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Multiyear Increase in the Stable Isotopic Composition of Stream Water From Groundwater Recharge Due to Extreme Precipitation

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Key Points:
- Stable isotopic composition of surface waters show a persistent increase due to summertime precipitation in the year 2011
- Length of isotopic recession of stream water is a strong function of watershed area
- Stream water isotopes consistent with a large pulse of water being stored and released from groundwater

Supporting Information:
- Supporting Information S1
- Data Set S1

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Abstract The isotopic composition of surface and groundwater is impacted by many hydrologic processes. The long-term stable water isotopic response of systems to hydrologic change is critical for interpreting isotopic information for streamflow generation, stream-aquifer-coupling, and recharge processes. To evaluate the response of stream-aquifer systems to extreme precipitation events we use 743 surface and groundwater isotopes with drainage areas ranging from 0.1 to >800 km^2. Results show multiannual trends from high to low isotopic compositions associated with increases in the composition of shallow groundwater. The year 2011 was one of the wettest years and the months of August and September were the wettest consecutive 2-month period in the 123-year record. This increase in the isotopic composition has long-term impact on the isotopic composition of surface and groundwater highlighting the importance of groundwater sources of baseflow to streams and the transient storage and release mechanisms of groundwater at the catchment scale.

Plain Language Summary We present and analyze surface and groundwater samples collected from late 2011–2016 across a large region of western Massachusetts. The data together show multiyear trends in the stable water isotope compositions, a tracer of water source and hydrological processes. These trends are not reflective of typical seasonal behavior and point to a change in the isotopic composition due to a unique hydrologic event. The year of 2011 was the wettest calendar year on record for western Massachusetts and the months of August and September of 2011 were the wettest consecutive 2-month period in the 123-year precipitation record. This wet period saturated the ground with excess water leading to large increases in the regional water table and high infiltration rates. The isotope data suggest that 4–5 years later we still observe this water draining from the groundwater system to surface streams. These results point to the important role of extreme precipitation events to surface and groundwater catchments, even in regions with high annual precipitation rates. The inclusion of groundwater processes (recharge, storage, and discharge) are important controls on surface water isotopic composition.

1. Introduction

The frequency of extreme precipitation events is increasing (IPCC, 2013). In addition, the annual precipitation rates are increasing in the Northeastern U.S. states (Higgins & Kousky, 2012; Mallakpour & Villarini, 2017). The impact of the magnitude and intensity of precipitation changes on the terrestrial hydrologic cycle (soil, surface, and groundwater storage) and biogeochemistry of waters is well documented (Vidon et al., 2017). Increases in precipitation and higher soil moisture conditions are presumed to have an impact on the timing and magnitude of flood events (Anderson et al., 2017; Blöschl et al., 2017; Trenberth et al., 2018; Weider & Boutt, 2010; Yellen et al., 2014, 2016). In fact, recent large precipitation events, such as those from Tropical Storms Irene and Lee, have led to widespread alteration of hydrologic and biogeochemical processes in many catchments along the U.S. Atlantic seaboard (Vidon et al., 2018, and references therein). Few studies have documented the impact of these changes in the precipitation regime on water quality or water isotopes in the terrestrial component of the water cycle. These large-scale impacts of extreme precipitation alter the hydrological landscape, making it difficult to interpret data collected over short time periods (Tetzlaff et al., 2017).

The understanding of changes in the isotopic composition of surface and shallow groundwater is important for documenting changes in climate and precipitation regime change (Puntsag et al., 2016). The use of stable

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isotopes in hydrological studies is becoming a widespread component of hydrologic analysis (Clark & Fritz, 1997; Dansgaard et al., 1993; Fricke et al., 1998; Gat et al., 2001; Gibson et al., 2005; Jasechko et al., 2017; Jouzel et al., 2000; Koeniger et al., 2016; Mazor, 2003; Rozanski, 1985). The development of distributed isotopic sampling of precipitation and surface water isotopes has led to landscape isotopic characterization—(isoscapes) and the proliferation of large isotope data sets (Bowen & Revenaugh, 2003; Bowen et al., 2011). A major assumption in most of these studies is that the isotopic composition of surface water and groundwater systems are time-invariant—at least on a multiannual basis. A recent documentation of ~40 years of precipitation in biweekly samples from Hubbard Brook (Puntsag et al., 2016) has shown an overall trend toward lower $\delta^{18}O$-H_2O values on an annual basis perhaps as a result of more moisture from Arctic or northerly sources. While precipitation isotopic composition plays a first order role in the spatial and temporal compositions of surface and groundwater (Kendall & Coplen, 2001), there are other processes that can impact surface and groundwater isotopic compositions. These include evaporation, recharge biasing, mixing, groundwater/surface water interaction, and the timing and form of precipitation (snow, rain, fog; Aggarwal et al., 2012; Clark & Fritz, 1997; Jasechko et al., 2014; Scholl et al., 2011; Schmitt et al., 2018). Few studies have documented the covariation or performed integrated assessment of both stream and groundwater isotopic composition, despite the fact groundwater provides the main source of water delivered to streams (Jasechko et al., 2016; Shanley et al., 2015). Therefore, surface water isotopic compositions to some extent are controlled by groundwater isotopic compositions.

In this contribution, we present the first paper to document stream water isotopic change at multiannual time scale due to large precipitation events. We analyze 743 samples of the isotopic composition of surface and groundwater stable isotopes from 5 years of sampling in the context of extreme summer precipitation in the year 2011. Results show multiannual trends toward isotopic depletion associated with large-scale enrichment of shallow groundwater. The work has implications for stream flow generation processes, residence time estimates, and interpretation of surface water isotopic composition and trends. Shallow glacial-derived soils and sediment in this region are important storage reservoirs for water at both annual and multiannual time scales (Boutt, 2017). The new insight gathered here supports current hydrological process thinking regarding source of water to streamflow and the multiannual memory of hydrologic systems with respect to shallow groundwater at the landscape scale.

2. Methods

2.1. HydroClimatic Information

We assemble hydroclimatic data for the region from a variety of public domain repositories. Monthly precipitation data are from Massachusetts Climate Division 1 (Western Massachusetts) products from NOAA climate at a glance (NOAA, 2017). We obtain monthly snow fall totals from station data (Amherst, MA 44 m asl, Lenox, MA 306 m asl). Stream discharge data are daily data from two USGS streamflow monitoring stations at Westfield River, Westfield, MA, USGS gage (USGS 01183500—drainage area 1,287 km^2) and Mill River, Northampton, MA, USGS gage (USGS 01171500—drainage area 136 km^2). Both streams are minimally impacted by upstream dam storage and have contrasting drainage areas of approximately a factor of 10. Groundwater anomalies, monthly value compared to historical monthly mean, are computed using water level measurements from 23 western Massachusetts USGS Climate Response Network wells following the procedures of Boutt (2017).

2.2. Water Sampling

We sampled 20 surface water locations approximately quarterly with upgradient contributing areas of 4 to ~1,000 km^2 from November 2011 to November of 2016 (Table S1 and Figure 1). Starting in April of 2014, 11 additional surface water locations with upgradient contributing areas of 1 to ~234 km^2 were sampled monthly adjacent to USGS Climate Response Network wells (Table S2 and Figure 1). Groundwater from four USGS Climate Response Network water-table wells were sampled monthly from September 2013 to November 2016 (Table S3). Mean water depths in the wells ranged from 2 to 3.7 m, with bottom screen depths from 5.3 to 11.9 m below surface. Groundwater samples were grab samples taken after three bailer withdrawals from the top of the water in the well. Discrete depth sampling of these wells shows a well-mixed borehole volume. Samples were place in 15 ml HDPE bottles with tightfitting caps and analyzed within a month of collection. Archived samples of the Deerfield River from May of 2010 (adjacent to

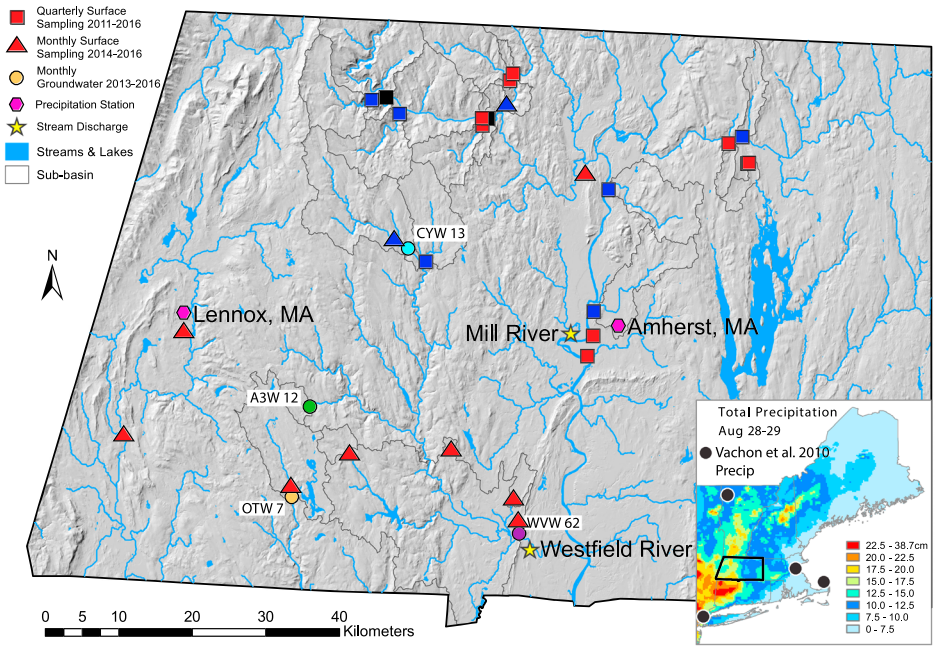

Figure 1. Shaded relief of Western Massachusetts indicating the location of meteorological stations, USGS stream gaging stations and surface and groundwater sampling sites for determination of the isotopic composition of water. Colors of surface water sampling sites (squares and triangles) correspond to drainage area (4–75 km^2—red; 75–500 km^2—blue; >500 km^2—black). Inset shows the accumulated precipitation during 28–29 August 2011 from Tropical Storm Irene. Black circles on inset show the locations of annual isotope measurements of precipitation in Vachon et al., 2010.

locations CTRW5 and 6) were also analyzed. Precipitation of Tropical Storm Irene (28–29 August 2011) were sampled in Holyoke, MA, approximately hourly during the storm and were weighted by local station data (Table S4).

2.3. Isotopic Analysis

All water samples were filtered and placed into 2 ml glass auto-sampler vials with a PTFE septa. The isotopic composition (^{2}H-H_2O, ^{18}O-H_2O) of hydrogen and oxygen of the water molecule of surface water, precipitation, and ground water are measured by wavelength scanned cavity ring-down spectrometry on unacidified samples by a Picarro L-1102i WS-CRDS analyzer (Picarro, Sunnyvale, CA). Samples were vaporized at 110 °C. A 5 μl Hamilton glass syringe draws 1 μl of sample to inject into a heated vaporizer port (110 °C). For each injection, the absorption spectra for each isotope are determined 20 times and averaged. To further eliminate memory effect between samples, each sample is injected six times and the results of the first three injections are discarded. Three standards that isotopically bracket the sample values are run alternately with the samples. Secondary lab reference waters (from Boulder, Colorado; Tallahassee, Florida; Amherst, Massachusetts) were calibrated with Greenland Ice Sheet Precipitation, Standard Light Antarctic Precipitation, and Vienna Standard Mean Ocean Water from the IAEA. Results are calculated based on a rolling calibration so that each sample is determined by the three standards run closest in time to that of the sample. Long-term averages of internal laboratory standard analytical results yield excellent instrumental precision of 0.51‰ for δ^2H-H_2O and 0.08‰ for δ^{18}O-H_2O. House waters analyzed from 2012 to 2017 show no drift or consistent offset in isotopic composition.

Estimates of young water fractions (Kirchner, 2016), defined as the fraction of water that is younger than 2–3 months, of streamwater is calculated by taking the amplitude of the detrended streamwater isotopic compositions (A_s) and dividing it by the amplitude of the precipitation annual isotopic composition (A_p). Amplitude estimates of an assumed sine-wave fit to the isotope data are calculated using the robust LAR nonlinear least squares algorithm in MATLAB with equation 4 of Kirchner (2016).

3. Results

3.1. Hydrologic Context

Figure 2 presents monthly precipitation, monthly snow totals from low (44 m asl Amherst) and high elevation sites (306 m asl Lenox); normalized basin yield for the Westfield River, Westfield, MA, USGS gage (USGS 01183500) and Mill River, Northampton, MA, USGS gage (USGS 01171500); and groundwater anomalies calculated from 15 USGS Climate Response Network wells in Western Massachusetts for the years 2011–2017 (Boutt, 2017). This period is characterized by precipitation extremes from the wettest year (165.9 cm/year in 2011) to one of the driest years (95.6 cm/year in 2016—eighth driest on record) in the period of record (1895–2017). Precipitation from the remnants of Irene impacted this region on 28–29 August 2011 resulting in intense rainfall ranging from 106 to 160 mm over the 2-day period across the study area. This part of Massachusetts experienced its second wettest August in the instrumental record (Olson & Bent, 2013) with the event from Irene making up to two thirds of the total precipitation during the month. Preceding and following Irene multiple frontal systems including Tropical Storm Lee during 8–9 September of 2011 also impacted the region resulting in the largest two consecutive months of precipitation (56.7 cm) in Western Massachusetts on record. The six largest consecutive months (ranging from 43.5 to 56.7 cm) of precipitation are all in the months of August to October. The composite effect of this lead to a substantial discharge event with a hydraulic recession lasting well into the summer of 2012 (Figure 2). Average groundwater levels (Boutt, 2017) reached a maximum in the winter of 2011–2012 and slowly fell into the winter of 2016.

3.2. Precipitation and Stream Water Isotopes

The amount weighted (~100 mm of precipitation) isotopic composition of the Tropical Storm Irene event sampled in Holyoke Massachusetts was −5.1 $\delta^{18}O\text{-}H_2O$ and −29.4‰ $\delta^{2}H\text{-}H_2O$, with individual samples ranging from −11.8 to −3.9‰ $\delta^{18}O\text{-}H_2O$ and −83.7 to −19.3‰ $\delta^{2}H\text{-}H_2O$ (Table S3). These values are broadly consistent with published summertime precipitation in the Northeast United States (Vachon et al., 2010). Figure 3 presents a time series of $\delta^{18}O\text{-}H_2O$ of stream waters from November 2011 to November 2016 for the surface water sampling network. Complete tables of all sample data and a $\delta^{18}O\text{-}H_2O$ versus $\delta^{2}H\text{-}H_2O$ plot are available in the supporting information (Figure S1). $\delta^{18}O\text{-}H_2O$ of stream waters range from approximately −5‰ to approximately −12‰ during the sampling period with any individual sampling event showing upward of 4‰ variation in $\delta^{18}O\text{-}H_2O$ across the sites. Average stream water composition from the Northeast United States based on Kendall and Coplen (2001) are −8‰ to −12‰ in $\delta^{18}O\text{-}H_2O$ although the Kendall and Coplen (2001) study has few samples in the local region. Lower (more negative values) isotopic compositions are observed in streamwater during the months of March–May with the years of 2014 and 2015 being the lowest values. This is consistent with the cold snowy conditions experienced during these years due to the polar amplification (Francis & Skific, 2015). Higher isotopic signatures (>−7‰ $\delta^{18}O\text{-}H_2O$, Figure 3) occur during the late fall periods and dominate the dry 2016 season. In general, stream waters with larger upgradient contributing areas have lower isotopic compositions and have less variable isotopic compositions from season to season. On average the highest stream waters compositions are found in November of 2011 and show a trend toward lower values through to the winter of 2015. Stream waters of similar sampling sites in summer of 2010 are substantially lower (approximately −11‰ $\delta^{18}O\text{-}H_2O$) than any of the values in the period of November 2011 to November of 2016. Time series of d-excess (defined as $\delta^{2}H\text{-}8^{*}\ \delta^{18}O$) do not show strong seasonal periodicity but generally display a trend toward higher values of d-excess.

The isotopic compositions of the surface water sampling sites are averaged based on upgradient contributing area and presented in Figure 3. These averages show strong seasonality and generally trend toward lower isotopic compositions from late 2011 to 2015. While the three groupings of watershed areas (4–60, 75–155, and >800 km^2) show a similar initial value (approximately −6.5‰), the rate and recovery time of the trend is a strong function of watershed area with samples from the largest watersheds showing a trend toward lower isotopic compositions over four seasons. There is also a shift in the timing of the summer/fall and winter/spring changes in oxygen isotopic composition that appears to be dependent on upgradient contributing area.

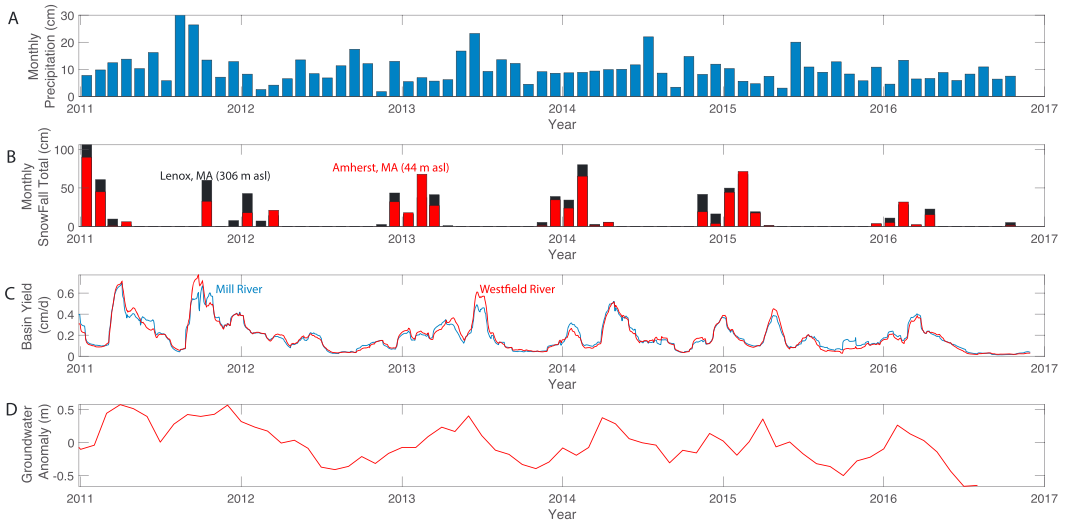

Figure 2. Summary of hydroclimate time series for Western Massachusetts from 2011–2016. (a) Monthly precipitation (mm) from NOAA climate at a glance, climate division 1 Massachusetts. (b) Monthly snow fall totals for the two stations on Figure 1 (black boxes—Lenox, MA; red boxes—Amherst, MA), locations in Figure 1 (pink polygons). (c) Drainage area normalized discharge (cm/day) for two drainages in Western Massachusetts (red—Westfield River; blue—Mill River). (d) Average groundwater anomalies for 16 groundwater level observations across western Massachusetts (Boutt, 2017).

Together these data indicate (1) a long descent in δ^{18}O-H_2O isotopic values from 2011 to 2015 no matter the size of the watershed; (2) Larger watersheds tend to have lower isotopic compositions than small watersheds; (3) All watersheds show strong seasonality but there is a response that is watershed size dependent.

3.3. Groundwater Isotopes

The four groundwater sampling sites have δ^{18}O-H_2O isotopic compositions that range from −8‰ to −10‰ over the period of sampling (Figure S3). The two high elevation sites (OTW 7 and A3W 12) have the lowest isotopic compositions and mimic each other. The lowest sampling site (WVW 62–64 m asl) possesses the highest isotopic signature. Groundwater sampling site OTW 7 shows some seasonal fluctuation in isotopic composition. There are monthly increases and decreases in isotopic composition but the dominant characteristic of the time series is the trend toward lower oxygen isotope values. Linear regression trend testing yields p values less than 0.01 for all four sites with slopes of δ^{18}O-H_2O of −0.11‰ to −0.34‰ per year. Statistically significant trends in δ^{2}H-H_2O (−0.10‰ to −2.12‰ per year) and d-excess (+0.27‰ to 0.81‰ per year) at low p (<0.05) values are present (Table S3). All of the sites show similar trends in δ^{18}O-H_2O, δ^{2}H-H_2O, and d-excess despite their differences in elevation, site characteristics, and screen depths.

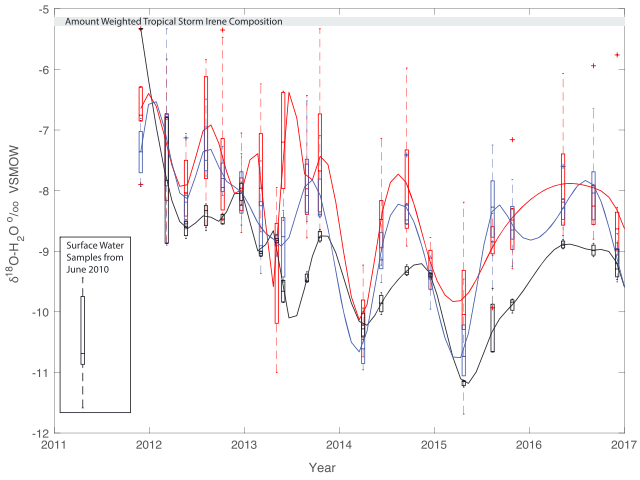

Figure 3. Box and whisker plot for quarterly isotope samples binned by watershed area (4–75 km^2—red; 75–500 km^2—blue; >500 km^2—black). Bottom and top edges of boxes are the 25th and 75th percentiles with outliers indicated by a +. Solid lines are cubic spline fits through data comprising different sized drainage basins. Tick marks indicate 1 January of specified year. VSMOW = Vienna Standard Mean Ocean Water.

4. Discussion

Stream and groundwater isotopic compositions across a 10,000 km^2 area show multiannual trends, lasting upward of 4 years, toward isotopic depletion following the wettest two consecutive months in the ~160-year record. Precipitation isotopic composition from the Tropical Storm Irene event is isotopically higher compared to all of the surface and groundwater samples. Together these data suggest a strong coupling of groundwater and surface water isotopic reservoirs following a conceptual model where groundwater is a dominant component of streamflow. A proposed mechanism to give rise to these observations is as follows: isotopically enriched (higher isotopic values) warm-event precipitation being

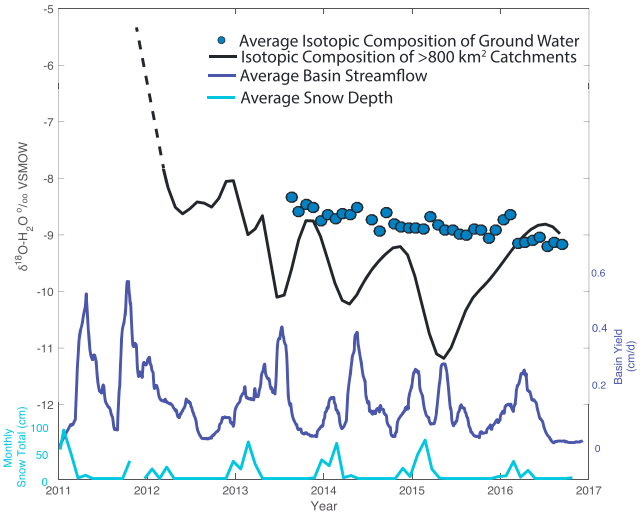

Figure 4. Summary plot of average surface water isotopic composition of large streams (>800 km^2—black line, dashed where controlled by a single sample), groundwater isotopic composition through time (blue dots) compared with basin yield from the Mill River (dark blue line) and snow fall total (light blue line) from the Amherst MET station. VSMOW = Vienna Standard Mean Ocean Water.

emplaced into both the surface drainage network, ponded and near surface storage (wetlands, ponds, etc.) and groundwater storage. The initial large increase in the surface water isotopic composition is likely from shallow, small storage near surface reservoirs that drain relatively quickly (~1 year). The longer-term trends in surface streamflow isotopic composition is due to the fact that regional shallow groundwater experienced a significant pulse of higher water isotope values that provides the baseflow to the stream network. Figure 4 illustrates this by comparing the average isotopic composition of groundwater from the four wells to the isotopic composition of the larger stream catchments. The multiyear trends in surface and groundwater isotopic composition are similar with the surface water having a slightly steeper slope and trends toward lower minimas. This is interpreted to either be due to more depleted runoff from the snowy and cold winter of 2015 or perhaps the return to more typical streamflow isotopic compositions (see summer 2010 pre-event values in Figure 3) as the baseflow values become lower.

Other mechanisms are possible to explain the observations presented here. The isotope data from May/June of 2010 establishes a key constraint on pre-event isotopic composition, but that does not necessarily rule out a prior long term trend. Pre-event values are typical of published data in the USGS NWIS database for this region and with those published in the literature (e.g., Bowen et al., 2011; Dutton et al., 2005; Kendall & Coplen, 2001; Landwehr et al., 2014). Additionally, there is a physical bound on how high the mean isotopic composition of precipitation can get in this region based on atmospheric circulation and vapor sources (Bowen et al., 2011). If the isotopic composition of surface waters we are observing was the decay from a prior (pre-2010) large precipitation event (or increase in temperature) there would need to be a large and unrealistic increase in the isotopic composition of the region, which is not supported by published precipitation isotope data (e.g., Vachon et al., 2010), temperature records, or model calculations of isotope composition of surface water (Bowen et al., 2011). Increases in the contribution of lower isotopic composition waters to streams from snowmelt (or cold season precipitation) could explain some of the trend toward lower values in the isotopic composition of water observed here. The winter of 2014–2015 was one of the snowiest on record but did not produce runoff events (Figure 4) anywhere close to the wet and less snowy winter of 2010–2011.

Stream water isotopes show seasonal and multiyear trends reflecting the seasonal fluctuation that is temperature dependent. The magnitude of the seasonal fluctuation does not appear to be dependent on watershed area. Yet, the magnitude of multiannual trends is clearly watershed area dependent suggesting that the amount of stored isotopically high groundwater in the larger watersheds has a longer residence time and longer temporal effect. During the period of the year (i.e., summer) when streamflow discharge is low, the isotopic compositions of the surface and groundwaters are similar. The large streams (black line in Figure 4) do not have isotopic compositions that rise above the averaged groundwater isotopic composition suggesting that in these waters evaporative isotopic fractionation is minimal, consistent with the d-excess values greater than 10 of these samples (Figure S1), and stream waters are essentially groundwater baseflow. The summer maxima of the surface water and averaged groundwater isotopic composition follows a very similar trend. This observation further supports a conceptual model that groundwater inputs to streams drive the isotopic evolution of surface water.

Seasonal amplitudes of precipitation or A_p calculated from Vachon et al. (2010) $\delta^{18}O$-H_2O precipitation sites are 1.7‰ (MA01), 1.9‰ (MA13), 4.4‰ (NY08), and 4.6‰ (VT99). Because these sites bracket the geographic location of the study region, we use an average A_p of 3.2‰. Seasonal detrended amplitudes of streamwater A_s grouped into contributing areas are 0.67‰ (4–60 km^2), 0.71 (75–155 km^2), while the greater than >800 km^2 was 0.50‰. Fraction of young water estimates calculated using the assumptions presented in Kirchner (2016; i.e., A_s/A_p) are then 0.21 (4–60 km^2), 0.22 (75–155 km^2), and 0.16 (>800 km^2). These calculations suggest that the streamwaters sampled here roughly represent 16% to 22% of water that is younger than 2–3 months.

High antecedent moisture conditions and these events taking place during summer/fall conditions led to the increased infiltration of high isotopic composition water. The majority of groundwater recharge in this region occurs during the nongrowing season, the shoulder seasons of fall and spring (Boutt, 2017). Wetter than average conditions caused soil moisture to be higher than normal (Yellen et al., 2016) allowing excess precipitation to recharge the water table. While rare in the instrumental record, these events in the past have likely occurred in wetter than average summers coincident with a land-falling tropical storm system. Because of this, the isotopic composition of this summer precipitation is distinct from typical groundwater recharge (fall/spring) and summer stream baseflow. Fall/spring precipitation tends to be more isotopically depleted (Vachon et al., 2010). Groundwater recharge is also seasonally biased (Jasechko et al., 2014) in this part of the world. This magnitude of increase in the isotopic composition of the groundwater suggests a significant amount of aquifer recharge during the late-growing season. Calculations based on the physical rise of the water table range from 0.1 to 0.3 m^3/m^2 during a 6-month period, which represents ~40% of the total recharge in an average climate year from 1960 to 2010 (Boutt, 2017).

These results have substantial implications for understanding the role of groundwater storage and release in humid-temperate catchments at the subregional scale. Groundwater mediated isotopic increases of surface water is a major driver of the observed isotope time series presented here. Fraction of young water estimates are consistent with baseflow recession analysis and confirm the importance of the shallow groundwater reservoir in maintaining flow in streams in this region. Recharge enhanced by extreme precipitation events to groundwater is necessary to explain the observations documented here. In fact, groundwater recharge from such large events may be more important than previously recognized (Weider & Boutt, 2010).

These results have important implications for isoscape reconstruction of surface and ground water systems. Grab samples of surface water isotopic composition may be biased by previous large storm events. There is immense power in cosampling and analyzing the isotopic composition of both surface and groundwater. Surface water isoscapes are not time-invariant and with anthropogenic climate change causing the isotopic composition of precipitation to evolve as dominant moisture sources change (e.g., Puntsag et al., 2016), it is even more important to understand the hydrologic and temporal context of surface and groundwater isotope results.

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