# Impact of Silverado Fire on soil carbon

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## SUMMARY

**The Earth's soil contains three times more carbon than our atmosphere. Small differences in how soil carbon is stored and released can impact the carbon cycling and accuracy of climate change models. One fraction of soil carbon, pyrogenic carbon (PyC) is produced from partial combustion of soil organic matter (SOM). It is more resistant to microbial decomposition, and its longer residence in the soil provides greater potential for carbon sequestration. We sought to understand to understand the effect of a wildfire event on PyC deposits, using nitrogen and carbon isotopes as a proxy due to the effect of fractionation on isotopes caused by changes in organic matter during combustion. We hypothesized that after the occurrence of a wildfire, there will be a higher $\delta^{15}N$ ratio ($\delta$ = delta notation) in the burned soil relative to unburned locations and that the $\delta^{13}C$ ratio will remain constant and that total carbon (C) and total nitrogen (N) of the burned sites will be lower than in unburned sites. We collected soil samples at five sites within Limestone Canyon Preserve, an area affected by the 2020 California Silverado Fire. The results showed significant variability in $\delta^{15}N$ and $\delta^{13}C$ as well as total C and total N between the sites but did not support the original hypothesis. Due to variations in nitrogen cycling processes, the fractionation during combustion did not overwhelm isotopic signals of N cycle processes, which highlights the importance of establishing location-based control samples when measuring $\delta^{15}N$ as an indicator of PyC.**

## INTRODUCTION

Soil is the largest terrestrial reservoir of carbon. It holds more than three times the amount of carbon that is in plants and the atmosphere combined (1). As a result, soil plays an important role in accumulating atmospheric carbon dioxide, called carbon sequestration, to help mitigate climate change (2). Healthy soils are rich in soil organic matter (SOM) and have a correspondingly high level of soil organic carbon (SOC). SOM consists of decomposing plant and animal matter, feces, and soil microbes (such as bacteria and fungi) and is responsible for storing and releasing nutrients for plant growth and supporting the retention of water, nutrients, and SOC (3).

SOC mainly consists of carbon, hydrogen, and oxygen, resulting from the decomposition of SOM. Carbon components of SOC can be released by a process called fractionation, which can occur by different physical, chemical, or isotopic processes such as wildfires, root respiration, and microbial respiration (4). Pyrogenic carbon (PyC, also known as black carbon, soot or charcoal) is estimated to comprise an average of 13.7% of the SOC stocks with estimates of up to 60% in some ecosystems (4, 5). PyC is a type of carbon that is produced from the incomplete combustion of SOM, most commonly due to wildfire. PyC is high in carbon and low in nitrogen, and more resistant to microbial decomposition than unburnt SOC. As a result, PyC has great potential for carbon sequestration. However, because we lack a comprehensive understanding of how PyC is formed, deposited, degraded, and mobilized depending on topography, it is not factored into carbon models or climate models (5, 6, 7).

Due to many factors, including dryer, hotter temperatures caused by climate change and fire suppression practices, wildfires have been increasing in frequency and intensity throughout the world (8). Fire suppression causes fuel to accumulate, which leads to more frequent and intense future fires (8). Fires now affect about 4% of global vegetated surface every year (9). In California in the last 10 years, approximately one out of every eight acres have been burned (5). Although scientists have a comprehensive understanding of the effects of fires on atmospheric carbon, our knowledge regarding the impact of fires on soil carbon, including on PyC, remains limited (4, 7, 10).

As wildfires increase in frequency, the proportion of PyC that constitutes global SOC may be increasing. Even small differences in how carbon is stored and released from the soil can have significant impacts on climate change models given that carbon storage directly affects the global carbon cycle and climate change dynamics (7). After a fire, elevated PyC can additionally cause the soil to be more hydrophobic, which can increase erosion because water tends to run off hydrophobic soil, unable to be absorbed into the soil (11). Combined with reduced vegetation cover, elevated PyC can also cause increased vulnerability to erosion in sloped topography (11).

There are several methods of estimating PyC. These include benzene polycarboxylic acid (BPCA), the ultraviolet nuclear magnetic resonance UV/NMR, and the carbon-13 nuclear magnetic resonance $^{13}C$ NMR (12). However, these methods measure the polycyclic aromatic carbon (PAC) in soil, which is found in humus, another fraction of SOC. As a result, the inclusion of some humic carbon in PyC measurements can lead to an overestimation of the actual amount of PyC present. Additionally, these methods require specialized machinery or laboratory analysis, such as chemo-thermal oxidation, UV oxidation, and NMR spectroscopy.

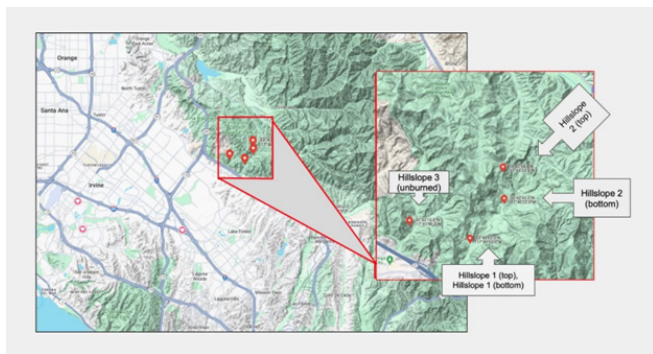An indirect method to measure PyC is the use of nitrogen

**Figure 1: Map of the five sampling sites and their location within Limestone Canyon Preserve in California.** At each site, both upper and lower slope samples were collected for three different slopes. Note that Hillslope 1 (top) and Hillslope 1 (bottom) are located very close to each other, and are indicated by the same red mark.

isotopes as a proxy (13). These two isotopes are indicated in delta notation ($\delta^{13}C$ and $\delta^{15}N$). $\delta^{13}C$ is a measure of the ratio of 13C to 12C. $\delta15N$ is the measure of the ratio of 15N to 14N. PyC is primarily composed of stable carbon isotopes, $^{12}C$ and $^{13}C$, and a lesser amount of stable nitrogen isotopes, $^{15}N$ and $^{14}N$. One indirect method of measuring PyC is to identify a change in $\delta^{13}C$ or $\delta^{15}N$ ratios (11). The combustion process results in selective consumption and loss of $^{14}N$. As a result of the larger relative amount of $^{15}N$, the remaining N pool will be enriched in $\delta^{15}N$ indicating greater PyC (4).However, prior research has shown that $\delta^{13}C$ does not change with charring and combustion (4).

Here we explored PyC deposits in five different sites within Limestone Canyon Preserve, an area affected by the 2020 Silverado Fire in Southern California. Specifically, our study sought to understand how PyC is deposited in land ecosystems after a wildfire by assessing changes in stable carbon and nitrogen isotopes across three separate hillslopes within the perimeter of the Silverado Fire: Hillslope 1 (bottom), Hillslope 1 (top), Hillslope 2 (bottom), Hillslope 2 (top), and the unburned hillslope (Hillslope 3). Based on the prior research relating to nitrogen and carbon isotopes, we know that different levels of combustion cause variations in the consumption of isotopes. We hypothesized that following a wildfire event, there will be an increased level of PyC and a correspondingly higher $\delta^{15}N$ ratio compared to unburned areas, while the $\delta^{13}C$ ratio will remain constant. We also hypothesized that both the total C and total N of the burned sites will be lower than in the unburned sites. We hypothesized this because during combustion, the process of fractionation occurs, where the lighter nitrogen isotope ($^{14}N$) is preferentially consumed in the combustion reaction (13). Our results showed significant variability in $\delta^{15}N$ and $\delta^{13}C$ between the sites but did not support the original hypothesis that there would be higher $\delta^{15}N$ in the burned soil and that the $\delta^{13}C$ ratio would remain constant.

## RESULTS

This study aimed to investigate the effects of a wildfire on pyrogenic carbon (PyC) deposits using nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotopes as proxies due to isotope fractionation during combustion. We hypothesized that burned soils would show a higher $\delta^{15}N$ ratio, constant $\delta^{13}C$ ratio, and lower
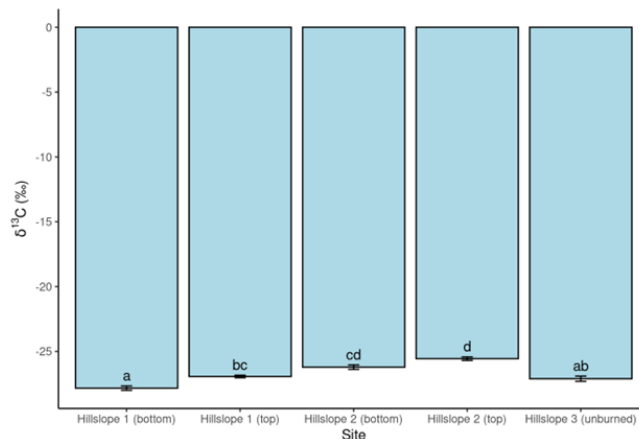


**Figure 2: $\delta^{13}C$ (‰) values in soil samples at each site (n=3).** Error bars represent estimated marginal means ± standard error. Data were analyzed using ANOVA followed by Tukey's HSD test at the 5% significance level. Bars with different letters above them indicate that the means are significantly different from each other. If two bars share the same letter, it means there is no significant difference between those groups (e.g., a bar with 'ab' would not be significantly different from a bar with 'bc,' but would be significantly different from a bar with 'cd').

total carbon and nitrogen compared to unburned soils. Soil samples from five sites affected by the 2020 Silverado Fire in Southern California were analyzed.

In this study, soil samples (5-inch cores) were collected at five sites within Limestone Canyon Preserve, an area affected by the 2020 Silverado Fire in Southern California (**Figure 1**). The five sampling sites consisted of one unburned site (Hillslope 3) and the tops and bottoms of two different burned hillslopes (Hillslopes 1 and 2). The unburned sample is labeled as Hillslope 3, and samples collected from burned sites are labeled as Hillslope 1 and 2. The tops of each of the two burned hillslopes had different elevations (850 ft versus 1340 ft, respectively). Approximately two years after the October 2020 Silverado Fire, we collected samples from hillslope tops and bottoms in order to observe potential differences in soil composition (and PyC, in particular) due to erosion down a hillslope, caused by rainfall after a wildfire. We additionally collected top and bottom samples from a nearby hillslope within the Limestone Canyon Preserve that was not impacted by the Silverado Fire. The samples were then dried, ground to homogenize the samples, weighed, and submitted to the UC Davis Stable Isotope Facility for analysis.

### Stable carbon isotopes

We expected that the stable carbon isotopes ($\delta^{13}C$ ratio) would remain constant. The $\delta^{13}C$ of the soil samples collected ranged from -28.09‰ to -25.40‰ in terms of isotopic composition of $^{13}C$ and $^{12}C$ (per mil) relative to the international Vienna Pee Dee Belemnite standard. We compared the samples taken from the unburned hillslope (Hillslope 3) and compared them to the samples collected in burned areas. We found that $\delta^{13}C$ unburned hillslope values were significantly more negative than our Hillslope 2 top and bottom samples (p < 0.001 and p = 0.017, respectively). However, the $\delta^{13}C$ values from the unburned hillslope were not significantly different from our Hillslope 1 samples.. When compared to Hillslope 1
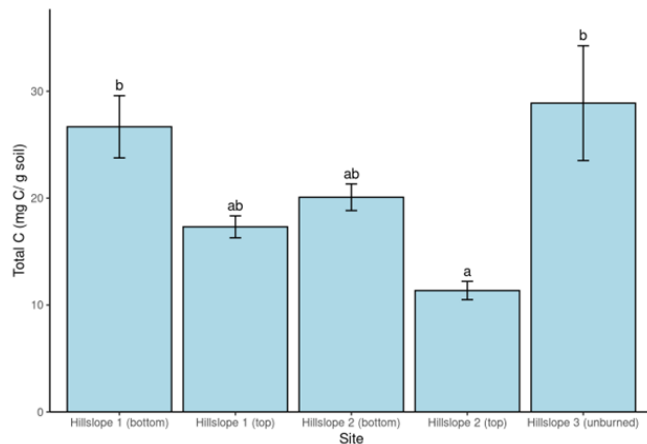
**Figure 3: Total carbon (mg) measured in soil samples at each site (n=3).** Error bars represent estimated marginal means ± standard error. Data were analyzed using ANOVA followed by Tukey's HSD test at the 5% significance level. Bars with different letters above them indicate that the means are significantly different from each other. If two bars share the same letter, it means there is no significant difference between those groups (e.g., a bar with 'ab' would not be significantly different from a bar with 'bc,' but would be significantly different from a bar with 'cd').



**Figure 4: $\delta^{15}N$ (‰) in soil samples collected at each site (n=3).** Error bars represent estimated marginal means ± standard error. Data were analyzed using ANOVA followed by Tukey's HSD test at the 5% significance level. Bars with different letters above them indicate that the means are significantly different from each other. If two bars share the same letter, it means there is no significant difference between those groups (e.g., a bar with 'ab' would not be significantly different from a bar with 'bc,' but would be significantly different from a bar with 'cd').

(bottom), Hillslope 1 (top), Hillslope 2 (bottom) and Hillslope 2 (top) had significantly more positive $\delta^{13}C$ values (p = 0.016, p < 0.001, and p < 0.0001, respectively). $\delta^{13}C$ values of Hillslope 1 (top) were also significantly more negative when compared to Hillslope 2 (top) (p < 0.001) (**Figure 2**).

**Total carbon**
We expected that the total C of the burned sites would be lower than in the unburned sites. Looking at total C in all of the samples, values ranged from 10.07 µg/mg soil to 39.41 µg/mg soil. total C from the unburned hillslope (Hillslope 3) was only significantly higher than Hillslope 2 (top) (p = 0.01). Amongst the burned sites, total C was also significantly higher in Hillslope 1 (bottom) compared to Hillslope 2 (top) (p = 0.023) (**Figure 3**).

**Stable nitrogen isotopes**
We expected that the $\delta^{15}N$ ratio would be higher in burned locations compared to unburned locations due to the combustion process. The $\delta^{15}N$ had values which ranged from 2.65‰ to 6.31‰. $\delta^{15}N$ in unburned hillslope (Hillslope 3) was significantly more positive than Hillslope 1 (top) (p =0.043) (Figure 4). In the burned sites, $\delta^{15}N$ in Hillslope 1 (bottom) was significantly more negative than Hillslope 2 (bottom) and Hillslope 2 (top) (p= 0.007 and p= 0.018). $\delta^{15}N$ in Hillslope 1 (top) was also significantly more negative than $\delta^{15}N$ in Hillslope 2 (bottom) and Hillslope 2 (top) (p = 0.006 and p = 0.016) (**Figure 4**).

**Total nitrogen**
We expected that total N) of the burned sites would be lower than in the unburned sites. In the total N graph, the values ranged from 1.04 µg/mg soil to 3.43 µg/mg soil. The unburned hillslope (Hillslope 3) had a significantly higher total N amount from Hillslope 1 (top) and Hillslope 2 (top) (p = 0.025 and p = 0.006). None of the total N amounts in the

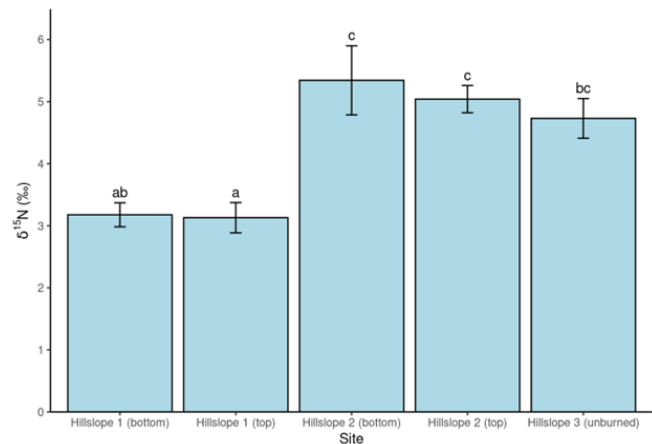unburned sites were found significantly different from each other (**Figure 5**).

**C:N ratios**
The carbon to nitrogen (C:N) ratios in all five sites ranged from 9.39:1 to 12.58:1. The ratio in the unburned hillslope (Hillslope 3) was significantly lower than from the ratio in Hillslope 1 (bottom) and significantly higher than the C:N ratio of Hillslope 2 (top) (p = 0.003 and p = 0.034, respectively). Also, the ratio of Hillslope 1 (bottom) was significantly higher than the C:N ratio of Hillslope 2 (bottom) and Hillslope 2 (top) (p = 0.001 and p < 0.0001). Hillslope 1 (top) was significantly higher than Hillslope 2 (bottom) (p = 0.02) (**Figure 6**).

**DISCUSSION**
This study aimed to investigate the effects of a wildfire on pyrogenic carbon (PyC) deposits using nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotopes as proxies due to isotope fractionation during combustion. We hypothesized that burned soils would show a higher $\delta^{15}N$ ratio, constant $\delta^{13}C$ ratio, and lower total carbon and nitrogen compared to unburned soils. Soil samples from five sites affected by the 2020 Silverado Fire in Southern California were analyzed, but the results showed variability in isotope and nutrient levels, contrary to the initial hypothesis.

We expected to find that the $\delta^{15}N$ values of the unburned hillslope (Hillslope 3) to be significantly different from the samples collected at burned sites. More specifically, we expected to see an increase in $\delta^{15}N$ values from Hillslope 3 (unburned) to the other sites. We also expected that the $\delta^{13}C$ values of the unburned hillslope (Hillslope 3) and the burned Hillslopes 1 and 2 to remain constant. However, the data showed unexpected differences between several of the sites. We expected that fractionation due to combustion could have influenced isotopic characteristics. However, other processes can influence isotopic characteristics as
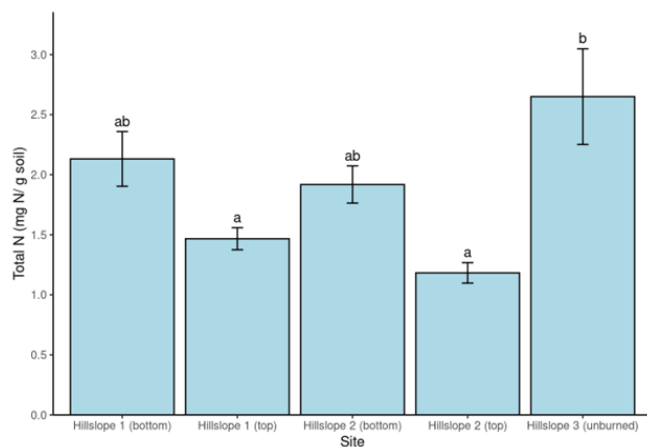
**Figure 5: Total nitrogen (mg) measured in soil samples at each site (n=3).** Error bars represent estimated marginal means ± standard error. Data were analyzed using ANOVA followed by Tukey's HSD test at the 5% significance level. Bars with different letters above them indicate that the means are significantly different from each other. If two bars share the same letter, it means there is no significant difference between those groups (e.g., a bar with 'ab' would not be significantly different from a bar with 'bc,' but would be significantly different from a bar with 'cd').



**Figure 6: Total carbon-to-nitrogen (C:N) ratio measured in soil samples at each site (n=3).** Error bars represent estimated marginal means ± standard error. Data were analyzed using ANOVA followed by Tukey's HSD test at the 5% significance level. Bars with different letters above them indicate that the means are significantly different from each other. If two bars share the same letter, it means there is no significant difference between those groups (e.g., a bar with 'ab' would not be significantly different from a bar with 'bc,' but would be significantly different from a bar with 'cd').

well, including other physical and chemical processes, and different types of vegetation in the area (4). Although we expected for fractionation to occur during combustion, we cannot rule out other processes (e.g., root respiration and microbial respiration) that could have influenced isotopic characteristics ($\delta^{15}N$ and $\delta^{13}C$) at each site before and after the Silverado Fire. Moreover, the background site variability may have been due to differences in nitrogen cycling processes with fractionation that also impact $\delta^{15}N$. This could have overpowered the differences arising from combustion during the wildfire and suggests that a location-specific control is important to account for this variability.

In this study, we were most interested in δ15N as an indirect estimate of changes in PyC. Our hypothesis was that PyC, and indirectly $\delta^{15}N$, would increase after a wildfire. We hypothesized this because during combustion, the process of fractionation occurs, where the lighter nitrogen isotope ($^{14}N$) is preferentially consumed in the combustion reaction (13). The N cycling process, which refers to how nitrogen cycles between atmosphere and soil and then transforms through microbial activity into biomass, soil organic matter and other nitrogen compounds, is influenced by many environmental factors (18). In particular, when nitrogen is released after a fire, the $\delta^{15}N$ value of soil is likely to change due to nitrogen mineralization (17).

Our research revealed that the fractionation produced during combustion did not overwhelm isotopic signals of other N cycle processes. This observation may be attributed to variations in nitrogen input rates, nitrogen sources, rates of physico-chemical nitrogen cycling, and nitrogen losses at individual sites. These variations led to differing isotopic fractionation, potentially resulting in distinct $\delta^{15}N$ values before the occurrence of the fire event.

This underscores the significance of establishing location-based control samples prior to any burn event whenever possible. Unfortunately, in many ecological studies, obtaining
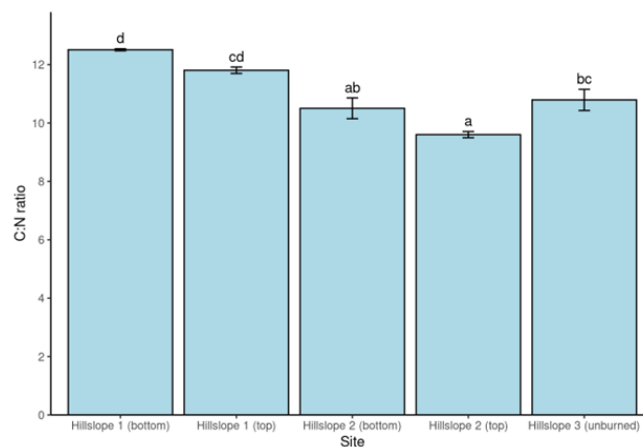
such baseline data is challenging. Consequently, it may be advisable to focus on studying a single location over time rather than attempting cross-location comparisons in the absence of baseline data when utilizing $\delta^{15}N$ as an indicator of PyC.

The results showed, however, that the only significant difference we saw was Hillslope 1 (top), where $\delta^{15}N$ was depleted. This suggests there are differences between the sites and the processes occurring in each one. These processes happen at different rates at different sites. N cycling can have an effect on the variability of $^{14}N$ and $^{15}N$ stable isotopes, which we expected had an effect on the variability of our results (18).

In our hypothesis, we stated that total C would be less in the burned sites than in the unburned site because we expected the burned sites to have released and lost carbon due to combustion. In total C, all of the burned sites had less carbon than the unburned site, but, statistically, Hillslope 2 (top) was the only significantly different burned site relative to the unburned site. Similar to total C, burned sites in total N were also generally lower than in the unburned hillslope (Hillslope 3). Hillslope 1 (top) and Hillslope 2 (top) were the two burned sites which were significantly different from Hillslope 3 (unburned) in total nitrogen.

We expected to find that Hillslope 3 (unburned) would have the highest carbon to nitrogen (C:N) ratio (8). However, our results showed that the C:N ratio in the unburned hillslope (Hillslope 3) was significantly higher than Hillslope 2 (top), and significantly lower than Hillslope 1 (bottom). This could be due to the physical variation between the sites. There could be a difference in the amount of organic matter, types of vegetation across sites, or simply variation in depth while sampling. We tried to control for this by ensuring that the samples were relatively similar in weight. However, the samples did vary in terms of content of rocks, leaves, twigs, and other natural items. In addition, the study from Kolka et al. found that soil

| Hillslope | Elevation | Fire intensity | Soil Map Unit | Soil Carbon Percent | Clay Percent | Sand Percent | Cation Exchange Capacity (meq/100g) | pH | K Factor, Whole Soil |
|---|---|---|---|---|---|---|---|---|---|
| Hillslope 1 (bottom) | 800 ft | high burn | Balcom clay loam, 30-50 percent slopes | 0.75 | 0.31 | 0.354 | 17.4 | 8.2 | 0.32 |
| Hillslope 1 (top) | 850 ft | high burn | Balcom clay loam, 30-50 percent slopes | 0.75 | 0.31 | 0.354 | 17.4 | 8.2 | 0.32 |
| Hillslope 2 (bottom) | 900 ft | high burn | Calleguas clay loam, 50-75 percent slopes, eroded | 0.75 | 0.3 | 0.35 | 23.6 | 8.2 | 0.32 |
| Hillslope 2 (top) | 1340 ft | high burn | Anaheim clay loam, 30-50 percent slopes | 2.00 | 0.31 | 0.35 | 25.3 | 6.5 | 0.28 |
| Hillslope 3 | 1610 ft | unburned | Calleguas clay loam, 50-75 percent slopes, eroded | 0.75 | 0.3 | 0.35 | 23.6 | 8.2 | 0.32 |

**Table 1: Location and measurements of the five sampling sites on three different hillslopes.** Samples were taken on August 8, 2022. The description of the fire intensity, soil map unit composition, clay percent, sand percent, cation exchange capacity, pH and K factor were all derived from the online Web Soil Survey according to the GPS coordinates of our soil sample (15).

depth and soil burn intensity impacts the C:N ratio (14).

A number of factors could have caused variability in our samples, which could have affected our results. For example, the samples may have been inadvertently taken at different depths of soil depending on the amount of compaction within the probe itself. Sampling could be improved by reducing the depth of the soil sampling. Rather than using five inches for each sample, we could concentrate sampling the soil close to the surface because the carbon we were testing is likely in the top layer of the soil most affected by the fire, and taking soil further down could dilute the samples. Additionally, we can also reduce variability in our results by collecting more samples at each site.

Additionally, since our samples were collected more than a year after the Silverado Fire, they may not be representative of the fire's immediate impact. Future studies can address this by immediate sampling and also longitudinal sampling to measure changes in soil composition across time, which would avoid the natural variability that exists across space.

The broader impact of this study on PyC and soil carbon sequestration relates to improving our understanding of how wildfires influence soil carbon dynamics. PyC, formed during combustion, plays a critical role in long-term carbon storage in soils. Examining how isotopes such as $\delta^{13}C$ and $\delta^{15}N$ shift after a wildfire can potentially help us better predict how carbon is stored or released post-wildfire, which has direct implications for carbon sequestration efforts. This study highlights the complexity and variability in post-fire carbon and nitrogen cycling, which suggests that fires do not have predictable effects on soil carbon storage and is important to understanding climate models.

## MATERIALS AND METHODS

### Study Site Description

The study was conducted in the Limestone Canyon Preserve in the Orange County Parks system of Southern California, in the area affected by the Silverado Fire in 2020 (Table 1). The Silverado Fire burned over 50.4 km2 of land from October 26 to November 7, 2020. This area has a mean annual precipitation of 383 mm (15). From November 2020 to the date of the soil sample collection in August 2022, the area had an average precipitation of 36.3 days a year on an annualized basis (15).

Sites were selected along three separate hillslopes within the perimeter of the Silverado Fire, with elevations ranging from 800 to 1610 ft above sea level (Table 1). We took three samples from each of the five different sites across Hillslopes 1-3. Hillslopes 1 and 2 experienced high severity burn and had very little vegetation cover. Hillslope 3 was unburned in the Silverado Fire.

### Sampling and Sampling Preparation Design

The five selected sites were in the location of the Silverado Fire between October 26, 2020 and November 7, 2020 (Figure 1). Hillslopes 1 and 2 were in burned areas and Hillslope 3 was in an unburned area. Samples from these sites were collected using a stainless steel, 12-inch, T-shaped soil probe (Lichtund brand). Three samples were collected at each site using the soil probe at a depth of five inches. The samples were randomly selected at each site. Table 1 contains a description of the fire intensity, soil map unit composition, clay percent, sand percent, cation exchange capacity, pH and K factor, which were all derived from the online Web Soil Survey according to the GPS coordinates of our soil samples (Table 1). The soil was stored in clear plastic bags. The individual soil samples were air dried for several days to remove any moisture. The soil was then ground and homogenized using a mortar and pestle. The sub-samples were weighed using a microbalance and placed into tin capsules for analysis.

### Soil Analysis

Samples were analyzed by the UC Davis Stable Isotope Facility for the following four data points: $\delta^{13}C$ (ratio of 13C and 12C stable carbon isotopes), total C, $\delta^{15}N$ (ratio of 15N and 14N stable nitrogen isotopes), and total N. The machine used to analyze the soil was an elemental analyzer coupled to an isotope ratio mass spectrometer (IRMS). The samples were combusted at extreme high temperatures (e.g., 1000° Celsius or higher). Then the oxides were removed from the reactor. Helium was passed through, trapping and heating the $CO_2$, and then releasing the $CO_2$ to the IRMS for analysis. The $\delta^{13}C$ values in the report we received from the Isotope Facility showed values relative to the international Vienna Pee Dee Belemnite standard.

### Data Analysis

Statistical analysis was performed using an ANOVA test (Analysis of Variance) to analyze the variation between the soils and determine any statistical differences. The Tukey Honest Significant Difference Test was also performed, which tested which means are different using a basis of p-value<0.05. All statistical analyses and graphs were generated in R (19).

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