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Keck Geology Consortium: Projects 2012-2013
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Annette Patton, Whitman College Geology Department
Research Advisor: Nicholas Bader

INTRODUCTION

Manganese (Mn) is a trace element found in soils, water, and solid minerals including Mn oxides, sulfides, carbonates, and silicate minerals (Klein and Dutrow, 2007). The dominant oxidation states of Mn in most soils are Mn^{3+} and Mn^{4+} in the solid component and Mn^{2+} ions in solution (Mundus et al., 2012). Manganese soil distribution generally follows addition profiles with higher concentrations near the surface resulting from atmospheric input and plant cycling (Herndon and Brantley, 2011). In areas of high industrial activity, additional anthropogenic inputs of Mn from the atmosphere can be significant. Gradual release of Mn from parent rock also contributes to its presence in soil (Mukhopadhyay and Sharma, 1991). In natural systems, soil functions as an Mn storage system by accumulating surface inputs of Mn and slowly releasing it into groundwater (Herndon and Brantley, 2011).

Manganese is an essential micronutrient for both plants and animals and is widely used as a cofactor in several photosynthetic and metabolic reactions (Mukhopadhyay and Sharma, 1991; Mundus et al, 2012). Plants acquire Mn through uptake of soluble Mn^{2+} ions; Mn^{3+} and Mn^{4+} oxides are unavailable to most plant species (Mukhopadhyay and Sharma, 1991; Mundus et al, 2012). In excessive quantities, Mn becomes toxic to plant functions as it effectively competes with magnesium and interferes with the uptake of this and other nutrient cations (Mukhopadhyay and Sharma, 1991). High levels of Mn in drinking water or food can also lead to health problems in human populations (U.S. Environmental Protection Agency, 2004).

Mn bioavailability depends upon several environmental factors, including Mn concentration, soil pH, presence of soil fauna, soil structure, abundance of organic matter, and saturation (Mukhopadhyay and Sharma, 1991). Soil pH generally plays a particularly important role in Mn availability. Due to the increased solubility in low pH systems, Mn becomes highly available in acidic environments and may become toxic to plants (Mundus et al, 2012). In alkaline soils, Mn is more likely to form Mn^{3+} and Mn^{4+} oxides, often resulting in Mn deficiency.

STUDY AREA

The study area is located in the Boulder Creek watershed in the Front Range, Colorado, USA. Dethier and Ouimet (this volume) provide a general location map. The Boulder Creek watershed is 1160 km^2 in area and extends from the Continental Divide to the Great Plains, ranging from 1480 m to 4120 m in elevation (Langston et al., 2011). Reservoirs throughout the watershed are used as a major water source for the City of Boulder and other small communities. Variations in the water chemistry of these drainage systems can therefore lead to reduced drinking water quality or difficulty in water treatment (Murphy and Writer, 2011).

GEOLOGIC BACKGROUND

The climate of the Colorado Front Range is strongly controlled by topography, which forces orographic precipitation of maritime weather systems originating from the Gulf of Mexico (Veblen and Donnegan, 2005). Annual precipitation increases with altitude and mean annual temperature decreases.

The Boulder Creek watershed is underlain primarily by highly fractured Precambrian granodiorites and high-grade metamorphic rocks (Langston et al., 2011). In higher areas of the watershed, bedrock is overlain by glacial sediment (Birkeland et al., 2003). Soils in the Boulder Creek watershed vary with respect to several climatic conditions, including elevation, topography and aspect (Birkeland et al., 2003). Soils throughout the watershed are also characterized by significant input of parent material from airborne dust.

Forest fires are common throughout the Front Range and have significant impact on biogeochemical cycles. Wildfires commonly alter the soil and hydrologic properties in the areas where they occur, in part by increasing surface runoff and physical erosion (Murphy and Writer, 2011). These changes often result in flooding and debris flows. Some studies suggest that fire may also reduce water quality by increasing pH, turbidity, and concentration of some metal ions in solution.

DESCRIPTIONS OF STUDY BASINS

Within the Boulder Creek watershed, soil samples were collected from four tributary basins including Fourmile Canyon, Betasso Gulch, and Gordon Gulch. The Betasso watershed ranges from 1810-2024 m in elevation and is characterized by a low-precipitation foothills climate regime (Boulder Creek CZO, 2013). This area is dominated by Ponderosa Pine (*Pinus ponderosa*) forests on south-facing slopes and mixed Ponderosa and Douglas Fir (*Pseudotsuga menziess*i) forests on cooler north-facing slopes.

Gordon Gulch lies within a montane climate zone at 2446-2737 m elevation and is characterized by mixed conifer forests with Ponderosa Pines, Douglas Firs, and Lodgepole Pines (*Pinus contorta*) (Boulder Creek CZO, 2013; Veblen and Donnegan, 2005). Precipitation in both Betasso and Gordon Gulch reaches a maximum of approximately 10 cm in May with a second peak in September to October. Precipitation at these sites reaches a minimum of less than 2 cm/month during the winter.

The Green Lakes Valley lies in the upper catchment of the Boulder Creek watershed between 3567-3745 m (Boulder Creek CZO, 2013). The site receives 100 cm/year of precipitation on average, of which approximately 80% is snowfall that occurs during the winter months (Caine, 1989). The upper portion of the basin is dominated by an alpine tundra environment with extensive talus exposure, sparse vegetation and relatively little exposed soil. The lower extent of the Green Lakes Valley is characterized by a subalpine climate and is inhabited primarily by forests of Subalpine Fir (*Abies lasiocarpa*) and Engelmann Spruce (*Picea engelmannii*) (Birkeland et al, 2003).

Fourmile Canyon is a large tributary watershed in the foothills north of Boulder Creek. Approximately 23% of the canyon ($26 km^2$) was burned in a forest fire on September 6-10, 2010 (Murphy and Writer 2012). In most areas, the fire burned needles and twigs but left standing trunks and large branches. The fire occurred during a dry period in September of that year and rainfall directly following the event was limited until the following spring (Murphy and Writer, 2011). Significant mobilization of sediment therefore did not occur until snow melted the following summer. Since that time, deforestation of the steep slopes in the burned area has lead to an increased risk of flooding and severe erosion (Murphy and Writer 2011; 2012). The fire also exposed historic gold mine tailings and waste rock, which may have resulted in increased transport of sediment and metals into Fourmile Creek.

METHODS

Soil samples were taken from soil pits throughout the Boulder Creek CZO that were chosen to represent variations in slope aspect, elevation, and exposure to wildfire. From these pits, samples were collected at representative metric intervals from the the surface litter to saprolite, where saprolite was defined as parent material that has undergone significant chemical alteration but has not been transported (Langston, 2011). At each of these sites, vegetation samples were also collected from dominant tree species. Sample sites of interest include four proximal sites in Fourmile Canyon, of which one site was outside of the main burn area of the 2010 fire, two sites were representative sites within the burned area, and one site was within a plot that was exposed to the 2010 fire and that has been protected from rainfall and surface disturbance by tarpaulins since the fire occurred. Figure 1 shows the soil profile of this protected sample site within

Figure 1: (Title = Sample Site in the Fourmile Burn Area. Sample site in the burn area that was protected from rainfall by tarpaulins since the 2010 fire. Samples were collected from depths of 1, 2, 8, 12, 16, 10, 30, 40 and 60 cm. Surface layers were very dark and ashy.

Fourmile Canyon. The upper 1-5 cm were composed primarily of a very fine, dark ash. Additional sample sites in Betasso Watershed, Gordon Gulch, and the high-elevation Green Lakes Valley were also examined.

The pH of each of the samples was measured in deionized water according to the Soil Science of America standard (Thomas, 1996). Soil-extractable Mn was measured according to the Canadian Society of Soil Science standard to estimate the Mn concentration available for uptake by plants (Liang and Karamanos, 1993). Ten g samples of air-dried soil were mixed in a solvent solution of diethylene triamine pentaacetic acid (DTPA), $CaCl_2$, treiethanolamine (TEA), HCl, and deionized water. The sample and solution mixture was placed on a horizontal shaker table for two hours and filtered. The filtrate was analyzed using a Flame Atomic Absorption Spectrometer. Bulk Mn concentrations were measured by Acme Analytical Laboratories using an ICP mass spectrometer. Total Mn of the dry-ashed vegetation samples was measured by the Oregon State University Central Analytical Laboratory using an ICP-MS.

RESULTS

Concentrations of extractable Mn are highly variable in the Boulder Creek Critical Zone soils and range from 0.5-145 ppm. In Figures 2 and 3, Mn concentrations of individual sample sites have been plotted against depth. Throughout the Boulder Creek watershed, soil profiles generally follow addition profiles with highest concentrations of both bulk and extractable Mn near the soil surface. Bulk Mn concentrations ranged from 600-2200 ppm in the soils of Fourmile Canyon. Figure 2 displays extractable Mn profiles for representative sample sites within each of the four watersheds. Soils in Betasso watershed generally contained higher concentrations of extractable Mn compared to samples collected from the other watersheds. These soils also demonstrate a more irregular soil profile pattern

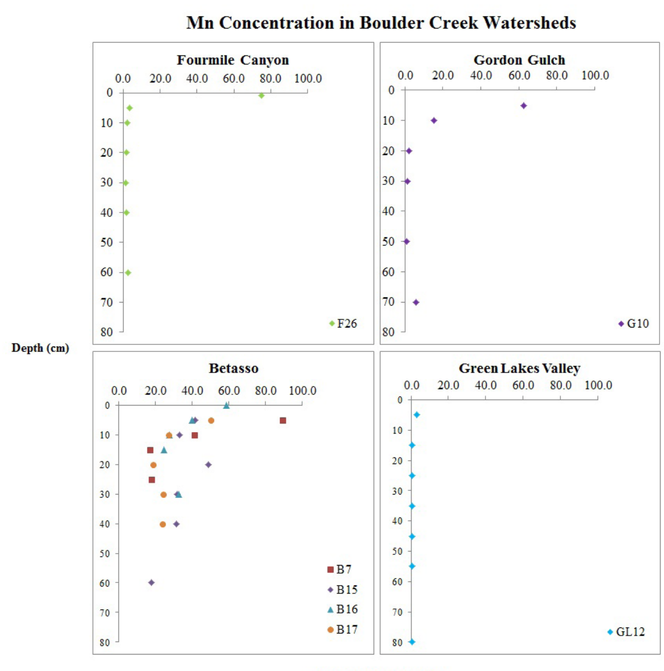

Figure 2: (Title = Extractable Soil Mn Concentrations in Boulder Creek Watersheds) Profiles of DTPA-extractable Mn for representative sample sites within each of the four study sites within the Boulder Creek watershed, CO. Depth is measured in cm from the soil surface.

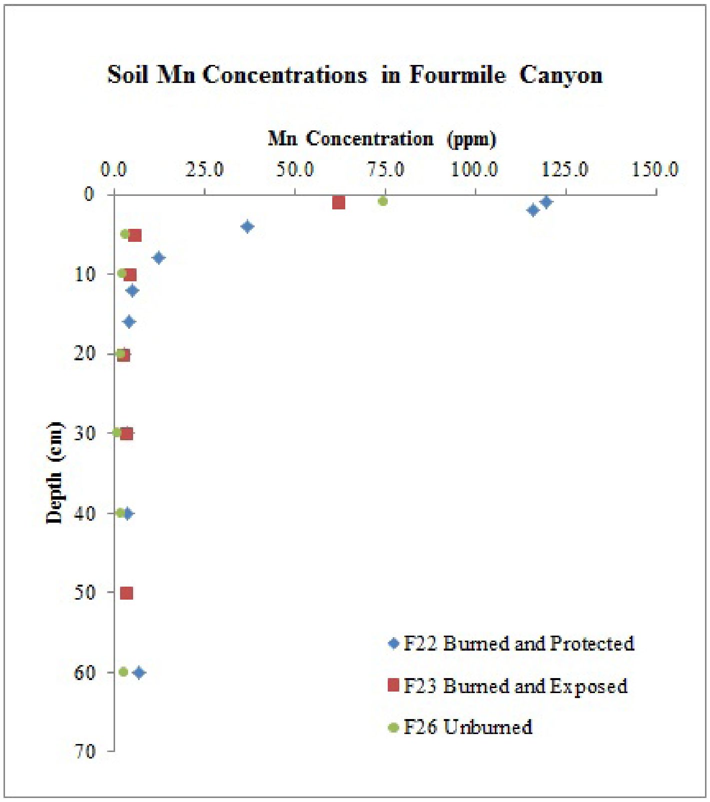

Figure 3: (Title = Extractable Soil Mn Concentration in Fourmile Canyon) Soil profiles of DTPA-extractable Mn in soils from burned and unburned sites in Fourmile Canyon, CO. Depth is measured in cm from the soil surface.

with respect to Mn concentration. Extractable Mn concentrations in the high-elevation soil of the Green Lakes Valley were generally lower than those found in low elevation sites.

The surficial soil in the Fourmile Canyon site that was burned in the 2010 fire and protected by tarpaulins demonstrates significant enrichment of extractable Mn concentration relative to the unburned soil in Fourmile Canyon and to the adjacent burned site that has been exposed since the fire (Fig. 3). Bulk Mn concentration in this sample site is approximately 2200 ppm in the top 1 cm. From 5-60 cm depth, bulk Mn ranges from 1100-1300 ppm. The ppm extractable Mn in the top centimeter of soil in the protected sample pit was nearly twice that of the top centimeter sample from the exposed site. The unburned site contained slightly higher concentration of extractable Mn in the top centimeter of soil relative to the site that was burned and exposed. Mn concentrations of all three sites at depths below 10 cm are similar.

Table 1 summarizes mean foliar Mn for the dominant species in the study catchments of the Boulder Creek Watershed. Total Mn concentrations are variable but appear to generally increase with altitude.

Table 1: (Title = Foliar Bulk Mn Concentrations of Dominant Tree Species) Mn concentration (ppm) in needles and twigs of dominant tree species in each of the study sites within the Boulder Creek watershed. Vegetation sampled within the Green Lakes Valley include spruce (Picea spp), willow (Salix spp) and Limber Pine (Pinus flexilis). Errors given are one standard deviation.

	Foliar Mn Concentration (ppm)				
Species	Fourmile	Betasso	Gordon Gulch	Green Lakes	All Samples
Juniper spp.	86 ±15 (n=2)	94 ± 34 (n=3)	-	-	91 ± 26 (n=5)
Ponderosa Pine	71 ± 3 (n=2)	98 ± 22 (n=11)	138 ± 26 (n=2)	-	99 ± 26 (n=15)
Lodgepole Pine	72 (n=1)	-	156 ± 35 (n=6)	-	144 ± 45 (n=7)
Douglas Fir	103 ± 37 (n=2)	107 ± 30 (n=4)	172 ± 32 (n=3)	-	127 ± 44 (n=9)
Total	84 ± 22 (n=7)	99 ± 23 (n=18)	157 ± 32 (n=11	123 ± 57 (n=4)	117 ± 39 (n=42)

Keane (2008) summarized foliar litterfall rates for these species in various forests in the western United States. Ponderosa Pines drop approximately 0.29 kg of needles/m^2/year in California and Arizona, Douglas Firs drop approximately 0.12-0.15 kg of needles/m^2/year in the northern Rocky Mountains, and Lodgepole Pines drop approximately 0.362 kg of needles/m^2/year. Table 2 summarizes estimated yearly inputs of Mn from needle-fall in each of the study watersheds based on the total mean Mn concentrations of needle samples in each watershed and the litterfall rates of the dominant species listed in Keane, 2008. Assuming that the Douglas Fir and Lodgepole Pine are not significant species in Fourmile Canyon and that 0.29 kg of needles/m^2/year is representative of annual litterfall in the burned area, the total yearly input of Mn from litterfall in would be approximately 24 mg/m^2/year or 630 kg/year total in the entire 26 km^2 burned area prior to the fire.

Measured pH values of soils from these sample sites did not perfectly follow the trend of increased acidity at high elevation. Average soil pH was 6.10 ± 0.50 (n=35) in the Fourmile sample sites, 5.67 ± 0.51 (n=30) in the Betasso sample sites, 5.61 ± 0.56 (n=13) in the Gordon Gulch sample sites, and 5.93 ± 0.36 (n=7) in the Green Lakes sample site.

Table 2: Calculated yearly input of Mn per area in each of the study basins. Needle-fall rate is averaged for the primary species listed as is estimated by Keane, 2008 and total mean foliar Mn is the average of all healthy vegetation samples collected in each basin. Errors given are one standard deviation.

Mn Input from Needle-fall

Watershed	Primary Species	Needle-fall Rate (g/m^2/year)	Total Mean Foliar Mn (μg/g)	Yearly Mn input (mg/m^2/year)
Fourmile	Ponderosa	290	84 ± 22 (n=7)	24
Betasso	Ponderosa	290	99 ± 23 (n=18)	29
Gordon Gulch	Ponderosa, Lodgepole, Douglas Fir	262	159 ±32 (n=11)	42
Green Lakes	Spruce spp, Limber Pine	200	123 ±57 (n=4)	25

DISCUSSION

Mn enrichment in soil samples of burned areas in Fourmile Canyon appears to reflect the release of Mn from vegetation as ash that was added to the soil surface during the fire. Based on the the calculated yearly input of Mn and on the pattern of enriched surface soils, needle-fall and decomposition of plant litter adds significant quantities of Mn to surface soils. Wildfires ash a large portion of this foliage as well as the accumulated duff layer on the soil surface, releasing all of the Mn contained in needles and surface duff in a single event.

The discrepancy between the protected and exposed pits within the burned area of Fourmile Canyon demonstrates the potential for mobilized Mn ions to be lost to surface runoff and groundwater flow. Surface Mn concentrations may even decline following a fire due to leaching of Mn ions and erosion of Mn-rich sediment that results from increased surface runoff. These data correlate with the high levels of Mn that have been measured in solution in Fourmile Creek in the summer following the 2010 fire (Beganskas, 2012). Mn-rich surface water poses an additional water quality concern in high-runoff post-wildfire hydrogeological regimes and may lead to reduced nutrient availability for future forest growth in Fourmile Canyon.

Variability in extractable Mn concentration between each of the study basins likely reflects variations in annual precipitation and forest type. Extractable Mn concentration in the Boulder Creek watershed does not appear to strongly reflect average soil pH. The Mn concentrations of sample sites within each watershed (Fig. 2) do appear to follow a pattern of lower Mn concentration at high elevation. Betasso watershed demonstrates a relatively high Mn concentration, while Gordon Gulch displays a slightly lower overall Mn concentration and the Green Lakes Valley displays very low concentrations of extractable Mn. This pattern likely reflects the increased precipitation at high elevations, which allows for leaching of soluble Mn from the soil profile. Lack of precipitation in lower elevation sites in Betasso allows for accumulation of higher concentrations of soluble Mn that is added to the soil either by continuous processes like litter-fall or by wildfire events.

CONCLUSIONS

Manganese concentration measurements clearly demonstrate the impact of fires on Mn nutrient cycling in Front Range soils. Immediate release of all foliar Mn adds significant extractable Mn to the soil surface and disrupts biogeochemical cycles. Increased sediment and ion mobility in post-fire soils may then release increased concentrations of soluble ions into stream systems.

The trends within each sample basin also demonstrate the influence of the climatic zone on extractable Mn concentration; high yearly precipitation appears to leach the soil of soluble Mn ions and results in very low Mn availability, while the limited precipitation at lower elevations appears to allow for a greater accumulation of soluble Mn in the soil profile. Consistent with the limited industrial activity of the region, the data do not suggest that natural processes are more significant than industrial Mn inputs in the Boulder Creek watershed. Additionally, soil pH does not seem to be a reliable indicator of extractable Mn concentration in the Boulder Creek watershed, indicating that abundance of organic matter and depth, climate regime, exposure to wildfire, and other factors are more important in influencing bioavailable Mn concentrations in soils of the Boulder Creek watershed.

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