Hydrologic tracers and thresholds: a comparison of geochemical techniques for event-based stream hydrograph separation and flowpath interpretation across multiple land covers in the Panama Canal Watershed

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Abstract

Stream hydrograph separation using naturally occurring geochemical tracers holds great potential for elucidating mineral weathering and solute transport. This study addresses a critical need to characterize catchment runoff generation in the humid tropics using multiple natural tracers for hydrograph separation and concentration/discharge (C/Q) hysteresis analysis. We use hydrometric and geochemical data collected at the start of the wet season from three small, steep catchments located in the humid seasonal tropics of central Panama that differ primarily in land cover. We apply a dual source hydrograph separation model between two end-members: new event water precipitation and pre-event water stored in the catchment. We compare the effectiveness of electrical conductivity (EC) and stable water isotopes (δD and $\delta^{18}O$) tracers for identifying precipitation event water in stream runoff using across forested (1.43 km²), mixed land use ‘mosaic’ (1.82 km²) and pasture (0.42 km²) catchments. Hysteretic C/Q loops are analyzed for flowpath interpretation using δD , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , and SO_4^{2-} . During a medium-large magnitude event on May 23, 2013, forest and mosaic stream δD , Ca^{2+} , Mg^{2+} , and Na^+ exhibited clockwise hysteresis, SO_4^{2-} exhibited anticlockwise hysteresis, and K^+ and Cl^- each showed no hysteresis. EC as a surrogate for total dissolved solids agrees acceptably with stable water isotope hydrograph separations during small peak runoff events (<3 mm/hr). However, isotope and conductivity tracers strongly disagree during a large runoff event (>10 mm/hr) in the mosaic catchment. Early wet-season events indicate lower event water fractions than events farther into the wet season. Despite previous work showing land cover strongly controls storm runoff efficiencies, hydrograph separation and hysteresis analyses only indicate weak event water delivery differences between the paired forest and mosaic catchments.

Keywords: tropical hydrology, stream chemistry, runoff mechanisms, land-use change

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1. Introduction

Many flowpath and runoff studies have been conducted in temperate regions, but the understanding of hydrologic processes in tropical catchments pales in comparison (Wohl et al., 2012). Further study in the humid tropics, which covers about 25% of the earth's land surface, becomes more urgent as the tropics face rising land cover disturbance pressures owing to population growth (Foley et al., 2005). Anthropogenic landscape disturbances to soil morphologies in the humid tropics further alter the flow regime, creating challenges in understanding hydrologic system behavior as land covers undergo change. Hydrograph separation studies using stable water isotopes and naturally occurring ion tracers present an opportunity to elucidate runoff process thresholds and infer flowpaths across a spectrum of anthropogenically altered tropical land covers (Buttle & McDonnell, 2004). Improved hydrological mechanistic understanding using natural tracers may advance hydrologic model development for predicting the impacts of change, with potential benefits for society (e.g. flood forecasting and hydropower) and interdisciplinary research (e.g. climate change, chemical weathering zones, plant water use and availability). Yet, only a few investigations have recently described event-based tracer studies in the tropics (e.g. Kurtz et al., 2011, Schellekens et al., 2004, Goller et al., 2005, Muñoz-Villers and McDonnell, 2012, and Bonell et al., 1998).

This study aimed to identify event-based runoff characteristics and evaluate electrical conductivity (EC) effectiveness as a hydrograph separation tracer relative to the stable water isotopes deuterium (δD) and oxygen-18 ($\delta^{18}O$) in three humid tropical catchments. These experimental catchments each span a spectrum of recovery from anthropogenic activity as part of the Agua Salud Project in the Panama Canal watershed. The same study catchments are described in detail in Ogden et al. (2013). We also utilized major ion hysteresis analysis (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , and Cl^-) in conjunction with the hydrograph separation results to interpret storm runoff water sources. Event scale runoff behavior in the Panama Canal watershed is characterized by highly responsive streams that rapidly deliver water as interflow (Niedzialek and Ogden, 2011). Variations in the effectiveness of EC and stable isotopes for hydrograph separation are analyzed based upon antecedent catchment conditions and event-based runoff behavior. This research presents potential applications for identifying storm runoff flowpaths and discriminating runoff fluxes from different sources in hydrologically responsive humid tropical catchments. Study results serve as a critical physical process characterization for later evaluating biogeochemical transport and cycling in the Panama Canal Watershed.

Naturally occurring geochemical constituents resulting from mineral weathering and biogeochemical processes can serve as flowpath tracers to help identify runoff generation processes. Hydrograph separation quantifies the relative contributing source water fractions (event water vs. pre-event water) to stream runoff during precipitation events. Decades of research on hydrograph separations using geochemical tracers have shown that in most alpine and temperate upland forested basins, the pre-event fraction is 50% or more of streamflow at peak discharge (Buttle, 1994). Past studies have compared different naturally occurring tracers on their effectiveness for hydrograph separation in temperate climates (e.g. LaDouche et al., 2001, Wels et al., 1991) and tropical montane Puerto Rico (Shellekens et al., 2004), yet there is a paucity of hydrograph separation studies comparing major ion tracers with stable water isotopes across small, steep, humid tropical catchments.

The ideal event-based tracers for humid settings are stable water isotopes δD and $\delta^{18}O$, as they are generally considered to behave conservatively when evaporative fractionation processes are negligible. Major ions and EC have also been successfully applied as tracers (e.g. Rice and Hornberger, 1998; Muñoz-Villers & McDonnell 2011), but this can be problematic due to their non-conservative behavior. Regardless of conservative behavior, C/Q hysteresis analysis can help determine solute flowpaths. Cl^- and Br^- are often assumed to act relatively conservatively in terrestrial ecosystems, though there is

some variation as to how different naturally-occurring geochemical tracers behave in different settings. In a meta-analysis of Cl^- conservative behavior in forest ecosystems, Svensson et al. (2010) found that Cl^- is more likely to be conservative in regions with high Cl^- deposition than in areas with low ($<6 \text{ kg ha}^{-1} \text{ yr}^{-1}$) Cl^- deposition. Given the proximity to both the Atlantic and Pacific Oceans, the Cl^- deposition rate in the Agua Salud catchments is expected to be high. Sklash et al. (1986) also report that Cl^- and EC both exhibit non-conservative behavior relative to the stable water isotopes in the Mai Mai catchment in New Zealand. EC can also exhibit non-conservative behavior (Pilgrim et al., 1979). Prior to this study, it was unknown how EC and Cl^- behave during runoff events in the Agua Salud catchments.

1.1 Runoff production in the Panama Canal Watershed

Hydrograph separation studies across varying land uses in the humid the tropics are lacking (Buttle and McDonnell, 2004). The initiation of the wet season is of particular interest for conducting a runoff tracer study, as anomalously high runoff ratios have been observed during this period in the Panama Canal Watershed (Calvo et al., 2005). Coupling hydrometric monitoring with event water and pre-event water fraction estimations using natural geochemical tracers could elucidate flowpath and runoff mechanisms as the Agua Salud Project catchments undergo a transition in moisture states. A dual component, rather than three component hydrograph separation influenced our approach per the Q-mode factor analysis by Kinner & Stallard (2004) of chemical constituents in the Lutz Creek catchment located 11km from the Agua Salud sites. They found that 95% percent of variance in Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NO_3^{2-} , PO_4^{2-} , Si(OH)_4 , and SO_4^{2-} can be explained by surface and subsurface runoff-contributing end members.

The objectives of this study are two-fold (i) to identify effective geochemical tracers for hydrograph separation purposes, and (ii) compare and contrast geochemically-derived hydrograph components and hydrometric runoff behavior among catchments of different land uses during the dry- to wet-season transition in moisture states.

1.2 Study location

In 2008, the Smithsonian Tropical Research Institute (STRI) began a landscape-scale study called the Agua Salud Project in the Panama Canal Watershed to investigate land use impacts on ecosystem services. The Agua Salud Project addresses tropical studies in biodiversity, forestry, and ecosystem services including hydrology across a spectrum of common tropical land uses (Stallard et al., 2010). Our study investigates early wet season precipitation runoff events using naturally occurring geochemical tracers across three catchments in Agua Salud Project.

Figure 1: Study site location within the Panama Canal watershed, with secondary forest ages relative to 2012 (Ogden et al. 2013). Stream, rainfall, groundwater, and soil water sampling locations are shown. The mosaic catchment weir is located at 9°13'07"N 79°46'15"W.

We studied three catchments draining into the Agua Salud River in the Panama Canal Watershed (Figure 1). The 1.43km² forest catchment is contained entirely within Soberanía National Park. Roughly 80% of the forest catchment is a mature forest (>80 years old) while secondary succession forest (<35 years old) makes up the remaining 20%. The second catchment is a mixed land-use mosaic

watershed draining 1.82km² adjacent to the forest catchment. It is characterized by a mix of young secondary forest (<15 years in age), older secondary forest (>15 years in age), actively grazed cattle pasture, and patches of subsistence agriculture. The third study sub-catchment is a 0.423km² actively grazed cattle pasture embedded within the mosaic catchment. All three study catchments share similar morphology, soils, underlying geology and rainfall.

1.3 Climate

Panama is located between 7° and 10° north of the equator with distinct wet and dry seasons governed by Inter-Tropical Convergence Zone movement. On average, the wet season begins on May 4 with a standard deviation of 11 days and ends on December 20 with a 15 day standard deviation (*Smithsonian Tropical Research Institute (STRI)*, 2013). We monitored the geochemistry of the three streams during rainfall events during a six week hydrologic transitional period at the start of the wet season beginning in May, 2013 and ending in mid-June, 2013. Average annual rainfall between 1960 and 2010 at Barro Colorado Island located about 11km west of the study catchments is 2700 mm (STRI, 2013).

1.4 Geology & soils

The Agua Salud Project catchments in this study are characterized by steep slopes and deeply incised channels ranging from 52 to 302m AMSL. The average hillslopes across the two paired forest and mosaic catchments are 24.0 % and 23.7% respectively (Ogden, et al., 2013). Soils in the Agua Salud experimental catchment are deeply-weathered oxisols typical of most tropical regions. Weathered tropical soils such as these are high in clay content and residual elements such as Fe, Al, and Si and low in alkali metals and alkaline earth metals (Harrison et al., 2005). These oxisols are up to 20m thick in the region and are derived from *in-situ* weathering of underlain basaltic parent rocks (Wegner et al., 2010; Harmon et al., 2005). Soil thickness generally decreases from ridge to stream channel, where saprolite and less weathered basaltic parent rock outcrops can be found in and near streams.

2. Methods

2.1 Physical monitoring & data control

The Agua Salud Project continuously monitors hydrologic fluxes using clustered tipping bucket rain gages, evapotranspiration gages, and V-notch weirs equipped with pressure transducers. This study presents data from two rain gage clusters and three streams whose weirs were instrumented with pressure transducers. Three clustered tipping bucket rain gages were situated on a grassy hilltop in the mosaic catchment at a point located 0.68, 1.2 and 2.6km from the pasture, mosaic, and forest weirs, respectively (Figure 1). Additionally, two clustered rain gages were located within 30m of the forest weir below a canopy opening resulting from a tree fall. In contrast to the mosaic rain gage cluster on an exposed hilltop, the forest rain gage cluster was mildly impacted by canopy interception. Davis rain gages (Rain Collector II, Davis Instruments Inc.) record 0.01 inch bucket tips using HOBO pendant data loggers. The rain gage clusters served as quality control checks for the occasional debris clogging. Tipping bucket data were binned into 15 minute periods.

Streamflow was monitored using V-notch weirs at each catchment's outlet. At each weir site, non-vented pressure transducers (In-Situ Leveltroll, model 300) measure the combined barometric and water depth pressure at 15 minute intervals. We used a time series data editor to perform barometric correction and to correct stage data when affected by debris and sensor drift. Stage data from 120° and 140° weirs were then converted to volumetric discharge Q (m³s⁻¹) using discharge coefficient values determined by 1:2 and 3:16 scale laboratory experiments (Creel, 2013).

2.2 Water chemistry collection & analysis

We gathered rainfall, within-event stream water, stream baseflow, and shallow groundwater samples for geochemical analyses. Rainwater and stream samples were collected adjacent to their respective nested rain gages and weirs. Sequential rainfall and stream water samples were automatically collected across each event's duration and streamflow fluctuations. All samples were analyzed for δD and $\delta^{18}O$ and EC. For major ion (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , and Cl^-) analysis, we collected pre-event baseflow and groundwater samples within the week leading up to the May 23 event when precipitation and runoff were sampled.

Adjacent to the mosaic and forest rain gage nests, a simplistic sequential rainfall sampler (Kennedy, 1979) automatically gathered stable water isotope and EC samples. Precipitation fell into a 15.5cm diameter funnel containing a ping-pong ball float to minimize evaporation. Funneled water was directed to a series of 12 capped, sequentially filling 125mL vials connected by tygon tubing. Precipitation was collected at 7.25mm increments corresponding to a full 125mL collection bottle with no head space. A 1L bottle connected to the twelfth 125mL vial served as an overflow reservoir in case all vials filled. Sequential rainfall samples were gathered within 24 hours from the end of the precipitation event. For the major ions, a separate pre-cleaned plastic funnel was used to manually fill sample vials. Unlike the isotope and EC samples, major ion precipitation samples were separately collected under a canopy to represent throughfall.

Within-event stream water was collected within 10m of each V-notch weir using solar-powered automatic samplers (ISCO 6712, Teledyne ISCO, Lincoln, NE). Each ISCO was equipped with a model 730 bubbler module and programmed to trigger an automated collection sequence when water level rose >1.5 mm in a 30 minute period. Once the sampling program was activated, 500mL plastic sample bottles within the ISCO were filled at sequentially decreasing temporal resolution at time intervals ranging from 30 minutes to 4 hours to adequately capture peak runoff and the receding hydrograph limb signatures. ISCO event samples were selected in the field to minimally represent a rise, peak, and receding limb based upon the bubbler module's stream stage data. At times we were not able to gather storm runoff samples across all catchments or during entire events due to collection equipment malfunction, mostly associated with insufficient solar power. For major ion collection, ISCO bottles were rinsed with baseflow stream water prior to the collection event. Any contamination of stream runoff samples as a result of rinsing bottles with baseflow water is minimized by the relatively large volume (500mL) of event water collected.

Shallow groundwater and soil suction lysimeter samples were also collected between events at varying frequencies. Three single piezometers were installed near streams in each study catchment (Figure 1). Wells were purged once and then sampled. Nested porous cup soil suction lysimeters (UMS, Munich, Germany) were installed at 15, 50, and 100cm depths across a hilltop and a mid-slope swale in both the pasture and forest catchments (Figure 1). 500mL lysimeter sample bottles were shallowly buried in soil downslope from the lysimeter points to prevent evaporation. We applied a 0.6 bar vacuum to the lysimeters and collected samples at each site between events when at least one lysimeter collection bottle had gathered a sufficient volume to fill the 20mL sample vials.

We collected all stable isotope and EC stream and rain water samples in 20mL HDPE vials with zero-head-space caps that prevent sample fractionation by eliminating air space. ISCO and sequential rainfall samples were collected within 24 hours from rainfall termination. We filtered aliquots for major ion analysis into 20 mL HDPE bottles using PP syringes and 0.45 μ m Whatman® syringe filters. Prior to the field campaign, bottles for cation analysis were soaked in 5% HCl bath for 24 hours, followed by 5

rinses with DI water. Bottles for anion analysis were soaked and rinsed in DI water only. Cation aliquots were preserved with approximately 0.1% HNO₃.

2.3 Laboratory analyses

δD and δ¹⁸O were analyzed at The Ohio State University using a Picarro L1102-i cavity ringdown spectrometer. Four internal laboratory calibration standards bracketing the expected sample range were analyzed every five samples to account for drift and memory effects. Internal standards were calibrated relative to Vienna Standard Mean Ocean Water (VSMOW) at the Ice Core Paleoclimatology Laboratory at The Ohio State University using gas-source mass spectrometry. Sample standard deviations were within 0.4‰ and 1‰ for δ¹⁸O and δD respectively.

Stable water isotope abundances are expressed in fractions relative to VSMOW. The abundance is given by:

$$\delta^{18}\text{O} \text{ or } \delta\text{D} = (R_{\text{sample}}/R_{\text{std}} - 1) \times 1000 \quad (1)$$

where R_{sample} and R_{std} is the ratio of ¹⁸O/¹⁶O or ²H/H for the sample and the VSMOW standard respectively.

EC was analyzed from each sample vial that had already been processed for isotopes. Conductivity readings were taken using an Accumet XL200 pH/mV/Conductivity meter with an Accumet 13-620-100 probe.

Anions were analyzed on a Dionex DX-120 ion chromatograph following the methods of Welch et al. (2010). Cations were analyzed on a Thermo Scientific Element2 ICP-MS using an Indium internal standard to account for matrix effects. Accuracy was tested against the NIST Standard Reference Material 1643e (Trace Elements in Water). The relative standard deviations of replicate samples for both anion and cation analysis were better than 5%.

2.4 Hydrograph separation

A dual-member hydrograph separation partitions runoff sampled at a catchment's outlet into two sources: event water representing 'new' rainfall runoff during an event, and pre-event water representing the integrated 'old water' runoff contributions prior to the rainfall event (Sklash & Farvolden, 1979). The two component mixing model using a mass balance approach for a geochemical constituent is given by:

$$Q_T = Q_P + Q_E \quad (2)$$

$$C_T Q_T = C_P Q_P + C_E Q_E \quad (3)$$

where Q is runoff, C is the concentration of the chemical constituent, and the T , P , and E subscripts represent total, pre-event, and event runoff respectively. This study focuses on the event water fraction in a dual component mixing model as the streamflow rises and falls in response to rainfall. The pre-event water fraction is given by:

$$F_P = (C_T - C_E)/(C_P - C_E) \quad (4)$$

The original key assumptions in applying this model have been revised by Moore (1989) and Buttle (1994). This study's use of the dual-member mixing model assumes the following:

1. The chemical concentration or isotopic signature of the event and the pre-event water are significantly different
2. The event water chemical signature is constant in space and can account for variations in time
3. The chemical signature of the pre-event water is constant in space and time
4. Contributions from the vadose zone must be negligible
5. Surface storage contributes minimally to the streamflow

From six storm events we performed dual-member hydrograph separations among the three study catchments using EC, $\delta^{18}\text{O}$ and δD when δD signatures were more than 10 ‰ between baseflow and precipitation samples. Conductivity and isotope event water signatures applied the incremental weighted mean rainfall signature prior to each stream sample time (McDonnell et al., 1990).

2.5 Concentration/discharge plots

Concentration vs. stream discharge plots were used to visualize major ion tracer results from two precipitation events. Major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , and SO_4^{2-} were analyzed alongside δD in the forest and mosaic catchments from the May 23, 2013 event. Only δD is presented since $\delta^{18}\text{O}$ mimics δD C/Q loop behavior.

3. Results and Discussion

3.1 Hydrometeorological conditions

The 2013 dry season began at the end of December, 2012 and ended in early May, 2013. Dry and wet seasons are pronounced (Table 1).

Table 1: Monthly rainfall totals recorded from the mosaic catchment rain gage nest in 2013.

	January	February	March	April	May	June
Monthly Rainfall (mm)	9	54	70	78	403	345

Event durations presented herein ranged between 45 minutes and 4 hours, with maximum 15 minute rainfall accumulations ranging between 7.6 and 24.6 mm. Event magnitudes and the antecedent rainfall leading up to each event are presented in Table 2.

Table 2: Event precipitation characteristics and antecedent precipitation for the six events analyzed for hydrograph separation. Reported antecedent precipitation refers to the mosaic rain gage record.

Event	Event Start (GMT)	48 hr Ant. Precip. (mm)	7 day Ant. Precip. (mm)	30 day Ant. Precip. (mm)	Event Precip. (mm)	Max Intensity (mm/15min)
May 9 Mosaic	2013-05-09 04:00	0.0	9.9	78.2	42.9	13.0
May 16 Mosaic	05/16/2013 20:15	22.1	131.3	236.0	25.1	3.8
May 18 Mosaic	2013-05-18 09:45	42.7	86.9	260.6	72.6	24.6
May 23 Forest	2013-05-23 19:00	7.6	110.5	294.1	50.8	23.4
May 23 Mosaic	2013-05-23 19:15	7.6	110.5	294.1	48.3	7.6
May 29 Forest	2013-05-29 12:45	1.3	87.6	374.7	62.5	16.3

June 11 Mosaic	2013-06-11 20:15	0.0	35.8	298.7	47.8	20.3
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3.2 Isotopic signatures

Rainfall isotope signatures ranged between -126.3‰ to +3.8‰ δD and -15.8‰ to 0.0‰ $\delta^{18}O$ (VSMOW) (n = 136). Stream signatures ranged between -62.3‰ to -21.5‰ δD and -8.9‰ to -3.5‰ $\delta^{18}O$ (n=157). Lysimeter signatures ranged between -69.7‰ to -10.5‰ δD and -9.6‰ to -2.0‰ $\delta^{18}O$ (n = 40). Shallow piezometer signatures ranged between -33.2‰ to -23.5‰ and -5.8‰ to -4.2‰ $\delta^{18}O$ (n = 25). The local meteoric water line (LMWL) from the study period refers to mosaic and forest catchment precipitation samples, and is similar to the global meteoric water line (GMWL) (Craig, 1961). No stream, groundwater, or soil water samples indicate a pronounced enrichment or deviation away from the LMWL (Figure 2) relative to variability in the precipitation signatures. This suggests that evaporative fractionation impacting stable water isotope signatures during the initial wet season period is unlikely.

Figure 2: Sample points from the 2013 campaign plotted against the local meteoric water line (LMWL) and global meteoric water line (GMWL). The LMWL is given by the equation $\delta D = 9.1\delta^{18}O + 8.3$ while the GMWL is $\delta D = 8\delta^{18}O + 10$. All points fall within the natural variability exhibited by rainfall at the forest and mosaic collection locations.

3.3 Hydrograph separation and tracer comparison

From sixteen geochemically-sampled events between May 9, 2013 and June 19, 2013, six events had an adequately distinct isotopic signature for comparison against EC. We generally present storm events with low temporal precipitation variability (Table 3). Typical event precipitation exhibited increasingly depleted isotopic signatures as each storm progressed. EC was highest at the start of each event

followed by increasingly dilute precipitation, which we attribute to aerosol fallout and/or dry deposition flushing in the rainfall sampler funnel as precipitation commenced. Spatial variability in precipitation amounts and chemical signature is possible, particularly for the smaller events. We assume that the sequential rainfall collection within each catchment best represents the event signature across the entire respective catchment.

Table 3: Event summary of baseflow collection and event characteristics between δD and $\delta^{18}O$ and EC tracers.

Event:	May 9 Mosaic	May 9 Pasture	May 16 Pasture	May 18 Mosaic	May 23 Forest	May 23 Mosaic	May 29 Forest	June 11 Mosaic	June 11 Pasture
Baseflow Collection Time (GMT)	May 2, 2013 14:00	May 3, 2013 18:45	May 15, 2013 16:35	May 17, 2013 15:55	May 21, 2013 18:00	May 22, 2013 17:30	May 28, 2013 17:25	June 9, 2013 20:30	June 9, 2013 23:00
Baseflow δD (‰)	-27	-28.9	-29.5	-24.6	-28.9	-30.4	-28.6	-32.4	-32.4
Baseflow $\delta^{18}O$ (‰)	-4.7	-4.6	-4.7	-4.3	-5.2	-5.2	-4.8	-5.3	-5.0
Baseflow EC ($\mu S/cm$)	134.0	101.5	92	105.4	142.0	101.0	141.0	134.6	83.0
Weighted Average Rainfall δD (‰)	-45.4	-45.4	-6.1	-52.9	-101.0	-105.1	-39.7	-17.6	-17.6
Weighted Average Rainfall $\delta^{18}O$ (‰)	-7.3	-7.3	-1.9	-7.8	-13.7	-14	-5.9	-3.8	-3.8
Weighted Average Rainfall EC ($\mu S/cm$)	11.4	11.4	26.4	4.9	13.3	12.2	17.7	6.1	6.1
Rainfall Weighted Std Dev δD (‰)	13.7	13.7	7.3	15.2	1.9	15.6	11.7	2.7	2.7
Rainfall Weighted Std Dev $\delta^{18}O$ (‰)	1.6	1.6	0.8	1.8	0.2	1.8	1.5	0.4	0.4
Rainfall Weighted Std Dev EC ($\mu S/cm$)	10.1	10.1	8.6	5.6	1.3	5.9	3.3	2.0	2.0

Figure 3:

2013 wet-season onset hydrograph separation results using EC, δD , and $\delta^{18}O$ as tracers across the forest, mixed land use ‘mosaic’, and pasture catchments.

As dual component hydrograph separation tracers, δD and $\delta^{18}O$ sometimes yielded mixed results (Figure 3). Low δD estimated event-water fractions are indicated at the first sample point in each pasture event (Figure 3). These first sample points’ event water fractions show physically impossible negative values during both the June 9 and June 11 events, highlighting a shortcoming when using the dual component hydrograph separation model. Both pasture events have relatively narrow differences between baseflow signatures and mean rainfall signatures: 16.8‰ δD 2.7‰ $\delta^{18}O$ on May 9 and 14.8‰ δD 1.2‰ $\delta^{18}O$ on June 11. Analytical instrument error inherent in cavity ring-down spectrometry may

explain these anomalies, with particular susceptibility to negative event water fractions at the first stream runoff sample point when isotopic signatures are close to baseflow. In contrast, the May 23 event presents the greatest confidence in hydrograph separation when the mean pre-event and event water δD and $\delta^{18}O$ signatures differ by more than 70‰ and 8.5‰ respectively (Table 3).

EC is generally a good surrogate for stable water isotopes tracers in small, early wet season events. Most samples collected during the stream response on May 9 show that conductivity falls within the event fraction range estimated by the stable isotopes and may thus serve as a more robust hydrograph separation tracer when event and pre-event baseflow isotopic signatures lack a strong distinction. The difference between δD and EC exhibit good agreement within a $\pm 8\%$ range during the May 29 forest event and within $+4$ to -13% for the June 11 mosaic and pasture events. The May 18 event water fraction estimates between EC and stable water isotopes are discussed in Section 3.7. During the May 23 and June 11 events, conductivity and stable water isotopes exhibit better agreement on the hydrograph rise than the hydrograph recession when dilute stream EC values overestimate the event fraction relative to δD and $\delta^{18}O$.

Hydrograph separation modeled using δD and $\delta^{18}O$ exhibited varying event water contributions across the six storms. As streamflow rose, runoff event fraction increased through the hydrograph peak in all streams (Figure 3). A delay in event fraction peak relative to the hydrograph peak is unequivocally apparent with stable water isotope and conductivity tracers in the May 23 mosaic, May 29 forest, and June 11 pasture catchments' events. If event water wasn't well mixed after infiltrating across the catchment, progressive isotopic depletion throughout the event duration could have caused a delayed maximum event water fraction. However this is unlikely as a post-peak maximum event fraction was also exhibited in the June 11 event when the precipitation isotopic signature was more enriched relative to the baseflow signature. As the June 11 event progressed, the rainfall signature weakly became more similar to the pre-event signature, thus potentially under-predicting the event fractions at later stream sample times. A lagged maximum event fraction may rather be indicative of catchment runoff processes.

The lagged maximum event fraction suggests that event water continues to travel through the catchment after precipitation has ceased and streamflow recedes. A lag in event fraction maximum has been attributed to event water storage that is slowly released as the hydrograph recedes. Bonell et al. (1990) observe a delayed event fraction in a New Zealand grassland catchment with extensive wetlands in valley bottoms. They attributed the lag to surface storage in wetlands. Such a storage mechanism is not possible in the Agua Salud Project catchments as catchments are steep and wetlands are nonexistent. Event water surface storage could take other forms, potentially through a delayed release from the soil matrix, matrix bypass to groundwater via macropores, or headwater riparian zones. Further research monitoring headwater runoff generation, stream-riparian zone interactions, and soil/macropore water fluxes shortly following an event may enhance understanding of this behavior.

Table 4: Physical runoff (RO) characteristics and interpretation using 2013 δD , $\delta^{18}O$, and EC tracer results corresponding to Figure 3. The tracer-sampled runoff percentage is the percent of the total storm runoff peak that may be accounted for using tracer results since sampling didn't always cover entire hydrographs. From each hydrograph's tracer-sampled runoff portions, the volumetric runoff event fraction is the total event water fraction throughout the tracer sampling period. *Considerable precipitation variability characterized the May 29, 2013 storm, with 18.3mm precipitation reported at the mosaic rain gage nest.

	May 9 Mosaic	May 9 Pasture	May 16 Pasture	May 18 Mosaic	May 23 Forest	May 23 Mosaic	May 29 Forest*	June 11 Mosaic	June 11 Pasture
Runoff Ratio (mm runoff/ mm precip.) (%)	4.1	3.1	7.0	21.8	4.7	14.4	3.0*	11.2	14.3
Gaged Rainfall (mm)	43	43	25	73	51	48	62*	48	48
Peak rainfall intensity (mm/15min)	13	13	5.6	24.6	23.4	7.6	16.3*	20.3	20.3
Tracer- Sampled Runoff (%)	59	53	65	79	49	46	94	87	44
Volumetric RO Event Fraction δD	0.26	-0.05	0.16	0.33	0.40	0.34	0.45	0.37	0.17
Volumetric RO Event Fraction $\delta^{18}O$	0.16	0.17	0.20	0.32	0.36	0.28	0.30	0.33	0.30
Volumetric RO Event Fraction EC	0.22	0.13	0.12	0.62	0.52	0.46	0.41	0.44	0.25

3.4 Major ions and δD as flowpath tracers using C/Q plots on May 23, 2013

The May 23 event fortuitously presented an opportunity to compare major ion tracers to a very strong isotopic signature contrast between event water and pre-event water in the mosaic and forest catchments (Table 3). Major ions often exhibit a cyclical relationship between concentration and stream discharge on the event basis. Hysteretic loops throughout a hydrograph's rise and fall may be used to qualitatively describe variations (or lack thereof) in runoff sources throughout the event (Evans and Davies, 1998). Concentration/discharge plots for δD , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} are presented in Figure 4 between the forest and mosaic catchments for the May 23, 2013 event. During this event, Ca^{2+} , Mg^{2+} , Na^{2+} and Cl^- baseflow concentrations are diluted with relatively low concentration event water, SO_4^{2-} baseflow concentration increases, and K^+ changes little (Table 5 and Figure 4).

Figure 4: May 23, 2013 event recording roughly 50mm of precipitation, highlighting contrasting hysteresis between forest and mosaic catchments. This event's $\delta^{18}\text{O}$ results are omitted since they agree strongly with δD . Additional late-recession sample points presented in this figure are not included in Figure 3 or its corresponding Table 4.

Table 5: Major ion summary of baseflow leading up to the May 23, 2013 event when throughfall was sampled.

Sample	Collection Date	Mg ²⁺ (ppm)	Ca ²⁺ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	Cl ⁻ (ppm)	SO ₄ ²⁻ (ppm)
Forest baseflow	2013-May-21	4.6	7.1	5.5	1.1	4.2	1.6
Mosaic baseflow	2013-May-22	6.5	10.7	6.8	1.2	5.6	1.7
Throughfall (mean)	2013-May-23	0.4	1.5	1.1	4.3	2.6	1.5

Major ion baseflow concentrations collected prior to the May 23, 2013 event and mean throughfall concentrations during the May 23, 2013 are presented in Table 5. Major ion baseflow concentrations in the forest are slightly more dilute than in the mosaic catchment, potentially as a result of less water

more dilute than the mean K^+ measured in throughfall. In both forest and mosaic streams, hysteresis or lack thereof is similar for each element.

Deuterium, Mg^{2+} , Ca^{2+} , and Na^+ exhibited clockwise hysteresis on May 23 (Figure 4). These clockwise loops most resemble the C3 type as described by Evans and Davies (1998). Clockwise hysteresis is expected for elements primarily derived from bedrock. In a two or three component system, a C3 loop is dominated by pre-event water, which agrees with the dual component hydrograph separations (Figure 3). This suggests that a third component (e.g. soil water) would be the least dominant contributor to runoff during this event. Mg^{2+} , Ca^{2+} , and Na^+ concentrations are lowest at sample points during the early stream recession. This behavior agrees with observed maximum event water fractions during the early stream recession (Figure 3), and implies event water becomes a relatively greater runoff contributor during the recession.

Potassium, Cl^- , and SO_4^{2-} each behaved differently from δD , Mg^{2+} , Ca^{2+} , and Na^+ (Figure 4). Potassium exhibited chemostatic behavior throughout the hydrograph's rise and fall across both catchments. Relatively high K^+ concentration throughfall samples range from 1.7 to 5.5 ppm with a mean of 4.3 ppm (Table 5), thus making K^+ the only ion whose event concentration is greater than the pre-event concentration. Non-conservative behavior with K^+ is expected owing to its biological importance as a nutrient. Potassium has been used as an indicator of overland and macropore flow in tropical soils when passing through leaf litter (Elsenbeer et al., 1995), but our results as an overland flow tracer are inconclusive. Chloride diluted with increasing discharge, while showing little to no hysteresis between the hydrograph rise and fall. Non-hysteretic behavior suggests that Cl^- is derived from multiple runoff sources with little distinction in end-member concentrations. Sulfate hysteretic loops moved in anticlockwise fashion. Considering how SO_4^{2-} is less present in the basalt and basalt-derived saprolites underlying Agua Salud catchments, SO_4^{2-} may have mixed with event water from near-surface sources. This is supported by SO_4^{2-} anticlockwise hysteresis contrasting bedrock-derived Mg^{2+} , Ca^{2+} , and Na^+ clockwise hysteresis.

No pronounced bedrock-derived solute flushing effects characterize the hydrograph rise in the Agua Salud catchments, while recessions are occasionally more dilute. Unobserved solute flushing contrasts the marked increase in EC and Cl^- during the rising limb observed by Sklash et al. (1986) in the Mai Mai, New Zealand catchment. When taken into the context of hydrograph separation, bedrock derived Ca^{2+} , Mg^{2+} , and Na^+ tracers during the May 23 event are more dilute during the receding limb, suggesting lesser pre-event water fractions following peak runoff (Figure 4). Laudon and Slaymaker (1997) suggest that pre-event component underestimation may be the result of failure in pre-event water to reach steady state equilibrium concentrations prior to the hydrological event. Considering the relatively low rainfall inputs prior to the May 23 event (Table 2), non-equilibrium reactions are unlikely in these highly weathered settings. Pre-event source underestimation could also be attributed to storm-flow soil zone flushing, where a decline in solute concentration during the hydrograph recession is attributed to soil water being flushed out and more dilute water contributing to storm recession runoff (Scanlon et al., 2001). We think a similar mechanism to Scanlon et al. (2001) likely occurs in Agua Salud catchments, where some storm event water flushes to groundwater via soil and/or preferential flowpaths, ultimately reaching streamflow during the post-storm recession.

Flowpath interpretation from hydrochemical results suggest similar mechanisms across the forest and mosaic catchments. Agreeing hysteretic loop directions between δD , Mg^{2+} , Ca^{2+} , and Na^+ in both catchments suggests similar storm runoff sourcing, where near-surface event water becomes relatively more dominant during the hydrograph recession. In the humid tropical northeast Australia Babinda study catchments, Bonell et al. (1998) credit a slow recovery to pre-event baseflow concentrations

during the late hydrograph recession to event water percolation to a slowly-draining permanent water table. Quick runoff responses in the Agua Salud streams have been attributed to macropore flow (e.g. Ogden et al., 2013), however, this does not mean near-surface water is a small contributor to runoff during the hydrograph rise. The rapid transport of water through preferential flowpaths could be displaced pre-event water from an infiltrating event water pulse (McDonnell, 1990). We confirmed pre-event water displacement in macropores during a 33mm storm peaking at 20.8mm rainfall within a 15 minute period in the subsequent field season on June 24, 2014. An isotopically sampled macropore flowing into an ephemeral, storm-activated headcut near the forest catchment within 30 minutes from rainfall cessation indicated -18.0 δD and -3.5 $\delta^{18}O$ signatures, while precipitation sampled at the forest rain gage station ranged between -34.4 and -49 δD and -5.7 and -7.4 $\delta^{18}O$. The activated macropore flow in the typically dry headcut provides convincing evidence of perched, near surface water tables driving runoff via macropores that aren't strictly conduits for event water.

3.5 Catchment wet-up and event fraction response

As the study catchments wet-up during the 2013 sampling period, runoff efficiencies generally increase within each respective catchment (Table 4). This is best observed between the May 9 (drier condition) and June 11 (wetter condition) events whose similar event magnitudes, rainfall intensities, and 7-day antecedent precipitation result in widely different runoff ratios (Table 2). Runoff ratios in the mosaic catchment change from 0.041 to 0.112 while the pasture catchment changes from 0.031 to 0.143 between the May 9 and June 11 events. (Table 4). These differing hydrometric results imply that a runoff threshold in these catchments was surpassed as the early rain season progressed to June 11. Potential explanations for increased runoff efficiencies include lower soil moisture storage deficits, macropore activation, and/or increasing coverage of variable source areas in the catchment.

A hydrochemical comparison between the mosaic and pasture sites during the early wet season May 9 and June 11 events also presents interesting differences in runoff event fractions. The mosaic catchment's EC, δD , and $\delta^{18}O$ volumetric runoff event fractions range from 0.16 to 0.26 on May 9, while volumetric runoff event fractions jumps to between 0.33 to 0.44 on the June 11 event (Table 4). Similarly, pasture EC, δD , and $\delta^{18}O$ volumetric runoff event fractions range between -0.05 and 0.17 on May 9, and 0.17 to 0.30 on June 11. The -0.05 event runoff fraction from the δD tracer on May 9 in the pasture is a physically impossible negative quantity for event water runoff volume, but is likely attributed to relatively narrow differences between δD and $\delta^{18}O$ event water and pre-event water isotope signatures, indicating that these are not appropriate tracers for this event. The more robust tracer for the May 9 event is likely EC, which falls between the range given by δD and $\delta^{18}O$ (Figure 3). The May 16 pasture event lent itself to better isotopic hydrograph separation certainty due to a larger contrast in baseflow and event water signatures (Table 3). The May 16 pasture runoff ratio is intermediate relative to May 9 and June 11, but this may be attributed to an earlier 17mm event wetting the pasture that ended 12 hours before the 25mm May 16 event start at the mosaic rain gages. Similar to the May 9 pasture event, the May 16 pasture event also exhibits lower event water volumes relative to June 11, with conductivity and δD and $\delta^{18}O$ tracer hydrograph separation results yielding between 0.12 and 0.20 volumetric runoff event fractions, however meaningful interpretation may be confounded by lower event magnitudes and rainfall intensities (Table 4). Rainfall intensity or a transition in catchment wetness states are two potential mechanisms for the event fraction differences between the early wet season May 9 event and the maturing wet season June 11 event.

Most isotope hydrograph separation studies show greater event water fractions with increasing catchment dryness (Klaus & McDonnell, 2013). A seasonal wet up event fraction transition is reported by Muñoz-Villers and McDonnell (2012) in a tropical montane cloud forest catchment in Veracruz, Mexico. They find that with increasing wetness stages, stream runoff shifts from a high event fraction

to a pre-event fraction dominance. Muñoz-Villers and McDonnell (2012) attribute a shift to greater pre-event fractions throughout the rain season onset to the highly permeable volcanic soils promoting vertical groundwater percolation to recharge groundwater. They suggest hydrophobicity on the soil surface developed throughout the dry season could potentially cause the initially higher event water fractions in storm runoff. Our observations do not indicate decreasing event water fractions under wetter, suggesting different runoff mechanisms than the Veracruz, Mexico catchments. A few studies have shown increasing event fractions with catchment wetness (e.g. Cey et al., 1998; Ocampo et al., 2006). Wetter conditions promoting saturation excess for higher event water fractions is a mechanism proposed by Ocampo et al. (2006). Furthermore, intensive studies at the Babinda study catchments in humid tropical northeast Queensland show that under wet antecedent conditions and monsoon rainfalls, stream hydrographs are dominated by event water (Bonell et al., 1998).

Increasing event-water fractions under wetter conditions are also a reasonable explanation for the behavior observed in the Agua Salud Project catchments. Lower runoff event water contributions under the drier antecedent catchment state on May 9 and May 16 in the mosaic and pasture sites (Table 4) suggest near-surface runoff flowpaths such as rapid shallow lateral flow may be subdued as the wet season begins owing to a high soil moisture deficiency. As antecedent moisture increases, the catchments become primed for promoting near surface, transient saturation-induced macropore activation.

3.6 Land cover

Land cover strongly influences hydrometric results, including differences in runoff ratios throughout the study period. Runoff ratios are lowest in the forest and highest in the pasture (Table 4). This behavior also agrees with runoff and precipitation results from the forest, mosaic, and pasture catchments between 2009 and 2012 (Ogden et al., 2013). Canopy interception losses can only partially explain the lower runoff ratios in the forest, with throughfall and stemflow likely totaling 84% in the forest (Niedzialek and Ogden, 2012) and between 84% and 100% in the mosaic and pasture catchments (Ogden et al. 2013).

Hydrograph separation results between land covers across the study period are less conclusive than the hydrometric results. Hydrograph separations in the highly disturbed pasture appear to report lower event water fractions than observed in the mosaic and forest catchments. Similar behavior has been reported during a large event between a disturbed and an undisturbed tropical rainforest catchment in northeast Queensland (Bonell et al., 1998). However the pasture's relatively small catchment size is a potential confounding factor on interpreting event water contributions relative to the mosaic and forest catchments. Many studies examining hydrograph separation results and catchment size yield equivocal or contradictory results (Klaus and McDonnell, 2013).

The May 23, 2013 event presents one of the more reliable hydrochemical comparisons between the mosaic and forest land covers due to the strong, spatially consistent precipitation isotope signals, similar precipitation amounts (50 mm), and reasonable tracer sampling intervals during the hydrograph peak. The slight difference in the volumetric event-water runoff fraction between forest and mosaic catchments (Table 4) may be attributable to the pasture catchment nested in the mosaic, which consistently reported lower volumetric event-water fractions throughout the study period. It is interesting to note that May 23 mosaic runoff magnitude was roughly three times larger than the forest, yet δD and $\delta^{18}O$ event water fractions did not show large contrasts (Table 4). Both catchments also exhibited similar hysteresis loops during the May 23 event (Figure 4). The delay in returning to pre-event solute concentrations in both the mosaic and forest adds further evidence that event water

delivery can be lagged through slower flowpaths, perhaps from storm-wetted soils and/or activated macropores draining into groundwater contributing to streamflow.

The hydrometric data indicate that the forest promotes greater infiltration and storage while hydrochemical clues suggest the processes driving runoff and its partitioning between pre-event and event water may be similar across the forest and mosaic catchments. Aerial photography analysis in 2012 indicated that the mosaic consists of 51% forest older than 15 years, 30% forest younger than 15 years, and 19% active cattle pasture (Ogden, et al. 2013). Near-surface tree rooting and biological activity in the mosaic catchment's forested areas may explain the general similarities in volumetric runoff event water fractions as observed in the forest catchment. Although hydrometric differences are strong, the hydrochemical similarities between the forest and mosaic catchments may serve as an indicator of the mosaic's recovery from intensive agriculture and grazing runoff controls towards forested runoff behavior.

3.7 Conductivity and isotope tracer disagreement

The May 18 conductivity tracer presents a stark event water contribution overestimation relative to δD and $\delta^{18}O$ event fractions. Such a strong disagreement is not apparent among the other events analyzed. Event magnitude is the most notable distinction of the May 18 event relative to the other precipitation events. The mosaic rain gage station recorded 72.6 mm during the May 18 event. By May 18, antecedent moisture conditions had increased considerably since the May 9 event (Table 2), which is a likely factor causing the peak runoff rate to be over an order of magnitude larger than peak runoff on May 9. In the Agua Salud catchments, a greater runoff ratio coupled with a larger event magnitude is consistent with findings by Ogden et al. (2013). A greater runoff ratio may be indicative of a hydraulic storage threshold that was surpassed, although δD and $\delta^{18}O$ volumetric event water runoff estimations at 0.33 and 0.32 are not particularly different from other observed event water volume fractions (Table 4).

A potential confounding factor is the within-event progressive stable isotope depletion ranging widely from -28.4 to -74.3 ‰ δD . The mosaic rain gage nest recorded 65 mm of precipitation from the 75 mm total by the time the first automated sample collection began at the mosaic weir. The event water travel time needed to reach the stream sample location at the mosaic catchment's weir would mean that not all 65 mm of rainfall had reached the stream sample locations. However even after the rainfall ceases and the event waters have presumably mixed, there is still a large disparity EC, δD , and $\delta^{18}O$ event water fraction estimations.

Another possible explanation for the May 18 tracer disagreement is non-conservative conductivity behavior during larger events. If pre-event water signature becomes more dilute across the course of an event, the event fraction would be overestimated. The mosaic rain gage recorded two events on May 16 measuring 17.8 and 24.6 mm. These events could have caused a spatially variable pre-event storage of dilute water sources that became connected and/or mobilized as the catchment responded to the large event. The May 23 and June 11 events also potentially exhibited a pre-event water dilution effect to a lesser degree during the hydrograph recessions after rainfall ceased (Figure 3).

The validity of the May 18 event's dual member hydrograph separation is suspect for potentially violating three critical assumptions: (i) the conductivity tracer may not be conservative for larger events and/or wetter antecedent conditions (ii) the pre-event water may be variable across space, and/or (iii) the vadose zone may have served as a third runoff source component. Considering how these assumptions appear reasonable for most of the other events we present herein when using isotope tracers, this behavior calls for further investigation on the potential for a different runoff mechanism.

Hoeg et al. (2000) suggest tracer discrepancies arise from spatial variability in reservoirs that only become activated during certain moisture contents in southern Black Forest, Germany. The heterogeneity in land cover across the mosaic catchment may lend itself to spatially variable solute concentrations if flowpaths are influenced by land cover. Whether this is a land cover response is uncertain, but new flowpath sources could have become activated.

Soil suction lysimeter data support the possibility that a hydrologic threshold had been reached on May 18. A third source from the soil could have potentially become activated and mixed with event water on May 18. Two lysimeters samples were collected on May 17th in the pasture site. A 50cm deep hilltop sample gave -52.3 ‰ δD and a 14.7 $\mu S/cm$ conductivity. At a mid-slope swale, a 100cm deep lysimeter collection was characterized by -25.8 ‰ δD and 9.8 $\mu S/cm$ signatures. Thus, the 100cm mid -slope swale lysimeter sample is a potential candidate as a third water source that is consistent with stream runoff observations on May 18. However, May 18 C/Q loops between δD , $\delta^{18}O$, and EC each behave similarly to the clockwise loops on May 23, 2013 (Figure 4) where a third source (e.g. soil water) is negligible or less significant than groundwater and event water sources.

3.8 Limitations and applications to the dual component hydrograph separation

Hydrograph separation serves to constrain event-based geochemical mass balances if a constituent's concentration is constant and distinct between sources. The variability in EC behavior relative to stable water isotopes across the study period suggests occasional non-conservative behavior or additional runoff source activation during the progression of event-based hydrologic catchment response. Identifying when tracers like EC behave conservatively could thus justify performing three-component hydrograph separations assuming the third source could be sufficiently characterized.

The varied hydrograph separation results presented in this study highlight the limitations to this dual member technique. By applying multiple naturally-occurring tracers we show that not all tracers behave similarly at all times, potentially due to differences with antecedent catchment conditions, event behavior, and runoff threshold activation. When tracers do agree, the inherent assumptions for a dual component hydrograph separation model are more likely to have been met, and greater confidence may be assigned to these events for further analysis of flow components. The hydrograph separation technique can also assist in identifying subsurface weathering zones via flowpath inference. As exhibited in this study, maximum event water fractions following the hydrograph peak suggest event water delivery to the stream isn't limited to activated lateral flowpaths. Further study should better characterize runoff thresholds by addressing potential within-event pre-event signature variations across soil, groundwater, and headwater areas as the catchment undergoes a dry to wet transition.

4. Conclusions

This event-based study in the small, steep tropical catchments within the Panama Canal Watershed shows that as the wet season progresses, runoff event fractions become more dominant than when the seasonal rains began. These results suggest that near-surface preferential flowpaths and/or shallow, perched lateral flowpaths activated in these oxisol soils approaching saturation are potential mechanisms for the observed event water runoff contributions. EC is a good surrogate for stable water isotope tracers during the hydrograph rise for smaller runoff events, however variable groundwater solute concentrations between contributing pre-event water sources may confound conductivity tracer hydrograph separations during some larger runoff events. EC over-predicted event fractions during a larger 72 mm event in the mosaic catchment. This may represent surpassing of a hydrological threshold by activating a third dilute source such as soil water. Clockwise hysteresis with Ca^{2+} , Mg^{2+} , and Na^{+} and SO_4^{2-} anticlockwise hysteresis further evidence a delayed event water flowpath after peak runoff, potentially as storm wetted soils and macropores drain into groundwater supplying stream recession

runoff. Runoff ratios are lowest in the forest, intermediate in the mosaic, and highest in the pasture, whereas hydrograph separation-estimated event fractions do not reveal strong differences between the paired mosaic and forest catchments. Similarities in hydrograph separation results and major ion hysteresis between mosaic and forest catchments imply similar runoff source water partitioning as the mosaic undergoes recovery towards forested runoff behavior.

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