# THESIS

# IMPACTS OF WILDFIRES AND RETARDANTS ON SURFACE WATER QUALITY

Submitted by

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# ABSTRACT

### IMPACTS OF WILDFIRES AND RETARDANTS ON SURFACE WATER QUALITY

Wildfire retardant is one of the most beneficial tools used to prevent the spread of wildfire, yet its presence has been found to be of big concern when dropped into aquatic habitats. Many retardants are composed mainly of ammonium and phosphates, which can lead to troubles with eutrophication and fish kills at high doses. Iron is often included to help with the identification of retardant drops, but can result in aesthetic issues when gotten into waterways. Despite the risks associated with its use, retardant is still a needed tool to help reduce the spread of wildfire and the effects of wildfire on the increase of organics, nutrients, and metals into waters. This study aims to quantify the effects of wildfire and wildfire retardant on the quality of surface waters.

A rainfall simulation was performed on soil plots to observe the influence of wildfire and wildfire retardant on the quality of runoff using Phos-Chek<sup>®</sup> LC-95A retardant. Soil plots were collected from a tallgrass prairie in Pingree, CO and plots were modified to simulate rainfall over unburned plots without retardant (Uwo), unburned plots with retardant (Uw), burned plots without retardant (Bwo), and burned plots with retardant (Bw). A Norton Ladder Type Rainfall Simulator was used to simulate rainfall over the plots at 165 mm/hr for 15 min and the runoff was collected and analyzed for ammonia, orthophosphate (P<sub>i</sub>), Fe, and TOC immediately following the experiment. The experiment was performed on 3 consecutive days and the entire process of the experiment was performed on the same plots 2 months after the first set of runs. Retardant use showed a significant increase in nutrient and iron concentrations for unburned

plots, while a significant increase was found for P<sub>i</sub> concentrations in burned plots. Burned plots showed a noticeable increase in TOC compared to unburned plots, but retardant showed no influence on either.

The second part of this study analyzed the leachate from soils collected from the burn area of the Royal Gorge on 3 separate occasions. Samples were collected from Uwo, Uw, Bwo, and Bw sites, as well as an unburned site with a high application of retardant (UwH). Nutrients and Fe were found to increase noticeably from Uwo to Uw + UwH soil, while ammonia was generally found to be higher in Bw than Bwo. Retardant was found to have no noticeable influence on TP and Fe in the first analysis, but Bw was found to show lesser concentrations than Bwo as the analyses carried on. Concentrations of Mn were generally less in Bw than Bwo for all of the analyses. These results show that concern is warranted when retardant is dropped near waterways.

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#### INTRODUCTION

As drought conditions continue to grow, so too does the occurrence of wildfires. Wildfires pose threats to human safety, property, aquatic habitats, and water quality so a preventative measure is needed to help curtail the threat. Aerial wildfire retardants have been found to be an effective tool in diminishing the spread of wildfires, but they can also pose a threat to water ecosystems if gotten into.

Retardant is generally composed of ammonium based fertilizer salts that often include ammonium polyphosphate, diammonium phosphate (DAP), and/or ammonium sulfate. If these compounds reach water bodies in high amounts the ecosystem is often affected by fish kills and algal blooms, while the economy can also feel the effect though a reduction in recreation and an increase in cost for water treatment plants. Iron is often included in retardants as well so that a clear sign can be made of where drops have occurred; however, if gotten into the water, iron can be a big concern for aesthetic issues. In order to curtail the concerns associated with retardant drops, a 90 m (300 ft) buffer zone has been imposed by the U.S. Forest Service between retardant drops and surface water. One caveat to this regulation is that drops are still allowed within the buffer zone if human life or property is at risk, but drops within the buffer zone are more likely to be done accidentally. In order to understand the potential impacts of retardant on water quality, the influence of runoff and erosion on the transport of retardant to waterways needs to be researched. This study investigates this concern by 1) simulating a rainfall event to analyze the water quality of the runoff and 2) analyzing the water quality of leached soils to observe the possible influence of sediments.

This thesis is composed of 3 main chapters. The first chapter contains a literature review that summarizes research already done on the impact of wildfire on the nutrients, metals, organics, and other parameters of soil, as well as what is known about wildfire retardants. The second chapter contains the methods and materials used, results, discussion, and conclusions of the experiments done. It is prepared in a manuscript format to be considered for an academic journal submission. The third chapter includes an update to a previous study done on the effects of the High Park Fire on the water quality of the Poudre River. Raw data of all experiments are provided in the appendices.

#### **1. LITERATURE REVIEW**

### 1.1 WILDFIRES

As climatic trends continue toward drier and warmer conditions, an increase in the frequency, severity, and size of wildfires is expected in the southern and western United States (Davis, 2001; Miller et al., 2009). The threat of wildfires in the United States is of great concern as 6.3% of the U.S. Population (17.5 million) reside within a wildland-urban interface (WUI) and 2.1% of the population lived within WUI areas where more than one fire occurred in the 2000s (Thomas and Butry, 2014). Additionally, the 10-year average federal wildland fire suppression expenditures were \$1.58 billion in 2000-2009, which were a 250% increase from the average expenditures of 1990-1999 (Gebert and Black, 2012).

## 1.1.1 FREQUENCY

Fire frequency is the number of fires in a study area over a given period of time and is defined by 2 attributes: 1) the mean fire return interval (the average number of years between fires in a given area over a given time period) and 2) the fire cycle (time required to burn an area the size of a given area) (Ryan, 2002). The frequency of wildfires can be dependent on a number of environmental factors including geographical location, flora type and size, elevation, and dryness of the forest. (Brown and Smith, 2000). Although two areas may be otherwise similar, one may still be less susceptible to frequent fires due to natural barriers such as lakes, avalanche paths, rivers, or barren ground (Turner and Romme, 1994). One reason fire frequency is a concern is because of the time available for a species of flora to regrow and reach its reproductive maturity (Noble and Slatyer, 1981). Fires that are frequent in their recurrence often lead to the growth of species of flora that have short life cycles, such as annual grasses (Keeley,

1981). Since the moisture content and energy on combustion are spatially heterogenous, the frequency of forest fires can be highly variable and vegetation more susceptible to frequent fires is often found on dry sites with more humidity (Rowe, 1983). Frequency of fires is often inversely related to patch size, and thus fire intensity as well (Malamud et al., 1998).

Various climatic trends, species types, and soil compositions vary throughout the world, which can lead to differing fire frequency in various forest types such as boreal, subalpine, or temperate forests. Higuera et al. (2014) compared wildfire frequency within the past 6000 years using pollen and macroscopic charcoal from lake-sediment records in a forest classified as subalpine in the Rocky Mountain National Park. Typical 500-year mean values for recurrences of wildfires fell between 150 and 250 years, with one 500-year mean recurrence exception centered around 3690 cal. year BP (before present, 1950) that was 77 years long, falling in line with a period of above average lake levels. The higher lake levels was suggested by Higuera et al. (2014) to be correlated to snow-dominated winters leading to drier summers. Despite the generally consistent 500-year mean recurrence, the range over the past 6000 years noticeably varied between 30-1035 years. Although climate variability occurred within the multidecadal and multi-centennial time-scales of the past 6000 years, fire frequency was found to contrast and stay relatively consistent. Alternatively, the increased evaporation and drought frequency in the summer months of the past 1500 years was found to align with an increase in crown-fire severity.

#### 1.1.2 SEVERITY

Fire severity is a qualitative way of expressing the disturbance imposed on an ecosystem by a wildfire (Neary et al., 2005). Wildfire has the capability to affect all components of an ecosystem, meaning the effects of wildfire are felt both above and below ground (Vierick and

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Schandelmeier, 1980). Fire severity consists of two components: intensity and duration. Fire intensity is the rate of energy release per area of wildfire and is expressed in units of kW/m<sup>2</sup> (Keeley, 2009). Higher intensity fires will result in a quicker spread of the fire from burning matter to unburnt matter. (Àgueda et al., 2008). The duration of burning plays a vital role on the effects within the soil layer since the rate that energy can transfer within the soil is limited by the soil's thermal properties (Frandsen and Ryan, 1986). Severity of wildfires is dependent on a number of environmental factors such as air temperature and humidity, fuel amount and moisture, topography, and wind speed. These criteria not only affect the severity of wildfires, but also the capability of fire suppression (Certini, 2005). Despite the large number of measurable traits associated with fire severity, fire intensity and fire severity remain relatively unassociated due to the variety of resource responses to the burning process (Ryan, 2002).

Fire severity is classified as low, moderate, or high. (Ryan, 2002). Low fire severity is typically associated with lower air temperature and fuel loadings, as well as higher fuel moisture, soil moisture, and relative humidity. High fire severity is typically associated with the inverse of low fire severity conditions (Neary et al., 2005). Ryan and Noste (1985) developed a two-dimensional matrix for fire severity based on depth of burn and fire behavior. Characteristics of low fire severity can reach up to a moderate depth of burn when residual duff is present for a creeping or spreading fire, but generally has a scorched depth of burn for spreading fires when the forest canopy remains, but can reach up to a moderate depth of burn for crowning fires when the there is residual duff left. Finally, high fire severity is always associated with a deep depth of burn, and can even be associated with a moderate depth of burn for crowning and spreading fires if duff is completely consumed. Plant tissue death typically begins at 40 -70 °C, seed death at 50-

120 °C, destructive distillation of organic matter (OM) at 200 - 315 °C, OM charring at 350-450 °C, volatilization of nitrogen at 300-500+ °C, and volatilization of phosphorus at 774+ °C (Hungerford et al., 1991). How intense a fire burns can have an influence on how much ash and nutrients from the burned flora are transported to waterbodies from runoff. Rhoades et al. (2011) found basins that were had >45% of the land burned at a high severity to have twice the instream nitrate concentrations compared to basins that burned at a lower severity after the Hayman Fire in Colorado (CO). The increased concentrations remained that way for up to 5 years after the fire event. The high presence of nitrate may be explained by Ball et al. (2010) who found a greater presence of nitrification and ammonia-oxidizing bacteria from the coal of wildfires that were up to 12 years old. Additionally, high severity fires have been associated with a higher likelihood of fish mortalities to occur, particularly with small streams that have a high fuel load (Rinne and Jacoby, 2005).

#### 1.1.3 LOCATION

Forests, ecosystems, and populations all over the world, especially in the western United States, Australia, and Mediterranean, are greatly affected by the impact of wildfires (FAO, 2012). The Rocky Mountains within the western United States are a distinct concern as they contain watersheds of high value that have been greatly impacted by wildfires in recent years. CO in particular has faced large scale fires such as the Hayman Fire in 2002 that burned 138,114 acres in Pike National Forest, the High Park fire in 2012 that burned 87,250 acres west of Fort Collins, the West Fork Fire Complex in 2013 that burned 110,405 acres, and the Black Forest fire in 2013, which destroyed 511 homes north of Colorado Springs and is the most destructive wildfire in state history (Schneider et al., 2012).

Just as geography and latitude influence the development of wildfires, so too do topography and vegetation. Gullies in particular are known to accumulate logs quicker than slopes do post-fire, which may result in more frequent and/or more severe wildfires (Bassett et al., 2015). If the growth of logs in gullies is extended over a longer period, it may lead to more severe wildfires compared to what slopes would experience. Alternatively, slopes will accumulate logs faster post-fire than gullies will.

#### 1.2 IMPACTS OF WILDFIRE

Wildfires have long been known as a necessary tool used to decrease the density of fuels that could lead to large-scale wildfires that are more difficult to control. However, the impact of wildfires on water quality is of great concern for the ecosystem and water utilities. The resulting effect of post-fire erosion in water basins often leads to increased loads of contaminants into water bodies, which leads to big concerns downstream (Meixner and Wohlgemuth, 2004; Stein et al., 2012).

#### 1.2.1 EROSION AND SEDIMENT TRANSPORT

Undisturbed soils in forested areas are known to have high infiltration rates that result in low runoff and low erosion rates (DeBano, 1981). When soils are disturbed by wildfires, the erosion potential is known to increase from the effect of heat on soil quality (DeBano, 1966). Erosion is affected by the intensity and duration of the fires, texture of soils, slope, and the vegetation present on the site (DeBano, 1990; USDA, 2006). High intensity fires are associated with a higher irreversible drying of OM in and on top of soils (Hooghoudt, 1950). The majority of the OM ends up being vaporized upward with the smoke, but a portion of it distills downward in the upper 5 cm of the soil to avoid the temperature gradient above (DeBano, 1966). As more OM is vaporized, the greater the hydrophobicity will be due to the non-polarity of the remaining OM (Michel et al., 2001). Dyrness (1976) found severely burned soils within the Willamette National Forest of Oregon to portray slight wettability 0-1 inches below the surface and significant non-wettability 2-9 inches below the surface. The formed wettability in the soils can impact the infiltration rates of soils for a few months to several years (Dyrness, 1976; MacDonald and Huffman, 2004). Alternatively, ash layers that collect on the surface of soils can lead to an increase in soil water retention due to the absorbance of water by the ash (Stoof et al., 2010).

Erosion potential is increased even further after a wildfire since the protective cover of the vegetation is no longer present to slow the velocity of raindrops. (DeBano, 1990). Areas with an increased slope often pose a greater threat to erosion as well, and the USDA (2006) suggests long-term erosion control for slopes with a 50% or larger gradient. Wischmeier and Smith (1960) developed the Universal Soil Loss Equation (USLE) to be applied to farmland erosion. The steepness value of the USLE was originally limited to an 18% (10.2°) maximum slope, but was later refined by Kitahara et al. (2000) to reach up to an approximate 30° inclination for mountainous forests. Slopes of 1 m<sup>2</sup> plots from the Colorado Front Range that were used for a rainfall experiment done by Benavides-Solorio and MacDonald (2002) ranged from 9° to 25°. Lower stability and uniformity within soils like loam, as opposed to sandy loam, decreases the hydraulic conductivity of the soil, which in turn decreases water infiltration and increases overland flow (Dong and Wang, 2013). All of these effects on the hydrophobicity of soils end up with a significant increase of sediment and solutes being transferred from the soils to runoff (Wallach et al., 2001). Excessive sedimentation from post-fire transport is of big concern to water utilities as well due to the cost and processing needs of the treatment, as well as the potential for damage or disruption to the treatment works (Meixner and Wohlgemuth, 2004).

DeBano and Krammes (1966) exposed a slightly water repellent naturally occurring soil to a range of temperatures for various times. The soil started with a 2 min. water drop penetration time (WDPT) and was not affected by a temperature of 150 °C for the maximum duration of 20 min. Soils exposed to temperatures of 260 and 315 °C for 10 min. increased WDPT > 40 and 60 min., respectively, and remained that way up to 20 min. Temperatures of 375 °C and above produced strong water repellency after 5 min., but decreased the WDPT after 15 min. of exposure.

The amount of ash left on the hillslopes plays a role in soil wettability as well. Cerdà and Doerr (2008) showed an 18-fold reduction of surface runoff in an ash only plot compared to a plot with bare terrain. The decrease in surface runoff was found to be attributed to a porosity of 83% in the ash layer. As the ash layer continued to be monitored, a heavy rainfall event (6") over 6 days was found to remove the ash layer almost completely. In addition to rain, wind has been found to play a role in the thinning of ash up to 15 days after a fire (Pereira, 2015). The first year after wildfires are contained is when the addition of nutrients and minerals from runoff has the biggest impact on surface water quality. Ash and particulates are often trans-located from soils to runoff within the first year, while nutrients and metals that are absorbed to the sediment often settle to the bottom of water bodies and can affect water quality for an extended period of time as they are leached off of the sediment (Stein et al., 2012).

#### 1.2.2 TOTAL ORGANIC CARBON

The burning of fuels in wildfires impacts the OM both above and below the soil surface. Smith (1970) has shown that the majority of OM is removed from a watershed through upward volatilization when a wildfire led to 79-91% of litter and humus being removed on a weight/area basis from a watershed in Ontario. Since such a large portion of the OM is volatilized, a portion of the OM may return to the surface as atmospheric deposited ash (Smith et al., 2011). Wildfire severity is a big component of the amount of OM volatilized, which in turn has a big impact on the amount of surface organic matter (SOM) post-fire. Post-fire SOM has been found to increase, decrease, or even remain relatively the same depending on many controlling factors such as wildfire severity, vegetation, regional climate, and topography (Santin et al., 2008). Varela et al. (2010) analyzed the top 5 cm of burned soil sites and found the amount of organic carbon to have little change for temperatures up to 220 °C, while a significant decrease was found for temperatures ranging from 380 - 460 °C.

When the OM of fuel is completely combusted, the ash that remains is white due to the presence of only inorganic matter; however, wildfires often leave more black ash and charred plant remains due to the length of time of burning (Boerner, 1982). A severe burn may lead to an ash layer up to 2-10 cm thick, which can equate to 2-10 kg/m<sup>2</sup> of ash (Doerr et al., 2008). Portions of the high organic carbon content from the ash often ends up being transported into rivers and water bodies from the anticipated runoff.

Particulate organic matter (POM) is often the form the majority of OM reaches the streams in (Smith et al., 2011). Once POM reaches the streams, it contributes to the total organic carbon (TOC) within the water. Gill (2004) studied impacts of the Rodeo-Chediski fire in Arizona on the quality of the Salt River and found TOC to increase from 5.42 mg/L-C pre-fire to 228 mg/L-C post-fire which exceeded maximum historical values. Organic matter can also take the form of dissolved organic carbon (DOC) in streams, which is a big concern to water treatment facilities. DOC is known to react with the disinfection process when oxidizers are used (often chlorination or chloramination) to form trihalomethanes (THMs), a disinfection by-product (DBP) that is often carcinogenic (Peterson et al., 1993). Writer et al. (2014) studied

impacts of the High Park Fire on the Poudre watershed in CO and found DOC concentrations to rise from 6.8 to 13.7 mg/L following thunderstorms that were spaced 9 days apart around the containment of the wildfire. Concentrations were found to drop to 3.5 mg/L three weeks after the fire was contained. However, DOC concentrations found in streams have remained elevated for up to 4 years after the Lost Creek fire in the Canadian Rocky Mountains (Emelko et al., 2011). Peterson et al. (1993) found the greatest THM yield to be approximately 11  $\mu$ g of THM per mg of DOC when chlorination was used. Since the current maximum contaminant limit (MCL) set by the EPA for THMs is 80  $\mu$ g/L (National Primary Drinking Water Regs, 2009) and the maximum DOC concentrations found in Writer et al. (2014) could potentially yield 150  $\mu$ g/L of THMs, water treatment plants should show concern about the amount of DOC in the source waters, as well as the disinfection process used.

### 1.2.3 NUTRIENTS

Nutrients, particularly nitrogen (N) and phosphorus (P), play a vital role in the lifecycle of aquatic ecosystems. However, the overabundance of nutrients within water bodies can lead to troubles within the ecosystem and lead to treatment concerns for water treatment plants downstream. When wildfires occur, the nutrients within OM become a great concern as it becomes transported to surface waters in post-fire runoff (Hauer and Spencer, 1998). Concentrations of nutrients within runoff are impacted by soil type, vegetation, fire severity, rainfall intensity and duration, and cumulative precipitation within the watershed. (Stein et al., 2012). Elevated concentrations of nutrients can last a few months to several years after the fire depending on fire severity, burn size, fuel type, or post-fire rainfall (Miller et al., 2013; Stein et al., 2012).

#### 1.2.3.1 PHOSPHORUS

Phosphorus (P) is a necessary element for life, and yet is known as being the limiting nutrient for aquatic life in many of the world's lakes (Khan and Mohammad, 2014; Schindler, 1977). The phosphorus cycle is fairly slow as it relies on the slow erosion off of rocks, as opposed to a gaseous cycle like many other compounds (Scharpley et al., 1994). Once inorganic P is eroded off of rock, plant life can take it up and convert it to organic P so that it can be consumed by fauna (Water: Monitoring & Assessment, 2012). Organic P is returned to the system through the wastes or decomposition of flora and fauna where bacteria will convert it back to inorganic P and the cycle will start all over again. Since the P cycle can often be sluggish, P is regularly found to be the limiting nutrient for microorganisms unlike other nutrients like nitrogen (Scharpley et al., 1994; Schindler, 1977). Goldman (1980) found the N:P chemical ratio of phytoplankton to be 100-150 at < 0.1 of the maximum growth rate ( $\mu_{max}$ ) and 10-20 at > 0.9  $\mu_{max}$ . Once P becomes high in concentration, eutrophication will become a substantial problem with the phytoplankton being much closer to reaching  $\mu_{max}$  (Khan and Ansari, 2005).

P is often adhered to soil particles, which gives it its low water solubility and makes erosion a big influence on its presence in water bodies (Khan and Mohammad, 2014). The adhesion of P to soil means that the slow desorption of phosphorus into water bodies can have a lasting effect on water quality, which in turn can make it difficult for the management of eutrophication (Stigliani et al., 1991). Once eutrophication begins, the water quality will inevitably restrict the use of water for fisheries, industry, recreation, power generation, and drinking (Khan and Ansari, 2005). Dissolved oxygen is taken up by the phytoplankton, which leads to a faster mortality rate for fish (Kahn and Ansari, 2005). As the algae die and decompose, the water quality will continue to be affected by 1) the odors that are released, 2) the dissolved oxygen that is used in the decomposition, and 3) the possible release of disease-causing bacteria. (Dodds, 2002; Kahn and Ansari, 2005). In order to prevent the spread of eutrophication, it has been recommended to have phosphorus limits of 50 ppb for streams entering lakes (Hinesly and Jones, 1990) and 25 ppb for lakes themselves (Addy and Green, 1996).

The analysis of P in waterways is often done in 2 ways: total phosphorus (TP) and total orthophoshate (Water: Monitoring & Assessment, 2012). Total phosphorus (TP) analysis measures all forms of P by converting all forms of organic and inorganic polyphosphates to orthophosphate (Hach, 2013). The conversion of polyphosphates to orthophosphate is enhanced even further with the use of high temperature and low pH (Sawyer et al., 2003). When all polyphosphate is converted to orthophosphate, the orthophosphate can then be measured colorimetrically by mixing the sample with molybdate and ascorbic acid to produce a blue color.

The easy transport of nutrients from burnt fauna often has a great influence on the concentrations in waterways. Son et al. (2015) reported TP loads to increase from a range of 4.3 to 1,517 kg/day pre-fire to a range of 1147 to 56,086 kg/day post-fire in the Cache la Poudre River after rainfall occurred after the High Park Fire in northern CO. The increase in loads led to a 390-fold increase in TP concentrations. Stein et al. (2012) found TP concentrations of post-fire runoff to increase 100-fold from pre-fire concentrations in southern California watersheds. Post-fire TP concentrations of runoff increased to approximately 15 mg/L. Concentrations of P often remain elevated for a greater period of time than nitrogen does, likely due to the higher temperatures needed for P to volatilize (Hungerford et al., 1991).

#### 1.2.3.2 NITROGEN

Nitrogen (N) is one of the most mobile compounds in the natural environment. Its mobility is one of the reasons why N has become a great concern for the environment since agriculture, industry, and utilities are increasing its presence in nature. (Sawyer et al., 2003). In waterways, N is present as dissolved dinitrogen  $(N_2)$ , ammonia, and the salts of nitrite  $(NO_2)$  and nitrate (NO<sub>3</sub><sup>-</sup>) (Khan and Mohammad, 2014). N starts off in the atmosphere as N<sub>2</sub> where it is taken into soil by nitrogen-fixing bacteria and converted to ammonia (Follett, 1995). Ammonia  $(NH_3)$  is subject to an equilibrium reaction with the ammonium  $(NH_4^+)$  that's present in the soil and the excess NH<sub>3</sub> of the reaction may be subject to a gaseous lost. The NH<sub>4</sub><sup>+</sup> in the soil is then nitrified by bacteria into the intermediate compound of NO<sub>2</sub>, which in turn is nitrified into NO<sub>3</sub>. Most of the NO<sub>3</sub><sup>-</sup> and some of the NH<sub>4</sub><sup>+</sup> are often taken in as desirable nutrients for plants, but most of the NH<sub>4</sub><sup>+</sup> is toxic to plant life and some of the NO<sub>3</sub><sup>-</sup> may be denitrified and released back into the atmosphere as N<sub>2</sub>. The consumption and decomposition of the plants and OM will then lead to  $NH_4^+$  entering back into the soil. Since  $NO_3^-$  is negatively charged, highly water soluble, and does not sorb well with the anionic sites in soil, it is easily mobile with runoff (Khan and Mohammad, 2014). Since ammonium has a positive charge it is much more sorbable into the soil layers and can be transported to water bodies once erosion occurs (Follett, 1995).

After N is transported to water bodies, concentrations of N generally lie around 15 to 20 mg/L for N<sub>2</sub> (Sawyer et al., 2003), < 0.1 mg/L for nitrite (Sawyer et al., 2003), and < 1 mg/L for nitrate (Water: Monitoring & Assessment, 2012). When N is in the form of N<sub>2</sub>, N is inert and does not affect the quality of the environment, nor can it be taken up by plant life (Follett, 1995). Ammonia on the other hand has been found to be chronically toxic to fish at 0.068 to 2.0 mg/L NH<sub>3</sub>-N (Eddy, 2005), so a range of 0.06 to 0.10 mg/L ammonia was set in CO as limits for cold

and warm waters, respectively, by the Colorado Department of Public Health and Environment (CDPHE) (Regulation No. 31, 2013). Since  $NO_3^-$  and  $NO_2^-$  have been found to cause blue baby syndrome in infants, the EPA has set MCLs of 10 mg/L-N and 1 mg/L-N for  $NO_3^-$  and  $NO_2^-$ , respectively (National Primary Drinking Water Regs, 2009).

Since N has a lower volatilization temperature (300-500+ °C) than P (774+ °C), it is still expected to affect water quality post-fire, but to a lesser extent than P (Hungerford et al., 1991). Son et al. (2015) analyzed the effect of the High Park Fire in CO and found total nitrogen (TN) loads to be modified from 1.0 to 1645 kg/day pre-fire to 416 to 1203 kg/day post-fire after the first rainfall event. The change in load led to a 6-fold increase of TN concentrations in the Cache la Poudre River, which was much smaller than the increase in TP concentrations (390-fold). Rhoades et al. (2011) studied the effects of the Hayman Fire on various streams within CO and found NH<sub>4</sub><sup>+</sup> concentrations to be non-detectable before the fire, but increase to a mean concentration of 0.21 mg/L-N for the first two months following the fire. Concentrations of NH<sub>4</sub><sup>+</sup> returned to normal after the first 2 months. Mean concentrations of  $NO_3^-$  were found to be 0.2 mg/L-N for both unburned and low-burned areas, while high burned areas had a mean concentration of 1.5 mg/L-N. The peak concentration was 2.3 mg/L-N and was reached after the snow melt 3 years after the fire. Stein et al. (2012) found similar results from many wildfires in Southern California. Mean concentrations of post-fire NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> was found to be 2.4 mg/L, which was 2-4 times larger than unburned concentrations.

#### 1.2.4 METALS

The presence of metals in water can lead to both aesthetic and health issues, and yet a certain amount of various compounds is beneficial for life. For example, soluble iron (Fe) can leave an orange color in the water in high concentrations, while high concentrations of soluble

manganese (Mn) will often leave a metallic taste, or stain laundry and fixtures (Crittenden, 2005; Macdonald and Stednick, 2003). Once Fe and Mn become oxidized to Fe(III) and Mn(IV), respectively, they can form colloidal precipitates, which can result in unacceptable aesthetics (Sawyer et al., 2003). This is even more likely when the pH is below 6 for Fe oxidation and below 9 for Mn oxidation. High concentrations of copper (Cu) may lead to poisoning, while gastrointestinal issues may arise at lower concentrations of 3-5 mg/L (Smith et al., 2011). Cu can also be used as a way to inhibit the growth of algae (Crittenden, 2005). In order to maintain the quality of water, secondary MCLs have been established by the EPA for Mn, Fe, and Cu at 0.05, 0.3, and 1.0 mg/L, respectively (National Primary Drinking Regs, 2009). The 3 metals mentioned can all be found within soils and rocks and often end up in the waterways through erosion and wind (Crittenden, 2005). Once in the waterways, the presence of the metals often leaves concentrations of Mn, Fe, and Cu within 0.01 to 1 mg/L , 0.05 to 0.2 mg/L, and 0.02 mg/L, respectively (Crittenden, 2005).

When wildfires breakdown the complex organics within OM, total and soluble metals are released and increased in mobility (Certini, 2005). Cu concentrations were found by Stein et al. (2012) to increase 112-fold from unburned to burned runoff in southern California watersheds. Since Mn, Fe, and Cu have high volatilization temperatures (2061, 2862, and 2562 °C, respectively), the compounds are more likely to be mineralized or deposited as opposed to being lost as a gaseous state. However, atmospheric deposition can still play a vital role in the transport of metals. Sabin et al. (2005) reported that the atmospheric deposition of Cu increased the runoff concentration 4-fold after the severe wildfire season of 2003 in Southern California.

#### 1.2.5 BULK WATER QUALITY PARAMETERS

pH is a valuable way of expressing the acidity or alkalinity of a solution. It is an important consideration in water resources for chemical coagulation, disinfection, water softening, biological processes, and corrosion control (Sawyer et al., 2003). Being aware of the pH of surface waters is useful in determining the solubility and biological availability of chemical constituents like nutrients and metals (pH - Water Properties, 2015). The effect that pH has on chemical constituents will lead to adjustments of concentrations, which in turn can increase the toxicity of a compound. Unpolluted rain has a natural pH of 5.6, but is often lower in many parts of the world due to acidic rain (Water Treatment Solutions, n.d.) The pH of most surface waters lies in a range of 5 to 8 units, while going below 6 to 5 or above 9 units often results in harmful ecological effects. When the pH falls below 5 the aquatic systems often develops a growth of unwanted plankton and many fish species will disappear, while a high pH (eg. >9) may increase the toxicity of other substances such as ammonia, or lead to the death of fish species (Water Treatment Solution, n.d.). pH is often increased after wildfires due to the release of inorganic ions from burnt residue (Certini, 2005). Son et al. (2015) found the average pH to increase from 7.9 to 8.5 units after the High Park Fire in CO. In regulating pH for human consumption, a secondary MCL of 6.5 to 8.5 has been recommended by the EPA (National Primary Drinking Water Regs, 2009).

Similarly, the inorganic ions released from the burnt residue may alter the electrical conductivity within waterways as well. Son et al. (2015) found the electrical conductivity to rise from 46.9  $\mu$ S/cm pre-fire to 123.94  $\mu$ S/cm after rainfall post-fire from the High Park Fire in CO. Electrical conductivity is in close relation to the total dissolved solids of a solution (TDS), while total suspended solids (TSS) is in close relation to turbidity (Sawyer et al., 2003). Suspended

particles are often found within surface waters, much of which are generally comprised of inorganic soil or organic materials found in nature. Turbidity from the Poudre River in Fort Collins, CO has been found to be 4,200 NTU following a storm 5 days after High Park Fire containment, but dropped to 31 NTU 3 weeks after containment (Writer et al., 2014). The increase in turbidity was likely due to mudslides that occurred upstream. High turbid waters can be a concern for drinking water utilities with the difficulties it can impose on aesthetics, the filterability, and the disinfection used in the treatment process (Sawyer et al., 2003).

Just as oxygen is needed for the functioning of terrestrial life, dissolved oxygen (DO) is vital for the survival of aquatic life. The solubility of oxygen within freshwaters can range from 7 mg/L at 35 °C to 14.6 mg/L at 0 °C under 1 atm (Sawyer et al., 2003). The lower solubility of oxygen at higher temperatures can be of concern in summer months since the rates of biological oxidation increase accordingly (Sawyer et al., 2003). Because of these reasons it is common to view 8 mg/L as the maximum available under critical conditions. The levels needed for fish to survive can vary with Trout needing 6 mg/L while bass and bluegill are fine at 5 mg/L (University of Wisconsin 2006). When constituents are added to streams, DO is often decreased because of the chemical reactions that occur. Earl and Blinn (2003) found DO to decrease from 6.3 to 5.7 mg/L after ash was input into a stream after a wildfire in New Mexico.

#### 1.3 WILDFIRE MITIGATION: RETARDANTS / SLURRY

One of the most current effective ways to prevent the spread of wildfires is the aerial application of wildfire retardants around the perimeter of the fire. As concern over wildfires continues to grow, so too does the use of wildfire retardant. An annual average of 31 million liters of retardant was used on US National Forest System lands between the years 2000-2010 (Tidwell, 2011b), while the annual average for US National Forest System lands had increased to

37.5 million liters between the years 2012-2014 (US Forest Service, 2014). Phos-Chek is one of the main distributors of wildfire retardant in the United States, and their iron colored retardant LC-95A-R accounts for the majority of retardant used. In 2006, a peak wildfire year, 51.5 million liters of Phos-Chek LC-95A-R was used, which was more than twice the amount of the other two Phos-Chek chemicals used that year. (Lecky, 2008). The composition of applied wildfire retardant is approximately 85% water, 10% fertilizer salts, and 5% additives (thickening agents, coloring agents, stabilizers and corrosion inhibitors). This composition helps prevent the spread of wildfires through 1) the wetting of fuel, 2) the depletion of oxygen to the fire, and 3) the slowing of fuel combustion through the use of inorganic salts (Tidwell, 2011). The fertilizer salts used in fire retardants are generally ammonia based and can consist of ammonium polyphosphate, diammonium phosphate, and/or ammonium sulfate (US Forest Service, 2016; Fire-Trol, 1999). When the salt is exposed to high temperatures, stable compounds are formed from the nitrogen that decrease the act of pyrolysis. Additionally, the act of combustion can be slowed even further when phosphorus is included in the salts. Phosphoric acid is released when phosphorus is exposed to high temperatures, leading to a charring of the fuel that forms a thick protective layer of carbon (Classes of Flame Retardants | Types of Flame Retardants, n.d.).

Buhl and Hamilton (2000) studied the effect retardants had on juvenile rainbow trout and found the lethal dose of retardant needed to kill 50% of the test subjects (LD50) after 24 hours to be 168 mg/L for Phos-Chek 259F, 942 mg/L for Fire-Trol LCA-F, and 1,141 mg/L for Fire-Trol LCM-R. Dietrich et al. (2012) found the 96 -hr LD50 of Phos-Chek 259F and LC-95A to be 140.5 and 339.8 mg/L, respectively, for salmon undergoing parr-smolt transformation. All of these concentrations are possible with an accidental spill of retardant directly into aquatic habitats. Calfee and Little (2003) found the toxicity of wildfire retardant to fathead minnows to

last over 21 days when used at normally applied concentrations. Additional research suggested that the toxicity of the retardant chemicals would be eliminated faster when applied to soils with increased organic carbon concentrations (Calfee and Little, 2002).

In order to protect aquatic ecosystems from retardant, the US Forest Service implemented a 90 m (300 ft) buffer between the retardant drop zone and surface waters (Tidwell, 2011). The 90 m (300 ft) buffer may only be circumvented if human life or public safety is at risk and the application of retardant is found to reduce the risk of public harm. Despite the regulations in place, retardant may still be dropped accidentally within a buffer zone. From 2008 to 2010 there were a total of 42 retardant drops within the buffer zone, 37 of which were accidental (Tidwell, 2011b). Of those 42 drops, 10 were only in the buffer zone, while 32 of them were directly in the water. In order to maintain the health of the ecosystem, retardant drops within avoidance zones must be reported to the Forest Service and the site will be assessed for impacts, monitored, and remediated if necessary. As long as wildfire retardant is applied appropriately, no significant impact is shown on the quality of surface waters from it. (Crouch et al., 2006).

#### 1.4 RUNOFF SIMULATION FOLLOWING WILDFIRES

Rainfall simulations on small plots are a convenient way of rapidly obtaining results, as well as controlling conditions of the rainfall and soil plots (Srinivasan et al., 2007). Dougherty et al. (2008) found small-scale, high-intensity, low-duration rainfall simulations (1.5 m<sup>2</sup>, 80 mm/h, 20 min) to be an effective tool for examining mobilization and treatment effects within a plot, while concentration and load data is more suitable for a large-scale, low-intensity plot.

Rainfall simulators are used as an effective way to analyze the characteristics and the effects of runoff by applying a consistent and uniform rainfall. There are two common designs of sprays used for rainfall simulators: 1) the spraying nozzle type that is designed to spray at a very

high intensity, but can use an oscillation boom with solenoids to give a lower overall intensity, and 2) the modular type with an array of hypodermic needles that are designed to produce larger rain drop sizes at near terminal velocity (Abudi, 2012; Miller, 1987). The modular type has a limited use for small plots, while pressurized nozzle sprayers are suitable for a variety of applications. Nozzle simulators have a wide variety of available intensities, are able to achieve terminal velocity faster by adjusting the pressures, and can use high discharge nozzles to achieve suitable drop sizes (Grierson and Oades, 1977). The most popular nozzle to use with the nozzle sprayers is the Veejet 80100. Intensities and raindrop size of natural rainfall can be closely simulated with a pressure of 41 kPa (6 psi) (Blanquies, 2003; Meyer and Harmon, 1979; Peterson et al., 2002). 75% of the kinetic energy of natural rainfall can be reached when the Veejet 80100 nozzles are hung 2.5 m above the soil plots (Meyer and McCune, 1958; Peterson et al., 2002).

Moody and Martin (2001) found the 30 min rainfall intensity for a 1, 10, and 100 year storm after a severe wildfire in the Spring Creek watershed in CO to be 22, 56, and 88 mm/hr, respectively, and in the Bear Gulch watershed of South Dakota he found intensities of 32, 70, and 106 mm/hr for the same storm frequencies, respectively.. Rainfall intensities used within small-scale (1-2 m<sup>2</sup>) rainfall simulations are usually done at high rates up to 105 mm/hr (Kleinman et al., 2004; Dougherty et al., 2008; Cornish et al., 2002) in order to represent storms between a 2-year and 10-year annual recurrence interval (ARI). Benavides-Solorio and MacDonald (2002) ran post-fire rainfall simulations on many soil plots of varying burn severities in the Colorado Front Range, and the simulations were executed using a maximum rainfall intensity of 94 mm/hr for a duration of 60 min.

Although high intensities are useful for a uniform distribution over the plot and for producing runoff quickly (Dougherty et al., 2008), the high amount of energy applied to the soil surface is often much higher than a natural system and can result in an unrealistic amount of sediment transport (Van Dijk, 2002). The increase in sediment transport may also be attributed to an increase in the soil infiltration rate associated with high intensities (Karssenberg, 2006; Stone et al., 2008).

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# 2. IMPACTS OF WILDFIRES AND RETARDANTS ON SURFACE WATER QUALITY

# 2.1 INTRODUCTION

Long-term wildfire retardant plays a vital role in the containment of wildfires. Increased temperatures and drought has led to a growth of uncharacteristically severe wildfires, which has made wildfire retardant an even greater necessity. Between the years of 2000 and 2010, an annual average of 31 million liters of retardant was dropped in the United States (Tidwell, 2011), while retardant use increased over 20% from 2012 to 2014 (US Forest Service, 2014). Retardant is typically applied aerially around the perimeter of the fire in order to create a long-term combustion barrier and is intended to be used specifically for terrestrial use. The composition of wildfire retardant, which is approximately 85% water, 10% fertilizer salts, and 5% additives (thickening agents, coloring agents, stabilizers and corrosion inhibitors) helps prevent the spread of wildfires through 1) the wetting of fuel, 2) the depletion of oxygen to the fire, and 3) the slowing of fuel combustion through the use of inorganic (fertilizer) salts (Tidwell, 2011). The fertilizer salts used in fire retardants are generally ammonia based and can consist of ammonium polyphosphate, diammonium phosphate (DAP), and/or ammonium sulfate, while iron oxide is a common coloring agent and guar gum or attapulgus clay are typical thickening agents (US Forest Service, 2016; "Fire-Trol LCG-F, Liquid Concentrate MSDS.", 1999). Additional substances are generally trade secrets.

Application to waterways is a big concern due to the potential of ammonia toxicity to fish (Buhl and Hamilton, 2000), which is a greater concern with high pH and high temperature (Eddy, 2005). In North America, Phos-Chek<sup>®</sup> is the standard retardant producer, while Fire-Trol<sup>®</sup> is typically applied in the EU. Buhl and Hamilton (2000) studied the effect retardants had

on juvenile rainbow trout and found the lethal dose of retardant needed to kill 50% of the test subjects (LD50) to be 168 mg/L after 24 hours for Phos-Chek<sup>®</sup> 259F, while Dietrich et al. (2012) found the 96-hr LD50 of Phos-Chek® 259F to be 140.5 mg/L and the LD50 of Phos-Chek® LC-95A to be 339.8 mg/L for salmon undergoing parr-smolt transformation. Increased levels of phosphorus pose a concern as well with the potential for eutrophication, which not only restricts the use of water for fisheries, industry, recreation, and drinking, but also poses a threat to fish by the depletion of dissolved oxygen (DO) (Khan and Ansari, 2005). If iron oxide is used as the coloring agent and the retardant is dropped over water, aesthetic issues can be a concern due to the orange color that can appear from high iron concentrations (Crittenden, 2005). Due to concern over the effect of retardant on water quality, a 90 m (300 ft) buffer has been imposed by Tidwell (2011) of the US Forest Service to protect aquatic life. Despite the restrictions imposed on retardant drops, it can still be dropped within the buffer zone either intentionally to protect life, property, or natural resources, or unintentionally via accidental drop. For example, from 2008 to 2010 there were a total of 42 retardant drops within the buffer zone, 37 of which were accidental (Tidwell, 2011). Of those 42 drops, 10 were dropped terrestrially, while 32 of them were dropped in the water.

Runoff from retardant dropped outside of the buffer zone is shown to have no significant impact on the quality of surface water, (Crouch et al., 2006), but little research has been done on the effects of runoff if retardant is dropped within the buffer zone. Unlike undisturbed soils in forested areas that are generally known to have high infiltration rates and low runoff (DeBano, 1981), soils disturbed by wildfires are much more prone to runoff and erosion due to the nonpolar organic matter (OM) that can distill downward in the upper 5 cm of the soil (DeBano, 1966). It is the purpose of this study to determine the effects that wildfire retardant can have on the levels of ammonia, total phosphorus (TP), iron, and total organic carbon (TOC) in the runoff collected from a rainfall simulation using soil collected from a prairie in Northern Colorado. More specifically, the differences between concentrations of both unburned and burned soil plots, with and without wildfire retardant are analyzed and compared to see the effect heat and ash can have on the transport of wildfire retardant.

# 2.2 METHODS AND MATERIALS

## 2.2.1 RAINFALL SIMULATION

#### 2.2.1.1 SOIL COLLECTION AND PREPARATION

Soil was collected from a tallgrass prairie in Pingree Park, CO on October 7 and 16, 2014 using soil plots made from stainless steel. The stainless steel was 1.6 mm thick and the dimensions used for the plot were 42.6 x 27.9 x 20.3 cm. A 20.3 cm depth was used to account for the non-wettability that can be applied to soils when subjected to high temperatures (Dyrness, 1976). The base of each plot was made as a separate piece of steel that fit tightly around the perimeter of the plot so that it could be removed when the plot was inserted into the soil for collection. A 30.5 cm long piece of 3.2 mm thick double-beveled steel was welded to the base of a slidehammer to knife along the perimeter of each plot during insertion.

Soil collection began by pounding empty plots slightly into the soil to make an indentation of the dimensions. The slidehammer was used to knife along the indentation in order to reach the needed depth of the plots (**Figure 2.1**). Once the needed depth was reached, the plot was inserted back into the indentation and force was applied to the top of it until the plot was level with the ground. A hole was dug in front of the plot and beveled steel was slidehammered underneath it so the plots could be removed from the ground. The steel base of each plot was placed back on so the plots could be covered and stored at room temperature until experimented

on. A total of 8 plots were collected to simulate the soil quality of unburned soil without retardant (Uwo), unburned soil with retardant (Uw), burned soil without retardant (Bwo), and burned soil with retardant (Bw).



Figure 2.1 Use of slidehammer to indent dimensions of the soil plot

Each plot had dried from sitting indoors, so 1 L of reverse osmosis (RO) water was spread out over the soil to achieve an approximate 10% moisture content 2 days prior to rainfall simulation. The soil gave the qualities of silt, so the volume of RO water needed to achieve the desired moisture content was based on the assumption of a 40% porosity (Yu et al., 2015). The tallgrass of each plot was trimmed to a height of approximately 2.5-5 cm. Trimmings were disposed of for unburned plots, while the burned plots had the trimmings placed on top prior to burning to allow for the influence of ash to be present. Phos-Chek<sup>®</sup> retardant LC-95A-R, consisting of ammonium polyphosphate (>85%), Iron Oxide (<5%), Attapulgus Clay, (<5%),

and Trade Secret Additives (<8%) (Phos-Chek<sup>®</sup> Fire Retardant Grade LC95A MSDS, 2014) was applied at a suggested application rate of 8.15 L/sq m (Recommended Retardant Coverage Levels, 2015), which came out to 96.9 mL for the 42.6 x 27.9 cm plots. Burned plots were put in a muffle furnace for an hour at 510 °C the day before the rainfall simulation so that the burning of flora and effects of heat from a severe wildfire could be simulated.

# 2.2.1.2 RAINFALL SIMULATION

Rainfall was simulated using a Norton Ladder Type Rainfall Simulator with Veejet 80100 spraying nozzles (**Figure 2.2**). Plots were placed under the rainfall simulator at a 20° angle to represent the steepness of the Colorado Front Range (Benavides-Solorio and MacDonald, 2002) and PVC pipe was placed under the end of the plot to catch and transport the runoff to a beaker (**Figure 2.3**). Fiberboard was taped along the perimeter of the plot using Gorilla Tape<sup>®</sup> as well as 2.5 cm above the front edge of the plot to prevent any rainfall from diluting the collected runoff (**Figure 2.3**). Water used for the simulation came from the Horsetooth Reservoir via direct line and rainfall was produced at an average pressure of 41 kPa (6 psi) so that drop size would be similar to that of natural rainfall (Blanquies, 2003). An average rainfall intensity of 165 mm/hr was used since it was the lowest possible to achieve with the available adjustments to the oscillation boom. Two plots were tested at a time for a total of 4 runs for the 8 plots.



Figure 2.2 Norton Ladder Type Rainfall Simulato



Figure 2.3 Setup of A) runoff collection and B) dilution prevention

The rainfall simulation was performed on 3 consecutive days (Runs 1, 2, and 3) and each plot was exposed to rainfall for 15 minutes per run. Runoff used for analysis was collected at 5 separate times per run from each plot using Nalgene<sup>®</sup> 125 mL HDPE bottles with no headspace remaining. The first 3 samples were collected consecutively and began as soon as the first runoff reached the end of the PVC pipe. The last 2 samples were collected at 10 and 15 minutes, respectively, to give a full representation of the entire run. Samples were immediately stored on ice after collection and analyzed the same day for orthophosphate, ammonia, and iron using Hach<sup>®</sup> methods 8048, 10031, and 8008, respectively, on a Hach<sup>®</sup> DR 2500 spectrophotometer. TOC was not able to be analyzed immediately due to problems with the Shimadzu<sup>®</sup> analyzer planned to be used, so samples were frozen and later analyzed for TOC using Hach<sup>®</sup> method 10129 on a Hach<sup>®</sup> DR 2500 spectrophotometer.

The same process used for the rainfall simulation and the analysis of samples was performed again approximately 2 months after the first set of runs. Only three samples of runoff were collected for each run of the second set. The first sample was collected as soon as runoff left the plots, while the collection of the last 2 samples remained at 10 and 15 minutes, respectively.

#### 2.2.2 SOIL LEACHATE ANALYSIS: ROYAL GORGE FIRE

## 2.2.2.1 SOIL COLLECTION AND PREPARATION

Soil samples were collected within the Royal Gorge wildfire site of Cañon City, CO on June 20, 2013 - 4 days after the fire was 100% contained. Soil was collected in triplicate from 5 separate sites: a high severity burned site with fire retardant applied (Bw), a high severity burned site without fire retardant applied (Bwo), an unburned site with fire retardant applied (Uw), an unburned site with a high application of fire retardant (UwH), and an unburned site without fire retardant (Uwo) to be used as a control (**Figure 2.4**). Samples were collected at an approximate depth of 2.5 cm using a trowel and 0.95 liter sized Ziploc<sup>®</sup> freezer bags were used to store the samples. Each sample was dried for a day at room temperature and then overnight in an oven at 105 °C to remove any moisture within the samples. A 0.991 mm sieve was used to remove large matter from the samples and triplicates were homogenized before being refrozen in new 0.95 liter Ziploc<sup>®</sup> freezer bags.



Figure 2.4 Sample sites of A) burned soil with retardant and B) unburned soil with retardant 2.2.2.2 LEACHATE TESTING

Soil samples were warmed to room temperature before analysis. Analysis was done by placing 100 g of each sample into a 1 L glass beaker and adding 1 L of reverse osmosis (RO) water (**Figure 2.5**). Each sample was done in duplicate along with 2 RO water blanks for a total of 12 samples. Beakers were stirred and placed in the dark for 6 hrs and then analyzed. Additional sets were used for analyses at 12 and 24 hrs. After each time frame, 100 mL was removed from the beakers via pipette and the leachate was temporarily placed in amber VOA

vials with Teflon lined caps. Samples from the VOA vials were measured for TP, Ammonia, Fe, and Mn as soon as possible via Hach<sup>®</sup> (Loveland, CO) methods 8190, 10031, 8008, and 8034, respectively, using a Hach<sup>®</sup> DR 2500 spectrophotometer. TOC was immediately analyzed using a Shimadzu<sup>®</sup> TOC-V CSH analyzer and turbidity was measured using Hach<sup>®</sup> Turbidimeter 2100N. Additional water quality parameters of pH, DO, and conductivity were measured using a Hach<sup>®</sup> SensION156 Portable Multiparameter Meter. Leachate analysis was repeated on 3 separate dates with samples frozen between each repetition. Analysis 2 and 3 were done approximately 2 and 6 months after Analysis 1, respectively.



Figure 2.5 Leachate from A) Bwo, B) Bw, C) Uwo, D) Uw, and E) UwH soils

## 2.3 RESULTS AND DISCUSSION

# 2.3.1 RAINFALL SIMULATION

## 2.3.1.1 TIMING OF RUNOFF COLLECTION

Burned soil had a noticeable impact on the start time of sample collection for the runoff. For example, collection times of Run 1.1 (for ease of understanding, Run numbers will be labeled with the Set number in the ones place and the Run number in the tenths place) for unburned samples started at or before 2.2 minutes, while 3 of the 4 burned samples started after 3.8 minutes. Although heat is known to increase the hydrophobicity of soil (Michel et al., 2001), the delayed collection time is likely due to the increased water retention from the ash (Stoof et al., 2010). The sample collection start time of all unburned samples started after 2.5 minutes for experiment 2, which was later than experiment 1. This is likely a result of the plots drying out before experiment 2 and having greater soil water retention than the unburned plots had before experiment 1. Burned plots showed start times that were less for experiment 2 than experiment 1, which may be attributed to the ash washing off of the plots. If the amount of ash on a plot is lessened, then the water retention of the ash would no longer be present and the hydrophobicity of the burned soil would likely play a bigger role. No consistent trend was observed between the sample collection start times between days.

# 2.3.1.2 GENERAL TREND

A decreasing pattern between concentrations could often be seen within runs and between runs, but the concentrations of some plots would occasionally differ in pattern compared to its duplicate. The variability in the results may be due to the differing vegetation patterns and geomorphology of the plots. Differing vegetation patterns may have obstructed and/or absorbed the runoff in differing ways, while the geomorphology of some plots may have led to pooling that could lead to differing effects on the patterns depending on where the pooling occurred. For example, it is hypothesized that a pooling located near the front of the plot could delay peak concentration due to the pooling becoming more concentrated from the runoff above it, while a pooling near the top of the plot would give a dip in the sample concentration due to the pooling building up in dilution.

# 2.3.1.3 TOC

TOC analysis was done for all runs of Set 1. Since samples had to be frozen before analysis, the samples were defrosted at room temperature for 6 hrs and then in the refrigerator overnight. Retardant application showed no consistent effect on TOC concentrations of unburned plots (**Table 2.1**). Uw Plot 2 TOC concentrations stayed significantly higher than both Uwo plots through Run 1, but did not remain that way for the remaining runs. Both Uwo plots began Run 1 at 42 mg/L, which is 0.8 times the initial concentration of Uw Plot 2. Uw Plot 1 began Run 1 at the same concentration as both Uwo plots. However, due to the initial misplacement of Uw Plot 1 and there being no significant difference between Uw Plot 1 and both Uwo plots, Uw Plot 1 was not included in TOC analysis. Overall, unburned plots showed a minimal decrease in TOC concentrations for Run 1, while concentrations decreased 1.1 to 3.8-fold by the end of Set 1. No significant difference was found between TOC concentrations of Bwo and Bw plots as well (**Table 2.1**). The average initial TOC concentration of burned plots was 382.5 mg/L with a standard deviation of 65.6, which is 9 times larger than the initial concentration of both Uwo plots. By the end of Set 1, Bw plots decreased an average 3.7-fold with a standard deviation of 0.0, while Bwo plots decreased 4.1-fold with a standard deviation of 1.6.

 Table 2.1 TOC concentrations of runoff from each run of Set 1

Run	1.1	1.2	1.3
Uwo	31-42 (37)	19-35 (26)	21-36 (27)
Uw		12-42 (30)	25-49 (35)
Bwo	314-346 (329)	140-335 (258)	82-183 (130)
Bw	297-419 (345)	112-327 (233)	83-123 (109)

Results shown as range (average)

# 2.3.1.4 AMMONIA

The biggest influence shown by the application of retardant can be seen in the ammonia concentrations of unburned plots (**Table 2.2**). Initial concentrations of ammonia for Uw plots were 27.7 mg/L for Plot 1, while Plot 2 was over range (OR) of the 50 mg/L-N detection limit. OR values persisted until sample 4 of the first run, but an initial reading of 4918.7 mg/L-N was found after the sample was diluted. This value may not be true however, since the dilution occurred after the sample reacted with the reagent. Regardless, such a difference between both

concentrations may be attributed to a misplacement of Plot 1 on Run 1 that had approximately half of it outside of the rainfall for about the first half of the run. This mishap would explain the lower concentrations of Uw Plot 1 when compared to Uw Plot 2, and its effect is noticeable in the concentrations of other analyses as well. Despite the initial misplacement, Uw ammonia concentrations generally decreased within runs, between runs, and between sets, and the difference in concentration between Plot 1 and Plot 2 was reduced fairly quickly. For example, Plot 1 decreased from the initial concentration 1.7-fold, 4.1-fold, and 5.7-fold by the end of Run 1, by the end of Set 1, and by the end of Set 2, respectively, while the diluted Plot 2 initial concentration decreased 215.7-fold, 607.3-fold, and 1003.8-fold for the same readings, showing a much quicker decrease. Uwo plots started Run 1 at 2.4 and 1.9 mg/L-NH<sub>3</sub> and reached concentrations to within the tenths place within the first run for both duplicates. In comparing Uwo to Uw plots, the effect of retardant on ammonia concentrations can be seen. When comparing the diluted samples from Uw Plot 2 to both Uwo plots, ammonia was on average 2319.2-fold, 47.5-fold, 13.5-fold, and 49-fold higher at the beginning of Run 1, at the end of Run 1, at the end of Set 1, and at the end of Set 2, respectively. Alternatively, when Uw Plot 1 is compared to both Uwo plots, ammonia concentrations were an average of 13.1-fold, 33.8-fold, 11.3-fold, and 49-fold higher for the same respective samples.

Table 2.2 Animonia concentrations of ranom nom cach ran						
Run	1.1	1.2	1.3	2.1	2.2	2.3
Uwo	0.4-2.15	0.3-0.6	0.0-0.6	0.5-1.0	0.4-0.8	0.0-0.2
	(0.88)	(0.37)	(0.26)	(0.80)	(0.67)	(0.07)
Uw		11.5-26.6	7.5-21.9	4.9-12.1	5.0-6.3	4.9-5.3
		(17.81)	(12.74)	(7.77)	(5.49)	(5.08)
Bwo	3.0-4.3	2.3-4.0	2.1-3.3	2.0-4.1	1.4-2.1	1.2-1.7
	(3.60)	(3.30)	(2.66)	(3.12)	(1.92)	(1.45)
Bw	3.8-4.5	3.2-4.2	1.6-2.9	1.9-2.5	1.2-1.9	1.1-1.3
	(4.01)	(3.68)	(2.09)	(2.27)	(1.75)	(1.13)

Table 2.2 Ammonia concentrations of runoff from each run

Ammonia concentrations between Bw and Bwo plots showed no credible difference (**Table 2.2**). Initial ammonia concentrations fell within 3.7 - 4.6 mg/L for all burned plots, showing no impact of retardant. This is likely due to the relatively low volatilization temperature of nitrogen (300-500+ °C), which volatilized the ammonia from the retardant when placed in the furnace. Ammonia concentrations generally fell between runs, but showed varied trends within runs. This may be attributed to the increased water retention of ash along with the varied amounts of ash per plot, which would have varied the ammonia/ammonium equilibrium per plot (Follett, 1995). Initial concentrations of burned plots decreased an average of 1.3-fold by the end of all 6 runs, while they decreased an average of 2.5-fold with a standard deviation of 0.72 by the end of both sets.

## 2.3.1.5 ORTHOPHOSPHATE

Retardant application showed a significant increase in orthophosphate (P<sub>i</sub>) concentrations for unburned plots (**Table 2.3**). The initial concentration for Uw Plot 2 started at a peak concentration of 22.30 mg/L for Run 1, while the misplaced Uw Plot 1 began Run 1 at 11.40 mg/L and reached a peak concentration of 23.40 mg/L at the 10 min mark. The use of wildfire retardant on unburned plots led to the peak concentrations of Run 1 for Uw plots being 7.7 times greater than the peak concentrations of Uwo plots with a standard deviation of 0.31. All Unburned plots showed a general trend of decreasing concentration within runs and within sets, but Uwo plots began decreasing at a more noticeable rate than Uw. For example, Uwo plots decreased on average 3.3-fold from the start of Run 1 to the end of Run 1, while Uw plots decreased 1.1-fold. Since different P sources can differ in concentrations of water-soluble P (WSP) (Shigaki et al., 2006), it may be that the phosphate within Phos-Chek<sup>®</sup> LC-95A is less soluble than P found in nature and is not transported as easily. What was unexpected was the sharp increase in concentrations between sets. Uw plots increased an average 3.2-fold with a standard deviation of 0.3 from the end of Set 1 to the peak concentration of Set 2, while Uwo plots increased an average 4-fold with a standard deviation of 0.8. Peak concentrations of Set 2 were not reached until Run 2 for 3 of the 4 unburned plots. The increase in concentration between sets was so significant for unburned plots that it led to the same 3 of 4 plots having higher concentrations at the end of Set 2 than the end of Set 1. This trend can be explained by the breakdown of polyphosphates (PolyP) to P<sub>i</sub> through hydrolysis in the soils. This process has been found to occur best in cool dry places and can hydrolyze up to 50% of the PolyP to P<sub>i</sub> within 2 weeks depending on soil type (Gowariker et al., 2009).

**Table 2.3** Orthophosphate concentrations of runoff from each run. Results displayed as range (average).

Run	1.1	1.2	1.3	2.1	2.2	2.3
Uwo	0.70-2.48	0.57-1.60	0.91-1.34	1.46-3.00	0.80-1.14	1.02-1.28
	(1.48)	(1.14)	(1.11)	(2.01)	(0.97)	(1.16)
L Isaz	14.50-22.85	12.98-17.83	12.75-18.13	25.86-41.10	21.89-46.84	22.93-36.24
UW	(18.85)	(15.85)	(15.12)	(33.45)	(32.04)	(29.60)
Dure	4.35-8.15	2.30-2.85	2.42-2.74	2.36-3.15	1.36-2.80	1.13-1.31
DWU	(5.91)	(2.58)	(2.59)	(2.79)	(2.15)	(1.22)
Bw	13.16-16.85	8.37-14.13	3.35-6.71	3.99-5.09	2.45-3.87	1.77-1.96
	(14.21)	(11.27)	(4.69)	(4.42)	(2.99)	(1.89)

Burned plots showed an increase in P<sub>i</sub> concentrations due to retardant application as well, but to a lesser degree as unburned plots. Bw plots had an average initial concentration of 15.94 mg/L with a standard deviation of 0.18, which was larger than the average initial concentration of Bwo plots 2.0-fold. Within Run 1, Bw plots decreased 1.2-fold with a standard deviation of 0.2, while Bwo plots decreased 1.8-fold with a standard deviation of 0.8. Run 1 showed an overall decrease in concentration, the change within runs showed varied trends for all burned plots. Concentrations of burned plots generally decreased within runs, but the end concentration of a run occasionally stayed consistent or even increased by the end of the run. This may be explained by the influence ash plays on the increase of  $P_i$  concentrations (Earl and Blinn, 2003), as well as the geomorphology of each plot. Despite the intermittent fluctuations in  $P_i$ concentrations, initial concentrations of burned plots decreased an average 3.8-fold with a standard deviation of 1.1 in Set 1 and an average 8-fold with a standard deviation of 2.3 by the end of Set 2. The change in concentrations between sets was negligent for burned plots, which may possibly be explained by the ash slowing the process of hydrolyzation in the soil. Overall, the presence of ash showed a trend of increasing  $P_i$  concentrations in plots without retardant, while decreasing the release of  $P_i$  in plots with retardant. For example, the average initial concentration of Bwo plots was greater than Uwo plots 2.7-fold with a standard deviation of 0.9, while the average concentration of Uw plots was greater than Bw plots 1.4-fold with a standard deviation of 0.04. While the ratio between Bwo and Uwo concentrations approaches 1 as the runs go on, the sharp increase in Uw concentrations led to the ratio between Uw and Bw plots increasing up to 20-fold.

## 2.3.1.6 IRON

Retardant application showed a general increase in Iron (Fe) concentration for unburned plots (**Table 2.4**). Peak concentrations of Uw plots in Run 1 gave an average concentration of 2.52 mg/L with a standard deviation of 0.01, which was 1.4 times greater than the average Uwo concentration. By the end of Run 1 Uwo plots decreased 6.6-fold with a standard deviation of 2.9, while the peak concentrations of Uw plots decreased 1.9-fold with a standard deviation of 0.0. The retardant application to burned plots showed a differing trend than unburned plots, with Bwo concentrations generally greater than Bw (**Table 2.4**). It was expected that the use of retardant would make Fe greater in Bw, but the unanticipated results can be explained by metal ions interacting with the available phosphate of the retardant to form phosphate salts that are

more insoluble and less able to be measured (Liodakis and Tsoukala, 2009). Bwo plots decreased 1.1-fold with a standard deviation of 0.4, while Bw plots decreased 1.5-fold with a standard deviation of 0.4. Concentrations of all burned plots were generally less than all unburned plots in Run 1, which may be explained by the ash inhibiting the release of Fe from the soil as shown by Gómez-Rey and González-Prieto (2014). A significant increase in concentrations was found for all plots between Run 1 and Run 2 of Set 1 and rust was observed on the plots on a later run, so the remaining data was considered invalid to use.

 Table 2.4 Iron concentrations of runoff from runs 1.1 and 1.2

Run	1.1	1.2
Lluvo	0.34-1.77	0.51-1.04
0w0	(0.98)	(0.67)
Lba	1.27-2.53	0.55-2.06
UW	(1.85)	(1.20)
<b>D</b> WO	0.24-0.86	0.48-2.72
BWU	(0.43)	(1.32)
Dur	0.16-0.29	0.23-0.90
DW	(0.23)	(0.48)

Results shown as range (average)

# 2.3.2 SOIL LEACHATE ANALYSIS – ROYAL GORGE FIRE

The 3 leachate analyses were performed approximately 2 months apart from each other and the results of all analyses were averaged together to give a broad range of possible concentrations. Only noticeable outliers were removed from the analysis. pH readings showed a generally consistent neutral pH for all soil types for all analyses, while DO readings showed a consistent decrease between collection times for all soil types. DO of each soil type started at approximately 6.5 mg/L for the 6 hr readings and decreased down to the high 4 to low 5 mg/L range for the 24 hr readings. Retardant showed a noticeable impact on the conductivity of both unburned and burned leachate and increased as time went on. Average conductivity increased from a range of 48 to 66.5  $\mu$ S/cm for Uw leachate to ranges of 223 to 318  $\mu$ S/cm and 434.5 to 587  $\mu$ S/cm for Uwo and UwH leachate, respectively.

# 2.3.2.1 TOC

Retardant showed no consistent effect on unburned samples, with unexplainable results for burned. TOC in Uw was greater than the respective Uwo samples 2.6-6.9-fold, but the unburned samples with a high application of retardant gave readings that were 2.8-3.2 times less than Uw (Uwo, 1.75-7.13 mg/L; Uw, 12.00-18.83 mg/L; UwH, 3.75-6.83 mg/L) (**Figure 2.6**). The inconsistency in TOC between retardant applications may only be due to site location, but additional research may be warranted. If the differences are due only to site location, then the results would fall in line with Hopmans et al. (2007) who found retardant to have no effect on unburned soil due to how low the amount of guar gum is in the solution. The overall increase in concentration from Uwo to Uw + UwH is likely all due to ash, as Badía et al. (2014) showed the carbon to decrease in the top 1 cm of soil from samples collected in NE Spain and analyzed 1 week post-fire.

Overall concentrations increased with contact time for all samples with the exception of one (Bwo), which fluctuated in concentration for each analysis. As expected, burned sites had the highest concentrations of TOC due to ash, with the highest range of concentrations found at site Bwo (57.1-67.7 mg/L). Bw showed lesser concentrations than Bwo, but that may be attributed to site location and/or differing amounts of flora. The increase in burned sites resulted in Bwo being 9.5-37.1 times greater than Uwo, with the difference in concentrations decreasing as contact time progressed. Gill (2004) found a similar increase between surface water samples pre- and post-fire from the Salt River in Arizona after the Rodeo-Chediski fire. She found

average TOC to increase 42-fold in Salt River post-fire, from 5.42 mg/L to 228 mg/L. Concentrations fluctuated between analyses for all unburned and burned samples.



Figure 2.6 Average results of TOC from all 3 leachate analyses

# 2.3.2.2 AMMONIA

Retardant increased ammonia concentrations in both unburned and burned samples, but the highest concentrations were found in unburned (Uw, 19-0-27.2 mg/L-N; UwH, 32.6-49.2 mg/L-N) (**Figure 2.7**). Uw + UwH gave results that were 63.3-368.8 times larger than Uwo, while Bw gave readings 1.1-1.2 times larger than the respective Bwo readings. Overall burned samples fell within a similar concentration of each other (2.2-3.1 mg/L). From a simulated rainfall event, Pappa et al. (2008) analyzed the water that leached through flower plots of various soil quality and they found ammonium to be highest in Uw as well (3-5 mg/L-N). Uwo concentrations (<0.5 mg/L-N for all) were found to be less than Uw by approximately 16-fold, which is much less than the results of this study. Their results are also from leachate that went through a whole soil layer as opposed to just the soil + ash from the surface like this study's. What was similar was the order of concentrations from lowest to highest (Uwo, Bwo, Bw, Uw). With how close the concentrations of Bwo and Bw can be, it's possible for Bw to have higher concentrations depending on the pH of the samples. Crouch et al. (2006) found median Bwo concentrations to be 11.5 times greater than Bw in various surface waters of North America (0.165 compared to 0.0145 mg/L-N, respectively). Overall, the concentrations still had no significant difference, however.



Figure 2.7 Average results of ammonia from all 3 leachate analyses

Overall, burned samples gave readings that were 10-20 times greater than Uwo, presumably from the ammonia found in ash (Rhoades et al., 2011). The noticeable amount of ammonia from ash is certain to have an effect on nearby water bodies due to the immediate impact of wildfires, as well as from post-fire runoff. Hauer and Spencer (1998) reported on the immediate and long term effects of the Red Bench Fire of Sept. 1988 in Glacier National Park, Montana and found the ammonia of nearby streams to increase over 26-fold from pre-fire measurements. Ammonia was found in excess of 260  $\mu$ g/L-N, a much smaller peak concentration than this study, but their samples were also diluted from the stream.

Concentrations increased between runs for each sample of Analysis 1, as was expected with contained leaching, but the trend between runs of the other analyses varied for each analyte. Just as the first analysis was the only experiment to show consistent patterns, so too was the first run, with peak concentrations found in Analysis 2 for all analytes. The freezing of the soil samples between analyses may explain why ammonia increased between the first two analyses, since the solubility of ammonia increases with colder temperatures (Budavari, 1996). The decrease between the last two analyses on the other hand may be attributed to the rise of the nitrification process.

# 2.3.2.3 TOTAL PHOSPHORUS

Retardant use showed a noticeable increase in total phosphorus (TP) for unburned samples, but generally decreased the concentrations of burned samples. Overall, TP increased between runs for both Uw (33.48-52.01 mg/L) and UwH (62.34-89.68 mg/L), which were larger than the respective Uwo readings 5.3-8.5 and 9.8-14.7-fold, respectively (**Figure 2.8**). Uw and UwH samples both showed an increase between runs for all analyses. Uwo samples on the other hand did show an increase between each run for Analysis 1, but showed varying trends for the last two analyses. When analyses are compared, Uw and UwH samples again showed similar trends to each other, with both showing peak concentrations during Analysis 2 for each run and minimum concentrations in Analysis 1. Peak concentrations of each run were generally found in Analysis 2 for Uwo as well, but minimum concentrations were all found in Analysis 3. Hopmans et al. (2007) analyzed unburned soils that were applied with Phos-Chek<sup>®</sup> D75-R wildfire retardant in the heathland of Australia. Phos-Chek<sup>®</sup> D75-R is mainly composed of diammonium sulfate (>65%), but also contains mono- and di'ammonium phosphate (>15 and >5%, respectively) ("PHOS-CHEK<sup>®</sup> FIRE RETARDANT GRADES D-75F AND D-75R, MSDS",

2010). They found P to increase gradually from 1 mg/kg to 9.4 mg/kg in the surface soil over 12 months at one of the sites, but at ano'ther site found similar trends as this study: P increasing sharply within the first 2 months, but rapidly decreasing afterward. They found that a large amount of P leached into the subsoil, which may lead to long term impacts on plant growth and nutrient uptake.



Figure 2.8 Average results of TP from all 3 leachate analyses

Bw readings of TP showed smaller concentrations than Bwo. The decrease in concentration from Bwo to Bw was fairly minimal (1.2-1.6 times less), while concentrations of each ranged from 7.83-10.96 and 5.48-7.07 mg/L, respectively. Crouch et al. (2006) also found phosphorus to be greater in the surface water of Bwo North American watersheds than Bw watersheds. They found Bwo to be 4.5 times greater than Bw watersheds (0.605 compared to 0.135 mg/L, respectively), but showed no significant difference with all the samples analyzed. TP being greater in Bwo samples is likely the result of many ions being released from the water soluble carbonate compounds in ash (i.e., Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>) (Liodakis and Tsoukala, 2009). When retardant is applied to the soil, the free ions are able to interact with the retardant to form

phosphate salts that are much more insoluble than their carbonate counterparts (i.e., Na<sub>2</sub>PO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>).

With the exception of Bw Run 3, all burned readings were higher than Uwo, with Bwo being 1.2-1.7 times greater than the respective Uwo concentrations. Hauer and Spencer (1998) found soluble reactive phosphorus (SRP) to increase due to fire as well, with a 45-fold increase of SRP found in streams immediately after the fire. Concentrations returned to normal within a few weeks, however. Peak concentrations were found in Run 1 for all analyses of burned samples with the exception of Bw Analysis 1. When analyses are compared, peak concentrations are found in Analysis 3 for all Bwo runs, while peak concentrations varied between Analysis 1 and Analysis 2 for Bw samples. The general decrease of Bw over time may represent it reacting with the free ions and becoming less soluble.

# 2.3.2.4 IRON

Iron concentrations increased noticeably from the retardant used in unburned soil, but like TP, showed a decrease from Bwo to Bw. Uw and UwH gave the highest concentrations of iron (0.70-0.73 and 0.85-0.95 mg/L, respectively), which were 2.6-3.3 and 3.4-3.9 times greater than Uwo, respectively (**Figure 2.9**). No consistent pattern was found between runs for each analysis of unburned samples. Iron readings of Uw and UwH samples, however, did show a general increase between each analysis with the exception of two Uw runs that generally stayed the same between two analyses. Uwo, however, showed varied trends between each analysis.



Figure 2.9 Average results of Fe from all 3 leachate analyses

The decrease in Fe between Bwo and Bw can also be attributed to the insoluble phosphate salts formed from the reaction of the iron ions with phosphate. Iron was found to be slightly higher in Run 2 for Bw, but also had a great significant difference in each analysis of Run 2. Over time, iron generally decreased in concentration between runs for each analysis of Bwo, while Bw generally peaked in Run 2 for each analysis. Like TP, peak concentrations were found in Analysis 2 for Bw, but were more varied for Bwo. García-Marco and González-Prieto (2008) compared soils in NW Spain and they found Bw to have the lowest readings of Fe as well. Readings of all burned soil remained low for 90 days, but returned to normal concentrations within 1 year. Liodakis and Tsoukala (2009) also found iron from the ash of various flora to decrease 1.5-2.0-fold when diammonium phosphate (DAP) retardant was applied before burning.

# 2.3.2.5 MANGANESE

Retardant use showed no consistent influence on manganese in unburned samples, but Bw was found to be less than Bwo in nearly all runs of each analysis (**Figure 2.10**). The lesser concentration in Bw may also be attributed to the formation of less soluble phosphate salts when Mn reacts with the available phosphate from the retardant. Nearly all runs of burned samples had higher Mn than the respective readings of Uwo. García-Marco & González-Prieto (2008) found Bwo and Bw soil to have higher Mn than Uwo 1 year after a prescribed fire, with peak content found 1 day after (Bwo>Uwo 11-fold; Bw>Uwo 16-fold). Their Bw samples being greater than Bwo may be related to their higher pH. Costa et al. (2014) studied the water quality from the Marão River watershed in Portugal after a wildfire in 2006 and found Mn to stay elevated 1 year after the fire, with concentrations 5 months post-fire being 6 times greater than pre-fire (Pre-fire:  $1.4 \mu g/L$ ; 5 months post-fire: 8.6  $\mu g/L$ ).



Figure 2.10 Average results of Mn from all 3 leachate analyses

No consistent trend was found between runs and analyses for Mn concentrations in unburned samples. Each analysis of Uw in Run 1 gave readings that were less than or equal to Uwo, while UwH gave readings that varied in comparison to Uwo. Each unburned sample decreased in concentration over time. Uw and UwH still had readings at Run 3 of Analysis 3, but nearly all Uwo analyses of Runs 2 and 3 showed no levels of Mn. Burned samples varied showed no consistent pattern between runs and analyses. All samples showed a sharp decrease after Run 1 of Analysis 1.

## 2.4 CONCLUSIONS

The rainfall simulation showed retardant to have a noticeable increase in concentrations of ammonia, P<sub>i</sub>, and Fe from unburned plots, as well as the P<sub>i</sub> from burned plots. No noticeable difference was found between ammonia in Bwo and Bw plots due to the high volatilization of ammonia. Fe was found to be higher in Bwo than Bw due to the metal reacting with the phosphate from the retardant to form more insoluble phosphate salts. Retardant use showed no impact on TOC concentrations in unburned or burned plots. P<sub>i</sub> increased dramatically between sets for all unburned plots sine the PolyP of the soils had time to hydrolyze to P<sub>i</sub>. The greatest influence retardant had on a concentration. The burning of plots led to the concentrations of TOC to be higher than all unburned plots, Fe to be lower than all unburned pots, and nutrients to fall between Uwo and Uw.

Leachate from Uw soils showed ammonia, TP, and Fe concentrations to have a noticeable increase compared to Uwo soils, while Bw only showed a small increase in ammonia when compared to Bwo. Bw was generally less than Bwo in TP, Fe, and Mn concentration because of the metals reacting with the phosphate from the retardant to form less soluble salts. No conclusive trends were found for Mn between Uwo and Uw sites. TOC was noticeably higher in burned sites, while no patterns were found from retardant use. Nutrients of burned sites were found to fall between Uwo and Uw + UwH, while metal concentrations of burned soils were found to show similar concentrations to all of the unburned soils.

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# 3. THE EFFECTS OF THE HIGH PARK FIRE ON CACHE LA POUDRE WATER QUALITY<sup>i</sup>

#### 3.1 INTRODUCTION

Wildfires are an important part of the natural lifecycle of a forest ecosystem. However, wildfires also pose threats to human safety, property and potable water sources. Many cities throughout the world obtain water for potable uses from forested areas. When forest fire occurs in a watershed, the water may be polluted with contaminants or off-flavor (smoky) compounds.

Colorado, with its mountainous and heavily forested terrain, has seen many large wildfires. In 2002, the Hayman fire grew to over 137,000 burned acres and impacted water supplies of the cities of Denver and Colorado Springs (Graham Technical Editor, 2003). Many other fires occurred in the summer of 2002 due to the severe drought conditions including the Missionary Ridge fire that burned 71,739 acres, the Bircher fire near Mesa Verde National Park, which burned 23,607 acres, and the Trinidad Complex fire that burned approximately 33,000 acres. The summer of 2012 had similar conditions as existed in 2002 including severe drought conditions and several large, intense fires that caused a state of emergency to be declared by State Forest, fire, and government officials (Longmont-Times-Call, 2012). The Waldo Canyon fire near Colorado Springs became the most destructive fire destroying 346 homes (Makings, 2012). The High Park fire near Fort Collins was a large, intense fire and is the focus of this study.

The High Park Fire ignited on June 9<sup>th</sup>, 2012, from a lightning strike and was contained on June 30<sup>th</sup>. **Figure 3.1** shows the burn area. In the summer of 2012, most of Colorado was

<sup>&</sup>lt;sup>i</sup> Chapter 3. authored by Clare L. Steninger and revised by Brent D. Morgensen.

under severe or worse drought conditions due to lack of precipitation in the preceding winter and warm temperatures occurring early in the spring (WWA and NIDIS, 2012). Due to the dry fuel and drought conditions, the fire grew to be 87,284 acres and is the second largest and second most destructive fire to occur in Colorado destroying 259 homes (*High Park Fire Burned Area Emergency Response Report*, 2012). Different areas burned with different severities, but 40.4% of the area had moderate severity and 6.5% with high severity (*High Park Fire Burned Area Emergency Response Report*, 2012). **Figure 3.2** shows the burn severity within the watershed.

The High Park Fire was located predominately in the Cache la Poudre watershed, which is a source for drinking water utilities in Fort Collins and Greeley, CO. Along with the Hewlett fire northeast of the High Park fire (May 14-22, 2012), 25% of the Poudre watershed was affected (Oropeza and Dustin, 2012). The other primary water source for Fort Collins utilities is Horsetooth Reservoir, which is a part of the Colorado-Big Thompson Project. Only 4% of the watershed draining into Horsetooth Reservoir was affected by the High Park fire (Oropeza and Dustin, 2012).

Wildfires induce changes within watersheds that affect soil composition, hydrology, and water quality. A higher severity fire destroys more vegetation than lower severity fires and can also change the composition of the soil by creating a hydrophobic layer (DeBano, 2000). This layer decreases infiltration capacity, so instead, precipitation is converted to runoff causing a higher sediment transport than in unburned areas (Gottfried et al., 2003; Gallaher and Koch, 2004; Neary, 2004; Kolka, 2012). The lack of vegetation post-fire destabilizes the hillside so erosion potential increases leading to runoff and turbidity (Morris and Moses, 1987; Wondzell and King, 2003). Increased turbidity poses difficulties for water treatment process, for example, the clogging of filters.



Figure 3.1 High Park Fire Burn Area map. Courtesy of US Forest Service.



**Figure 3.2** Burn Severity map of High Park Fire (High Park Fire Burned Area Emergency Response Report, 2012).

#### 3.1.1 TOTAL ORGANIC CARBON

Total organic carbon (TOC) in rivers within fire affected watersheds increases due mobilization of organics from the soil and ash. Gill (2004) found an increase in average total organic carbon (TOC) concentrations from 5.42 mg/L-C pre-fire to 228 mg/L-C after the fire in the Salt River one year after the Rodeo-Chediski fire in Arizona. Although the most prevalent form of organic C depositing into streams is the particulate form, increases in dissolved organic carbon (DOC) after fires also occur. DOC in the streams after the Mortar Creek fire correlated with storm events although the concentrations did not exceed 4 mg/L-C in the first year after the fire (Minshall et al., 2001). After the Lost Creek fire in the Canadian Rocky Mountains in 2003, the median DOC concentration in the discharge from the watersheds affected by wildfire for the first two years post-fire was 3 mg/L whereas the reference stream had only 1-2 mg/L DOC (Emelko et al., 2011). The increase in TOC or DOC could cause issues for drinking water utilities because of increased potential for taste and odor issues and the formation of disinfection-by-products.

### 3.1.2 NUTRIENTS: NITROGEN AND PHOSPHORUS

Fires also change nutrient concentration, specifically nitrogen and phosphorus, in receiving water bodies. After the Lost Creek fire, Emelko et al. (2011) found that the dissolved organic nitrogen (DON) increased from a mean of 120 to 205.3  $\mu$ g/L-N and total phosphorus increased from a mean of 5.7 to 42.2  $\mu$ g/L-P in the four years after the fire occurred. The Cerro Grande fire near Los Alamos, New Mexico, also showed increases in nutrient levels within months of the fire (Gallaher and Koch, 2004). The phosphate concentration was historically at a maximum at 1.74 mg/L-P but peaked to 14.5 mg/L-P two months after the fire. In another study that focused on fires in southern California, a region with a history of frequent fires, Stein et al.

(2012) discovered an increase in mean concentrations of nitrate+nitrite from 0.5 mg/L-N preburn to 2.45 mg/L-N post-fire as well as a 921 fold increase in total phosphorus (from 0.15 mg/L-P to 15 mg/L-P). In the first spring runoff after the Red Bench fire in Montana in 1988, the soluble reactive phosphorus (SRP) peaked at 69.2  $\mu$ g/L-P compared to <10  $\mu$ g/L-P in control streams, while ammonium peaked at 220 µg/L-N, 2 orders of magnitude higher than control streams. Nitrate peaked at 427  $\mu$ g/L-N compared to <75  $\mu$ g/L-N in the first post-fire spring runoff (Hauer and Spencer, 1998). Leaching of nutrients from riverbed sediments unaffected by fire from the Haihe River in China was studied by (Wu et al., 2012). The ammonia-nitrogen reached a maximum of 1.4 mg/L after 3 days for 5 cm dredging depth and a maximum of about 2.5 mg/L after 12 days for undredged samples. Total phosphorus and total dissolved phosphorus (TDP) were low for the first 3 days of the test and then linearly increased until day 20 (approximately 0.30 mg/L-P). The results also indicate that the release of nutrients and organic matter is significantly higher from riverbed sediment than from bank sediment. Lim et al. (2011) reported similar results for an artificial lake in South Korea unaffected by fire. The phosphate concentrations increased from 0.014 to 0.276 mg/L-P over a period of 20 days and ammonianitrogen on day 11 with a concentration of approximately 5 mg/L-N. Presence of nitrogen and phosphorus in surface waters promote algal blooms that result in release of algal metabolites, and lower dissolved oxygen levels when algae die and decompose (Dodds, 2002). Algal metabolites including impart off-flavors to the surface and drinking waters (Omur-Ozbek and Dietrich, 2005; Ho et al., 2009; Zuo et al., 2009), so are a concern to potable water utilities.

## 3.1.3 METALS

After fires, total and soluble manganese is increased in soils due to the breakdown of complex organics containing manganese that are present in ash (Smith et al., 2011). Iron, zinc,

and copper follow the same trend as manganese (Certini, 2005). The increase in these soluble metals in soils support an increase in streams once precipitation occurs. In Lithuania after drought and fires, copper concentrations increased from a background range 0.6-11.7  $\mu$ g/L-Cu to 0.6-26.1  $\mu$ g/L-Cu (Sakalauskiene and Ignatavicius, 2003). Stein et al. (2012) reported a 3 fold increase in the event mean concentrations of copper, lead, nickel and zinc in rivers after southern California fires. After the Cerro Grande fire, the copper concentration ranged from 4-290  $\mu$ g/L-Cu, which is higher than concentrations prior to the fire (Gallaher and Koch, 2004). Metals, especially iron and manganese, can become soluble and cause aesthetic issues in drinking water including discoloration or metallic taste (MacDonald and Stednick, 2003). Anticipating increases in metals in water after fires permit drinking water utilities to plan for treatment changes.

# 3.2 MATERIALS AND METHODS

## 3.2.1 SEDIMENT LEACHING

#### 3.2.1.1 SAMPLE COLLECTION

Sediment samples were collected from five locations within the Cache la Poudre watershed within the fire burn area: Century Park, Stevens Gulch, Young Gulch, Mile Marker 115, and Fort Collins Intake, as shown in **Figure 3.3**.


Figure 3.3 Map of Poudre River with Sediment Sampling Locations

At each location, samples were collected in triplicates from the riverbed (bottom), the riverbank (middle), and just above bankfull (upper). **Figure 3.4** shows examples of the riverbed locations. A total of 45 sediment samples were collected from the five sites. Each sample was collected using a shovel and placed in a gallon-sized plastic bag with seal. Samples were dried first at room temperature and then in a muffle furnace at 105 °C. The 105 °C evaporated the water to give dry weight of the soil, but may have also volatilized some compounds, such as ammonia. The samples were then sifted through a 0.991 mm sieve, which represents fine silt and clays in the American Society for Testing Methods (ASTM) classification (Gee and Or, 2002). The 0.991 mm sieve excluded sands, gravels and cobbles >0.991 mm in diameter. The sifted sediment was placed in another gallon-sized plastic bag with seal and placed in the freezer until analysis.



Figure 3.4 Riverbed Sediment Sample Locations

Sediment samples were collected at approximately the same locations from each of the same sites along the Cache la Poudre River approximately 1 year following the first collection of samples in order to observe any lingering effects from the High Park Fire. Samples were also collected from an additional site preceding the burn area, Poudre before Rustic (PBR), to be used as a control sample. The second collection of sediment was done in the same manner as the first collection, resulting in a total of 54 samples. Samples were preserved for the second analysis in the same manner as done for the first one (dried at room temperature, heated at 105 °C, sifted through a 0.991 mm sieve, homogenized, and frozen in sealed bags until used for analysis).

## 3.2.1.2 BENCHSCALE LEACHING TESTING PROCEDURES

For leaching test preparations, the samples from one site location, the riverbed sediment (bottom) were mixed, the middle sediments were mixed, and the upper sediments were mixed until homogenous. For each layer of sediment (bottom, middle and upper) 100 g of sediment was placed in a Pyrex glass beaker and received 1 L of Poudre River water,(Fisher Scientific, Pittsburgh, PA) and mixed, in duplicate. This grouping of 6 beakers was designated the "6 hour" leaching samples. Two additional groups of 6 beakers (2 Bottom, 2 Middle, and 2 Upper) were

made in the same manner as described above and designated "12 hour" leach and "24 hour" leach groups. Additionally, 2 1 L glass beakers were each filled with 1 L Poudre River water and served as controls. The same procedure was used for the 2<sup>nd</sup> collection of samples, but samples were analyzed only after 6 hrs and 24 hrs. **Figure 3.5** shows the setup of the leaching beakers. The samples were then kept in dark at room temperature.



Figure 3.5 Sediment Leaching Beaker Setup

After 6 hours, 100 mL of the leachate from the "6 hour" beakers were removed, passed through a Whatman 25mm-diameter glass microfiber filter (1.6 μm retention GF/A, Maidstone, UK), and placed in 40 mL amber volatile organic analysis (VOA) vials with Teflon lined caps (Fisher Scientific, Pittsburgh, PA) and kept in the refrigerator at 4 °C until they were analyzed. Metals (iron, copper and manganese) were tested immediately after extraction. Also after 6 hours, 100 mL of each control sample was removed and analyzed. The 1.6μm filter excluded molecules with diameters larger than 1.6μm, which limits the number of larger particles, greater than sand/silt size, from influencing results. The leachate and controls were analyzed for Total Organic Carbon (TOC), Total Nitrogen (TN), Total Phosphorus (TP), iron (Fe), copper (Cu), and manganese (Mn), according to Hach Methods (Hach DR 4000, Loveland, CO) 10129, 10071, 8190, 8008, 8506, and 8034, respectively. Water quality parameters including pH (Hach model

51940), Dissolved Oxygen (DO) (Hach DO probe model 51970), temperature, and conductivity (Hach model 51975) were measured using a Hach SensION156 Portable Multiparameter Meter (Loveland, CO). Turbidity was measured using Hach Turbidimeter 2100N (Loveland, CO). After 12 hours of leaching, leachate from the "12 hour" beakers were removed and the same analyses were conducted. The same procedure was repeated after 24 hours. Analyses of samples collected 1 year after the first collection (Analysis 2) were done in the same manner as the first analysis (Analysis 1) excluding temperature and DO. Analysis 2 was done after 6 hours and 24 hours of leaching, but 12 hour analysis was not included.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 SEDIMENT LEACHING

Statistical analyses were performed using a 1-way analysis of variation (ANOVA) with  $\alpha$ =0.05. Results for organics and nutrients (TOC, TN, and TP) from both analyses are provided in **Table 3.1**. In comparing the controls concentrations for each parameter, significant differences were not observed except for TOC and TP. The control concentrations at Stevens Gulch for TOC and TP were much lower than controls at other sites, so removing these outliers, there was not a significant difference observed. In comparing the leaching contact times (6, 12, 24 hours) for each riverbed location and site, there is a significant difference in TOC concentrations (p<0.05) for 8 of the 15 locations. The highest concentrations occurred after the 24-hour leaching time, which indicates TOC release increased with time. For each site, comparisons of riverbed location concentrations were significant for 3 of the 5 sites (p<0.027). The middle riverbed locations had the highest TOC concentrations (averages: Century Park = 41.23 mg/L, Young Gulch = 20.6 mg/L, FCWTF Intake=42.07 mg/L). In comparing the TOC concentrations from riverbed locations at each site, there was a significant impact of sites on

TOC concentrations (p<5x10<sup>-6</sup>). The FCWTF Intake had the highest concentrations for all riverbed locations (averages: Bottom=36.33 mg/L, Middle=42.07 mg/L, Upper=40.85 mg/L), indicating the accumulation of sediments downstream may affect water quality more. The concentrations were much less than the average post-fire concentration found in the Salt River in Arizona (228 mg/L-C) collected within 2 years after the Rodeo-Chediski fire (Gill, 2004). The increase determined with this study was not as significant because the controls obtained from the Poudre River water were already impacted by the fire. Whereas an increase of 4107% was observed for the Salt River when the before and after fire TOC levels were compared. In contrast, the TOC levels in the leachate (average maximum ranged 19.16 to 44.15 mg/L) from this study contained higher concentrations than the dissolved organic carbon concentrations (<4 mg/L-C) reported after the Mortar Creek fire (Minshall et al. 2001). This may indicate that even though the samples for this study were filtered with a 1.6 µm glass fiber filter, the particulate organic carbon may contribute a significant amount.

TOC concentrations decreased significantly between analysis (p<0.014) with the exception of 2 locations: Stevens Gulch, middle (p=0.057) and Mile Marker 115, upper (p=0.426). The similarity in concentrations between analyses at Stevens Gulch is shown by its noticeably smaller readings in Analysis 1 compared to all other sites. The upper location at Mile Marker 115 not only had the least change in TOC concentrations between analyses, but also showed an increase in concentration for the 6 hour reading. This may be because of an additional source that contributed to TOC at that location, which would also explain why it is the highest average reading in both analyses. Another possible factor could be that the upper location had measures to reduce the impact of runoff and erosion, such as a vegetable or ground cover. The presence of TOC can also reduce runoff through an increase of infiltration into the soil (Relf,

2015), which may explain the high concentrations of other analytes at this location. Although Mile Marker 115 had the highest average overall reading for the upper location (26.62 mg/L), FCWTF Intake was still shown to have the highest average readings for the two locations closest to the river (bottom=19.05 mg/L, middle=9.46 mg/L). Despite these high readings, over half of the locations still fell within the range of 5-7 mg/L. The presence of TOC decreased so significantly that the 3 locations with the average highest readings were also the only locations higher in concentration than the respective locations of PBR, showing how much the river was able to adjust TOC 1 year after the fire. TOC and many of the other analytes showed the overall lowest concentrations at Young Gulch, which suggests an increased impact of runoff and river flow at that site. The variability between concentrations due to contact time was also lessened in Analysis 2, showing a decrease in the available TOC to be desorbed from the sediment. Overall, TOC was found to significantly change between only 2 sites, with a significant increase from Young Gulch to Mile Marker 115 (p=0.0159).

	PBR	Century Park	Stevens Gulch	Young Gulch	Mile Marker 115	FCWTF Intake
TOC		45.30	22.00	20.75	48.45	45.30
2012		M 24 hr	B 24 hr; U 24 hr	M 6 hr	U 24 hr	M 24 hr
TOC	13.27	9.02	10.01	6.79	28.75	22.62
2013	U 24 hr	B 24 hr	U 24 hr	U 24 hr	U 24 hr	B 24 hr
TN		6.85	3.60	3.60	5.15	7.3
2012		M 24 hr	U 6 hr	U 6 hr	U 6 hr, U 24 hr	M 6 hr
TN	1.89	2.23	1.92	1.92	3.74	2.58
2013	U 24 hr	B 24 hr	U 6 hr	U 6 hr	U 24 hr	B 24 hr
ТР		0.75	0.53	0.53	0.44	0.96
2012		U 6 hr	U 6 hr	U 6 hr	M 6 hr	M 6 hr
ТР	0.53	0.50	0.53	0.53	0.68	0.68
2013	U 24 hr	B 6 hr	U 24 hr	U 24 hr	U 6 hr	M 6 hr

Table 3.1 Maximum concentrations of nutrients and TOC from sediment leaching

Concentrations are in mg/L. Each reading is followed by its location (B: bottom; M: middle; U: upper) and contact time. --: readings were not taken

In comparing the TN concentrations from each riverbed location over time, a significant difference was not observed (p>0.05). Time did not significantly affect TN concentrations for 13 of the 15 riverbed locations tested. However, riverbed location had a significant impact on TN concentrations (p<0.013). The middle and upper locations had the highest concentrations at Century Park and Young Gulch (averages: 6.68 mg/L-N, 5.02 mg/L-N), and Stevens Gulch and Mile Marker 115 (averages: 4.04 mg/L-N, 5.08 mg/L-N), respectively. Sites also had a significant impact on TN concentrations (p<4.8x10<sup>-5</sup>) with the highest concentrations for the middle and upper locations from Century Park (averages: 6.68 mg/L-N, 5.17 mg/L-N, respectively). The highest concentration from all the bottom locations came from the FCWTF Intake (average=4.93 mg/L-N).

The maximum average TN concentrations determined by this study ranging from 3.83 to 5.67 mg/L-N are higher than the levels reported for the leaching tests conducted by Wu et al. (2012) in China (1.4 and 2.5 mg/L-N). However the concentrations from Wu et al. (2012) were reported for ammonia-nitrogen so does not account for the other forms of nitrogen that might be present in the leachate, so the TN concentrations would possibly be higher. This study was conducted with 100 g/L of sediment, while the Wu et al. (2012) tested 5 to 10 cm of sediment in 2 L of water (container 10 cm diameter, 50 cm height), which may contribute to the lower nitrogen concentrations. The Wu et al. (2012) study also was not concerned with post fire conditions, but rather a severely contaminated river. In another study by Lim et al. (2011), leaching tests were performed with lake sediments and reported the peak ammonia-nitrogen concentration of 5 mg/L-N. Although this value is similar to the TN values reported in this study, the experiment involved lake sediments that might have higher accumulation of nitrogen

species, providing higher leaching potential of nitrogen. The lake's watershed was also unaffected by fire, so concentrations may not be directly compared.

The TN concentrations found in this study are similar to the concentrations found after southern California fires (Stein et al., 2012). The mean concentration of nitrate+nitrite after the California fires was 2.45 mg/L-N in river water samples. This study was conducted in a batch system so the higher concentrations found (max average 3.83-5.67 mg/L-N) would be diluted if in the Poudre River, which would correlate better to the concentrations reported in the Stein et al. (2012) study. This study determined much higher levels of nitrogen leaching compared to other studies. For instance, Emelko et al. (2011) reported the dissolved organic nitrogen (DON) at 205.3 µg/L-N after fire in 3 fire affected creeks in 4 years post-fire, which is an order of magnitude smaller than this study's results for TN. It should be noted that the DON concentration does not account for all forms of nitrogen present in the sample. The Red Bench fire in Montana produced a peak of ammonia at 220 µg/L-N and nitrate at 427 µg/L-N (Hauer and Spencer, 1998), also an order of magnitude less than the current study's results, yet ammonia and nitrate were not looked at individually in the current study.

TN was significantly less at all sites between analyses (p<0.015), while the controls between the analyses remained close. Analysis 2 showed 11 of the 15 locations to be less in concentration than the respective locations of PBR. Extreme concentrations of TN followed the pattern of TOC, with the overall lowest concentration found at Young Gulch and the highest concentration at the upper location of Mile Marker 115. Levels of TN stayed relatively consistent between sites, with only the progressions to the extremes being significantly different: Stevens Gulch to Young Gulch (p=0.002) and Young Gulch to Mile Marker 115 (p=0.004). The bottom location remained the lowest concentration for 4 of the 6 sites, while it was the highest at the

locations toward the end of the burn area: Century Park and FCWTF Intake. Overall, TN was found to be less than 1 mg/L at 11 of the 15 sites in Analysis 2, which resulted in a 1.4 to 12.2-fold decrease from the respective locations of Analysis 1.

Contact time did not have a significant impact on TP concentrations (p>0.05) for 13 of the 15 riverbed locations in Analysis 1. However, riverbed location does significantly affect TP leaching concentrations from all sites (p < 0.03). The highest TP concentrations were from the upper location from Century Park, Stevens Gulch, and Mile Marker 115 (averages: 0.71 mg/L-P, 0.572 mg/L-P, 1.32 mg/L-P, respectively). The site the sediment comes from also is significant to TP concentrations ( $p < 5x10^{-6}$ ) with the highest concentrations for the bottom and middle locations from FCWTF Intake (averages: 0.75 mg/L-P, 0.87 mg/L-P, respectively. The site with the highest average TP concentration for the upper location was Mile Marker 115 (1.32 mg/L-P). The maximum total phosphorus concentrations in Analysis 1 ranged from 0.57 to 1.35 mg/L-P. This is in the same range as in a Lost Creek fire study (maximum average 42.2  $\mu$ g/L-P) (Emelko et al., 2011). This study's range is lower than the Cerro Grande fire concentrations (14.5 mg/L-P) because this value was observed within the first 2 months after fire so a large proportion of nutrient-containing ash and sediment would still be suspended in the river, giving a high concentration (Gallaher and Koch, 2004). Similar phosphorus concentrations (peak of 15 mg/L-P) were seen in the Stein et al. (2012) study mentioned above. The Red Bench fire gave a soluble reactive phosphorus (SRP) peak of 69.2 µg/L-P (Hauer and Spencer, 1998). This concentration is lower than the range in the current study, but SRP does not account for the other forms of phosphorus that may be present in the water.

Controls of TP were found to be twice as large for Analysis 2 than Analysis 1. Concentrations varied both between sites and in contact time, but fell within an average range of 0.15-0.60 mg/L-P per site. TP was significantly different between analyses (p<0.033) for 13 of the 15 sites. All but one site decreased in concentration, with the majority decreasing 2-fold or greater. The one site that increased in concentration, Century Park, bottom, was the location furthest upstream of the burn area, showing a minimal impact of dilution from the river or runoff. Of all organics and nutrients measured, TP was the one that had the least significant change between analyses, possibly due to the strong adherence of phosphorus to soil (Khan and Mohammad, 2014), which would reduce its rate of desorption. Like other analytes measured, phosphorus in the sediment acclimated back to pre-burn levels for TP, with 11 of the 15 average temporal concentrations of each site, falling less than the respective sites of PBR. The highest concentration of TP occurred at FCWTF Intake, middle due to an outlying concentration, but if the outlier is removed the average peak concentration again falls at Mile Marker 115, upper with a 6 hour reading of 0.68 mg/L-P. Young Gulch again showed the least variance between sample locations. Statistical consistency was shown for 4 of the 5 progressions (p>0.053), with the only statistical difference again falling between Young Gulch and Mile Marker 115 (p=0.031).

Results for metals leaching from Poudre River sediment are given in **Table 3.2**. For the majority of riverbed locations (9 of 15), there was not a significant impact of contact time on iron concentrations in the leachate. However, the riverbed location had a significant impact on iron concentrations (p<0.0008). The highest concentrations were observed for the upper location (averages: Century Park=1.40 mg/L, Stevens Gulch=2.08 mg/L, Young Gulch=1.25 mg/L). The middle and upper riverbed locations significantly impacted the iron concentrations ( $p<1.0x10^{-5}$ ). The highest iron concentrations for middle location was observed at the FCWTF Intake (average=1.32 mg/L) while the upper location concentration was highest at the Stevens Gulch (average=2.08 mg/L). The maximum averages of iron leached ranged from 0.974 to 2.08 mg/L.

Fe. All sites showed an increase in iron concentrations in sediment-spiked samples than the controls. This confirms that the fire increases solubility of iron (Smith et al., 2011).

The average site concentrations of iron decreased at 14 of the 15 sites, while 9 of the 15 sites decreased significantly (p<0.014). Controls showed a significant decrease as well (p=0.011). Century Park, bottom was again the only site to show an increase. Sites within the burned area decreased from the respective sites of PBR at 11 of the 15 sites, while the 4 sites that increased were all above the bottom sampling location. If outlying concentrations are removed, peak iron concentration was found at the 24 hour reading of Young Gulch, bottom (0.94 mg/L). Of all the analytes tested, iron was the only one that had a peak concentration at a different site than Mile Marker 115, upper. The only statistical difference found between sites in Analysis 2 was from Mile Marker 115 to FCWTF Intake (p=0.005), while 11 of the 15 sites were significantly different due to contact time (p<0.047).

	PBR	Century Park	Stevens Gulch	Young Gulch	Mile Marker 115	FCWTF Intake
Fe		1.65	2.13	1.36	0.98	1.65
2012		U 6 hr	U 6 hr	U 24 hr	M 6 hr	M 6 hr
Fe	0.68	0.69	0.57	0.94	0.43	0.64
2013	B 6 hr	B 6 hr	U 6 hr	B 24 hr	U 6 hr	B 6 hr
Cu		0.34	0.51	0.30	0.22	0.09
2012		B 6 hr	U 6 hr	U 6 hr	M 24 hr	M 24 hr
Cu	0.26	0.31	0.61	0.20	0.98	0.71
2013	U 24 hr	B 6 hr	U 6 hr	U 6 hr	U 6 hr	M 6 hr
Mn		0.4	0.9	0.4	0.4	0.4
2012		M 24 hr	M 6 hr	U 6 hr	M 6 hr	B 24 hr
Mn	0.4	1.2	1.4	0.4	1.9	0.8
2013	U 6, 24 hr	B 6 hr	U 6 hr	M 6 hr	U 6 hr	B 6 hr

 Table 3.2 Maximum concentrations of metals from sediment leaching

Concentrations are in mg/L. Each reading is followed by its location (B: bottom; M: middle; U: upper) and contact time. --: readings were not taken

Results for copper leaching are provided in Table 3.2 as well. For the majority of riverbed locations (11 of 15), contact-leaching time did not have a significant impact on copper concentrations in the leachate (p>0.05). The riverbed location also did not significantly change the concentrations except at Century Park where the highest concentrations of copper were located in the bottom region (0.19 mg/L, p=0.033). However, the sites have a significant impact on the bottom and middle locations. The highest copper concentrations were observed at Stevens Gulch (averages: Bottom=0.34 mg/L, Middle=0.38 mg/L). The maximum averages of copper concentrations ranged from 0.121 to 0.361 mg/L-Cu. These concentrations are similar to the values of copper after the Cerro Grande fire (4-290 µg/L-Cu) (Gallaher and Koch, 2004). The current study's concentrations are slightly higher, probably due to the batch conditions in the beakers. The concentrations would be diluted in the actual Poudre River. The copper results in **Table 3.2** are much higher than the concentrations in a study by Sakalauskiene and Ignatavicius, (2003) in Lithuania (maximum post fires: 26.1 µg/L-Cu) most likely because of the closer proximity of the High Park fire to the Poudre River than the fires in Lithuania were to their respective rivers. The sediment-leaching test showed higher concentrations of copper than in the controls, so copper is expected to leach into the river, especially with agitation of the riverbed sediment.

Average concentrations of copper increased between analyses at 8 of the 15 sampling locations, with the last 2 sites downstream taking up 6 of them. Despite approximately half of the sites showing an increase in concentration, only 3 of the 15 sites were significantly different (p<0.025). No significant difference was found between the analyses for controls. Concentrations remained at such high levels that 11 of 15 locations had higher average concentrations than the respective locations of PBR. The average peak concentration was found to move downstream

between analyses, from Stevens Gulch, middle in Analysis 1 (0.38 mg/L) to Mile Marker 115, upper in Analysis 2 (0.65 mg/L). Stevens Gulch still showed the highest average concentration at each location of all sites preceding Mile Marker 115, however. Contrary to Analysis 1, contact-time in Analysis 2 showed a significant difference between concentrations (p<0.05) at the majority of locations (9 of 15). Of the locations that significantly changed due to contact time, all but 1 decreased over time, showing a more immediate desorption of Cu. Overall, Cu showed variability between sites in Analysis 2, with statistical differences found between 4 of the 6 sites (p<0.016).

Results for manganese in the leachate are also given in **Table 3.2**. There was not a significant impact of contact times on manganese concentrations in the leachate (p>0.05). Riverbed locations also did not impact manganese concentrations. Sites were only significant for the upper riverbed location (p=0.006) and the highest concentration was observed at Young Gulch (0.32 mg/L). The lack of significance for the ANOVA tests may be due to the limited number of data points for manganese. Hach method 8034 has a detection limit of 0.1 mg/L-Mn, and many samples had non-detectable manganese levels. The maximum averages of manganese ranged from 0.32 to 0.45 mg/L-Mn. These values were larger than the typical control concentration of 0.2 mg/L-Mn, which indicates that manganese will leach into water from fire affected soils.

Average Mn concentrations increased at 8 of the 15 locations between analyses, but showed no significant change (p>0.05) between the majority of locations (10 of 15). No significant difference was found between analyses for controls as well. Along with the similarity between analyses, the majority of locations within the burn area of Analysis 2 (10 of 15) showed higher concentrations than the respective locations of PBR, suggesting that the wildfire may have

had a long term effect on Mn concentrations. Peak concentration of Analysis 2 was found at Mile Marker 115, upper (1.18 mg/L) which more than doubled from the peak concentration of Analysis 1, while the second largest concentration was found at the same site as the peak concentration of Analysis 1 (Stevens Gulch). Mn generally decreased as contact time increased in Analysis 2, but showed varied trends between locations of each site. Overall, Mn only significantly changed between 2 sites in Analysis 2 (p=0.022), with concentrations increasing from Young Gulch to Mile Marker 115.

The concentrations of organics, nutrients and metals observed in this study are compared to the Environmental Protection Agency (EPA) regulations for drinking water in **Table 3.3** (EPA, 2009). There is not a specific EPA regulation for TOC, but the concentrations are higher than the typical TOC concentrations in the Poudre River of 2 to 4 mg/L. The average concentrations discussed above are also larger than the concentration (11 mg/L) found just after the fire on June 30<sup>th</sup> by the FCWTF. Based on data by Milhous (2009) for the Poudre River during spring flow, the volume to surface area ratio in the river is 0.37 m<sup>3</sup>/m<sup>2</sup>. The laboratory settings in the beakers have a volume to surface area ratio of 0.11 m<sup>3</sup>/m<sup>2</sup>, so even with approximately 1:3 dilution the TOC concentrations in the river would be much higher than concentrations found historically.

Parameter	EPA Regulation	2012 Min	2013 Min	2012 Max	2013 Max
TOC (mg/L)	N/A	8.45	5.39	48.45	28.75
TN (mg/L-N)	NO <sub>3</sub> -N: 10 NO <sub>2</sub> -N: 1	1.0	0.39	7.3	3.74
TP (mg/L-P)	Limiting algal growth: 0.025-0.05	0.33	0.15	1.28	0.60
Fe (mg/L)	0.3	0.31	0.08	2.64	0.97
Cu (mg/L)	Action level:1.3 Secondary: 1	0	0.03	0.56	1.11
Mn (mg/L)	0.05	0	0	0.9	2.0

Table 3.3 Comparison of average sedim'ent leaching concentrations to EPA regulations

The high concentrations may still be problematic for treatment practices, especially the possibility of disinfection-by-product (DBP) formation. TN is not specifically regulated, but nitrate and nitrite have Maximum Contaminant Levels (MCLs) of 10 and 1 mg/L, respectively, due to their harmful health effects including reducing the capability of red blood cells to hold oxygen in young children. The concentrations found in this study for both analyses do not exceed the regulations, even though the specific forms of nitrogen were not delineated. The EPA does not regulate TP, but literature has shown that the concentration of TP that above which algae flourish ranges from 0.005 to 0.01 mg/L-P (Koester, 2011). The TP concentrations found in this study greatly exceed this level in both analyses, which may induce algae growth in the river in the future. Even with dilution in the river, these concentrations would be problematic due to the resulting algal metabolites producing taste and odor issues. Several of the iron concentrations in this study exceed the EPA secondary MCL, which may impact the aesthetics or corrosion of the distribution system. However, this study focused on the source water, not treated water, so much of the iron would be removed through conventional treatment. Copper concentrations did not exceed either the MCL of 1.3 mg/L-Cu or the secondary, aesthetic MCL of 1 mg/L, so copper would not be problematic for drinking water utilities after the High Park Fire. Manganese

concentrations did exceed the secondary MCL of 0.05 mg/L and remained that way in Analysis 2, however the concentrations would not only be more dilute in the river but would also be reduced with conventional treatment.

An approximate dilution factor can be calculated based on data from Milhous (2009) concerning spring conditions in the Poudre River. The flow rate of 2.85 m<sup>3</sup>/s, average depth of0.75 m, and average width of 13 m, would give a velocity in the river of approximately 1 m/s. The length of river in the burn area that is of interest is about 24,000 m, which would give the water in the river 6 to 7 hours to travel through the burn area. The contact surface area in the river (~314,000 m<sup>2</sup>) and the volume of water (~117,000 m<sup>3</sup>) would give a volume to surface area ratio of 0.37 m<sup>3</sup>/m<sup>2</sup>. The volume to surface area ratio in the beakers is 0.11 m<sup>3</sup>/m<sup>2</sup>. The dilution of the concentrations from the beakers to the river would be approximately 1:3. Even with a 1:3 reduction in concentration, some of the parameters (TOC, TP, iron, and manganese) would not be acceptable for EPA standards. However, with conventional treatment, these parameter could decrease and be acceptable for EPA regulations.

Typical water quality parameters for the sediment leaching tests are found in **Table 3.4**. Maximum average pH values occurred at the upper riverbed location and ranged from 7.09 to 7.23. Several of the locations (3 of 5) had pH values that decreased from 6 to 12 hours, but then increased after 24 hours. This change in pH may be because of the changing water chemistry over 24 hours. For instance, hydroxide ions could precipitate with iron in the water, thus increasing the pH. Values of pH of Analysis 2 generally stayed within the same range at each site of Analysis 1. Dissolved oxygen (DO) maximum averages ranged from 5.325 to 5.98 mg/L. There was no distinct trend of how location or duration of leaching affected DO values. Temperature was relatively uniform across all samples at 24-25 °C except for Stevens Gulch samples which were kept in the refrigerator just before analysis. Maximum averages of conductivity ranged from 129.2 to 197.98  $\mu$ S/cm. The upper and middle riverbed locations had the highest conductivity averages, and the values increased with time. This is perhaps due to compounds dissolving into the water over time. Conductivity measurements decreased between analyses to an average range of 83.20 to 143.25  $\mu$ S/cm per location in Analysis 2, showing an overall decrease in compounds. The highest averages of turbidity ranged from 80.3 to 209.02 NTU and which typically occurred at the upper riverbed location. There is not a distinct temporal trend for turbidity. The type of particles greatly influences settling rates, so this may be the cause of the variability amongst samples. Turbidity also decreased between analyses to a range of 9.42 to 28.05 NTU for Analysis 2. Such a decrease may be due to a decrease in available TOC and particles to influence the readings.

	PBR	Century Park	Stevens Gulch	Young Gulch	Mile Marker 115	FCWTF Intake
рН		7.22	7.21	7.38	7.32	7.26
2012		U 24 hr	U 6 hr	U 24 hr	U 24 hr	U 24 hr
рН	6.80	6.96	6.94	7.40	6.91	7.38
2013	B6, 24 hr; M 6 hr	U 6 hr	B 24 hr; M 24 hr	B 6 hr; M 6 hr	B 24 hr	U 6 hr
Conductivity (µS/cm)		153.3	136.7	167.4	175.1	152.2
2012		M 24 hr	U 24 hr	M 24 hr	U 6 hr	U 24 hr
Conductivity (µS/cm)	120.4	92.3	106.9	103.9	136.7	155.1
2013	U 24 hr	B 24 hr	M 24 hr	M 24 hr	U 24 hr	B 24 hr
Turbidity (NTU)		278	210.5	93.2	118.9	88.8
2012		U 6 hr	U 6 hr	U 24 hr	U 6 hr	U 6 hr
Turbidity (NTU)	25.0	24.8	33.9	13.0	35.6	35.7
2013	U 6 hr	B 6 hr	U 6 hr	M 6 hr	U 6 hr	M 6 hr
DO (mg/L)		5.61	7.07	7.11	6.29	6.04
2012		B 6 hr	B 6 hr	B 6 hr	M 6 hr	B 6 hr
DO (mg/L)						
2013						

Table 3.4 Maximum water quality parameter measurements from sediment leaching

Concentrations are in mg/L. Each reading is followed by its location (B: bottom; M: middle; U: upper) and contact time. -- readings were not taken

# 3.4 CONCLUSIONS

Although the High Park fire was one of Colorado's largest fires, the water quality of the Cache la Poudre was not significantly impacted 5 to 10 months after the fire. Concentrations of organics and nutrients from Poudre River sediment showed elevated concentrations immediately after the High Park Fire, but were significantly decreased 1 year after. Metals also showed increased concentrations following the fire, but varied in response 1 year later. Iron was shown to generally decrease between analyses, while copper and manganese generally increased, but showed little significant difference between analyses. The results suggest a good influence of runoff and river flow on the reduction of organics and nutrients over time, while metals were likely released from the organics into the sediment and remained at elevated concentrations.

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APPENDIX

							Plot	t 1, Anal	ysis 1							
				Run 1					Run 2					Run 3		
	Sample #	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	Start Time	1.83	3.17	5.00	10.00	15.00	2.50	4.03	5.80	10.00	15.00	2.30	4.63	5.88	10.00	15.00
	NH3-N	2.4	0.4	0.4	0.3	0.4	0.8	0.6	0.5	0.5	0.8	0	0.4	0	0	0
Uwo	$P_i$	3.06	2.66	2.11	1.14	0.9	1.7	1.34	1.34	1.06	0.67	1.19	1.06	0.99	0.74	0.61
	Fe	1.81	1.02	1.2	0.82	0.49	0.67	0.48	0.61	0.48	0.39	Х	Х	Х	Х	Х
	ТОС	42	38	35	36	28	26	28	18	14	16	10	12	22	23	11
	Start Time	2.17	6.50	8.67	10.17	15.00	1.88	6.70	7.93	10.00	15.00	2.82	6.08	7.67	10.00	15.00
	NH3-N	27.7	41.8	33.5	27.1	16.2	13.2	13.8	13.3	12.1	11.3	19.1	10.6	8.9	8.8	6.8
Uw	$P_i$	22.3	21.25	17.6	20.05	19.92	16.9	17.1	16.5	13.9	15.95	17.85	15.25	13.85	15.4	14.6
	Fe	1.2	1.53	1.76	2.54	1.4	2.75	1.1	1.17	1.21	0.51	Х	Х	Х	Х	Х
	ТОС	42	39	40	38	39	34	29	6	20	37	36	27	43	29	25
	Start Time	5.33	9.00	11.00	13.00	15.00	3.70	6.45	7.93	10.43	15.00	4.00	5.75	7.22	10.00	15.00
	NH3-N	4.2	3.4	3.6	3.7	4.1	3.1	5.3	4.7	5	4.1	2.4	2.9	2.9	2.6	2.2
Bwo	$P_i$	5.39	4.39	5.16	5.47	5.3	3.52	3.29	Х	3.02	2.81	2.48	2.76	Х	2.72	2.68
	Fe	0.52	0.29	0.29	0.98	0.36	1.75	0.81	0.66	0.57	0.5	Х	Х	Х	Х	Х
	ТОС	384	378	370	380	372	334	122	386	362	340	272	236	214	192	154
	Start Time	5.58	9.08	11.33	13.92	15.00	3.50	5.60	6.60	10.00	15.00	4.13	5.65	6.65	10.00	15.00
	NH3-N	3.7	3.8	3.3	3.3	3.5	2.9	3.5	3.4	3.2	3	3.5	3.1	1.7	1.4	1.4
Bw	$P_i$	15.76	11.73	11.4	11.16	10.98	12.99	13.83	13.14	Х	11.25	5.01	8.22	5.16	Х	3.79
	Fe	0.31	0.28	0.15	0.13	0.16	1.07	0.51	0.45	0.4	0.18	Х	Х	Х	Х	Х
	TOC	352	308	292	284	286	280	30	260	224	210	114	80	92	110	96

Table 2.5 Rainfall Simulation results for ammonia (NH<sub>3</sub>), orthophosphate (P<sub>i</sub>), Iron (Fe) and TOC from Plot 1, Analysis 1

X – Results not gathered due to inefficient supplies or interference with readings

			Plot 1, Analysis 2								
			Run 1			Run 2			Run 3	1	
	Sample #	1	2	3	1	2	3	1	2	3	
	Start Time	3.53	10.00	15.00	2.55	10.00	15.00	2.10	10.00	15.00	
Uwo	NH3-N	0.80	0.50	0.60	0.70	0.30	0.40	0.10	0.00	0.00	
	$P_i$	2.29	1.43	1.32	2.94	1.40	1.12	1.30	1.20	1.00	
	Start Time	3.00	10.00	15.00	2.67	10.00	15.00	2.30	10.00	15.00	
Uw	NH3-N	13.60	6.30	5.00	6.20	5.40	4.80	5.50	5.30	4.90	
	$P_i$	42.24	37.95	29	50.38	28.05	23.65	39.73	36.29	20.93	
	Start Time	4.67	10.00	15.00	3.28	10.00	15.00	2.45	10.00	15.00	
Bwo	NH3-N	3.60	3.20	1.80	2.30	2.20	2.40	1.80	1.30	1.30	
	$P_i$	2.82	2.58	2.10	1.75	2.09	1.88	1.03	0.97	1.09	
	Start Time	2.88	10.00	15.00	2.92	10.00	15.00	3.40	10.00	15.00	
Bw	NH3-N	2.70	2.20	2.40	1.80	1.80	1.60	0.90	1.20	1.00	
	$P_i$	4.03	3.89	3.87	1.97	4.03	2.24	1.53	1.62	1.39	

Table 2.6 Rainfall Simulation results for ammonia (NH<sub>3</sub>), orthophosphate (P<sub>i</sub>), Iron (Fe) and TOC from Plot 1, Analysis 2

			Plot 2, Analysis 1													
			-	Run 1	-	-			Run 2	-	-		-	Run 3	-	
	Sample #	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	Start Time	1.83*	3.17*	5*	10.00	15.00	0.88	5.08	6.30	10.00	15.00	2.92	6.05	7.35	10.00	15.00
	NH3-N	1.9	0.5	1.3	0.6	0.6	0	0.2	0	0.3	0	0.3	0.7	0.6	0	0.6
Uwo	$P_i$	2.87	1.42	Х	0.92	0.91	0.92	1.49	1.27	1.16	0.47	1.49	1.2	1.26	1.34	1.15
	Fe	1.72	1.24	1.04	0.23	0.18	1.4	0.66	0.64	0.62	0.7	Х	Х	Х	Х	Х
	ТОС	42	40	38	34	39	27	28	41	24	37	31	35	41	49	40
	Start Time	1.42	4.00	5.42	10.00	15.00	1.03	3.90	5.03	10.00	15.00	0.67	3.80	5.58	10.00	15.00
	NH3-N	4919	1670	329	31.9	22.8	39.3	26.7	22.6	14.2	11.6	24.7	16.1	14.2	10.1	8.1
Uw	$P_i$	11.4	19.45	19.2	23.4	15.5	12.05	18.55	14.15	16.9	16.1	14.25	15.15	18.4	11.65	14.8
	Fe	2.52	1.93	1.94	2.3	1.34	1.37	1.22	1.2	0.59	0.8	Х	Х	Х	Х	Х
	ТОС	52	49	47	50	49	31	18	42	35	47	25	42	55	30	37
	Start Time	1.13	6.33	7.33	10.00	15.00	1.23	4.70	5.57	10.00	15.00	2.85	4.82	5.80	10.00	15.00
	NH3-N	4.3	3.9	3.4	2.9	2.5	2.1	2.6	2.6	2	1.5	3.3	3.6	2.5	2.2	2
Bwo	$P_i$	10.83	8.19	5.34	4.72	4.3	1.79	2.02	2.15	1.93	2.06	2.42	2.35	2.4	2.72	2.66
	Fe	0.48	0.23	0.24	0.18	0.74	3.68	2.02	1.86	0.82	0.46	Х	Х	Х	Х	Х
	ТОС	308	286	282	272	258	196	284	224	172	158	93	60	10	12	55
	Start Time	3.80	5.82	7.08	10.00	15.00	2.42	5.67	6.25	10.00	15.00	2.28	4.83	5.88	10.00	15.00
	NH3-N	4.6	4.3	5.2	4.2	4.2	4.2	4.8	4.4	3.9	3.5	2.2	1.9	1.9	1.8	2
Bw	$P_i$	16.11	15.42	17.9	16.2	15.33	14.43	11.49	10.29	6.96	5.49	3.76	2.9	5.2	3.92	3.31
	Fe	0.24	0.19	0.27	0.27	0.21	0.73	0.45	0.42	0.31	0.27	Χ	Χ	Х	Χ	Х
	ТОС	486	420	364	346	310	260	280	374	210	194	132	132	114	86	130

Table 2.7 Rainfall Simulation results for ammonia (NH<sub>3</sub>), orthophosphate (P<sub>i</sub>), Iron (Fe) and TOC from Plot 2, Analysis 1

X - Results not gathered due to inefficient supplies or interference with readings \* - Estimated collection time

			Plot 2, Analysis 2								
_			Run 1			Run 2			Run 3		
	Sample #	1	2	3	1	2	3	1	2	3	
	Start Time	2.63	10.00	15.00	2.88	10.00	15.00	2.32	10.00	15.00	
Uwo	NH3-N	1.20	1.00	0.70	0.90	0.80	0.80	0.00	0.20	0.10	
	$P_i$	3.70	1.69	1.60	1.19	1.67	1.46	1.25	1.17	1.03	
	Start Time	2.52	10.00	15.00	1.37	10.00	15.00	0.70	10.00	15.00	
Uw	NH3-N	10.60	5.70	5.40	6.30	5.20	5.00	4.90	5.00	4.90	
	$P_i$	22.68	39.96	28.80	43.29	26.73	20.13	32.75	22.96	24.92	
	Start Time	1.22	10.00	15.00	1.58	10.00	15.00	0.80	10.00	15.00	
Bwo	NH3-N	4.60	3.00	2.50	1.70	1.50	1.40	1.60	1.60	1.10	
	$P_i$	3.15	2.62	3.47	2.46	3.72	0.97	1.53	1.38	1.29	
	Start Time	1.82	10.00	15.00	1.65	10.00	15.00	3.00	10.00	15.00	
Bw	NH3-N	2.00	2.20	2.10	1.80	2.00	1.50	1.30	1.20	1.20	
	$P_i$	6.15	4.45	4.10	3.70	3.03	2.92	2.38	2.26	2.15	

 Table 2.8 Rainfall Simulation results for ammonia (NH3), orthophosphate (Pi), Iron (Fe) and TOC from Plot 2, Analysis 2

		Leaching 1			Leaching 2		Leaching 3			
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr	
Plank	0			0			0.0			
DIAIIK	0.4			0			0.1			
Uwo	7	5.5	6.5	1.5	2.5	6.5	1.0	0.0	1.5	
UWU	2	1	8	2.5	2.5	7	0.5	0.0	1.0	
Uw	9	30.5	20	14	14	20	14.5	16.0	14.0	
Uw	14	12	18	10	17.5	23	10.5	12.0	18.0	
Dwo	71.5	66.5	73	61.5	57.5	66	69.0	57.5	70.5	
DWU	56.5	55.0	70	80	60.5	72	51.0	45.5	54.5	
Dw	37	37	46	48	52.5	56	49.0	54.0	55.0	
Dw	36	33	57	37	53	53	53.0	73.5	55.0	
UwU	2.5	5.0	8	5	5.5	7	3.5	4.0	2.5	
UWH	6	3	9	3	6.5	5	2.5	4.5	6.0	

Table 2.9 Total Organic Carbon (mg/L) results from soil leaching

		Leaching	g 1		Leaching 2	2		Leaching 3	1
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlank	0.3			0.7			0.0		
DIAIIK	0.0			0			0.3		
Uwo	0.2	0.5	0.4	0.5	0	0.1	0.3	0.2	0.0
Uwu	0.1	0.0	0.6	0.5	0	0	0.2	0.1	0.1
<b>L</b> I vy	12.5	18	29.5	25	34.5	32	18	19	22
UW	18.5	22	32.5	24	33.5	30.5	16	21	17
Dava	2.3	3.2	3.3	3.4	1.9	2.8	2.8	1.5	1.7
DWO	2.4	2.7	3.2	3.2	2.4	2.7	3.2	1.5	1.3
Dw	2.1	3.2	3.2	3.6	2.5	3.6	3.5	2.2	2.0
DW	2.5	3.4	4.3	3.8	2.5	3.3	2.8	2.3	2.2
Umuli	24	45.0	50	38	63	59.5	27	32	26
UWI	38.5	50.5	58.5	47	71	60	21	34	33

 Table 2.10 Ammonia (mg/L-N) results from Soil Leaching

		Leaching	g 1		Leaching	2		Leaching 3	3
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlank	0.07			0.06			0.00		
Біанк	0.07			0.25			0.01		
Uwo	4.57	8.80	7.83	7.83	4.24	7.50	6.85	9.78	3.91
Uwo	6.85	4.57	6.85	7.83	7.50	7.50	4.24	3.26	2.93
Uw	19.57	40.11	44.68	41.74	47.61	61.96	33.59	41.74	47.61
Uw	34.89	39.78	45.33	37.50	40.11	59.35	33.59	44.35	53.15
Duvo	7.50	1.30	5.87	31.96	7.83	6.20	16.96	14.35	12.72
DWO	6.85	4.24	6.20	9.78	6.85	9.78	13.70	12.39	7.83
Dw	5.87	9.13	0.98	7.17	8.48	9.13	4.89	7.17	2.28
DW	8.48	7.83	5.22	8.48	3.26	4.89	7.50	4.89	5.87
Uwu	40.11	65.55	82.83	61.96	74.35	96.20	64.89	72.72	80.55
UWH	72.72	72.39	87.72	69.79	81.85	97.50	64.57	80.87	93.27

 Table 2.11 Total Phosphorus (mg/L) results from Soil Leaching

		Leaching	g 1		Leaching	2		Leaching 3	3
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlank	0.06			0.01			0.03		
Біанк	0.02			0.02			0.01		
Umo	0.39	0.25	0.19	0.27	0.32	0.25	0.21	0.26	0.19
Uwo	0.29	0.24	0.16	0.27	0.24	0.26	0.26	0.30	0.25
<b>U</b> ww	0.43	0.49	0.53	0.85	0.76	0.86	0.80	0.82	0.76
Uw	0.71	0.63	0.64	0.74	0.71	0.74	0.79	0.81	0.82
Davia	0.77	0.08	0.15	0.63	0.21	0.11	0.48	0.26	0.20
DWU	0.50	0.08	0.10	0.44	0.24	0.16	0.49	0.21	0.19
Dwy	0.08	0.10	0.01	0.15	0.08	0.03	0.09	0.08	0.08
DW	0.12	0.06	0.03	0.42	0.73	0.08	0.08	0.28	0.04
I Jaw II	0.64	0.75	0.73	0.87	0.92	0.84	1.10	1.08	0.93
UWH	1.00	0.81	0.87	1.04	0.89	0.83	1.06	1.08	0.91

 Table 2.12 Iron (mg/L) results from Soil Leaching

		Leaching	g 1		Leaching 2	2		Leaching 3	1
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlawla	0.0			0			0.5		
DIAIIK	0.2			0.2			0.1		
Uwo	1	0.0	0.0	0.8	0	0	0.1	0.0	0.0
Uwo	1	0.1	0.0	0.3	0	0	0.2	0.0	0.0
TI	0.5	0.0	0.1	0.2	0.1	0.1	0.1	0.2	0.1
UW	1	0.6	0.2	0.2	0.1	0	0.2	0.4	0.1
Davia	2	0.1	0.2	0	0.4	0.2	0.2	0.2	0.2
DWO	1.5	0.1	0.2	0.2	0.2	0.2	0.3	0.4	0.2
Bw	1	0.0	0.1	0.6	0	0	0.2	0.0	0.3
	1.5	0.1	0.1	0.4	0.2	0.2	0.2	0.1	0.3
U U	2	0.0	0.1	0.2	0.5	0.3	0.1	0.1	0.1
UWH	1	0.2	0.0	0.3	0	0	0.2	0.1	0.1

 Table 2.13 Manganese (mg/L) results from Soil Leaching

		Leaching 1		Leaching 2			Leaching 3		
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlauk	7.95			6.6			7.17		
DIAIIK	7.98			6.67			7.20		
Uwo	7.97	Х	Х	7.17	7.3	7.19	5.73	7.21	7.23
Uwu	7.95	Leaching 1         Leaching 2         Leaching 3           12hr         24hr         6hr         12hr         24hr         6hr         12hr           6.6         7.17         6.67         7.20         7.20           X         X         7.17         7.3         7.19         5.73         7.21           X         X         7.25         7.44         7.21         5.90         7.25           X         X         6.89         6.74         6.63         6.78           X         X         7.41         7.42         7.22         6.61         6.80           X         X         7.37         7.4         7.19         6.65         6.75           X         X         6.89         6.74         6.76         6.63         6.78           X         X         7.37         7.4         7.19         6.65         6.75           X         X         7.33         7.42         7.16         6.94         6.61           X         X         7.33         7.42         7.16         6.94         6.61           X         X         7         6.95         6.93         6.95         6.92	7.41						
I Iwy	7.36	Х	Х	6.92	6.79	6.8	6.59	6.86	6.78
UW	7.09	Х	Х	6.89	6.74	6.76	6.63	6.78	6.84
Dwo	5.95	Х	Х	7.41	7.42	7.22	6.61	6.80	7.32
DWU	6.41	Х	Х	7.37	7.4	7.19	6hr           7.17           7.20           5.73           5.90           6.59           6.63           6.61           6.65           6.81           6.94           7.05           6.95	6.75	7.18
Dw	7.19	Х	Х	7.26	7.3	6.89	6.81	6.64	7.24
BW	7.45	Х	Х	7.33	7.42	7.16	6.94	6.61	7.23
UwU	6.55	X	X	6.98	6.97	6.94	7.05	7.11	7.01
UWI	6.55	Х	Х	7	6.95	6.93	6.95	6.92	7.03

Table 2.14 pH results from Soil Leaching

X – Readings were not able to be taken due to errors with reading

	Leaching 1           6hr         12hr         24hr           4.64		Leaching 2			Leaching 3			
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlauk	4.64			5.88			5.25		
DIAIIK	3.30			6.66		3.23           3.69           69.3         47.7           56.0           69.1         48.3           341         211           257           331         235           294         238           296         186.2			
Umo	44.1	50.9	62.3	50.7	57.2	69.3	47.7	56.0	67.0
Uwu	37.3	46.8	58.6	Leaching 26hr12hr24hr6hr $5.88$ $5.25$ $6.66$ $3.69$ $50.7$ $57.2$ $69.3$ $47.7$ $50.8$ $57.5$ $69.1$ $48.3$ $239$ $291$ $341$ $211$ $215$ $274$ $231$ $235$ $217$ $246$ $294$ $238$ $227$ $255$ $296$ $186.3$ $333$ $411$ $460$ $332$ $406$ $491$ $599$ $425$ $403$ $471$ $579$ $444$	52.8	65.9			
T	138.9	203	276	239	291	341	211	257	312
UW	201	234	288	215	274	331	235	276	324
Davio	242	264	295	217	246	294	238	262	294
DWO	222	238	271	227	255	296	186.3	218	254
Bw	292	314	352	333	411	460	333	371	434
	282	312	355	318	381	430	332	376	416
	251	330	507	406	491	599	425	480	548
ОМП	394	441	531	403	471	579	444	543	626

Table 2.15 Conductivity ( $\mu$ S/cm) results from Soil Leaching
		Leaching 1			Leaching 2	2	Leaching 3		;
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlank	5.51			6.9			6.82		
Біанк	5.48			7.21			7.01		
Uwo	5.85	4.49	3.75	6.72	5.79	5.04	7.22	7.01	6.78
Uwu	5.75	4.52	3.80	6.18	5.85	4.81	6.92	6.68	6.48
I law	6.09	4.62	3.38	6.9	5.63	5.34	7.19	6.38	5.79
UW	5.75	4.73	3.43	6.83	5.83	4.59	7.29	6.56	5.51
Duvo	5.73	4.72	2.82	6.58	5.42	4.92	6.09	5.88	5.79
DWO	5.23	4.66	3.72	6.19	5.46	5.04	6.19	6.09	5.92
Dw	6.40	4.71	3.63	6.07	5.39	4.84	6.85	6.08	5.87
DW	5.52	5.30	3.13	6.31	5.39	5.46	6.49	6.31	6.18
UwII	5.10	4.72	3.50	7.12	6.52	6.03	7.13	6.90	6.61
UWI	5.35	5.08	3.99	7.15	6.5	5.88	7.28	6.68	6.07

 Table 2.16 Dissolved Oxygen (mg/L) results from Soil Leaching

		Leaching 1			Leaching	2	Leaching 3		}
	6hr	12hr	24hr	6hr	12hr	24hr	6hr	12hr	24hr
Dlank	0.106			0.045			0.127		
DIAIIK	0.057			0.083			0.132		
Uwo	14.0	12.3	14.0	22	24.5	18.4	33.8	34.6	34.4
Uwo	16.0	9.55	11.5	19	20.5	20.9	34.2	34.3	30.6
Uw	9.59	8.87	13.1	21.5	18	18.3	32.6	31.6	27.3
Uw	11.7	17.4	13.1	20.7	14.8	14.3	29.1	27.2	27.2
Dava	14.0	11.1	12.7	15.4	13.3	11.1	23.1	26.1	20.8
DWU	35.1	7.98	11.9	17.3	17.8	11.7	22.4	25.0	14.8
Day	17.9	5.82	7.13	16.9	9.57	6.48	18.1	14.8	13.2
DW	15.7	5.64	9.93	24.6	11.6	7.13	20.2	18.0	12.2
	15.1	13.0	13.9	23.4	23	18.3	47.2	48.3	40.5
UWH	23.1	11.7	17.9	19	19.6	17.3	48.2	49.8	42.1

Table 2.17 Turbidity (NTU) results from Soil Leaching

	Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	9.9		33.8	38.2	1.5	11.5	8.5	12.3	9.8	16.9	20.6	
0 III	8.4	38.0	38.4	37.8	1.7	8.4	8.4	15.8	8.8	19.3	20.9	19.6
12 hr		34.2	41.7	39.3		10.6	22.0	22.0		15.5	20.5	19.6
12 11		34.5	42.9	41.1	-	12.5	22.0	22.0	-	14.7	20.5	19.1
24 hr		33.9	46.2	45.6	<u> </u>	22.0	21.4	22.0		16.8	20.5	19.6
24 11		36.6	44.4	40.5	-	22.0	21.3	22.0	-	18.2	20.6	20.0

Table 3.5 Total Organic Carbon (mg/L) results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6 hr	9.4	20.1	20.4	20.4	14.4	39.0	38.0	39.4	
0 III	7.7	19.9	20.3	20.3	9.2	39.8	39.2	39.2	
12 hr		28.8	37.2	37.6		34.2	41.7	39.3	
12 11		29.8	36.6	36.8		34.5	42.9	41.1	
24 hr		47.1	41.4	38.7		33.9	46.2	45.6	
2.11		36.9	42.6	58.2		36.6	44.4	40.5	

	Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.5	2.5	6.0	4.8	1.2	1.7	1.8	3.6	0.2	1.2	5.4	1.1
UII	0.2	3.2	17.7*	5.7	0.6	2.1	1.5	16.1*	0	0.8	5.5	1.4
12hr		3.9	7.0	4.8		2.6	3.8	4.9		0.6	5.0	2.0
12111		3.8	6.7	5.9		3.0	3.0	5.7		1.9	4.7	2.1
24hr		4.1	7.2	5.5		2.7	2.3	2.4		1.3	4.8	2.3
24111		3.1	6.5	4.3		2.0	1.8	3.6		2.0	4.7	3.4

Table 3.6 Total Nitrogen (mg/L-N) results from Sediment Leaching, Analysis 1

		Mile Mar	·ker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	0.3	1.3	3.5	5.6	0.5	5.6	9.4	4.8	
UII	0.3	1.5	17.2*	4.7	0.6	4.5	5.2	17.7*	
12hr		2.5	6.4	4.9		4.8	5.4	5.9	
12111		2.3	5.4	5.0		5.3	5.2	5.6	
24hr		2.1	3.5	4.9		4.3	4.1	4.6	
		1.4	4.2	5.4		5.1	4.2	4.1	

\* - outlier not used in calculations

	Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.08	0.34	0.42	0.74	0.04	0.34	0.3	0.54	0.07	0.84	0.81	0.24
UIII	0.07	0.39	0.37	0.77	0.05	0.28	0.42	0.52	0.07	0.24	0.8	0.38
12hr		0.38	0.36	0.72		0.31	0.45	0.45		0.19	0.64	0.32
12111		0.36	0.4	0.68		0.34	0.41	0.98		0.19	0.66	0.35
24hr		0.26	0.44	0.72		0.35	0.35	0.51		0.27	0.78	0.35
24111		0.34	0.4	0.6		0.34	0.31	0.43		0.26	0.79	0.33

Table 3.7 Total Phosphorus (mg/L-P) results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	0.07	0.43	0.46	1.3	0.06	0.72	0.96	0.84	
UII	0.07	0.32	0.41	1.26	0.05	0.66	0.96	0.82	
12hr		0.29	0.6	1.5		0.72	0.84	0.51	
12111		0.3	0.56	1.3		0.87	0.93	0.69	
24hr		0.3	0.42	1.26		0.72	0.72	0.75	
- 1111		0.37	0.4	1.3		0.78	0.81	0.57	

	Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.051	0.520	0.678	1.393	0.058	0.530	0.739	2.200	0.094	0.303	0.518	0.840
UIII	0.248	0.670	0.805	1.908	0.07	0.406	0.976	2.065	0.115	0.358	0.539	1.465
12hr		0.580	0.675	1.374		0.777	1.580	2.637		0.375	0.473	0.917
		0.487	0.577	1.147		0.731	1.044	2.489		0.279	0.584	1.549
24hr		0.383	0.403	1.247		0.645	0.679	1.514		0.533	0.629	1.369
		0.470	0.217	1.345		0.332	0.646	1.578		0.637	0.534	1.347

Table 3.8 Total Iron (mg/L-Fe) results from Sediment Leaching, Analysis 1

		Mile M	arker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	0.088	0.802	1.057	0.870	0.083	0.562	1.708	0.942	
UIII	0.051	0.846	0.894	0.644	0.176	0.646	1.588	0.953	
12hr		0.563	0.987	0.621		0.524	1.182	0.855	
12111		0.562	1.085	0.473		0.442	1.263	0.829	
24hr		0.379	0.910	0.404		0.484	1.005	0.558	
24111		0.371	0.909	0.423		0.455	1.144	0.421	

	Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.008*	0.328	0.059	0.044	0.030*	0.350	0.405	0.556	0.066	0.258	0.369	0.290
UIII	0.062	0.345	0.085	0.038*	0.157	0.305	0.355	0.465	0.009	0.175	0.044*	0.301
12hr		0.167	0.088	0.044*		0.365	0.450	0.172		0.084	0.346	0.039
12111		0.196	0.153	0.013		0.355	0.300	0.285		0.029	0.044*	0.029
24hr		0.057	0.154	0.208		0.340	0.266	0.013		0.290	0.166	0.043
27111		0.069	0.114	0.004		0.341	0.501	0.038		0.161	0.291	0.102

 Table 3.9 Copper (mg/L-Cu) results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	0.036	0.189	0.167	0.250	0.121	0.024	0.008	0.030	
UII	0.011	0.209	0.219	0.003*	0.044*	0.112	0.045	0.096	
12hr		0.111	0.166	0.044*		0.065	0.146	0.151	
		0.214	0.137	0.044*		0.044*	0.215	0.095	
24hr		0.124	0.199	0.298		0.138	0.140	0.022	
		0.144	0.288	0.086		0.031	0.177	0.114	

\* - below detection limit, zero used for calculations

		Century Park			Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	1	0.5	0.4	-0.3*	0.2	0.7	0.8	0	0.2	0.1	0.2	0.8
	0.2	0.2	0.3	-0.3*	0.5	0.3	0.9	0	0.3	0.3	0.4	-0.1*
12hr		0.3	0.5	-0.3*		-0.3*	-0.1*	-0.3*		0.1	0.5	0.3
		0.5	0.5	0.2		-0.2*	0.2	-0.3*		0.3	0.1	0.1
24hr		0.1	0.4	-0.3*		0.2	0	0.1		0	0.2	0.5
2 111		0.2	0.4	0		0.7	0.4	-0.1*		0	0.3	0.2

Table 3.10 Manganese (mg/L-Mn) results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6hr	0.2	0.2	0.2	-0.3*	0.1	-0.1*	0.1	-0.3*		
UIII	0.2	-0.3*	0.5	-0.3*	0.3	0.5	-0.3*	0		
12hr		0.3	0.6	-0.3*		0.1	-0.3*	0.3		
		0.2	0.3	-0.3*		0.2	-0.3*	-0.2*		
		-0.1*	-0.1*	-0.3*		0.4	0.1	0.1		
24hr		0.1	0.2	-0.3*		0.4	0.2	0.2		

\* - below detection limit, zero used for calculations

		Century Park				Stevens	Gulch		Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	6.77	6.82	6.84	7.02	6.58	6.97	7.07	7.18	6.91	6.79	6.74	6.96
0 III	6.88	6.86	6.89	7.12	6.92	6.98	7.14	7.24	6.84	6.94	6.92	7
12 hr		6.86	6.74	6.93		6.75	6.73	6.95		6.96	6.94	7.03
12 111		6.81	6.84	7.02		6.7	6.9	6.93		7.02	6.99	7.1
24 hr		7.07	7.06	7.19		6.97	7.16	7.18		7.24	7.2	7.37
27 11		7.09	7.12	7.24		7.05	7.17	7.19		7.35	7.26	7.38

Table 3.11 pH results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6 hr	6.74	6.88	7	7.23	6.72	6.76	6.94	7.02		
0 III	6.76	6.93	7.13	7.32	6.78	6.88	6.98	7.07		
12 hr		6.81	6.97	7.03		6.74	6.97	7.12		
12		6.87	7.02	7.16		6.89	7.04	7.11		
24 hr		7.28	7.26	7.28		7.15	7.21	7.26		
		7.33	7.29	7.35		7.17	7.28	7.25		

		Century Park			Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	6.09	5.57	5.59	5.49	7.3	7.08	7.01	6.85	7.41	7.13	6.74	6.71
0 111	5.92	5.64	5.48	5.39	7.25	7.05	6.66	6.56	7.12	7.08	6.94	6.7
12 hr		6.26	6.02	5.84		5.56	5.82	5.96		5.53	4.14	5.45
12 111		6.2	5.94	5.82		5.57	5.86	5.86		5.9	4.46	5.36
24 hr		5.57	5.52	5.52		5.33	5.32	5.25		4.75	3.42	4.59
24 111		5.53	5.46	5.48		5.24	5.34	5.31		4.8	3.3	4.64

 Table 3.12 Dissolved Oxygen (mg/L) results from Sediment Leaching, Analysis 1

		Mile Ma	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6 hr	6.2	6.03	6.37	6.07	6.45	6.07	5.88	5.53		
0 III	6.38	6.33	6.21	6.1	6.49	6.01	5.84	5.23		
12 hr		5.86	5.66	5.57		3.79	4.77	3.7		
12 11		5.9	5.48	5.79		3.55	4.89	4.26		
24 hr		5.4	4.49	5.06		3.45	5.33	4.27		
2.111		5.34	4.51	5.21		3.58	5.24	3.95		

		Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6 hr	25.6	24.9	24.8	24.8	24.7	24.8	24.8	24.9	24.1	23.9	23.4	23.6	
0 III	25.2	24.9	24.8	25	24.4	24.8	25.7	24.7	24.4	23.8	23.5	24.1	
12 hr		25.1	25.2	25.2		19.9	19.4	20.3		25.3	25	24.8	
		25.1	25.2	25.1		19.5	20.1	19.1		25.5	24.7	25.2	
24 hr		25.4	25.1	25		19.2	19	18.7		24.7	24.9	24.5	
		25.3	25.1	25.1		18.8	18.4	19.3		25.1	24.6	24.4	

 Table 3.13 Temperature (°C) results from Sediment Leaching, Analysis 1

		Mile Mar	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6 hr	24.8	24.4	24.4	24.4	26.2	25.5	25.4	25.3		
0 III	25.2	24.4	24.4	24.5	25.7	25.6	25.5	25.5		
12 hr		23.6	24	24.2		24.2	24.1	24.2		
		24.1	24	24		24.4	24	24.4		
24 hr		24.1	25.1	25.1		24.8	24.4	24.4		
		24.3	25	25.1		24.6	24.2	24.2		

		Century Park			Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	67.7	91	131.4	115.9	79.1	112.5	109.5	121.1	81	180.6	132.5	112.8
0 111	67.5	91	134.6	115.3	78.7	110.6	112.3	122.2	82.4	87.7	134	117.6
12 hr		92.7	138.8	124.2		121.8	120.7	126.6		87.9	137.1	117.1
		93.6	140.9	121.6		121.1	118.6	132		87.6	138.7	122.4
24 hr		100.3	151.7	141.1		126.5	128	137.5		93.6	166.3	138.1
		100.5	154.8	138.1		132.8	123.3	135.8		93.5	168.4	143

Table 3.14 Conductivity (µS/cm) results from Sediment Leaching, Analysis 1

		Mile Mar	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6 hr	78.7	96.3	129.8	179.4	79.6	134.4	128.7	139		
	78.5	95.4	130.3	170.8	77.6	132	130.2	141.7		
12 hr		97.3	154	195.8		140.9	130.9	142.8		
		96.6	136.6	191.9		145.8	133.8	140.4		
24 hr		102.6	150.2	228		142.9	137.6	152.5		
		102.8	150.7	222		148	141.9	151.8		

		Century Park				Stevens Gulch				Young Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6 hr	2.12	50.7	53.3	296	3.2	40.8	45.3	123	1.93	32.2	59.5	46.9	
0 III	2.79	63.1	51.1	260	7.24	36.4	67.6	298	1.36	27.4	54.3	83.9	
12 hr		26.1	41	130		49.6	52.5	244		23.8	47.7	78.4	
12 11		36.3	36.6	127		48.3	68.1	363		26	42.5	105	
24 hr		35.9	47.4	126		16.4	31.7	97.1		35.5	43	88.9	
2111		31	29.8	109		25.3	29.8	129		34.7	65.8	97.5	

 Table 3.15 <u>Turbidity (NTU) results from Sediment Leaching</u>, Analysis 1

		Mile Mai	rker 115		FCWTF Intake					
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper		
6 hr	1.63	53.4	53.4	140	3.07	86.1	89.4	89.5		
0 III	2.38	43.8	40.9	97.8	5.73	87.7	78.4	88		
12 hr		43.3	72.5	99.8		62.9	92.6	75.1		
		43.6	50.7	96.6		75.5	94.5	74.2		
24 hr		36	33.6	55.3		43.7	68.9	44.2		
2.111		28.4	28.9	84.6		56.2	58	35.8		

		PBR					Centur	y Park			Stevens	Gulch	
_		Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6	hr	6.55	10.28	9.65	12.23	4.67	8.75	6.00	5.40	6.55	5.78	6.19	9.92
0	6 hr	5.42	9.02	9.34	12.51	3.89	8.56	6.04	5.38	5.42	5.89	6.12	9.46
24	24 hr		9.81	9.14	13.07		9.70	6.34	5.76		6.12	6.22	9.44
24			9.04	8.86	13.47		8.33	6.24	5.69		5.49	6.07	10.58

 Table 3.16 Total Organic Carbon (mg/L) results from Sediment Leaching, Analysis 2

	Young Gulch					Mile Ma	rker 115			FCWTF	Intake	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	7.50	6.36	6.58	6.27	6.55	6.69	7.32	24.48	7.50	16.07	9.11	6.45
	5.35	5.64	5.96	6.00	5.42	6.64	7.73	24.48	5.35	14.88	9.03	6.68
24 hr		6.87	6.27	6.62		6.88	7.50	29.51		23.03	9.90	6.92
		6.02	6.62	6.97		6.87	7.74	27.99		22.21	9.80	6.66

	PBR					Centur	y Park			Stevens	Gulch	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	0.498	0.889	0.912	1.762	0.450	1.861	0.582	0.458	0.498	0.612	0.671	1.931
	0.465	0.867	0.883	1.805	0.373	1.772	0.595	0.471	0.465	0.612	0.667	1.903
24 hr		0.916	0.913	1.865		2.317	0.593	0.506		0.636	0.663	1.912
24 III		0.898	0.940	1.918		2.147	0.624	0.489		0.599	0.656	1.898

 Table 3.17 Total Nitrogen (mg/L-N) results from Sediment Leaching, Analysis 2

	Young Gulch					Mile Ma	rker 115			FCWTF	Intake	
	Control Bottom Middle Upper				Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	0.368	0.409	0.444	0.430	0.498	0.581	0.825	3.177	0.368	1.736	0.624	0.408
	0.358	0.425	0.450	0.394	0.465	0.603	0.852	3.076	0.358	1.538	0.641	0.395
24 hr		0.393	0.444	0.391		0.656	0.906	3.802		2.600	0.651	0.383
		0.386	0.439	0.402		0.641	0.934	3.668		2.565	0.683	0.389

	PBR					Centur	y Park			Stevens	Gulch	
	Control Bottom Middle Upp				Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	0.01	0.29	0.27	0.37	0.14	0.46	0.24	0.15	0.01	0.17	0.16	0.39
	0.13	0.24	0.38	0.58	0.10	0.55	0.16	0.15	0.13	0.18	0.14	0.48
24 hr		0.20	0.24	0.43		0.42	0.16	0.15		0.17	0.16	0.54
		0.51	0.36	0.64		0.38	0.19	0.15		0.16	0.23	0.51

 Table 3.18 Total Phosphorus (mg/L-P) results from Sediment Leaching, Analysis 2

	Young Gulch					Mile Ma	rker 115			FCWTF	Intake	
	Control Bottom Middle Upper				Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	0.15	0.19	0.14	0.17	0.01	0.17	0.22	0.79	0.15	0.44	0.38	0.21
	0.14	0.33	0.15	0.16	0.13	0.20	0.17	0.56	0.14	0.61	0.98	0.39
24 hr		0.17	0.23	0.15		0.16	0.16	0.54		0.46	0.25	0.16
		0.13	0.13	0.16		0.17	0.23	0.51		0.38	0.39	0.14

		PB	R			Centur	y Park			Stevens	Gulch	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.03	0.72	0.37	0.31	0.01	0.79	0.33	0.22	0.03	0.30	0.21	0.57
	0.00	0.63	0.37	0.33	0.03	0.59	0.35	0.28	0.00	0.24	0.23	0.56
24hr		0.55	0.21	0.15		0.49	0.24	0.19		0.17	0.10	0.25
		0.48	0.24	0.15		0.34	0.19	0.16		0.14	0.11	0.08

Table 3.19 Total Iron (mg/L-Fe) results from Sediment Leaching, Analysis 2

	Young Gulch					Mile Ma	rker 115			FCWTH	Intake	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.02	0.23	0.17	0.24	0.03	0.27	0.27	0.45	0.02	0.56	0.34	0.45
	0.06	0.22	0.20	0.21	0.00	0.26	0.21	0.40	0.06	0.72	1.43*	0.52
24hr		0.90	0.40	0.13		0.17	0.10	0.25		0.21	0.31	0.27
		0.97	0.40	0.14		0.14	0.11	0.08		0.27	0.33	0.48

		PBR				Centur	y Park			Stevens	Gulch	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.12	0.08	0.17	0.20	0.03	0.35	0.14	0.21	0.12	0.15	0.13	0.56
	0.41	0.03	0.22	0.22	0.01	0.26	0.20	0.19	0.41	0.18	0.39	0.66
24hr		0.04	0.23	0.32		0.07	0.04	0.20		0.34	0.17	0.32
		0.06	0.14	0.19		0.03	0.12	0.13		0.30	0.26	0.20

Table 3.20 Copper	(mg/L-Cu)	) results from	Sediment 1	Leaching,	Analysis 2
				L))	-/

		Young	Gulch			Mile Ma	rker 115			FCWTH	<sup>7</sup> Intake	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.00	0.11	0.15	0.20	0.12	0.40	0.50	1.11	0.00	0.44	0.69	0.40
	0.02	0.21	0.20	0.19	0.41	0.32	0.37	0.84	0.02	0.48	0.73	0.40
24hr		0.12	0.04	0.08		0.29	0.34	0.25		0.16	0.21	0.15
		0.10	0.03	0.07		0.20	0.46	0.39		0.13	0.17	0.20

\*- below detection limit, zero used for calculations

		PBR Control Bottom Middle Upper				Centur	y Park			Stevens	Gulch	
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.00	0.20	0.10	0.40	0.20	1.50	0.20	0.20	0.00	0.20	0.30	1.20
	0.00	0.20	0.20	0.40	0.20	0.90	0.30	0.10	0.00	0.10	0.20	1.60
24hr		0.20	0.10	0.50		0.60	0.10	0.00		0.20	0.00	0.60
		0.10	0.00	0.30		0.30	0.20	0.00		0.10	0.30	0.30

 Table 3.21 Manganese (mg/L-Mn) results from Sediment Leaching, Analysis 2

		Young	Gulch			Mile Ma	rker 115		FCWTF Intake			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	0.20	0.00	0.20	0.20	0.00	0.80	0.30	2.00	0.20	0.80	0.60	0.20
onr	0.10	0.00	0.60	0.20	0.00	0.50	0.30	1.80	0.10	0.80	0.50	0.30
24hr		0.00	0.10	0.00		0.20	0.00	0.60		0.40	0.20	0.20
		0.00	0.10	0.10		0.10	0.30	0.30		0.30	0.40	0.20

	PBR					Centur	y Park		Stevens Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	6.78	6.81	6.78	6.73	6.80	6.68	6.82	7.00	6.78	6.87	6.84	6.91
onr	6.81	6.78	6.81	6.76	6.82	6.62	6.85	6.91	6.81	6.85	6.91	6.90
24hr		6.82	6.78	6.76		6.51	6.68	6.80		6.95	6.93	6.82
		6.78	6.75	6.74		6.54	6.74	6.86		6.93	6.94	6.94

 Table 3.22 pH results from Sediment Leaching, Analysis 1

		Young	Gulch			Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	7.35	7.38	7.39	7.37	6.78	6.48	6.65	6.71	7.35	7.29	7.35	7.34	
	7.32	7.40	7.41	7.42	6.81	6.59	6.72	6.74	7.32	7.15	7.36	7.41	
24hr		6.88	6.87	6.95		6.91	6.88	6.82		7.05	7.12	7.06	
		6.83	6.94	7.00		6.90	6.90	6.82		7.06	7.12	7.11	

	PBR					Centur	y Park		Stevens Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6 hr	94.60	102.20	102.40	112.90	81.20	90.40	83.10	83.10	94.60	97.70	100.50	102.40
onr	94.40	102.30	103.10	113.60	81.40	89.20	83.20	83.10	94.40	98.60	100.30	102.30
24hr		103.60	104.50	120.80		93.00	83.50	83.50		97.60	106.80	106.40
		102.20	104.70	120.00		91.50	83.80	83.10		100.40	107.00	101.90

**Table 3.23** Conductivity ( $\mu$ S/cm) results from Sediment Leaching, Analysis 2

		Young	Gulch			Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	95.40	95.30	100.20	98.00	94.60	105.00	110.10	127.50	95.40	133.00	105.10	99.20	
	93.70	96.90	100.20	97.60	94.40	104.50	108.80	125.50	93.70	129.90	104.80	99.30	
24hr		96.40	103.90	101.10		104.90	111.40	138.30		154.80	109.90	103.10	
		96.50	103.90	100.70		103.60	111.30	135.00		155.30	110.20	103.90	

		PB	BR			Centur	y Park		Stevens Gulch			
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper
6hr	0.84	15.30	17.30	25.50	0.37	24.60	16.10	13.10	0.84	12.90	10.80	35.50
	0.71	13.60	20.30	24.40	0.40	25.00	17.20	13.00	0.71	10.70	10.80	32.30
24hr		9.66	10.70	13.40		24.40	12.70	10.50		8.27	7.21	18.10
		9.55	12.20	12.90		18.30	12.60	9.58		7.62	7.71	17.60

 Table 3.24 Turbidity (NTU) results from Sediment Leaching, Analysis 2

		Young	Gulch			Mile Ma	rker 115		FCWTF Intake				
	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	Control	Bottom	Middle	Upper	
6hr	0.42	10.70	11.60	13.20	0.84	20.50	16.00	39.60	0.42	21.40	39.00	28.20	
	0.53	10.50	14.40	11.90	0.71	18.40	13.00	31.50	0.53	17.70	32.40	28.90	
24hr		12.80	5.75	6.75		16.40	10.50	22.70		16.50	17.40	15.70	
		7.04	5.91	6.62		15.40	11.00	18.40		19.20	18.90	18.00	



Figure 3.6 Total Organic Carbon results from Sediment Leaching, Analysis 1



Figure 3.7 Total Nitrogen results from Sediment Leaching, Analysis 1



Figure 3.8 Total Phosphorus results from Sediment Leaching, Analysis 1



Figure 3.9 Iron results from Sediment Leaching, Analysis 1



Figure 3.10 Copper results from Sediment Leaching, Analysis 1



Figure 3.11 Manganese results from Sediment Leaching, Analysis 1



Figure 3.12 pH results from Sediment Leaching, Analysis 1



Figure 3.13 Dissolved Oxygen results from Sediment Leaching, Analysis 1



Figure 3.14 Temperature results from Sediment Leaching, Analysis 1



Figure 3.15 Conductivity results from Sediment Leaching, Analysis 1



Figure 3.16 Turbidity results from Sediment Leaching, Analysis 1