NM WRRI Student Water Research Grant
Final Report June 30, 2017

1. **Student Researcher:** Amanda Otieno
   Faculty Advisor: Rebecca Bixby

2. **Project title:** Characterization of metals in soil contributions to runoff events following wildfires

3. **Description of research problem and research objectives.** The objective of this project is to characterize the chemical composition of soils from unburned, low, moderate and high burn areas within the Valles Caldera National Preserve, five years post Las Conchas Fire.

4. Description of methodology employed.

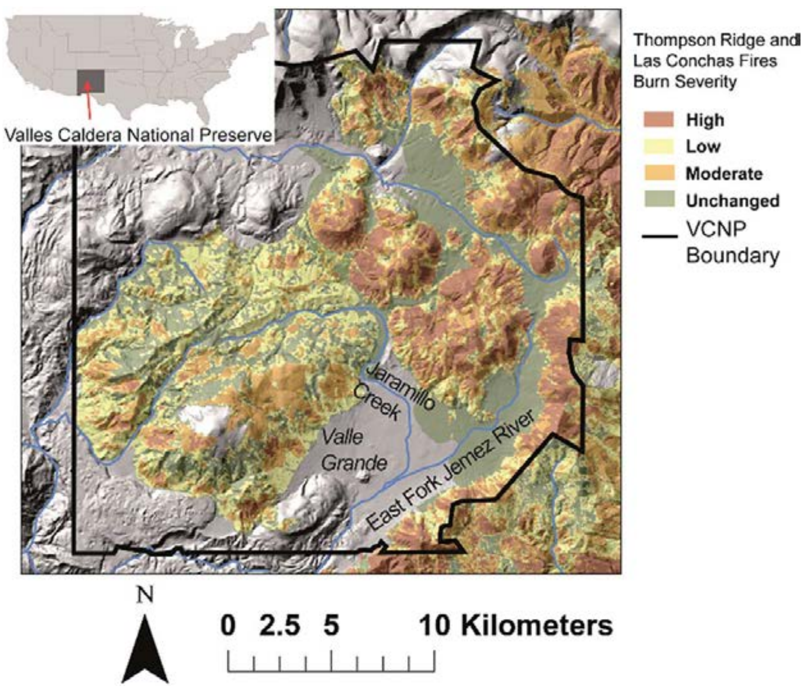


Figure 1: Site map of the Valles Caldera National Preserve, New Mexico. The white triangle indicates the Sierra de los Valles dome sample site.

Thirty-two soil samples were collected from the Sierra de los Valles dome within the Valles Caldera National Preserve (VCNP) in Jemez, New Mexico. Eight samples were collected from each burn severity previously classified by Burned Area Emergency Response (BAER) as high, moderate, low, and unburned (Figure 1). Sixteen samples were collected on two occasions in December 2016 and April 2017 using a random stratified sampling method. Random stratified sampling involves collecting soil in a random fashion within designated sections, in this case the four burn categories. The top three inches of soil were collected using the methods designated by the EPA SESD operating manual, which requires the removal of vegetation prior to soil assortment (United States Department of Energy, 2014). The soil type was characterized on site using the guide to texture by feel flow diagram as modified by the USDA's Natural Resources Conservation Service (United States Department of Agriculture, 1979). The soil samples were refrigerated at 4°C at the University of New Mexico.

Soil samples were air dried for 72 hours and ground using a mortar and pestle. Each sample was sieved using a 2 mm sieve. Two-gram soil samples were digested in triplicates using 5 mL of HNO_3, 2 mL of 30% H_2O_2, and 5 mL of HCl. The samples were placed in a DigiPrep block digestion system for 145 minutes at 100°C then brought to 25 mL volume using 2% HNO_3. They were filtered using 0.45μm filter for ICP-OES analysis. Dissolved metal concentrations of Al, Ba, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sr, V, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Concentration amounts were at the upper end of the ICP-OES detection limit for Al, K, and Fe so these samples were re-analyzed after 1:100 dilution using 2% HNO_3.

Subsamples were also prepared for anion analysis in triplicates, using 4-5 g of sediment and 25 mL of 18 MΩ water. The samples were placed in a tumbler for one hour and centrifuged for 10 minutes. They were filtered using 0.45μm filter and partitioned into 10 mL vials for analysis in the ion chromatography system. The results of which provide the concentrations of F, Cl, NO_2, Br, NO_3, PO_4, and SO_4.

One-way analysis of variance (ANOVA) determined any statistically significant differences between the means of the four burn severities with respect to the cation and anion concentrations. The means that were statistically different were further analyzed using a Tukey Kramer post-hoc test, a multiple comparison procedure used to identify the differences among the four burn severities.

5. **Description of results; include findings, conclusions, and recommendations for further research.**

The soil texture was determined for all 32 samples (Table 1). Soil texture describes the mineral fraction of soil through the distribution of the relative content of sand, silt, and clay particles (Figure 1) (Barbarick et al., 2000). Classification is based on one of four major categories: sand, silt, clay and loam. Texture influences physical factors, such as erosion and permeability, and allude to the soil's anion and cation holding capacity. The texture class, loam, was constant at the high, moderate, and low burn severity sites. Loam soils have a medium infiltration rate and water storage ability, moderate movement of oxygen into the root-zone and low erosive rates for wind but high erosive rates for water (Barbarick et al., 2000). The unburned sites were collected near the grasslands at the base of the Sierra de los Valles dome adjacent to the East Fork of the Jemez River headwaters. The soil classification was sandy loam. Sandy loam soils have slightly higher infiltration rates, lower water storage availability, very good movement of oxygen into the root-zone, higher erodibility via wind but lower by water (Barbarick et al., 2000). The soil texture of these sites prior to the Las Conchas fire was not determined thus wildfire impacts to the soil texture cannot be determined.

Metals occur naturally in soils through the weathering of underlying bedrock. Concentrations of elements differed depending on the season they were sampled (Table 2 and Table 3). The notable differences between the data in Table 2 versus Table 3 are the undetected elements: As and Ni for the December samples and Cd, Li and Mo for April (the concentration of these elements were simply too low for ICP-OES detection in these months). The distribution of metals change due to biochemical cycling by microorganisms in soils and plant roots (Kabata-Pendias, 2004). The April samples are prone to higher variances in metal concentrations due to the growing season, which does not occur to the same extent in the cold month of December (Kabata-Pendias, 2004). Further analysis will determine if any statistically significant differences appear between seasons. The mean of the December and April samples were tabulated (Table 4). There is no discernable order to the concentrations of metals by burn severity, however nine of the twenty-one elements present highest in concentration within the high severity as compared to the other three burn categories (Table 4). The concentrations range from a factor of 10^{-1} mg/Kg to 10^{3} mg/Kg. Elements such as Al, Ba, Ca, Fe, Mg, Mn and Si occur at higher levels due to their natural abundance in earth's crust (Rice et al., 2012). Heavy metal concentrations (Cd, Co, Cr, Cu, Pb, Mo, Sr, V and Zn) are typically low in soils, as is reflected in the Sierra de los Valles dome.

Wildfires simultaneously mobilize heavy metals in the soil that are typically inert and restrained, and introduce metals from the overlying vegetation as ash deposits. The one-way ANOVA was used to determine differences among group means per burn severity (Figure 2: A-D). The statistically significant differences are those whose p-value is less than $\alpha = 0.05$. Twelve of the twenty metals represented in the December samples had significant p-values: Ba, Co, Cr, Cu, Fe, K, Li, Mn, Na, Si, Sr, and V. The post hoc test identified the sample means that were significantly different by burn category. Elements Cr, Li, Mn, Mo, Na, and Sr showed variances mostly between the high/moderate and low/unburned. Co and V showed differences between all or most of the burn severities and Ba, Fe, K, Si distinguished between high and moderate as well as high/moderate, low and unburned. Fe was the only element to have a significant difference between the low and unburned sites.

Seven of the nineteen elements in the April samples had significant p-values: Al, As, Co, Mg, Ni, Pb, and V (Figure 3: A-D). Again, no burn severity alluded to specific trends when considering these elements collectively. Much like the December samples, the difference among the four burn severities occurred on a metal-by-metal basis. The metals Al, As, Co, and V differ between high/moderate and low/unburned. Pb was one of the few elements to show differences between the high and moderate burns. Concentrations of Mg and Ni in the low burn severity sites differed with the remaining three categories.

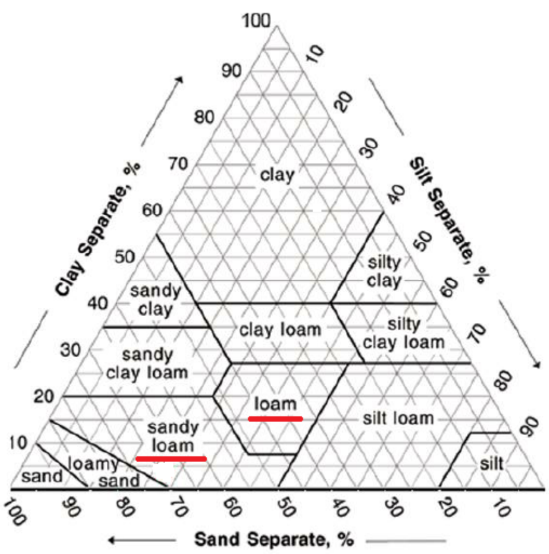
Mean anion concentrations varied with burn severity (Figure 4). The moderate burn severity has the highest anion concentrations with respect to the other three burn categories for both sampling dates. Research has documented decreases in the total nutrient pool directly after a wildfire but increases in moderate/low burn severities as succession occurs (De la Rosa et al., 2012). Temperature determines the volatizing of nutrients, with high burn severities causing the greatest loss in total nutrients post wildfire. Seven years after the Las Conchas fire anions present in higher concentrations for the high-burn samples than the low and unburned. The presentation of high concentrations of anions for the moderate and high burn were not statistically significant despite appearances (Figure 4). The only anions having a significant difference among the four burn categories was Br in December (Figure 4) and NO_2 in April (Figure 5). Br in April was not analyzed using one-way ANOVA because concentrations were not detectable within the high and unburned categories for the ion chromatography system.

The Las Conchas fire has had long lasting impacts on the chemical composition of soil in the VCNP. This research alludes to the distribution of metals and specific anions being a result of burn severity. Twenty-two metals were analyzed and 16 were significantly different between burn severity; the majority of which were between the high/moderate and low/unburned groups. Co and V were the only two metals showing a significant mean difference among sites for both December and April samples. The overall distribution of anions was higher in high/moderate burns, whereas the concentrations of metals depended on the element and not the burn category.

Soil is a medium for metals and anions to collect, but may also be a transporter of these substances when a disturbance is introduced into a system. A wildfire will disrupt the aggregate capacity of soils, making them more susceptible to erosion during precipitation events. In the southwestern US, the wildfire season is followed by the monsoon season. Thus, burnt soils have a high potential of being introduced into waterways in areas like the VCNP. It will be important to understand how the distribution of metals and anions in surface soils of different burn severities interact with nearby surface water. Further investigation will be done to study the leaching effects of metals and anions in water.

Table 1: Categorization of soil texture class by burn severity for the 32 soil samples collected at the VCNP.

Burn Severity	Samples	Texture Class
High	8	Loam
Moderate	8	Loam
Low	8	Loam
Unburned	2/6	Loam/Sandy loam



Loam is a soil with roughly equal proportions of sand, silt and clay.	
Sandy loam consists of less than 7% clay, 50% silt and 43-50% sand.	

Figure 1: Textural triangle for determining soil texture by the feel method. The red underlines indicate the two texture classes for the soil samples collected in the VCNP, with the definition tabled to the right (United States Department of Agriculture, 1999).

Table 2: Mean and standard deviation of the metal concentrations (mg/Kg) for the 16 soil samples collected in December 2016 from the VCNP. As and Ni were below the detection limit for the ICP-OES.

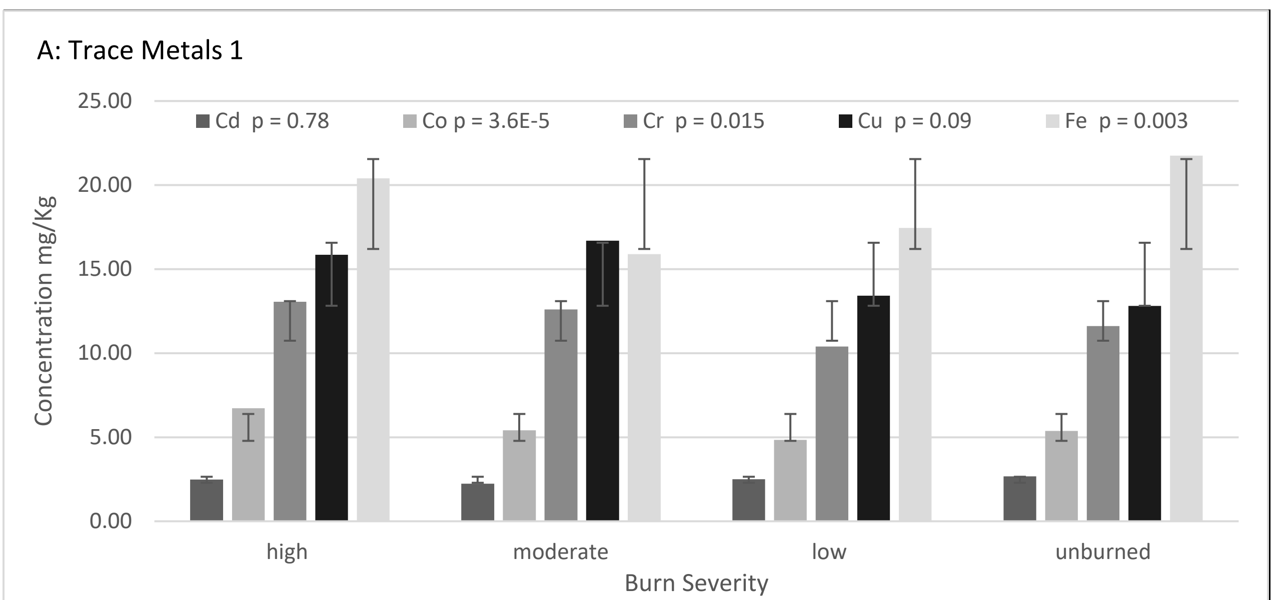
	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Pb	Si	Sr	V	Zn
Mean	172.68	21.41	174.99	764.29	2.47	5.59	11.92	14.69	188.73	51.61	9.81	318.86	263.06	.32	58.74	21.85	2478.73	30.08	28.17	38.72
Median	177.93	21.16	170.95	632.01	2.50	5.37	11.88	14.19	188.07	52.41	9.52	362.97	246.33	.36	59.13	21.71	2490.36	28.83	27.49	37.67
Std. Deviation	30.12	1.45	40.84	358.15	.25	.78	1.40	2.15	29.13	4.09	3.94	103.66	59.56	.15	11.27	1.68	263.92	9.03	3.63	5.61
Range	125.24	5.37	156.45	1222.27	1.00	2.56	5.00	7.53	112.02	16.83	14.07	363.99	168.39	.49	39.37	6.48	993.40	28.02	12.11	22.31
Minimum	78.72	19.28	94.87	366.51	1.77	4.65	10.02	11.10	132.77	42.15	1.95	44.37	179.00	.04	32.87	17.62	1806.66	18.54	22.87	31.90
Maximum	203.96	24.65	251.32	1588.78	2.77	7.21	15.02	18.63	244.79	58.98	16.02	408.36	347.39	.52	72.24	24.10	2800.06	46.56	34.98	54.21

Table 3: Mean and standard deviation of the metal concentrations (mg/Kg) for the 16 soil samples collected in April 2017 from the VCNP. Cd, Li and Mo were below the detection limit for the ICP-OES.

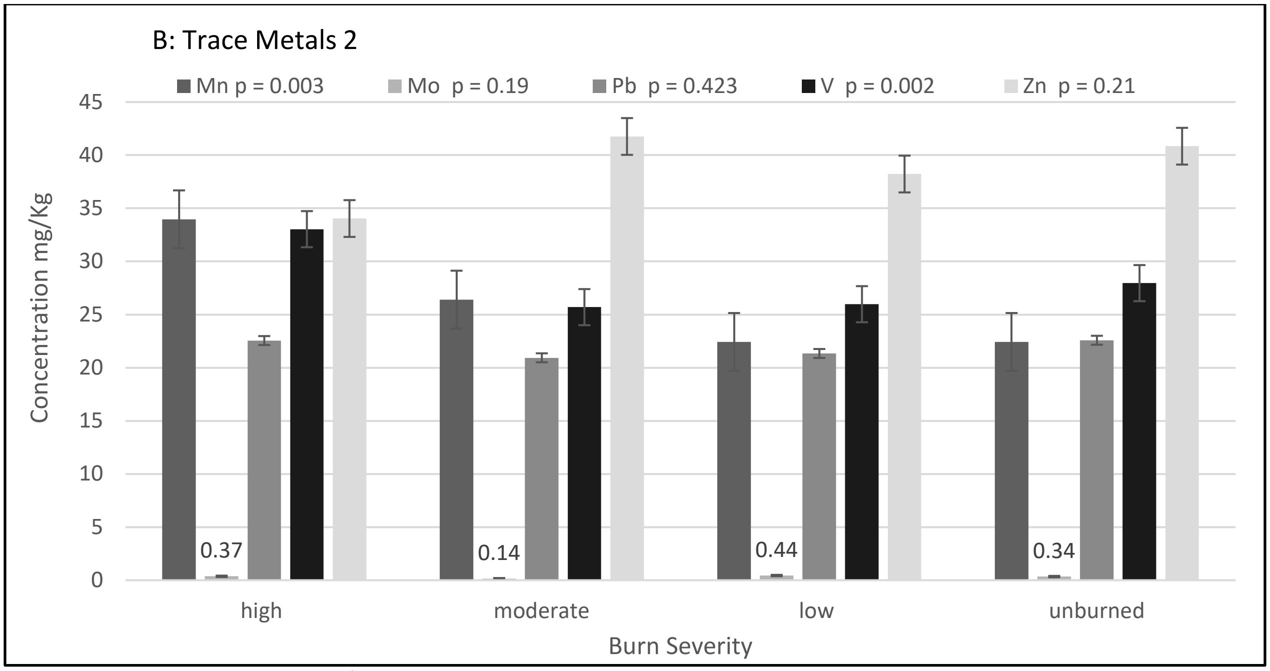
	Al	As	B	Ba	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Si	Sr	V	Zn
Mean	102.32	4.24	18.22	126.92	2512.04	2.62	6.41	8.30	114.33	13.10	308.14	39.59	3.48	7.74	133.89	27.09	20.51	29.34	38.72
Median	100.88	4.35	18.10	130.26	2402.43	2.26	6.43	8.59	112.21	12.61	294.68	36.76	3.39	7.63	138.01	27.15	20.20	28.47	37.67
Std. Deviation	16.11	.68	1.88	19.90	716.50	.89	.94	.91	15.12	1.91	75.53	10.02	.50	1.12	14.02	7.32	3.21	5.95	5.61
Range	60.65	2.31	8.17	63.06	2948.12	3.54	3.78	3.74	63.97	5.62	267.95	34.11	1.93	4.24	50.17	27.04	14.44	18.64	22.32
Minimum	74.99	2.98	14.06	94.96	1183.70	1.91	4.96	5.97	86.37	10.10	186.26	31.34	2.76	6.13	107.58	14.69	16.79	19.49	31.90
Maximum	135.64	5.29	22.23	158.02	4131.82	5.45	8.74	9.71	150.34	15.72	454.21	65.45	4.69	10.37	157.75	41.73	31.23	38.13	54.21

Table 4: Mean metal concentrations (mg/Kg) for all 32 samples collected in December and April. The gray cells in the table indicate the highest values for the element.

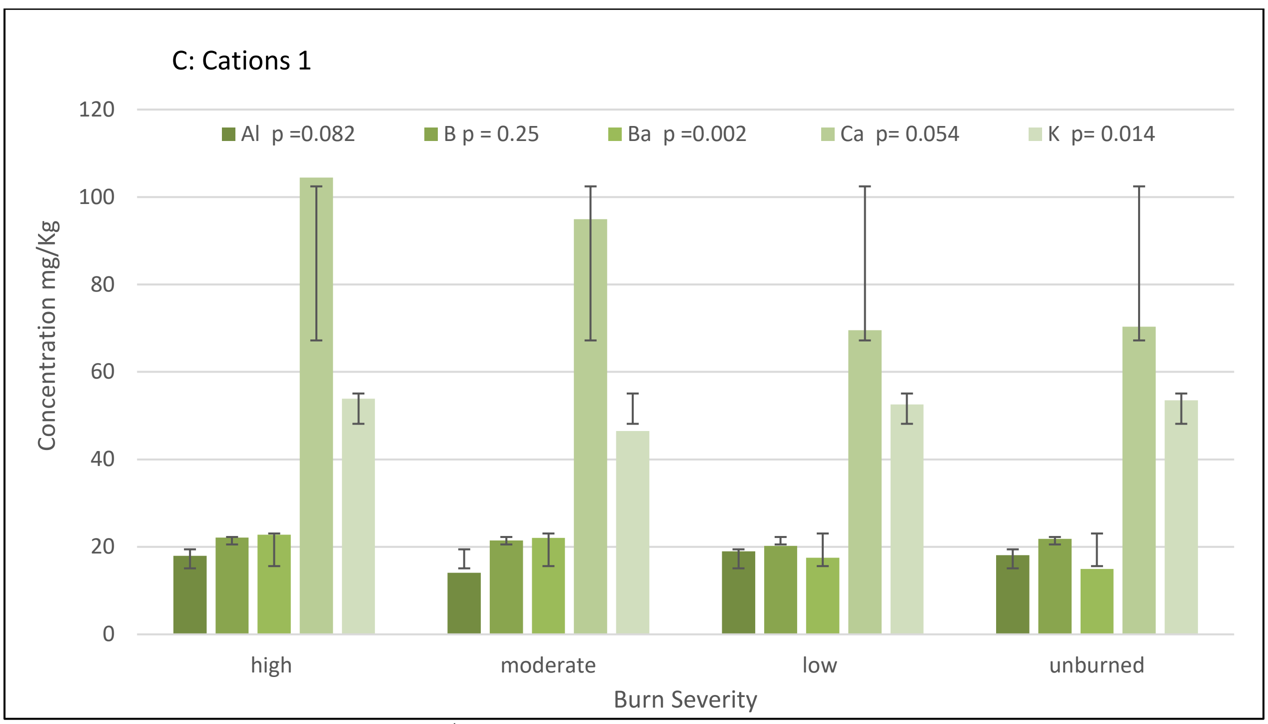
	Burn severity			
Metal	high	moderate	low	unburned
Al	131.91	122.84	147.91	147.27
As	84.25	104.93	106.32	113.79
B	20.46	18.90	19.62	20.29
Ba	176.32	137.15	159.19	131.16
Ca	1915.00	1719.74	1657.76	1260.15
Cd	2.49	2.23	2.49	2.66
Co	5.23	3.93	3.49	3.76
Cr	10.11	9.41	8.03	9.12
Cu	11.90	12.35	11.15	10.58
Fe	162.42	132.70	143.02	168.00
K	32.64	29.81	33.41	33.55
Li	7.55	5.52	12.42	13.81
Mg	558.28	551.36	616.16	571.96
Mn	313.89	259.98	318.60	249.93
Mo	0.37	0.14	0.44	0.34
Na	43.47	46.42	54.16	52.60
Ni	3.99	3.37	3.24	3.32
Pb	14.79	14.12	15.28	14.99
Si	1331.41	1142.79	1317.86	1433.19
Sr	34.53	31.72	26.63	21.45
V	28.53	22.21	22.85	23.76
Zn	28.99	33.26	36.70	37.16



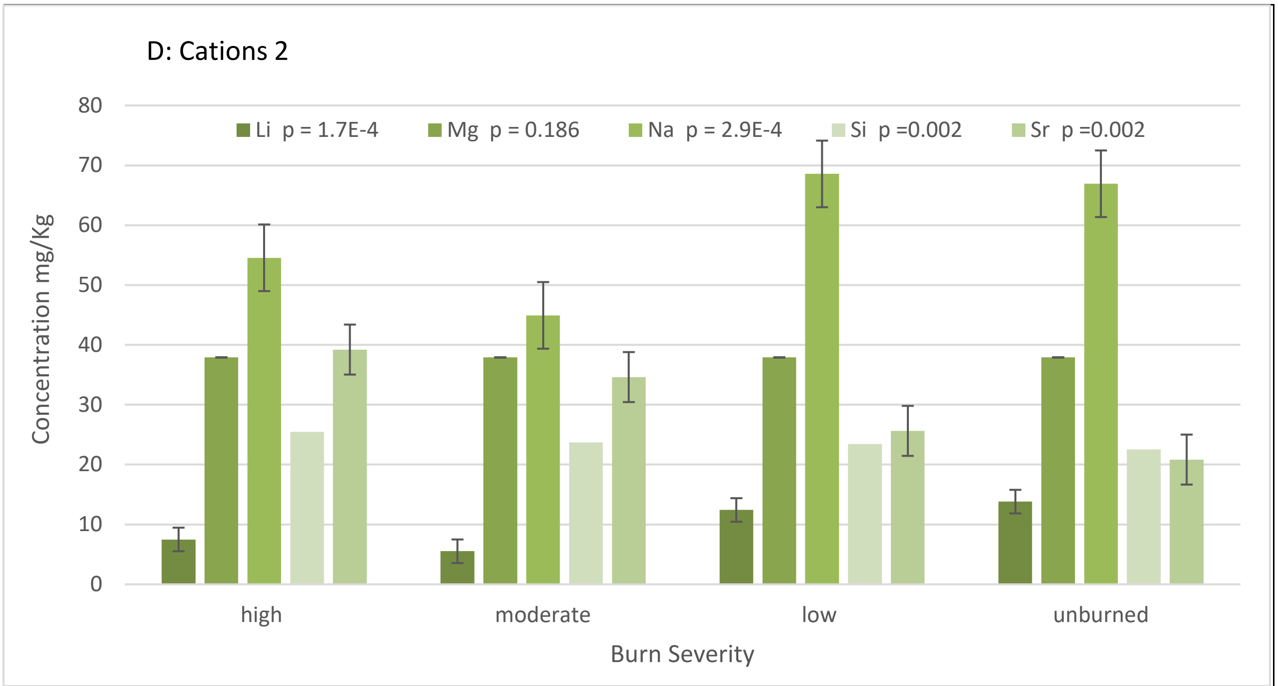
*Fe has been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentrations see Table 2.



*Mn has been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentrations see Table 2.

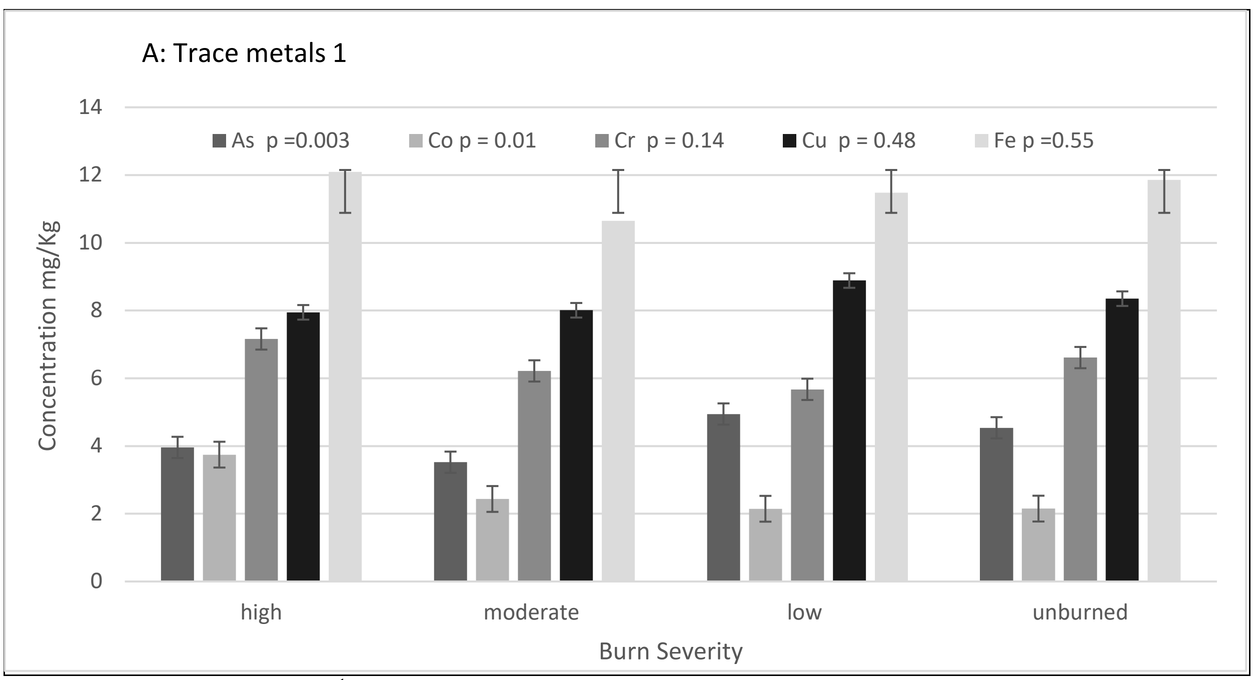


*Al, Ba and Ca have been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentrations see Table 2.

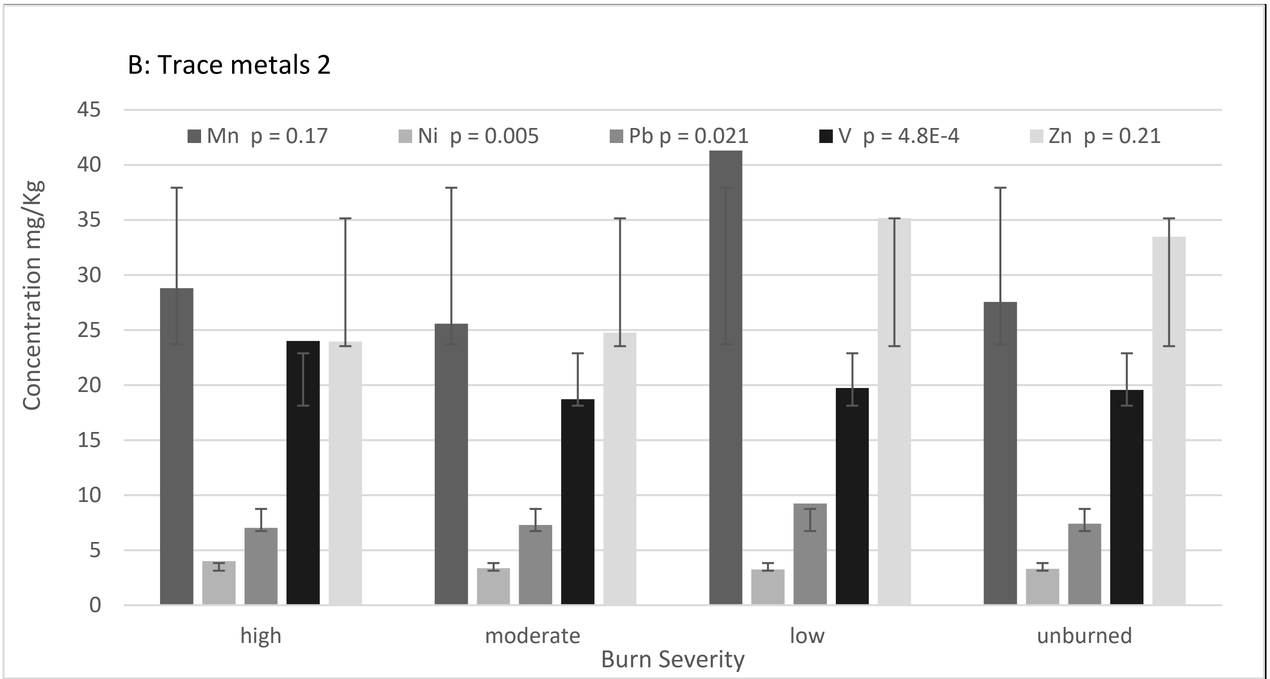


*Mg has been reduced by a factor of 10^{-1} and Si by a factor of $^{10-2}$ for graphical purposes. For the actual concentration see Table 2.

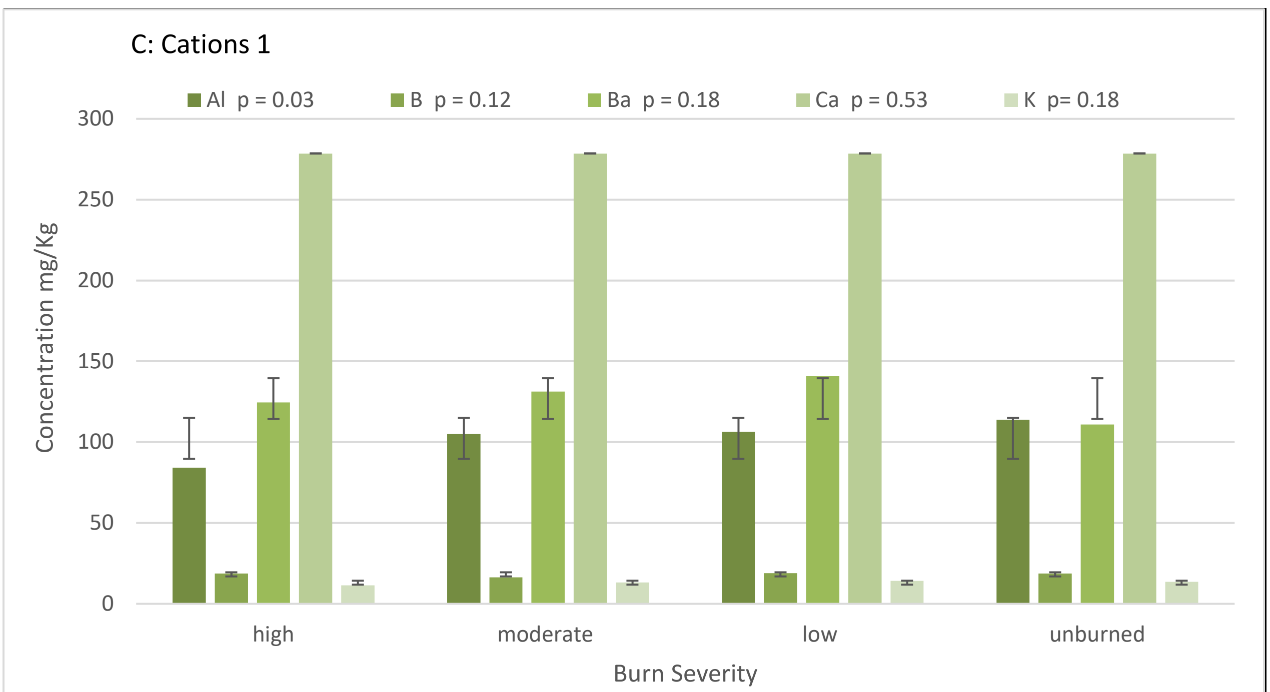
Figure 2 (A-D): Mean concentration and standard deviation for trace metals (A and B) and cations (C and D) by burn severity for the 16 December samples. The p-values calculated by the one-way ANOVA positioned to the right of the element specify which element's concentration differs significantly among burn severities.



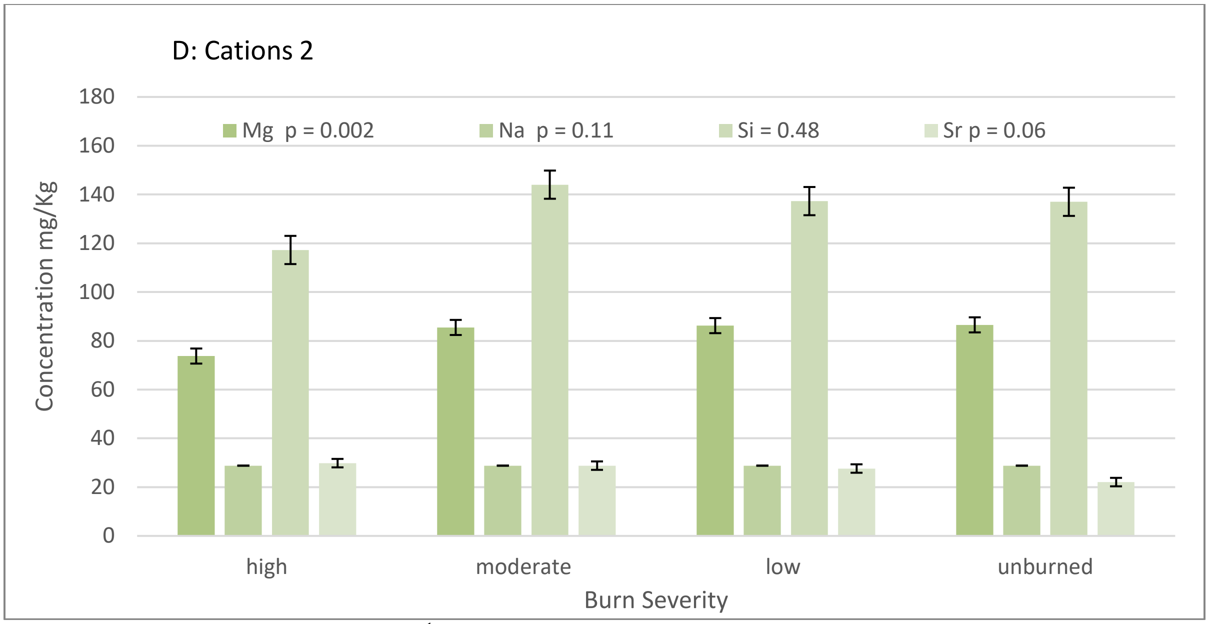
*Fe has been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentration see Table 3.



*Mn has been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentration see Table 3.



*Ca has been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentration see Table 3.



*Mg and Na have been reduced by a factor of 10^{-1} for graphical purposes. For the actual concentration see Table 3.

Figure 3 (A-D): Mean concentration and standard deviation for trace metals (A and B) and cations (C and D) by burn severity for the 16 samples collected in April. The p-values calculated by the one-way ANOVA positioned to the right of the element specify which element's concentration differs significantly among burn severities.

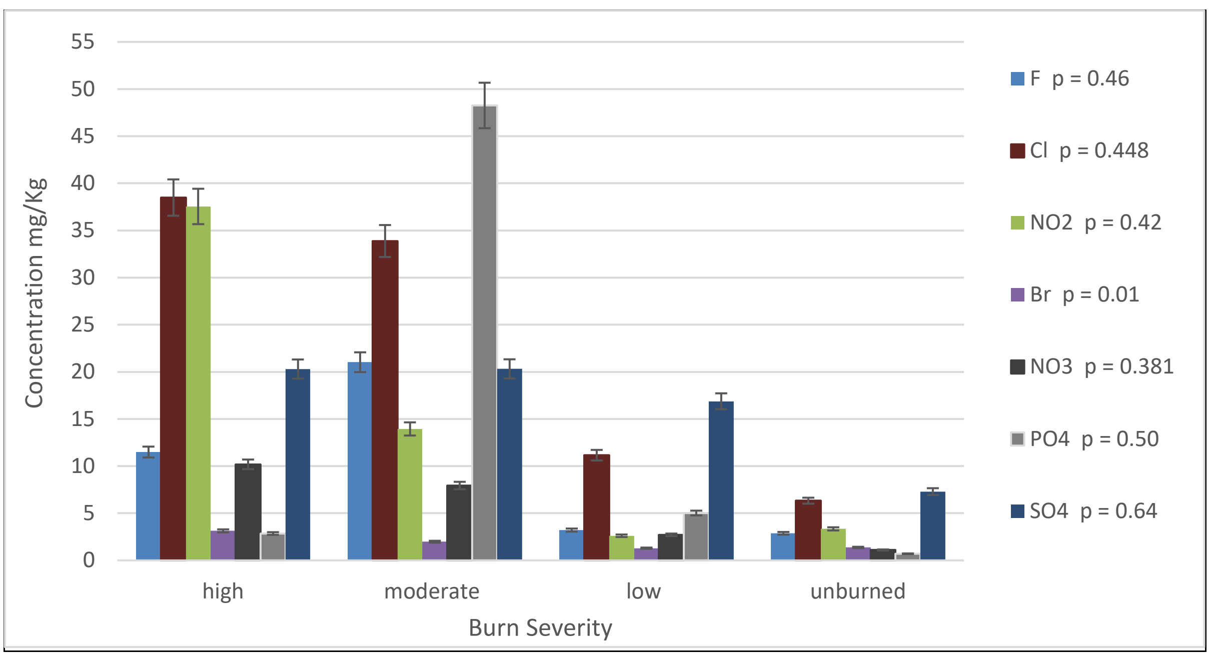


Figure 4: Mean concentration and standard deviation for anions analyzed in December. The p-values calculated by the one-way ANOVA positioned to the right of the element specify which element's concentration differs significantly among burn severities.

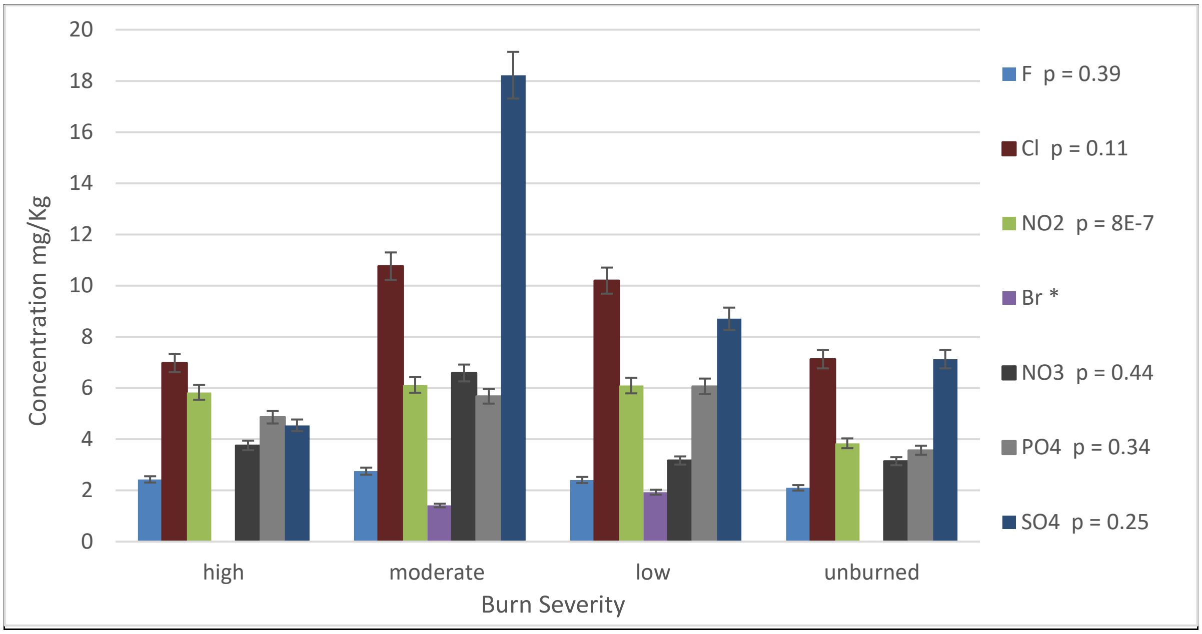


Figure 5: Mean concentration and standard deviation for anions analyzed in April. The p-values calculated by the one-way ANOVA positioned to the right of the element specify which element's concentration differs significantly among burn severities. Br was not represented in the high and unburned categories; thus no one-way ANOVA was performed.

6. **Provide a paragraph on who will benefit from your research results.** A variety of agencies could benefit from this research, specifically those concerned with forest ecosystems and watershed health. Runoff from wildfire may pose a threat to aquatic species making New Mexico Game and Fish an agency that could find value in this data. After the Las Conchas fire, Albuquerque's water quality was severely impacted. Thus, water treatment facilities such as Albuquerque Water Utility Authority may find this research helpful. Wildfire is a natural process; however, the effects in the southwestern U.S. have been compounded due to fire suppression management schemes and climate change. Increase fire severity can drastically change a landscape, the changes undergone in soils are increasingly important to understand for best management practices. New Mexico Environment Department, the Valles Caldera National Preserve, and the Forest Service are all agencies that may benefit from such analysis.

7. **Describe how you have spent your grant funds. Also, provide your budget balance and how you will use any remaining funds.** The funds were spent on salary, laboratory and field supplies, travel and analysis in the UNM analytical chemistry lab. The remaining funds of $376.71 were not spent.

Actuals	Distributed	Balance
		$4,632.09
Salary	Billed	$1081.76
Laboratory supplies and field supplies	Billed	$299.24
Travel (truck rentals)	Billed	$312.16
Analytical Chemistry Laboratory Costs	Billed	$3,480.00
		$376.71

8. **List presentations you have made related to the project.** No presentations have been made at this time.

9. **List publications or reports, if any, that you are preparing. Remember to acknowledge the NM WRRI funding in any presentation or report that you prepare.** No publications have been prepared to date. My professional project is being developed and presented for completion of the Water Resources Program in the Fall of 2017.

10. **List any other students or faculty members who have assisted you with your project.** The faculty members include Professor Rebecca Bixby of the Biology Department, Professor Ali of the Earth and Planetary Science Department and Professor Cerrato in of the Civil Engineering Department. Dr. Johanna Blake from the USGS is a not a faculty member but is a part of my committee and has been providing assistance. The students who have aided in this research include post-doc Dr. Eliane Hayek, MS student Asifur Rahman and undergraduate student Keely Miltenberger.

11. **Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.** There are none at this time.

12. **Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.** I will finish my degree in the Fall of 2017, earning a Master's of Water Resources from the Water Resources Program with a concentration in hydro science. My future career plans are to apply for hydrology positions within the National Park Service, U.S. Forest Service and water agencies within the Tribal Nations throughout New Mexico. It is my hope to gain more field experience, specifically in rural ground water use/management within the state.

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