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**Investigation of physical and chemical characteristics of soils
from high, moderate, low and unburned severity areas
following the 2011 Las Conchas fire**

by

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ABSTRACT

Soils play an essential role in ecosystem health as they are the medium for terrestrial and aquatic life. Soils can be drastically altered by wildfire as seen in the Jemez River watershed following the 2011 Las Conchas fire which burned over 31,800 acres. The aim of this research is twofold: 1) to characterize the effects of fire on the cation and anion composition in soil by burn severity following the 2011 Las Conchas wildfire and 2) to assess the leaching capacity of nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), aluminum (Al^{3+}), calcium (Ca^{2+}), iron (Fe^{2+}), potassium (K^+), and magnesium (Mg^{2+}) from soils. The pH, % organic matter (OM), and anion and cation from 32 soil samples collected at the Valles Caldera National Preserve from four burn categories: high, moderate, low and unburned in December 2016 and April 2017. The pH was highest in the moderate burn severity category and statistically different between the moderate/low burn severity categories. The % OM was higher in burned soils than unburned soils and statistically different between the moderate/unburned soils. Principal component analysis showed a clear separation between the chemical composition of soils collected in December and those collected in April; the analysis also showed that sites within the unburned/low severity categories were more homogenous than those from the high/moderate, high/low or moderate/low categories. Sulfate was the only anion that did not differ significantly by season. Three of eight ions, NO_3^- , Ca^{2+} and Fe^{2+} , were statistically different between burn severity categories. The leaching of these eight ions in 10 mmol Na_2CO_3 resulted in higher concentrations in solution over 0 and 30-minutes for every ion except Mg^{2+} (concentrations for Mg^{2+} were below detection for ICP-OES). All three anions either adsorbed back onto the soil surface or were removed from solution after 1 hour. The results suggest that post-fire recovery of soils may differ among burn severity category but the burned soils following the Las Conchas fire as indicated by the measurements used are at least as fertile as the unburned areas examined.

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INTRODUCTION

Soil Productivity

Soils are formed from plants, microorganisms, animals, water, and weathering rock (Breemen and Buurman, 1998). The main mineral inputs are composed of rock from the underlying geological layers that break-up through a process known as weathering. The soil organic matter covers all the living and dead organisms contained within the soil that will decompose through mineralization (Breemen and Buurman, 1998). Collectively this formed soil results in the creation of well-defined soils that provide the physical and chemical characteristics that can support plant growth. Additionally, soils have a leading role in the biogeochemical cycling of water, nutrients, and other trace metals and elements (SSSA, 1998). The vital role of soils, as it pertains to ecosystems, makes its health a key environmental focus. Several soil components can be studied as indicators of soil quality/productivity. There is no single assessment that provides a comprehensive assessment of soil functions. Thus, soil scientists use a variety of chemical, physical, and biological indicators to provide a wide range of information about soil function. This research focused on four indicators: the texture, pH, percent organic matter (% OM), and the chemical composition by measuring eight anions and cations (NO_3^- , PO_4^{3-} , SO_4^{2-} , Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ and Mg^{2+}).

Soil texture describes the mineral fraction of soil through the distribution of the relative content of sand, silt, and clay particles (Barbarick et al. 2000). The categories for soil particles are divided by size; clay being the smallest and sand the largest of these categories. The proportion of the different particles defines its texture, whose classification is based on one of four major categories: sand, silt, clay, and loam (Ashman and Puri, 2002). Soil texture is an important characteristic that affects a whole range of physical and chemical properties such as erosion, water holding capacity, permeability/leaching of nutrients, soil fertility, and the cation holding capacity (Breemen and Buurman, 1998).

The soil pH is an indication of the acidity or alkalinity of soil. In addition to providing the best physical conditions for plant growth as mentioned previously, there is also an optimal chemical environment for productive soils to maintain. The optimal pH is not the same everywhere, but the pH range between 5-9 typically prevents the buildup of toxins, supplies

nutrients for the overlying vegetation, and is optimal for microorganisms (Breemen and Buurman, 1998; SSSA, 1998).

Organic matter (OM) is derived primarily from the decomposition of plant tissue and is a dynamic aspect of soil in that soil is continually being broken down through the work of soil microorganisms (Winegardner, 1996; Brady, 1974). Organic matter acts as the primary reservoir for major nutrients and the chemically active cation exchange site (Brady, 1974). Soil OM supplies nutrients to plants and alters the physical nature of the soil by binding aggregating particles (Ashman and Puri, 2002).

There are numerous components incorporated into the soil fraction, but components of interest are typically those that have a beneficial effect on plant growth. There are several ions supporting/aiding plant growth; six of which will be the focus of this research; nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), calcium (Ca^{2+}), iron (Fe^{2+}), potassium (K^+) and magnesium (Mg^{2+}). Aluminum (Al^{3+}) is an element of interest due to it being toxic to plants and animals in relatively small amounts and the influence on soil fertility due to its ability to reduce soil pH (Ashman and Puri, 2002). Availability of these ions is an important measure of soil health. The promotion of a sustainable environment and healthy ecosystem is rooted in the productivity and health of soils. The capacity of a soil to function within its ecosystem can be hindered by wildfire, thus, for best management practices it is of great importance to investigate the recovery of soils long after such a disturbance.

Wildfire impacts on soils

Although wildfires are often naturally occurring, they can be detrimental to a landscape by impacting the biological, physical, and chemical properties of forest soils. Components, such as pH, % OM and NO_3^- , PO_4^{3-} , SO_4^{2-} , Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ , and Mg^{2+} concentrations, directly affect the productivity of soils. Studies show that pH in soils will increase during and after a wildfire due to ash deposits (Gray and Dighton, 2006; Schafer and Mack, 2010). In every ecosystem there is an optimum pH that makes certain ions more available to plants, and changes in pH can inhibit the cycling of cations and anions (Brady and Weil, 2016). Wildfires can partially sterilize the soil surface, decreasing soil biota, and OM (Xue et al. 2014). Reducing soil OM inhibits the supply of major anions (NO_3^- , PO_4^{3-} , and SO_4^{2-}), and disrupts the capacity of soils to hold and exchange cations and buffer against changes in pH (Ulrey et al. 2017). Heating

will affect the chemical components in soil as fire liberates both organic and inorganic constituents. Results vary depending on the anion or cation in question, but most studies attest to decreased concentrations in the soil as components oxidize or volatilize directly following a fire (DeBano, 2000; Gonzalez-Perez et al. 2004; Bento-Goncalves et al. 2012). However, with time soil ions can accumulate through the process of mineralization, where the chemical or element is released from plant matter after burning, and make their way into the soil profile (Smith et al. 2011; Gray and Dighton, 2006). Smith et al. (2011) noted increased concentrations of Ca^{2+} , K^+ and Mg^{2+} in their literature review of wildfire effects on water catchments, while Pereira and Ubbeda (2010) reported increases in Al^{3+} and Fe^{2+} in soils after a wildfire in Lithuania. The addition of ions into the soil is a complex process and may not always increase soil ions because of the different properties of ions, vegetation burned, wildfire properties and burn severities. Current research tends to distinguish wildfire impacts on soil solely between burned and unburned soils. One of the greatest factors affecting the results of these impacts is burn severity. In post fire assessment there is an effort to categorize the effects of wildfire on soils (Keely, 2009). The soil burn severity differentiates post fire soil properties from fire effects on vegetation, focusing specifically on ground surface characteristics (Keely, 2009). The temperature, duration and fuel source differentiate burnt soils, separating them into one of four categories: high, moderate, low, and unburned. The different categories of burn will result in the loss, char, or scorching of trees, roots, and surface litter. The degree to which soils have been impacted could provide more insight into post-fire soil recovery.

Wildfire impacts on surface waters

The leaching of ions is important for two reasons; one, the mobility of ions is a major factor in the maintenance of ecosystems and two, wildfire impacts on the availability of ions within soil which can impact water quality following rainfall or snowmelt events (Burton et al. 2016; Burke et al. 2013; Smith et al. 2011). Suspended sediment in post fire runoff is a transport mechanism for anions and cations and has the potential to impair water surfaces. In research by Townsend and Douglas (2000) and a review by Smith et al. (2011), elevated levels of anions and trace metals were reported in forest catchment streams post wildfire. In 2011, the Las Conchas wildfire, one of the largest wildfires in New Mexico's history, burned through the Valles Caldera National Preserve (VCNP) drastically changing the soil conditions and surrounding surface

water quality (NPS, 2012). The introduction of large sediment loads had an immediate effect on the Jemez River and its tributaries, as well as the Rio Grande (Dahm et al. 2015). Real time data captured drastic changes in conductivity, pH, turbidity, and dissolved oxygen. During the Las Conchas fire, Sherson et al. (2015) assessed event responses in surface water nutrient concentrations in the East Fork of the Jemez River, noting sags in dissolved oxygen, increases in nitrate concentrations by an average of 50% and large multi-day increases of dissolved phosphate. Further investigation was made to better understand the impacts of the runoff, specifically wood ash, on the water quality by Cerrato et al. (2016). Results from this study suggest that the dissolution of metal-bearing carbonate and oxide phases in ash and metal re-adsorption were important processes affecting water chemistry. In the recently published Total Maximum Daily Load (TMDL) report, the East Fork of the Jemez River was deemed impaired due to an excess of plant nutrients; the Jemez River was considered impaired due to high Al concentrations (NMED, 2016). It is important to think about the fate of these ions, not only to understand how much is incorporated in the soil for ecosystem health and management but also how much is introduced to surrounding surface waters via erosion, seasonal rains, and snowmelt.

Wildfire and climate change

Wildfires pose a threat to the forested watersheds in the arid southwestern United States. The Jemez Mountains in northern New Mexico is one region that has been strongly affected by recurring wildfire activity. About 5,200 fires have been mapped in the Jemez Mountains from 1909-1996 (USGS, 2017). Westerling et al. (2003) showed increased wildfires in western forests since the mid-1980s, noting higher frequencies, longer durations and longer seasons. These wildfire trends were witnessed within the Jemez Mountains with the more recent fires, the Cerro Grande in 2000, Las Conchas in 2011, and Thompson Ridge in 2013. Wildfire activity is projected to worsen as climate change trends increase regional temperatures and change precipitation patterns (Graham et al. 2004). The prevalence of drought conditions across the southwestern United States will lead to earlier snowmelt, more rain and less snow, greater vapor pressure deficits in spring and autumn and, ultimately, more severe wildfires within mid-elevation ranges such as the Jemez Mountains (Abatzoglou and Williams, 2016; Dahm et al. 2015; Miller et al. 2012).

Current research on the impacts of the Las Conchas fire provides an opportunity to investigate the lasting effects of fire on soil chemistry. Little is known about the longer-term effects of wildfire on soil constituents, specifically by increased burn severity. Soils are an essential resource for all organisms, a unique and irreplaceable resource. The direct connection of terrestrial impacts to stream water quality runoff prioritizes this investigation in the arid southwest. The objectives of this paper are to (1) *characterize the effects of fire on the cation and anion composition in soil by burn severity following the 2011 Las Conchas wildfire*; and 2) *assess the leaching capacity of NO_3^- , PO_4^{3-} , SO_4^{2-} , Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ and Mg^{2+} from soils.*

METHODS

Site Description

Research was conducted within the Jemez River watershed in north central New Mexico. The basin expands Sandoval, Rio Arriba and Los Alamos counties. The study site was located on the west flank of the Jemez Mountains within the Valles Caldera National Preserve (Figure 1). Soil samples were collected from the Sierra de los Valles dome which was formed after a series of volcanoes erupted approximately 1.25 million years ago (Goff, 2009). The dome gains over 600 meters in elevation northeast of the East Fork of the Jemez River. The sampling site was approximately 200 square meters (Figure 2). The lowest sampling point sits roughly at 2,620 meters in the grassland valley near the banks of the East Fork of the Jemez River. The highest sample site was midway up the Sierra de los Valles dome at an elevation of 2,830 meters.

The geology of Jemez Mountains is comprised mostly of Tertiary-aged volcanic rocks: basalt, andesite, dacite, and rhyolite (Goff, 2009). The Sierra de los Valles dome geology was characterized as dacite, with major elemental compositions consisting of SiO_2 , TiO_2 , Al_2O_3 , FeO , MnO , MgO , CaO , Na_2O and K_2O (Shackley, 2012; Goff, 2009). The United States Department of Interior –Natural Resource Conservation Service categorized the soils at the head of the East Fork of the Jemez River into two groups based on the geomorphic features: the moderate to steep rim rock slopes and those of domes, and the alluvial/colluvial fans along the valleys (Figure 3) (Muldavin and Tonne, 2003). The forest soils are primarily Andisols, Alfisols and Inceptisols derived from volcanic rock and gravel while the grassland soils are mostly Mollisols derived from the weathered volcanic alluvium (Muldavin and Tonne, 2003). The Jemez Mountains are considered part of the Southern Rocky Mountains Ecoregion; classification used by the U.S.

Forest Service indicates open woodland coniferous forest and alpine meadows (Muldavin and Tonne, 2003).

Las Conchas Fire

The Las Conchas fire began in June 2011 in the Jemez Mountains just west of the VCNP. The weather and fuel conditions permitted for an aggressive fire that spread quickly, burning approximately 156,593 total acres within five weeks (NPS, 2012). Within the VCNP, 19% of the total acres were burned, where the high burn severities were seen on the eastern portion of the preserve at higher elevation zones, including the Sierra de los Valles dome (NPS, 2012). The array of burn was similar for each dome on the western portion of the park, with the highest elevations receiving the highest burn severities that decreased down the flanks (Figure 4).

Sampling Methods

A total of 32 soil samples were collected from the Sierra de los Valles dome within the VCNP. Four samples were collected and bagged from the high, moderate, low and unburned severity category sites in December 2016 and April 2017 respectively. The soil burn severity differentiate post fire soil properties from fire effects on vegetation, focusing specifically on ground surface characteristics and the Burn Area Emergency Response (BAER) team constructs post fire maps from these impacts (Safford, 2006). The Las Conchas BAER map was used to determine the GPS coordinate boundaries for the stratified sampling done within the four burn severity categories. Stratified random sampling involves the arbitrary collection of samples within defined, divided areas (e.g., four burn severity categories) (US EPA, 1997). Following the methods in the US EPA Science and Ecosystem Support Division operating manual, vegetation was removed prior to soil collection using an Ames Ergo hand trowel (USDOE, 2014). The top six centimeters of soil were bagged and stored in individual one-quart Ziploc bags. The soil type was characterized at each collection site by hand using the guide to soil texture by feel modified by the USDA's Natural Resources Conservation Service (USDA, 1979). The soil samples were refrigerated at 4°C at the University of New Mexico until laboratory analysis was conducted.

Laboratory Analysis

Soil samples were air dried for 72 hours and ground using a mortar and pestle. Each sample was sieved using a 2-mm sieve. The soil pH was measured on a 1:1 soil-water ratio by

mixing 5g of soil and 5 mL of 18 MΩ water in a digitube. The Oakton 300 series hand held pH probe was held just above the settled soil layer to measure the pH directly after mixing. Percent organic matter was determined by calculating loss on ignition. Approximately 6 g of soil was placed in pre-weighed aluminum boats, and dried in a Boekel Scientific desiccator for 72 hours to remove water. The weight was recorded. The sample was then ashed at 550° C in a muffle furnace for four hours, left to cool overnight, and weighed again. This was done for all 32 soil samples collected. The percent of OM was calculated using the following equation:

$$\text{LOI} = \frac{\text{pre-ignition weight (g)} - \text{post-ignition weight (g)}}{\text{Pre-ignition weight (g)}} * 100$$

For anion analysis, 4-5 g of each soil sample was weighed, partitioned into digestion tubes (Digitube®) in triplicates, and 25 mL of 18 MΩ water was added. The samples were placed in a tumbler for one hour and centrifuged for 10 minutes at 6,000 RPM prior to filtration through a 0.45 μm filter. The filtered samples were partitioned into 10 mL vials for analysis with a Dionex 1100 ion chromatography (IC) instrument determining the concentrations of F⁻, Cl⁻, NO₂²⁻, NO₃⁻, Br⁻, PO₄³⁻, and SO₄²⁻. The detection limits ranged from 0.050 mg/kg for SO₄²⁻ and approximately 0.010 mg/kg for NO₃⁻, and PO₄³⁻.

For cation analysis, 2 g soil samples were digested in triplicates using HNO₃, HCl and H₂O₂. Five mL of HNO₃ was added to the samples and heated for 30 minutes at 35° C using a block digestion (DigiPrep®). One mL of 30% H₂O₂ was added and again heated for 30 minutes at 35° C. One mL aliquots of 30% H₂O₂ were added until no reaction would take place. Five mL of HCl were added and the sample and was heated for two hours. The samples were left to cool and evaporated down to 5 mL. The digested sample solution was brought to 25mL using 2% HNO₃. Cation concentrations (Al³⁺, B³⁺, Ba²⁺, Ca²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, Pb⁴⁺, Sr²⁺, V⁵⁺, and Zn²⁺) were determined using a Perkin Elmer Optima 5300 DV inductively coupled plasma optical emission spectrometry (ICP-OES) instrument. The limits of detection ranged from 0.008 mg/kg to 0.5 mg/kg depending on the individual elements.

The leaching of cations and anions from the high, moderate, low, and unburned soil samples were determined via batch analysis. Approximately 5 g of soil (n = 2) from each burn severity category were placed in digitubes and 50 mL of 10 mmol Na₂CO₃ solution was added.

The mixture was tumbled continuously over a 24-hour period. Six mL aliquots were collected at times 0, 0.5, 1, 4, and 24 hours for anion and cation analysis using the IC and ICP-OES instruments described above. The pH was measured and recorded at each time step.

Data Analysis

Principal component analysis (PCA) was used to explore the soil compositional patterns for ions among the four burn severity categories with PC-ORD software 6.0. This multivariate method investigated all 21 ions simultaneously. Further investigations were made using univariate statistics for pH, % OM, and eight ions; NO_3^- , PO_4^{3-} , SO_4^{2-} , Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ and Mg^{2+} . These ions were chosen due to their naturally high abundance in the underlying geology formation of dacite rock, and their importance as soil productivity measures. Two-way analysis of variance (ANOVA) compared the mean differences in multiple variables (pH, % OM and ion concentrations) between sample collection seasons December and April, and among the burn severity categories (high, moderate, low and unburned) using SPSS 2015 software. The two-way ANOVA was used to determine if the differences between seasons or among burn severity category were statistically significant for pH, % OM and ion concentrations. The null hypothesis for each two-way ANOVA were: (1) The means (pH, % OM and ion concentrations) for each season are equal, (2) the means (pH, % OM and ion concentrations) among burn severity category were equal, and (3) there is no interaction between season and burn severity. The significance level was denoted as $\alpha < 0.05$, concluding any p-value less than α as significant and the related hypothesis false. In conjunction with the two-way ANOVA, a multiple comparison procedure was used. The Tukey Kramer post-hoc test determined the statistical differences among burn severity categories for each variable tested (pH, % OM and ion concentrations). The factor season was not analyzed with the Tukey Kramer post hoc test because the test requires more than two treatments to test for significant differences.

RESULTS

Physical soil properties

The texture class for the samples collected at the high, moderate, and low burn severity sites was loam, with soil texture identified as loam for six of the eight unburned samples and sandy loam for the remaining two (Table 1). The soil pH values across the four burn severity

categories did not differ significantly by season (2-way ANOVA, $p = 0.962$), but did vary significantly by burn severity category (Table 1 and Table 2). Soil pH was statistically different between the moderate and low burn sites ($p = 0.016$), but not among other burn severities (Table 3). Percent OM did not differ significantly by season (2-way ANOVA, $p = 0.782$) but did differ significantly by burn severity category. The % OM was statistically different between the high/unburned severity categories (Tukey Kramer, $p = 0.004$) (Table 3). Nearly all the burned soil samples had higher % OM than the unburned samples (Figure 5).

Anions and Cations

The ions NO_3^- , PO_4^{3-} , SO_4^{2-} , Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ and Mg^{2+} were the focus of univariate statistical analysis due to their high concentrations in dacite and important role in soil productivity. There was a significant difference between sampling seasons (December and April) for two of three anions examined, NO_3^- and PO_4^{3-} , and all five cations Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ , and Mg^{2+} (Table 2). On the other hand, SO_4^{2-} was not statistically different between seasons (2-way ANOVA, $p = 0.237$). The trends for the samples collected in December had higher concentrations of SO_4^{2-} , Al^{3+} , Fe^{2+} , and K^+ compared to the April samples which had higher concentrations of NO_3^- , PO_4^{3-} , Ca^{2+} and Mg^{2+} (Figure 6 and 7). The only ions that showed statistical differences among burn severity categories were NO_3^- , Ca^{2+} , and Fe^{2+} (Table 3). The significant differences for NO_3^- concentrations were between high/unburned ($p = 0.003$) and moderate/unburned ($p = 0.045$) severity categories. The differences for Ca^{2+} concentration was between the high/unburned ($p = 0.019$) severity categories. Lastly, the statistical difference for Fe^{2+} concentrations was between the high/moderate ($p = 0.018$) and moderate/unburned ($p = 0.008$).

Soil Characterization

Principal component analysis was used to analyze all 21 ions analyzed for December and April. The first principal component (PC1) explained 51% of the variance and the second principal component (PC2) explained 15% of the variance in overall ion composition among sites. There is a clear delineation of sites by season with samples clustered in the left and right portion of the graph differentiating those samples collected in December and April, respectively (Figure 8). PC1 has higher loadings of Al^{3+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , and K^+ with values $> \pm 2$,

indicating higher concentrations of these ions for these sites in the December samples. PC1 had higher loadings of Ca^{2+} and Mg^{2+} with values $> \pm 2$, indicating higher concentrations for the sites on the right half of the plot, for the samples collected in April. PC2 has higher loadings of Sr^{2+} , Cl^- , NO_2^{2-} , NO_3^- , PO_4^{3-} , and SO_4^{2-} indicating higher concentrations of these ions for soils in different burn severity categories. Again, PC2 explains only 15% of variance and the graph shows less differentiation in soils along the y-axis. This PCA graph also demonstrates higher sample homogeneity between the low/unburned severity categories, and more sample variation between soil chemical composition from the high and moderate burn severity categories.

Batch Experiment

There was a decrease in pH of at least one unit over the 24-hour duration in the batch experiment for all soils within all four burn severity categories. Soil from the moderate burn had the greatest decrease in pH from 10.28 at time 0 to 8.58 at 24 hours (Figure 9). The unburned soil had the least change in pH, with a decrease from 10.28 at time 0 to 9.25 at 24 hours (Figure 9).

The leaching of all anion and cation concentrations was greatest at 0 and 30 minutes in all treatments. However, the concentrations of anions and cations released to solution decreased at later time points. For example, PO_4^{3-} and SO_4^{2-} had detectable concentrations at the 0 and 30 minutes only, but had concentrations from the 2, 4, and 24-hour collections that were below the IC detection limit. Only NO_3^- has concentrations that were high enough to be detected in solution throughout the 24-hour duration of the experiment (Figure 10). Potassium had the highest leached concentration values between 0-15 mg/kg while Mg^{2+} did not have detectable concentrations throughout the experiment (Figure 11). Iron and Ca^{2+} were the only two ions having higher concentrations for all burn severity categories at 30 minutes, compared to the initial sampling (Figure 11).

DISCUSSION

Physical soil properties

The soil texture class was loam at the high, moderate, and low burn severity sites. Six of the unburned soil samples had the same classification, loam, but two samples were designated as sandy loam. Loam consists of roughly equal proportions of sand, silt, and clay while sandy loam consists of less than 7% clay, 50% silt, and 43-50% sand (Barbarick et al.

2000). Research suggests that wildfires change soil structure as heat aggregates clay particles into sand-sized particles, making the soil structure coarser (DeBano, 1990). However, the results of this investigation that the Las Conchas fire is not the only factor affecting these properties. The difference in texture may be associated with location, rather than burn severity, as the unburned sites were collected in the grasslands at the base of the Sierra de los Valles dome. The sample location places unburned soils nearer the East Fork of the Jemez River, where the higher water table could introduce soil moisture as a factor of influence. The texture classification was identified on site and was thus lacking the more precise results that laboratory analysis could provide. Deviations from the percentages of clay, silt and sand mentioned above, may not be obvious with the field method used; therefore, it is difficult to say with any certainty how and if the Las Conchas fire impacted the soil texture.

Studies show that pH is affected by seasonal fluctuations with lower soil pH occurring in winter (Murdock and Call, 2006; Salim et al. 2015). The soil moisture, temperature, and microbial activity can cause soil pH to vary. The pH for soil samples collected in December and April did not differ significantly by season, but trends were seen. When averaging the pH across all four burn severity categories, December samples had a lower mean pH (5.74) when compared to the soils collected in April (mean pH of 5.81). Research suggests salt concentrations increase as soils dry and soluble cations replace negatively charged anions or hydronium ions on the surface resulting in a higher pH, a process likely to have occurred in the more alkaline soils collected in the month of April (USDA, 2001).

Differences among burn severity categories indicated that wildfire did affect soil pH. The pH measured in soils from the high and moderate burn severity categories was higher than the pH in soil from the unburned category. Studies show that pH in soils will increase during and after a wildfire due to alkaline ash deposits (Gray and Dighton, 2006; Smith et al. 2011). The buffering capacity of soils within the pH range of 4-7 is small; therefore, increases in sorption of cations causes increases in soil pH. The pH of these samples was within this range (5.54-5.94); seemingly the addition of cations from burned vegetation did increase the soil pH (Sollins et al. 1988). The conditions found in the low burn severity are such that minimal changes occur through the soil profile. The mean pH as recorded in the low burn severity category was lower than the pH from the unburned category; the results of which are not clearly explained, but have been found in prior research. In a study conducted by Xue et al. (2014), burned soil pH increased

one year after the wildfire and decreased progressively four and seven years later to concentrations lower than the unburned soils. The soil pH from the high and moderate burn severity categories did not return to pre-burn conditions illustrating that wildfire impacts on pH is not a straightforward process.

Changes in soil organic matter typically occur slowly under natural conditions, as changes through soil microbiological processes or by external physical or chemical factors (Gonzalez-Perez et al. 2004; De la Rosa et al. 2012). In this investigation the soil % OM was not statistically different between seasons; however, fires can quickly alter OM (De la Rosa et al. 2012). The consumption of OM begins at relatively low temperatures (200-250°C) that occur within the low burn severity category (Certini et al., 2011; Keely, 2009). The immediate decreases in OM are transient and OM will often re-accumulate over years due to primary succession (Ulery et al. 2016). Within the Sierra de los Valles dome, the burned soils had higher % OM when compared to the unburned soils. The highest concentrations occurred in the moderate burn severity category which differed significantly from the unburned severity category. As indicated by Certini et al. (2011), fire-induced gain or loss in OM results from the dominance of one of two processes: removal of the litter layer and organics from the topsoil or input of charred materials from the scorched vegetation. All the burned soils seemed to benefit from the input of charred materials as these soils had higher % OM.

Anions and Cations

Various factors, such as fluctuating temperatures, freezing, precipitation, and snowmelt can affect the concentrations of anions and cations in soil (Roberts, 1978; Diaz-Ravina et al. 1993). These factors may have contributed to the statistical differences in ion concentrations in soils collected in December and April. In December inches of snow had accumulated above ground and the soil was frozen. In April soil conditions were drastically different: the snow had melted, and enough time had passed to leave the top soil dry. Seven of eight ion concentrations differed between these months. The anions NO_3^- and PO_4^{3-} and cations Ca^{2+} and Mg^{2+} had lower concentrations in the December samples, while Al^{3+} , Fe^{2+} , and K^+ had higher concentrations in the December samples. In saturated soils concentrations of NO_3^- can leach further down into the profile causing a decline in levels at the surface, which was seen in the lower concentrations for December. In warmer seasons release from OM can occur, contributing to the higher

concentrations seen in the soils collected in April. Salim et al. (2015) found higher PO_4^{3-} concentrations in winter followed by spring >autumn> summer under natural forest conditions in slightly acidic soils in India. The concentrations of PO_4^{3-} in the April samples were nearly double those collected in December. The fluctuations of Al^{3+} and Fe^{2+} are not explored as in depth as the other cations (Ca^{2+} , Mg^{2+} , and K^+), but one study by Cuesta et al. (1993) found higher concentrations of these cations later into the year (October) than in spring/summer months. Soil K^+ is often released from the clay minerals in soil under saturated conditions, validating its higher concentrations in December. Research by Diaz-Ravina et al. (1993) investigated seasonal changes in Ca^{2+} and Mg^{2+} showing higher concentrations of these cations in autumn>spring>>winter \geq summer. Sulfate was the only ion that was not statistically different between seasons. Sulfate pools have been shown to vary over time with changes in soil moisture and temperature like the other ions studied; however, as this research indicates the timing and environmental seasonal differences did not affect the concentrations of SO_4^{2-} (Ghani et al. 2012).

Wildfire can be an important factor on the cycling of anions and cations through an ecosystem, liberating elements previously withheld by vegetation. The results of this research show that after wildfire some ions can accumulate in soils over time. Cerrato et al. (2016) found very high concentrations of Al^{3+} , Ca^{2+} , Fe^{2+} and Mg^{2+} in the ash from pine, aspen and spruce, the dominant trees of the VCNP. Raison (1979) found deposition of overlying burned vegetation resulted in increased concentrations of Ca^{2+} , Fe^{2+} and Mg^{2+} in the residual soil material. In this study, Ca^{2+} was the only cation to have higher concentrations for the all the burned soils compared to unburned soils. Of the four burn categories, the Ca^{2+} concentrations were greatest in the high severity burn, potentially due to its high volatilization temperatures (1240-1484°C) (Gray and Dighton, 2006). A similar situation occurred for Mg^{2+} which also has a high volatilization temperature (1107 °C), but the differences among burn severity category for Mg^{2+} were not statistically different. The production of ash post wildfire does not always manifest to an increase of nutrients in soil as seen for Fe^{2+} , Al^{3+} and K^+ . In December samples Fe^{2+} concentrations were highest in the unburned severity category. The significant difference between the moderate and unburned sites are supportive of the findings by MacLean et al. (1983) who found Fe^{2+} concentrations lower in burned soils years after a wildfire. A similar trend can be seen in the distribution of cation concentrations in the moderate burn severity category where Al^{3+} , Fe^{2+} , K^+ , and Mg^{2+} had the lowest concentration levels out of any burn severity category in

the December soils, and Fe^{2+} had the lowest concentrations in the April soils. The soil samples from the moderate burn severity category had the highest %OM, as well as a pH and texture like the soil from the other burn severity categories, suggesting equal or greater ability for cation adsorption capacity. Yet, the soils collected within the low and unburned severity categories had higher Al^{3+} , Fe^{2+} , K^+ , and Mg^{2+} concentrations than the moderate burn in December and/or April. The low burn severity undergoes the least amount of change in that, the surface organic layers are not completely consumed, nor is the structural aggregate stability of the soil changed. The concentrations of cations in these soils were most like the unburned soils, as indicated by PCA. Aluminum in the December soil samples was the only cation with the highest concentrations in the low burn severity category. The concentrations of K^+ were highest in the unburned soils in both months. Wildfires have been documented to immediately decrease K^+ by 43-66%, which is higher than the reported losses of all the other components except nitrogen and nitrogen containing compounds (Raison, 1979). Neither of these cations however had statistical differences among burn severities, thus the factors inducing the change may not be fire induced.

The temperatures reached among the four burn severities have different effects on NO_3^- , PO_4^{3-} , and SO_4^{2-} because volatilization happens at relatively low temperatures (Schafer and Mack, 2010; Gray and Dighton, 2006; Sherson et al. 2015). Nitrate concentrations were higher in burned soils than unburned soils for all the burn severity categories in both months. Research indicates that soil NO_3^- concentrations increase immediately after a fire (Lehmann and Schroth, 2002; MacLean et al. 1983; Murphy et al. 2006; Schafer and Mack, 2010). Nitrate is readily adsorbed by plants and soil colloids but can also be easily leached (Yang and Hai-qing, 2007; Recheigl, 1995) which may be the reason this constituent had the overall lowest concentrations of all the anions in this experiment. In this study, the burned soils in December had nearly ten times the PO_4^{3-} concentrations as the unburned soils. While testing for Phosphorous-availability post-wildfire, Rodriguez et al. (2009) noted increases in PO_4^{3-} in burned plots versus unburned plots. Sulfate is the only anion to have higher concentrations in unburned samples (Recheigl, 1995). Little research has reported the effects of fire on SO_4^{2-} , but due to its chemical similarities to PO_4^{3-} , its interaction with soil OM and the cations within the clay fraction its presentation could vary depending on the degradation/combustion of soil OM and desorption from soil particles over time (Murphy et al. 2006).

Batch Experiment

The decrease in pH recorded over the 24-hour duration of the batch experiment alludes to the slightly acidic nature of these soils. All the burned soils caused a greater decrease in soil pH than the unburned soils over 24 hours. The burned soils decreased by nearly 1 pH unit from times 0 to 30 minutes and nearly 2 pH units over 24-hours. The changes in pH can be understood by the leaching of cations and anions and their exchange with Al^{3+} , Fe^{2+} , and H^{+} ions on the soil surface. An early release of cations and anions is likely due to water soluble phases, or desorption due to reactions with Na_2CO_3 .

The clay minerals and organic matter have a negative net charge that attracts the positively charged cations. The cations Ca^{2+} , K^{+} and Mg^{2+} are known as basic cations and are more easily displaced into solution, with decreasing affinities: $\text{Ca}^{2+} > \text{Mg}^{2+} \gg \text{K}^{+}$ (Sollins et al. 1988; Breemen and Buurman, 1998). Potassium leached between 2-15 mg/L at each time-step over the 24 hours, the most leaching of any cation. Potassium has the lowest affinity for the exchange site, meaning it is not held as tightly to the negative interface as the other cations and has been found to leach at significant quantities in organic soils (Lehmann and Schroth, 2002). The consistent leaching of Ca^{2+} over time (2-5 mg/L at 0, 30, 1, 4 and 24 hours) could be due to its high concentration levels within soil. Iron has a higher solubility in less alkaline conditions, at a pH nearer 9, accounting for its higher leached concentrations at 30 minutes. Iron and Al^{3+} can act like Lewis acids, creating hydrogen ions through their interactions with water. Both cations are held more tightly by the soil particles. Aluminum can also form oxide complexes making it more difficult to be displaced by the other basic cations; in this experiment the leaching of Al^{3+} over time was relatively small, between 0.5-5 mg/L. The burn severities displayed different leaching concentrations. The low burn and unburned soils had higher leached concentrations for Ca^{2+} , K^{+} and Fe^{2+} after 30 minutes, which may be correlated to the lower percentages of OM found in these samples. Again, OM has negatively charged sites that are able to adsorb cations, and a lower % OM may correlate to decreased cation exchange.

Unlike the cations the anions near the outer surfaces are not easily adsorbed onto soil particles (Dale and Cole, 1980). Application of the Na_2CO_3 solution will quickly transfer the anions into solution from the soil, because of their weaker association with the soil surface. When adsorption occurs, the affinity for anions at the exchange site is: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^{-}$ (Breemen and Buurman, 1998). Phosphate is immobile in most soils, due to its high adsorptive

capacities which is most likely why the leached concentrations were < 1 mg/L overall (Lehmann and Schroth, 2002). On the other hand, SO_4^{2-} and NO_3^- are readily leached by surface soils. Leached concentrations of SO_4^{2-} were well below that of NO_3^- . Nitrate had the highest leached concentrations over time, 6-27 mg/L over four hours, because of its weak interaction with the negatively charged matrix of soils. The three anions leached in a similar fashion for each burn severity, where the highest concentrations were collected at the 0 hour. The concentrations of leached anions correlated closely with their concentrations in soil among burn severity category; most anions had higher leached concentrations from the moderate burn. The decline in anion concentrations in solution over time is a likely indication of their formation of aqueous complexes with cations and their adsorption back onto the soil interface (Alam et al. 2017; Sollins et al. 1988).

CONCLUSION

In this investigation the top six cm of soils had significant changes in pH, %OM and anion and cation concentrations among burned soils. Due to soils heterogeneity, time and other geospatial/environmental factors the differences noted cannot be attributed burn severities only. Working within the restraints of the experiment however, the long-term impacts of wildfire on soils suggest a positive outcome for soil productivity. The heating of soils overall increased the %OM, NO_3^- and PO_4^{3-} in soil from all burn severity categories, as well as the pH in the high and moderate burn severity categories. The results for Ca^{2+} and Fe^{2+} had significant difference between burned and unburned soils, but Al^{3+} , K^+ and Mg^{2+} did not. The pH of burned soil does not indicate a presence of free acids (pH < 4) or a presence of CaCO_3 (pH $> 7.8-8.2$). The pH range is slightly acidic, promoting maximum uptake of vital ions sustaining plant growth and providing a suitable environment for bacteria, and the formation of OM. The mobility of these ions affects the rate at which plant roots can extract them from soil, the higher concentrations of K^+ and NO_3^- indicate that these cations and anions were more soluble (under the laboratory conditions laid out). The movement of ions through the soil is important, but so is ion loss due to runoff. The East Fork of the Jemez River is impaired because of high plant nutrients and Al^{3+} (NMED, 2016). During the leaching experiment all the ions entered solution, and leaching losses were higher for burned soils than unburned. This could be an indication that burned soils have greater leaching effects and could contribute to the ongoing impairment of the East Fork of the Jemez River. Along with their addition to surface water, certain elements can decrease pH. A

large enough change could prove hazardous to aquatic and terrestrial organisms reliant on specific pH ranges.

The results suggest that burned soils, even within areas of high burn severity, may return or surpass pre-fire soil conditions given adequate time. It is important to keep in mind that effects of fire on soil properties are complex and can present differently within the same watershed depending on the characteristics of the fire and overlying vegetation. Despite the statistically different outcomes found for the soil parameters discussed above, burn severity can be correlated to other ecosystem responses in a negative manner. Various authors show ties between burn severity and alien plant invasion (Turner et al. 1999), decreased regrowth of herbs and shrubs (Flinn and Weinn, 1977; Keely, 2006), and species richness and patterns of seedling recruitment (Whelan, 1995; Bond and van Wilgen, 1996; Ryan 2002; Johnstone and Chapin, 2006; Keely, 2009). In a time where climate change threatens increased wildfire activity, the changes to soil parameters following wildfire become increasingly important to understand. The implications of investigating wildfire impacts by burn severity and season may become important in research of this kind as it influences results; and could impact watershed management.

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Figure 1: Site map for the study site on the west flank of the Jemez Mountains within the Valles Caldera National Preserve at the Sierra de los Valles dome outlined by the blue box.

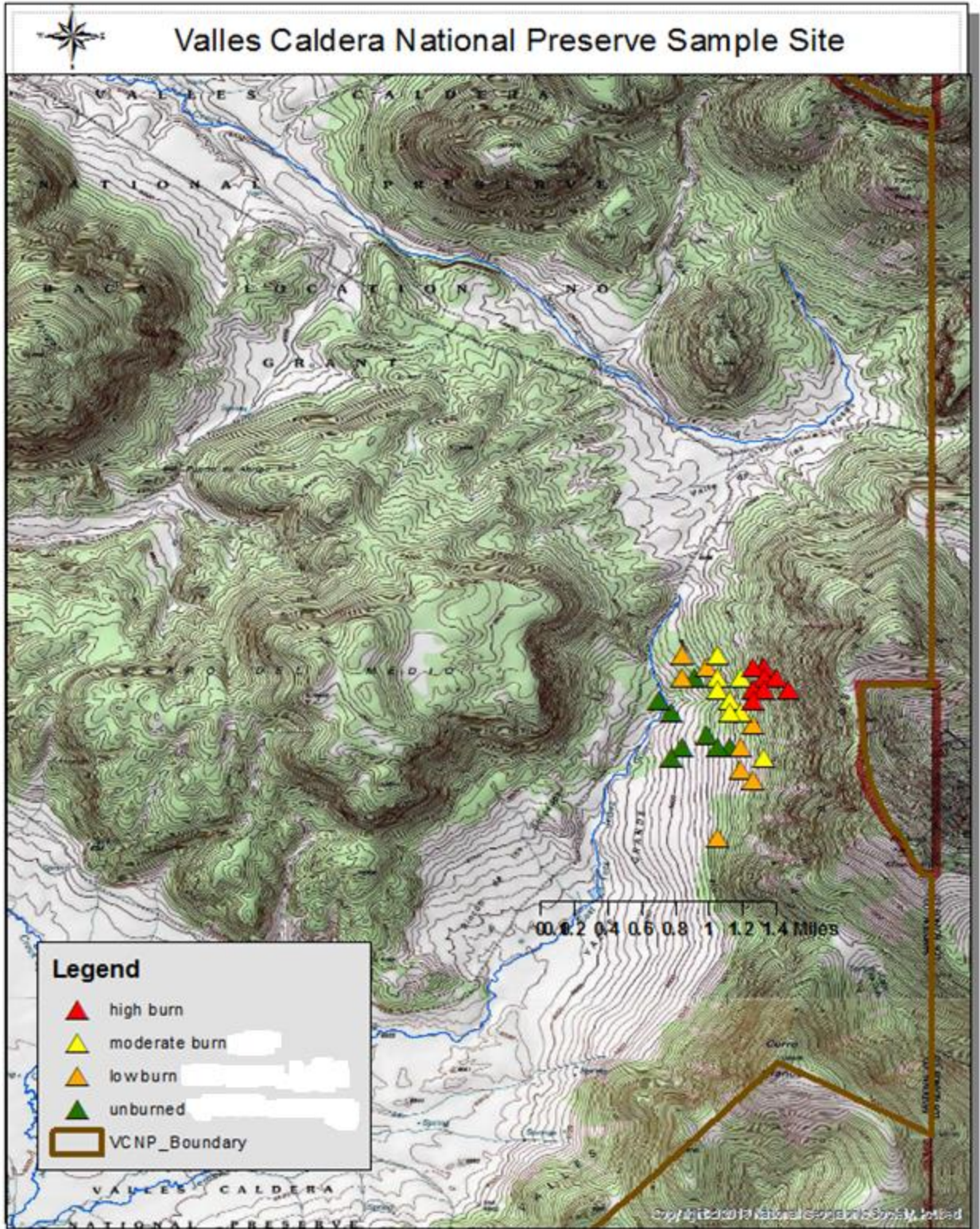


Figure 2: Site map showing locations of the 32 soil samples collected on the hill slope of the Sierra de los Valles dome. Eight samples were collected from each burn severity category; the colors of each burn severity are coded and labeled in the map legend.

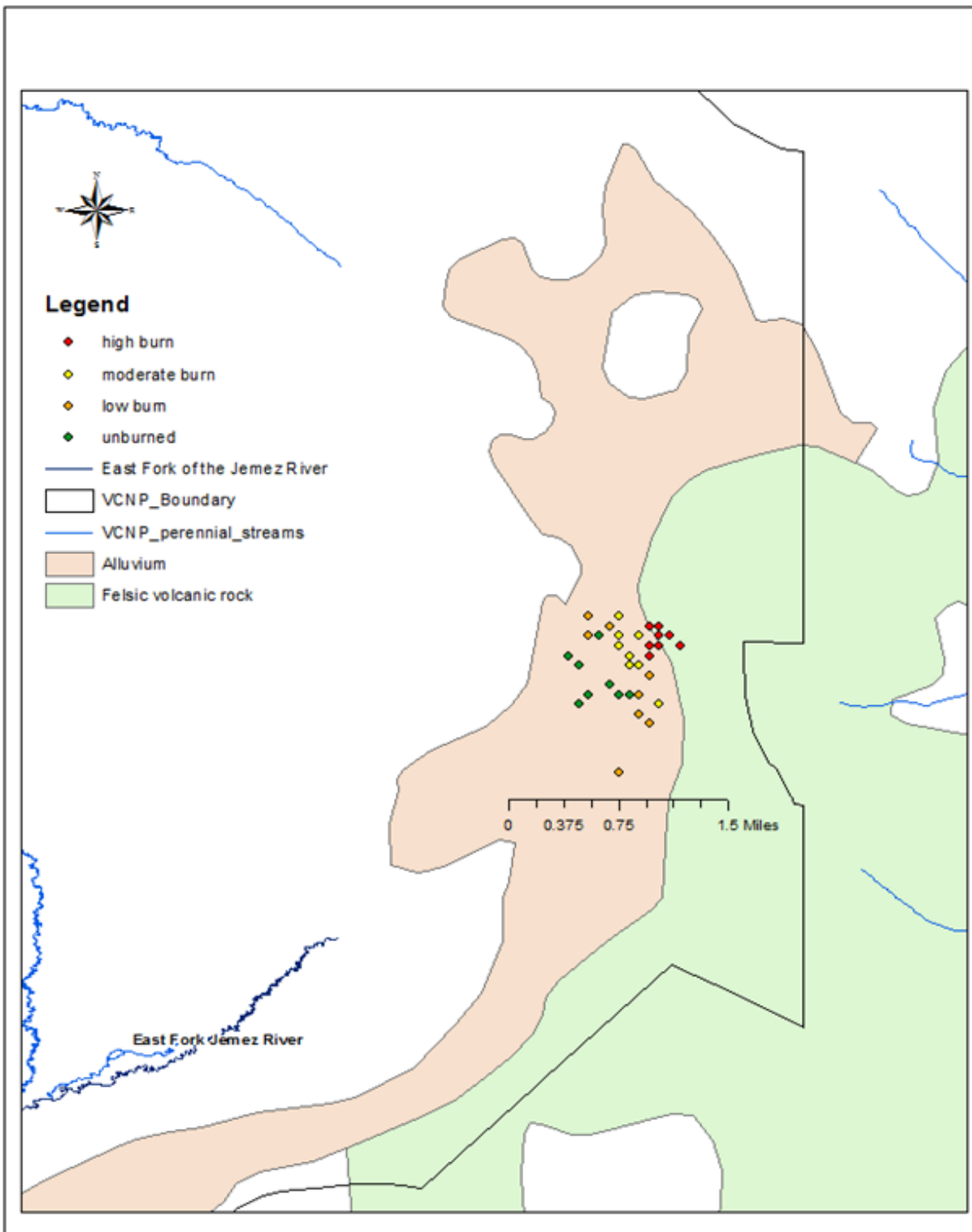


Figure 3: Site map showing the locations for the 32 soil samples by burn severity category over the geology for the Sierra de los Valles dome. The geomorphic features are alluvium and felsic volcanic rock, which were further characterized as being comprised of dacite (Shackley et al. 2016; Goff, 2009).

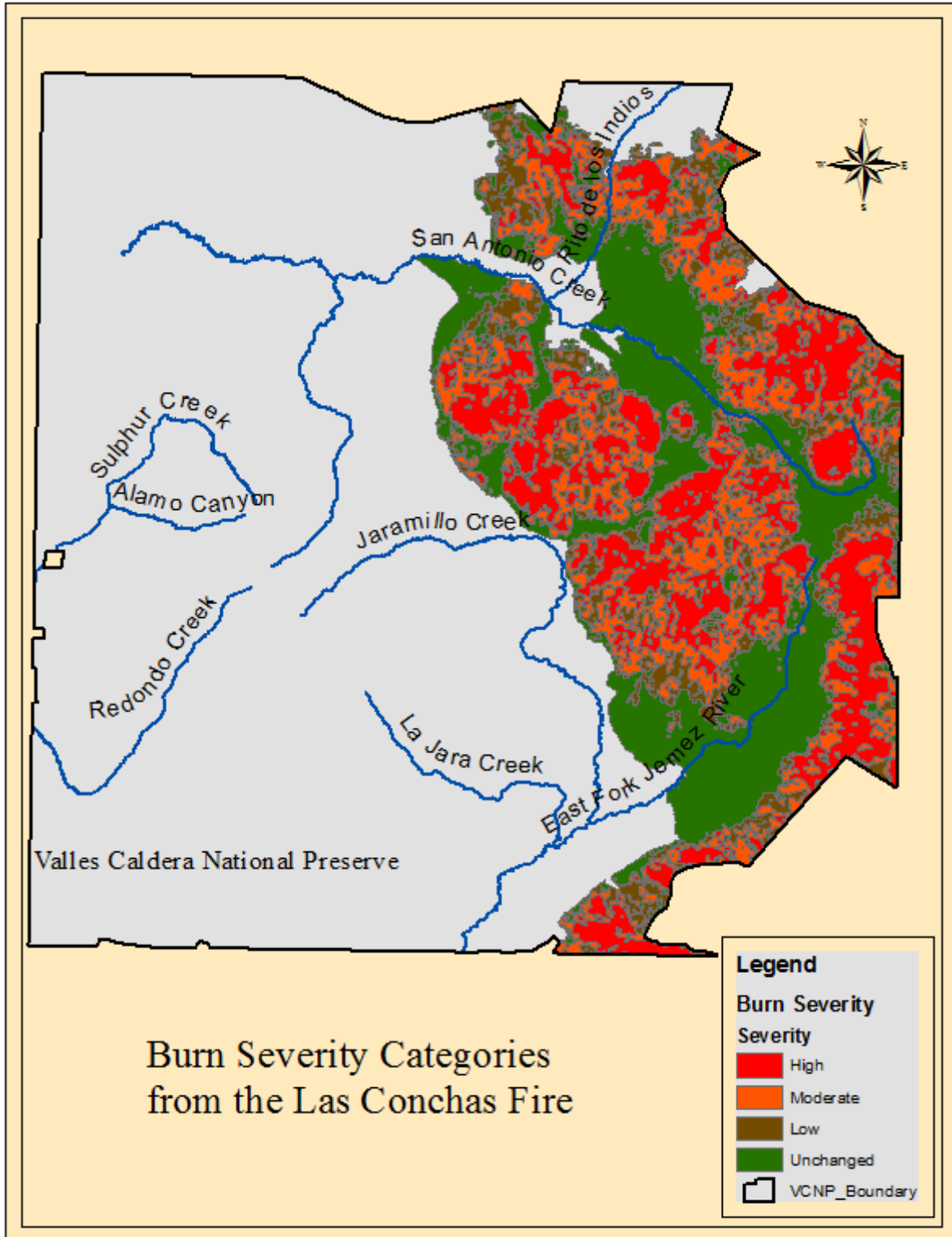


Figure 4: Site map showing the BAER burn severity map. The Las Conchas fire occurred on the east side of the Valles Caldera National Preserve boundary.

Table 1: The soil texture class, mean % OM \pm standard deviation, and mean pH for soil from all four burn severity categories. The highest values for % OM and pH are in bold.

<i>Burn Severity</i>	<i>Texture Class</i>	<i>% OM</i>	<i>pH</i>
High	8 Loam	12.7 \pm 0.42	5.93
Moderate	8 Loam	15.0 \pm 2.35	5.94
Low	8 Loam	12.3 \pm 1.07	5.54
Unburned	6 Loam/ 2 Sandy	9.73 \pm 0.11	
	Loam		5.70

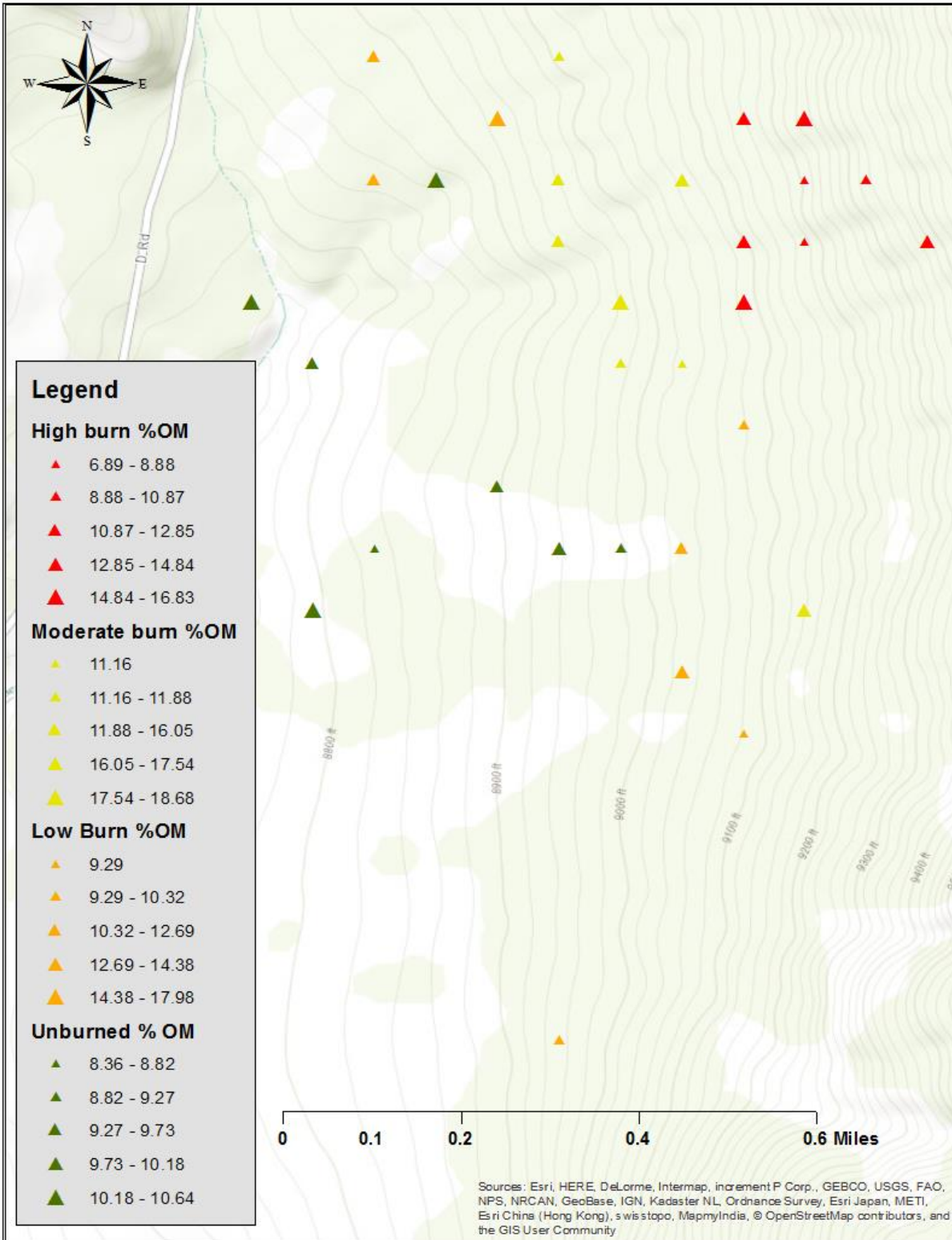


Figure 5: Site map showing the % OM per soil sample on the Sierra de los Valles dome.

Table 2: Results of the two-way ANOVA for all the measurable soil characteristics; pH, % OM, anions and cations; $p < 0.05$ level.

Two-Way ANOVA		
<i>Variable</i>	<i>Seasonal p-value</i>	<i>Burn severity category p-value</i>
pH	0.962	0.021
% OM	0.782	0.008
Anions		
NO ₃ ⁻	0.015	0.022
PO ₄ ³⁻	0.001	0.721
SO ₄ ²⁻	0.237	0.073
Cations		
Al ³⁺	<0.0001	0.069
Ca ²⁺	<0.0001	0.022
Fe ²⁺	<0.0001	0.004
K ⁺	<0.0001	0.099
Mg ²⁺	<0.0001	0.337

Table 3: The statistic test results for pH, % OM, NO_3^- , Ca^+ , and Fe^{2+} . These three anions were the only ions to differ significantly among burn severity category. The level of significance is $p < 0.05$ and denoted in the table with an asterisk (*).

pH			% OM		
(I) burn	(II) burn	Significant	(I) burn	(II) burn	Significant
high	moderate	0.606	high	moderate	0.335
	low	0.092		low	0.995
	unburned	1.000		unburned	0.166
moderate	high	0.606	moderate	high	0.335
	low	*0.016		low	0.233
	unburned	0.567		unburned	*0.004
low	high	0.092	low	high	0.995
	moderate	0.016		moderate	0.233
	unburned	0.102		unburned	0.247
unburned	high	1.000	unburned	high	0.166
	moderate	0.567		moderate	*0.004
	low	0.102		low	0.247

NO_3^-			Ca^{2+}			Fe^{2+}		
(I) burn	(II) burn	Significant	(I) burn	(II) burn	Significant	(I) burn	(II) burn	Significant
high	moderate	0.999	high	moderate	0.944	high	moderate	*0.018
	low	0.185		low	0.524		low	0.244
	unburned	*0.003		unburned	*0.019		unburned	0.982
moderate	high	0.999	moderate	high	0.944	moderate	high	*0.018
	low	0.139		low	0.843		low	0.578
	unburned	*0.045		unburned	0.066		unburned	*0.008
low	high	0.185	low	high	0.524	low	high	0.244
	moderate	0.139		moderate	0.843		moderate	0.578
	unburned	0.974		unburned	0.294		unburned	0.127
unburned	high	*0.003	unburned	high	*0.019	unburned	high	0.982
	moderate	*0.045		moderate	0.066		moderate	*0.008
	low	0.974		low	0.294		low	0.127

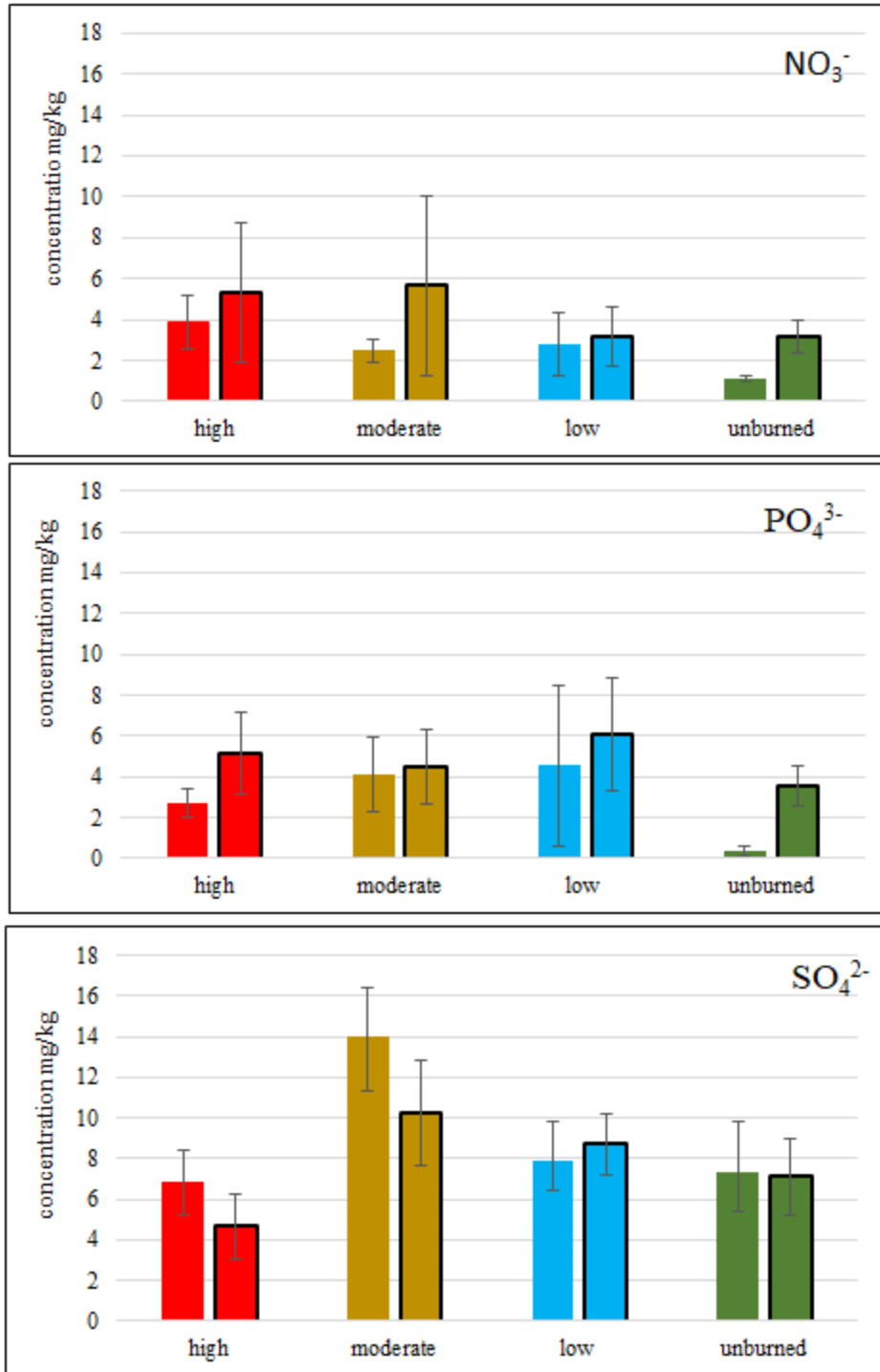


Figure 6: Mean ion concentrations (mg/kg) \pm standard deviation for the soil samples collected in December and April for NO_3^- , PO_4^{3-} , and SO_4^{2-} in each burn severity category. The bars outlined in black represent the soil samples collected in April.

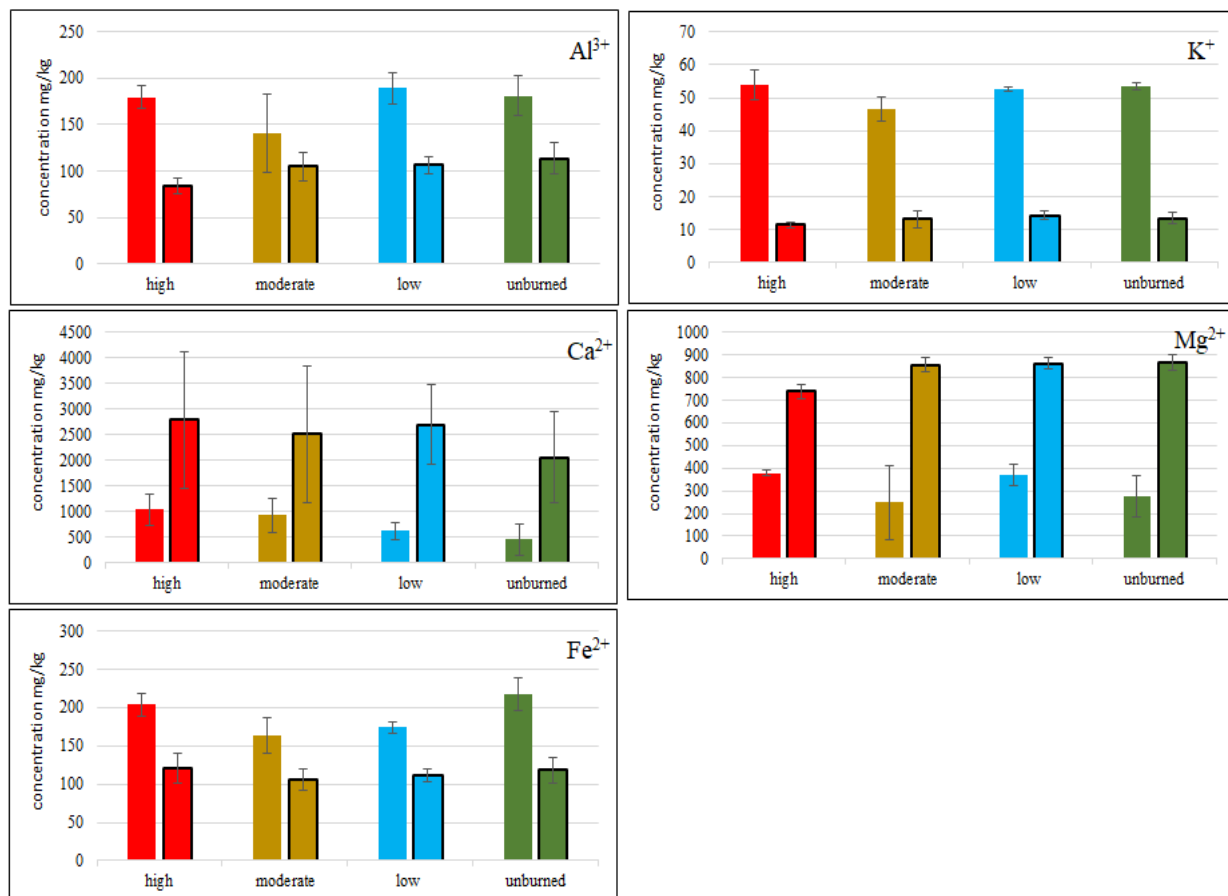


Figure 7: Mean ion concentrations (mg/kg) \pm standard deviation for the soil samples collected in December and April for cations Al^{3+} , Ca^{2+} , Fe^{2+} , K^+ , and Mg^{2+} in each burn severity category. The bars outlined in black represent the soil samples collected in April.

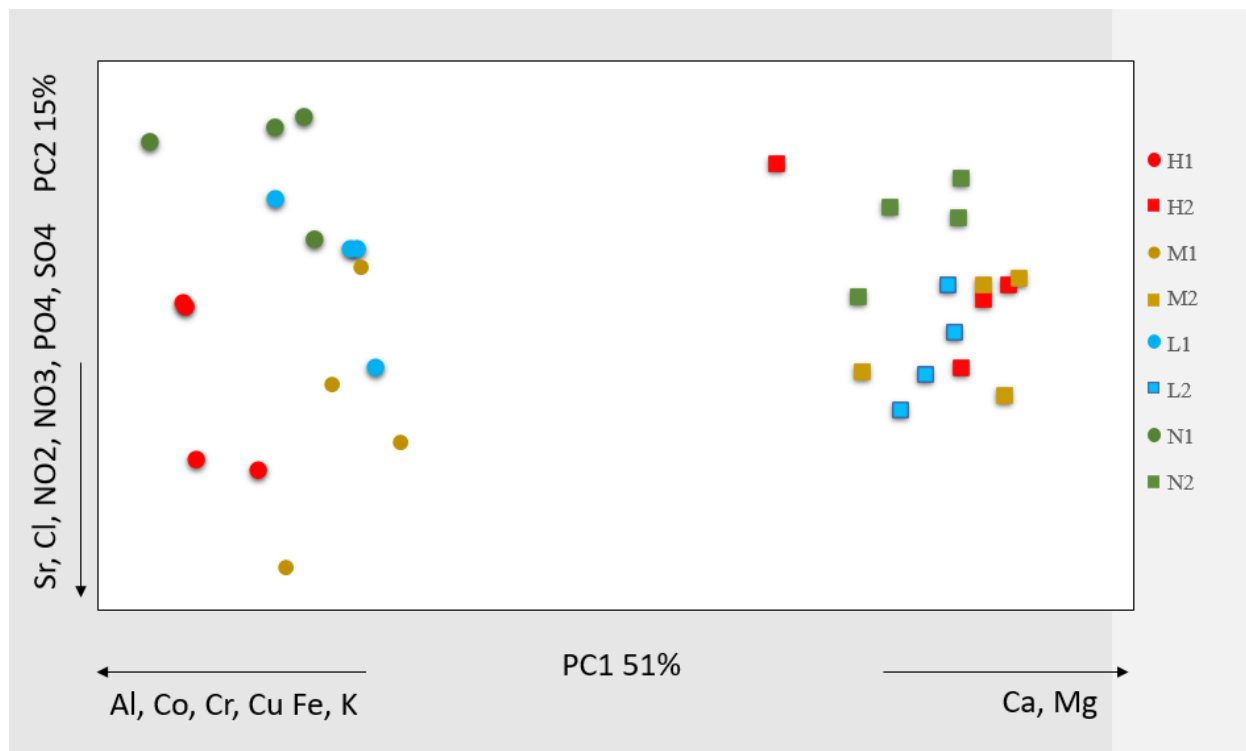


Figure 8: Principal component analysis illustrating the loadings $> \pm 2$ along the x and y-axis for PC1 and PC2. All 21 ions were analyzed from the 32 soil samples collected. The legend to the right organizes the burn severity categories by color and the collection seasons by number and shape (1-circles) December and (2-squares) April.

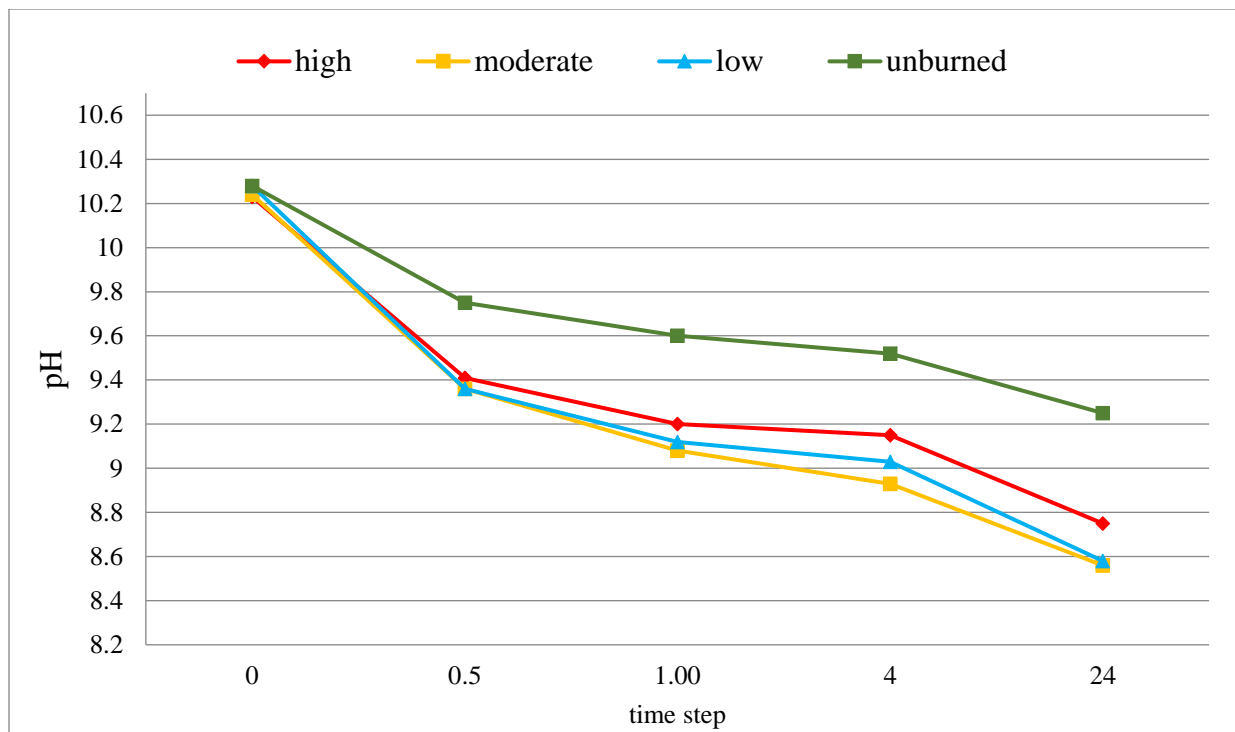
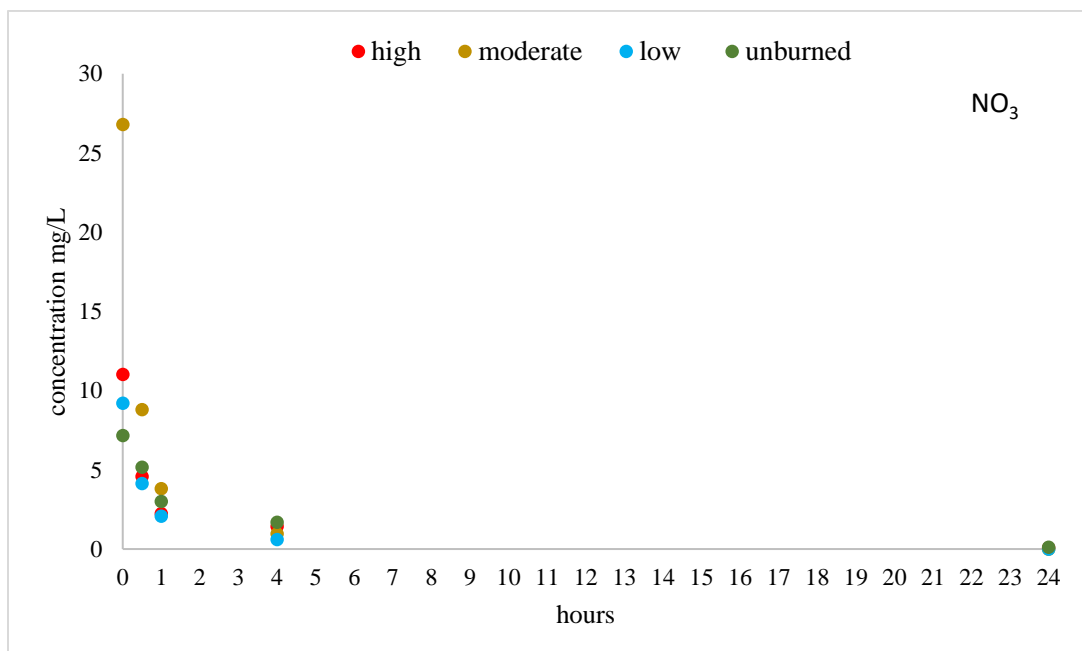


Figure 9: The pH taken over 0, 0.5, 1, 4 and 24 hours during the batch experiment, for each of the 5:50 mL soil: 10mM NaCO₃ solution from the four different burn severities.



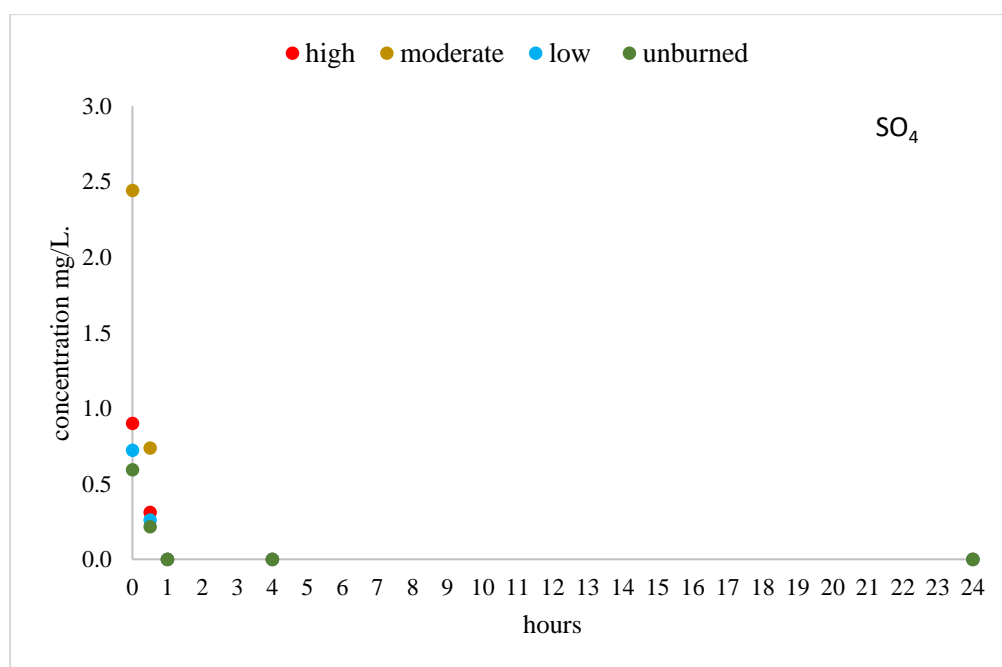
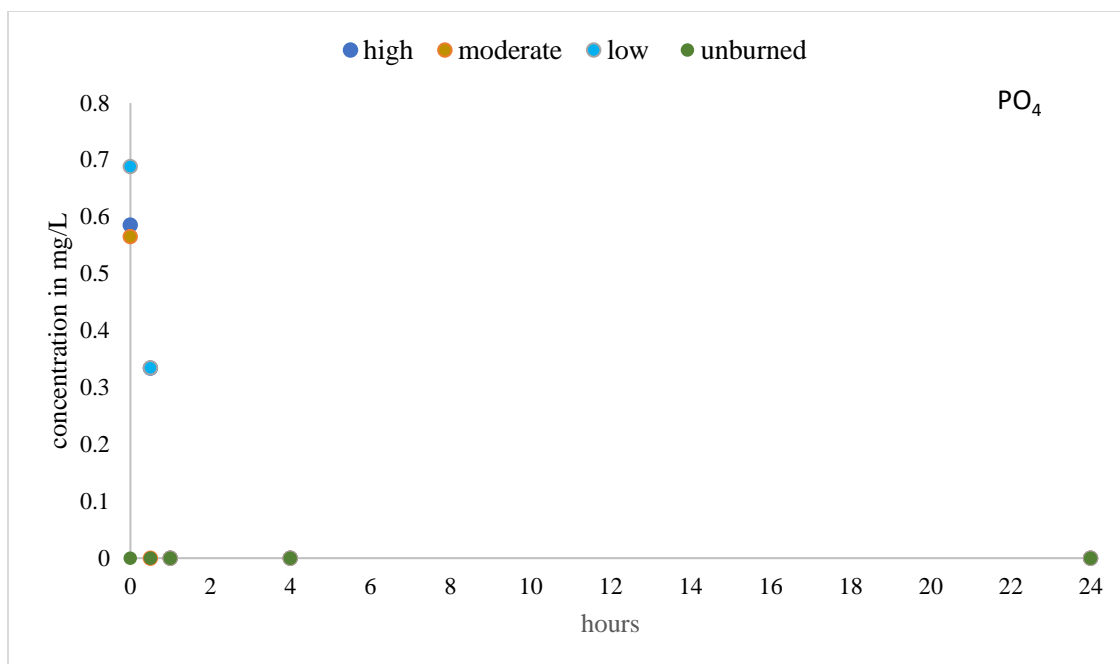
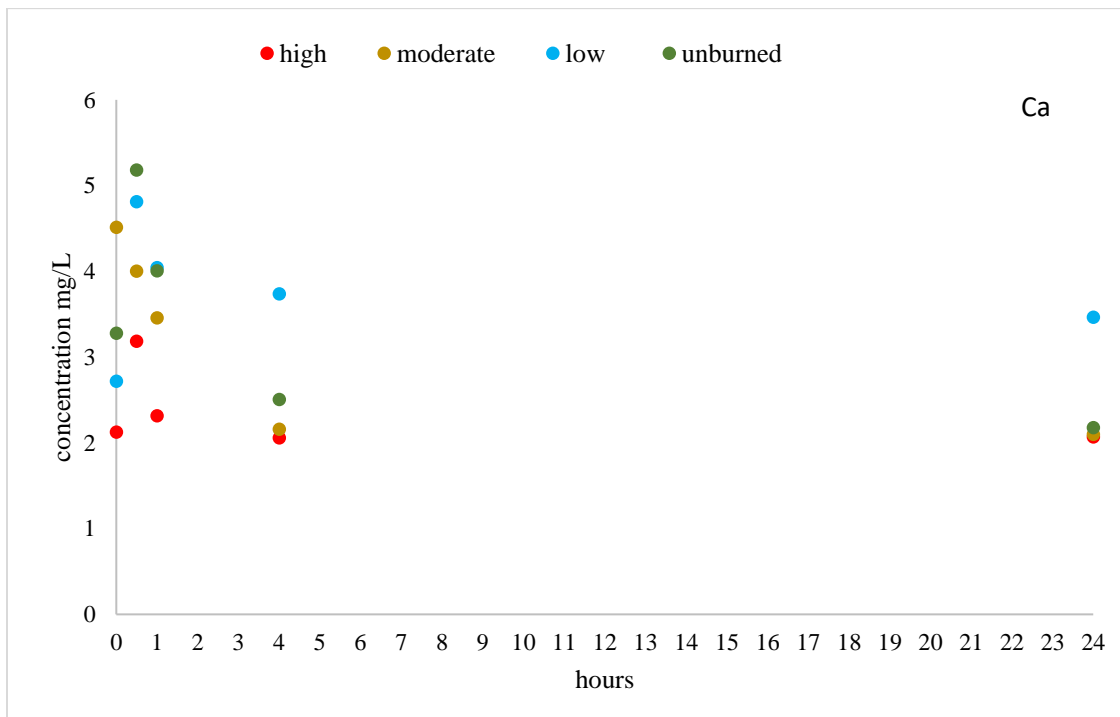
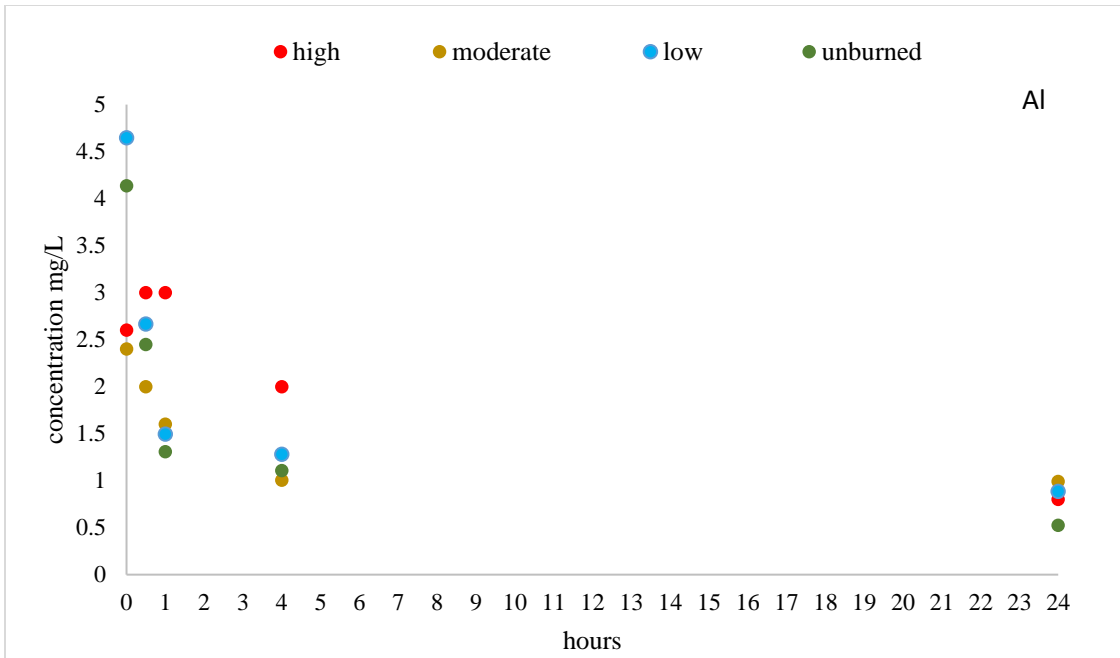


Figure 10: The leached concentration mean \pm standard deviation of NO_3^- , PO_4^{3-} , and SO_4^{2-} (mg/L) over 0, 0.5, 1, 4 and 24 hours, time steps 0,1,2,3 and 4 respectively for the high, moderate, low and unburned severity categories in the batch experiment



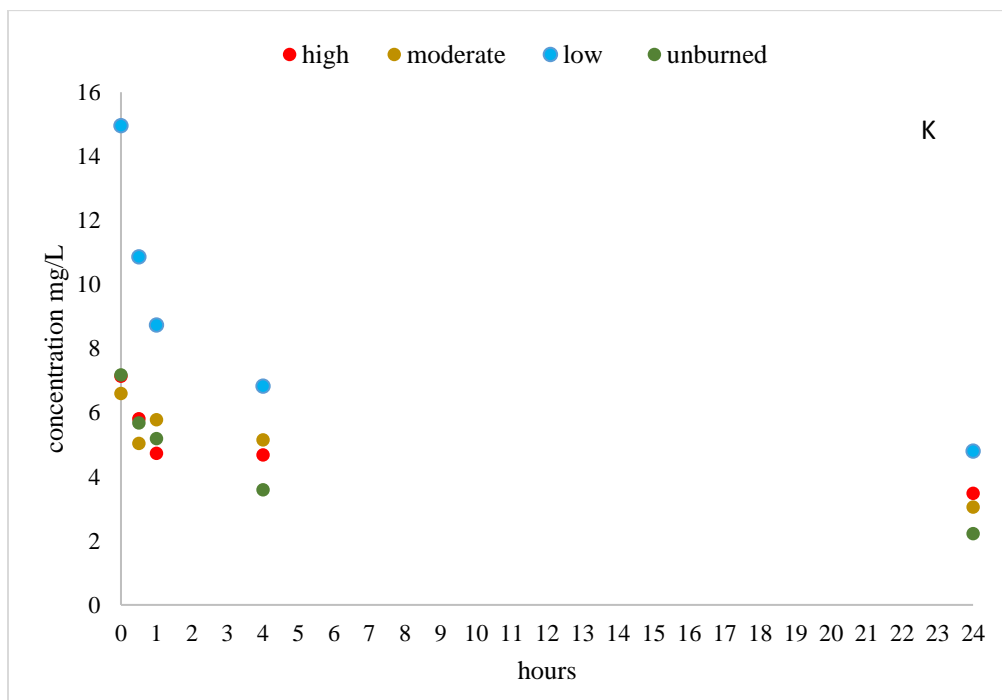
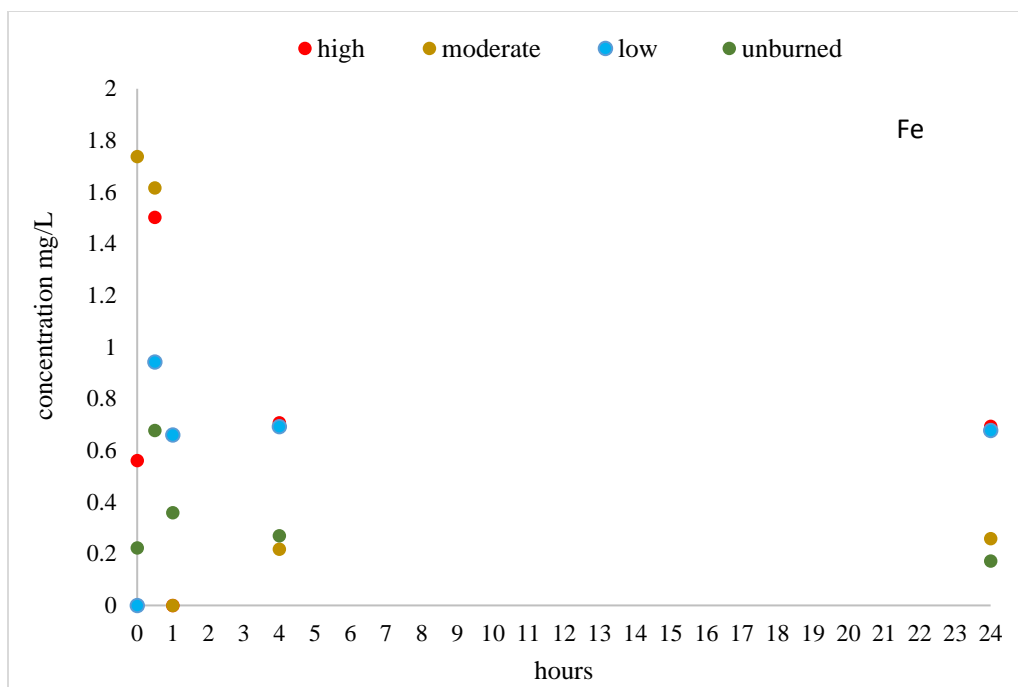


Figure 11: The leached concentration means \pm standard deviation of Al^{3+} , Ca^{2+} , Fe^{2+} , and K^{+} (mg/L) over 0, 0.5, 1, 4 and 24 hours respectively for the high, moderate, low and unburned severity categories in the batch experiment