

Fisher J¹, Sullivan PL², Neal A², Brantley SL²

1 Geological Sciences Department, Brown University, Providence, RI

2 Earth and Environmental Systems Institute, The Pennsylvania State University, University Park, PA

Abstract

The integration of climate, weathering, and biological processes across the critical zone is conveyed in stream water solute concentrations and fluxes. As concentration-discharge behaviors vary between catchments of differing lithology, land use, and vegetation cover, the underlying control on stream water solute behavior remains elusive. This study examined these relationships to find correlations between nitrate and land use, sulfate and underlying lithology and the dominance of Ca or Si to water fluxes in the watershed.

Introduction

Understanding the vast network of soils and streams that transport water at the earth's surface is paramount to quantifying chemical weathering and biotic processes in the Critical Zone. As precipitation makes its way into the stream it can infiltrate into the soil where it picks up ions. Though streams integrate the signal of many flow paths, stream water ion concentrations vary differently in response to changes in discharge of several orders of magnitude (Godsey et al, 2009).

Solute concentrations can vary with stream discharge so that in some cases solutes are enriched, diluted, or chemostatic. Enrichment and dilution describe changes with discharge, while chemostasis describes stream chemical environments in which solute concentrations remain relatively constant despite variations in discharge. Determining the mechanisms for fluxes in solute behavior can help us understand and protect stream environments.

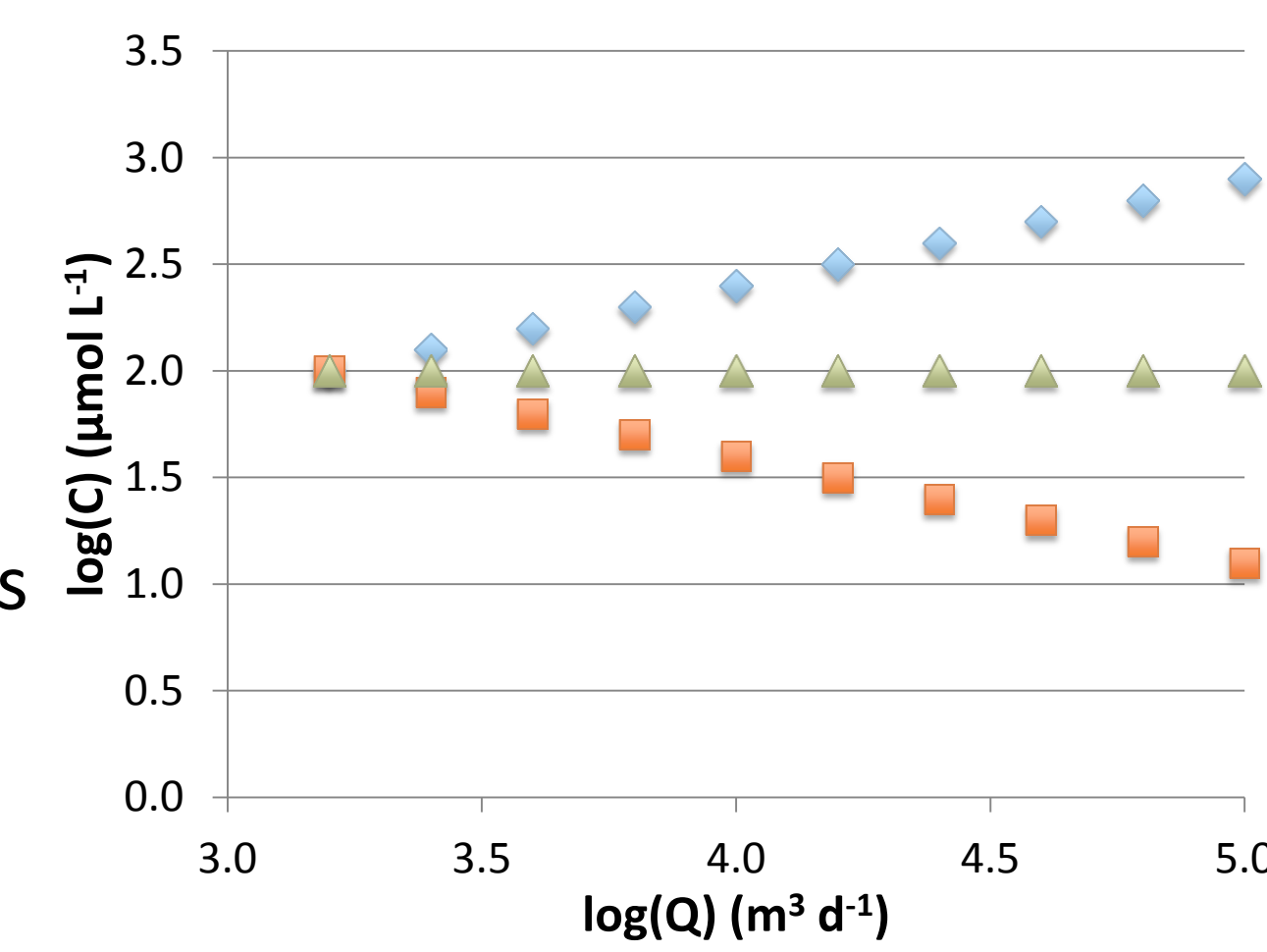
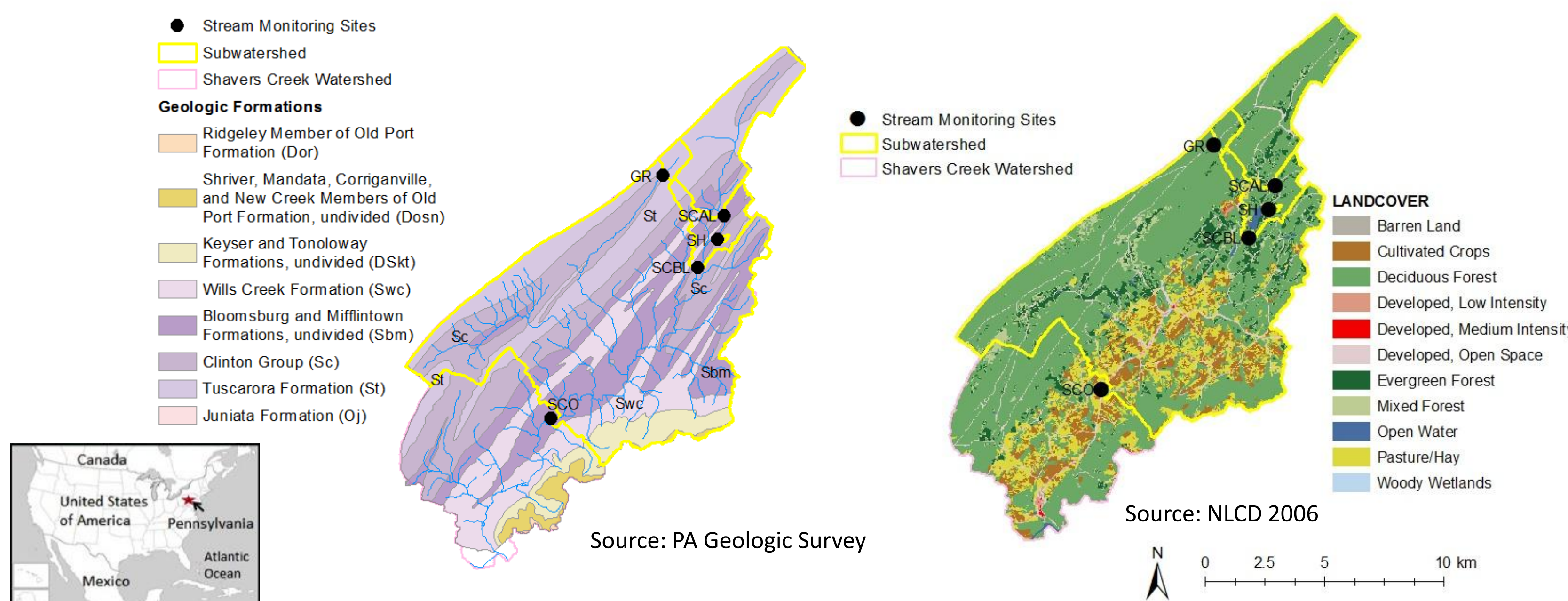


Figure 1: This represents the three potential scenarios of stream behavior: **enrichment**, **chemostasis**, and **dilution**

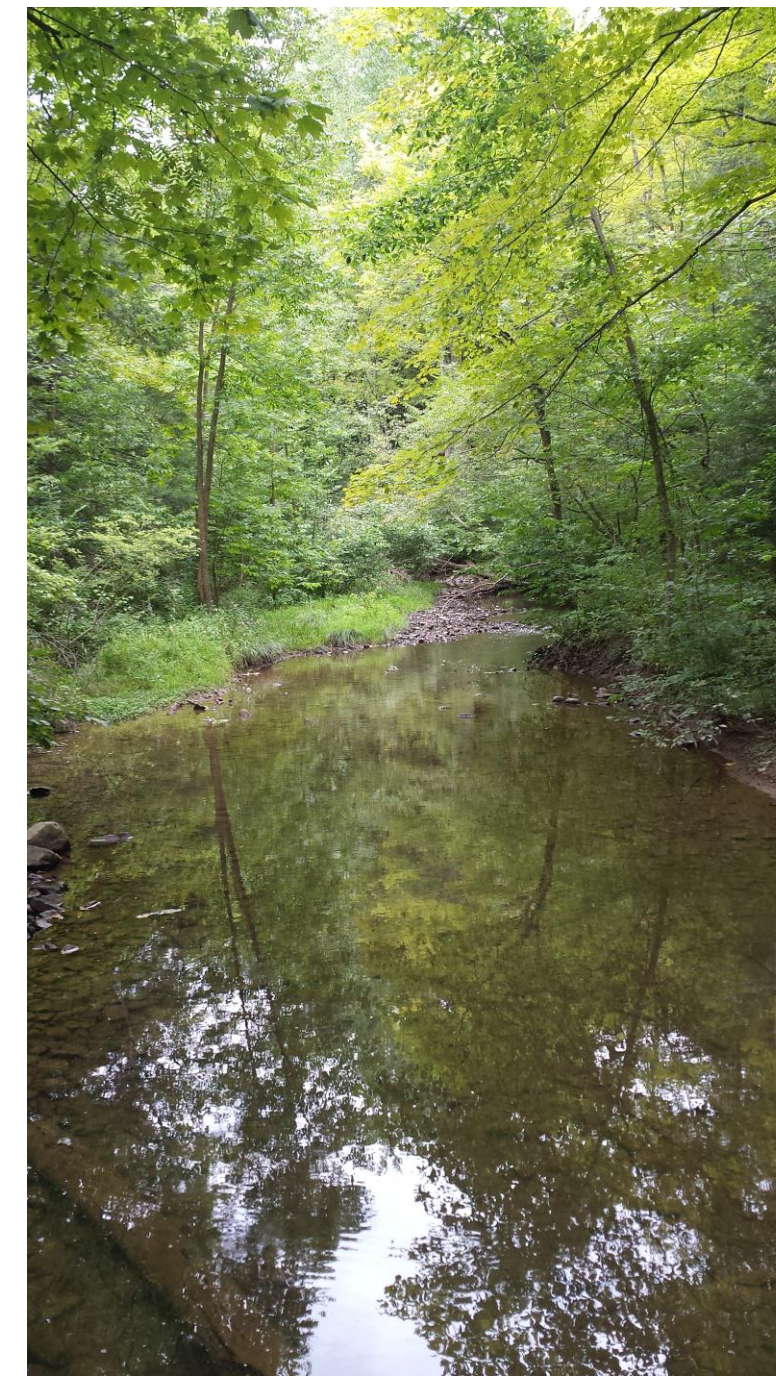
Study Site

The Shavers creek watershed is located in the Valley and Ridge physiographic province of central PA and feeds the Susquehanna River by way of the Juniata River. The land within the watershed is a mix of temperate forest and agricultural land, and much of the forest was cleared as recently as the 1930's. This study focuses on five sites within the Shavers Creek watershed: one on a small catchment completely underlain by shale (Shale Hills; SH), one on a small catchment underlain by sandstone/quartzite (Garner Run; GR), one above and one below Lake Perez (SCAL and SCBL), and one representing the outlet of Shavers Creek (SCO).

Figure 2: The Shavers Creek Watershed in relation to the greater United States and showing the five sites studied with a) the underlying lithology and b) the overlying landcover



Methods



Discharge measurements (Q ; $m^3 s^{-1}$) and stream water grab samples were taken at five sites in the Shavers Creek watershed to examine the relationship between concentration (C) and discharge.



- Discharge (Q ; $m^3 s^{-1}$) measured: Acoustic Doppler Current Profiler (ADCP; SonTek IQ, SCO) or Acoustic Doppler Velocimeter (ADV; Flow Tracker, SonTek inc; SCAL & SCBL & GR.), v-notched weir using the rating curve (Nutter 1964; SH)
- HOB0 Pressure Transducers collecting stage measurements every thirty minutes were installed at SCAL, SCBL, and SCO
- Water samples were collected and filtered ($0.45 \mu m$ nylon filter) weekly to biweekly for anion and cation analysis on a Dionex ICS 2500 and a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer, respectively.

Results and Discussion

- Nitrate and sulfate increase rapidly between the upstream sites (SCBL, SCAL) and the outlet (SCO)
- Observed increase in nitrate is consistent with a shift in land use from a forested to agricultural setting.
 - The fertilizers and cow manure used locally could increase nitrate towards the outlet.
- Elevated sulfate at the outlet could be due to a transition in bedrock lithology to the Wills Creek formation, which contains both celestite ($SrSO_4$) and gypsum ($CaSO_4$) (Cotter, 1986).
- While sulfate dilutes at SCO it remains chemostatic at SCBL and SCAL.
 - This may be a sign of the weathering limitations of the sulfate sources in the Wills Creek formation.

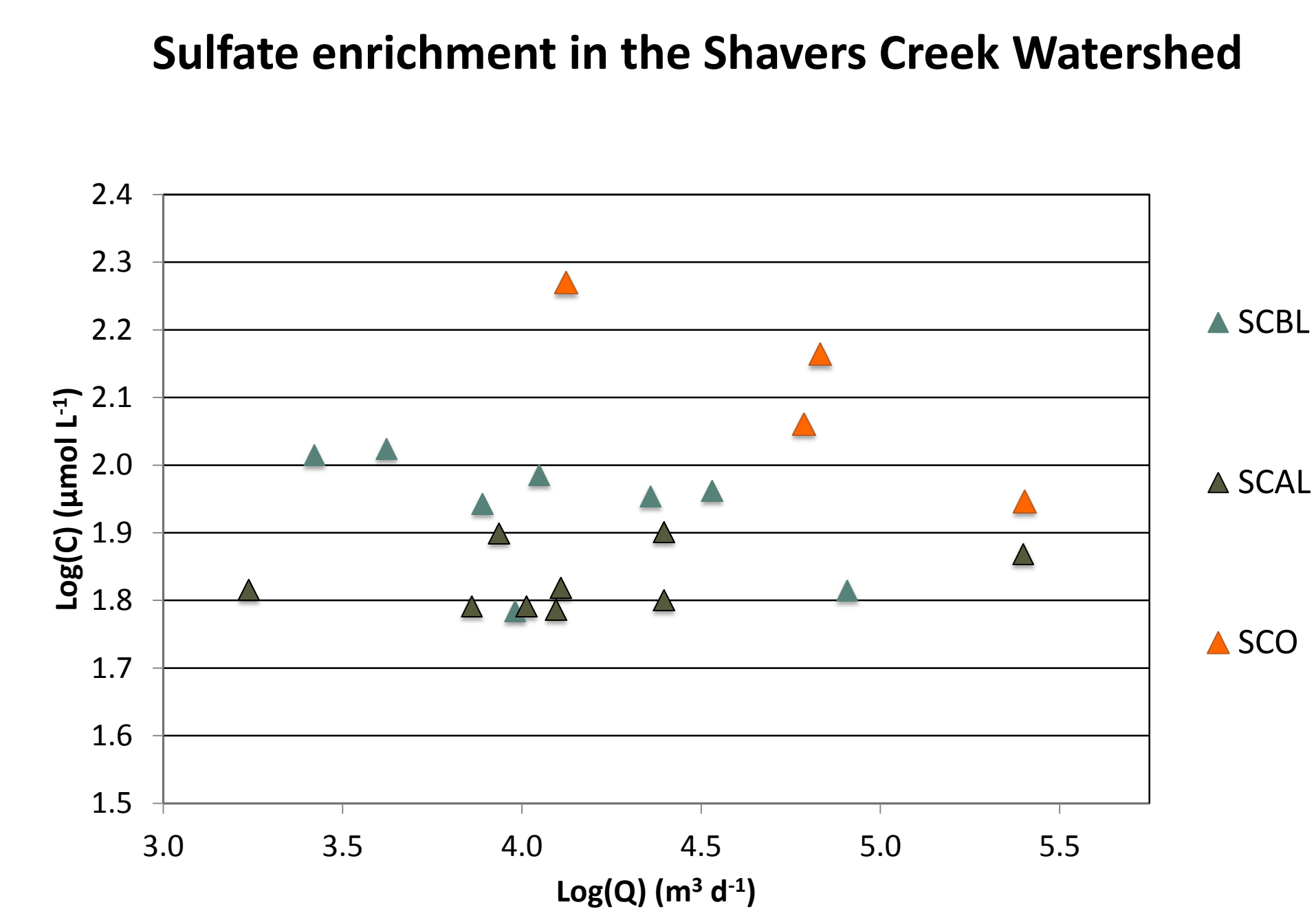
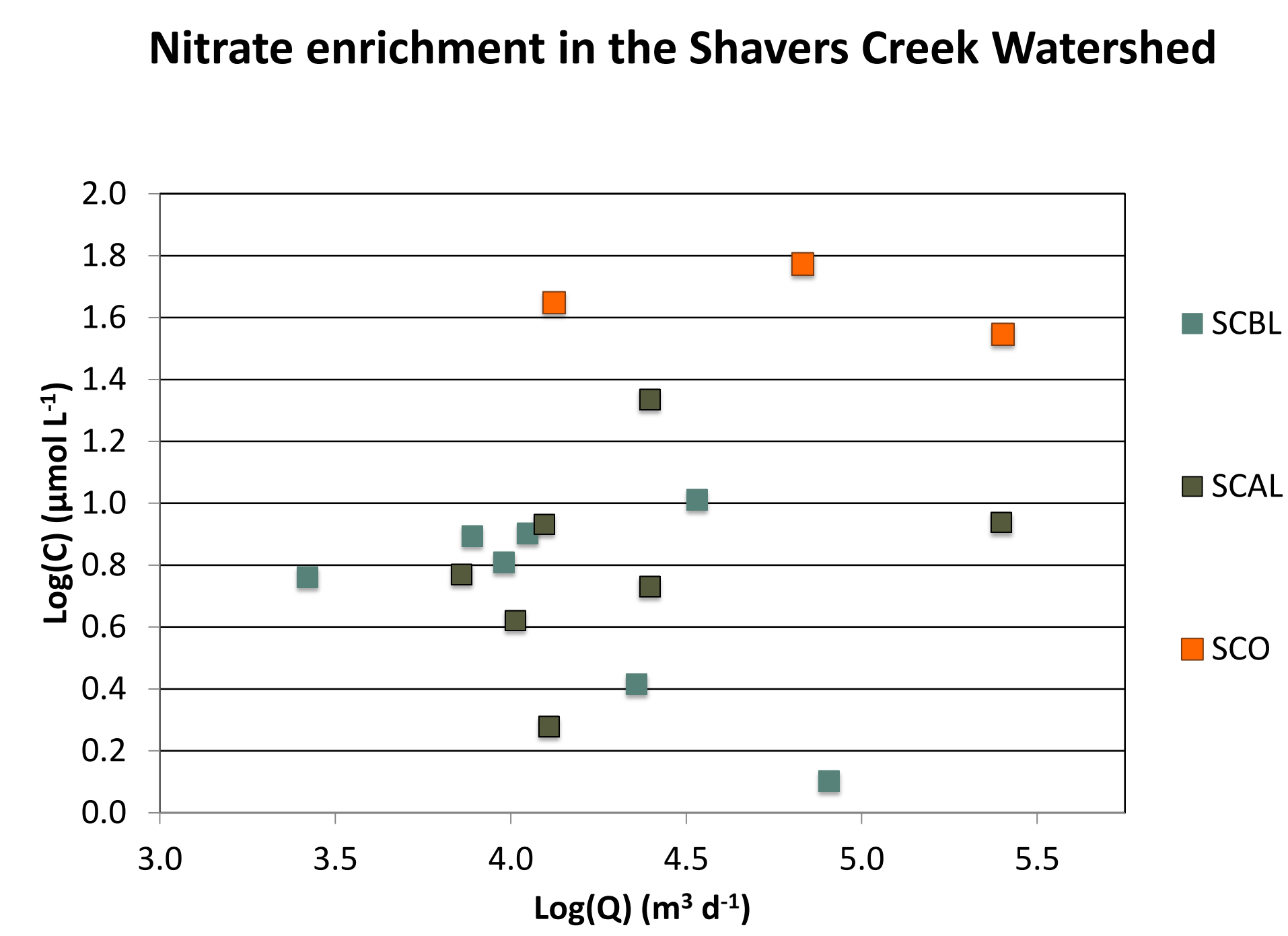
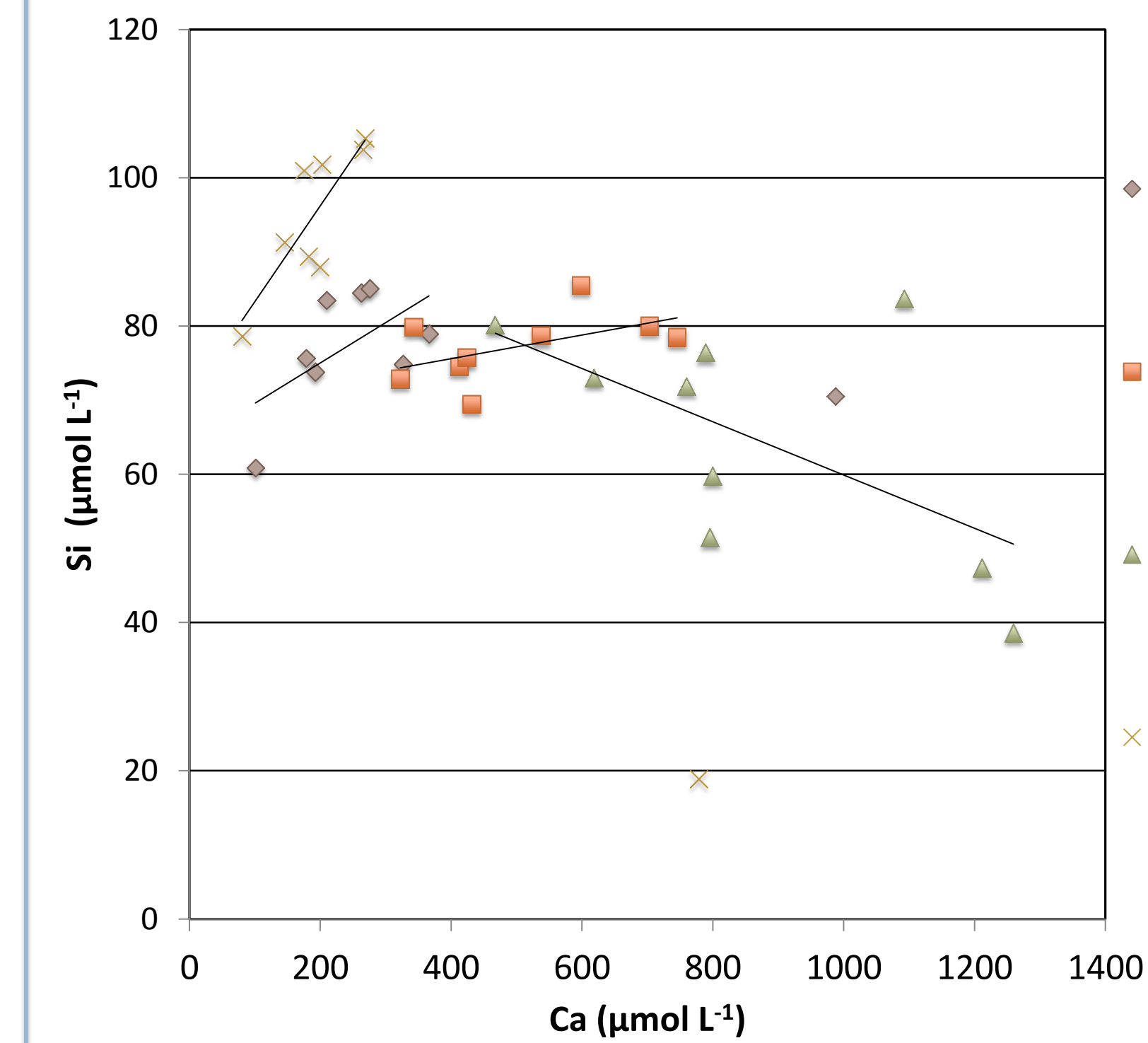


Figure 3: Nitrate and Sulfate Concentrations along Shavers Creek as a function of discharge

Stream water Ca and Si concentrations in the Shavers Creek Watershed



Stream water Ca and Mg concentration in the Shavers Creek Watershed

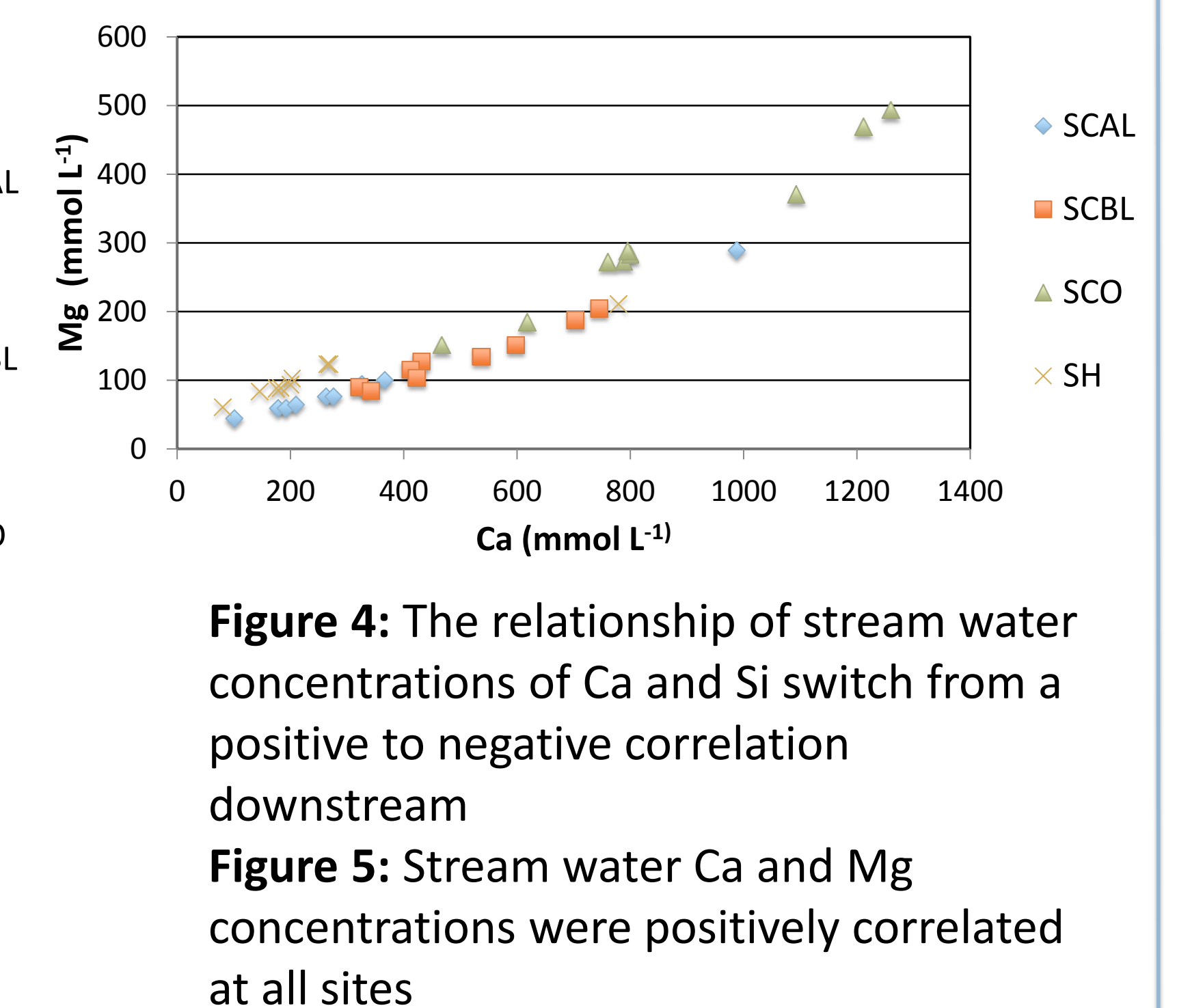


Figure 4: The relationship of stream water concentrations of Ca and Si switch from a positive to negative correlation downstream

Figure 5: Stream water Ca and Mg concentrations were positively correlated at all sites

- Ca and Mg are positively correlated at all sites (Fig. 5). However, the correlation of Ca and Mg with Si transitions from positive to negative when approaching the outlet (Fig. 4). This exhibits the shift in underlying lithology from a shale to a carbonate setting.
- While the majority of the data conforms to the trend for each site (Fig. 4), there are two outliers to the data, one at SCAL and one at SH, which were measured in October 2013. Boron isotope data (not shown) from this time suggest the anomaly may be driven by leaching of nutrients from leaf litter.
- Mg and Ca dilute in response to discharge while other ions such as Si remain largely chemostatic.

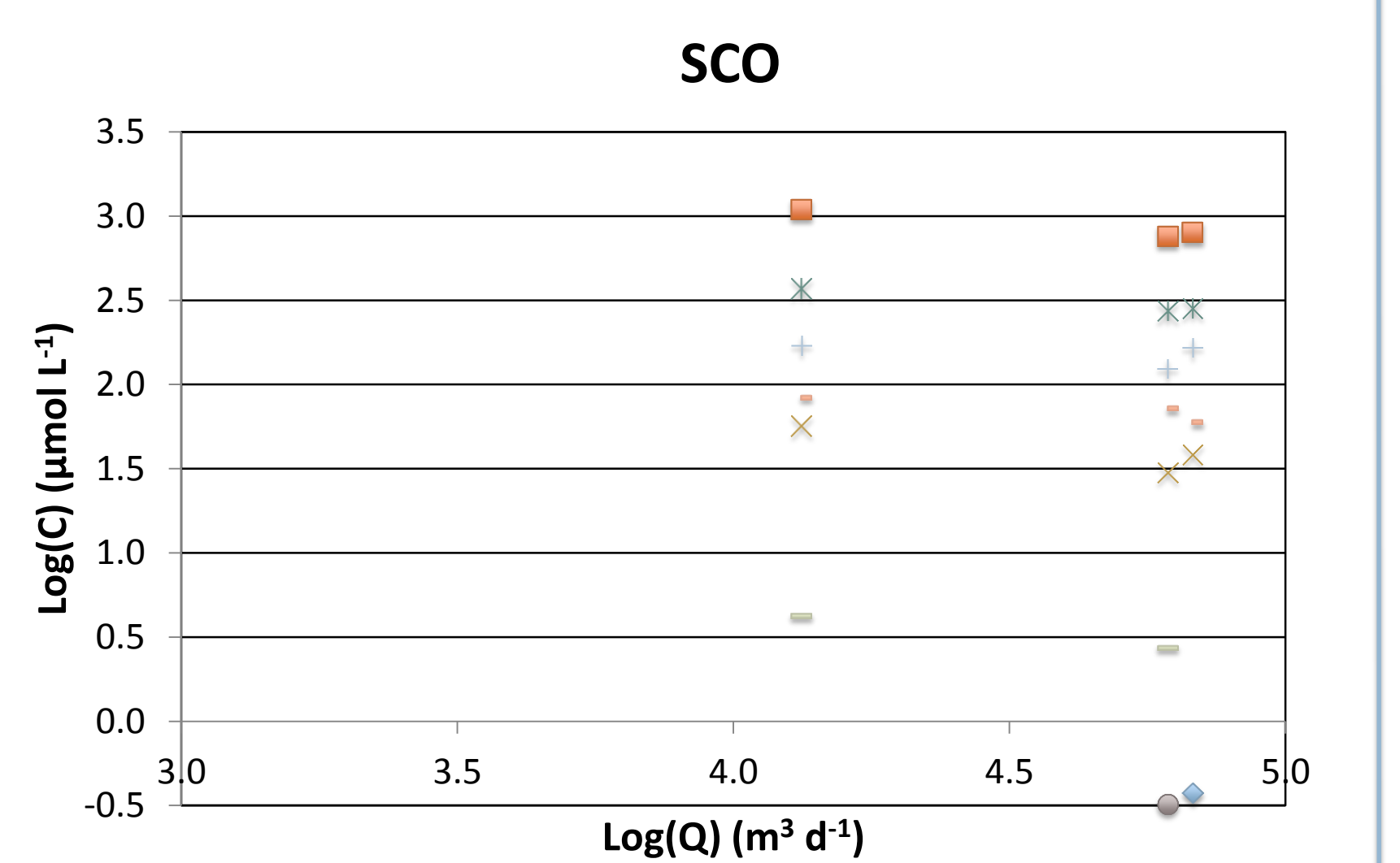
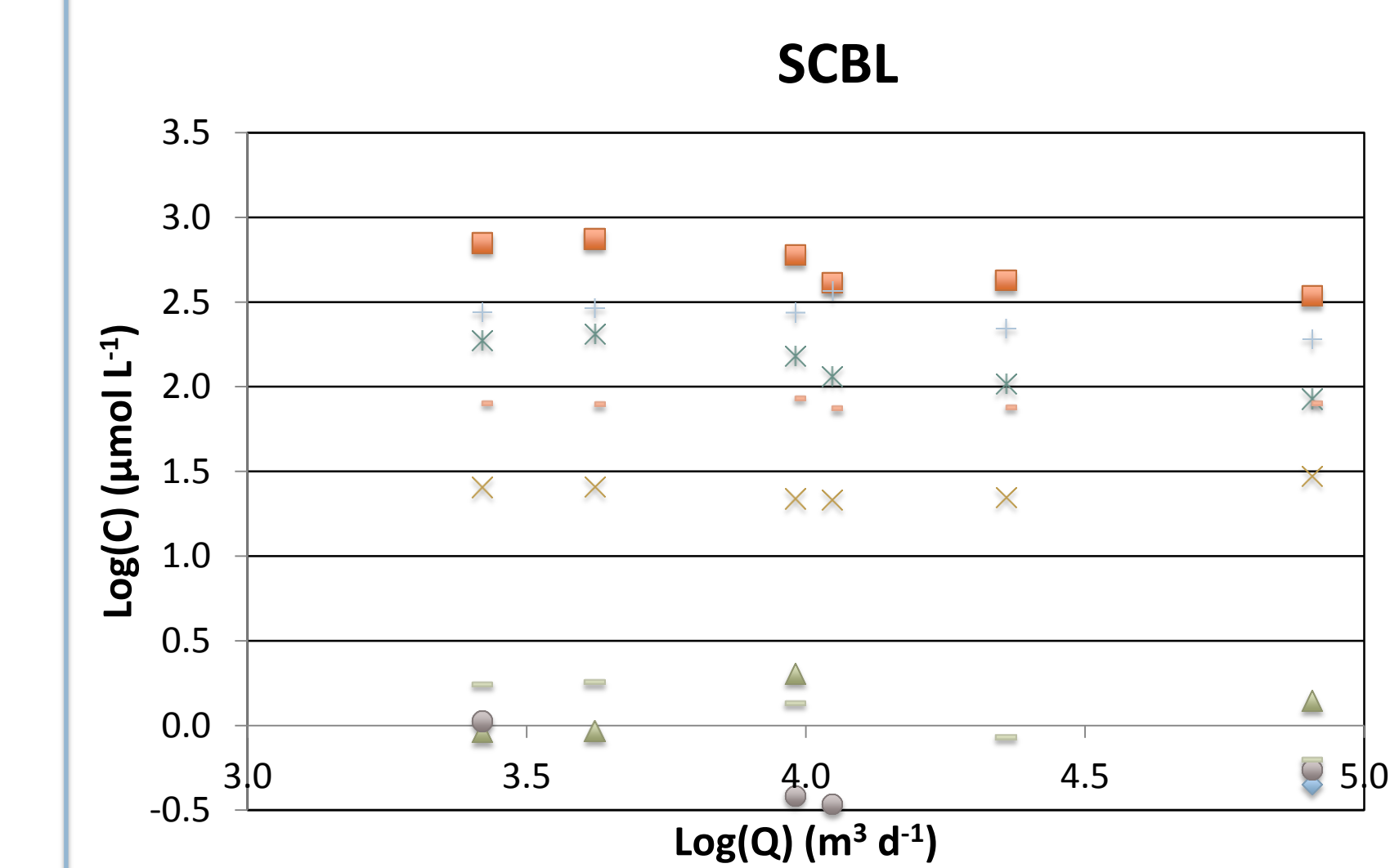
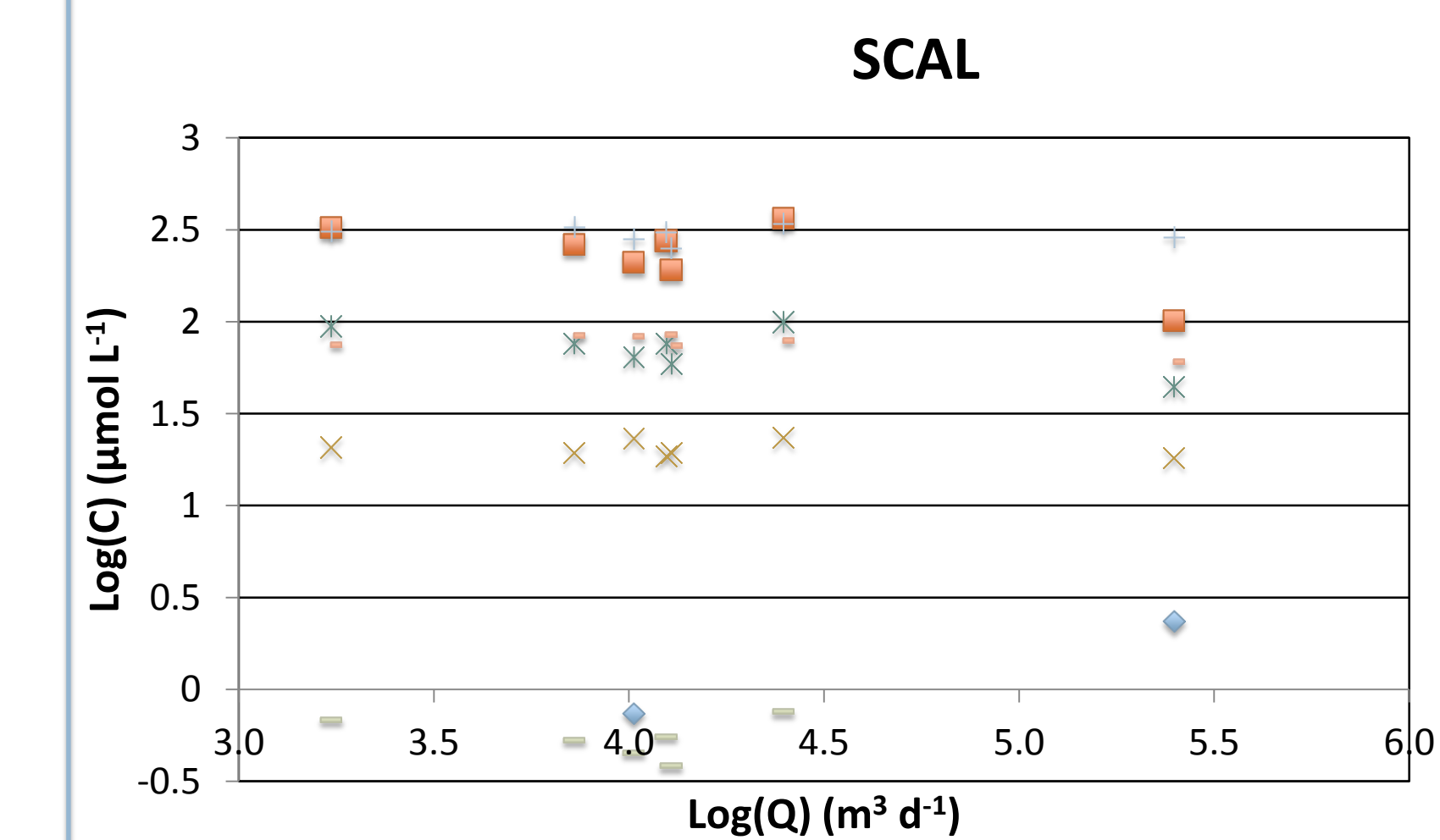


Figure 6: Log-log plots show dilution of Ca and Mg at the Shavers Creek main stem sites: SCAL (a), SCBL (b), and SCO (c)

Conclusions

These results suggest that under low-flow conditions stream water is recharged largely from carbonate sources while under high flow conditions, water interacting with Si-rich sandstone becomes increasingly important to stream chemistry. This further supports the need to integrate the geologic setting into hydrogeochemical models in order to accurately predict the anthropogenic impact on stream water quality. Additionally more work needs to be done sampling the area to get more conclusive stage-discharge relationships for each stream site.