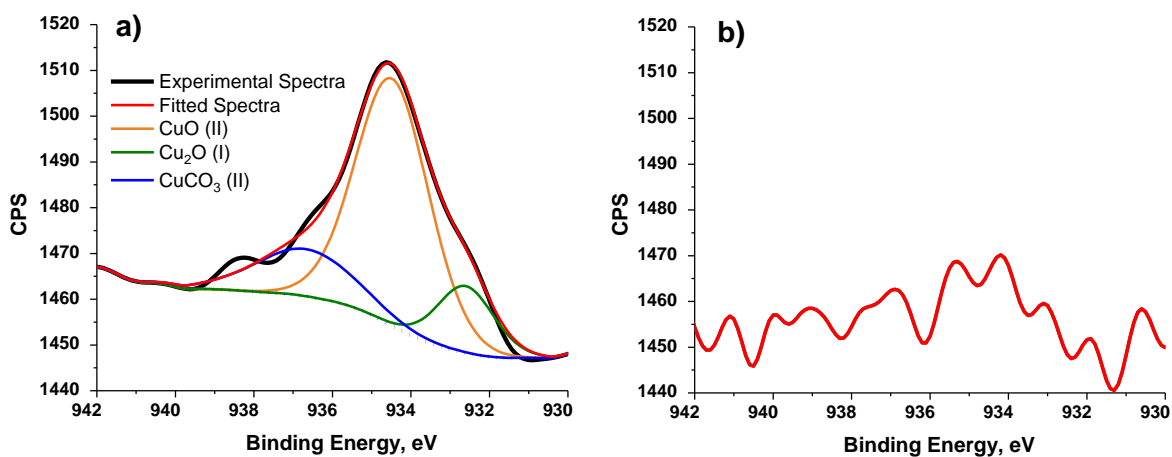


Figure 5. Results from the metal sorption experiments ($n=3$, sampling interval = 5 min, 15 min, 30 min, 1 hr, 2 hrs and 3hrs) conducted by reacting $10 \mu\text{M}$ of (a) Cu(II) and (b) Cr(VI) separately in a solution containing 0.1g of 350°C Pine ash with 50mL of $18\text{M}\Omega$ water. Note that the control experiments were conducted by reacting $10\mu\text{M}$ of Cu(II) and Cr(VI) in $18\text{M}\Omega$ water without ash.



c)

Sample	% Content		
	Cu ₂ O (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

¹Below detection limit

Figure 6. 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, CuCO₃, Cu₂O and Cu metal.

Appendix: Supporting Information

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

Additional Materials and Methods.

Wood Sampling Methods. Wood samples of Ponderosa Pine, Quaking Aspen and Colorado Blue Spruce were collected from the Valles Caldera National Preserve area in New Mexico. We collected tree branches with attached twigs, leaves and needles from unburned live trees. The collected tree branches were crushed to powders using a laboratory milling machine and then oven dried for at 60°C for 48 hours before burning.

Water and Soil Sampling Methods. Surface water samples were collected as grab samples in 125 mL polypropylene bottles after three rinses. Samples for dissolved analysis were filtered through a 0.45 µm filter. Samples for metals' analysis were acidified to a pH of 2 with nitric acid. Soil samples were collected using a soil auger down to 6 inches and homogenized prior to preparation for analysis.

Solid Phase Analyses. Elemental composition and the oxidation states in the near surface (5-10 nm) were acquired using a Kratos Axis DLD Ultra X-ray photoelectron spectrometer. A monochromatic Al K α source was used, operating at 225W with no charge compensation. The Cu 2p spectra from reference Cu samples were used to identify the species of Cu present on the near surface region of the reacted ash sample. Reference Cu samples (Cu metal, Cu(I, II) oxide and Copper(II) carbonate basic) were purchased from Sigma Aldrich, Strem Chemicals and Alfa Aesar respectively. All the chemicals were >99% pure except the Copper(II) carbonate basic (\geq 95% purity). The high-resolution spectra, along with the binding energies obtained for the Cu 2p regions

for these reference materials are shown in Figure S10. Curve fitting and quantification were performed using CasaXPS software. Spectra of all the samples were calibrated using gold powder deposited on each sample with respect to the Au 4f peak position at 84 eV. Electron scattering background was removed using a Shirley background; curve fitting of spectra was done using a 70% Gaussian/30% Lorentzian [GL (30)] line shape. Qualitative mapping of the ash samples was done using an electron probe microanalyzer (EPMA) using wavelength dispersive X-ray spectroscopy (WDS). A JEOL JXA-8200 Super-Probe was used, operating at 10 kV with a 10 μm probe diameter and 30 nA probe current.

Characterization of 60°C, 350°C and 550°C samples (BET, zeta potential and C, H, N, O analysis). The Brunauer-Emmett-Teller (BET) specific surface area for the 350°C and 550°C ash samples were measured using a Gemini 2360 V5 surface area analyzer. The zeta potential of the ash samples was determined using a Malvern Zetasizer Nano-ZS equipped with a He-Ne laser (633nm) and non-invasive backscatter optics (NIBS). N and C contents (wt %) for 60°C, 350°C and 550°C samples were measured using a Costech ECS 4010 Elemental Analyzer coupled to a Thermo Fisher Scientific Delta V Advantage mass spectrometer via a CONFLO IV interface. O and H contents (wt %) were measured using a Thermo Chemical Elemental Analyzer (TCEA) coupled to a Thermo Fisher Scientific Delta V Advantage. Wt % C, H, N and O values were calculated using the Elemental Spruce Powder Standard B2213.

Table S1. Mass of wood (e.g., pine spruce and aspen) samples for (a) oven drying and (b) burning procedure of wood samples.

a)

Sample Name	Mass before oven drying at 60°C for 48 hours (g)	Mass after oven drying at 60°C for 48 hours (g)	% mass lost (moisture content)	% mass remaining due to loss of moisture content
Pine	2164	1612	25.5	74.5
Spruce	3342	2762	17.4	82.6
Aspen	2802	2173	22.4	77.6

b)

Sample Name	Mass before burning at 550°C for 4 hours (g)	Mass after burning at 550°C for 4 hours (g)	% mass remaining after burning	Mass before burning at 350°C for 4 hours (g)	Mass after burning at 350°C for 4 hours (g)	% mass remaining after burning
Pine	450.2	22.55	5.01	200.2	7.32	3.66
Spruce	450.4	17.16	3.81	200.2	6.96	3.48
Aspen	450.1	24.01	5.33	200.2	10.94	5.47

Table S2. Detection limits for analyses using: a) inductively coupled plasma optical emission spectrometry (ICP-OES), and b) inductively coupled plasma mass spectrometry (ICP-MS).

a) ICP-OES

Element	IDL (mg L⁻¹)	MDL (mg L⁻¹)
Al	0.0280	0.0280
Ca	0.0100	0.0100
Cu	0.0054	0.0054
Fe	0.0062	0.0062
Mg	0.0030	0.0030
Mn	0.0014	0.0014
Ni	0.0150	0.0150
Pb	0.0420	0.0420
V	0.0064	0.0064
Zn	0.0018	0.0018

b) ICP-MS

Element	IDL (mg L⁻¹)	MDL (mg L⁻¹)
Cu	0.004	0.009
Ni	0.006	0.02
Pb	0.0003	0.0004
V	0.006	0.01
Zn	0.04	0.1

**IDL = Instrument Detection Limit

**MDL = Method Detection Limit

Table S3. Maximum Contaminant Level (MCL) and different standards for exposure limits set by USEPA for Cr, Cu, Fe, Mn and Zn. Additionally, average concentrations of these 5 metals in natural soils (without known anthropogenic additions) are also provided for comparison with soil samples collected along the East Fork Jemez river ranges for this study.

Element	Drinking water standard- Maximum Contaminant Level (MCL) ($\mu\text{g L}^{-1}$) ²	Drinking water action level ($\mu\text{g L}^{-1}$) ³	Drinking water secondary standard ($\mu\text{g L}^{-1}$) ¹	Surface water human health for the consumption of water + organism ($\mu\text{g L}^{-1}$) ³	Aquatic Life Freshwater CMC Acute Exposure ($\mu\text{g L}^{-1}$)	Aquatic Life Freshwater CCC Chronic Exposure ($\mu\text{g L}^{-1}$)	Average concentrations of metals in non-anthropogenically affected soils in the US (mg kg^{-1}) by Burt et al. ⁵
Chromium (III)					570	74	
Chromium (total)	100						88.7
Chromium (VI)					16	11	
Copper (Cu)		1300		1300	2 ⁴	1.3 ⁴	24.7
Iron (Fe)			300			1000	19000
Manganese (Mn)			50	50			62.6
Zinc (Zn)			5000	7400	120	120	589

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- (1) USEPA, Secondary Drinking Water Standards: Guidance for Nuisance Chemicals, accessed on Dec 22, 2017 at <https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals>
- (2) USEPA, National Primary Drinking Water Regulations, accessed on Dec 22, 2017 at <https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants>
- (3) USEPA, National Recommended Water Quality Criteria - Human Health Criteria Table, accessed on Dec 22, 2017 at <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table>
- (4) USEPA, Fact Sheet: Draft Estuarine/Marine Copper Aquatic Life Ambient Water Quality Criteria, accessed on Dec 22, 2017 at <https://www.epa.gov/sites/production/files/2016-08/documents/copper-estuarine-marine-draft-factsheet.pdf>
- (5) Burt, R.; Wilson, M.; Mays, M.; Lee, C., Major and trace elements of selected pedons in the USA. J. Environ. Qual. 2003, 32, (6), 2109-2121.

Table S4. Acid extractable elemental content (mg kg⁻¹) for wood samples (Pine, Spruce, Aspen) at 60°C, 350°C and 550°C. Data are presented as Mean \pm standard deviation.

Acid Extractable Elemental Content (mg kg ⁻¹)												
Temperature: 550°C												
Sample	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	Si	Sr	Zn
Pine	4138.40	181967.73	476.16	2765.07	5050.52	78075.67	27881.15	1575.62	803.60	814.26	505.93	938.27
	\pm 100.17	\pm 6195.55	\pm 9.12	\pm 302.26	\pm 767.95	\pm 1781.05	\pm 35.82	\pm 14.15	\pm 22.81	\pm 93.11	\pm 1.75	\pm 4.94
Spruce	4734.25	164204.50	81.50	71.88	4154.38	33847.64	9807.35	3933.69	242.56	334.93	551.96	590.30
	\pm 64.55	\pm 3723.07	\pm 1.07	\pm 1.59	\pm 40.74	\pm 628.85	\pm 106.4	\pm 41.92	\pm 2.91	\pm 29.36	\pm 6.25	\pm 7.67
Aspen	177.41	307080.02	12.91	72.42	238.57	47800.02	14193.24	175.14	277.82	289.68	1372.46	1209.62
	\pm 3.19	\pm 4896.33	\pm 2.01	\pm 1.62	\pm 14.5	\pm 728.85	\pm 129.61	\pm 0.74	\pm 1.64	\pm 1.58	\pm 15.07	\pm 12.29
Temperature: 350°C												
Pine	2384.54	122157.57	543.31	4996.51	4151.65	55823.72	19205.62	1179.05	524.65	310.14	332.28	638.32
	\pm 96.48	\pm 4502.43	\pm 123.69	\pm 261.96	\pm 441.79	\pm 2122.64	\pm 747.69	\pm 61.36	\pm 101.22	\pm 18.17	\pm 12.89	\pm 23.33
Spruce	4477.69	186287.82	112.24	81.47	3598.13	37261.72	6168.71	4760.57	266.93	322.53	646.79	799.14
	\pm 175.93	\pm 5459.71	\pm 3.06	\pm 5.42	\pm 908.11	\pm 1050.50	\pm 48.12	\pm 315.24	\pm 3.04	\pm 23.09	\pm 27.32	\pm 36.21
Aspen	184.81	294197.49	11.83	62.89	225.13	45153.30	13275.79	182.36	264.34	241.02	1390.40	1206.46
	\pm 1.67	\pm 1343.51	\pm 0.13	\pm 0.60	\pm 4.72	\pm 242.64	\pm 73.52	\pm 1.08	\pm 3.52	\pm 5.76	\pm 3.89	\pm 8.47
Temperature: 60°C												
Pine	91.1	9364.2	4.97	58.2	114.7	8696.5	466.3	59.6	6.1	202.8	13.1	23.3
	\pm 3.05	\pm 220.03	\pm 1.29	\pm 18.24	\pm 45.69	\pm 35.69	\pm 8.47	\pm 2.81	\pm 0.25	\pm 11.56	\pm 0.61	\pm 1.81
Spruce	131.5	11294.7	12.9	4.6	198.9	8628.5	419.1	185.1	12.5	258.8	24.3	33.2
	\pm 3.32	\pm 248.46	\pm 0.46	\pm 0.31	\pm 7.93	\pm 28.68	\pm 15.13	\pm 6.5	\pm 0.9	\pm 1.67	\pm 0.61	\pm 0.4
Aspen	22.2	22359.3	5.1	5.7	22.4	9709.04	858.5	10.6	17.9	23.7	86.8	78.6
	\pm 1.15	\pm 565.51	\pm 0.03	\pm 0.88	\pm 8.53	\pm 25.86	\pm 4.22	\pm 0.15	\pm 0.82	\pm 3.9	\pm 0.35	\pm 1.49

Table S5. The Kruskal Wallis test was used to determine if significant differences exist (defined as p -value < 0.05) between the tree species (Pine, Spruce, Aspen) at three temperatures (60°C, 350°C and 550°C) with respect to acid extractable metal concentrations (\log_{10} transformed). Individual contribution of the metals was not considered here due to limited number of observations ($n=3$) for each metal. No significant difference (highlighted, p -value = 0.4007 > 0.05) was observed for Pine, Aspen and Spruce at 60°C. The limitation of Kruskal Wallis test is that it does not specify which specific sample is contributing to the overall difference. To address this, Mann Whitney U test was done to do pairwise comparisons between the samples.

Comparison between Pine, Spruce and Aspen at 60°C, 350°C and 550°C (n=9)

<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations (\log_{10} transformed)	89.85	4.982×10^{-4}

Comparison between Pine 60, Spruce 60 and Aspen 60 (n=3)

<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations (\log_{10} transformed)	1.8293	0.4007

Comparison between Pine 350, Spruce 350 and Aspen 350 (n=3)

<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations (\log_{10} transformed)	8.1227	0.01723

Comparison between Pine 550, Spruce 550 and Aspen 550 (n=3)

<u>Data</u>	<u>χ^2 statistic</u>	<u>p-value</u>
acid extractable element concentrations (\log_{10} transformed)	9.5225	0.00855

Table S6. The Wilcoxon rank sum test (Mann-Whitney U test) was used to do pairwise comparisons ($n=9$ samples, ${}^9C_2 = 36$ combinations of pairs) of tree species (Pine, Spruce, Aspen) at 60°C, 350°C and 550°C to test for significant differences (defined as $p < 0.05$) in metal concentrations (\log_{10} transformed). Individual contribution of the metals was not considered here due to limited number of observations ($n=3$) for each metal.

Serial No.	Pair considered	Diff.	W	<i>p</i> -value	Serial No.	Pair considered	Diff.	W	<i>p</i> -value
1	Aspen 350 – Aspen 60	1.078	990	1.20×10^{-4}	19	Pine 60 – Aspen 60	0.164	726	0.383
2	Aspen 550 – Aspen 60	1.108	991	1.15×10^{-4}	20	Spruce 60 – Aspen 60	0.331	765	0.190
3	Spruce 550 – Aspen 60	1.407	1043	8.87×10^{-6}	21	Spruce 60 – Pine 60	0.642	690	0.103
4	Spruce 350 – Aspen 60	1.477	1053	5.22×10^{-6}	22	Aspen 550 – Aspen 350	0.021	672	0.793
5	Pine 350 – Aspen 60	1.678	1080	1.18×10^{-6}	23	Spruce 550 – Aspen 350	0.401	788	0.117
6	Pine 550 – Aspen 60	1.748	1101	3.47×10^{-7}	24	Spruce 350 – Aspen 350	0.462	798	0.092
7	Aspen 350 – Pine 60	0.761	960	3.38×10^{-4}	25	Pine 350 – Aspen 350	0.532	912	2.64×10^{-3}
8	Aspen 550 – Pine 60	0.780	967	2.43×10^{-4}	26	Pine 550 – Aspen 350	0.634	927	1.45×10^{-4}
9	Spruce 550 – Pine 60	1.261	1043	3.67×10^{-6}	27	Spruce 550 – Aspen 550	0.371	775	0.155
10	Spruce 350 – Pine 60	1.284	1042	3.91×10^{-6}	28	Spruce 350 – Aspen 550	0.434	783	0.130
11	Pine 350 – Pine 60	1.413	1110	3.06×10^{-8}	29	Pine 350 – Aspen 550	0.542	911	2.75×10^{-3}
12	Pine 550 – Pine 60	1.547	1133	4.36×10^{-9}	30	Pine 550 – Aspen 550	0.651	927	1.45×10^{-3}
13	Aspen 350 – Spruce 60	0.774	903	3.73×10^{-3}	31	Spruce 350 – Spruce 550	0.043	694	0.610
14	Aspen 550 – Spruce 60	0.777	910	2.86×10^{-3}	32	Pine 350 – Spruce 550	0.140	738	0.316
15	Spruce 550 – Spruce 60	1.238	1008	2.91×10^{-5}	33	Pine 550 – Spruce 550	0.324	783	0.130
16	Spruce 350 – Spruce 60	1.235	1008	2.91×10^{-5}	34	Pine 350 – Spruce 350	0.150	713	0.470
17	Pine 350 – Spruce 60	1.339	1114	2.21×10^{-8}	35	Pine 550 – Spruce 350	0.282	761	0.207
18	Pine 550 – Spruce 60	1.431	1134	3.99×10^{-9}	36	Pine 550 – Pine 350	0.150	738	0.316



 = p -value < 0.05 = Significant difference
 = p -value > 0.05 = No significant difference

Table S7. Specific surface areas (m^2/g) of the Pine, Spruce and Aspen ash samples measured by Brunauer-Emmett-Teller (BET) method.

Sample	BET Multipoint Surface Area (m^2/g)
Pine Ash 350°C	36.91
Pine Ash 550°C	294.37
Spruce Ash 350°C	20.29
Spruce Ash 550°C	124.77
Aspen ash 350°C	7.06
Aspen ash 550°C	12.9

Table S8. Elemental composition (C, H, N, O) and ratios of Pine, Spruce and Aspen samples at 60°C, 350°C and 550°C. H/C is the atomic ratio of hydrogen to carbon; O/C is the atomic ratio of oxygen to carbon and (O+N)/C is the atomic ratio of the sum of nitrogen and oxygen to carbon.

Sample	Elemental composition				Molar H/C	Molar O/C	Molar (O+N)/C
	C (%)	H (%)	N (%)	O (%)			
Pine 60°C	52.1	6.91	0.5	37.7	1.589	0.542	0.549
Spruce 60°C	50.3	6.86	0.3	41.2	1.638	0.614	0.619
Aspen 60°C	51.1	6.87	0.4	39.4	1.615	0.578	0.585
Pine 350°C	31.8	1.10	2.4	26.9	0.414	0.634	0.699
Spruce 350°C	15.0	0.48	0.7	21.5	0.384	1.078	1.115
Aspen 350°C	14.0	0.42	0.3	28.6	0.361	1.537	1.555
Pine 550°C	16.3	0.57	0.4	21.8	0.421	0.998	1.018
Spruce 550°C	25.3	0.62	0.4	19.7	0.294	0.583	0.598
Aspen 550°C	6.1	0.26	0.4	27.1	0.513	3.326	3.379

Table S9. Atomic content for the unreacted and reacted 350°C pine ash as determined by X-ray photoelectron spectroscopy (XPS) survey scan.

Sample	% Atomic Content		
	C 1s	O 1s	Cu 2p
Unreacted 350°C pine ash	66.2	33.8	BDL ¹
Reacted 350°C pine ash	73.2	26.7	0.11

¹*Below detection limit*

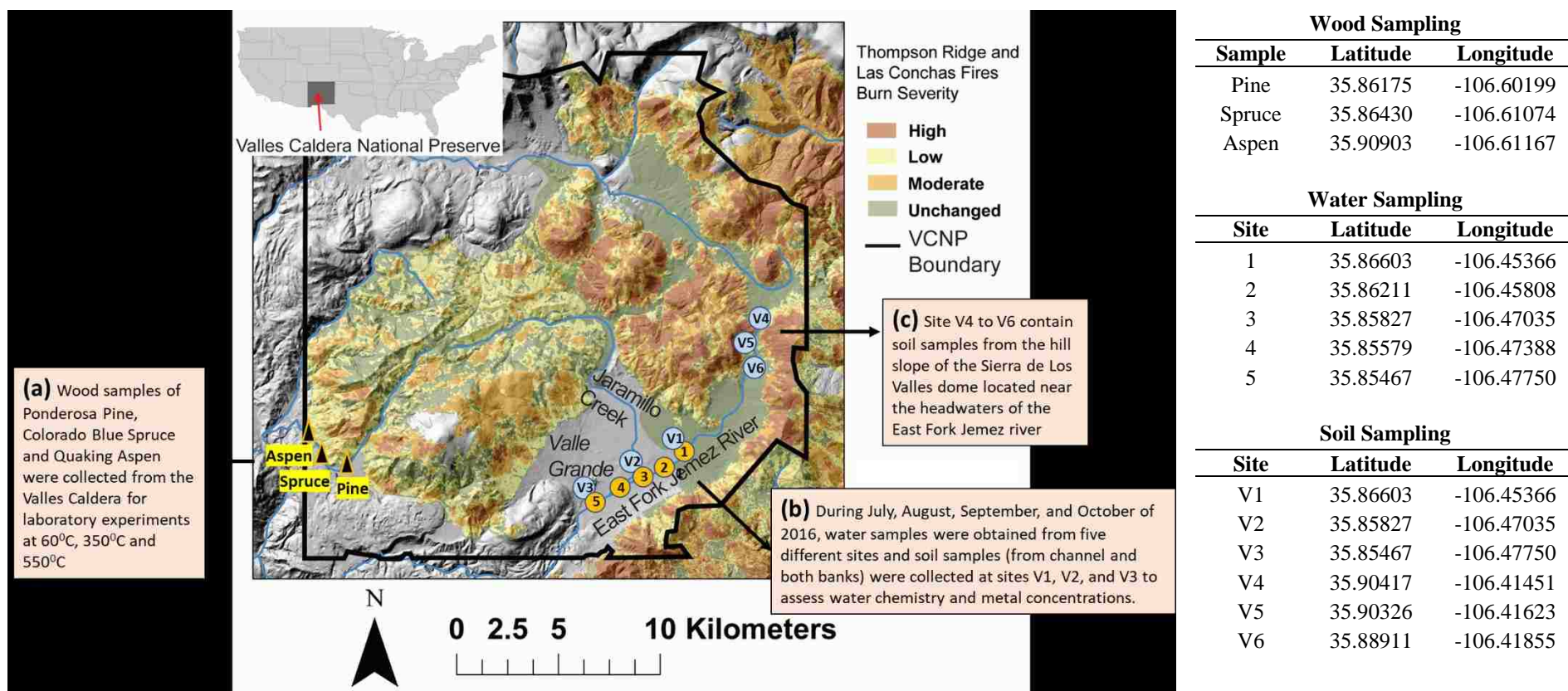
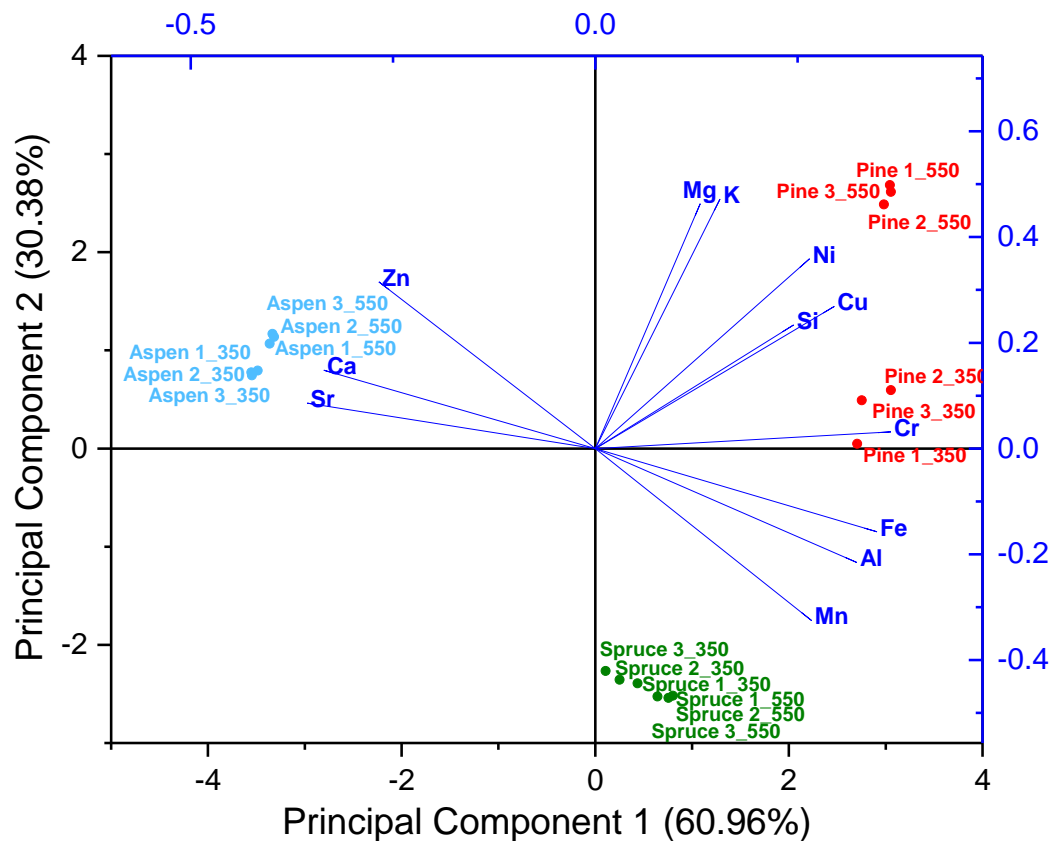


Figure S1. Map showing the sampling locations for (a) wood, (b) water and soil and (c) soil samples in Valles Caldera. The co-ordinates of the sampling locations are shown beside the map. This site map is adapted from the map published in a previous study by Cerrato et al.²³

Reference

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Element	Coefficients of PC 1	Coefficients of PC 2
Al	0.32329	-0.2157
Ca	-0.33562	0.14808
Cr	0.36557	0.03147
Cu	0.29553	0.26884
Fe	0.34826	-0.15737
K	0.15423	0.47189
Mg	0.12975	0.46318
Mn	0.26729	-0.32558
Ni	0.26484	0.35895
Si	0.24515	0.2337
Sr	-0.35604	0.08592
Zn	-0.26742	0.31536

Figure S2. Principal component analysis was run on metal concentrations for 350°C and 550°C triplicate measurements of ash samples (Pine, Spruce, Aspen). The first two principal components explained 91.34% of the total variance. The metals such as Al, Cr, Cu, Fe, Mn and Si showed high positive loadings on PC 1; and PC 2 showed high positive loadings for the major elements (Ca, K, Mg) and metals such as Ni, Sr and Zn. Coefficients of the metals on the principal components are shown in the table. The figure also shows the component scores of the Pine, Spruce and Aspen ash samples. 350°C and 550°C Pine ash samples had positive scores on the both the principal components.

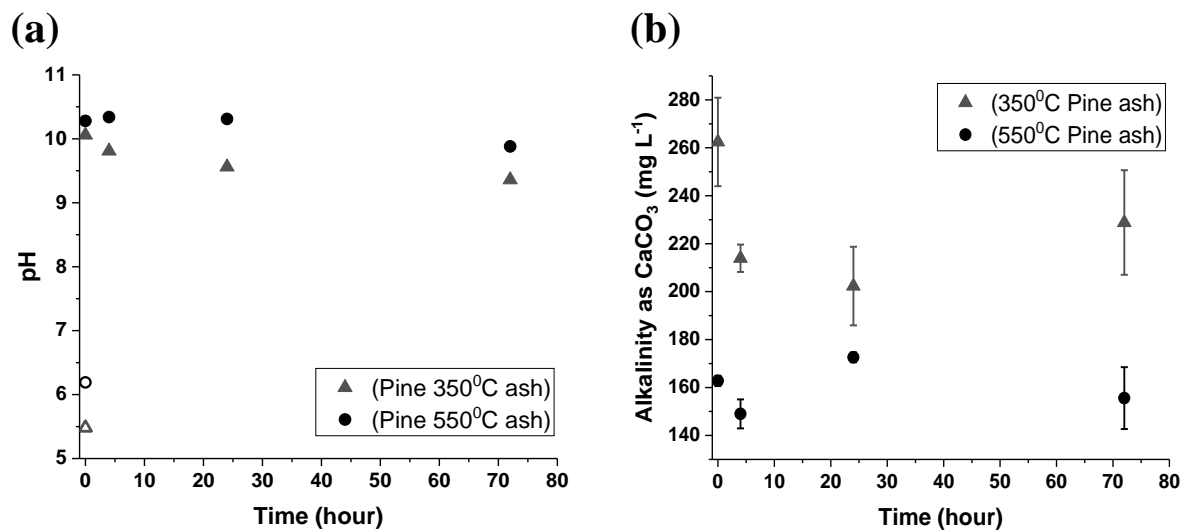
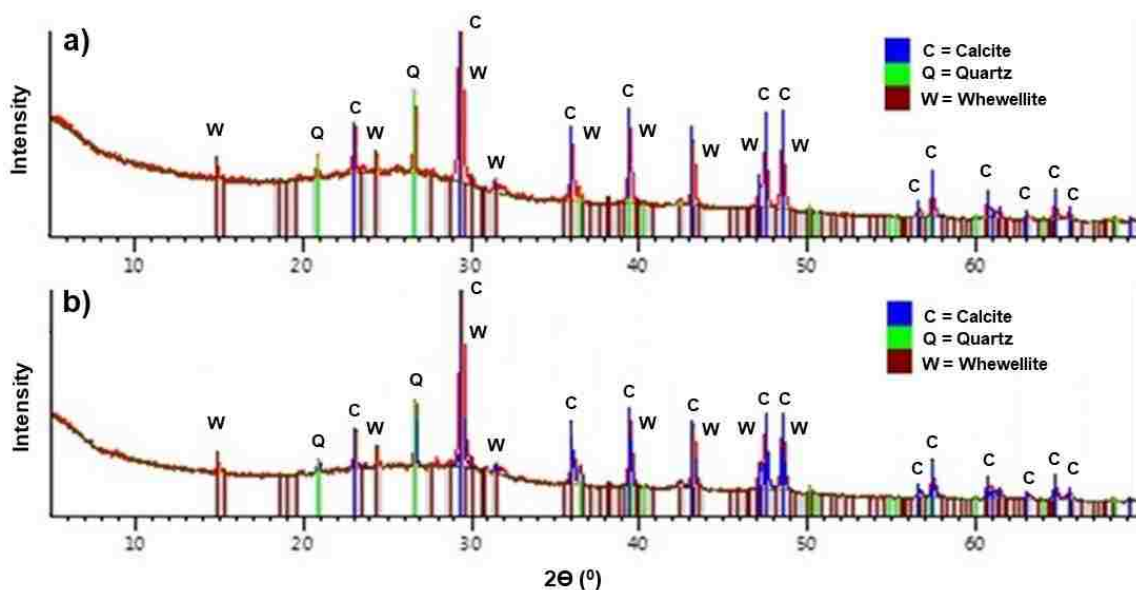


Figure S3. pH and alkalinity measured at 0, 4, 24 and 72 hours are shown in figure (a) and (b) respectively. In figure (a), the open symbols represent the pH of 18MΩ water.



Compound Name	Unreacted Ash (atomic wt.%)	Reacted Ash (atomic wt.%)
Calcite (CaCO ₃)	79%	78%
Quartz (SiO ₂)	12%	11%
Whewellite (Ca(C ₂ O ₄).H ₂ O)	9%	11%

Figure S4. XRD patterns of the (a) reacted and the (b) unreacted 350°C Pine ash sample from the batch sorption experiments with Cu(II). The two samples are very similar in terms of crystalline composition which is predominantly calcite (78-79 %) with lesser amounts of quartz (11-12 %) and whewellite (9-11 %).

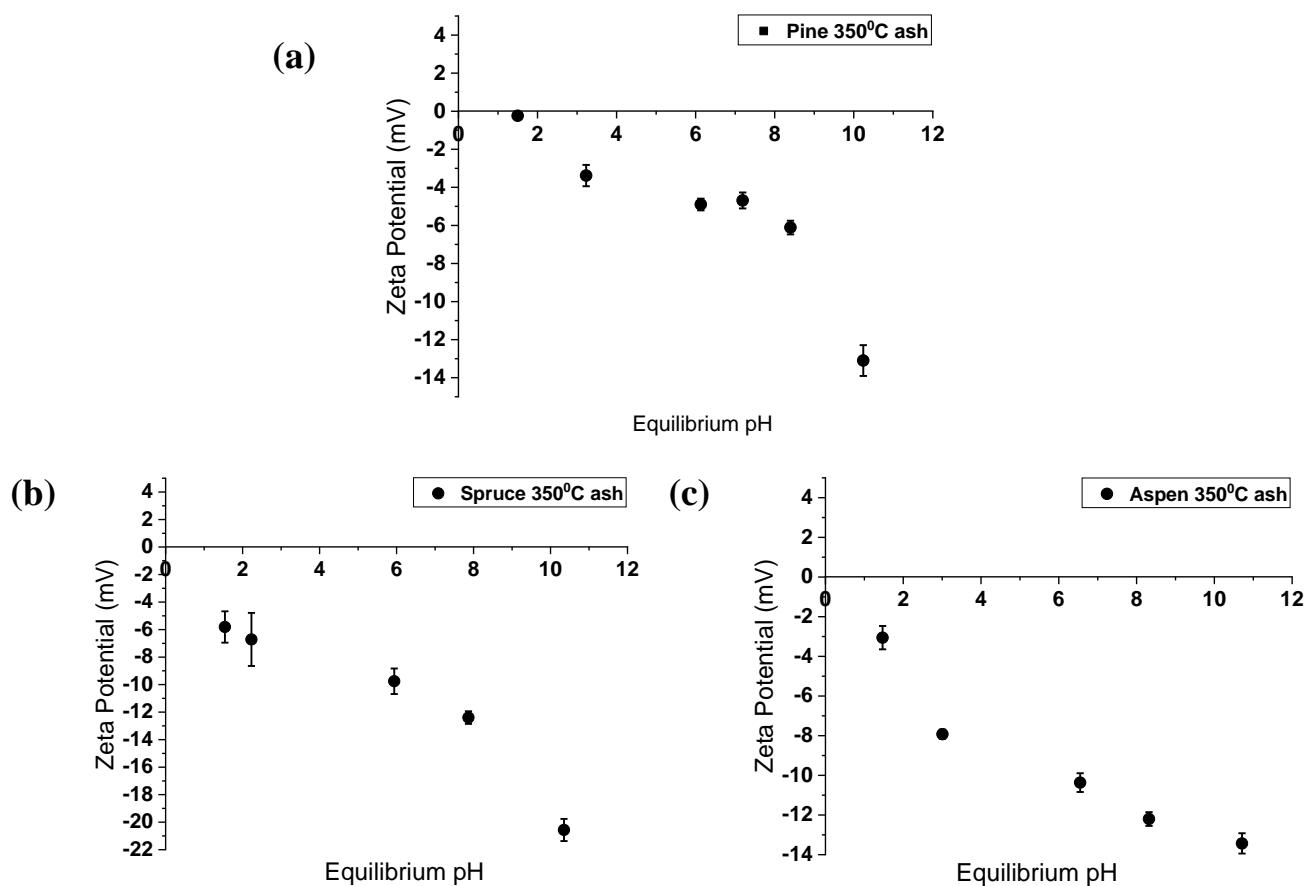


Figure S5. Zeta Potential (mV) measurements of (a) Pine 350°C ash, (b) Spruce 350°C ash and (c) Aspen 350°C ash in different solution pH values. The reported values are the average of three measurements.

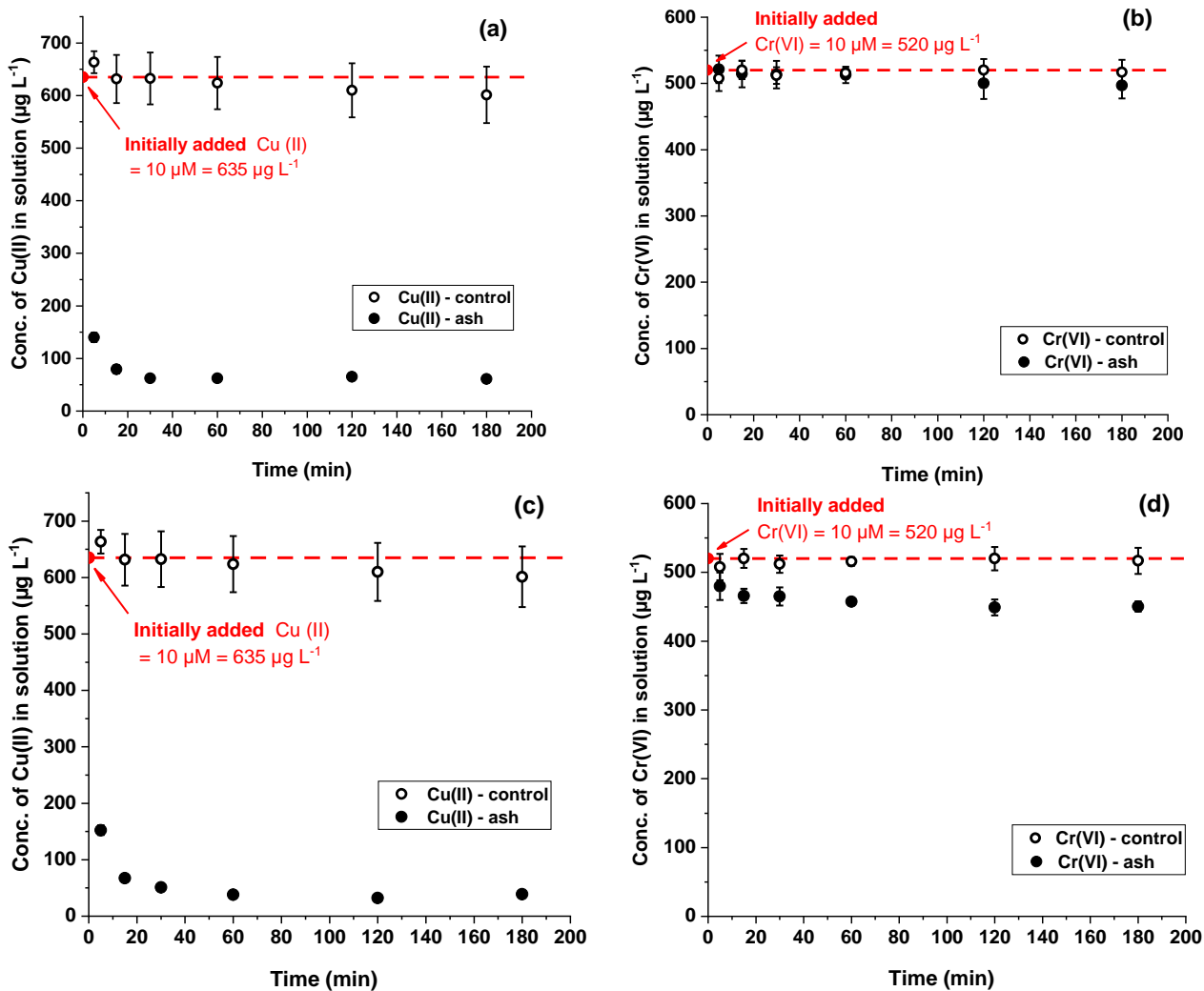


Figure S6. Results from the metal sorption experiments ($n=3$, sampling interval = 5 min, 15 min, 30 min, 1 hr, 2 hrs and 3hrs) conducted by reacting $10 \mu\text{M}$ of (a) Cu(II) and (b) Cr(VI) separately in a solution containing 0.1g of 350°C Spruce ash with 50mL of $18\text{M}\Omega$ water. Figures (c) and (d) show the same analysis with Aspen ash. Results from the control experiments without the ash are included in all the figures.

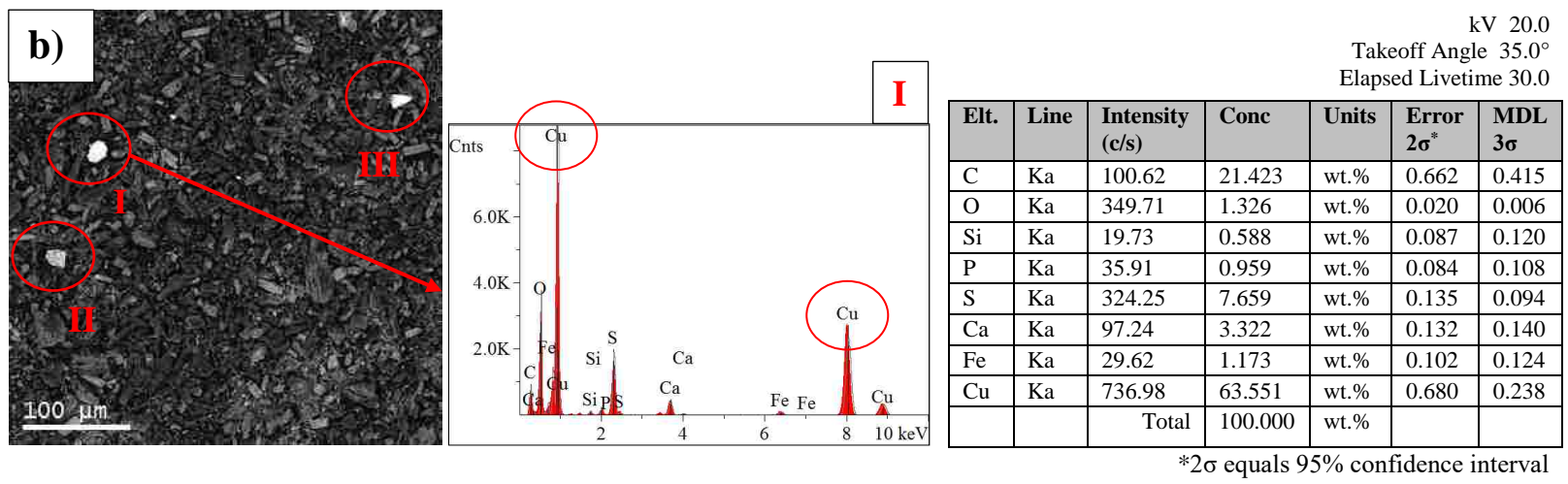
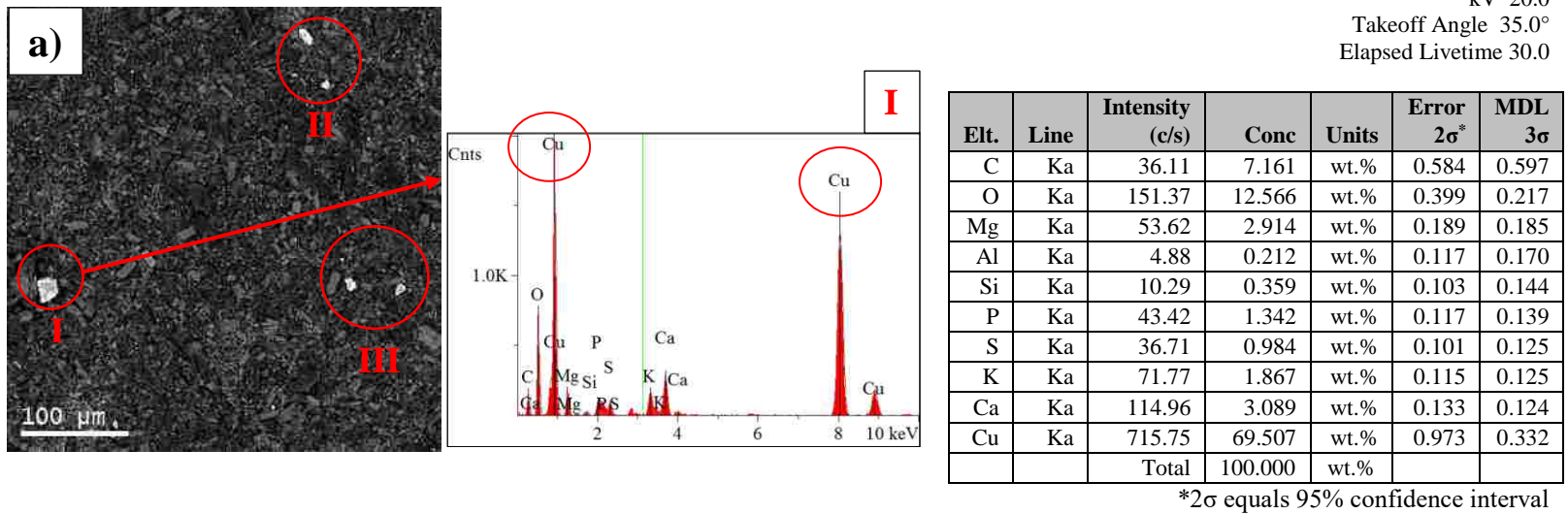
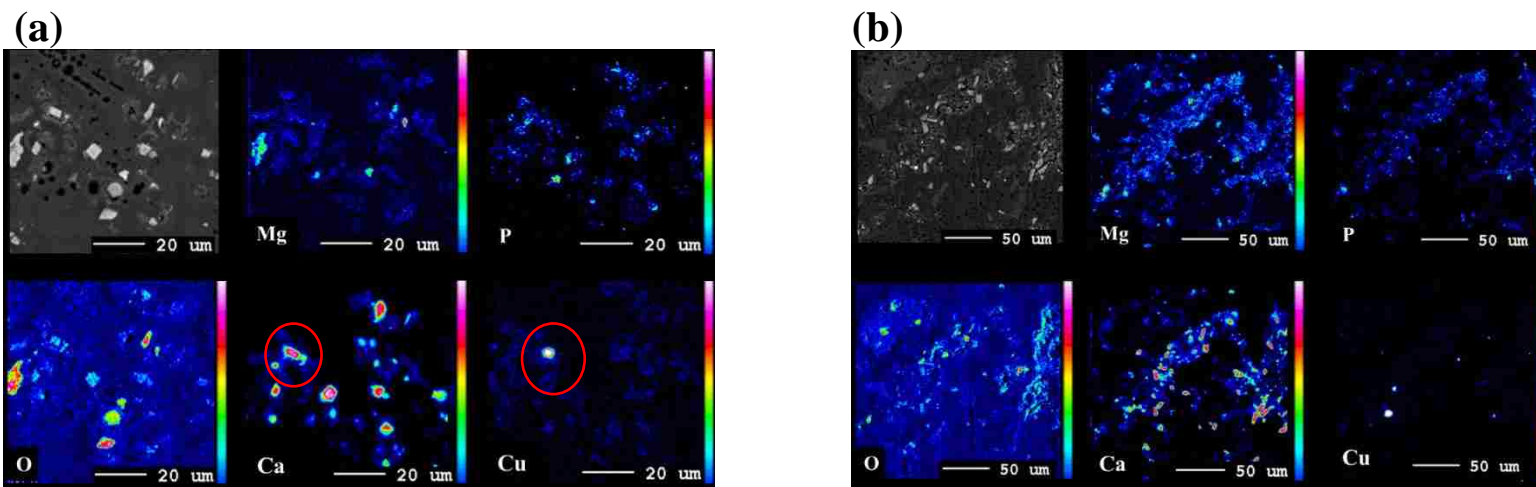
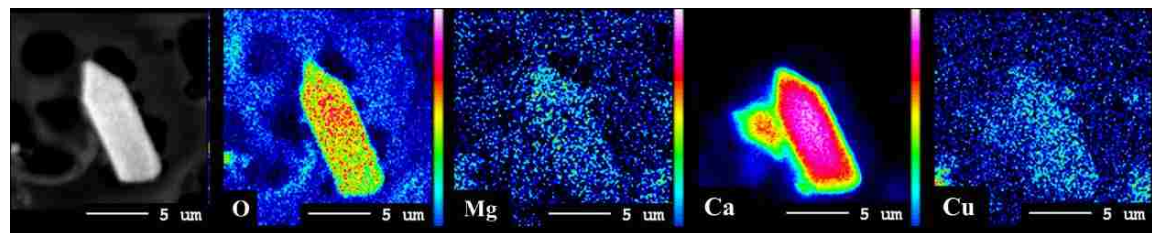


Figure S7. SEM images of the (a) unreacted and the (b) reacted 350°C Pine ash from the batch sorption experiments with Cu(II). EDS spectrum from a Cu grain on both the ash samples shows presence of Cu peaks. The atomic wt.% distribution for the respective spectrum is also shown for a specific Cu grain highlighted in red circle.



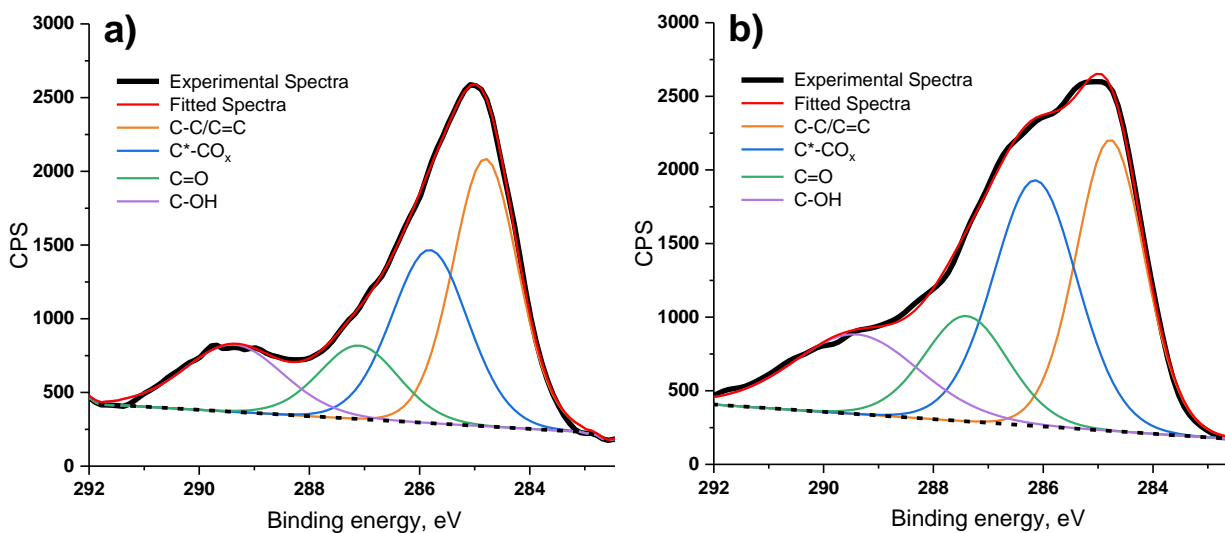
(c) Microprobe mapping of the mineralized Ca region [red circled in figure (a)] of the reacted ash



(d)	<u>K (wt%)</u>	<u>Ca (wt%)</u>	<u>Mg (wt%)</u>	<u>Cu wt%</u>	<u>Si (wt%)</u>	<u>S (wt%)</u>	<u>P (wt%)</u>	<u>O (wt%)</u>	<u>C (wt%)</u>	<u>Total (wt%)</u>
Average of 7 reference lines (Reacted sample)	0.033	16.957	0.018	0.012	0.006	0.007	0.097	46.430	14.825	78.384
Average of 7 reference lines (Unreacted sample)	0.137	17.557	0.014	BDL*	BDL	0.054	0.013	46.270	14.691	78.727

*BDL = Below detection limit at 95% confidence interval

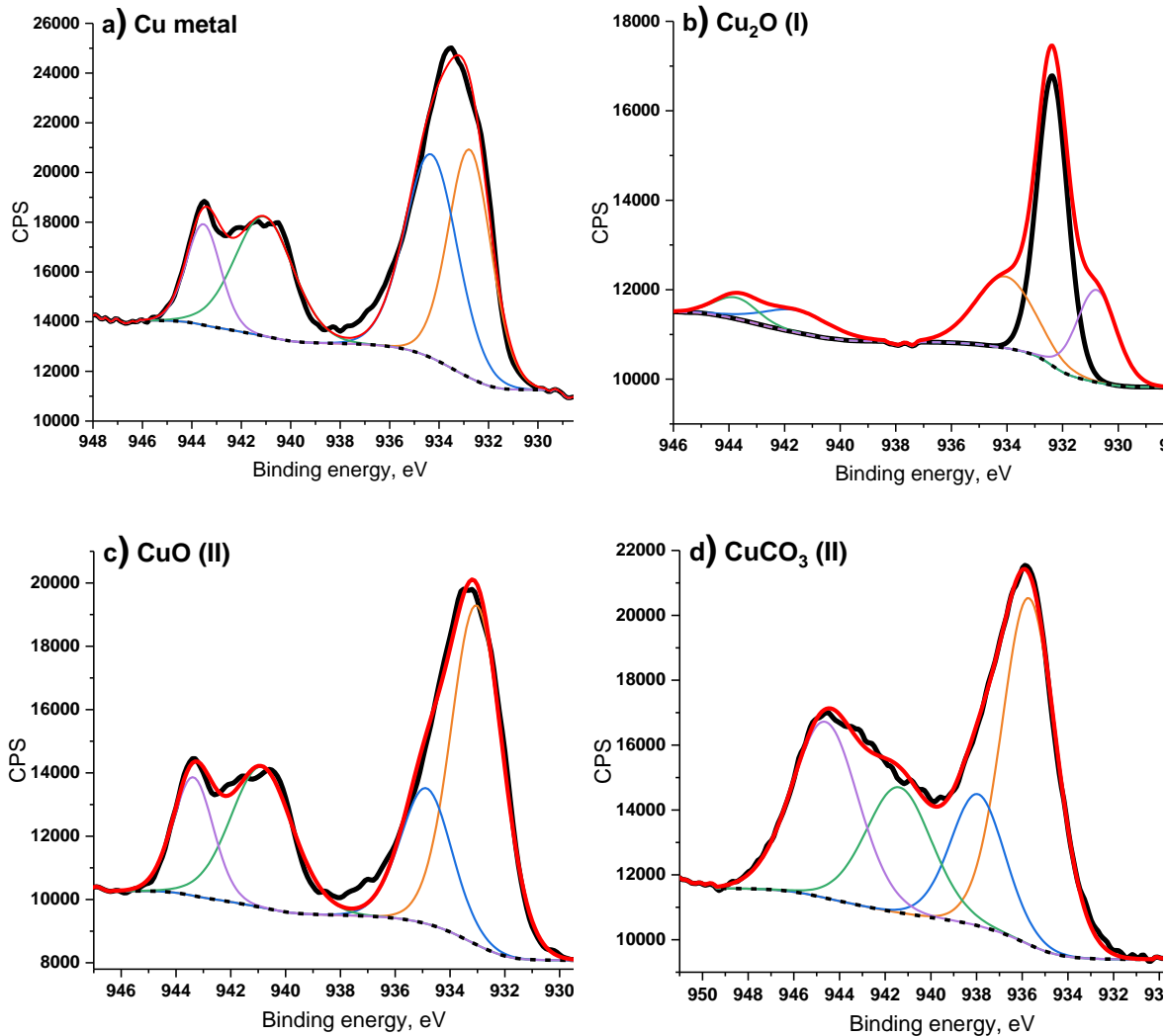
Figure S8. Microprobe mapping of Mg, P, O, Ca and Cu on the (a) reacted and (b) unreacted 350°C Pine ash. Microprobe analysis showed presence of low level of detectable Cu associated with mineralized Ca in the reacted ash, shown in figure (c). In table (d), the wt% of the elements associated with the mineralized Ca region is shown. At 95% confidence level, the Cu in the reacted sample is detectable at 0.012 wt% but below detection limit in the unreacted sample. Detection limit for Cu at 95% confidence level was 0.009 wt%.



c) Percentages of surface carbon bonds determined from curve fitting of C 1s high resolution XPS spectra

	C-C %	C*-CO _x %	C=O %	C-OH %
Binding energy, eV	285	285.6	287.5	289.5
Untreated ash	35.3	16.8	4.7	9.4
Reacted ash	25.3	24.2	11.9	11.8

Figure S9. XPS high resolution C 1s spectra for the (a) Unreacted 350°C Pine ash sample and (b) the reacted 350°C Pine ash sample. (c) Percent compositions of the C 1s spectra for the unreacted and the reacted ash.



(e) Binding energy values obtained for reference samples using XPS high resolution Cu 2p spectra

Reference Samples	Binding Energy (eV)
Cu metal	932.8
Cu ₂ O (I)	932.4
CuO (II)	934.9
CuCO ₃ (III)	935.7

Figure 10. XPS high-resolution Cu 2p spectra for (a) Cu metal, (b) Cu₂O (I), (c) CuO (II) and (d) CuCO₃ (II). (e) The binding energies obtained for the Cu 2p regions for these reference materials are shown.

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