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Evaluation of Hydrograph Separation Techniques with Uncertain End-member Composition

Running Head: Evaluating Hydrograph Separation Techniques

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Abstract

Hydrograph separation is one of many approaches used to analyze shifts in source water contributions to stream flow resulting from climate change in remote watersheds. Understanding these shifts is vital, as shifts in source water contributions to a stream can shape water management decisions. Because remote watersheds are often inaccessible and have poorly characterized contributing water sources, or end-members, it is critical to understand the implications of using different hydrograph separation techniques in these data-limited environments. To explore the uncertainty associated with different techniques, results from two hydrograph separation techniques, mass balance and principle component analysis, were compared using three years of aqueous geochemical data from the East River watershed located in the Elk Mountains of Central Colorado. Solute concentrations of the end-members were characterized by both a limited set of direct chemical measurements of different sources and detailed seasonal instream chemistry to examine the influences of uncertain end-member compositions in a data-limited environment. Annual volumetric end-member contributions to stream flow had relatively good agreement across separation techniques. Large variations in time were observed in the hydrograph separations, depending on the end-member type, and estimated flow contributions varied between the selected solutes. End-member concentrations characterized by stream chemistry showed several limitations including a reduced number of distinguishable end-members and differences in timing of flow contributions. Results highlight the benefits of using multiple hydrograph separation techniques by providing a 'weight-of-evidence' approach to environments with limited end-member concentration data.

Keywords: hydrograph separation, mass balance, end-member mixing, instream chemistry, data-limited, solutes

1. INTRODUCTION

The hydrology of high-elevation mountain environments has changed dramatically over the past decade (Hock et al., 2019). April 1st snow water equivalent, an important hydrologic indicator, has been in decline across the western United States in part due to rising global temperatures (Mote et al., 2005; Mote et al., 2018; Huning & AghaKouchak, 2018) and an increase in the fraction of precipitation falling as rain (Hamlet et al., 2005; Knowles et al., 2006). This is significant as a decrease in the fraction of precipitation falling as snow has been identified as one cause of decreased streamflow (Berghuijs et al., 2014; Foster et al., 2016), along with shifts in evaporative losses (Foster et al., 2016). Additionally, the timing of snow derived runoff has been observed to occur earlier than long term averages across western North America (Brahney et al., 2017a; Clow, 2010; Stewart et al., 2005), which has been exacerbated by dust deposition on snow (Painter et al., 2007; Skiles et al., 2012). Earlier snowmelt may cause high elevation reservoirs to exceed storage capacities, forcing early releases (Barnett et al., 2005 & references therein; Kopytkovskiy et al., 2015). This loss of storage as snow and storage within reservoirs means less water during periods of summer drought when water demand is high. This is consequential as agriculture is particularly vulnerable to shifts in snowmelt quantity in the western United States (Qin et al., 2020), where 53% of annual runoff is snow derived (Li et al., 2017). This is even higher in mountainous regions where 70% of annual runoff is snow derived (Li et al., 2017). Changes to the timing, duration, and quantity of snowmelt may also impact sensitive endemic instream biota (Brahney et al., 2020; Brown et al., 2007) and may affect the biodiversity of cold water adapted organisms (Hotaling et al., 2017 & references therein). Given that shifts in source water contributions to instream flow are influential in the genetic diversity and management of mountain stream systems, techniques to track these changes in remote environments are critical.

Hydrograph separation techniques are often used to separate the chemically distinct source waters (end-members) contributing to instream flow. Traditionally, hydrograph separations are performed using mass balances with one or two chemical or isotopic solutes (see Klaus & McDonnell, 2013; Wels et al., 1991). Another more robust form of hydrograph separation additionally utilizes principal component analysis (PCA) and end-member mixing analysis (EMMA). This second method offers an advantage by employing a larger suite of chemical and isotopic information than a traditional mass balance to separate the end-members

(see Bearup et al., 2014; Carroll et al., 2018; Liu et al., 2017). This partitioning of flow into the end-members through hydrograph separation techniques is useful for analyzing changes in the hydrology of mountain catchments. For example, hydrograph separation has been used to track temporal changes in glacial contributions to streamflow (Brahney et al., 2017b), analyze base flow patterns in the Upper Colorado River Basin (Miller et al., 2014), and examine how forest bark beetle infestations affect the local water balance (Bearup et al., 2014). Studies such as these demonstrate the power and versatility of hydrograph separation techniques. Using multiple separation techniques offers both a method of comparison and also a potential 'weight-of-evidence' approach to working in catchments where a single separation technique on its own may not fully characterize the contributing end-members.

Components that contribute to instream flow can generally be categorized into "old" (pre-event) and "new" (event) waters, as summarized by Genereux & Hooper (1998). Old water is usually described as all water that exists in the watershed before hydrologic perturbation, such as a rainstorm or snowmelt event that generally reaches the stream through subsurface pathways. New water may reach the stream by infiltrating and taking short residence time subsurface pathways or may enter the stream through surface pathways (Freeze, 1974). Residence time in the watershed is an important factor as it will affect the chemical signal a packet of water accumulates as it moves towards the stream. Sueker et al., (2000) summarizes this well, describing water that undergoes significant chemical changes as 'reacted' water and water that goes unaltered through the watershed as 'unreacted' water. Thus, instream chemistry represents the complex mix of source waters existing as new and old water and having undergone (or not undergone) a chemical alteration. To parse the contribution of these unique water types to streams, hydrograph separations can be used in tandem with geochemically relevant solute information from the stream and the contributing end-members. For accurate separations, solute concentrations of the contributing end-members should be representative of the end-members throughout the basin. However, detailed spatial and temporal information about end-member solute concentrations are very difficult to establish. As highlighted by Bales et al. (2006), spatially detailed hydrologic observation networks in mountainous environments are often unavailable.

As such, data limitations often affect the number of possible end-members that are identified and how end-member concentrations are characterized. Studies often choose to

approach characterizing end-member concentrations one of two ways. Some studies (Jenkins et al., 1994; Liu et al., 2017; Williams et al., 2009) characterize end-member concentrations through detailed temporal and spatial sampling directly from the sources. The second way is through a type of 'hydrologic rationalization' in which end-member concentrations are characterized solely by instream data during certain flows or at certain locations (Pinder & Jones, 1969, Miller et al. 2014, and Foks et al., 2019). For example, the stream's chemical composition during periods of low flow is often assigned to a groundwater end-member. Still, other studies use a combination of detailed sampling and hydrologic rationalization to characterize end-member concentrations. For example, James & Roulet (2009) utilized diverse spatial sampling to characterize a concentration range for a new-water end-member. Detailed instream sampling during baseflow along with samples from a single spring in the study area were used to characterize concentrations of an old-water end-member. Many studies have highlighted the issues with using poorly characterized end-member concentrations to perform hydrograph separations (Cayuela et al., 2019; Kiewiet et al., 2020; Penna & Meerveld, 2019), but characterizing end-member concentrations via detailed spatial and temporal sampling is not always possible, particularly in remote catchments. This highlights the need to develop methods to overcome inevitable end-member data limitations.

Understanding the strengths and weaknesses of different hydrograph separation techniques in predicting end-member contributions when end-member information is limited is a critical first step. Therefore, this study focuses on *how two similar hydrograph separation techniques compare in their prediction of annual volumetric end-member contributions to rivers with limited end-member data, but detailed instream data across multiple years.* Of specific interest are 1) the consequences of using different end-member characterizations informed by detailed instream data to address challenges related to spatially limited end-member data with two commonly applied hydrograph separation techniques and 2) if any general conclusions about catchment hydrology can be made as a result of using multiple separation techniques and a 'weight-of-evidence' approach.

2. METHODS

2.1 Study Area

The experimental watershed is located in the Gunnison National Forest near Gothic, Colorado (Figure 1) and serves as the primary drainage of the main stem East River (ER). The study site includes the Rocky Mountain Biological Laboratory (RMBL) and hosts a diversity of hydrogeochemical studies performed as part of the Lawrence Berkeley National Laboratory (LBNL) Watershed Function Science Focus Area (WFSFA) funded by the U.S. Department of Energy. The headwaters of the ER are in a high-alpine region of the Elk Mountains of Central Colorado at an elevation of 3190 m, and with the confluence of the Taylor River near Almont, Colorado form the Gunnison River at an elevation of 2245 m. The sub-watershed of interest has a drainage area of approximately 85 km^2. The ER represents one of the many small watersheds that drain to the Upper Colorado River Basin (UCRB), a critical water resource for much of the western United States. The ER WFSFA receives 1200 mm yr^{-1} of precipitation (PRISM, 2021) that primarily falls as snow (Hubbard et al. 2018). The ER watershed is generally considered pristine and runoff is composed primarily of snowmelt, rain, and groundwater (Carroll et al., 2018) with little to no human impact in the study area apart from atmospheric deposition events. The arid regions of the southwestern United States have been identified as a likely source of dust deposition in the Colorado Rockies (Lawrence et al. 2010). Dust in the Colorado Rocky Mountains is commonly calcareous (Brahney et al., 2013; Clow et al., 2016) and has been observed to shift snowmelt by one to three weeks earlier than pre-dust loading conditions (Clow et al. 2016; Painter et al., 2010; Skiles et al. 2015). The geology of the area is dominated by Mancos shale of Cretaceous age with intrusions of Paleogene igneous laccoliths and ore-rich stocks (Hubbard et al. 2018). For additional information about the study site, see Hubbard et al. (2018).

[Insert Figure 1]

2.2 Data Collection

2.2.1 Instream Sampling

Associated with ongoing research as part of the WFSFA, LBNL investigators have been collecting stream discharge and solute data at daily to weekly intervals beginning in May 2014 at one instream monitoring site located at the watershed outlet (Pumphouse (PH), Figure 1). The PH site is located at an elevation of 2760 m and includes an automated water sampler (Model

3700; Teledyne ISCO, NE, USA) to recover stream water samples from a fixed location in the stream channel via a peristaltic pump into uncapped 1 L polyethylene bottles. Geochemical analysis of all water samples includes cations, trace metals, and anions. Prior to analysis, samples were filtered (Pall, NY, USA; polytetrafluoroethylene: 0.45μm) and stored at 4 C. Anion samples were stored in high-density polyethlene vials with Cl, NO3, and SO4 measured using an ion chromatograph (ICS-2100, Dionex, CA, USA) equipped with AS-18 analytical and guard columns with concentrations determined using factory-provided calibration standards. Cation samples were preserved with trace metal grade 12N HNO3 and analyzed using ion coupled plasma mass spectrometry (Element 2, Thermo Fisher, MA, USA). For this study, only solutes from the 2016, 2017, and 2018 water years (WYs) were used (where the 2016 WY is defined as October 1st, 2015 to September 30th, 2016). The PH site also includes a multi-parameter sonde (EXO2; YSI, Inc.; Yellow Springs, OH, USA) equipped with an EXO conductivity/temperature sensor for measuring the specific conductivity (SC) of stream water at 5-minute intervals over the WY2016-2018 interval.

2.2.2 End-member sampling

Two potential end-members were sampled (snow and deep groundwater). Snow samples were collected from 2017 to 2020 with the majority of samples collected in 2020 at six locations around the basin (Snow pits, Figure 1). Snow pits were dug in open, flat areas with anion, cation, and trace metal concentrations determined by filtering (Pall, NY, USA; polytetrafluoroethylene: 0.45μm) melted samples collected at 10 cm intervals over the pit depth. Pit depths ranged from 67 to 140.5 cm depending upon location. Solute data representative of deep (~60 m) groundwater sourced from Mancos shale bedrock has been monitored weekly to monthly since 2015 at the Inouye Well, which is drilled to a depth of 61 m with water pumped to the ground surface from this depth using a fixed downhole pump. Samples were filtered upon collection and stored at 4 °C until analysis. For this study, only groundwater samples collected in the 2016 – 2018 WYs were used.

2.3 Hydrograph Separation Approaches

Two methods of hydrograph separation and two characterization methods for end-member concentrations were used to compare volumetric contributions to instream flow using limited end-member data, but detailed instream chemistry data for three water years (WYs). The

first hydrograph separation technique used PCA and EMMA. PCA is a statistical tool that uses the variances and co-variances of datasets to highlight collective trends. The purpose of this type of analysis is to identify a shared factor (such as an end-member) that may explain trends exhibited in a mixing space. EMMA employs a statistical analysis of the mixing space to identify end-members based on instream chemical signals (Christophersen & Hooper 1992). However, this method is fundamentally reliant on mass balance principles and since the mixing space consists of projected solute concentration data, it can be used in tandem with flow data in a constrained system of equations to solve for the contributions to instream flow due to each end-member. This approach of using PCA and EMMA for hydrograph separation is herein referred to as the 'statistically-based approach' although it utilizes mass balance principles for the final step of the hydrograph separation. Several important assumptions are made to ensure the validity of this approach. First, EMMA requires the assumption of the conservative (linear) mixing of end-members (Christophersen et al., 1990; Christophersen & Hooper, 1992). In addition, EMMA requires end-members to have a constant composition or the variability in end-member composition must be known through time and/or space. The last requirement is that end-member concentrations must be sufficiently different from each other for at least one solute (Christophersen et al., 1990; Hooper et al., 1990).

The second method of hydrograph separation used was a simple chemical mass balance. Chemical data are collected to characterize the composition of each source water. These data, along with instream concentration and discharge data, are then used in a constrained system of equations where mass is conserved to parse the contribution of each source water (Pinder & Jones, 1969). This approach is herein referred to as the 'mass-based' approach. Several assumptions are applied that are similar to those established by Sklash & Farvolden (1979) and those from the statistically-based method of separation. These include: 1) that end-member composition is assumed constant or else the variability in time and/or space is known, 2) solutes mix conservatively, 3) the number of end-members are known, 4) instream concentrations are only composed of waters originating from the identified end-members or else all other waters contributing are considered negligible, and 5) end-member concentrations are sufficiently different for at least one solute.

End-member concentrations were characterized using two methods because of the uncertainties associated with limited end-member measurements. The first characterization of the

end-member concentrations was by direct sampling of two potential end-members (groundwater and snowmelt) at a limited number of sites across the basin (Figure 1). The second method of characterizing end-member concentrations was done by inferring potential end-members from instream chemistry during certain flow regimes at certain times of the year at the outlet of the catchment. Hereinafter, end-member concentrations characterized by direct sampling of the source waters will be referred to as 'measured end-member concentrations' and end-member concentrations characterized by instream sampling at the outlet of the catchment during certain flows and times of the year will be referred to as 'hydrologically rationalized end-member concentrations'. These two characterizations of the concentrations of the end-members have unique ranges and both of these will be discussed in further detail in the following sections.

By using these two hydrograph separation techniques and two different characterizations of the end-members, five types of separations were performed for the 2016, 2017, and 2018 WYs (Figure 2). Each separation offers insight into the possible separation of the hydrograph and the associated variability.

[Insert Figure 2]

2.3.1 Solute Selection

The solutes used in both methods play an essential role in determining the outcome of the hydrograph separation. Different combinations of solutes will yield slightly different answers. Non-conservative solutes or solutes without geochemical relevance to the basin will result in poor separations. Four different methods were used to select the solutes for both analyses. First, commonly used conservative solutes in hydrograph separations were examined. Second, conservative solutes used previously at this specific study site were examined. Third, the temporal behavior of instream solutes was examined. Fourth, solute behavior in relation to flow was examined. In the statistically-based approach, a posteriori method can also be used to select solutes. This posteriori method involves plotting measured instream concentrations against predicted instream solute concentrations, resulting from end-member concentrations and fractional flow contributions informed by the statistically-based hydrograph separation. If predictions are sufficient, as evaluated by coefficients of determination and slopes, the solutes can be retained in the analysis. If not, new solutes can be selected.

Commonly used conservative solutes in hydrograph separation methods include calcium, magnesium, potassium, silicon, and sodium, as was shown by Wels et al. (1991), Hooper (2003), and Liu et al. (2017). Less commonly used solutes include rubidium, barium, strontium, uranium, and (sometimes) sulfate as shown in Ladouche et al. (2001) and Barthold et al. (2011). A previous study done in ER WFSFA used calcium, uranium, strontium, sulfate, and two stable isotopes to perform their separation in the 2016 WY; but, they suggested that sulfate not be used in future studies in the basin due to observed non-conservative behavior (Carroll et al., 2018).

Time series of solute data were also analyzed (Figures S1-S3). This was helpful for identifying solutes with clear temporal patterns (e.g., Ca or Na) and those without clear temporal patterns (e.g., Sn or V). After examining temporal behaviors, the solute's relation to flow was used as the final *a priori* metric of selection for solutes to be used in the analysis (see, Ladouche et al., 2001; Pinder & Jones, 1969). Examining the temporal behavior of solutes is important as it can change from year to year. The linearity of solute concentrations in this study was quantified and classified based on hydrologic responsiveness to changes in flow. High coefficients of determination (R^2), slope, and low root mean square error (RMSE) produced from the comparison of a linear best-fit on logarithmic concentration – discharge (C-Q) plots were used as indicators for the strength of the relationship (Table 1) (Godsey et al., 2009). If solutes qualified as "Best" or "Moderate" in two of the three categories, they were retained for use in the analysis for that WY (Table S1). This was done to find solutes that mobilize with changes in runoff generation and to highlight seasonal end-members. It is important to note that linearity in C-Q plots indicates conservative mixing, likely between just two end-members; however, it is possible there could be more if two end-members had similar solute concentrations. Because this method of selecting solutes is also highly effective at highlighting solutes that are responsive to changes in end-member contributions that influence instream concentrations, it was used in tandem with the other three methods described previously.

[Insert Table 1]

2.3.2 End-member Characterization

2.3.2.1 Hydrologically Rationalized End-member Concentrations

Using our general understanding of hydrology in this area, three potential end-members (deep groundwater, snowmelt, and soil water) were identified and then characterized from the detailed instream solute data at the outlet of the catchment. These hydrologically rationalized end-member concentration ranges were chosen to capture the chemical variability instream over time. This characterization of end-member concentration ranges may be helpful indicators of changes in end-member contributions to the stream throughout the year when detailed end-member concentration data are limited or unavailable.

Commonly, deep groundwater concentrations are inferred from instream chemistry during base flow (see James & Roulet, 2009; Miller et al., 2014, Pinder & Jones 1969). As such, solute concentrations during the lowest 5% of discharge were used to represent deep groundwater chemistry. Similarly, solute concentrations during the highest 5% of discharge were used to represent snowmelt when deep groundwater contributions are limited and snowmelt dominates runoff in mountainous systems such as the UCRB. While this characterization of the snowmelt end-member concentrations will not perfectly represent the variability in snow composition, it does provide a reasonable representation of the variability in the integrated snow end-member contributions to instream chemistry. Finally, shallow soil waters were characterized by using the highest 15% of discharge from the summer storm events in August through October. This period was chosen as any deviation in base flow chemistry late in the water year that was likely due to storm events and could represent older and reacted water. It is important to note that characterizing end-member concentrations based on instream chemistry will bias hydrograph separation results to 100% contribution of the defined end-member during the respective flow regimes. To account for variability in the hydrologically rationalized end-member concentrations, a normal distribution was assumed using the mean and standard deviation of each end-member. This distribution was randomly sampled 1000 times to establish a range of possible source compositions for each solute to be used in the hydrograph separations.

2.3.2.2 Measured End-member Concentrations

The second method of characterizing end-member concentrations used measured values. To establish measured end-member concentration ranges for each solute representing two potential end-members (snowmelt and deep groundwater), we created distributions based on a limited number of available solute samples. This provided insight into acceptable concentration ranges for the two measured and potential end-members. The snowmelt sample size was small (n

= 18 – 36) and represented six sample sites from the basin from 2017 to 2020. Because of the small sample size, we established a uniform distribution based on the min and max of the field samples and randomly sampled it 1000 times to get at the possible source concentrations for each solute (Figures S4 – S8). This was done to better represent the uncertainty in the measured end-member concentration for each solute to be used in hydrograph separations.

The number of measured groundwater samples was spatially limited. The field samples collected from 2016 WY through the 2018 WY (n =122-124) from a single location, the Inouye Well, were nearly normally distributed (Figures S9 – S13). A distribution was generated for each solute based on the distribution inherent to the field samples collected by LBNL and sampled 1000 times to determine possible groundwater compositions. The resulting concentrations from each sampled distribution were then used in the hydrograph separation techniques.

As with hydrologically rationalized end-member concentrations, characterizing end-member concentrations via direct measurements also poses challenges. Acquiring representative source samples can be difficult in mountain environments where there may be significant spatial variation. In addition, end-member concentrations can change significantly while en route to the stream. This is why creating distributions from our limited set of measured data was important to represent uncertainty in end-member composition.

2.3.3 PCA and EMMA

To begin the statistically-based method of hydrograph separation, first the PCA must be performed. Through PCA, stream chemistry is projected into a mixing space (referred to as the *U*-space) defined by the principal components retained for analysis (Equations S1-S3). Determining the number of principal components to retain is significant as the number of end-members is one greater than the number of principal components retained. To do this, $\boldsymbol{X}$ – which represents the standardized matrix containing time series of stream chemistry - is projected into the *U*-space while maintaining the units in the solute space (*S*-space) following (Christophersen & Hooper, 1992; Equation 1)

$$\widehat{\boldsymbol{X}} = \boldsymbol{X}\boldsymbol{V}'(\boldsymbol{V}\boldsymbol{V}')^{-1}\boldsymbol{V} \quad (1)$$

where $\widehat{\boldsymbol{X}}$ is the de-standardized but projected matrix of $\boldsymbol{X}$ that has units equivalent to that of the *S*-space, and $\boldsymbol{V}$ is the eigenvector obtained from the PCA. The residuals (Hooper, 2003; Equation

2) between the modeled stream chemistry in the projected matrix and the measured stream chemistry are calculated as

$$\boldsymbol{E_j} = \widehat{\boldsymbol{X_j}} - \boldsymbol{X_j} \quad (2)$$

where $\boldsymbol{E}$ is the matrix of residuals between the projected jth solutes and the measured jth solutes. Generally, if the modeled data is a good fit to the observed data, the residuals should be identical and normally distributed with a mean of zero and constant variance (Draper & Smith, 1981). If the residuals violate any of these conditions, it suggests that there is a pattern within the data that the model is not capturing. As such, residuals were analyzed using the coefficient of determination (R^2) and relative root mean square error (RRMSE) to evaluate structure and variance. Residuals were also analyzed using p-values to find significant ($p < 0.05$) linear trends in the residuals and analyzed with quantile-quantile plots to evaluate normality. RRMSE (Equation 3) was calculated as

$$RRMSE = \frac{\sqrt{\frac{\sum \boldsymbol{E_j^2}}{n}}}{\overline{\boldsymbol{X_j}}} \quad (3)$$

where $\overline{\boldsymbol{X_j}}$ represents the average solute concentration and n represents the number of samples. Similar studies have also used R^2 and/or RRMSE (e.g. Ali et al., 2010; Bearup et al., 2014; Carroll et al., 2018) to quantify the residuals (Table S2). These studies were used as a basis for comparison to determine appropriately low R^2 and RRMSE values. Using these metrics, the number of principal components (m) as well as the predicted number of end-members were determined. To complete the analysis, all solutes and end-members were projected into the *U*-space (Equations S4 & S5).

2.4 Hydrograph Separation

2.4.1 Statistical Hydrograph Separation

The final steps of the statistically-based approach result in a set of linear equations, which can then be solved using the constrained least-squares method. A constrained least-squares method was used in order to accommodate end-member concentrations characterized by hydrologic rationalization. To separate the hydrograph, the system of equations (Equation 4) is solved for f , the fraction of instream signal due to each end-member. An example of the system

of equations in the instance of three end-members is shown below; but, it can be easily reduced in the instance that only two end-members are found to describe the mixing space.

$$\begin{cases} 1 = f_1 + f_2 + f_3 \\ \boldsymbol{U_1} = \boldsymbol{W_1^1} f_1 + \boldsymbol{W_1^2} f_2 + \boldsymbol{W_1^3} f_3 \\ \boldsymbol{U_2} = \boldsymbol{W_2^1} f_1 + \boldsymbol{W_2^2} f_2 + \boldsymbol{W_2^3} f_3 \end{cases} \quad (4)$$

$$where\ f \quad due\ to\ each\ end - member \geq 0$$

$\boldsymbol{W}$ is known and represents the projected end-member in the *U*-space, with subscripts indicating the principal component and superscripts indicating the identity of the end-member. $\boldsymbol{U}$ represents the projected solutes instream with the subscripts again indicating the corresponding principal component. In instances of just two end-members, the system of equations was reduced accordingly. $\boldsymbol{W}$ was selected from the end-member distributions described previously to solve the system of equations. This was done 1000 times to produce 1000 different solutions to Equation 1. For each iteration, the end-member fraction was multiplied by the stream flow to calculate the flow due to that end-member. This resulted in a 1000 possible separated hydrograph solutions for each time-step to reflect the variability in potential end-member concentrations.

2.4.2 Mass Balance Separation

For mass balance separations, the number of end-members and the identity of the end-members are decided *a priori*. Since the ER is a snow-dominated basin in the UCRB, deep groundwater and snowmelt were two logical and likely choices for end-members, but they were assumed end-members. A third end-member was not included in this method of separation, but could be in future studies. To separate the hydrograph using a mass balance, discharge and concentration data were combined in a system of just two equations. The first equation in the system below represents a flow balance where unaltered groundwater and snow water are assumed to mix instantaneously in the water column. This equation (Equation 5) represents a mass balance with a particular solute.

$$\begin{cases} Q_{tot} = Q_{gw} + Q_{sm} \\ C_{tot} Q_{tot} = C_{gw} Q_{gw} + C_{sm} Q_{sm} \end{cases} \quad (5)$$

Q_{tot} is the total instream discharge measured at the Pumphouse, Q_{gw} and Q_{sm} and represent discharges from groundwater and snowmelt. C_{tot} is the concentration instream at the

Pumphouse. C_{gw} and C_{sm} are the measured concentrations at the groundwater and snow end-members, respectively. Like the statistical separation, C_{gw} and C_{sm} were selected from the generated distributions described previously for both measured and hydrologically rationalized end-members. The system of equations was solved 1000 times for Q_{gw} and Q_{sm} for each time step to generate 1000 possible hydrograph separations.

3. RESULTS

3.1 Solute Selection

The C-Q plots revealed that the solutes with the strongest relationship to discharge were generally calcium, uranium, and strontium for all years analyzed (Table S1; Figures S14 -S16). Solutes were often inversely correlated with discharge (Figures S17 – S19). Barium strongly correlated to discharge in both the 2016 and 2018 WYs, and as a result, it was also used in the 2017 WY. Given that strontium met all criteria sufficiently in 2016 WY and 2018 WY, it was also used in 2017 WY despite only meeting one out of the two criteria for retention defined in Table 1. Magnesium correlated strongly with discharge in the 2016 WY and was included for that water year only. Sulfate, a commonly used solute in mixing analyses, albeit one that is not conservative, had a strong correlation to discharge. Previous research by Carroll et al. (2018) suggested it may not be conservative in this watershed owing to anaerobic forms of microbial reduction, and therefore, it was subsequently excluded from this analysis. In summary, the selected solutes used in all years were barium, calcium, strontium, and uranium, with magnesium used only in the 2016 WY.

3.2 End-members

3.2.1 End-member Concentration Distributions

The individual end-member solute concentration distributions that were sampled for hydrograph separation differed based on the method of characterization (hydrologically rationalized or measured). For end-member concentrations characterized by hydrologic rationalization, solute concentrations were randomly sampled from the generated normal distributions described previously. For end-member concentrations characterized by field measurements, solute concentrations were sampled from generated uniform distributions for the snow end-member (Figures S4-S8). Solute concentrations for the groundwater end-member were

sampled from the generated distributions inherent to the field samples of groundwater (Figures S9-S13).

3.2.2 End-member Retention

Following an analysis of the residuals and principal component space, the number of end-members contributing to instream flow was determined. For all water years, the residuals as evaluated by R^2 and RRMSE indicated the retention of two to three principal components (Table 2). The number of end-members is one more than the number of principal components; hence, three to four end-members were predicted. Although R^2 and RRMSE values are reasonable based on accepted ranges in similar studies (Table S2), none of the residuals were normally distributed according to the quantile-quantile plots (Figures S20 – S31). This indicates that there could be aspects of mixing space that are not entirely captured by the solutes included in the analysis. Results from the residuals as evaluated by p-values are variable, but generally agree that four end-members could adequately describe the mixing space. P-values often (although not always) indicated slopes significantly ($p < 0.05$) different that zero for $m \leq 2$, which suggests some remaining pattern in the residuals at low levels of principal component retention. An example of these results for the 2016 WY are shown below for strontium (Figure 3). Overall, R^2 and RRMSE indicated that the calculated principal components adequately described the mixing space for the purposes of this study, but quantile-quantile plots and p-values results vary and suggest that this analysis could be improved in the future, such as by testing different solute combinations in an aim to reduce structure in residuals.

[Insert Table 2]

[Insert Figure 3]

For all water years, similar trends in the projections of solutes into the mixing space (*U*-space) were observed (Figure 4). Projection into the *U*-space indicates that solutes have seasonal variation. The stream signal tends towards the snow end-member during peak runoff and then towards the groundwater end-member during periods of base flow. The collective non-linear shape of the projected solutes in the *U*-space support the findings from the residuals analysis and

suggests the existence of more end-members than identified. Thus, based on the collective information from all analyses, three major end-members are likely. Given the ER WFSFA is a snow-dominated basin with seasonal melt, it was assumed that groundwater and snow water were two likely contributors to the stream. The possibility of a potential third major end-member (soil water) was tested using hydrologically rationalized end-member concentrations with the statistically-based method of hydrograph separation. However, this was not possible in separations with measured end-member concentrations due to limited end-member data. Since groundwater and snow are assumed, it is possible that they are not the primary streamflow controls, rather they are likely contributors based on previous work done in the ER basin by Carroll et al., (2018). In summary, instream flow was assumed to be composed of water originating from two to three end-members, with three end-members being most likely. The implications of potential missing end-members in hydrograph separations done with only two end-members are discussed in more detail in the following sections.

[Insert Figure 4]

3.3 Hydrograph Separations

With the solutes and the number of end-members selected, hydrograph separations proceeded. Recall the hydrographs were separated using two different methods with two different end-member characterizations (Figure 2). In addition, both two and three end-member separations were tested.

3.3.1 Statistically-based Hydrograph Separation

3.3.1.1 Three End-members Characterized by Hydrologic Rationalization (3 H-EM)

Using hydrologically rationalized end-member concentrations, a separation was performed to yield a groundwater component, a snow water component, and a soil water component (Figure 5). Error bands show the interquartile ranges (IQR) resulting from the sampling of the end-member distributions. The initial flush of groundwater generally peaks in May while the snow signal tends to peak in June, with this behavior being generally replicable across water years. In contrast, soil water contributions vary across years. Increases in soil water contributions during June may be related to precipitation events (Figure S32), but direct

causation is unclear. Large variations seen in the 2017 WY may be due to the inclusion of barium even though it lacked a strong relationship with discharge in the 2017 WY. A feature to note in all separations done with hydrologically rationalized end-member concentrations is the short period of time in June where there is no evident contribution of groundwater. This is an artifact of using hydrologically rationalized end-members and will be discussed in detail in the following sections.

3.3.1.2 Two End-members Characterized by Hydrologic Rationalization (2 H-EM)

Using two end-members with hydrologically rationalized concentrations, the hydrograph was separated into a groundwater and a snow water component (Figure S33). While the discharge contribution of each end-member differs slightly from that of a three end-member separation, the timing of the peak groundwater contribution is the same. Similar to the separation with three end-members, there is again an artifact from the methodology where groundwater contributions in all water years go to zero for one to two weeks in June.

[Insert Figure 5]

3.3.1.3 Two End-members Characterized by Measurements (2 M-EM)

Using two end-members characterized by measured concentrations rather than the hydrologically rationalized concentrations, there is a difference in the timing of peak groundwater contributions (Figure 6). In this separation, where two measured end-member concentrations are used, groundwater peaks with peak snowmelt rather than before peak snowmelt. This difference in timing is likely due to the two different characterizations of the end-members. In addition, discharge contributions from snow are greater than groundwater contributions at most times of the year. This occurs even when there is no snow in the basin (e.g., during the late summer and early winter months). However, a potential missing soil water end-member may help to explain this discrepancy as soil water can enter the stream during these times.

3.3.1.4 Model Evaluation

As stated previously, selected solutes were examined posteriori by comparing predicted versus measured instream concentrations in the statistically-based method. In general, predicted versus measured instream concentrations showed strong relationships across all years as indicated by high R^2 values (Figures S34 – S40). However, separations with measured end-member concentrations showed consistent underestimations of instream concentrations of calcium and barium, and consistent over estimations of strontium (Figures S34 - S35). This is demonstrated well in the 2016 WY (Figure 7). Uranium was well predicted with measured end-member concentrations. Instream concentrations of solutes were well predicted with models using hydrologically rationalized end-member concentrations, which was expected as the hydrologically rationalized end-member concentrations were derived from the stream chemistry (Figure 8; Figures S6 – S40). In general, residuals indicate that most solutes were able to predict instream concentrations reasonably well (as seen by the relatively normal distribution of the residuals) with the exception of barium in the 2017 WY; however, end-member concentrations characterized by measurements generally over or under predicted instream concentrations in some capacity. This suggests that the model could be improved in future studies by testing different solutes and solute combinations in an effort to estimate instream concentrations more consistently (Barthold et al., 2011).

[Insert Figure 6]

[Insert Figure 7]

[Insert Figure 8]

3.3.2 Mass-based Hydrograph Separation

3.3.2.1 Two End-members Characterized by Hydrologic Rationalization (2 H-EM)

Using two end-members with hydrologically rationalized concentrations in a mass balance separation yielded similar results as the statistically-based method of separation (Figure 9). Again, the timing of peak groundwater contribution is shifted so that it occurs before peak snowmelt, which is an artifact of using hydrologically rationalized end-member concentrations. However, the mass balance method reveals how the separation is affected by different solutes

(Figure S41). There is a clear separation of the hydrograph in all water years and good agreement among all solutes with the exception of barium in 2017 WY (Figure S41).

3.3.2.2 Two End-members Characterized by Measurements (2 M-EM)

Similar to a statistical separation of the hydrograph using two end-members based on field measurements, the mass-based separation method also showed groundwater and snowmelt peaking at the same time. When the median response of all solutes is assessed, the IQR is quite large (Figure S42). However, using the mass-based method, the influence of each solute can be examined (Figures S43). Viewing solutes individually, it is clear that calcium is very different from the other solutes, predicting an almost 50/50 split in the flow contributions of each end-member during the entire water year. When calcium is removed from the analysis (Figure S44), the IQR is greatly decreased and there is a better separation of groundwater and snow water contributions (Figure 10). Again, barium is a poor solute for separation the 2017 WY.

[Insert Figure 9]

[Insert Figure 10]

3.4 End-member Fractions of Total Annual Volumes

Since there are several differences in the time series of the separated hydrographs due to the different methods and end-member characterizations, annual volumetric contributions of end-members to stream flow were used as another method of comparison (Figure 11, Table 3). Across methods, the median percent of total annual volume from groundwater ranged from 21% to 41% from 2016 - 2018 (regardless of the number of end-members or the characterization of the end-members). Median annual groundwater contributions from hydrologically rationalized end-member concentrations ranged from 21% – 41%, while median groundwater contributions estimated from measured end-member concentrations had a slightly smaller range from 22% – 35%. In general, the IQR of the same end-member number and characterization overlap regardless of the method of hydrograph separation. Overall, these results suggest that the median percent annual volumes of the end-members are similar across hydrograph separation techniques

583 and vary more across end-member characterization. However, there are large variations in the
584 mass-based method of separation depending on the solute used (Figure S45).
585
586 [Insert Table 3]
587
588 [Insert Figure 11]
589
590 **4. DISCUSSION**
591 Hydrograph separations via statistically-based and mass-based methods with two unique
592 end-member characterizations were used to analyze the hydrology of a catchment with limited
593 end-member data but detailed instream data. Results highlight the importance of solute choice as
594 well as end-member retention and characterization in separations. In addition, annual volumes
595 were similar despite differences in timing caused by different end-member characterizations.
596
597 **4.1 Selected Solutes**
598 Selected solutes influenced results in both statistical and mass-based methods of
599 separation. Although solutes were selected using multiple methods, selection procedures were
600 heavily reliant on the solute's hydrologic responsiveness to flow, which generally assumes
601 simple mixing of two end-members. In addition, choosing solutes that changed with flow
602 prioritized solutes that mobilized strongly (as opposed to periodically or weakly) with flow. In a
603 detailed end-member mixing study by Barthold et al. (2011), it was found that geochemically
604 similar elements like magnesium and calcium (both of which mobilize fairly well with
605 discharge) could potentially deliver similar information and suggested it may be better to include
606 more minor elements. Thus, our analysis may be flawed in that minor elements that did not
607 mobilize with flow were not included, even though they may have offered a broader perspective
608 of basin hydrology.
609 Limiting the number of solutes could also unintentionally exclude important
610 hydrogeochemical indicators in the watershed. This is well demonstrated by mass-based
611 separation results wherein two solutes stand out as behaving very differently from the others.
612 The first is calcium in separations with measured end-member concentrations, which often
613 predicts a 50/50 contribution of end-members at all times of the year across all water years

(Figure S43). As a result, when examining the median response from all solutes, including calcium (Figure S42), there is a much larger total IQR than without calcium (Figure 10). Interestingly, in contrast to the analysis with measured end-member concentrations, a mass-based separation with hydrologically rationalized end-member concentrations has a very clear separation using calcium (Figure S41). This variation across end-member characterization is very different from other solutes, such as strontium and uranium, that produce clear separations regardless of being derived from measured or hydrologically rationalized end-member concentrations. Barium also tends to act like strontium and uranium in all years except in the 2017 WY. In this year, barium tends to dramatically and rapidly change end-member response (Figures S41 and S44). Barium shows the significant temporal variations a solute can have in a catchment from year to year and it may not have behaved conservatively or been appropriate to include in the analysis for 2017 WY.

Although the barium's 2017 WY behavior may be partly due to its weak relationship with discharge in this year (Table S1), it also illustrates the utility of more solutes or different combinations of solute in providing additional information. Perhaps other minor elements would behave similarly and prompt investigation into the presence of additional unidentified end-members (e.g., ephemeral springs or creeks sporadically discharging to the river after storm periods). Alternatively, the use of additional solutes could highlight non-conservative behaviors or other reactive processes occurring via different hydrologic flows paths. Non-conservative behavior is a critical consideration while examining the separated hydrograph as it could affect the amount of water attributed to an end-member during the water year. Beyond considering the selection of solutes, testing multiple combinations of solutes within PCA is one advantage of the statistically-based method that was not included here. Testing additional solute combinations in the future may allow for better estimates of instream solute concentrations for solutes such as calcium, which was consistently underestimated using measured end-member concentrations (Figure 7; S34 - S35). All in all, the behaviors demonstrated by individual solutes stress the importance of choosing appropriate solutes that can capture the full basin hydrology, particularly in environments where sampling is limited. A broader range of conservative solutes based on multiple catchment characteristics (hydrology, geology, atmospheric deposition patterns, etc.) may prove to be beneficial. Future studies will need to explore the solute selection process more

deeply and perhaps establish additional methods that can guide researchers to the hydrogeochemically pertinent solutes for their catchment.

4.2 Implications of End-member Characterization and Retention

4.2.1 End-member Characterization

In this study, end-member data was limited. Besides direct end-member measurements, hydrologic rationalization of end-members based on instream chemistry was used to characterize end-member concentrations. Using these two end-member characterization methods led to several substantial differences in the resulting separated hydrographs.

4.2.1.1 Hydrologically Rationalized End-member Concentrations

Figures 5 and 9 display two features that are unique to hydrograph separations done with hydrologically rationalized end-member concentrations. The first is a difference in the timing of peak groundwater contributions to earlier in the year than separations performed with measured end-member concentrations. This is because hydrologically rationalized end-member concentrations are close in magnitude to (or at times, the same as) the instream concentrations. This similarity to instream concentrations makes it so small chemical shifts in the stream can indicate more dramatic shifts in end-member contributions, hence the earlier increase in peak groundwater contribution to the stream as compared to separations performed with measured end-member concentrations. Subsequently, the difference between instream concentrations and measured end-member concentrations is much larger, so small changes in the instream concentration of solutes indicate small changes in end-member contributions. Hence, only when there are substantial changes in the composition of the stream are dramatic shifts in the contributing end-members indicated.

The other important feature of hydrograph separations done with hydrologically rationalized end-members is the period of zero contribution of groundwater during peak snowmelt. The reason for this is well demonstrated by the principal component mixing space (Figure 4). It is clear that hydrologically rationalized end-member concentrations can overlap with the instream solutes allowing 100% contribution of that end-member to instream flow at a given time of year (Figures 5 & S41). This is a violation of the end-member mixing model assumptions that state end-members must be a convex combination that encompass the solutes in

675 the mixing space (Christophersen & Hooper, 1992; Hooper, 2003; Hooper et al., 1990).
676 Furthermore, the mixing space can be encompassed by any number of end-members, but with
677 hydrologically rationalized end-member concentrations it is very hard to distinguish more than
678 three contributing end-members that can encompass the solutes in the mixing space.
679 Despite this, hydrologically rationalized end-member concentrations may pose an
680 advantage in data-limited environments. Hydrologically rationalized end-member concentrations
681 – unlike measured end-member concentrations - do not require spatially and temporally uniform
682 end-member data or detailed sampling schemes. Rather, hydrologically rationalized end-member
683 concentrations derived from instream data are able to provide a snapshot of the major end-
684 member contributors to streamflow during the year. Hence in studies where distinctions between
685 more than three end-members are not needed, hydrologically rationalized end-members may
686 offer unique and desirable benefits such as the reduced sample location requirements (just
687 needing one at the outlet of the catchment).
688
689 *4.2.1.2 Measured End-member Concentrations*
690 Some measured end-member concentration data was available for use in the hydrograph
691 separations. This was important, as it gave evidence for the observed solute concentration ranges
692 of the possible end-members. Ideally, the measured composition of an end-member for a
693 hydrograph separation should be representative of the end-member composition for the entire
694 watershed. In this study, a single sampling point at the Inouye Well was used to represent all
695 groundwater regardless of depth or bedrock composition. However, a USGS geologic survey of
696 the area shows a diverse geologic profile (Gaskill et al., 1991) that suggests such spatially
697 limited sampling of the groundwater end-member likely insufficiently captured the range of
698 possible groundwater concentrations within the 85 km^2 basin. Other studies have also noted
699 spatial (Penna & Meerveld, 2019) and temporal (Feng et al., 2002; Liu et al., 2004) variability in
700 end-member composition. Furthermore, the spatial and temporal variability in end-member
701 composition and its effect on the hydrograph has been observed in catchments < 1 km^2 in size
702 (Cayuela et al., 2019; Kiewiet et al., 2020). Studies such as these emphasize the importance of
703 spatially diverse and temporally detailed end-member data for hydrograph separation. However,
704 this is not always possible in remote catchments with limited access, financial, and/or personnel

resources and highlights how multiple methods of separation may be useful when detailed end-member data is limited or unavailable.

4.2.2 End-member Retention

With limited end-member data available, this study included two possible end-members with concentrations characterized by field measurements (groundwater and snowmelt) and three possible end-members with concentrations characterized by hydrologic rationalization (groundwater, snowmelt, and soil water). However, residuals and *U*-space analysis indicated that three to four end-members would best capture basin hydrology (Tables S3 – S5; Figure 4). As such, there is likely an over attribution of flow to the end-members that were available for use in the separations. For example, in separations where just two end-members characterized by measured concentrations are present, snowmelt contributions are predicted even when was no snow was present in the basin like during the late summer (after July) and early fall months (Figures 6 and 10). This over attribution of flow to the snow end-member may have been due to missing end-members in the analysis, such as soil water or rainfall producing overland flow.

4.3 Annual Volumetric End-member Contributions

Across hydrograph separation methods, total percent of annual volume from each end-member was generally similar with median groundwater contributions ranging between 21% and 41% (Table 3; Figure 11). These findings agree reasonably well with other studies of the UCRB. Miller et al. (2014) performed a solute separation across multiple sub-basins in the UCRB finding that annual contributions of base flow to discharge ranged between 21 and 58% in large basins (>1000 km^2). This estimate is expected to be greater as the study areas are much larger. However, there was a study conducted previously in a sub-basin of the ER WFSFA where a hydrologic water budget revealed groundwater contributions ranged from 21 to 52% with an average of 35% (Carroll et al., 2019). Our findings using a limited set of end-member data appears relatively consistent with the much more data-detailed study Carroll et al., (2019) in the same watershed; although, there is variation based on the characterization of the end-member concentrations and the solutes used in the analysis. Overall, these findings seem to suggest that in the face of limited data, multiple methods of hydrograph separation may be useful in tracking shifts in the hydrology of mountainous and seasonally snow-dominated catchments.

5. CONCLUSIONS

Using limited end-member data and multiple conservative solutes, two hydrograph separation techniques were compared. Results showed that there can be large temporal differences in the predicted hydrograph based on the characterization of end-members and solutes used. Consequences of characterizing end-member concentrations through hydrologic rationalization include reduced numbers of distinguishable end-members, shifts in the timing of end-member contributions to the stream, and periods of time where some end-member contributions go to 100% and others become zero. However, the benefits of using hydrologically rationalized end-member concentrations include the requirement of a single sampling point which could be advantageous in data-limited environments so long as their limitations are appropriately considered within the context of individual catchments. Results additionally show that annual volumetric contribution of the end-members to instream flow were similar across hydrograph separation techniques and provided reasonable annual volumetric estimates of the groundwater end-member. However, estimates of annual volumetric contributions of the end-members do vary depending on the characterization of end-member concentrations (measured or hydrologically rationalized). The results suggest that in remote mountainous catchments where data is limited, the use of multiple hydrograph separation techniques could provide valuable information about shifting water resources. This is critical considering the growing significance of water coming from remote catchments and the role such water plays in the security and management of our water future and sensitive mountain ecosystems.

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770

771 **DATA AVAILABILITY**

772 All data used in the analysis are available through the Lawrence Berkley National Laboratory at
773 https://data.ess-dive.lbl.gov/view/doi:10.21952/WTR/1495380 and https://data.ess-
774 dive.lbl.gov/view/doi:10.15485/1668055. Snow pit data from the Lawrence Berkley National
775 Laboratory will be made available soon at https://data.ess-dive.lbl.gov/, along with a data
776 package specific to this publication.

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TABLES

Table 1: Criteria for evaluating C-Qplots. Criteria are relative to the water year. Slopemax and R^2_{max} are the maximums found in a single water year. $RMSE_{min}$ was the minimum for the water year.

Rating	Slope	R^2	RMSE
Best	$\geq 0.7 \, \lvert slope_{max} \rvert$	$\geq 0.8 \, R^2_{max}$	$\leq 1.2 \, RMSE_{min}$
Moderate	$\geq 0.5 \, \lvert slope_{max} \rvert$	$\geq 0.7 \, R^2_{max}$	$\leq 1.5 \, RMSE_{min}$
Poor	$< 0.5 \, \lvert slope_{max} \rvert$	$< 0.7 \, R^2_{max}$	$> 1.5 \, RMSE_{min}$

Table 2: The mean relative root mean square error (RRMSE) and R^2 for the residuals for each water year. Average values for retaining two to three principal components (m = 2 and m = 3) fit ranges defined by Table S2. Expanded tables which include p values by solutes are available (Tables S3 – S5)

	2016 WY		2017 WY		2018 WY	
m	RRMSE (%)	R^2	RRMSE (%)	R^2	RRMSE (%)	R^2
1	5.6	0.109	9.6	0.233	8.1	0.141
2	4.1	0.057	4.9	0.055	4.8	0.054
3	2.5	0.024	1.8	0.007	1.4	0.010
4	1.1	0.006				

Table 3: Median fraction of annual end-member contributions to volume water leaving basin the statistically-based (STAT), mass-based (MB) and end-member (EM) characterizations: measured (M) or hydrologically rationalized (H).

		Snowmelt (%)		Groundwater (%)	
WY	End-Member Characterization	STAT	MB	STAT	MB
2016	3 H-EM	58		27	
	2 H-EM	66	65	34	35
	2 M-EM	75	65	25	35
2017	3 H-EM	67		21	
	2 H-EM	73	75	27	25
	2 M-EM	78	72	22	28
2018	3 H-EM	58		35	
	2 H-EM	59	59	41	41
	2 M-EM	74	69	26	31

FIGURE LEGENDS

Figure 1: Study area of the East River Basin Located in the Elk Mountains of Central Colorado. Service Layer Credits: Esri, HERE, Garmin, ©OpenStreetMap contributors, and the GIS user Community.

Figure 2: Experimental design matrix for all three water years. In general, solutes were selected for use in the analysis, then an end-member characterization method was chosen. Next, the hydrograph was separated using one of two techniques. Finally, two or three end-members were used to complete the separation. This led to five unique separations being performed, as indicated by the light grey arrows.

Figure 3: Residuals analysis for the 2016 WY for the solute strontium. Plots on the left show residuals at different numbers (m) of principal component retention and the associated R2, RRMSE. p-values indicate if slope is significantly ($p < 0.05$) different than zero. Open dots represent data points; line evaluates trends in data. Right hand plots assess normality at each level of principal component retention. Plus signs represent the residuals, dashed line represents the theoretical normal distribution residuals would follow if they were normally distributed.

Figure 4: Data projected into the *U*-space across all WYs as defined by the principal components (PCs). All years include projections using Ba, Mg, Sr, and U. The 2016 WY additionally includes Mg. Error bars represent one standard deviation of the end-member concentrations about the mean from the field data, not the generated distributions of end-member concentrations used for hydrograph separation. Solutes are in grey. Hydrologically rationalized end-members (H-EM) concentrations are represented by triangles. Measured end-member (M-EM) concentrations are represented by squares.

Figure 5: Hydrograph separation of three end-members with hydrologically rationalized concentrations (3 H-EM) using the statistically-based method of separation. Lines indicate median response from 1000 samplings around the mean and standard deviation of the end-member concentrations. The interquartile range (IQR) of the model traces shaded around the median represents the lower 25^{th} to upper 75^{th} quantiles.

Figure 6: Hydrograph separation of two end-members with measured concentrations (2 M-EM) using the statistically-based method of separation. Lines indicate median response to 1000 samplings of the end-member concentration distributions. The interquartile range (IQR) of the model traces shaded around the median represents the lower 25^{th} to upper 75^{th} quantiles.

Figure 7: Plots on the left show predicted versus measured concentrations of the instream using 2 end-members characterized by measured concentrations in the 2016 WY. Trends indicated by red line. Dashed lined shows the theoretical perfect predicition of instream concentrations. Middle plots show residuals between predicted and measured instream concentration data. Histogram on the right show the distribution of residuals.

Figure 8: Plots on the left show predicted versus measured concentrations of the instream using two end-members characterized by hydrologic rationalization in the 2016 WY. Trends indicated by red line. Dashed lined shows the theoretical perfect predicition of instream concentrations. Middle plots show residuals between predicted and measured instream concentration data. Histogram on the right show the distribution of residuals.

Figure 9: Hydrograph separation of two end-members with hydrologically rationalized concentrations (2 H-EM) using the mass-based method of separation. Lines indicate median response from four solutes (Ba, Ca, Sr, U) where each end-member concentration for each solute was sampled 1000 times. The

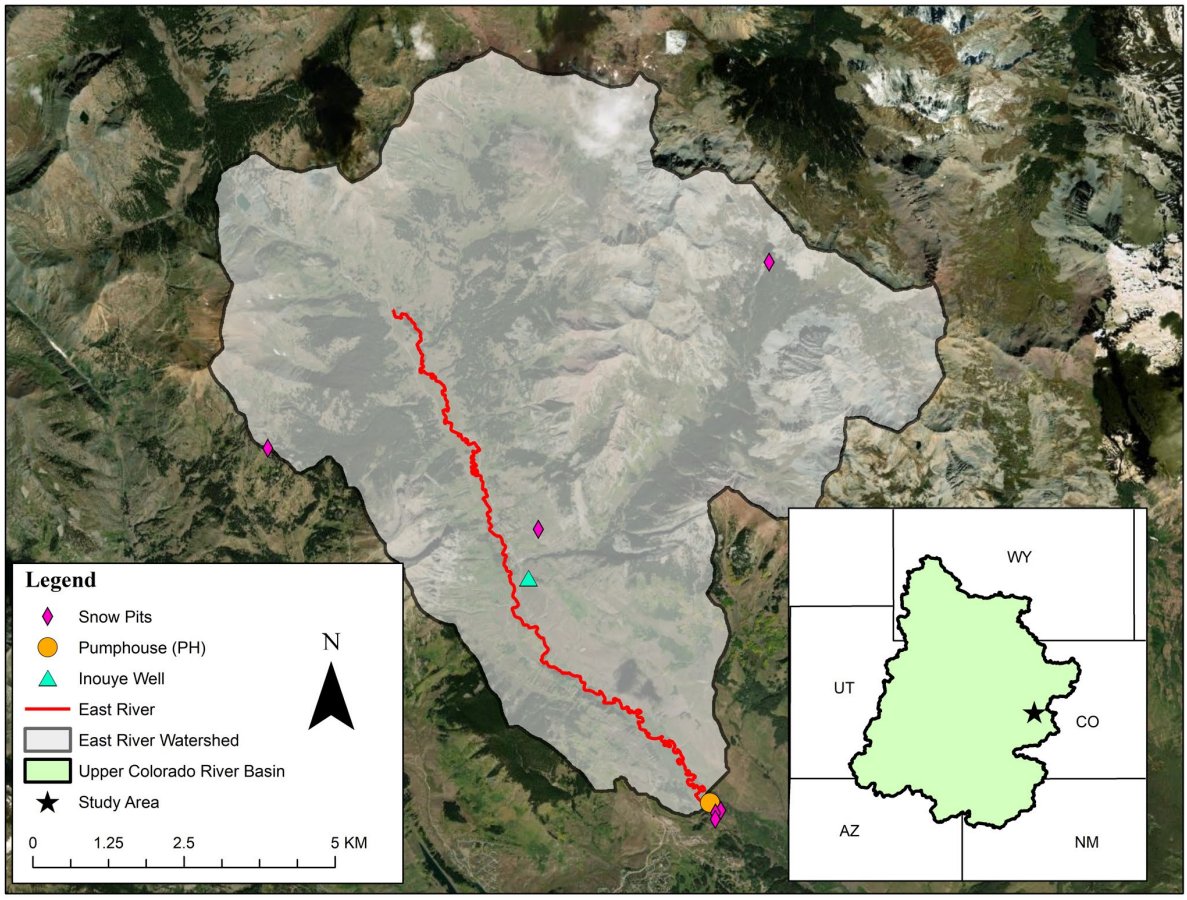
interquartile range (IQR) of the model traces shaded around the median represents the lower 25th to upper 75th quantiles.

Figure 10: Hydrograph separation of two end-members with measured concentrations (2 M-EM) using the mass-based method of separation. Lines indicate median response from all solutes except calcium where each end-member concentration for each solute was sampled 1000 times. The interquartile range (IQR) of the model traces shaded around the median represents the lower 25th to upper 75th quantiles.

Figure 11: Total percent of the annual volume of water leaving the catchment coming from each end-member – groundwater (GW) or snowmelt (snow)- via statistically-based (STAT) and mass-based (MB) methods of separation with hydrologically rationalized end-members concentration (H-EM) and measured end-member concentrations (M-EM). Targets represent the median, boxes represent the interquartile range (IQR) spanning the 25th to 75th quantiles with error bars representing the minimum and maximum, and boxes representing outliers (1.5IQR). The snow end-member is represented in orange, groundwater in blue. H-EMs show n = 1000 for all years while M-EMs show n = 4000 (n = 5000 for 2016WY only)

SUPPLEMENTAL INFORMATION

Supporting information contains more detailed methods for the principal component analysis. Additionally, it contains figures and tables to support the main text, particularly with regards to the residuals analysis and hydrograph separations.



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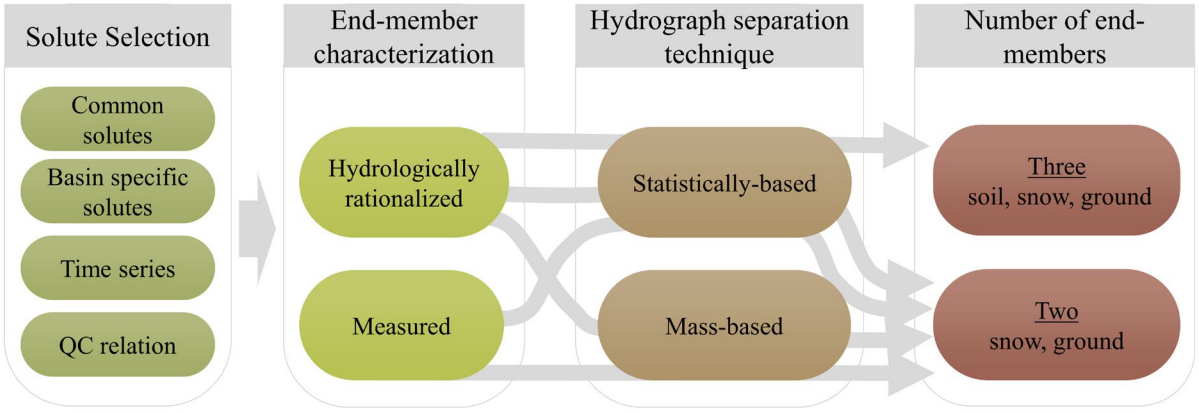

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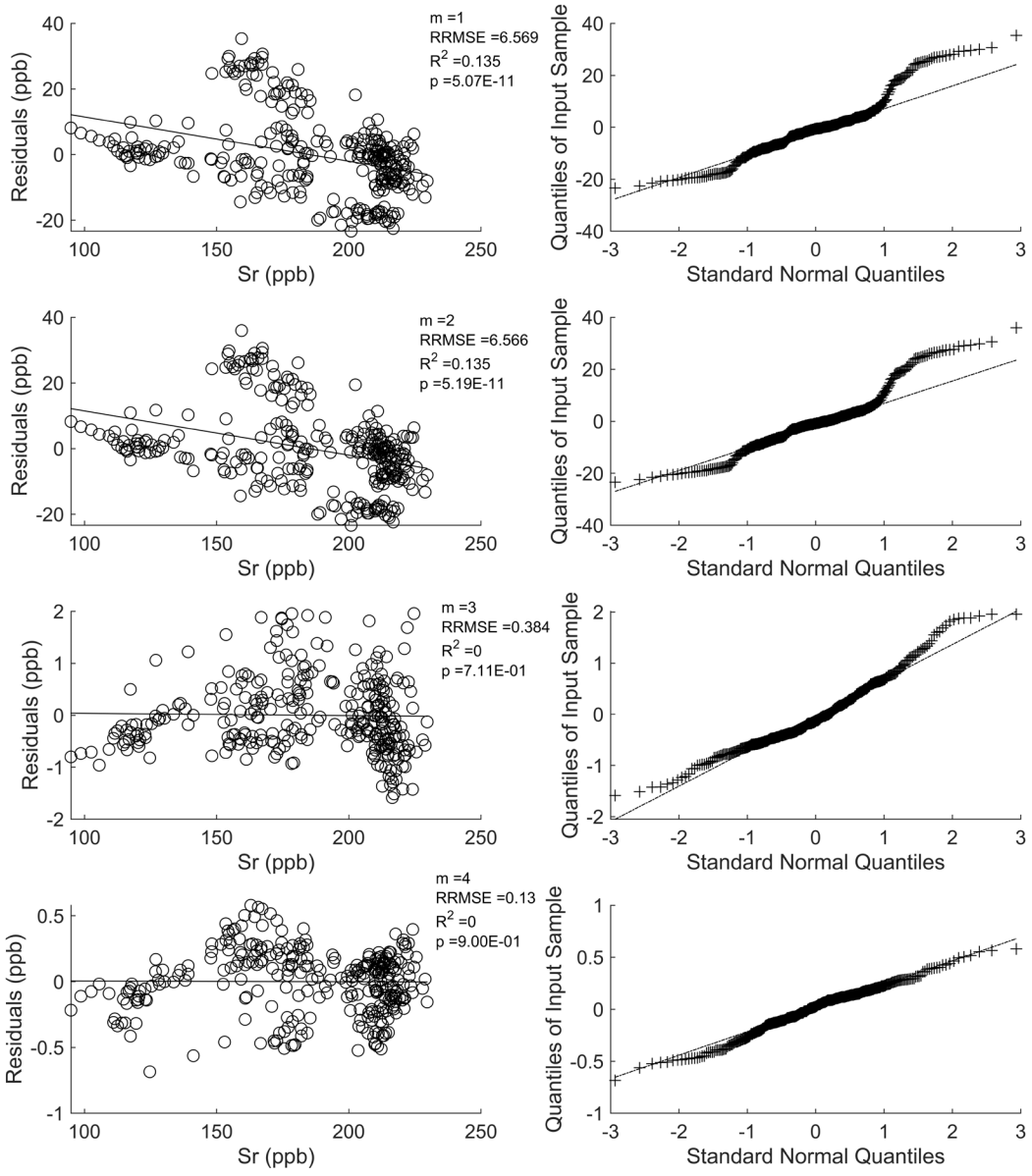

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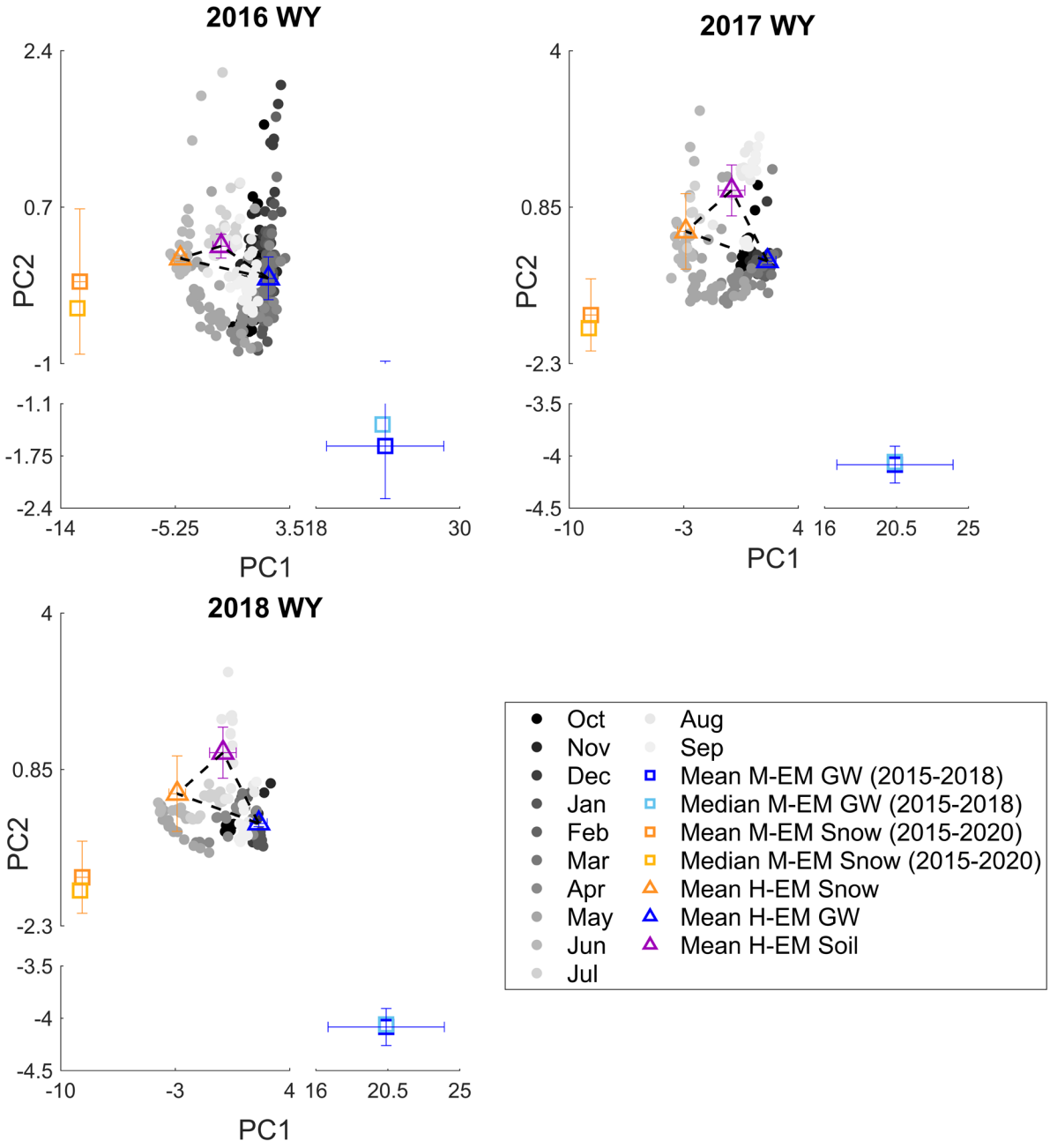

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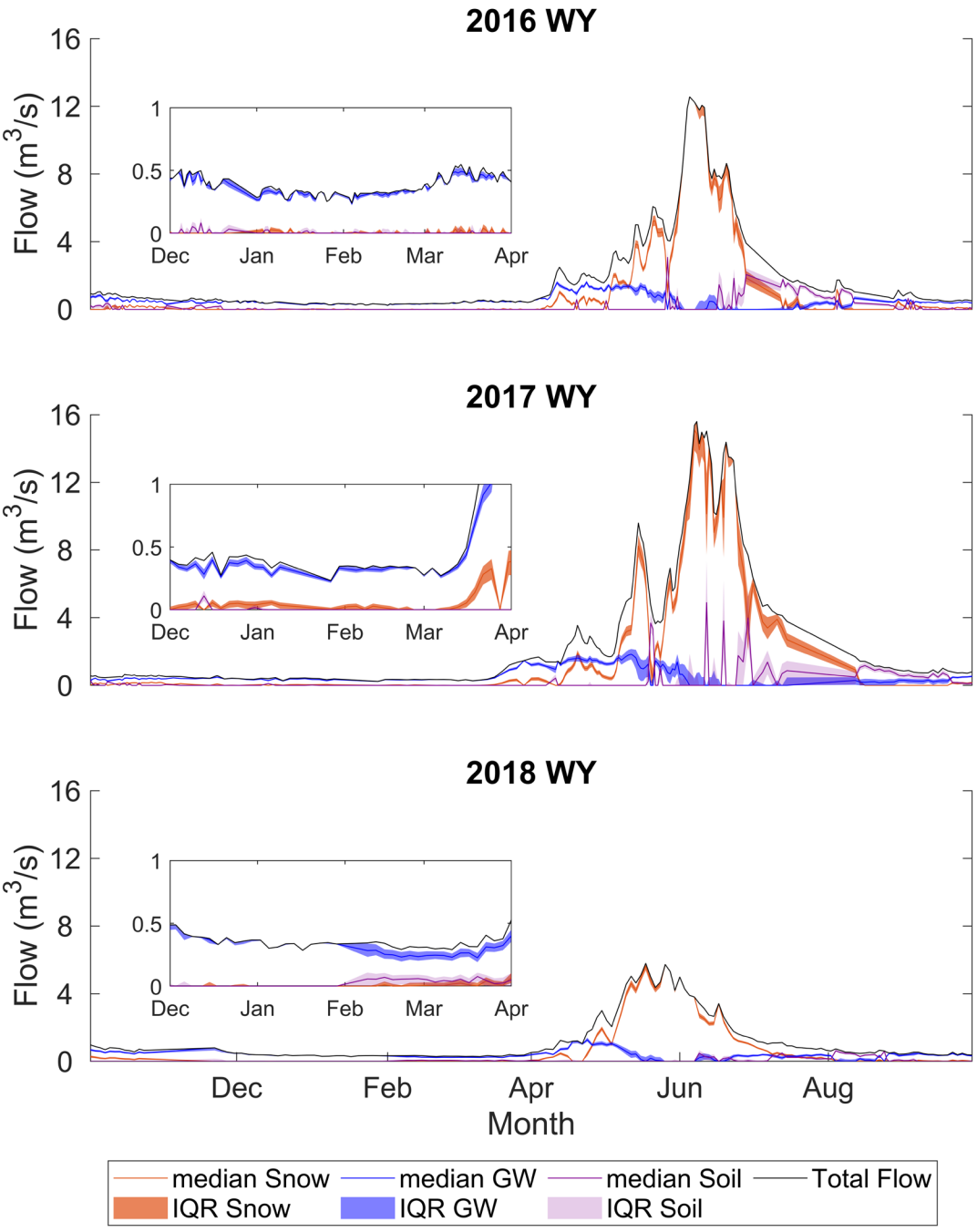

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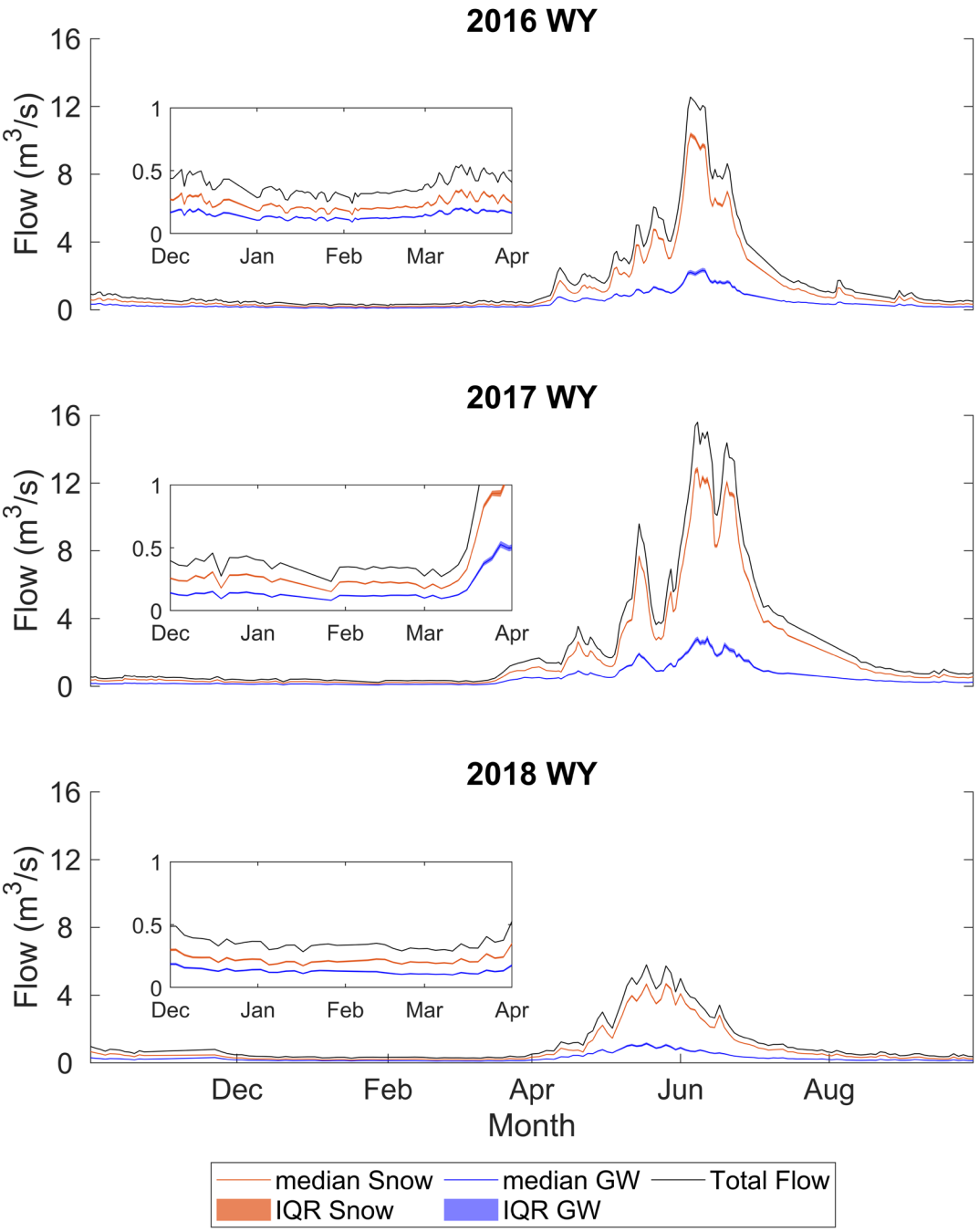

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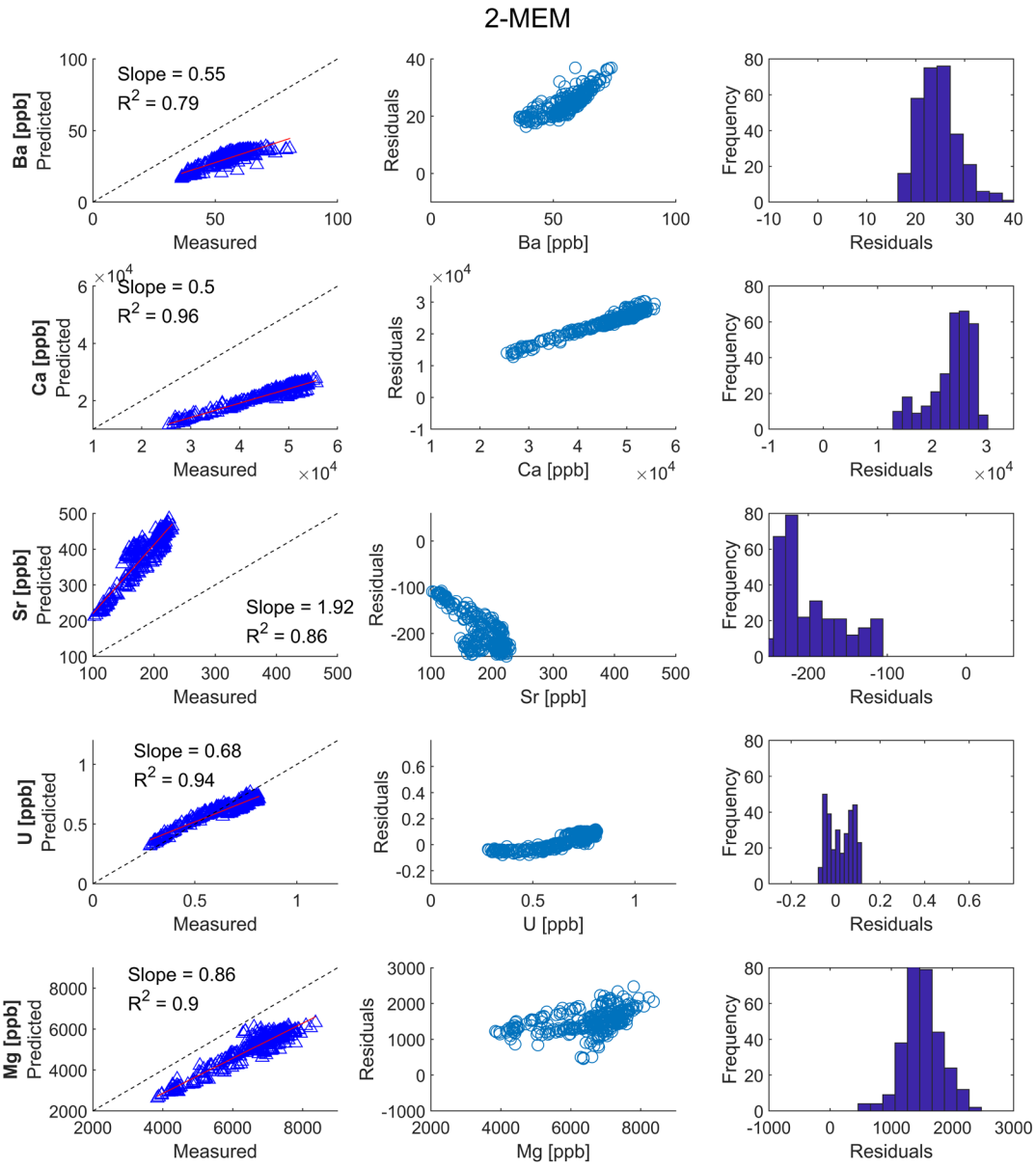

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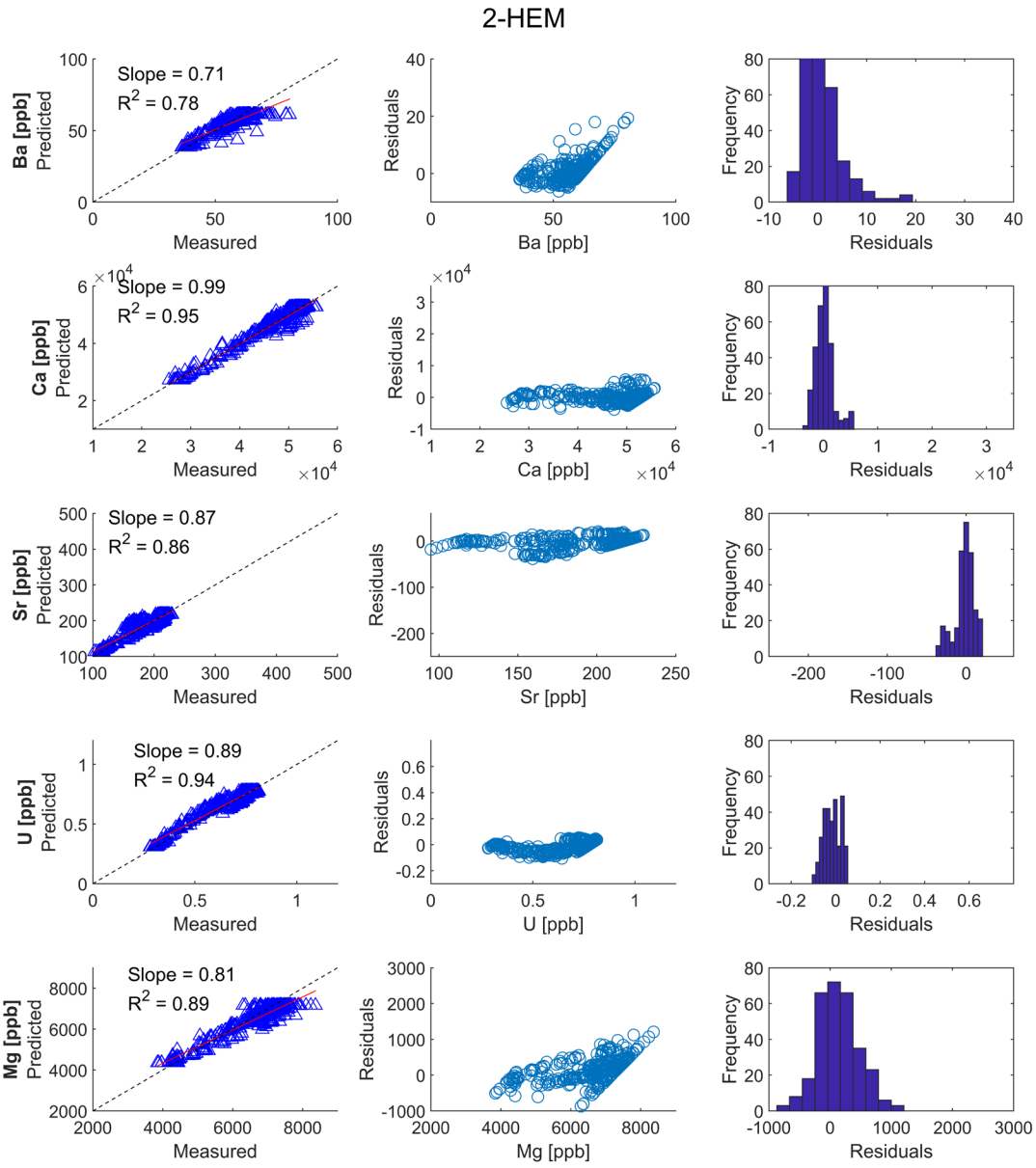

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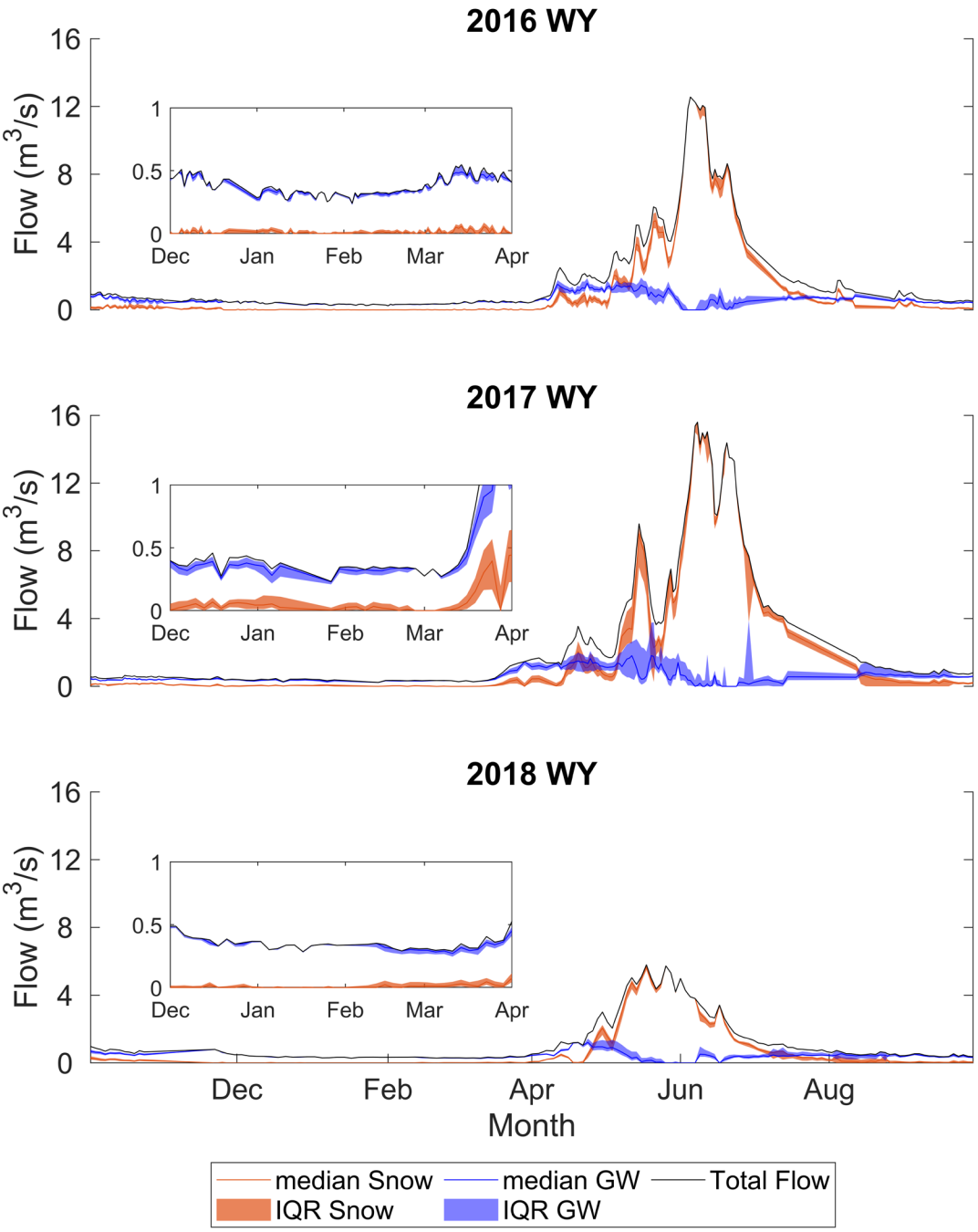

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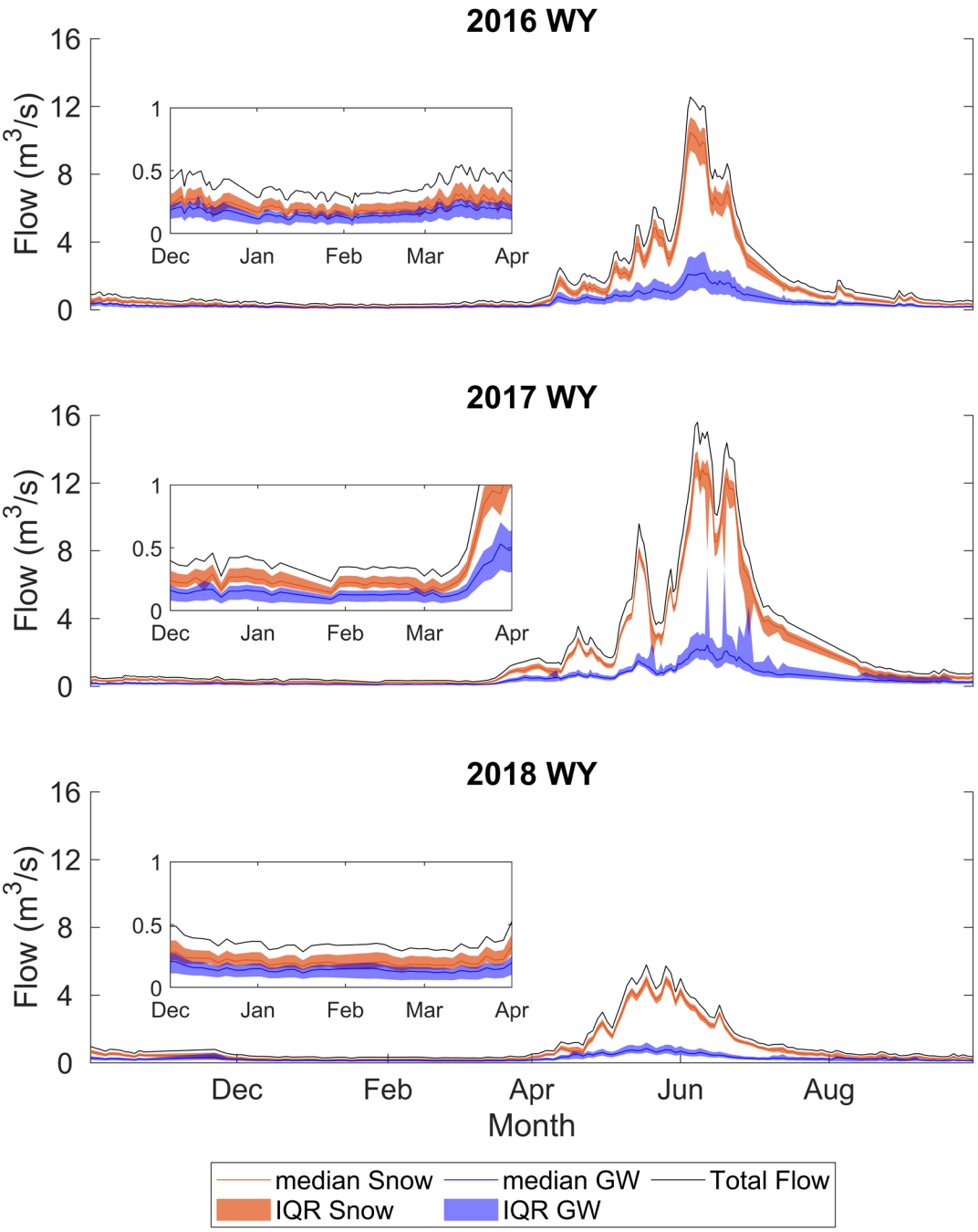

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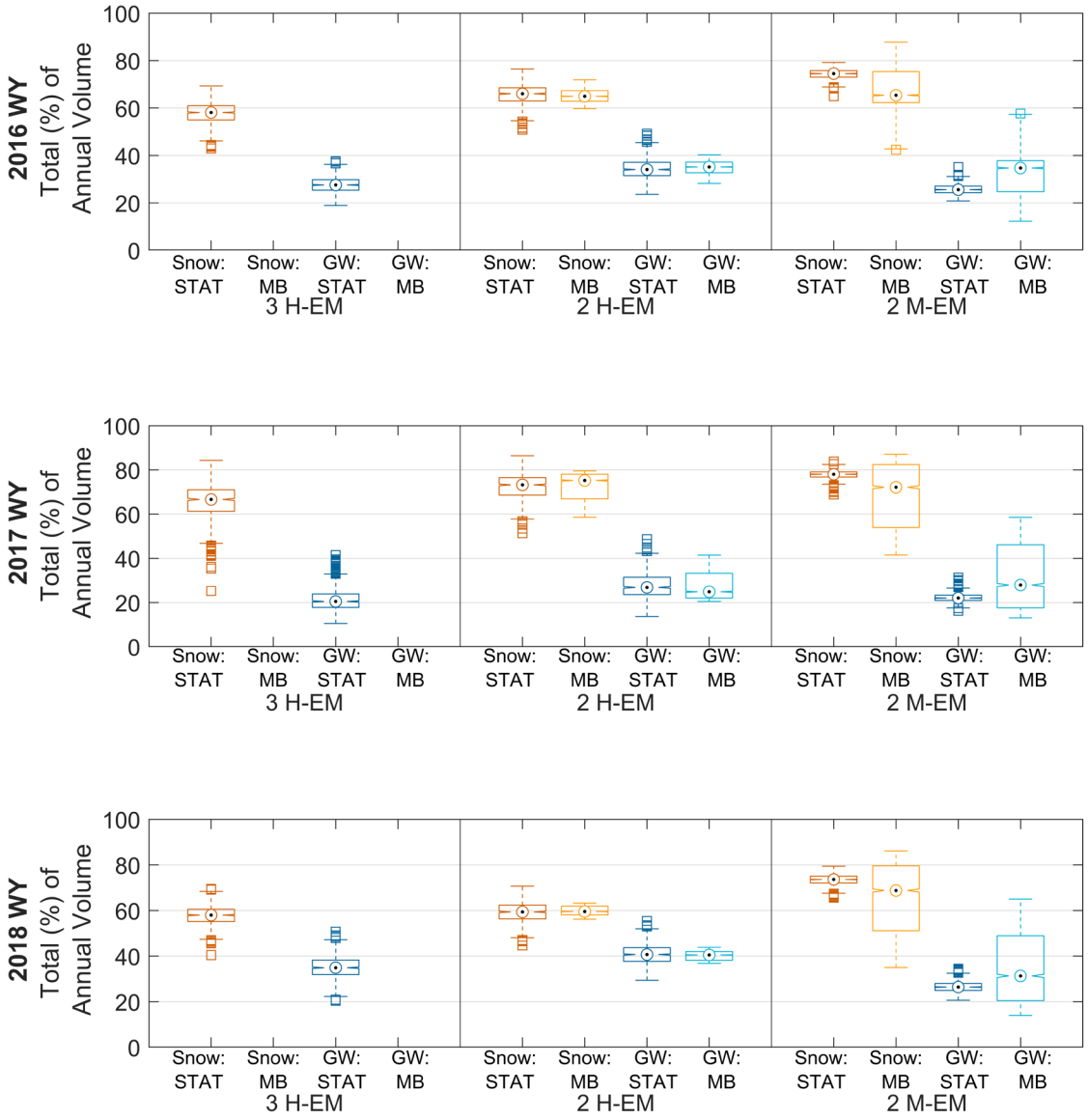

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