

Concentration-discharge behavior as an indication of groundwater
contribution in Copper Creek sub-catchment of the Upper East River
Basin

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Full Time Independent Research

Summer 2017

Abstract

Groundwater in high elevation watersheds is difficult to quantify, but remains a major component in the hydrologic budget for the western United States. Concentration-discharge (C-Q) data can provide a framework for characterizing groundwater flow in small alpine catchments by indicating fluid residence times and solute fluxes. Such factors heavily influence biochemical processes and mixing behaviors downstream. Complimenting field measurements, End Member Mixing Analysis (EMMA) was conducted to apply a statistical approach for identifying solutes. Most small catchments exhibit chemostatic behavior which is defined as nearly constant solute concentration with changing discharge rates (Maher, 2011) therefore, SF₆ and N₂/Ar samples were collected to estimate fluid residence time and recharge temperature. We investigated these relationships in the Copper Creek sub-catchment by analyzing solute concentrations of anions, cations, and dissolved organic and inorganic carbon coupled with discharge measurements to assess its groundwater and solute contributions to East River.

1. Introduction

The Colorado River is the largest source of water across the west, and receives 90% of its flow from snowmelt-dominated systems in high elevation watersheds (Rumsey *et al.*, 2015). Groundwater and shallow subsurface flow in headwater source basins are major components in the hydrologic budget for the Colorado River. Snowmelt-dominated systems typically have short residence time, making them susceptible to contamination and sensitive to climate change (Newman *et al.*, 2010). A recent study on high elevation watershed sensitivity to climate observed that an increase in temperature of 4°C would decrease the snowpack in alpine and sub-alpine terranes by 50% (Baron *et al.*, 2000). A decrease in snowpack resulted in earlier peak runoff and faster regression to baseflow conditions (Baron *et al.*, 2000). Runoff timing directly affects biogeochemical processes and feedbacks within the critical zone (Carroll *et al.* HESS in prep) (Figure 1).

Snowpack that percolates into the subsurface becomes groundwater and impacts baseflow conditions in streams. Baseflow is water that keeps perennial streams flowing all year and is predominately groundwater (Miller *et al.*, 2014). Source water components in mountain catchments are difficult to quantify due to mountain block recharge and areas inaccessible for gaging. Concentration-discharge relationships (C-Q) are simple and effective methods for characterizing groundwater by providing a numeric approach to understanding hydrologic partitioning and solute export (Carroll *et al.* HESS in prep). We supplement this with a statistical approach, End Member Mixing Analysis (EMMA), to compliment physical measurements (Carroll *et al.* HESS in prep).

The Copper Creek sub-catchment drives solute export to East River (Carroll *et al.* HESS in prep), and is estimated to be the highest contributor of groundwater, accounting for 25% of discharge (Winnick *et al.*, 2015). Solutes are generated from biogeochemical weathering and provide information on groundwater residence time and flow paths (Godsey *et al.*, 2010). In this study, we administer various techniques such as C-Q relationships and EMMA to quantify groundwater contribution and solute export within the alpine and sub-alpine terranes of the critical zone (Figure 1).

2. Study Area

The Upper East River Basin spans 85 km² of montane, sub-alpine, and alpine terrane in central-Colorado (Winnick *et al.*, 2015). Copper Creek is located on the eastern side of the basin and flows from

Copper Lake to its confluence with East River in the Gothic townsite. We sampled from 10 sites on Copper Creek, major tributaries, and springs collectively (Figure 2). Copper Creek is accessible through the Copper Creek Trailhead, north of Gothic, Colorado.

The Copper Creek sub-catchment overlies Paleozoic Gothic, Maroon, and Jurassic Morrison Formations, Cretaceous Mancos Shale Formation, and Tertiary porphyritic igneous intrusives (Winnick *et al.*, 2015). Lithologies include red-brown conglomerates with interbedded sandstone and limestone, dark-grey marine shale, granodiorites and quartz monzonites, respectively.

3. Sampling Methods

3.1 Discharge

Discharge was measured at five sites along Copper Creek, and two sites along tributaries: Triangle Pass Creek, and one site from Queen Basin Creek (Figure 2). Discharge was measured using a SonTek Flowtracker acoustic doppler velocimeter. We used a tag line and recorded location using 15-30 cm intervals, using the stream bank as a datum. At each location, depth was measured using the Flowtracker meter stick and the height of the doppler was adjusted to measure average velocity. Discharge was calculated by integrating the product of cross sectional area and velocity. The largest uncertainties in discharge were in velocity measurements and were within 10% to 20% error.

3.2 TDS, pH, and Temperature

Total dissolved solids, pH, and temperatures were recorded using a Myron and Hanna Instruments probe for sites on Copper Creek, Triangle Pass Creek, Queen Basin Creek, and West Side Spring. Electrical conductivity and pH measurements range in error due to problems with probe calibration and resulted in some unstable values.

3.3 Stream Chemistry

Water chemistry samples were obtained from seven sites along Copper Creek, one site from Triangle Pass Creek, and one site from Queen Basin Creek. Samples were collected for stable isotopes, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, dissolved organic and inorganic carbon (DOC/DIC), cations, and trace metals. Syringes and filters were flushed three times to remove possible manufacturing contaminants.

Stable Isotopes

Stable isotopes samples were obtained using 5ml syringes with 0.45 μm Hydrophilic Polyvinylidene Fluoride Filters (PVDF) and collected in a 1.5 ml sterile vial.

Dissolved Organic and Inorganic Carbons

DOC/DIC samples were obtained using 60 ml syringes with 0.45 μm PVDF and collected in sterile glass vials.

Cations and Trace Metals

Cations and trace metal samples were obtained using 60 ml syringes with 0.45 μm PVDF and collected in plastic vials containing 0.4 ml of nitric acid.

3.4 Sulfur hexafluoride (SF₆) and Dissolved Gases (N₂/Ar)

Two SF₆ samples were collected in a spring located immediately west of Copper Creek on a hillslope. A piezometer was placed 35 cm deep into soft soil a few centimeters from where the spring emerged. Water was pumped out of the spring into 1L plastic coated amber bottles. 2.5-3L of spring water was flushed through the bottles before being capped in open atmosphere, leaving no headspace. The caps were sealed using electrical tape wrapped in a clockwise direction.

Two dissolved gas samples were collected in the same spring. Spring water was pumped through the piezometer filling a sterile glass bottle. Once filled, the bottle was immersed into a 2.5L plastic container allowing approximately 500ml to flush through. The glass bottle was capped underwater using a plastic stopper with a needle pushed through. The needle was removed underwater following the release of bubbles from inside the bottle.

SF₆ is an inert, anthropogenic gas that is incorporated in the groundwater interface and can provide information on fluid residence time (Newman *et al.*, 2010). Such environmental tracers have been widely used for age dating groundwater less than 50 years old (Figure 3). We opted for SF₆ over other tracers such as chlorofluorocarbons (CFCs), due to large concentrations of vegetation in the study area.

4. Results

Lab results for stream chemistry, SF₆ samples, and dissolved gases are expected in late August to early September. We will continue monitoring stream discharge through October, when streams return to baseflow conditions.

PH, temperature, and totally dissolved solid measurements show TPC and CC-04 with the lowest average temperatures, high TDS, and low pH (Figure 4). Discharge measurements show a significant increase at CC-04 (Figure 5).

5. Discussion

We anticipate our stream chemistry results to show mostly chemostatic behavior, where solute fluxes vary little from changing discharge (Maher, 2011). Stream discharge measurements showed the greatest flow at the confluence with East River at 1.3009 m³/s therefore, stream chemistry analysis of solute concentration may decrease at this point. For solute identification, we will use a bi-mixing plot from EMMA and look for linear behavior between solutes in monthly changes in concentration (Carroll *et al.* HESS in prep). This technique has already been administered for the Pumphouse site on East River (Figure 6).

Field measurements such as pH, temperature, and TDS indicate that site CC-04 and Triangle Pass Creek are large sources for groundwater contribution. Both sites had the lowest average temperatures, highest TDS, and low pH. Water picks up dissolved solids as it travels through the subsurface and contributes to geochemical weathering producing more acidic water compared to shallow subsurface flow or rain water.

Lab results for SF₆ and dissolved gas samples collected at West Side Spring are anticipated to age date less than 50 years, but greater than 1 year, and have low recharge temperature. If the results indicate a recent age, less than or equal to a year, flow is likely shallow subsurface or our piezometer was not deep enough to pump out groundwater.

Continuing discharge measurements through September and October will provide data on baseflow conditions and solute concentrations, which are typically highest during baseflow (Carroll *et al.* HESS in prep).

Literature Cited

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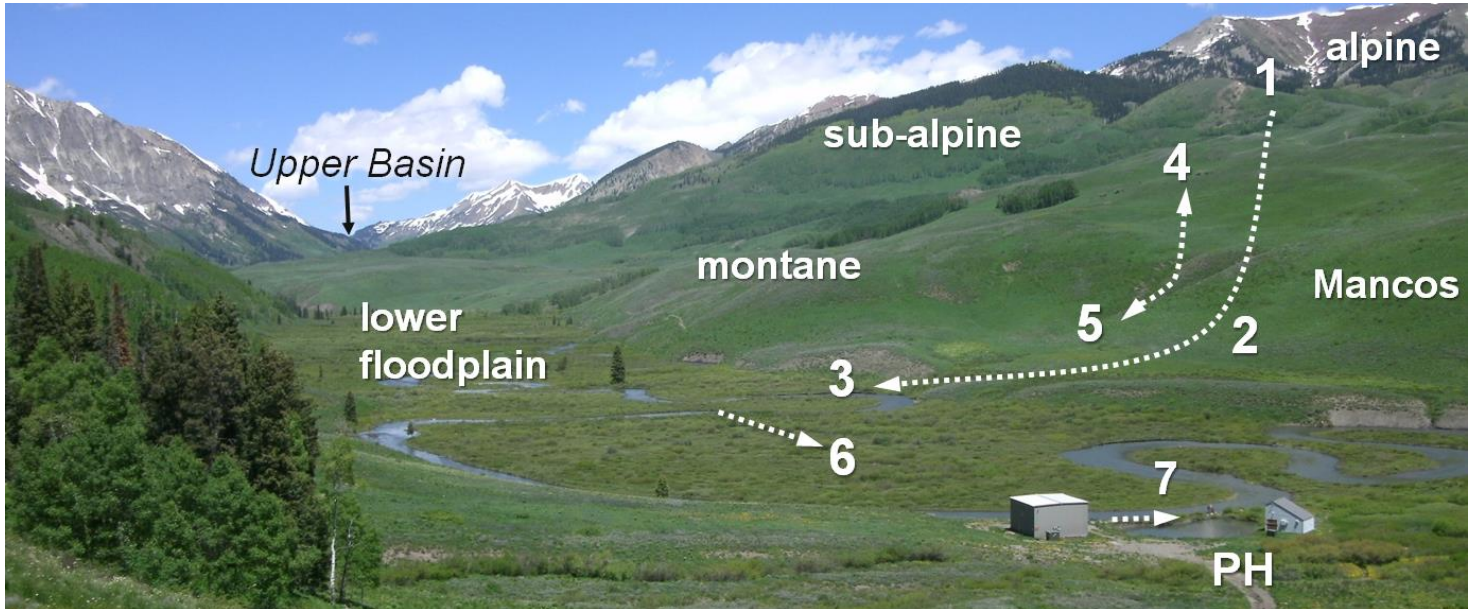


Figure 1. Terranes of the East River Basin including feedbacks in the critical zone.

- (1) GW recharge zone with deep water tables and ET limited to soil and fractured rock.
- (2) Hillslope processes of carbonate weathering and water-rock equilibrium
- (3) GW discharge zone – ET not limited
- (4) Seasonal GW recharge-discharge zone dependent on water table fluctuation & veg. structure
- (5) Shallow flow paths and ephemeral seeps during spring melt
- (6) Floodplain transformations.
- (7) Integrative C-Q

From Carroll et al. HESS (in prep).

Copper Creek Research Sites 2017

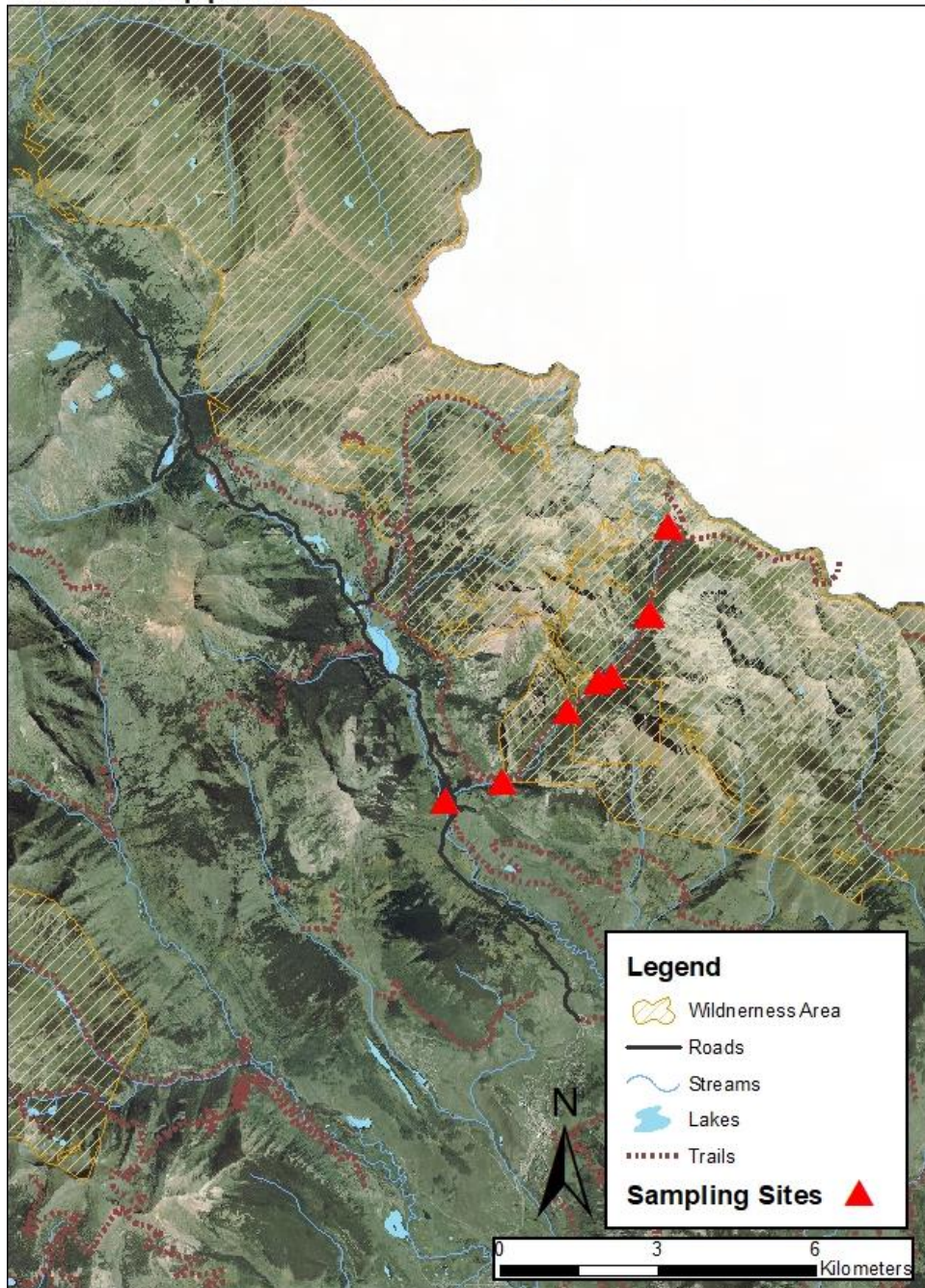


Figure 2. Location of Copper Creek sub-catchment and research sites.

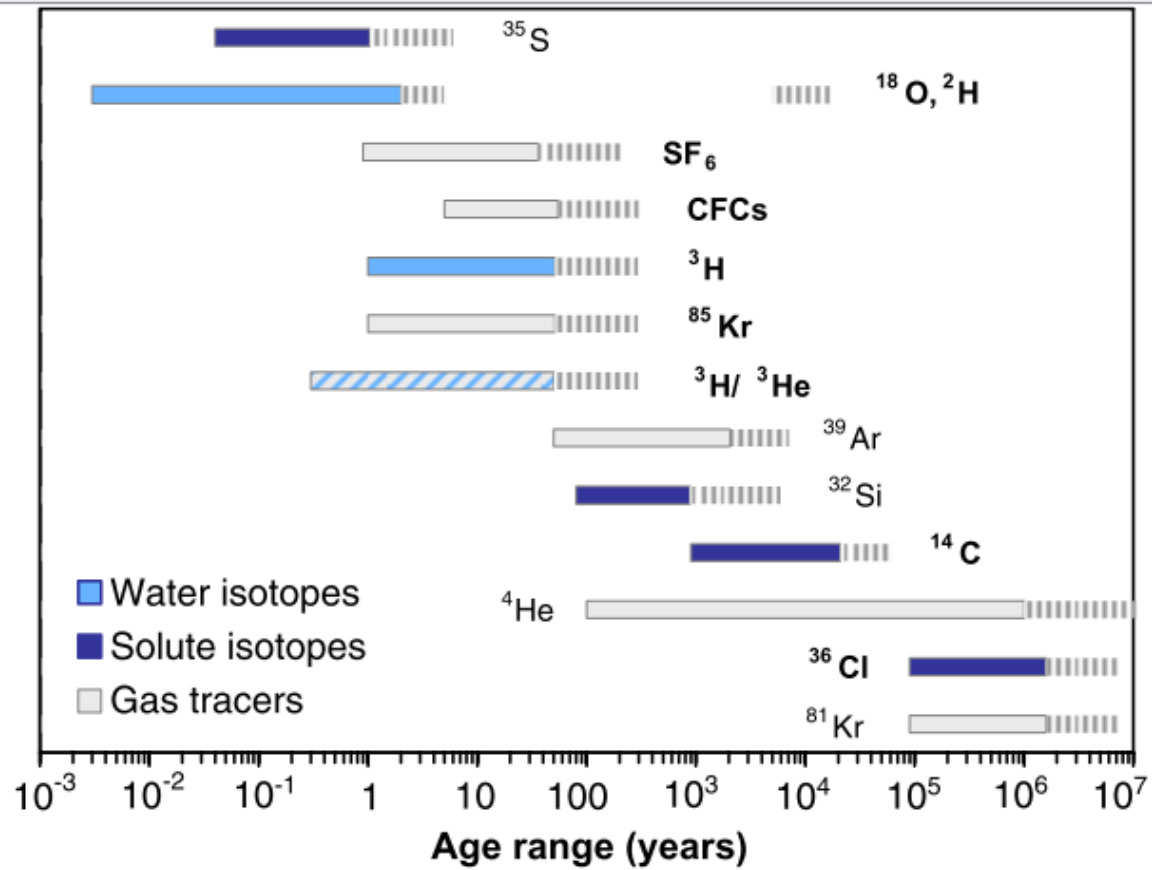


Figure 3. Age ranges for various environmental tracers used for groundwater dating. From B.D. Newman et al., 2010.

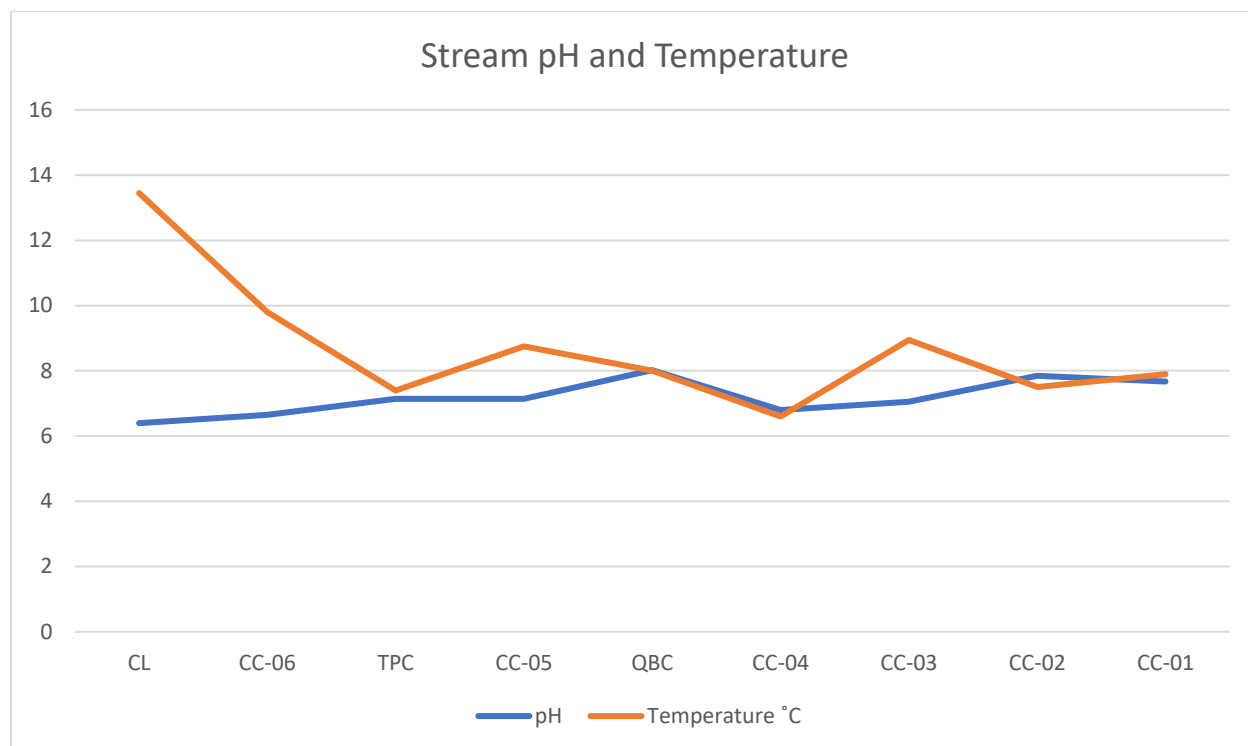


Figure 4. pH and temperature distributions for Copper Creek sites.

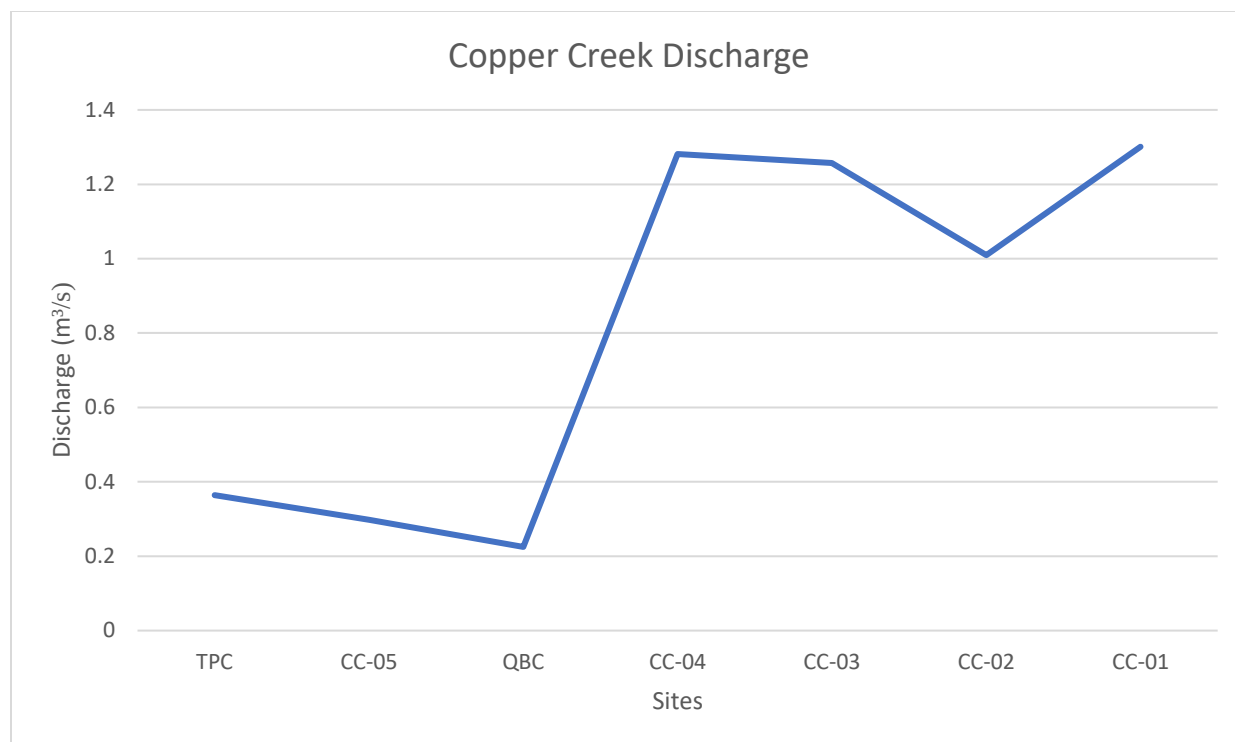


Figure 5. Discharge distribution of Copper Creek sites.

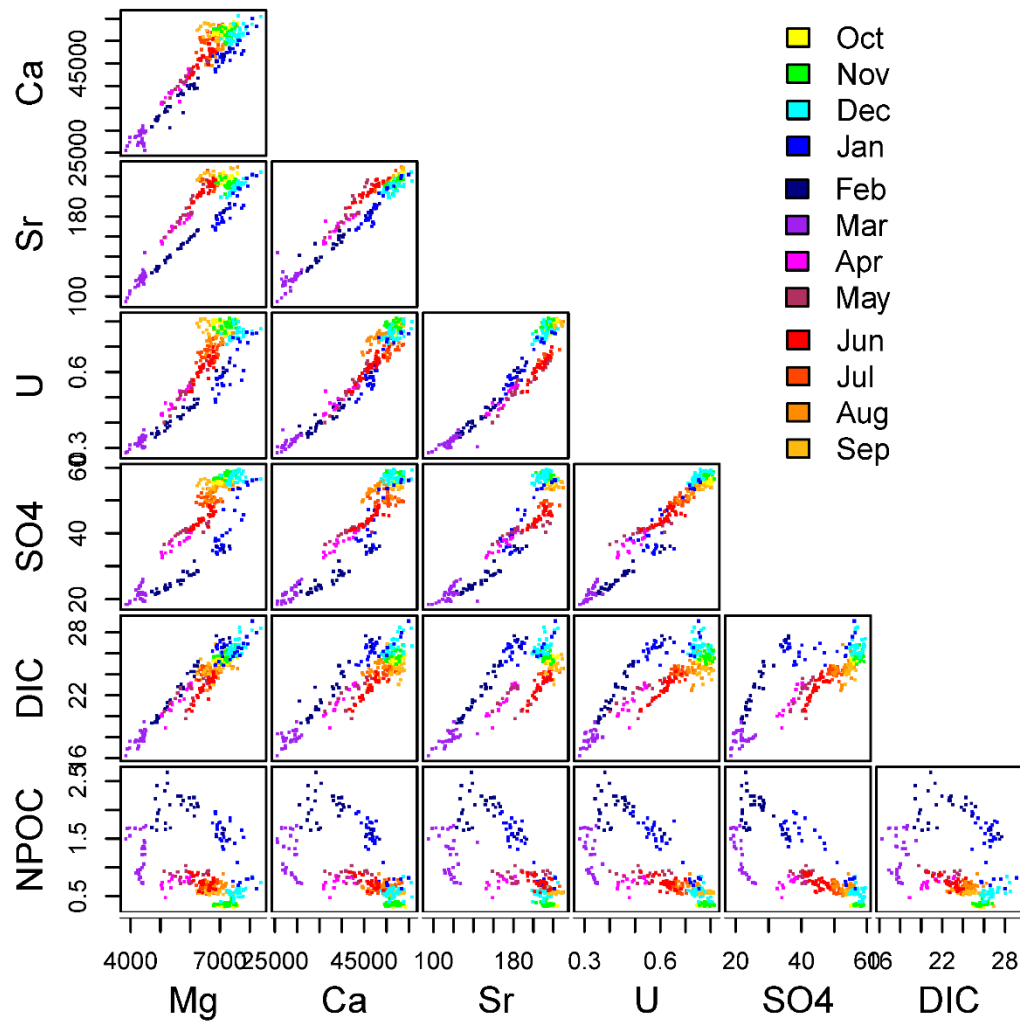


Figure 6. Example of EMMA bi-mixing plot for Pumphouse. Linear relationships between monthly solute concentrations are used for solute identification. From Carroll et al. HESS (in prep).