

Speciation and reactivity of redox-sensitive metals in wildfire ash: Implications for nutrient and metal cycles

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Wildfire is raising unprecedented challenges in the western United States. Its effects are manifest as both abrupt and long-term changes in ecosystem function. The catastrophic fire seasons across the western U.S. in 2020 and 2021 provided a preview of the environmental impacts and large costs that will be associated with future fire events. One key feature of post-fire landscapes is the transformation of above-ground biomass and litter into a surface layer of ash. This ash layer is commonly enriched in pyrogenic carbon and minerals. While the chemical composition of ash particles is expected to vary with fuel-type, oxygen regime, moisture content, and degree of combustion or pyrolysis, the molecular-scale speciation and reactivity of ash particles have been scarcely investigated.

Here we collected ash, soil, and unburnt biomass samples from four dominant vegetation types (chaparral shrub, pond riparian zone, mixed spruce-fir, and oak forest), which experienced high and moderate burn severity during the 2020 Glass Fire in Napa and Sonoma Counties. Metal speciation was determined using bulk XANES and micro-XANES analyses. We found that ash particles were enriched in calcium, iron and manganese compared to unburned surface soils. Calcium was present either in carbonate minerals or in association with organic matter, with no detection of calcium oxide or hydroxide phases. Iron and manganese mineralogy differed markedly between the ash particles and the unburned surface soil. While iron in the unburned soils was present as 2-line ferrihydrite, we identified large fractions of hematite and maghemite in the ash. For manganese, we found mixed-valent and trivalent Mn phases, including hausmannite (Mn_3O_4) and bixbyite (Mn_2O_3), but also detected Mn(III)-rich birnessite and Mn(II). In unburned soil, Mn was present either as Mn(IV) or Mn(II) species. These analyses point to the formation of distinct redox-sensitive phases during fire that originate from metals contained with the vegetation and litter layer. Additionally, these point-scale analyses can be used to estimate stocks and fluxes of *de novo* minerals and metals, respectively, within the burn perimeter, to better understand how wildfires impact on nutrient and metal cycles.