**Examining Spatial Differences in Soil Solute Chemistry in a Semi-arid Montane Catchment, Manitou Experimental Forest, Colorado.**

by

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## Abstract

Biogeochemical properties of soils play a crucial role in soil and stream chemistry throughout a watershed. How water interacts with soils during subsurface flow can have impacts on water quality, thus, it is crucial to understand where and how certain soil water chemical processes occur within a catchment. In this study, ~200 soil samples were evaluated throughout a small catchment in Manitou Experimental Forest to examine spatial and vertical patterns in major soil solutes among different landscape units: riparian areas, alluvial fans, and steep hillslopes. Solutes were extracted from the soil samples in the laboratory and analyzed for major cation (Li, K, Mg, Br, and Ca) and anion (F, Cl, $NO_2$, $NO_3$, $PO_4$, and $SO_4$) concentrations using ion chromatography. Concentrations of most solutes were greater in near surface soils (10cm) than in deeper soils (100cm) across all landscape units, except for fluoride which was found to increase with depth. Potassium was found to have the highest variation between depths, with the largest range of 1.039 mg/l (100 cm) to 3.127 mg/l (10 cm) being in riparian areas. Nearly every solute was found to be enriched in riparian areas, with mean concentrations being higher than the hillslopes and fans, $NO_3$ being the only notable exception with concentrations greater in the alluvial fans. Br, $NO_2$, and $PO_4$ concentrations were often below the detectable limit, and Li and Na were not variable between depths or landscape units. Overall, based on the comparisons between depths and landscape units, findings suggest that K, Ca, F, and $NO_3$ solutes may serve as valuable tracers to identify subsurface flowpaths from different landscape units and depth within this catchment.

**Introduction:**

Montane ecosystems and their complex topography play a crucial role in the quality and availability of water in the Colorado Front Range (Godsey et al., 2019). Understanding montane catchment hydrologic connectivity and flowpaths informs and aids forest and hydrologic management, which is especially important for dry environments with seasonal precipitation inputs (Bukoski et al., 2021). Topography influences surface and subsurface hydrology, and thus vegetation, soil chemistry, and nutrient patterns (Molina et al., 2019; Sadiq et al., 2021; Seibert et al., 2007). How water flows along and beneath the surface determines local soil wetness and decomposition behaviors, which in turn alters soil chemistry (Seibert et al., 2007). Additionally, topographically-driven flowpaths influence soil structures via weathering, altering the physical and chemical characteristics and hydrologic capacities of soils (Sadiq et al., 2021). Gaining knowledge on how topography controls soil water chemistry and flowpaths is essential for managing forest and water resources, especially when considering anthropogenic climate change and disturbances in montane systems (Covino, 2017; Dai et al., 2018). With climate change impacting montane zones at a disproportionally high rate, information regarding topographic variation in soils and their control on water quality is of growing importance (Bukoski et al., 2021)

Several characteristics of soil composition, such as distribution of organics or subsurface geologic structure, can alter soil water solute concentrations and stream chemistry. Variations in soil water chemistry can aid in determining flowpaths from upland soils to the stream (Botter et al., 2020; Covino, 2017; Herndon et al., 2015; Jencso & McGlynn, 2011). Soil solutes have been evaluated in previous studies mainly through the concentration-discharge ratio from stream samples, which infer how different flowpaths in the subsurface impact stream solute

concentrations (Botter et al., 2020; Godsey et al., 2009; Herndon et al., 2015). Generally, high discharge leads to a diluting effect, resulting in lower levels of geogenic or biogenic solutes in the water, however, this effect varies by the specific solute (Botter et al., 2020; Godsey et al., 2019). For instance, stream samples with elevated concentrations of magnesium (Mg), fluoride, (F), and sodium (Na) are commonly considered to indicate deep flowpaths along bedrock (Kiewiet et al., 2020). In contrast, nitrogen (N), calcium (Ca), phosphate ($PO_4$), and potassium (K) concentrations are typically related to shallow flow through vegetated areas, and sulfate ($SO_4$) is associated with redox conditions (Christopher et al., 2006; Kiewiet et al., 2020). Stream solute concentration-discharge (C-Q) relationships can provide valuable information regarding general flowpath characteristics, but do not allow for an in-depth spatial evaluation to be conducted. By knowing how different topographic features and positions effect soil solute production and transport, a greater understanding can be gained on where dominant flowpaths exist within a catchments and the how flow through certain landscape units can effect stream chemistry (Godsey et al., 2009).

Stream water chemistry has been evaluated through C-Q ratios to indicate how different discharge levels effect solute transport; however, it has not been examined on the smaller scale of direct soil solute measuring spatially or at depth. In the most comprehensive stream solute evaluation, Botter et. al. (2020) used solute concentrations from stream samples across hundreds of catchments around the world and evaluated the vertical and temporal relationships between different C-Q ratios. Numerical models accompanied with known solute information (i.e. geogenic vs. biogenic solutes) were used to infer the depth of subsurface flow, with geogenic solutes indicating deep bedrock flow and biogenic solutes reflecting shallow subsurface flow. Through these numerical experiments they found varying dilution effects among solutes,

different C-Q ratios among different catchment environments, and a reduction in solutes with depth. This finding of differing solute concentrations at depth suggests heterogenous subsurface flow throughout the catchments, however, they did not apply any further inferences on which landscape units contribute to different solutes, or their implications on water quality or availability (Botter et al., 2020). While this study has found valuable relationships among solutes at depth and catchments through modeling, the scale of research and the methods used do not allow for in-depth spatial relationships to be made about how local topography and soil structures can influence water chemistry within a single headwater catchment.

While stream sampling has been the main avenue for water solute analysis, fewer spatial inferences can be made aside from the relative depth where the solutes generally originate (i.e. shallow versus deep; Botter et al., 2020). One method to evaluate spatial hydrologic connectivity and flowpaths is to examine soil solute chemistry from laboratory extraction of soil. This lab-based procedure is a less resource- and labor-intensive way to determine the potential spatial variability in water chemistry. By extracting cation and anions via soil extractions (simulated infiltration and runoff), the spatial variability in soil chemistry can be determined and thus, the flowpath that water takes as it passes through the soil and enters stream systems (Covino, 2017). Additionally, by examining soil solute concentrations across different landscape units within a catchment directly rather than through modelling with stream samples, a more local analysis of hydrologic connectivity and subsurface flowpaths can be conducted, providing more information on where certain solutes originate within a catchment and at which depths.

The goal of this study is to determine how soil solute concentrations vary across landscape units (hillslope, riparian, and alluvial fan) in a montane catchment. I specifically investigated: how do major cations and anions vary with depth within a given landscape unit;

and how do cations and anions differ among the landscape units within the catchment? By conducting thorough soil sampling throughout the catchment and extracting the solutes, a more comprehensive and direct analysis can be made regarding soil chemistry and how it may affect stream chemistry.

**Methods:**

*Site Description:*

This study was conducted in Manitou Experimental Forest (MEF, 39.1006°N, 105.0942°W), located roughly 77 kilometers northwest of Colorado Springs, Colorado, USA. At about 2,750 meters elevation, this montane zone has a semi-arid climate, receiving 39.6 cm of precipitation annually, most of which occurs in afternoon thunderstorms during the growing season (April through August). The climate is generally cool, ranging in average temperatures of -2° C low in January and a 19° C high in July. Topography of the area is variable, ranging from steep hillslopes to gradual alluvial fans and densely vegetated riparian areas. Dominant plants species include ponderosa pine (*Pinus ponderosa),* Douglas-fir (*Pseudotsuga menzisii*), and aspen (*Populus tremuloides*), with Engelmann (*Picea engelmannii*) and blue spruce (*Picea pungens*) growing in the damper areas of the landscape (USFS, n.d.). Soils in the area are primarily sandy loam and sandy gravelly loams, weathered from sandstone and granitic formations, ranging from slightly acidic to alkaline (pH 6.1-7.8) (Ortega et al., 2014). The drier south-facing slopes are characterized by looser, very gravelly coarse sandy loam, and the north-facing slopes had slightly more fine gravelly coarse sandy loam (NRCS, 2022). Soils become more organic and fine in the alluvial fan and riparian areas, with fine and very fine sandy loams

accompanied by increased vegetation (NRCS, 2022). Bedrock lies about 1.8 m below the soil, however there are numerous outcroppings across the landscape (Ortega et al., 2014).

Soil samples were collected from the headwaters of Hotel Gulch within MEF, which includes a main unnamed stream system (Hotel Stream for the purposes of this study) consisting of three subcatchments: A, B, and AB corresponding to different tributaries and their drainage areas. Samples were taken from three sites along stream segment A (A0, A3, and A5 with the site code increasing with distance from the headwaters). The smaller tributary, B, only had one sampling site, B2, as it has a shorter stream length and had a more homogenized environment compared to the A reach. Similarly, sampling was only conducted at one site of the convergence of reach A and the smaller reach B stream (AB), called AB3. In order to observe spatial patterns in soil chemistry, the study area was aggregated into three major landscape units: hillslope, alluvial fan, and riparian. Hillslopes are characterized by steep slopes with sandy soiled features on each side of the stream. Dominated by larger conifers, hillslopes are vegetated more sparsely than the riparian or south-facing fan landscapes. Riparian landscapes are densely willow dominated areas in close proximity to the stream. These landscapes have more diverse vegetation patterns than the other landscapes, and have dense, damp, and heavily organic soils. Alluvial fans are similar to riparian, but have sandier soils deposited from upslope areas and more homogenous, slender cinquefoil (*Protentilla gracilis*) dominated vegetation. Fans were mostly present on the south-facing side of the stream, and differed from the hillslopes in both vegetation patterns and in slope, with more grassy vegetation and gradual grades (NRCS, 2022).

Each A site had alluvial fan landscape units, typically present on the south-facing side of the stream, which B2 and AB3 did not. B2 is characterized by a narrower landscape, with steep slopes on both the north and south-facing slopes, intermediated by a riparian area around the

stream. AB3 is similar to other A sites, with a wide area between slope aspects, however, it did not have a distinct fan landscape unit.

*Sampling:*

At each sample point, bucket-type augers were used to sample from four depths: 10, 30, 50, and 100 centimeters. Three replicate samples were taken at each sampling location, which were then placed in a plastic bag and labelled, including the site, landscape unit, depth, slope aspect, and sample code. Each of the three sampling plots were backfilled once sampling was complete for each depth. Location coordinates were recorded using a handheld GPS. Once collected, the samples were placed in coolers with ice packs for transportation to the laboratory and were kept in a -28° C freezer until processing.

*Sample Processing:*

Samples were processed using a soil water extraction method in order to measure solute chemistry. Once thawed, large rocks and organic materials were removed from the soils using a 2 mm sieve. Next, 10 g of sieved soils were measured, placed in an Erlenmeyer flask, saturated with ultra-pure deionized water, overturned to mix the solution, and placed on a shaker table for 24 hours at 200 rpm. Once removed from the shaker table, samples were placed in a centrifuge (ThermoFisher Sorvall ST 16) to separate the sediment from the extraction solution. 50 mL of the mixed solution was placed into centrifuge vial and spun at 5000 rpm for 20 minutes. The extracted water was then transferred from the centrifuge vials to HDPE bottles for filtering, removing most of the sediments. The extracted water samples were kept at 2° C and were filtered within 48 hours of centrifuging. Filtering was conducted using several vacuum pump assisted

filtering towers with Whatman 42 Nuclepore 1 μm filters. First, the filters are rinsed with deionized water, followed by 10 mL of sample to prime the filters. The filtering tower was then emptied, and the remainder of the sample was filtered. Samples were filtered twice, as small particles of sediment were still present after the first pass of filtering. Filtered extractions were then transferred to opaque Nalgene bottles and frozen at -28° C until ion chromatography (IC) analysis.

To measure solute concentrations, the soil extractions were analyzed by ion chromatography for both anions (F, Cl, $NO_2$, Br, $NO_3$, $PO_4$, $SO_4$) and cations (Li, Na, $NH_4$, K, Mg, Ca). Sample duplicates along with analytical blanks and known standards were ran in each run to ensure instrument accuracy. The mean accuracy for the ion chromatography was +/- 2.5% of the known concentrations from the standards.

*Data Analysis:*

In order to evaluate spatial and vertical differences among solutes, several series of t-tests were run among depths, landscape units, and depths at specific landscape units. First, t-tests were run for each total solute at each landscape unit to identify any significant differences in solutes between depth for each landscape. Next, t-tests were run for average solute concentrations among all depths between landscape units in order to see if there were any significant differences in concentration among different areas. Last, another series of t-tests were conducted among each landscape, for each solute, at every individual depth. These different levels of statistical testing allowed for solute concentration differences to be identified between landscape units, depths, and landscape units at each depth. All t-tests were evaluated at the $\alpha = 0.05$ level of significance.

**Figure 1:** Sampling sites and subcatchments of the study area within Hotel Gulch in the Manitou Experimental Forest.

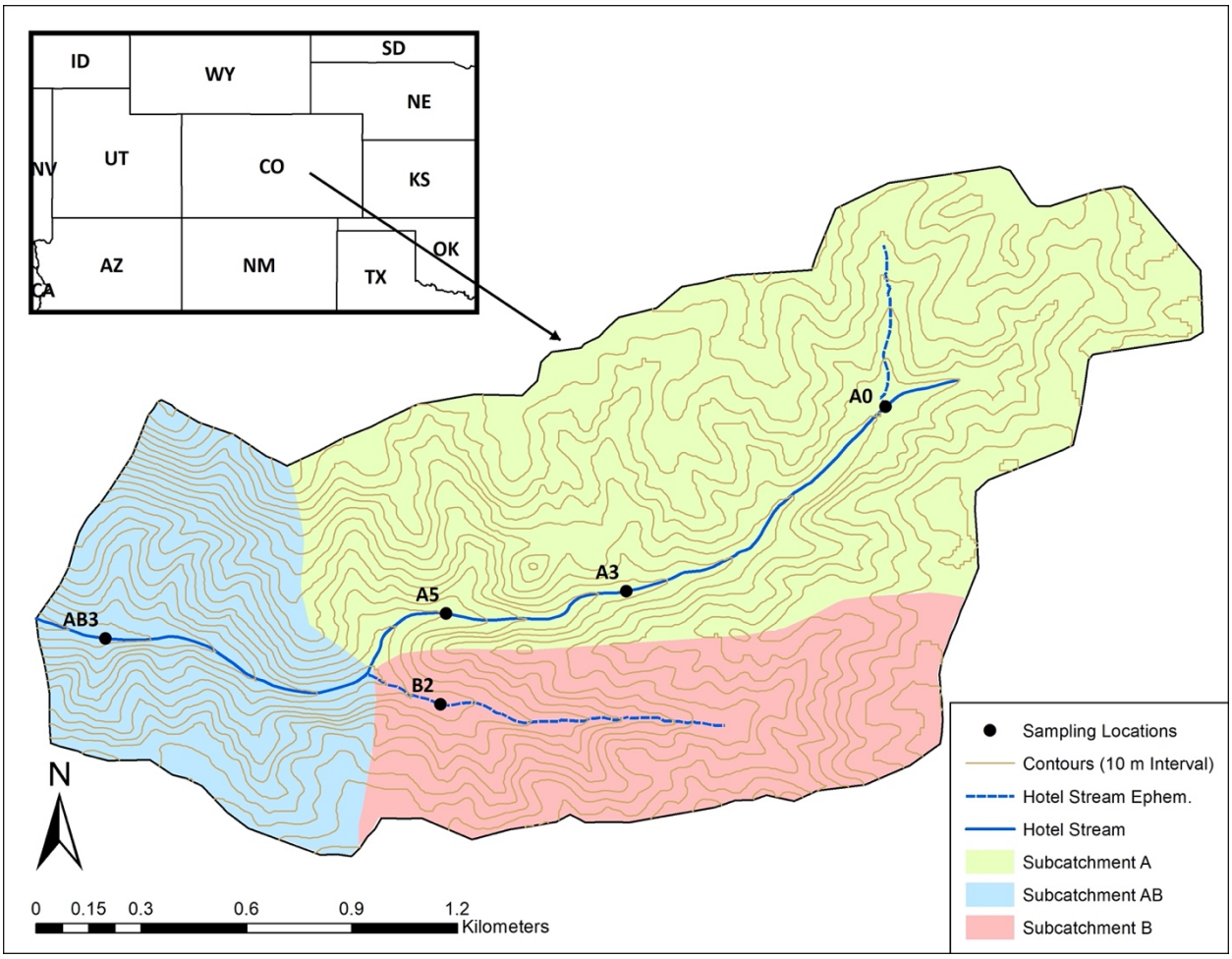



**Table 1:** Vegetation characteristics at each landscape unit and number of samples at each landscape unit and depth.

| **Landscape Unit** | **10 cm** | **30 cm** | **50 cm** | **100 cm** | **Vegetation Characteristics** |
|---|---|---|---|---|---|
| North-Facing Hillslope | 13 | 13 | 12 | 11 | Douglas-fir (*Pseudotsuga menziesii*), Lodgepole pine (*Pinus contorta*) |
| South-Facing Hillslope | 11 | 11 | 10 | 9 | Ponderosa pine (*Pinus ponderosa*) |
| Alluvial Fan | 10 | 11 | 10 | 8 | Grasses, Cinquifoil (*Potentilla reptans*) |
| Riparian | 15 | 13 | 17 | 10 | Grasses, Coyote willow (*Salix Exigua*) |

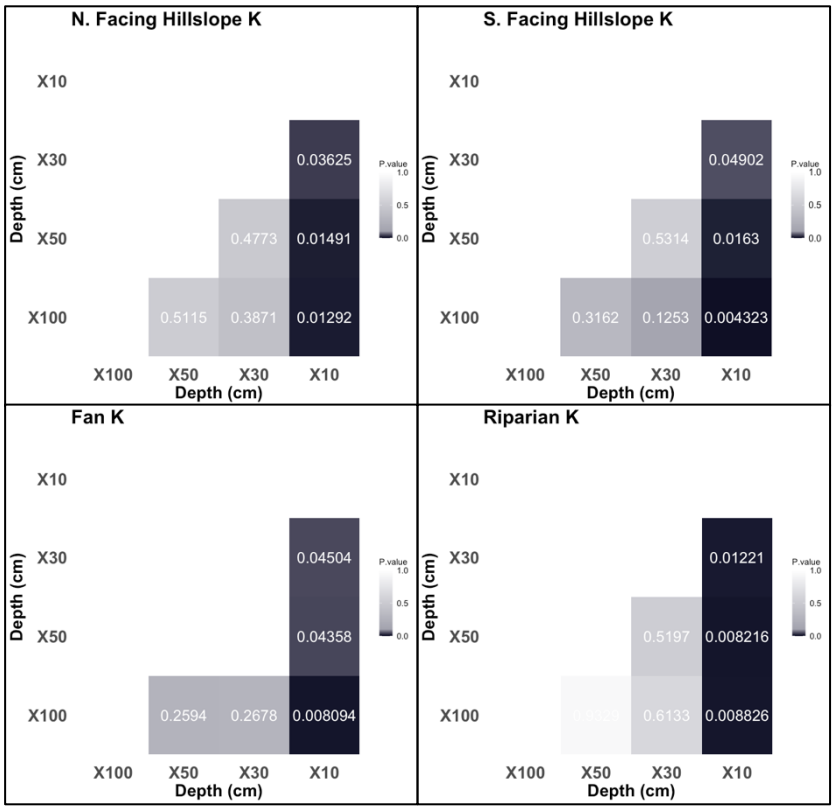
**Table 2:** Mean and standard error for each of the studied cation concentrations at each depth, and bulk, for every landscape unit.

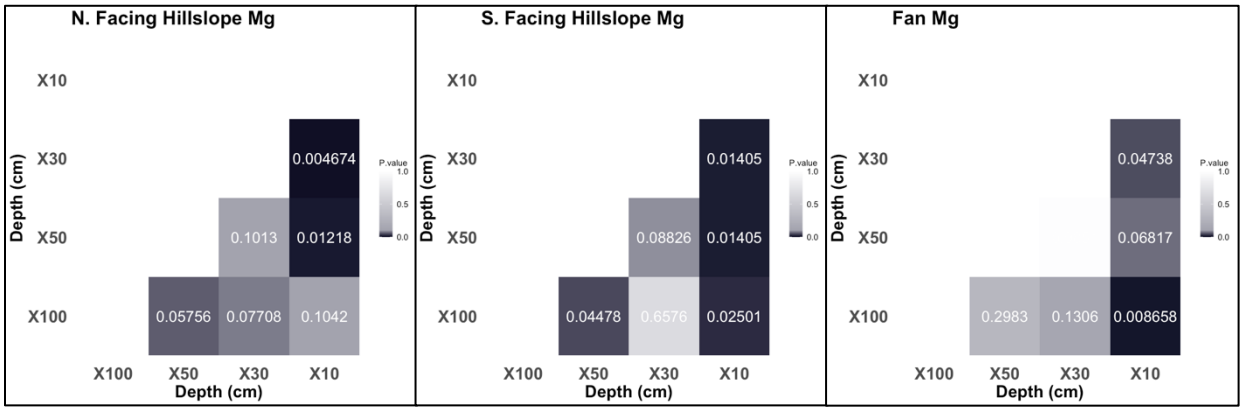
| **Landscape Unit** | **Li** | **Na** | **K** | **Mg** | **Ca** |
|---|---|---|---|---|---|
| | Mean / STD Error | Mean / STD Error | Mean / STD Error | Mean / STD Error | Mean / STD Error |
| **North Facing Hillslope** | | | | | |
| 10 cm | 0.043 / NA | 0.659 / 0.09 | 1.775 / 0.327 | 0.334 / 0.033 | 2.275 / 0.302 |
| 30 cm | 0.036 / 0.004 | 0.546 / 0.054 | 0.958 / 0.149 | 0.22 / 0.006 | 1.483 / 0.602 |
| 50 cm | 0.034 / 5e-04 | 0.666 / 0.087 | 0.824 / 0.11 | 0.237 / 0.007 | 1.625 / 0.074 |
| 100 cm | 0.038 / 0.004 | 0.567 / 0.042 | 0.761 / 0.165 | 0.226 / 0.023 | 1.715 / 0.156 |
| Bulk | 0.037 / 0.002 | 0.647 / 0.042 | 1.093 / 0.114 | 0.267 / 0.012 | 1.785 / 0.095 |
| **South Facing Hillslope** | | | | | |
| 10 cm | 0.039 / NA | 0.69 / 0.06 | 2.208 / 0.41 | 0.435 / 0.035 | 3.09 / 0.035 |
| 30 cm | 0.035 / 8e-04 | 0.674 / 0.048 | 1.171 / 0.267 | 0.328 / 0.015 | 2.545 / 0.015 |
| 50 cm | 0.032 / 4e-04 | 0.681 / 0.012 | 0.93 / 0.17 | 0.336 / 0.031 | 2.686 / 0.031 |
| 100 cm | 0.038 / 0.001 | 0.541 / 0.206 | 0.702 / 0.102 | 0.338 / 0.017 | 2.354 / 0.017 |
| Bulk | 0.035 / 0.001 | 0.606 / 0.054 | 1.326 / 0.15 | 0.355 / 0.013 | 2.607 / 0.129 |
| **Alluvial Fan** | | | | | |
| 10 cm | 0.042 / 0.002 | 0.686 / .074 | 2.318 / 0.408 | 0.512 / 0.054 | 3.849 / 0.445 |
| 30 cm | 0.039 / 0.003 | 0.752 / 0.173 | 1.262 / 0.261 | 0.38 / 0.027 | 2.689 / 0.209 |
| 50 cm | 0.039 / 0.002 | 0.839 / 0.201 | 1.26 / 0.252 | 0.379 / 0.042 | 2.636 / 0.275 |
| 100 cm | 0.036 / 0.002 | 0.836 / 0.219 | 0.933 / 0.112 | 0.33 / 0.015 | 2.279 / 0.171 |
| Bulk | 0.039 / 0.001 | 0.803 / 0.089 | 1.428 / 0.153 | 0.398 / 0.02 | 2.855 / 0.162 |
| **Riparian** | | | | | |
| 10 cm | 0.038 / 0.001 | 0.722 / 0.108 | 3.127 / 0.681 | 0.563 / 0.08 | 4.213 / 0.689 |
| 30 cm | 0.039 / 0.001 | 1.135 / 0.284 | 1.148 / 0.153 | 0.486 / 0.068 | 3.469 / 0.45 |
| 50 cm | 0.037 / 0.001 | 0.733 / 0.137 | 1.082 / 0.122 | 0.419 / 0.027 | 3.003 / 0.179 |
| 100 cm | 0.037 / 0.001 | 0.952 / 0.158 | 1.039 / 0.147 | 0.386 / 0.025 | 2.673 / 0.185 |
| Bulk | 0.038 / 0.001 | 0.846 / 0.092 | 1.633 / 0.219 | 0.467 / 0.028 | 3.373 / 0.225 |

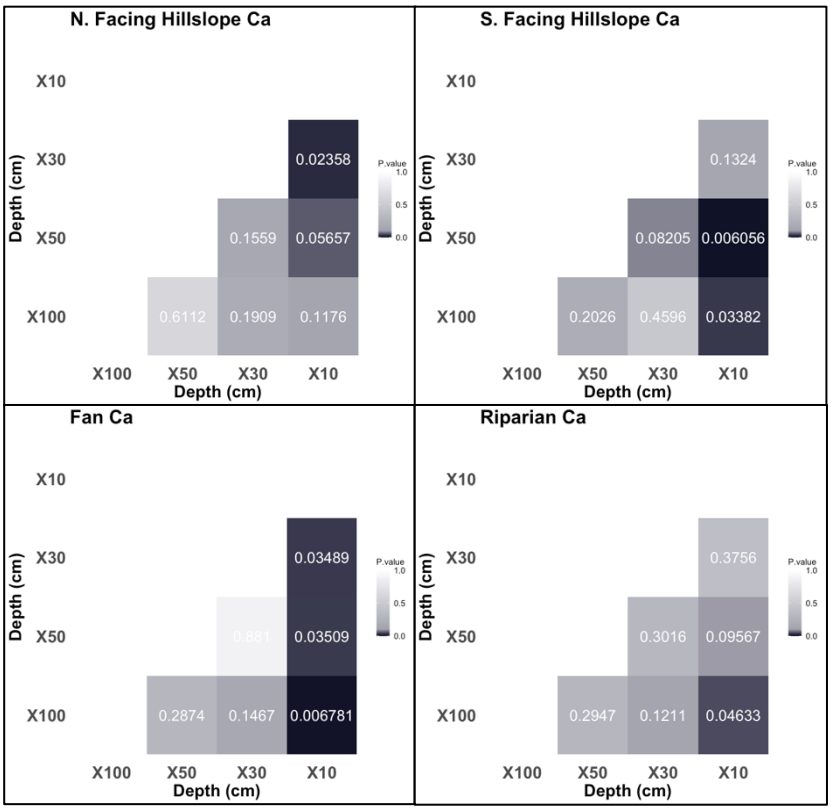
**Table 3:** Mean and standard error for each of the studied anion concentrations at each depth, and bulk, for every landscape unit.

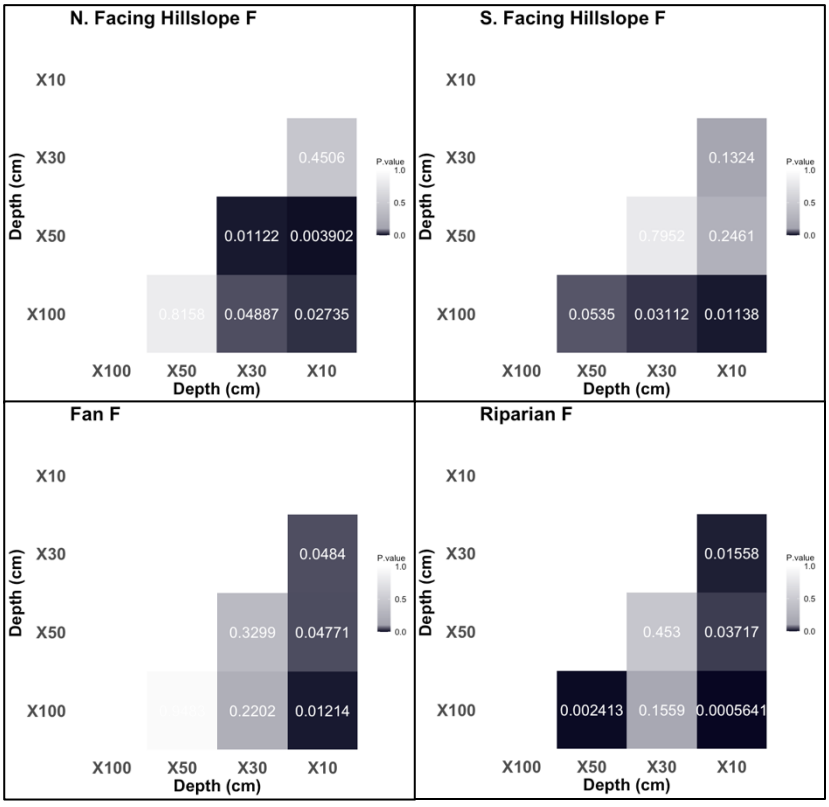
| **Landscape Unit** | **F** | **Cl** | **$NO_2$** | **$NO_3$** | **$PO_4$** | **$SO_4$** |
|---|---|---|---|---|---|---|
| | Mean / STD Error | Mean / STD Error | Mean / STD Error | Mean / STD Error | Mean / STD Error | Mean / STD Error |
| **North Facing Hillslope** | | | | | | |
| 10 cm | 0.0741 / 0.005 | 0.578 / 0.062 | 0.231 / 0.025 | 0.341 / 0.020 | 0.596 / 0.11 | 0.642 / 0.028 |
| 30 cm | 0.081 / 0.007 | 0.369 / 0.057 | NA / NA | 0.299 / 0.009 | 0.389 / NA | 0.649 / 0.052 |
| 50 cm | 0.122 / 0.013 | 0.512 / 0.067 | NA / NA | 0.376 / 0.026 | 1.202 / 0.855 | 0.855 / 0.257 |
| 100 cm | 0.128 /0.02 | 0.387 / 0.056 | NA / NA | 0.553 / 0.209 | 0.395 / 0.023 | 0.578 / 0.03 |
| Bulk | 0.108 / 0.009 | 0.476 / 0.032 | 0.231 / 0.025 | 0.387 / 0.048 | 0.726 / 0.242 | 0.679 / 0.062 |
| **South Facing Hillslope** | | | | | | |
| 10 cm | 0.141 / 0.019 | 0.398 / 0.067 | 0.282 / 0.023 | 1.19 / 0.209 | 0.531 / 0.1 | 0.651 / 0.033 |
| 30 cm | 0.258 / 0.083 | 0.549 / 0.042 | 0.219 / 0.005 | 0.615 / 0.089 | 0.3295 / 0.043 | 0.606 / 0.031 |
| 50 cm | 0.5 / 0.166 | 0.365 / 0.072 | 0.224 / 0.005 | 0.547 / 0.07 | NA / NA | 0.566 / 0.049 |
| 100 cm | 0.797 / 0.201 | 0.377 / 0.069 | 0.202 / 0.003 | 0.341 / 0.018 | NA / NA | 0.627 / 0.062 |
| Bulk | 0.403 / 0.066 | 0.434 / 0.031 | 0.242 / 0.011 | 0.667 / 0.075 | 0.46 / 0.069 | 0.603 / 0.019 |
| **Alluvial Fan** | | | | | | |
| 10 cm | 0.336 / 0.147 | 0.524 / 0.067 | 0.347 / 0.043 | 3.102 / 0.623 | 0.582 / 0.13 | 0.716 / 0.051 |
| 30 cm | 0.602 / 0.198 | 0.494 / 0.048 | 0.246 / 0.0102 | 1.157 / 0.179 | 0.566 / 0.18 | 0.639 / 0.045 |
| 50 cm | 0.895 / 0.215 | 0.58 / 0.072 | 0.224 / 0.008 | 0.709 / 0.111 | 1.143 / 0.602 | 0.617 / 0.057 |
| 100 cm | 0.912 / 0.14 | 0.491 / 0.092 | 0.207 / 0.005 | 0.449 / 0.047 | 0.584 / NA | 0.527 / 0.036 |
| Bulk | 0.7 / 0.096 | 0.524 / 0.031 | 0.256 / 0.014 | 1.405 / 0.239 | 0.671 / 0.126 | 0.647 / 0.028 |
| **Riparian** | | | | | | |
| 10 cm | 0.551 / 0.116 | 0.777 / 0.112 | 0.264 / 0.016 | 0.878 / 0.305 | 0.707 / 0.305 | 1.002 / 0.087 |
| 30 cm | 1.184 / 0.208 | 0.683 / 0.123 | 0.209 / 0.007 | 0.718 / 0.247 | NA / NA | 0.7 / 0.049 |
| 50 cm | 1.25 / 0.156 | 0.515 / 0.061 | 0.212 / 0.003 | 0.555 / 0.131 | 0.315 / 0.131 | 0.691 / 0.051 |
| 100 cm | 1.623 / 0.213 | 0.516 / 0.055 | 0.213 / NA | 0.447 / 0.078 | NA / NA | 0.835 / 0.104 |
| Bulk | 1.131 / 0.095 | 0.613 / 0.048 | 0.231 / 0.009 | 0.649 / 0.104 | 0.658 / 0.182 | 0.804 / 0.038 |

**Figure 2:** Significance matrices for t-test comparisons of solutes among depths for each landscape unit. The shade of the comparison is dependent on the level of significance, with lower p-values being darker, and higher p-values being lighter. Matrices shown are limited to those with significant p-values ($p < 0.05$), as matrices with no significant values have been excluded.




N. Facing Hillslope Ca
X10
X30
X50
X100
Depth (cm)
0.02358
0.1559
0.05657
0.6112
0.1909
0.1176
P.value
1.0
0.5
0.0
X100
X50
X30
X10
Depth (cm)
S. Facing Hillslope Ca
0.1324
0.08205
0.006056
0.2026
0.4596
0.03382
Fan Ca
0.03489
0.881
0.03509
0.2874
0.1467
0.006781
Riparian Ca
0.3756
0.3016
0.09567
0.2947
0.1211
0.04633


N. Facing Hillslope F
X10
X30
X50
X100
Depth (cm)
0.4506
0.01122
0.003902
0.8158
0.04887
0.02735
P.value
1.0
0.5
0.0
X100
X50
X30
X10
Depth (cm)
S. Facing Hillslope F
0.1324
0.7952
0.2461
0.0535
0.03112
0.01138
Fan F
0.0484
0.3299
0.04771
0.2202
0.01214
Riparian F
0.01558
0.453
0.03717
0.002413
0.1559
0.0005641

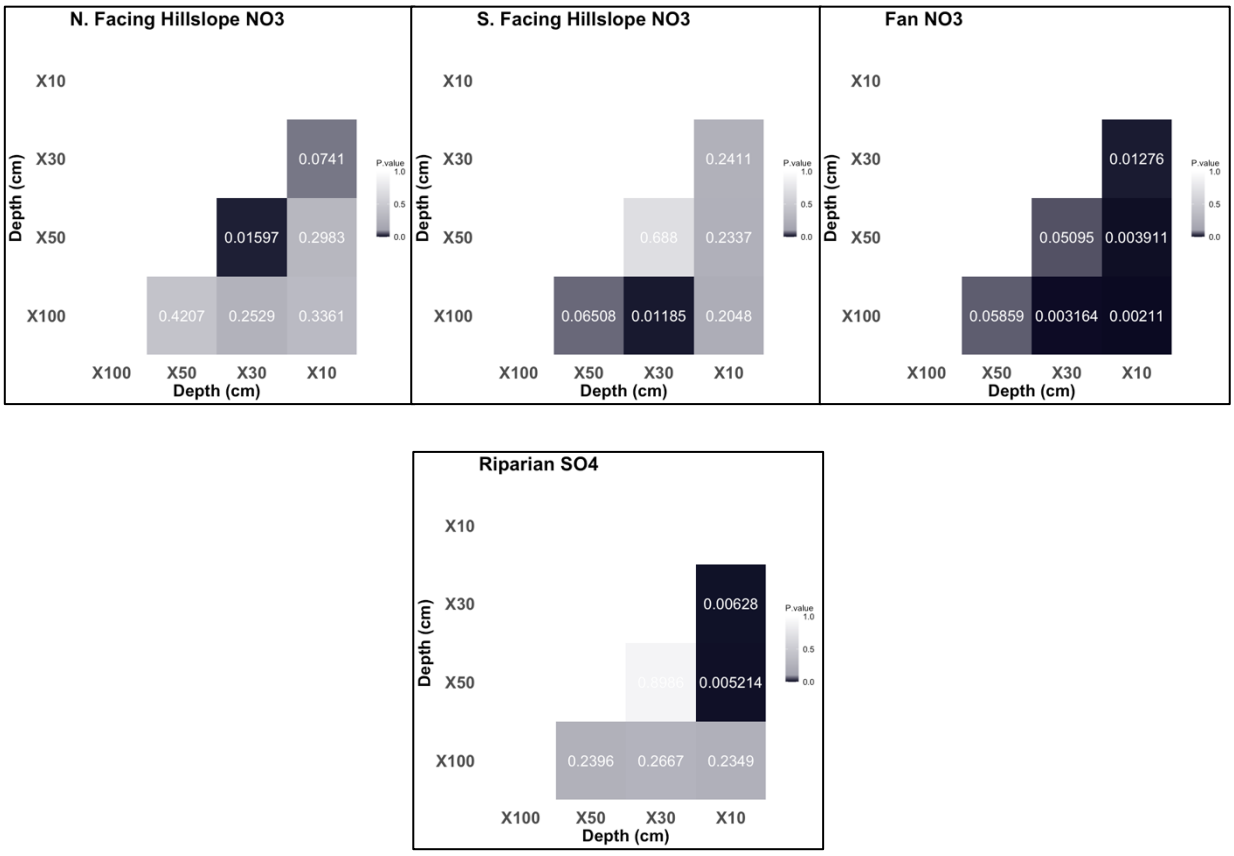
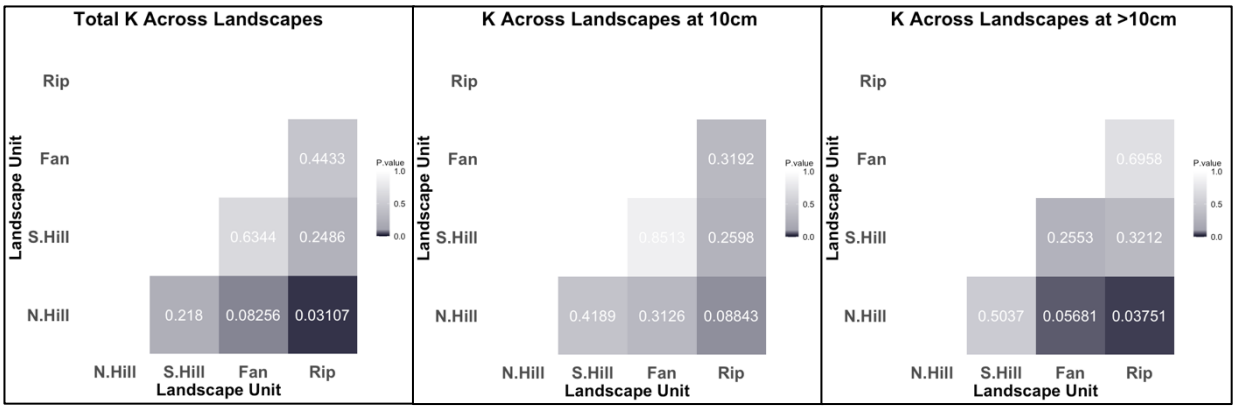
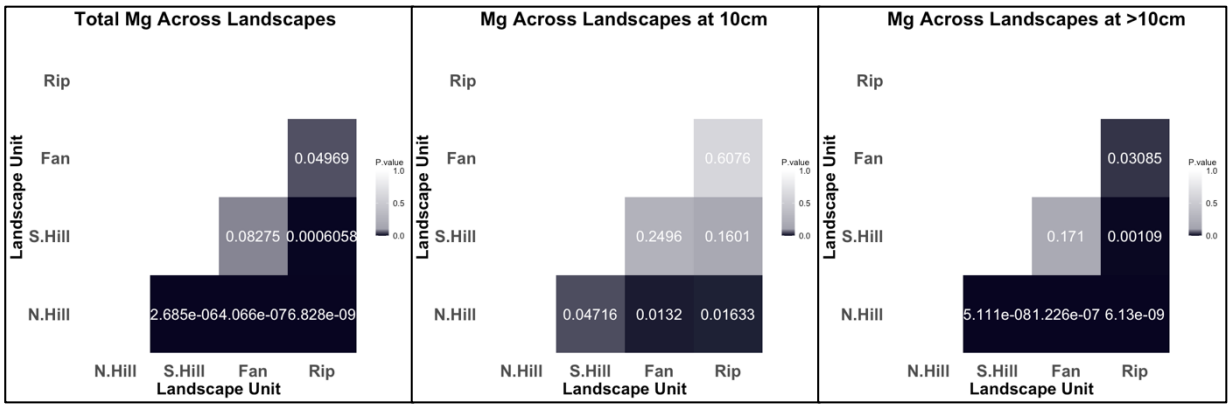
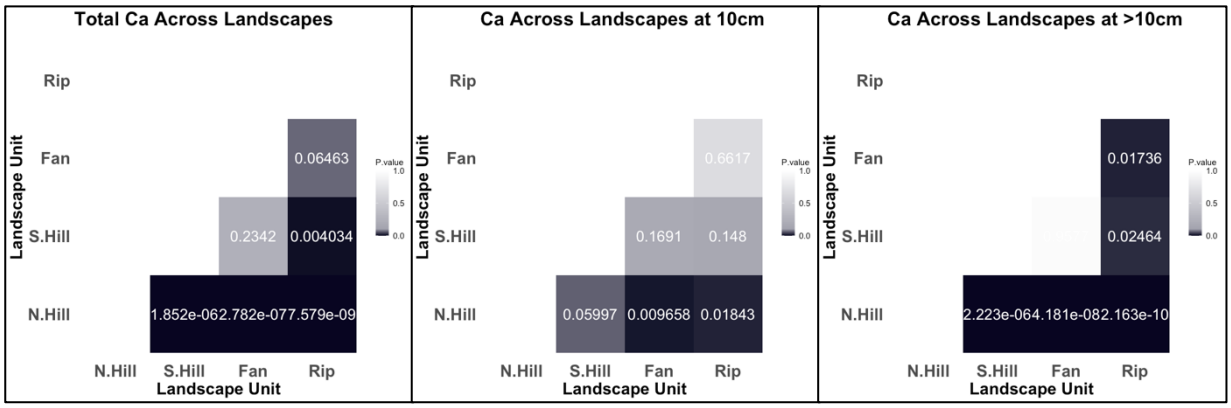
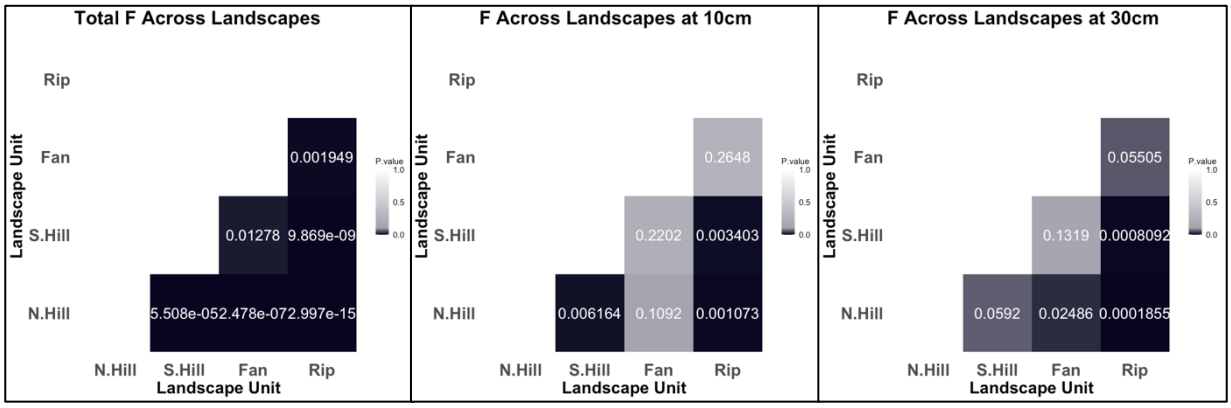


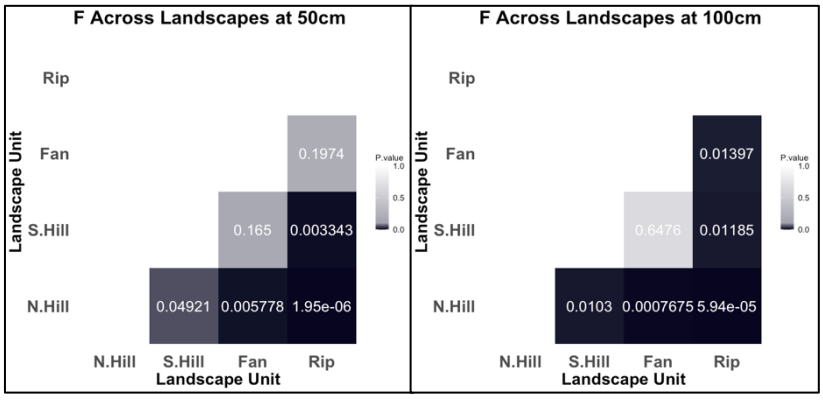

**Figure 3:** Significance matrices for t-test comparisons of solutes among different landscape units at each depth. The shade of the comparison is dependent on the level of significance, with lower p-values being darker, and higher p-values being lighter. Matrices shown are limited to those with significant p-values ($p < 0.05$), as matrices with no significant values have been excluded.

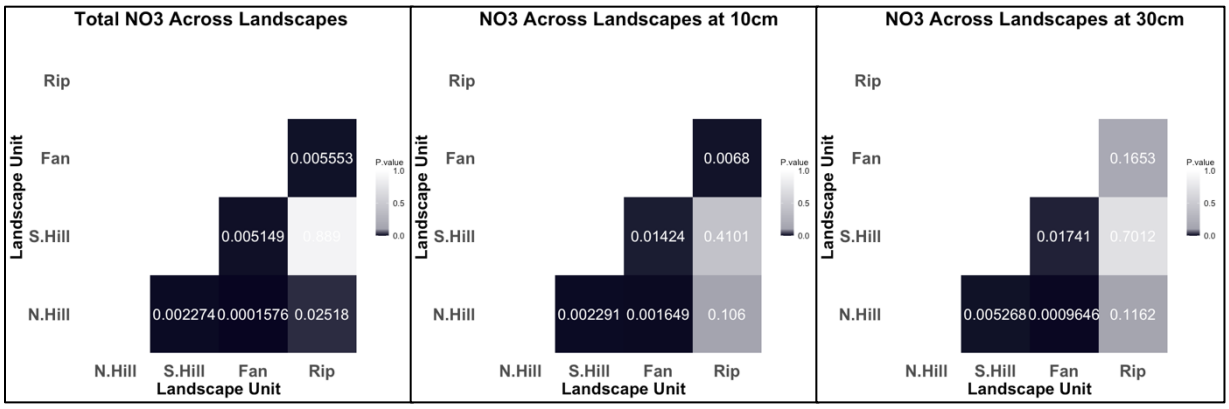


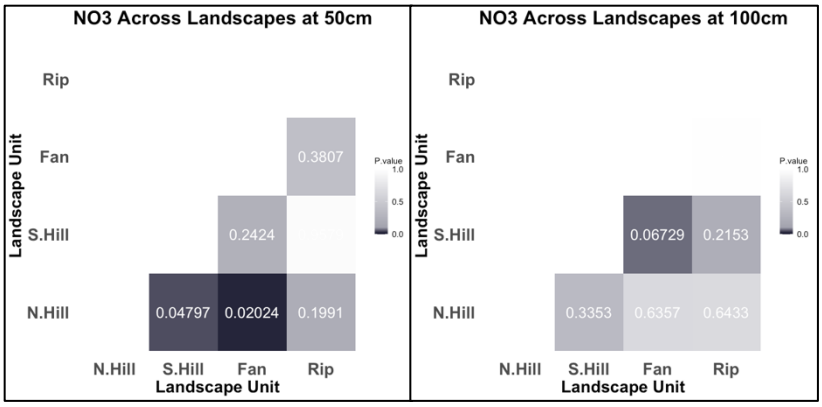

Total Mg Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.04969
0.08275
0.0006058
2.685e-06
4.066e-07
6.828e-09
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
Mg Across Landscapes at 10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.6076
0.2496
0.1601
0.04716
0.0132
0.01633
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
Mg Across Landscapes at >10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.03085
0.171
0.00109
5.111e-08
1.226e-07
6.13e-09
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0

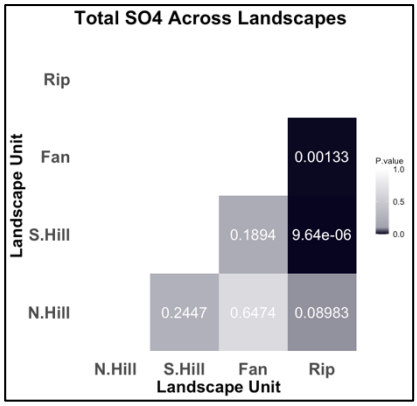

Total Ca Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.06463
0.2342
0.004034
1.852e-06
2.782e-07
7.579e-09
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
Ca Across Landscapes at 10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.6617
0.1691
0.148
0.05997
0.009658
0.01843
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
Ca Across Landscapes at >10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.01736
0.02464
2.223e-06
4.181e-08
2.163e-10
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0

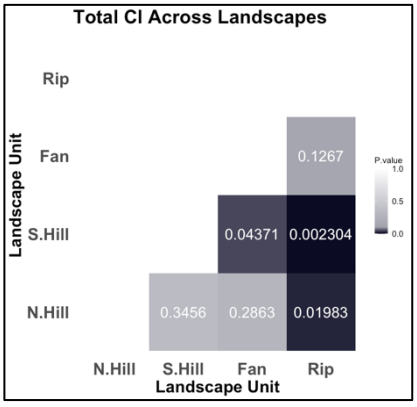

Total F Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.001949
0.01278
9.869e-09
5.508e-05
2.478e-07
2.997e-15
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
F Across Landscapes at 10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.2648
0.2202
0.003403
0.006164
0.1092
0.001073
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
F Across Landscapes at 30cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.05505
0.1319
0.0008092
0.0592
0.02486
0.0001855
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0


F Across Landscapes at 50cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.1974
0.165
0.003343
0.04921
0.005778
1.95e-06
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
F Across Landscapes at 100cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.01397
0.6476
0.01185
0.0103
0.0007675
5.94e-05
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0


Total NO3 Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.005553
0.005149
0.839
0.002274
0.0001576
0.02518
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
NO3 Across Landscapes at 10cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.0068
0.01424
0.4101
0.002291
0.001649
0.106
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
NO3 Across Landscapes at 30cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.1653
0.01741
0.7012
0.005268
0.0009646
0.1162
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0


NO3 Across Landscapes at 50cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.3807
0.2424
0.04797
0.02024
0.1991
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0
NO3 Across Landscapes at 100cm
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.06729
0.2153
0.3353
0.6357
0.6433
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0


Total SO4 Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.00133
0.1894
9.64e-06
0.2447
0.6474
0.08983
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0


Total Cl Across Landscapes
Rip
Fan
S.Hill
N.Hill
Landscape Unit
0.1267
0.04371
0.002304
0.3456
0.2863
0.01983
N.Hill
S.Hill
Fan
Rip
Landscape Unit
P.value
1.0
0.5
0.0

**Results:**

*Solutes Concentrations Within Each Landscape Unit:*

Concentrations of Br, and for the most part $NO_2$, in the soil extracts were below the IC detection level; therefore, these solutes were not included in statistical comparisons. While significance was found between depths and landscapes in $NO_2$, differences in concentrations were minimal. Additionally, no significant differences were found in Na at any landscape unit across depths. No significant differences were found among any solutes ($p > 0.05$) between the north- and south-facing aspects of the riparian areas. Consequently, these data were combined when comparing the riparian area solutes to other landscape units. Additionally, all fan landscapes were on the south-facing aspect.

Riparian Differences with Depth

i. Cations

Significant differences at riparian landscape units were found in K and Ca across depths (Figure 2). In K concentrations, significant differences were found between 10 cm and >10 cm ($p < 0.01$), with mean concentrations ranging from 1.039 mg/l (100 cm) to 3.127 mg/l (10 cm), decreasing with depth (Table 2). Mean Ca concentrations ranged from 2.673 mg/l (100 cm) to 4.213 mg/l (10 cm), decreasing with depth (Table 2). The only significant difference among the depths for Ca was 10 cm versus 100 cm ($p < 0.05$) (Figure 2).

ii. Anions

Significant differences were found in F and $SO_4$ for riparian landscapes across depths (Figure 2). Fluoride was found to have a significant difference between 10 cm and >10 cm ($p < 0.05$), and between 50 cm and 100 cm ($p < 0.01$) (Figure 2). Mean concentrations of F ranged

from 0.551 mg/l (10 cm) to 1.623 mg/l (100 cm), increasing with depth (Table 3). Sulfate showed a different pattern of significance across depths in riparian areas, with significant differences found at 10 cm and 30 cm, and 10 cm and 50 cm ($p < 0.01$) (Figure 2). Concentrations of $SO_4$ ranged from 0.691 mg/l (50 cm) and 1.002 mg/l (10 cm) with no clear pattern across depths (Table 3).

Alluvial Fan Differences with Depth

i. Cations:

Significant differences were found in K, Mg, and Ca for alluvial fans across depths (Figure). Potassium showed the same significant differences in fans as in riparian areas, with significance found between 10 cm and >10 cm depths ($p < 0.05$) (Figure 2). Mean concentrations for K ranged from 0.933 mg/l (100 cm) to 2.318 mg/l (10 cm), decreasing with depth (Table 2). Significant differences in Mg were found between 10 cm and 30 cm ($p < 0.05$), as well as 10 cm and 50 cm ($p < 0.01$) (Figure 2). Mean concentrations of Mg ranged from 0.33 mg/l (100 cm) to 0.512 mg/l (10 cm), decreasing with depth (Table 2). Calcium had a similar pattern of significance as K, with significant differences found between 10 cm and >10 cm ($p < 0.05$) (Figure 2). Mean concentrations of Ca ranged from 2.279 mg/l (100 cm) to 3.849 mg/l (10 cm), decreasing with depth slightly, but with a substantial drop in concentration below 10 cm (Table 2).

ii. Anions

Significant differences were found in F, and $NO_3$ across depths (Figure 2). Fluoride had significant differences between 10 cm and >10 cm ($p < 0.05$) (Figure 2), and mean concentration ranged from 0.336 mg/l (10 cm) to 0.912 mg/l (100 cm), increasing with depth (Table 3). Nitrate

had significant differences between 10 cm and >10 cm ($p < 0.01$), with additional significant difference found between 30 cm and 100 cm (Figure 2). Mean concentrations of $NO_3$ were all relatively low and ranged from 0.447 mg/l (100cm) to 0.878 (10 cm), decreasing with depth (Table 3).

North-facing Hillslope Differences with Depth

i. Cations

North-facing hillslopes had significant differences in Li, K, Mg, and Ca across depths (Figure 2). While a significant difference was found between 50 cm and 100 cm ($p < 0.01$) for Li (Figure 2), concentrations only ranged 0.034 mg/l (50 cm) to 0.043 (10 cm) and were below the detection level for many samples, consequentially removing them from further analysis. Potassium had significant differences between 10 cm and >10 cm ($p < 0.05$) (Figure 2), with mean concentrations ranging from 0.761 mg/l (100 cm) to 1.775 mg/l (10 cm), decreasing with depth (Table 2). Significant differences in Mg concentrations were between 10 cm and 30 cm, as well as 10 cm and 50 cm ($p < 0.01$) (Figure 2). Mean concentrations of Mg ranged from 0.22 mg/l (30 cm) to 0.334 mg/l (10 cm), with higher concentrations at 10 cm and relatively constant concentrations below 10 cm (Table 2). Calcium was found to have significant differences only between 10 cm and 30 cm ($p < 0.05$), with borderline significance between 10 cm and 50 cm ($p = 0.057$) (Figure 2). Mean concentrations ranged from 1.48 mg/l (30 cm) to 2.275 mg/l (10 cm), with a significantly higher concentration at 10 cm, and then increasing with depth slightly between 30-100cm (Table 2).

ii. Anions:

Significant differences were found in F, Cl and $NO_3$ concentrations in north-facing hillslopes at different depths (Figure 2). Fluoride was found to have significant differences at 10 cm and 50 cm ($p < 0.01$), as well as 10 cm and 100 cm ($p < 0.05$) (Figure 2). Additionally, significance was also found between 30 cm and 50 cm ($p < 0.05$), as well as 30 cm and 100 cm ($p < 0.05$) (Figure 2). Mean concentration of F increased with depth, ranging from 0.074 mg/l (10cm) to 0.128 mg/l (100 cm) (Table 3). Chloride was found to have significant differences at 10 cm and 30 cm ($p < 0.05$), as well as 10 cm and 100 cm ($p < 0.05$) (Figure 2). Concentration of Cl ranged from 0.369 mg/l (30 cm) to 0.578 mg/l (10 cm), with no obvious pattern among depths (Table 3). The only significant difference found for $NO_3$ across depths was at 30 cm and 50 cm ($p < 0.05$) (Figure 2). Mean concentrations of $NO_3$ ranged from 0.299 cm (30 cm) to 0.533 mg/l (100 cm), generally increasing with depth, but with the lowest concentration being at 30 cm (Table 3).

South-facing Hillslope Differences with Depth

i. Cations

At south-facing hillslopes, significant differences were found in K, Mg, and Ca (Figure 2). Potassium had significant differences between 10 cm and >10 cm ($p < 0.05$) (Figure 2), with mean concentrations ranging from 0.702 mg/l (100 cm) to 2.208 mg/l (10 cm), decreasing with depth (Table 2). Significant differences in Mg were found between 10 cm and >10 cm ($p < 0.05$), as well as between 50 cm and 100 cm ($p < 0.05$) (Figure 2). Magnesium mean concentrations ranged from 0.328 mg/l (30 cm) to 0.435 mg/l (10 cm), with concentrations being generally stable below 10 cm (Table 2). Significant differences in Mg were found between depths 10 cm

and 50 cm ($p < 0.01$), as well at 10 cm and 100 cm ($p < 0.05$) (Figure 2). Concentrations of Ca ranged from 2.354 mg/l (100 cm) to 3.09 mg/l (10 cm), decreasing with depth (Table 2).

ii. Anions:

Significant differences were found in F and $NO_3$ in south-facing hillslopes at different depths (Figure 2). Fluoride was found to have significant differences between 10 cm and 100 cm ($p < 0.05$), and 30 cm and 100 cm ($p < 0.05$) (Figure 2). Mean concentrations of F ranged from 0.141 mg/l (10 cm) to 0.797 mg/l (100 cm), increasing with depth (Table 3). Nitrate had one significant difference at depth between 30 cm and 50 cm ($p < 0.05$), and mean concentrations decreased with depth, ranging from 0.341 mg/l (100 cm) to 1.19 mg/l (10 cm) (Table 3).

*Bulk Differences Among Landscape Units:*

Riparian:

i. Cations:

Significant differences in total cation concentrations between riparian and other landscape units were found for K, Mg, and Ca (Figure 3). For K, significant differences were found between riparian and north-facing hillslope landscape units ($p < 0.05$) (Figure 3), with mean concentrations of 1.633 mg/l and 1.093 mg/l, respectively (Table 2). Magnesium was found to have significant relationships between riparian and all other landscapes ($p < 0.05$) (Figure 3). Bulk Mg concentrations ranged from 0.267 mg/l to 0.467 mg/l with north-facing hillslopes being the lowest and riparian areas being the highest (Table 2). Calcium was found to have significant differences between riparian areas and both aspects of the hillslopes ($p < 0.01$) (Figure 3). Bulk Ca concentrations ranged from 3.373 mg/l at riparian areas to 1.785 mg/l at north-facing hillslopes (Table 2).

ii. Anions:

Significant differences in total anions concentration between riparian areas and other landscape units were found in F, Cl, $NO_3$, and $SO_4$ (Figure 3). Fluoride was found to have significant differences between riparian areas and all other landscape units ($p < 0.01$) (Figure 3). Mean concentrations of total F ranged from 0.108 mg/l to 1.131 mg/l, with north-facing hillslopes having the lowest concentration, and riparian having the greatest (Table 3). Chloride was found to have significant differences among riparian areas and both aspects of hillslopes ($p < 0.05$) (Figure 3), with mean concentrations ranging from 0.434 mg/l in south-facing hillslopes to 0.613 mg/l in riparian areas (Table 3). Nitrate was found to have significant differences between riparian areas and north-facing hillslopes ($p < 0.05$), as well as riparian areas and alluvial fans ($p < 0.01$) (Figure 3). Total mean concentrations of $NO_3$ ranged from 0.387 mg/l to 1.405 mg/l, with the lowest concentrations being in north-facing hillslopes and the greatest in the alluvial fans (Table 3). Total $SO_4$ concentration were found to have significant differences among riparian areas and fans, as well as riparian areas and south-facing hillslopes ($p < 0.01$) (Figure 3). Mean concentrations of total $SO_4$ ranged from 0.603 mg/l in south-facing hillslopes to 0.804 mg/l in riparian areas (Table 3).

Alluvial Fans

i. Cations:

In addition to the significant differences found between riparian and alluvial fan landscapes, significant differences in total cations among alluvial fans and other landscapes were found in Mg and Ca (Figure 3). Magnesium was found to only have a significant difference

between fans and north-facing hillslopes ($p < 0.01$) (Figure 3). Calcium was found to have a significant difference between fans and north-facing hillslopes (Figure 3).

ii. Anions:

Along with the significant differences found between riparian and alluvial fan landscapes for anions, significant differences were also found between alluvial fans and other landscape units for F, Cl, and $NO_3$ (Figure 3). Fluoride was found to have significant differences between fans and both aspects of the hillslopes ($p < 0.05$) (Figure 3). Similarly, $NO_3$ was also found to have significant differences between fans and both aspects of the hillslopes ($p < 0.01$) (Figure 3). Chloride was found to have a significant difference between fans and south-facing hillslopes ($p < 0.05$) (Figure 3).

North- and South-facing Hillslopes:

i. Cations:

In addition to the above noted comparisons, significant differences in total cation concentrations were found between north- and south-facing hillslopes in Mg and Ca ($p < 0.01$) (Figure 3).

ii. Anions:

Lastly, along with the significant comparisons evaluated above, significant differences in total cations were found between north- and south-facing hillslopes in F and $NO_3$ ($p < 0.01$) (Figure 3).

*Comparisons Between Landscape Units at Depth:*

Based on the previous analyses, comparisons of solutes among each landscape unit at specific depths were limited to solutes which were found to have clear patterns in significant differences. Thus, K, Mg, and Ca were evaluated at 10 cm and >10 cm depths as they displayed a clear pattern of significance, and F, and $NO_3$ at each sampled depth, as their significance patterns were less identifiable (Figure 3). $SO_4$ was only analyzed at bulk concentrations, as it was found to only have significance at a single landscape unit (Figure 3). The following analysis will build upon each other, with the previously noted landscape significance patterns being included in the analysis of the following landscape comparison.

Riparian vs. Other Landscape Units:

i. 10 cm

Significance between riparian areas and other landscape units at 10 cm was found in Mg, Ca, F, and $NO_3$ (Figure 3). Magnesium was found to only have significance between riparian areas and north-facing hillslopes ($p < 0.05$) (Figure 3). Similarly, Ca was found to have the same pattern of significance between riparian areas and north-facing hillslopes ($p < 0.05$) (Figure 3). Fluoride was found to have significant differences in concentrations among riparian areas and both aspects of the hillslopes ($p < 0.01$) (Figure 3). Lastly, $NO_3$ was found to only have significant differences between riparian areas and alluvial fans ($p < 0.01$) (Figure 3).

ii. >10 cm

For solutes analyzed at >10 cm, K, Mg, and Ca had significant differences between riparian and other landscape units. Potassium was found to have significance between riparian areas and north-facing hillslopes ($p < 0.05$) (Figure 3). Significant differences in Mg were found

among riparian and all other landscape units ($p < 0.05$) (Figure 3). Calcium was found to have a similar pattern to Mg, with significant differences among riparian areas and all other landscape units ($p < 0.01$) (Figure 3).

iii. 30 cm

Of the solutes evaluated at 30 cm, F was the only one to have significant differences among riparian areas and other landscape units. Fluoride was found to have significant differences in concentrations among riparian areas and both aspects of the hillslopes ($p < 0.01$), with additional borderline significance found between riparian areas and fans ($p = 0.055$) (Figure 3).

iv. 50 cm

Fluoride was the only solute analyzed at 50cm to have significant differences between riparian areas and other landscape units. Similar to 30 cm, F was found to have significant differences in concentration among riparian areas and both aspects of hillslopes at 50cm ($p < 0.01$) (Figure 3).

v. 100 cm

At 100 cm, F was the only solute of those evaluated to have significant differences between riparian areas and other landscape units. Fluoride was found to have significant differences in concentrations among riparian areas and all other landscape units ($p < 0.05$) (Figure 3).

Alluvial Fan vs. Other Landscape Units

i. 10 cm

In addition to the significance found between riparian areas and other landscape units, significant differences in solute concentrations between alluvial fans and other landscape units were found in Mg, Ca, and $NO_3$. Magnesium was found to have significant differences between fans and north-facing hillslopes ($p < 0.05$) (Figure 3). Similarly, significant differences in Ca were only found between fans and north-facing hillslopes ($p < 0.01$) (Figure 3). Nitrate was found to have significant differences among fans and both aspects of hillslopes ($p < 0.05$) (Figure 3).

ii. >10 cm:

For solutes evaluated at >10 cm, significant differences between fans and other landscape units were found in Mg and Ca. For Mg, significant differences were found only between fans and north-facing hillslopes ($p < 0.01$) (Figure 3). Calcium was found to have a similar pattern, with a significant difference between fans and north-facing hillslopes ($p < 0.01$) (Figure 3).

iii. 30 cm:

Of the solutes analyzed at 30 cm, significant differences in concentrations between fans and other landscape units were found in both F and $NO_3$. Fluoride was found to have significant differences between fans and north-facing hillslopes at 30 cm ($p < 0.05$) (Figure 3). Nitrate was found to have significant differences in concentrations among fans and both aspects of the hillslopes ($p < 0.05$) (Figure 3).

iv. 50 cm

At 50 cm, significant differences in solute concentrations between fans and other landscape units were found in both F and $NO_3$. For fluoride, significant differences were found

between fans and north-facing hillslopes ($p < 0.01$) (Figure 3). Nitrate was found to have a similar pattern, with significance found between fans and north-facing hillslopes ($p < 0.05$) (Figure 3).

v. 100 cm

At 100 cm, significant differences in solute concentration between fans and other landscape units were found in only in F. Significant differences in F were found between fans and north-facing hillslopes ($p < 0.01$) (Figure 3).

North- and South-Facing Hillslopes:

As all other comparisons have been exhausted by the analysis detailed in the prior sections, significant differences in solute concentrations will be evaluated between north- and south-facing hillslopes in this section.

i. 10 cm

At 10 cm, significant differences between north-facing hillslopes and other landscape units (for the remaining comparisons) were found in Mg, F, and $NO_3$. Each of these solutes were found to have significant differences between north- and south-facing hillslopes, with p-values less than 0.05 for Mg, and less that 0.01 for F and $NO_3$ (Figure 3).

ii. >10 cm

Of the solutes evaluated at >10 cm, significant differences among north-facing hillslopes and other landscape units at >10cm were found in Mg and Ca. Both solutes were significant in north- and south-facing hillslope comparison ($p < 0.01$) (Figure 3).

iii. 30 cm

At 30cm, significant differences in solute concentrations were found among north-facing hillslopes and other landscape units only in $NO_3$. A significant difference was found between north- and south-facing hillslopes for $NO_3$ concentrations ($p < 0.01$) (Figure 3).

iv. 50 cm

Significant differences in solutes at 50 cm between north-facing hillslopes and other landscape units were found in both F and $NO_3$. Both solutes were found to have significance differences between north- and south-facing hillslopes ($p < 0.05$) (Figure 3).

v. 100 cm

At 100 cm, significant difference in solutes among north-facing hillslopes and other landscape units were found in only in F. Fluoride was found to have significance between north- and south-facing landscape units ($p < 0.05$) (Figure 3).

**Discussion:**

*Solute Concentrations Between Landscape Units*

As seen in the results above, aspect was not a significant cause of difference in solute concentrations in riparian and alluvial fan landscapes; however, differences were found between north- and south-facing hillslopes. All solute concentrations were greater in the near-stream landscape units (riparian and alluvial fan) than in the hillslopes, and nearly all solutes were higher in riparian areas than alluvial fans, with the exception of $NO_3$ (Table 2 & 3). Additionally, south-facing hillslopes were found to have higher concentrations than north-facing hillslopes in nearly all solutes ($PO_4$ and $SO_4$ were marginally higher on north-facing hillslopes). Increased concentrations of solutes in these near-stream landscape units was expected and can be partially

due to the increased vegetation density leading to higher concentration of biogenically derived solutes in riparian (willows, grasses, and forbs) and alluvial fan areas (higher density of grassy vegetation), as well as the tendency for subsurface flow to flush downslope towards the stream (Christopher et al., 2006; Herndon et al., 2018; Jin et al., 2011; Pei et al., 2021; Piatek et al., 2009). Concentrations of biogenically derived solutes, such as K and $NO_3$ being greater in riparian and fan landscapes is clear, as there is more leaf litter and root materials in those soils when compared to hillslopes (Piatek et al., 2009). Increased concentrations in near-stream units can also be described spatially by the flushing of solutes from hillslopes toward riparian areas, which is consistent with the data found in this study (Jin et al., 2011; Mosimane et al., 2017). Additionally, wooded areas with less dense, tree-dominated vegetation have generally been found in previous studies to have greater rates of flushing and less solute retention of base anions and cations when compared to the dense grassy and willow dominated riparian areas, supporting my results (Pei et al., 2021).

Regarding soil structure, coarser soils with larger pore spaces more actively transport solutes through subsurface flow when compared to more dense and finer grained soils, explaining the increase in concentrations in riparian and fan landscapes, as those soils were more dense and fine-grained than the hillslopes (NRCS, 2022; Pei et al., 2021). Additionally, soil with a relatively high clay fraction, as seen in the riparian and alluvial fan areas, retain solutes more readily than coarser and sandier soils, further supporting the increase in most solute concentrations in riparian and alluvial fan areas (NRCS, 2022; Pei et al., 2021). While a quantitative assessment of soil textures was not conducted in this study, a qualitative evaluation of the soils for riparian and alluvial fans soils showed finer soils with higher clay content when compared to those of the hillslopes.

While the vegetative and topographic explanations for solute behaviors are clear for differences between near-stream and hillslope landscapes, these factors do not clearly explain the increased concentrations of solutes in south-facing hillslopes when compared to north-facing hillslopes. The north-facing hillslopes, while having more vegetation and finer soils, were observed to have lower concentrations of solutes, working opposite of the processes described above (Tables 2 & 3) (NRCS, 2022). A possible explanation is that preferential subsurface flowpaths along root systems could potentially flush the solutes from the north-facing hillslopes at a higher rate than on the south-facing hillslopes, as vegetation was denser in the north-facing aspect (Pei et al., 2021). Another reason that solutes were lower in the north-facing hillslopes may be due to the temperature and wetness of the soils (Piatek et al., 2009). In addition to the flushing of solutes from hillslopes to valleys, wetter soils can dilute and transport soil solutes more readily when compared to drier soils, which have a higher level of solute retention (Piatek et al., 2009). The temperature of soils is also connected to wetness, as it had been found that hotter soils retain soil solutes more than cooler soils. These processes were found for $NO_3$ in particular in existing literature (Piatek et al., 2009). Even with gradual topography, significant temperature differences between slope aspect occur due to the increased insolation that south-facing hillslopes receive compared to north-facing hillslopes (Bennie et al., 2008). As the north-facing hillslopes are both cooler and wetter than the south-facing due to decreased direct insolation, greater canopy cover and delayed snowmelt, these processes could possibly explain the increased concentrations in south-facing hillslopes. Nitrate has been found to get flushed out of hillslopes in particularly large amounts in persistently wet soils and during snowmelt events, supporting the data of this study further (Piatek et al., 2009).

The amount of variation among landscape units varied among specific solutes, with some having larger differences in concentrations by location. Of the studied solutes, F, Ca, and $NO_3$ had notably large variations among depths and landscape units (Tables 2 & 3). Less spatial variation was found in $SO_4$ and Cl, with higher concentrations in riparian areas than the other landscape units. For the geogenically derived solutes (F, Ca, Cl, and $SO_4$), these large differences between the riparian areas and hillslopes could be partially due to the deposition of geogenically derived solutes from stream flow into the near-stream riparian areas (Piatek et al., 2009). Geogenically derived solutes in stream waters have been found in a previous study to increase in summer months, leading to the deposition of these solutes into the riparian areas, which could be a factor in the found increase in solutes in riparian areas when compared to the hillslopes (Piatek et al., 2009). While variations of $SO_4$ were less than other solutes, higher concentrations in riparian areas could be explained by the release of $SO_4$ from the erosion of pyrite, a mineral prominent in MEF soils, which was then flushed down the hillslopes and remineralized in riparian areas from subsurface flow (Herndon et al., 2018; Piatek et al., 2009). Nitrate behaved differently than other solutes in that there were much higher concentrations in the fan landscapes than any other, and mean concentrations in riparian areas were closer to those of the hillslopes (Table 3). One possible explanation for this could be due to the particularly high transport of $NO_3$ during snowmelt, rainfall events, and areas of high runoff (Piatek et al., 2009). While other solutes show a flushing pattern from the hillslopes to storage in the riparian areas, this behavior of $NO_3$ to be flushed more actively in areas with high flow may be able to explain the high concentrations in fans, as there is not as much flow in the fans when compared to riparian landscapes (Piatek et al., 2009).

*Solute Concentrations at Depth*

For nearly all of the studied solutes, mean concentrations either decreased with depth (K and $NO_3$) or showed a clear pattern of high concentrations in shallow depth (10 cm) and constant lower concentrations underneath (30-50 cm) (Mg and Ca), with the exception of F, which increased with depth (Table 2 & 3). Smaller variations were found in Li, Na, Cl, and $SO_4$, with more homogenous mean concentrations between depths. While this pattern of high surface concentrations was expected for the biogenically derived solutes, it contrasted expectations for geogenically sources solutes like Mg and Na, except for F. For the organic solutes, higher surface concentrations can be explained by greater amounts of leaf litter and roots within the shallowed depths (Christopher et al., 2006; Herndon et al., 2018). Calcium was particularly high in the surface level soils, which is supported by other studies finding high concentrations of Ca associated with the decomposition of plant material in shallow soils (Christopher et al., 2006). Magnesium, despite being found to be geogenically derived in other studies (Pei et al., 2021), did not have the expected pattern of increasing concentrations with depth. This contrast in findings may be caused by the uptake and redeposition of Mg by plants within the catchment, making it behave more like the biogenically derived solutes (Jin et al., 2011). While this process has been found to be minimal in other studies, this could be a driver for high surface concentrations of Mg within MEF, as the Pikes Peak granite bedrock of the area is quite poor in Mg (Jin et al., 2011; Smith, 1999). Another process that could lead to high concentrations of solutes in surface soils is evapoconcentration of solutes in shallow soils. While subsurface flow has a flushing effect on solutes, the evapoconcentration of solutes when the near surface soil is dried can lead to higher concentrations of solutes above the deeper subsurface (Mosimane et al., 2017). High surface

levels of K, Mg, Ca, Cl, and $SO_4$ have been attributed to evapoconcentration in previous studies and is supported by the data of this study as well (Mills, 2016; Mosimane et al., 2017).

Of the studied geogenically derived solutes, F was the only one to show the expected pattern of increasing concentrations with depth. This was the case across all landscape units; however, there was more variation within the fans and south-facing hillslopes than riparian areas and north-facing hillslopes (Table 3). This clear pattern of increase in depth may be attributed to the high concentration of F within the Pikes Peak granite bedrock being weathered through subsurface flow (Smith, 1999). The decreased variability with depth in the riparian areas and north-facing hillslopes may be caused by the trend of increased flushing on the north-facing hillslopes, and the consequent channeling of concentrations within the downslope riparian areas across all depths (Piatek et al., 2009).

*Possible Hydrologic Tracers*

When evaluating the data for possible hydrologic flow tracers, factors include which solutes were found to have distinct patterns among landscape units and at depths. When patterns of variation can be identified between these two factors, knowledge of where subsurface flow occurs both spatially and vertically can be obtained. With these considerations, and supported by the results of this study, possible valuable solute tracers within Hotel Gulch appear to be K, Ca, F, and $NO_3$, as each of these solutes show distinct patterns of variation either spatially, at depth, or both. While significant patterns were found in other solutes between landscape units and depth, solutes such as Mg, Cl, and $SO_4$ may not be as valuable of tracers due to the relatively low variations in concentrations.

Potassium was found to be spatially distinct, with larger variations of mean concentrations among depths, and to a lesser degree, between landscape units. While K concentrations were not found to be significantly variable among different landscape units, high variations were found among depths, with high concentrations in the shallow soils. If high concentrations of K are found in streams, this could potentially be an indicator of shallow subsurface flow through a vegetated area. Calcium exhibited the highest mean concentrations of the studied solutes, with distinct patterns of significance between both landscape units and at depth. Similar to K, high Ca concentrations in surface soils are most likely attributed to organic matter decomposition and could indicate shallow subsurface flow through areas of high vegetation. Nitrate also displayed patterns similar to these two solutes, with variation among landscape units and depths. High concentrations of $NO_3$ in the stream could also indicate shallow flow through organic enriched soils, and specifically alluvial fans, where concentrations were particularly high. Lastly, F was found to be an opposite indicator than the three other solutes, with clear significant differences among both landscape units and depth; however, with concentrations being higher at deeper depths. Higher concentrations of F in the stream could be an indicator of deeper subsurface flow from erosive environments, as it is most likely bedrock derived.

**Conclusion**

Through the sampling and analysis of ~200 samples within a headwater catchment of MEF, inferences can be drawn to the possibility of certain solutes serving as indicators of flow through different landscape units and depths. Of the studied soil solutes, it was found that K, Ca, F, and $NO_3$ could potentially be valuable tracers of subsurface flow through a catchment and

provide information on how and where water is travelling beneath the surface towards a stream. With knowledge of these tracers, inferences can be made about flow origins and water quality, as flowpaths can be identified using solute data.

Limitations to this study include: the comprehensiveness of replicate sampling within each landscape unit, the use of soil extractions using ultra-pure deionized water rather than simulated rainwater solutions, and the comparison of solute data to other data within the catchment such as stream, precipitation, and groundwater data. While limitations to the depth of which inferences can be made based on this study exist, it can be used as a preliminary resource for further study of soil solute behaviors, tracers within a catchment, and their implications on water quality and availability.

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