The Use of Gravitational Filtration to Preserve Water Samples to Measure High-Frequency Dissolved Organic Carbon and Nutrients

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Introduction

Despite extensive employment of automated water samplers, the temporal variability of dissolved organic carbon (DOC) and nutrient species e.g., nitrate at a high-frequency during storm events is rarely documented. These elements are biologically active: microorganisms readily utilize these elements, causing a decrease in their concentrations over the sampling period. For DOC analyses, the water samples must be filtered immediately and acidified. Furthermore, both DOC and nutrient species samples must be stored at a cool temperature.

High-frequency DOC and nutrient species observations may contribute to our understanding on the dynamics of trace metals and the role of biology in geochemical processes. Trace metals readily complex with DOC, allowing for easier transport in water. Nitrate and sulfates are important components of proteins and plant growth.

In this study, we evaluated the validity of a gravitational filtration system (GFS), which is an amended sampling method for automated samples that filter water by gravity upon sampling (Kim et al., 2012), for the preservation of sample integrity for DOC and nutrient species. The evaluation was carried out using water samples from streams and lakes in the Shaver's Creek Watershed. We monitored the concentration of DOC and nutrient species in the GFS samples over two weeks and compared them to reference samples collected by a standard method. The results indicate that DOC is preserved in Lake Perez, but not in Shaver's Creek Outlet or Garner Run. For nutrient species, both sulfate and nitrate are well preserved in Lake Perez and Shaver's Creek, but not Garner Run. However, the control samples were preserved just as well at certain sites.

Sampling Sites

The sampling sites were selected based on their variability in lithology and land use.
- Lake Perez is located on shale in a mixed forest.
- Garner Run Outlet is a first order stream that lies in deciduous forest.
- Shaver's Creek Outlet is located on agricultural land underlain by shale and sandstone.
- The Susquehanna Shale Hills stream was dry due to the lack of rain and was therefore not included in the study.
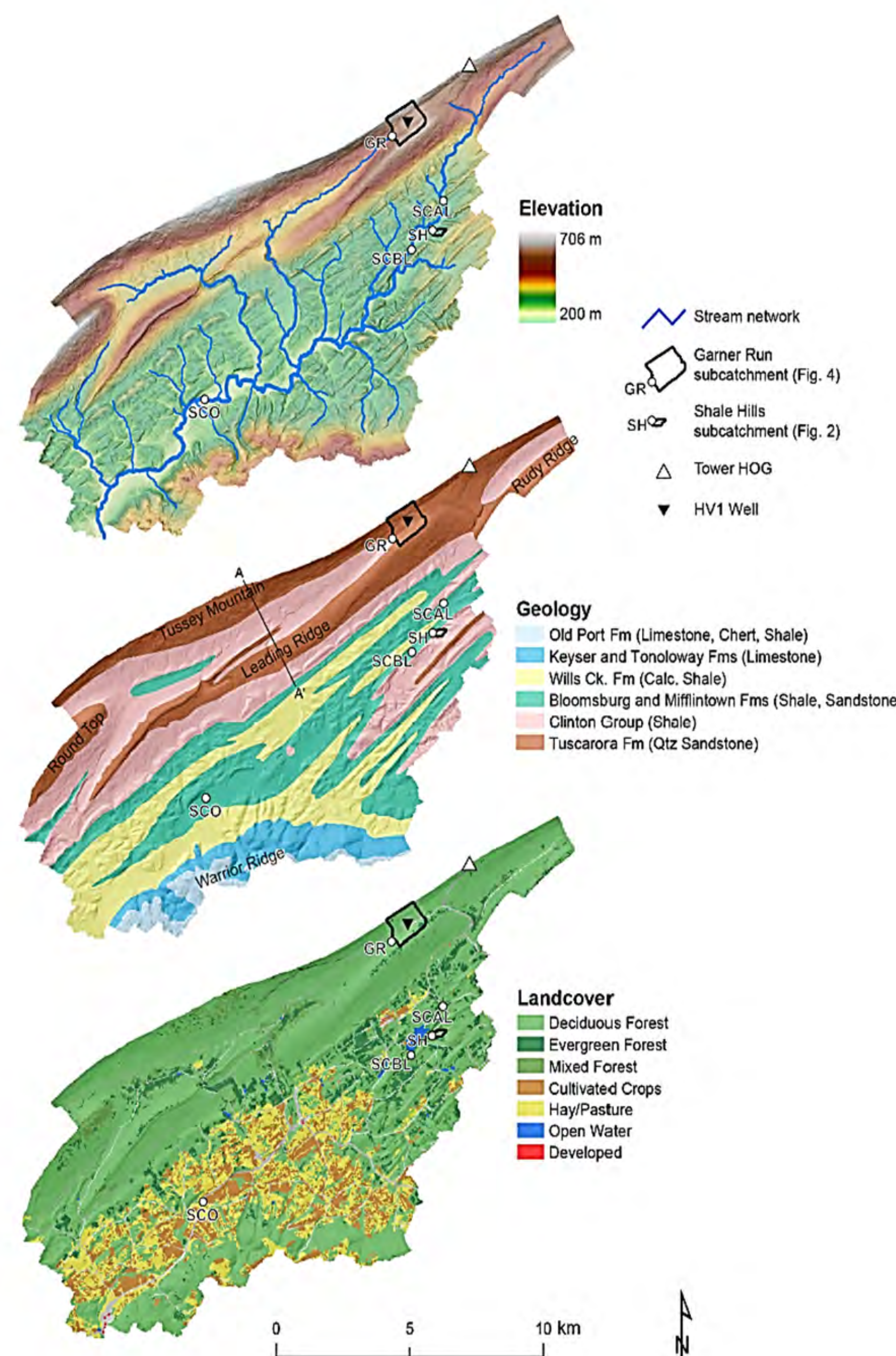
Figure 1: Map showing lithology and land use across Shaver's Creek Watershed (Brantley et al., 2016)

Methods

Bulk and reference samples collected in the field:
- Reference samples were filtered using a 0.45 μm filter
- DOC samples were immediately acidified with 2N HCl
- Bulk samples were transferred into ISCO samplers in the lab

Following the aging period:
- DOC samples were acidified with 2N HCl and analyzed on the Shimadzu TOC-5300a
- Anion samples were analyzed on the Thermo Scientific Dionex ICS2500
- Samples were stored at 4°C until tested.

Picture: ISCO sampler components: 150 mL syringe, 25 mm filter, 60 mL and 30 mL bottles with tubing as connection

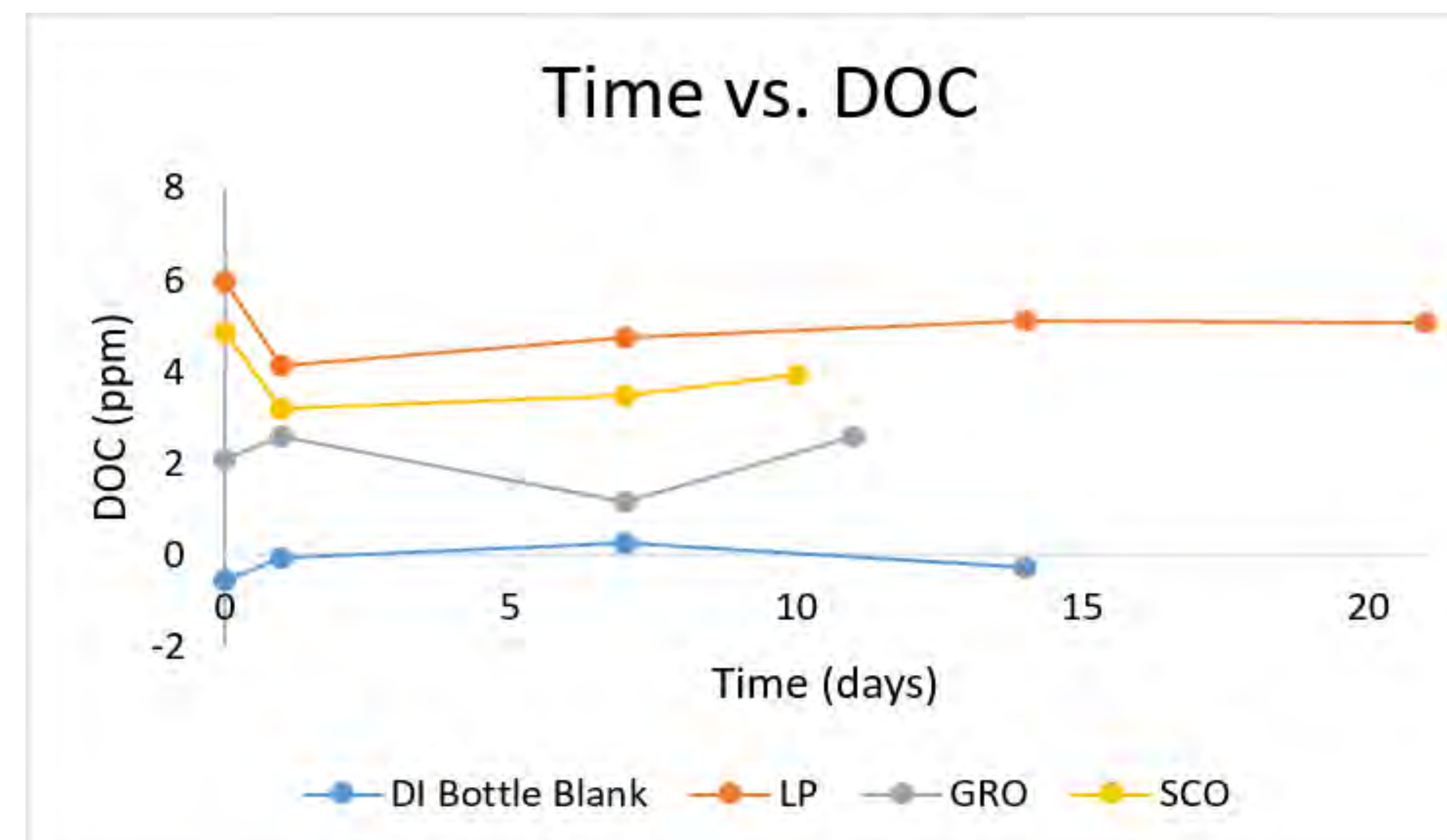## DOC Results

Time vs. DOC

Figure 2: DOC concentration with age

The DOC at the sites exhibited three different behaviors:

Lake Perez: DOC from the reference sample was 5.97 ppm. The concentrations remained consistent across three weeks. After and aging period of 26 days, the control sample was filtered and tested. Over this time period, 62% of the sample was recovered. The samples from the automated sampler had recoveries ranging from 69 to 86%.

Garner Run Outlet (GRO): The DOC concentration for the reference sample was 2.09 ppm. The control sample, which was tested after 12 days, had a recovery of 78%. Samples from the GFS had recoveries at approximately 81%, but only 55% of the day 7 sample was recovered.

Shaver's Creek Outlet (SCO): The DOC concentration for the reference sample was 4.86 ppm, and the control sample, which was tested after 11 days, had a recovery of 73%. The samples from the GFS had recoveries ranging from 65 to 81%.

The DI bottle blanks had values from -0.57 to 0.64 ppm.
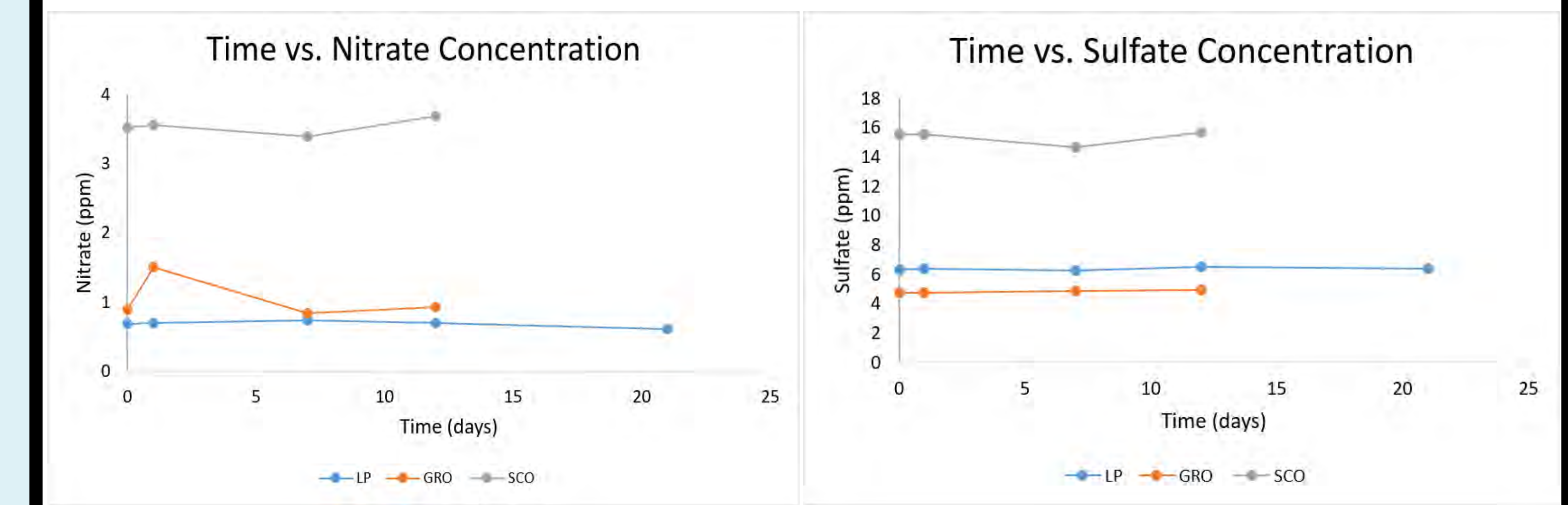
Nutrient Species Results

Lake Perez (LP): The reference sample contained 6.32 ppm sulfate and 0.68 ppm nitrate. The sulfate concentrations remained consistent across three weeks, with percent recoveries ranging from approximately 96 to 99%. For nitrate, the recoveries ranged from 89 to 98% over the aging period. After an aging period of 26 days, the control sample was filtered and tested. The control sample had a recovery of 95.37% for sulfate and 93.19% for nitrate. The sample was well preserved for both nutrient species.

Garner Run Outlet (GRO): The reference sample contained 4.74 ppm sulfate and 0.89 ppm nitrate. Sulfate samples from the GFS had recoveries ranging from 95 to 99%. Nitrate samples had recoveries at approximately 93 to 96%, but only 59% of the day 7 sample was recovered. The control sample, which was tested after 12 days, had a recovery of 95.25% for sulfate and 99.40% for nitrate. Filtration may not be necessary at this site.

Shaver's Creek Outlet (SCO): The reference sample contained 15.55 ppm sulfate and 3.51 ppm nitrate. Samples from the GFS had recoveries at ranging from 94 to 99%. The control sample, which was tested after 11 days, had a recovery of 99.68% for sulfate and 94.28% for nitrate. The high concentrations of these anions are due to runoff from nearby farms.

The DI bottle and filter blanks read at or below 0.41 ppm for sulfate, and below 0.2 ppm for nitrate.

Figure 3 (Left): Nitrate concentration with time; FIgure 4 (Right): Sulfate concentration with time

Time vs. Nitrate Concentration

Time vs. Sulfate Concentration

Future Study

While the nutrient species were well preserved in the sampler, the DOC samples had varying percent recoveries. Samples are normally filtered with a 0.45 μm, acidified with HCl, and stored at a low temperature to reduce microbial activity. This can be difficult to accomplish if samples remain in the field for long periods of time. One way to improve DOC recovery is to preacidify the sample bottles with a few drops of HCl, so the samples are acidified as they enter the bottle. Reducing the pore size of the filter would increase the filtration time of the sample. This could give the sample more time to react in the syringe.

Further study of this method would include creating a time series of 30 days or longer, and perhaps testing the control sample weekly to better understand the rate of microbial activity.

References

Kim H, Bishop JKB, Wood TJ, Fung IY (2012) Autonomous Water Sampling for Long- Term Monitoring of Trace Metals in Remote Environments. Environ. Sci. Technol. 46, 11220-11226.

Brantley, S. L., DiBiase, R. A., Russo, T. A., Shi, Y., Lin, H., Davis, K. J., Kaye, M., Hill, L., Kaye, J., Eissenstat, D. M., Hoagland, B., Dere, A. L., Neal, A. L., Brubaker, K. M., and Arthur, D. K (2016): Designing a suite of measurements to understand the critical zone. Earth Surf. Dynam. 4, 211-235.

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