Stream discharge is a key water balance component and important factor in global change evaluations. Nevertheless, the mechanisms for streamflow generation are poorly understood. Near-stream surface saturation during precipitation events is one of the most iconic, visible indicators of rapid runoff production in upland humid catchments around the world. Despite years of study, we lack understanding of what occurs within the near-stream saturated area, its mixing dynamics and how this affects catchment geochemical- and flow-response dynamics during events. This thesis explores the mechanisms that control near-stream saturated area behavior in a headwater catchment.

First, I explore the relation between catchment geochemical response and the flow duration curve (FDC) for the 46-ha Weierbach catchment in Luxembourg across 10 years of runoff monitoring. The shape of the Weierbach FDC suggested a two-phase system, a high-flow, precipitation-driven period and a dry, evapotranspiration-driven, low-flow period. I hypothesized that the two phases were correlated with activation of shallow hillslope and subsurface streamflow sources and that the activation of these sources would be reflected in stream chemistry and surface saturation dynamics. During high-flow periods of the FDC, stream geochemistry was largely unchanging, lacking a dilution effect and appeared a mix of the highly variable soil and groundwater. Thermal infrared (TIR) imagery suggested large surface saturation dynamics at high flows. The geochemical
signature of streamflow and soil riparian water during low-flow periods most closely resembled groundwater chemistry and led to increasing base cation concentrations and electrical conductivity.

Secondly, to better understand the effect of rain falling on saturated areas and the contribution of rainfall to saturation excess overland flow, I quantified surface saturation dynamics in a near-stream area during rainfall events using high-frequency TIR imagery. During 10 rainfall events across a 34-day period starting December 2013, a total of 161 mm of rainfall elicited 133 mm of runoff at the 6-ha outlet. Surface saturation within a 25-m² thermal infrared imaged area increased from 2 to 20% but was highly variable and weakly correlated to discharge and precipitation. Rainfall onto mapped, near-stream saturated areas accounted for little of the flow generated within a headwater reach. Streamflow isotopic composition at the 6-ha, headwater outlet deflected little throughout the 30-day rainfall period, 0.7 and 1.2 ‰ for δ¹⁸O and δ²H, respectively. Groundwater exfiltration within the saturated area generated nearly all of the streamflow as well the persistent saturation throughout the event.

Thirdly, I examined the underlying controls on streamwater chemostasis in a forested, headwater catchment. Thermal infrared imagery was simultaneously used to quantify saturation expansion and groundwater exfiltration hotspots within the headwater reach. Streamflow during a series of rainfall events responded chemostatically, most measured geochemical species (Ca²⁺, Mg²⁺, Na⁺, SiO₂, Cl⁻, SO₄²⁻ and NO₃⁻) varied little (< 0.5 mg/L), despite discharge increases from 0.2 to 4 L/s. Groundwater levels within the saturated zone increased after an initial 24 mm of event rainfall and remained within 0.05 m of the soil surface throughout the runoff period. TIR imagery identified consistent groundwater exfiltration zones from temperature differences across the event-period in the saturated zone. This suggested that unlike many headwater systems, the alluvial aquifer was well connected to groundwater outside the riparian zone and the mapped seepage area was a focused discharge point for the catchment-scale groundwater flow system.

Overall this work suggests that for this catchment, groundwater exfiltration in the near-stream zone strongly controls stream geochemical response as well as the timing, duration and quantity of streamflow generation.
The role of near-stream zones on flow, chemistry and isotopic composition at the headwater scale.

by

Jay Frentress

A DISSERTATION

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Approved:

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Director of the Water Resources Graduate Program

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Dean of the Graduate School

I understand that my dissertation will become a part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Jay Frentress, Author
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Near-stream surface saturation during precipitation events is one of the most iconic, visible indicators of rapid runoff production in upland humid catchments. The importance of such areas for generating rapid runoff has been demonstrated in countless studies, beginning with the pioneering work of Dunne and Black (1970a, 1970b), the saturated mapping work of Dunne et al. (1975) and Taylor (1982) as well as more recent incorporation of saturated area mapping into field-modeling synthesis (Birkel et al., 2009). Saturation excess overland flow (SEOF) as a formal runoff mechanism is comprised of rain falling onto saturated areas and ‘return flow’, defined as emergence of subsurface stormflow originating from upslope sources (as originally defined by Hewlett and Hibbert, 1967; McDaniel et al., 2008) and the near-stream exfiltrating groundwater (described first by Hursh and Brater, 1941). While some work has quantified exfiltration gradients in the near-stream saturated zone (Abdul and Gillham, 1989; McGlynn et al., 1999), most work has assumed that the volumetric contribution of rain falling onto saturated areas far exceeds this ‘return flow’ component. Some studies (McGlynn and McDonnell, 2003; Dahlke et al., 2012) have shown that the groundwater contribution to streamflow remains constant throughout events, where hillslope inputs increased to provide the bulk of storm runoff. Others have found that elevated groundwater levels in the near-stream zone induce hillslope connectivity and lead to surface saturation and resulting overland flow (Taylor et al., 2002; Lyon et al., 2006; McDaniel et al., 2008; Jencso et al., 2009; Harpold et al., 2010). Indeed, disentangling groundwater and hillslope water from rain falling onto saturated areas is difficult with current methodology.

But, near-stream saturated areas are often patchy internally and highly irregular along their margins and spatial extent. Within-saturated area dynamics are rarely considered. Rather, characterizing simply the areal extent of saturated areas has been the focus of field-mapping (Dunne et al., 1975; Latron and Gallart, 2007; Birkel et al., 2009; Rinderer et al., 2012), aerial photograph analysis (Wigington et al., 2005), field surveys of vegetation and soil type (Kulasova et al., 2014), surface flow detector deployments (Srinivasan et al., 2000; Needelman et al., 2004; Srinivasan and McDowell, 2009) and GPS-field surveys at larger spatial scales (Godsey and Kirchner, 2014). This areal extent of saturation has been incorporated into hydrograph separation models (Dewalle et al., 1988) of event and pre-event partitioning of the storm hydrograph.
Despite years of study, we lack understanding of what occurs within the near-stream saturated area, its mixing dynamics and how this affects catchment geochemical- and flow-response dynamics during events. Because of technological limitations, we lack detailed knowledge of temporal dynamics of surface saturation extent throughout events and how this may be related to within-saturated area mixing of rainfall and return flow.

This thesis mechanistically assesses near-stream saturated area behavior in a headwater catchment by isolating a stream reach with weirs placed upstream and downstream to quantify inputs from the near stream zone to the stream. I make detailed process observations within the saturated zone using thermal infrared imaging of the saturated area, groundwater measurements as well as geochemical and isotopic tracing to ask the overarching question:

*What internal mechanisms drive near-stream saturated area dynamics and how does this express itself in flow and chemistry at the catchment outlet?*

This thesis consists of three manuscripts that assess the importance of surface saturation in the near-stream zone on streamflow and solute dynamics. I use a nested catchment approach, interrogating sources of runoff across multiple scales to shed light on linkages between plot-scale hydrologic process and catchment-scale runoff dynamics. I begin with a top-down approach in Chapter 1 and then shift to more bottom-up (reductionist) approaches in Chapters 2 and 3. My goal is not a method for upscaling observations though, but an attempt to better understand how streamflow source and streamflow chemistry are affected via mixing within the riparian area.

*Thesis outline*

In Chapter 1, I assess stream and solute response within the 0.46-km² Weierbach study catchment based on multiple years of chemistry and flow data. I query these data in search of threshold-like response patterns of geochemistry in relation to streamflow and groundwater dynamics. I also compare flow and solute concentrations to saturation dynamics at an event-scale. This chapter shows the dynamic surface saturation response at the event-scale and provides evidence from inter-annual comparison of flow and geochemistry that chemostatic responses (where discharge varies by order of magnitude but stream chemical dynamics vary less than one order of magnitude) dominate under wet conditions.
In Chapter 2, I focus on time periods when surface saturation dynamics, solute and water flux are the greatest, during wet, winter conditions. I use thermal infrared imagery to quantify surface saturation at a high-frequency throughout a series of rainfall events and compare these dynamics to streamflow isotopic composition. This chapter shows that despite increases in surface saturation, the direct contribution of rain to the stream hydrograph is minimal. Moreover, streamflow isotopic composition is exceptionally well-mixed, suggesting large groundwater sources during events. Discharge and groundwater levels within the catchment and near-stream saturated zone both respond in a threshold-like manner to rainfall.

Chapter 3 builds on the results of Chapter 2 and assesses the role of groundwater behavior on geochemical export. I compare geochemical composition of streamflow, rainfall, groundwater, soil solution and overland flow within the saturated riparian zone to understand streamflow sources and composition. This chapter shows very little difference between the geochemical composition of riparian endmembers or streamflow. With so little event water present in streamflow, groundwater dominates the chemistry within the near-stream zone and outlet. This chapter provides insights into subsurface controls, gained by electrical resistivity tomography, riparian water table monitoring and riparian groundwater temperature mapping that reveal the causes of the catchment chemostatic behavior observed in Chapter 1. Large groundwater storage within the fractured schist layers underlying the catchment facilitate long flowpaths and transit times that lead to well-mixed, low-variability geochemical composition that emerges within near-stream zone and controls streamflow geochemistry.
References


Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. Forest hydrology: 275–290


Chapter 2 Unraveling hydrological controls on stream water chemistry in a headwater catchment

Abstract

The links between a catchment’s flow duration curve (FDC) and its geochemical response are poorly understood. Here we explore the relation between catchment geochemical response and the FDC for the 46-ha Weierbach catchment across 10 years of runoff monitoring. The shape of the Weierbach FDC suggested a two-phase system, a high-flow, precipitation-driven period and a dry, evapotranspiration-driven, low-flow period. We hypothesized that the two phases were correlated with activation of shallow hillslope and subsurface streamflow sources and that the activation of these sources would be reflected in stream chemistry and surface saturation dynamics. We projected discharge into the probability domain of the FDC and tested this hypothesis by examining the catchment geochemical response. Near-stream surface saturation dynamics for a series of runoff events were determined thermal infrared (TIR) imagery. The stream geochemical response was largely bracketed by soil and groundwater geochemistry during high-flow periods of the FDC. The geochemical signature of streamflow and soil riparian water during low-flow periods most closely resembled groundwater chemistry and led to increasing electrical conductivity and base cation concentrations. Stream geochemical response during high-flows was uncorrelated to increased discharge. The response of surface saturation within the 100-m² TIR-imaged area was highly dynamic, responding strongly to increased flows and groundwater levels during the high-flow FDC period. TIR-imaged overland flow dynamics occurred during one of the largest flows recorded within the catchment, where surface saturation increased from 11 to as much as 51% of the TIR-imaged area, suggesting that surface overland flow may play a significant role in flow generation and stream geochemistry during large events. The lack of correlation between flow probability and geochemistry during during high-flows likely resulted from extensive mixing between soil and groundwater sources - though large variability in groundwater and soil water geochemistry suggested additional controls on mixing dynamics. Geochemical variability throughout the FDC as well as the dynamic response of surface saturation require additional, higher-frequency examination.
Introduction

The links between streamflow and stream chemistry have received much study. Event-based investigations have used geochemical and isotopic tracers to apportion streamflow sources into time and space components (Sklash and Farvolden, 1979; Hooper et al., 1990; Christophersen and Hooper, 1992; Burns, 2002) and extensive applications with end member mixing (Burns et al., 2001; James and Roulet, 2006; Vidon et al., 2008). Non-event streamflow investigations have focused on low-flow and drought characteristics (Musiake et al., 1975; Smakhtin, 2001; Dahm et al., 2003), as well as biogeochemical responses during drought (Morecroft et al., 2000; Dahm et al., 2003) or concurrently with prescribed burns (Williams and Melack, 1997). Concentration-discharge relationships across many years at multiple sites were examined by Godsey et al. (2009), who found that solute export was almost proportional to discharge, leading to nearly chemostatic behavior. In a small glacial catchment in the Swiss Alps, Hindshaw et al. (2011) have shown how the time-dependent stoichiometry of cation to Si ratios are controlled by catchment hydrological state and subsequent changes in residence time. Along similar lines, Maher and Chamberlain (2014) have shown that weathering rates of silica depend on residence times and flowpath length. The stream geochemical signature integrates catchment functions of collection, storage and release - reflecting a moving average of active catchment sources, flowpaths and residence times. Understanding the catchment’s geochemical state across the full range of observed flow conditions is needed to better predict how catchments will respond under changing climatic conditions. Concentration-discharge relationships have been used as a means to ascertain geochemical and flow linkages across multiple flows and time scales (Johnson et al., 1969; Clow and Drever, 1996; Hinton et al., 1997; Kendall and McDonnell, 1999; Xenopoulos et al., 2003; Godsey et al., 2009; Warrner et al., 2009). Concentration-discharge relationships alone, even those spanning multiple years, may mask geochemical behavior during certain flow conditions, particularly during high flows where samples are often sparse.

Here, we propose to look on stream chemistry-discharge relationships from a slightly different perspective – integrating flow, element concentrations and saturated area dynamics with regards to flow probability. This, graphically represented by the flow duration curve (FDC), distributes discharge according to exceedance probability, and is a potential means to link catchment hydrologic and geochemical states.
The FDC has many uses in water resource planning (Foster, 1934; Brutsaert, 2005), as well as sediment (Cordova and Gonzalez, 1997) and stream pollution management (Searcy, 1959). The FDC graphically represents the probability of exceeding any given flow, projecting streamflow information into the probability, rather than time, domain. The FDC, reviewed extensively by Vogel and Fennessey (1994, 1995), provides a summary of catchment behavior over seasonal to multi-year time scales, integrating stormflow, baseflow and low-flow basin responses.

The shape of a catchment’s FDC has been linked with catchment geology and climate (Musiake et al., 1975), vegetation (Burt and Swank, 1992), as well as soils and land use (Sefton and Howarth, 1998). Recent investigations into controls on FDC shape have incorporated rainfall runoff models to relate physical basin and climactic factors to corresponding catchment FDCs (Yokoo and Sivapalan, 2011). As part of their investigation of physical controls on the FDC across 200 basins, Yaeger et al. (2012) found that climate and catchment properties controlled FDC shape. Climatic inputs strongly control the upper tail shape in the FDC, closely corresponding to the rainfall probability curve, while the lower tail is controlled by basin-scale evapotranspiration (Yokoo and Sivapalan, 2011; Cheng et al., 2012).

The mid-slope region of the FDC reflects subsurface flow processes that drain the basin and connect the high-flow and low-flow periods; Yokoo & Sivapalan (2011) showed that decreased soil depth and increased soil conductivity resulted in shorter mid-slope regions that transitioned more quickly to the lower evapotranspiration tail, likely due to decreased subsurface storage and higher conductivity, both of which enhance the effect of evapotranspiration on discharge. The lower FDC tail reflects the probability that evapotranspiration processes dominate subsurface flow (Yokoo and Sivapalan, 2011) and is strongly controlled by geology and soils (Yaeger et al., 2012). Dominant hydrologic flow processes have also been linked to FDC shape; the FDC flow ratio – the ratio discharge at 0.5 and 0.95 probabilities – has been used to ascribe dominant flow processes, with high and low ratios corresponding to surface runoff processes and surface-groundwater runoff processes, respectively (Peters and Driscoll, 1987).

While physical catchment characteristics, climatic inputs and hydrologic processes have been linked to FDC shape, little research has related stream geochemical response to catchment FDC. Instead, the flow ratio has been used as a proxy for dominant flow processes. Peters and Driscoll (1987) determined that the sum of base cation (Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$) concentrations as well as
acid-neutralizing capacity were negatively correlated to the FDC flow ratio (low ratios indicate groundwater sources), which emphasized the important role of groundwater in lake and stream systems. Verry (1975) applied the FDC to calculate annual nutrient yield and smooth discharge from groundwater bogs and fens (see also Johnson, 1979). To our knowledge though, no studies to date have specifically examined the evolution of the stream geochemical signature across the range of the catchment FDC.

Flow-driven, nearly chemostatic relationships between concentration and discharge have been observed (Godsey et al., 2009). We hypothesize that similar chemostatic behavior will be evident in the 0.46-km² catchment studied here, and seek to better understand the flow processes that control geochemical signatures in this small catchment. Our overarching question driving this research is: How does the FDC relate to streamflow geochemistry?

If the high-flow FDC tail is strongly influenced by climatic forces and the low-flow tail by catchment geology and soils, we hypothesize that streamflow geochemistry, an integrate signal of catchment geochemical response, should reflect: 1) strong groundwater inputs at the low-flow tail and 2) surface/rainfall inputs at the high-flow tail. To test this, we compare biweekly observations of stream base cations (Ca²⁺, Mg²⁺, and Na⁺), electrical conductivity, and surface saturation dynamics (as inferred from thermal infrared imagery) in a headwater reach to corresponding flow conditions within the projected domain of the flow duration curve. Here we leverage existing stream chemistry and discharge data to explore the relation between streamflow sources and the flow duration curve in a headwater forested catchment in Luxembourg. We then use mapped patterns of saturated area dynamics to further test the linkages between FDC and streamflow sources.

Study Site

We pose our research questions at the 0.46-km² Weierbach catchment within the 250-km² Attert Experimental Basin (Luxembourg). Previous work in the Weierbach has documented catchment storage, flowpath dynamics, and connectivity from observations of the geochemical and hydrometric response of the stream, soil, and groundwater compartments over multiple years (Krein et al., 2006; Pfister et al., 2009, 2010; Martínez-Carreras et al., 2010; Fenicia et al., 2013). We build upon this work and test our hypotheses that streamflow sources impart observable
differences in the streamflow geochemical signature and this is related to the FDC. The Weierbach has 10 years of continuous discharge measurement for constructing annual FDCs and 6 years of bi-weekly stream chemistry observations including base cations (Ca$^{2+}$, Mg$^{2+}$, and Na$^+$) and electrical conductivity.

The Weierbach catchment is 85% forested, with mixed hardwood and conifer species including Fagus and Picea. The catchment ranges in elevation from 422 to 512 m above sea level with hillslopes as steep as 15° though with a mean slope of 5° (Martínez-Carreras et al., 2010). Leptic cambisol soils, with a well-developed organic horizon, extend to depths of 0.5 to 1 m above highly fractured, Devonian schists. This regolith above the hard, schist bedrock is made up of fractured bedrock and periglacial slope deposits (Juilleret et al., 2011), that form the main groundwater body in the catchment (Krein et al., 2006). Mean annual precipitation measured at a nearby rainfall gauge, 25 km from the catchment, is 845 mm with little seasonality (Pfister et al., 2005).

Discharge from the catchment generally peaks between December and February (1 - 1.5 mm/h), when evapotranspiration is low (Salvia-Castellví et al., 2005). Summer flows are very low, ceasing altogether during the driest years. Annual water balance calculations indicate that the catchment sheds 60% of precipitation as discharge, releasing slightly more (74%) during the winter and less (28%) during summer. Subsurface geology in the Weierbach is thought to exert a first-order control on runoff generation with winter events typically consisting of stored, pre-event water though event water composition can be much higher in the summer when hydrograph response is more muted (Martínez-Carreras et al., 2015; Wrede et al., 2015). Storm hydrographs exhibit muted, delayed peaks, as much as 24 hours after peak rainfall, with non-linear threshold relationships to incident precipitation and antecedent wetness conditions. The perceptual model of rainfall-runoff is that precipitation satisfies the subsurface storage capacity and spills to the stream channel in a threshold-like manner; overland flow is typically only visible along man-made impervious surfaces (Wrede et al., 2015).

**Methods**

*Computing the flow duration curve*
We used Matlab R2011a to generate the flow duration curve as a cumulative distribution function of the recorded discharge values (Vogel and Fennessey, 1994). The cumulative distribution function generated a probability of exceedance for each flow by fitting a distribution to the recorded flows. Flow in the Weierbach, ceased during some summer periods (2004-2006, 2009-2011). Weierbach discharge was estimated using established rating curves as a function of water stage, recorded on 15-minute intervals since 2004 using ISCO (™) 4120 flow loggers. In order to calculate the FDC using a cumulative distribution function, zero values were adjusted to one-half the value of the lowest recorded flow (0.0002 m³/s). For the Weierbach FDC, zero flow values plot at 0.0001 mm/h. We computed period-of-record FDCs that incorporated the entire flow record (2004-2014) and represented a composite of flow during the discharge period. It should be noted that as all flows were contained in the period of record FDC, the high and low-flow tails are more susceptible to over-representation of high and low flow characteristics – i.e. the highest flow recorded during a 10-year period will necessarily make up the high-flow tail even if flow during most years may not reach this level (Vogel and Fennessey, 1994).

**Water sample collection and analysis**

Stream, soil lysimeter and groundwater samples, taken bi-weekly over the course of six years, were analyzed for electrical conductivity and major cations. Stream water samples were taken manually at the Weierbach outlet (Figure 2.1), while groundwater samples were taken manually from four wells within the catchment. Soil water samples were taken from two soil tension lysimeter nests with various depths (0.2, 0.4, 0.6 and 1 m) located in upslope areas; a third soil lysimeter in the riparian zone was at 0.1-m depth.

Collected water samples were filtered to 0.45 µm and analyzed for Ca²⁺, Na⁺, and Mg²⁺ by ion chromatography (Dionex HPLC). Samples were stored at 4 °C until filtration and chemical analyses. Electrical conductivity was determined in situ via a WTW LF 323 conductivity meter.

**Thermal infrared imagery collection and analysis for quantifying saturated area dynamics**

Thermal infrared imagery (TIR) has recently been used to identify groundwater and hillslope inputs to the stream (Loheide and Gorelick, 2006; Cardenas _et al._, 2008; Pfister _et al._, 2010), investigate mixing in wetlands (Schuetz _et al._, 2012) and streams (Schuetz and Weiler, 2011), as
well as quantify stream temperatures along large stream reaches (Cardenas et al., 2014). Given that there was a measurable difference between the temperature of water within the saturated zone (streamflow, exfiltrating groundwater and standing water) and that of the surrounding soil and vegetation, temperature could be used to calculate the extent of saturation within a given area in the Weierbach catchment.

A FLIR ™ b425 camera was used to capture infrared imagery of a periodically-saturated headwater reach during the winter 2010-2011 (Figure 2.1). Winter discharge from this reach, which drains 6 ha of the Weierbach catchment, was highly correlated to discharge at the 46-ha catchment outlet. As the discharge record for this headwater reach is limited (gauged since March 2013), we sought to relate surface saturation at the headwater reach directly to catchment discharge via the FDC. In order to assess saturation dynamics within the 184-m² headwater reach (Figure 2.1), several images were captured and later assembled into a full-extent panorama. Imagery was collected, roughly bi-weekly for a five-month period, from the same spot along the eastern bank, facing west. Infrared imagery was exported as raw temperature matrices using FLIR QuickReport ™ software. Atmospheric temperature and relative humidity parameters for the infrared camera were adjusted according to the date and time images were captured. The emissivity parameter was set to 0.95, appropriate for liquid water and saturated soil and within the range of emissivity values used by others (Robinson and Davies, 1972; Schuetz and Weiler, 2011; Cardenas et al., 2014). A standardized grey-scale colormap, corresponding to a range of observable temperatures, was created and allocated to each image before images were stitched into a panorama using PTgui ™. The panoramic TIR imagery was then classified into saturated and unsaturated pixels, using the temperature range of known saturated areas (stream channel). The extent of saturation was calculated as the proportion of the total number of saturated pixels relative to the total number of pixels within the image extent.

**Results**

*Stream geochemical response to the FDC*

Concentration-discharge plots of stream chemistry and discharge were constructed on logarithmic axes for major cations (Ca²⁺, Mg²⁺, Na⁺) and electrical conductivity (Figure 2.2). Cation
concentrations decreased with increasing discharge. Discharge ranged by more than nearly 3 orders of magnitude, from 0.001 to ~1 mm/h, while cation concentrations ranged by factors of 2 – 4. Electrical conductivity ranged by a factor of nearly 2.

Flow duration curves in the Weierbach have sharp low-flow and high-flow tails, separated by slightly convex-shaped intermediary flows in the mid-region of the FDC during most water years (Figure 2.3). The convex-shaped region of the period-of-record FDC occurs near the 0.5 probability value, effectively separating the FDC into two halves – an evapotranspiration-associated, low-flow tail and a rainfall-dominated, high-flow tail. Figure 2.4 shows bi-weekly cation concentrations and electrical conductivity plotted against the exceedance probability associated with the flow during sampling. Stream cation concentrations and electric conductivity increase with increasing exceedance probability (decreasing flow) however, their behavior above and below the mid-point of the convex-shaped intermediate region of the period-of-record FDC is markedly different. Stream cation concentrations and electrical conductivity were largely flat during high-flows (0 to 0.5 exceedance probability) while during low-flow conditions cation concentrations and electrical conductivity increased (0.5 to 1 probability). Regression analysis showed that exceedance probability explained up to 43% of the variability in stream cation concentrations and electrical conductivity above probabilities of 0.5. All regression analyses determined for probabilities greater than 0.5 were statistically significant (p < 0.05) with probability explaining 18, 26, 36 and 43% of the variability in calcium, magnesium, sodium concentrations and electrical conductivity, respectively.

Groundwater and soil lysimeter sample concentrations of calcium, magnesium, sodium and electrical conductivity were plotted with exceedance probability (Figure 2.4). Because of the high variability of soil and groundwater samples, they are depicted with boxplots, representing the mean, median and interquartile (25-75%) geochemical range. Though variable, groundwater and soil lysimeter samples tended to bracket stream concentrations throughout the FDC. Groundwater samples tended to have higher cation concentrations and electrical conductivity than stream samples while cation concentrations from soil lysimeters tended to be lower than stream samples. Electrical conductivity, Na+, Ca2+, and Mg2+ show a general increasing trend with increasing probability, with mean soil lysimeter concentrations greater than groundwater concentrations at the highest exceedance probabilities.
**Saturation Dynamics**

TIR imagery were collected during greater-than-average flow conditions, with exceedance probabilities less than 0.5. TIR images were collected within a headwater reach within the Weierbach. (Figure 2.5). TIR images were collected at ground level and focused on the right-bank riparian and exfiltration zone – which makes up 100 m² of the 184-m² zone. Differences in the observed temperature of stream and standing saturated water with surrounding vegetation allowed for the extent of saturation to be determined throughout the imaged area.

The extent of surface saturation within this headwater reach, calculated via the TIR imagery, was plotted against the corresponding FDC exceedance probability (Figure 2.6). The proportion of saturated area was highest during high flows – more than 50% of the imaged plot area was saturated during a rain on snow event in January 2011 when discharge was equivalent to exceedance probabilities of less than 0.05 – and decreased with increasing exceedance probability. Though highly variable, the proportion of saturation increased with decreasing exceedance probability (Figure 2.6). Discharge varied directly with proportion of saturated area, though low-discharge saturation values were highly variable and this relationship is largely skewed by the effect of the two observations of surface saturation near 50% (Figure 2.7).

Groundwater level duration curve (GWDC) was constructed from groundwater measured approximately 100 meters from the headwater reach (Figure 2.6). The GWDC exhibited a very similar shape to the flow duration curve, especially at high and low flows. Groundwater levels increased during high-flow (low exceedance probability) conditions and with observed saturation (Figure 2.7). The inflection point of the GWDC differed from that of the FDC, with the GWDC’s slope changing near an exceedance probability of 0.8 while the FDC slope changes at 0.5 probability. Instead, groundwater levels decreased little between 0.4 and 0.8 exceedance probabilities (Figure 2.6).

**Discussion**

*How does the FDC shape relate to catchment geochemical response?*
The Weierbach FDC was sloped with well-defined high and low-flow tails. The intermediate region of the Weierbach period-of-record FDC was slightly convex, with an inflection point at 0.5 dividing the high and low-flow tails and lacked an elongated intermediate region typically associated with subsurface drainage (Yokoo and Sivapalan, 2011). Annual FDC (AFDC) reflected similar morphology with the inflection point largely occurring between 0.4 and 0.6. AFDC from 2011 and 2012 differed from this overall trend. In the AFDC from 2012, an elongated intermediate region is present and results in a low-flow tail emerging at an exceedance probability > 0.8. The 2011 AFDC exhibited much lower flows overall, lacking well-defined upper and lower tails, potentially due to less annual precipitation; there were 533-mm of rainfall in the 2011 water year compared to an average of 750-mm per water year during this study.

The presence of a convex-shaped intermediate region defined by sharp, upper and lower tails suggested a simple, two-phase system: A high-flow, precipitation-driven period and a dry, evapotranspiration-driven, low-flow period. This interpretation was supported by the stream geochemical response, which differed markedly at exceedance probabilities above and below 0.5. Cation concentrations and electrical conductivity values were lowest at low exceedance probabilities and increased non-linearly with increasing probability. Regression analyses for solute constituents, above and below the exceedance probability of 0.5, indicated that exceedance variability accounted for 0.18, 0.26 and 0.36 of the variability observed in calcium, magnesium and sodium concentrations, respectively. Regression analysis also found that 43% of the variability in electrical conductivity, at exceedances greater than 0.5, was due to increasing probability.

How do our findings compare with the concentration-discharge literature?

Our findings are consistent with others who have found that groundwater-related solutes showed general decreasing trends with decreased flow probability (high-flows) (Peters and Driscoll, 1987). While the general trend of increasing solute concentration with decreasing flow has been more widely observed (Clow and Drever, 1996; Godsey et al., 2009), our results indicate that the probability domain of the flow duration curve suggests this trend is mostly evident during low-flow conditions. Low-flow conditions observed by Hindshaw et al. had long residence times and low ratios of major cations to silica, indicating greater weathering of silica (2011). Concentration-discharge plots for our dataset showed that stream base cation concentrations and electrical conductivity decreased with increasing discharge. Ideal chemostatic concentration-discharge
relationships would have a slope of 0, effectively remaining constant at all discharges. Ideal dilution behavior of the same chemical constituents would have a slope of -1, with discharge diluting a constant source of solutes (Godsey et al., 2009). Concentration-discharge plots for major cations and electrical conductivity from the Weierbach have corresponding slopes between -0.04 and -0.08 (Figure 2.2).

Groundwater and soil water geochemical concentrations in the Weierbach were highly variable but generally bracketed stream concentrations across the flow duration curve. This suggests that streamflow was a mixture of these two sources. At higher flows associated with exceedance probabilities greater than 0.5, stream, groundwater and soil lysimeter solute concentrations were largely constant. Stream cation concentration and electrical conductivity response suggested well-mixed streamflow sources during high to medium-flow conditions between 0 and 0.5 probability. There was also a lack of dilution in solute chemistry during the high-flow tail, which is in agreement with the findings of Godsey et al. (2009) who found only small effects of dilution in concentration-discharge relationships across 59 catchments.

**FDC, groundwater storage and streamflow**

During low-flow periods, stream, groundwater and soil water solute concentrations increased, likely reflecting the draw-down of subsurface storage and increasing proportion of groundwater sources with high electrical conductivity and cation concentrations. This finding also supports model-based (Yokoo and Sivapalan, 2011) and regionalized (Cheng et al., 2012; Yaeger et al., 2012) conclusions drawn by others who have found that soils, subsurface drainage and geology play a strong role in shaping the low-flow tail of catchment flow duration curves. Observed increases in solute concentrations are likely due to increased contact time of water. Burns et al. (2003) found positive correlations between groundwater residence time (on the scales of months and years) and groundwater concentrations of weathered minerals (Ca²⁺, Mg²⁺ and SiO₂) at the Panola Mountain Research Watershed. Campbell et al. (1995) found stream solute concentrations were controlled by snowmelt moving through small groundwater reservoirs that indicated geochemical mixing and denudation processes that occurred on time-scales of hours to days.

Tritium-derived estimates of residence time during baseflow conditions in the Weierbach are 4.7 years. These estimates were based on samples collected when flow levels corresponded to an
exceedance probability of 0.78, which also appeared to be when the groundwater duration curve (GWDC) decreased rapidly (Figure 2.6) and groundwater geochemistry differed markedly from higher-flow periods (Figure 2.4). The GWDC low-flow tail remained elevated relative to the FDC at exceedance probabilities greater than 0.5. This could be due to a mismatch in units between the FDC (volume/time) and the GWDC (height), where a unit decrease in streamflow is equivalent to a smaller change in groundwater level. This does not appear evident at flow probabilities less than 0.5, where the GWDC and FDC are closely aligned (Figure 2.6).

The similarity between groundwater, riparian soil water and stream solute concentrations above exceedance probabilities of 0.8 is most likely explained by groundwater exfiltrating through the riparian zone into the stream (Figure 2.4). During the low-flow tail, only riparian soil lysimeters produced water for soil water sampling. During the lowest flows of the FDC, rainfall inputs and hillslope contributions to streamflow are minimized; riparian soils are largely sourced by groundwater. This likely explains why soil lysimeter and groundwater cation concentrations and electrical conductivity were very similar above probabilities of 0.8.

**Saturated area effects**

Surface saturation dynamics at the 184-m² headwater reach, as quantified by ground-based TIR imagery, increased with discharge and groundwater levels. The highest saturation values (~51%) occurred during an intense rain-on-snow event. This was one of the highest discharges observed in this catchment and in support of model-based findings that climatic conditions strongly influence the shape of high-flow FDC tails (Yokoo and Sivapalan, 2011). Previous work has suggested that the shape of the high-flow tail reflects climate inputs, ‘filtered’ somewhat by the catchment geology and fast, subsurface flow (Yokoo and Sivapalan, 2011; Cheng et al., 2012; Yaeger et al., 2012; Ye et al., 2012). A number of studies have contributed streamflow generation to expanding surface saturated areas (Dunne and Black, 1970a, 1970b; Steenhuis et al., 2004; Birkel et al., 2009; Weill et al., 2013) though this is difficult to quantify. We hypothesized that the conditions suitable for generating high-flow FDC tails (high rainfall, fast subsurface flowpaths) would also increase surface saturation, and subsequent increases in rainfall inputs and dilution effects to streamflow. We documented the expansion of surface saturation using TIR imagery, albeit in a small area (100-m²). Surface saturation was linearly correlated to both increasing discharge and groundwater levels (Figure 2.7), though this was largely driven by two data points at the highest saturation (51%). During
high-flows, the groundwater and flow duration curves overlapped and disentangling the relative causes of surface saturation expansion became difficult. Geochemically, streamflow appeared to be a mixture of groundwater and soil water sources. If surface saturation affected streamflow chemistry, we did not observe it in this dataset – though the temporal resolution (bi-weekly chemistry and TIR imagery) may have overlooked periods of incident precipitation. Higher-frequency observations of surface saturation, as well as observations at greater spatial scales, are needed.

Conclusions

We tested how the shape of flow duration curve related to changes in stream geochemistry across multiple years. During low-flow periods, we found that groundwater sources, likely reflecting long residence times with increased contact time with the subsurface, appeared largely responsible for increased streamflow concentrations of major cations and electrical conductivity. During high-flow periods, streamflow geochemical composition responded chemostatically and was uncorrelated to discharge. Groundwater and soil water were highly variable throughout the FDC, though mixing of groundwater and soil water sources appeared to explain stream geochemical composition during high-flows. The FDC and GWDC are in close agreement during the high-flow period but at exceedance probabilities greater than 0.5, groundwater levels decreased at a smaller rate relative to decreases in discharge until decreasing sharply near 0.8 exceedance probability, when groundwater, soil water and stream concentrations of cations and electrical conductivity increased. High groundwater concentrations of major cations and electrical conductivity are likely caused by increased subsurface contact time, as much as 5 years based on tritium-derived estimates of residence time at similar flows.

The proportion of saturated area, as quantified from infrared imagery taken within a headwater reach, increased with both discharge and groundwater levels. Despite this increase in surface saturation, we did not observe changes to stream geochemical signatures during these high-flow periods, which suggested that streamflow sources remained constant and lacked a dilution effect due to direct inputs of rainfall. Higher frequency observations of surface saturation during rainfall events, as well as geochemical and isotopic characterizations of endmember sources, could help to explain some of the surface saturation variability we observed here and disentangle the combined
effects of incident precipitation, hillslope outflow and exfiltrating groundwater on surface saturation dynamics. At the temporal and spatial resolution implemented here, we found that groundwater drove stream geochemical and flow behavior across the FDC. Dynamic surface saturation expansion was likely due to groundwater exfiltration in the riparian zone, which explained the positive correlation between surface saturation and discharge as well as between surface saturation and groundwater level.
References


Figure 2.1 The 0.46-km² Weierbach catchment located in Luxembourg. TIR imagery was collected along a 20-m headwater reach.
Figure 2.2 Stream concentrations of Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and electrical conductivity are plotted against discharge (log-log axes).
Figure 2.3 Period-of-record and annual flow duration curves from the Weierbach catchment. Annual FDCs were constructed from discharge records from individual water years (water year 2004 is based on discharge between April 2004 and March 2005).
Figure 2.4 Source cation concentrations plotted against FDC exceedance probability. Boxplots reflect the median, mean, interquartile range (25-75%) and outliers of groundwater (red) and soil lysimeter (blue) samples. Six individual boxplots depict the geochemical variation across the FDC, with each boxplot capturing 0.166 of the FDC probability.
Figure 2.5 Digital photo panorama (above) of the 100-m$^2$ semi-saturated zone along a headwater reach, with the location of the main channel and flow direction indicated by a yellow line. Saturation extent within the reach, as determined via ground-based thermal infrared imagery taken before, during and after a significant rain-on-snow event (winter 2010-2011). Saturated areas, as identified by similar temperatures to known saturated points, are identified by the deep red color. Change image to greyscale with red or yellow indicating saturation, increase % font to show saturation.
Figure 2.6 Weierbach flow duration curve (black) and groundwater duration curve (blue). Percent saturated area (red asterisks) from infrared imagery. Groundwater and proportion of saturation (right) and discharge (left) use log-scale.
Figure 2.7 Saturation plotted against discharge (upper). Saturation plotted against groundwater height (lower).
Chapter 3 A mechanistic assessment of near-stream saturated area dynamics

Abstract

Saturation excess overland flow (SEOF) generated in near-stream saturated areas is a mixture of rainfall and exfiltrating sub-surface water that can be quickly transported to the stream network during rainfall events. Mixing processes within these heterogeneous zones are poorly understood, despite much research focused on quantifying the extent of such saturated areas and their links to the storm hydrograph. Here, we quantified surface saturation dynamics in a near-stream area during rainfall events using high-frequency thermal infrared imagery. We isolated a 184-m² headwater reach with upstream and downstream weirs to mechanistically assess how rain falling on near-stream saturated zones contributes to the storm hydrograph. During 10 rainfall events across a 34-day period starting December 2013, a total of 161 mm of rainfall elicited 133 mm of runoff at the 6-ha outlet. Specific discharge generated within the 2 ha separating the 4 and 6-ha weirs was more than twice as large than at the 6-ha outlet. Surface saturation within a 25-m² thermal infrared imaged contributing area increased from 2 to 20% but was highly variable and weakly correlated to discharge and precipitation. Rainfall onto mapped, near-stream saturated areas was unable to explain the difference in flow generated within this small reach and explained less than 2% of the variance of flow change through events. Groundwater, soil lysimeter and surface saturated zone isotopic composition were very similar that at the 6-ha outlet, which was nearly unchanging and varied little throughout the 30-day period: -9.1 to -7.9 ‰ (s.d. = 0.16) and -57.8 to -54.7 ‰ (s.d. = 0.50) for $\delta^{18}O$ and $\delta^2H$, respectively. Rainfall isotopic composition ranged widely, -17.9 to -4.8 ‰ for $\delta^{18}O$ (s.d. = 3.06) and -134 to -23.7 ‰ for $\delta^2H$ (s.d. = 25.5). Streamflow isotopic composition at the 6-ha outlet deflected little throughout the 30-day rainfall period, 0.7 and 1.2 ‰ for $\delta^{18}O$ and $\delta^2H$, respectively. Groundwater exfiltration within the saturated area generated nearly all of the streamflow as well the persistent saturation throughout the event. This work suggests that for some catchments groundwater exfiltration in the near-stream zone dominates the isotopic composition of SEOF component as well as the storm hydrograph.

Introduction
Near-stream surface saturation during precipitation events is one of the most iconic, visible indicators of rapid runoff production in upland humid catchments. Figure 3.1 shows a selection of such areas across headwater zones in different hydro-regions. In each case, rain falling onto these zones would be expected to run off and contribute to the fast portion of the storm hydrograph. The importance of such saturation overland flow processes, largely dominated by rain falling onto saturated areas, has been demonstrated in countless studies, beginning with the pioneering work of Dunne and Black (1970a, 1970b), the important process-based work of Dunne et al. (1975), Taylor (1982) and recent model work by Frei et al. (2010), field-modeling synthesis by Birkel et al. (2009) and countless other studies.

Saturation excess overland flow (SEOF) is comprised of rain falling onto saturated areas and return flow (Dunne and Black, 1970a, 1970b), generally thought to be the emergence of subsurface stormflow originating from upslope sources (originally described by Hewlett and Hibbert, 1967; McDaniel et al., 2008) and exfiltrating groundwater (Hursh and Brater, 1941). While some work has quantified exfiltration gradients in the near-stream saturated zone (Abdul and Gillham, 1989; McGlynn et al., 1999), most work has assumed that the volumetric contribution of rain falling onto saturated areas far exceeds this ‘return flow’ component. Some studies (McGlynn and McDonnell, 2003; Dahlke et al., 2012) have shown that the groundwater contribution to streamflow remains constant throughout events, where hillslope inputs increased to provide the bulk of storm runoff. Others have found that elevated groundwater levels in the near-stream zone induce hillslope connectivity and lead to surface saturation and overland flow (Taylor et al., 2002; Lyon et al., 2006; McDaniel et al., 2008; Harpold et al., 2010). Indeed, disentangling groundwater and hillslope water from rain falling onto saturated areas is difficult with current methodology.

Near-stream saturated areas are often patchy internally and highly irregular along their margins and spatial extent (as illustrated in Figure 3.1). Within-saturated area dynamics are rarely considered. Rather, characterizing simply the areal extent of saturated areas has been the focus of field mapping (Dunne et al., 1975; Latron and Gallart, 2007; Birkel et al., 2009; Rinderer et al., 2012), aerial photograph analysis (Wigington et al., 2005), field surveys of vegetation and soil type (Kulasova et al., 2014), surface flow detector deployments (Srinivasan et al., 2000; Needelman et al., 2004; Srinivasan and McDowell, 2009) and GPS-field surveys at larger spatial scales (Godsey and Kirchner, 2014). This areal extent of saturation has been incorporated into hydrograph separation
models (Dewalle et al., 1988; Harris et al., 1995) and more recently by Birkel et al. (2009) and others. However, topographic and soil topographic indices can over-predict saturation extent and thus saturation excess overland flow contributions (Harpold et al., 2010). Similarly, we lack understanding of the detailed temporal dynamics of surface saturation extent throughout events and how this may be related to within-saturated area mixing of rainfall and return flow.

Here we assess mechanistically the near-stream saturated area behavior in a headwater catchment by isolating a stream reach with weirs placed upstream and downstream to quantify inputs. Detailed process observations focused on the streamflow generation and mixing dynamics within the saturated zone between the weirs are applied: thermal infrared imaging of the saturated area, groundwater measurements as well as geochemical and isotopic tracing of storm rainfall, discharge and endmember sources within the saturated zone (groundwater, riparian soils, overland flow). I ask: What internal mechanisms drive near-stream saturated areas development and interact with rainfall and exfiltrating groundwater to contribute to the streamflow signal?

Thermal infrared imagery (TIR) has recently been used to identify groundwater and hillslope inputs to the stream (Loheide and Gorelick, 2006; Cardenas et al., 2008; Pfister et al., 2010; Schuetz and Weiler, 2011) as well as to investigate mixing in wetlands (Schuetz et al., 2012). Thus far, proof-of-concept monitoring of saturated area dynamics monitoring with thermal infrared imagery has been restricted to snap-shots during near-optimal conditions with large temperature contrasts between target substrates: water, rock, soil, litter and vegetation (Frentress et al., this thesis). Here, we build on this work and apply ground-based, high-frequency, thermal infrared imagery over a 25-m² saturated area to quantify linkages between surface saturation, incident precipitation, exfiltrating groundwater, and the stream hydrograph response. Past work has shown that interactions between surface and subsurface processes strongly influence runoff dynamics in bog-forest upland watersheds (Gibson et al., 2000). Interactions between groundwater and surface water are thought to strongly influence stream geochemistry. Understanding the controls on mixing of surface and subsurface sources that contribute to runoff generation during rainfall events is paramount to better understanding stream biogeochemical export (Sophocleous, 2002).

At our study site at the Weierbach catchment in Luxembourg, Wrede et al. (2015) found that hydrographic response suggested a strong groundwater influence, one that lagged incident precipitation with peak discharges occurring as much as 20 hours after rainfall. However, runoff
ratios between 0.4 and 0.7 during intense rainfall events suggested an important role for SEOF in generating runoff (Pfister et al., 2002). Indeed, previous work within the Weierbach has documented the surface saturation expansion during intense rainfall events; surface saturation in one monitored riparian zone expanded 4-fold during a rain on snow event (Frentress et al., this thesis).

Here, we isolate a 184-m² section of the near-stream saturated zone along a 37-meter, headwater reach of the Weierbach using weirs upstream and downstream of the observed saturated zone. We monitor the saturated zone water table dynamics, determine the spatial extent of surface saturation using TIR imagery, as well as sample internally the saturated zone and streamflow for isotopic analysis. We mechanistically assess linkages between groundwater rise, surface saturation dynamics, streamflow response, and stream isotope composition to address the following questions:

- How does rain falling on near-stream saturated zones contribute to the storm hydrograph?
- How does the isotopic composition of SEOF evolve during events?
- How are near-stream saturation dynamics, precipitation, groundwater levels and streamflow related?

**Study Site**

We chose the Weierbach catchment to investigate controls on SEOF dynamics and contribution to storm runoff (Figure 3.2). The 0.46-km² Weierbach (Luxembourg) is ideally suited to investigate interaction and mixing between surface and subsurface sources because of a strong groundwater response and documented surface saturation expansion at the headwater scale (Frentress et al., this thesis). The Weierbach catchment is 85% forested and underlain by hard, schist bedrock. Catchment elevation ranges from 422 to 512 m above sea level with a mean slope of 5.25° (Martínez-Carreras et al., 2010). Pleistocene periglacial slope deposits (PPSD) define the development of the Leptic Cambic soils, with a biologically active layer occurring within 0.5 m of the soil surface. The silty loamy soils have large (> 40%) quantities of gravels and coarse materials, with fine-textured soils becoming a small portion of soil volume at depths greater than 0.5 m. The
poreous, weathered PPSD extend to the fractured schist bedrock, and are thought to supply much of the delayed, groundwater flow runoff (Krein et al., 2006; Juilleret et al., 2011). Mean annual precipitation is 845 mm with little seasonality (Pfister et al., 2005). Catchment discharge peaks (0.5 – 1.5 mm/h) between December and February when evapotranspiration is low (Salvia-Castellví et al., 2005).

Within the Weierbach catchment, a 37-m headwater reach draining the upper 6 ha (Figure 3.2) was selected due to the responsive surface saturation dynamics previously documented with panoramic infrared imagery (Frentress et al., this thesis). This study reach and saturated area was vegetated with herbaceous plants (Impatiens noli-tangere L., Chrysosplenium oppositifolium L. and Oxalis acetosella L.) as well as common fern (Dryopteris carthusiana (Vill.) H. P. Fuchs) (Martínez-Carreras et al., 2015). Organic riparian soils, 0.2 – 0.5 m thick, overlay the fractured schist bedrock throughout the 184-m² near-stream zone, which was saturated, or nearly saturated, much of the year. Starting May, 2013 streamflow from a 2-ha sub-watershed was monitored using two, sequential weirs: a lower weir quantified discharge at the 6-ha scale while an upper weir quantified discharge at the 4-ha scale. The lower weir was in a naturally-constricted area of the channel, 10 m downstream of the 184-m² saturated zone and 37 m downstream from the upper weir (Figure 3.2). Flow generated from the 2-ha sub-watershed, which contained the 184-m² saturated zone, was quantified by subtracting the upper weir (4-ha drainage) from the lower weir (6-ha drainage). Uncertainty in the discharge measurements were estimated following (Graham et al., 2010; McMillan et al., 2010).

**Methods**

*Infrared Imagery Collection and Analysis*

A FLIR™ AC250 was used to capture TIR imagery of a 25-m² area within the 184-m² monitored saturated zone. TIR imagery were collected every 15 minutes throughout multiple rainfall events during a 4-week period between December 16, 2013 and January 17, 2014. Temperature within the saturated zone was a useful proxy for determining the spatial extent of saturation. During much of the year, there were measurable differences between the temperature of superficial water within the saturated zone and that of the surrounding soil and vegetation. During winter months,
streamflow and exfiltrating groundwater in the Weierbach were typically warmer than surrounding vegetation and easily distinguished (Figure 3.3).

Atmospheric temperature and relative humidity parameters for the infrared camera were adjusted according to the image date and time. Trial and error showed that these parameters did not have a large effect on temperature differences. We applied an emissivity parameter of 0.95, which was appropriate for liquid water, saturated soil as well as green vegetation and was within the range of emissivity values used by others, 0.95-0.98 (Robinson and Davies, 1972; Deitchman and Loheide II, 2009; Schuetz and Weiler, 2011; Cardenas et al., 2014). FLIR imagery were exported as temperature matrices using FLIR ResearchIR™. TIR imagery were then analyzed to determine the number of pixels with the temperature of water, using the temperature range of a known saturated area to classify pixels. A pair of known saturated patches, one at a “pour-over” where surface saturation spilled into the channel and one just upslope with persistent saturation, were used to define the temperature of saturation for that image. Pixels within the temperature range of the known saturated zone were classified as saturated while warmer and/or colder pixels were classified as unsaturated (Figure 3.3). Low temperature contrasts between water, soil and vegetation can diminish accuracy in differentiating saturated from non-saturated areas. For images when the temperature of the known saturated patches was within 0.5 °C of known non-saturated areas (vegetated hillslopes, woody debris etc.), the saturation estimate was omitted from the time-series. The FLIR™ AC250 was able to differentiate temperatures as small as 0.1 °C; we therefore used 0.5 °C threshold as a conservative estimate of saturation.

Rainfall, Streamflow and Groundwater

Rainfall was measured near the Weierbach (46 ha) outlet, (Figure 3.2), using a tipping bucket gauge (Model 52203, 0.1-mm increments). A rainfall auto-sampler was installed to collect rainfall from the tipping bucket rain gauge in 2-mm increments. Rainfall samples were stored at 4 °C until isotopic analysis. Water stage at the 4, 6 and 46-ha outlets was recorded on 15-minute intervals using ISCO (™) 4120 flow loggers. The 4-ha weir was a box-flume with a 27° v-notch. The 6-ha weir constricted streamflow using two long planks, forcing the flow over a small impoundment. Rating curves for each weir were developed using the salt-tracer dilution technique (Dingman, 1994); volumetric calibration was used at the 4-ha weir whenever possible.
Water tables were monitored at two locations within the riparian zone. Each location consisted of a well at 0.4-m depth with a 0.15-m screen at the bottom. Water levels within piezometers were recorded every 15 minutes by Diver™ pressure transducers and corrected for barometric effects using a Diver™ barometric pressure sensor.

Riparian area was used as a proxy for the maximum saturation extent to estimate the potential maximum contribution of rainfall to saturation excess overland flow, and subsequently, the event water component of the hydrograph. The riparian extent throughout the Weierbach was estimated manually using handheld GPS (4,400 m², J. Iffly, pers correspondence). This manual delineation agreed well with GIS estimates using 1 and 2-m riparian buffers along the channel (3,500 and 7,000 m², respectively). Assuming the riparian extent was fully saturated and hydraulically connected to the channel, the maximum contribution from direct precipitation on saturated areas (DPS) was calculated by multiplying riparian area * rainfall and compared to the total storm runoff. Saturation extent above the 6-ha outlet was measured manually, 184-m², and maximum contributions during rainfall estimated in the same manner as above. Saturation extent above the 4-ha outlet was small yet variable and maximum contribution of saturation to runoff at the 4-ha weir was not estimated.

Isotopic Composition and Hydrograph Separation

ISCO auto-samplers were installed to collect streamwater and saturated zone water moving as overland flow. One auto-sampler was installed immediately upstream of the 6-ha weir. A second auto-sampler was installed within the saturated zone and was used to sample surface water just upstream of the stream channel (Figure 3.2). During the most intense rainfall periods, streamflow was sampled as often as every 3 hours, less frequently between events. Additional manual samples of surface water at select locations throughout the 184-m² saturated area were collected every few days. All collected samples were kept at 4 °C until isotopic analysis. Measurements of δ¹⁸O and δ²H in the liquid water samples were performed using a LGR Liquid-Water Isotope Analyzer and reported relative to δ¹⁸O and δ²H in VSMOW with a lab precision of 0.1 per mil for δ²H and 0.5 per mil for δ¹⁸O.

Results
Saturation Excess Overland Flow

A series of 10 rainfall events were monitored and sampled between December 13, 2013 and January 17, 2014. Rainfall events occurred every 3-4 days, averaged 16-mm depth and contributed 161 mm of rainfall during the 36-day period. Total specific discharge at the 46, 6 and 4-ha weirs was 124, 133 and 59-mm, respectively. Large specific discharge, and subsequent baseflow-adjusted rainfall runoff ratios (Table 3.1) are possibly due to sub-weir losses at the 4-ha gauge, anomalous precipitation records, gauge error or the inter-basin transfer of water. These are dealt with in more depth in chapter 4 (Frentress et al., this thesis). Specific discharge at the 6 and 46-ha scales were quite similar, with much smaller discharges observed at the uppermost 4-ha weir. The sum total of streamflow production from the 4-ha area was 30% of the total flow at the 6-ha outlet. The majority of streamflow generation was generated in the 184-m² saturated zone between the 6 and 4-ha stream outlets (Table 3.1).

The proportion of surface saturation within the 25-m² IR-monitored area expanded from a 2% on the 16th December, prior to the first, significant rainfall event and expanded to a maximum of 17% on the 13th January (Figure 3.4). Saturated area expansion during the initial rainfall period – between 18th and 28th of December – was correlated to net discharge generated within the saturated zone (r = 0.93, Figure 3.5). There was no significant correlation between surface saturation and discharge after the 28th of December. We also tested for, and did not find, correlation between saturation extent and air temperature or antecedent precipitation at antecedent time lag frequencies of 1, 3, 7 or 14 days.

Direct contributions of rainfall to the storm hydrograph were very small relative to total discharge produced at the 6 and 46-ha scales. We estimated the contributions due to direct precipitation on saturated areas (DPS) using surface saturation extent at the 6 and 46-ha scales by multiplying rainfall depth (mm) by the maximum area of saturation (184 m² and 4,400 m², respectively) and was expressed volumetrically (L/s, Figure 3.6). Field surveys of the riparian extent at the 46-ha scale were used as proxies of surface saturation. Figure 3.6 shows that direct rainfall contributions to runoff, calculated in this manner were 2% and 0.4% at the 6 and 46-ha scales, respectively. DPS at the 4-ha scale was not estimated due to large uncertainty in saturation extent.

Isotopic composition of streamflow
Streamflow isotopic composition measured at the 6-ha weir responded little to rainfall inputs, which varied from -17.9 to -4.8 ‰ for $\delta^{18}O$ (s.d. = 3.06) and -134 to -23.7 ‰ for $\delta^2H$ (s.d. = 25.5). Isotopic composition of streamflow at the 6-ha outlet ranged from -9.1 to -7.9 ‰ for $\delta^{18}O$ (s.d. = 0.16) and -57.8 to -54.7 ‰ for $\delta^2H$ (s.d. = 0.5) as shown in Figure 3.7. Streamflow isotopic composition at the 6-ha outlet deflected little throughout the 30-day rainfall period, 0.7 and 1.2 ‰ for $\delta^{18}O$ and $\delta^2H$, respectively. Isotopic separation of the hydrograph was not possible because rainfall isotopic composition was highly variable and crossed over the streamflow signal, with isotopic composition higher and lower than streamflow isotopic composition. Samples of overland flow within the saturated zone were correlated to the isotopic composition at the 6 ha outlet ($r = 0.36$ and $r = 0.53$ for $\delta^{18}O$ and $\delta^2H$, respectively) and were significantly different ($p < 0.05$) from the 6-ha isotopic composition. However, the difference in mean isotopic composition at the 6-ha outlet and samples within the saturated zone was small, 0.09 and 1.2 ‰ for $\delta^{18}O$ and $\delta^2H$, respectively; though the isotopic composition within the saturated zone was slightly lighter and more similar to the isotopic composition of volume-weighted rainfall (Figure 3.7). Meteoric water line plots (Figure 3.8a, b) indicated that $\delta^2H : \delta^{18}O$ ratios within rainfall varied widely though stream, groundwater, soil lysimeter as well as overland flow samples reflected highly similar ratios across a small range.

**Groundwater**

Groundwater levels in two wells within the 46 ha Weierbach (Figure 3.2), were monitored continuously between 2009 and 2014. Riparian groundwater levels (RP1 and RP2) and groundwater levels distant from the headwater reach (GW1 and GW2) were highly correlated during the December 2013 – January 2014 event. The water table level within RP1 rose above the soil surface although in RP2, located 2 m distant, the water table remained below the soil surface throughout the event (Figure 3.9). Discharge and groundwater level response throughout the year were highly correlated when groundwater levels are within 1.5 – 2 m of the soil surface (Figure 3.10). Seasonal differences in correlation between groundwater and streamwater were evident; groundwater levels were not related to streamflow during summer months. Transmissivity feedback (Rodhe, 1998) between groundwater height and stream discharge was evident and exhibited similar threshold behavior inferred in the time-series. Above groundwater heights of 0.5 m, discharge responded linearly to groundwater level (Figure 3.11). Well location and proximity to the channel network did not appear to influence groundwater behavior. Groundwater well 1 was
located more than 200 m from the channel, though the groundwater table dynamics were very similar to those of well 2, located within 10 m of the stream channel.

**Discussion**

*A saturated zone red herring?*

We were able to quantify the extent of saturation expansion within the gauged headwater reach during a series of rainfall-runoff events. Despite expansion of surface saturation, rain falling on saturated areas within the 184-m² riparian zone could only account for 2% of the total storm runoff generated. This hydrometric finding was supported by isotopic composition during the 4-week monitored period, where streamflow isotopic composition at the 6-ha outlet was effectively unchanging, reflecting well-mixed sources. Exfiltrating groundwater within the riparian zone generated the bulk of storm discharge and overwhelmed the rain falling on saturated areas.

Surface saturation within the 25-m² TIR imaged area responded dynamically and was initially correlated to discharge – during the first ten days - but was poorly correlated with discharge throughout the rest of the 4-week monitoring campaign. This finding contrasts with the work of Birkel *et al.* (2009), whose incorporation of dynamic surface saturation into model structure improved model performance in peaty Girnock catchments in Scotland. Instead of directly contributing to flow generation, surface saturation in our study catchment appeared an extension of subsurface flow. Near-stream zones and other wetland areas are generally considered hotspots for flow generation (Ambroise, 2004; Steenhuis *et al.*, 2004; Dahlke *et al.*, 2012) and geochemical transformation (Gilliam, 1994; Burns *et al.*, 2003; Agnew *et al.*, 2006; Lischeid *et al.*, 2007). Near-stream riparian areas in particular have been identified as key zones where streamflow sources mix (Bishop *et al.*, 2004; Tetzlaff *et al.*, 2014). Langhoff *et al.* (2006) found that mixing of surface and groundwater sources could be inferred from the ratio of the wetted width to the effective stream width, with large ratios (i.e. large wetted widths) associated with greater groundwater seepage through the streambed, either as diffuse seepage through riparian soils or as lateral hillslope flow. If we apply the same ratio approach, our mapped riparian zone should reflect large groundwater seepage (as large as 10 m riparian width / 0.25 m channel width). This in fact supports our results that suggest that groundwater seepage through the riparian soils, rather than rain falling on
dynamically expanding surface saturation, dominated discharge. Indeed, groundwater seepage in the 184-m² zone (2 ha, Table 3.1) generated large, per-area-unit response relative to the 4, 6 and 46-ha scales.

The role of groundwater exfiltration in SEOF generation

Surface saturation in the near-stream zone responded rapidly to incident precipitation, similar to saturation dynamics observed by Birkel et al. (2009) and estimated via distributed, rainfall-runoff models by Weill et al. (2013). While we did not map catchment-wide distribution of saturation, we do know that the near-stream zone makes up 1 and 0.3% of the area in the 46 and 6-ha catchments, respectively. This narrow zone appears to be a concentrated delivery zone for groundwater to the stream. The underlying catchment geology, fractured schist bedrock overlain by gravelly, periglacial slope deposits, supports this continuum. Streamflow generation in this geological setting is perhaps analogous to sandy, lake-dominated catchments of the North Temperature Lakes Long Term Ecological Research site in Wisconsin where streams and lakes occur at the interface of shallow groundwater tables and landscape position determines groundwater flowpath and subsequent lake chemistry (Cheng and Anderson, 1994; Webster et al., 1996).

Rather than generating significant streamflow via rain falling onto the saturated area, the near-stream saturated zone at Weierbach appears to be a conduit for streamflow sourced within groundwater stores. Streamflow increased non-linearly with increasing groundwater levels – located near and quite distant to the stream channel, appearing to respond only once a threshold groundwater level has been reached – a catchment-wide fill-and-spill process. Similarly, Weill et al. (2013) found that during periods of extensive saturation, a one-to-one relationship between groundwater storage and streamflow emerged. These threshold-mediated dynamics suggest that groundwater levels rise and intersect the channel and associated low-lying riparian areas, inducing streamflow and surface saturation expansion. These findings are similar also to Harpold et al. (2010) who found that as subsurface heterogeneity decreased, the variable source area emerged as an extension of the stream channel itself.

Within this catchment, water table dynamics within the riparian zone appear closely related to groundwater behavior at 10 and 200 m from the stream. Groundwater levels across the catchment appear highly synchronized, with streamflow response mediated by a groundwater threshold,
above which the stream responds directly to increasing groundwater levels. This finding contrasts with rank correlation analysis of groundwater wells across a catchment where correlation between wells and between wells and streamflow decreased significantly beyond a few meters of the channel (Seibert et al., 2003). The highly fractured schist bedrock underlying the catchment may provide the mechanism by which groundwater levels and streamflow can respond so uniformly. It seems the fractured schist and periglacial slope deposits act as a highly conductive and hydraulically connected reservoir, filling and spilling to the stream channel – the exposed interface between catchment storage and drainage. The synchronized behavior of groundwater wells between 0.5 and 2.2-m depths, as well as observed low variability in isotopic composition of streamflow and laterally-homogenous subsurface layers within ERT imagery, suggests that the subsurface is hydraulically well-connected throughout the Weierbach catchment.

An evolving perceptual model of the Weierbach catchment

Previous perceptual models of streamflow generation at the Weierbach suggest that water flows along the interface between the soil and fractured schist (Krein et al., 2006; Wrede et al., 2015). Streamflow response in the Weierbach is muted with peaked delays lagging streamflow by as much as 20 hours and suggestive of strong subsurface contribution to flow (Wrede et al., 2015). We build on this and suggest that streamflow generation in the Weierbach is an extension of groundwater dynamics and that the fractured schist forms a well-connected groundwater storage reservoir that fills and spills into the lowest-lying exposed area of the catchment – the near-stream zone and channel. Highly permeable soils overlying deeply fractured bedrock materials facilitate the downward movement of rainfall to groundwater storage. Rainfall percolates through the soil and periglacial till until it meets less conductive layers of schist, filling void space before spilling and moving downslope toward the stream channel. Unlike catchments where surface and near-surface saturation facilitates rainfall contributions to event runoff dynamics (Srinivasan and McDowell, 2009; Appels et al., 2011; Dahlke et al., 2012), the Weierbach represents perhaps a SEOF catchment endmember, with documented surface saturation dynamics and little to no event-water contributions to the storm hydrograph. Rather, groundwater exfiltration within the saturated near-stream zone drives saturation and discharge dynamics.

Conclusion
Surface saturation dynamics during events have been used to account for rapid streamflow response during events. However, they may mask underlying streamflow generation processes in some catchments. Indeed, we show that though surface saturation responded visibly and dynamically to input precipitation, it was poorly correlated to discharge dynamics and did not affect the event water composition of channel stormflow. Exfiltrating groundwater within the saturated riparian zone appeared to be the sole source of streamflow and surface saturation, as evidenced by the unchanging isotopic composition of streamflow and the synchronicity between groundwater levels and streamflow. Riparian groundwater dynamics and well response 200 m normal to the stream channel responded in unison. Our mechanistic assessment of near-stream saturated area dynamics suggests that this groundwater – and not the visible surface saturation dynamics – is the real driver of headwater streamflow at this site.
References

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Frentress J, Pfister L, McDonnell JJ. this thesis. Unraveling hydrological controls on stream water chemistry in a headwater catchment (Weierbach, Luxembourg)

Frentress J, Pfister L, McDonnell JJ. this thesis. The role of near stream groundwater exfiltration of headwater stream chemostasis


Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. *Forest hydrology* 275–290


Figure 3.1 Photographs showing surface saturation at multiple study sites – clockwise from upper left – Weierbach, Luxembourg (A); Paroma, Ecuador (B); Aberdeen, UK (C); Sleepers River, Vermont USA (D).
Figure 3.2 Stream gauges and groundwater well locations within the 46-ha Weierbach catchment (Luxembourg). Inset: LIDAR DEM of the saturated riparian area found along a headwater reach. S1 and S2 drain 6 and 4-ha hillslopes, respectively.
Figure 3.3 Digital (a), TIR (b) and classified imagery (c) of the gauged saturated zone; above, left and right, respectively. The 184-m² saturated zone lies between weirs at the 6 and 4-ha outlets, Figure 2. The infrared image shows the stream channel and groundwater exfiltration areas (red). Temperature within a small blue patch, center of both lower images, was used to classify all pixels within the IR image into saturated (red) or unsaturated (blue) categories, lower-right image. The digital image is taken from ground-level and therefore has a slightly different extent than the infrared imagery.
Figure 3.4 Rainfall, discharge and saturation development in the Weierbach. Rainfall (mm/h) shown above. Discharge (left axis) at the 4, 6 and 46-ha outlets are shown below. Proportion of saturation (right axis) in the 25-m² TIR imagery in lower plot.
Figure 3.5 Proportion of saturation calculated from TIR imagery plotted against net discharge generated within the 184-m² riparian zone. Blue points ($r = 0.93$) identify saturation values observed between 18th and 28th December (the initial wetting-up period for the event). Red points ($r = -0.37$).
Figure 3.6 Discharge (L/s) generated at the 6 and 46-ha outlets (top and bottom plots, respectively). Outlet discharge is in blue while discharge due to direct precipitation on the saturated area (DPS, L/s) is in red.
Figure 3.7 Deuterium (above) and δ^{18}O (below) composition of rainfall, volume weighted rainfall and streamflow at the 6-ha outlet.
Figure 3.8a Global and meteoric water lines and isotopic composition of streamflow (6-ha (green) and 4-ha (cyan)) as well as saturated zone within TIR (SZ – blue), groundwater (red), and soil lysimeter solution (magenta).
Figure 3.8b Same as 3.8a scaled to show streamflow isotopic composition. Global and meteoric water lines and isotopic composition of streamflow (6-ha (green) and 4-ha (cyan)) as well as saturated zone within TIR (SZ – blue), groundwater (red), and soil lysimeter solution (magenta). Same plot scaled to isotopic composition of streamflow.
Figure 3.9 Riparian (RP1, RP2) and groundwater (GW1, GW2) levels in the Weierbach during the December 2013 – January 2014 event. Riparian groundwater levels plotted on right-axis, groundwater wells located distant to the headwater reach plotted on the left-axis. Note the soil (zero) line corresponds to the riparian groundwater levels.
Figure 3.10 Groundwater height (blue and red) at two groundwater wells. Discharge (black) at the 46-ha outlet is also shown.
Figure 3.11 Discharge vs groundwater levels at two wells between October 2012 and October 2013. GW1 is located 200 meters from the nearest perennial channel while GW2 is located within 10 meters of perennial channel. Rainbow colors (ROYGBIV) indicate when data were taken and proceed from red (October 2012) to violet (October 2013).
Table 3.1 Rainfall (mm), specific discharge (mm), baseflow-adjusted runoff (mm) and runoff ratios during the December 13, 2013 – January 17, 2014 event

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Chapter 4 The role of near stream groundwater exfiltration on headwater stream chemostasis

Abstract

The causes of chemostatic behavior in streams at the headwater catchment scale remain poorly understood. Here we examine the underlying controls on streamwater chemostasis in a forested, headwater catchment. We used a nested catchment approach, bracketing flow at 4 and 6-ha scales of a headwater reach within the 46-ha Weierbach. A 184-m² near-stream saturated zone separated the 4 and 6-ha weirs. To understand the effect of within-saturated zone mixing processes on streamflow chemistry we sampled upstream and downstream streamflow, lateral groundwater inflows, soil water and overland flow within the 184-m² near-stream, saturated zone. Thermal infrared imagery was simultaneously used to quantify saturation expansion and groundwater exfiltration hotspots within the headwater reach. A series of consecutive rainfall events, spanning 34 days and totaling 161 mm, produced 133 mm of discharge at the 6-ha outlet, 70% of which was generated between the 4 and 6-ha outlets. Streamflow responded chemostatically, most measured geochemical species (Ca²⁺, Mg²⁺, Na⁺, SiO₂, Cl⁻, SO₄²⁻ and NO₃⁻) had low concentrations and that varied little (< 0.5 mg/L) throughout the rainfall events, despite discharge increases from 0.2 to 4 L/s. As streamflow solute concentrations changed little, solute export mimicked the storm hydrograph. Groundwater levels within the saturated zone increased after an initial 24 mm of event rainfall and remained high and within 0.05 m of the soil surface throughout the runoff period. Hydraulic gradients measured at two piezometer nests within the saturated zone suggested that heterogeneous flowpaths, with upwards and downwards gradients controlled exfiltration within the mapped saturated zone. Increases in hydraulic head at 0.15 m induced down-welling in one piezometer nest while hydraulic head increases at 0.40 m caused upwelling at the other piezometer nest. At the same time, surface saturation extent increased 20% within the TIR-imaged near-stream zone. No significant dilution of geochemical species was observed over the 30-day monitoring period, despite the 10 rainfall events and massive groundwater flux of water through the 184-m² zone. This suggested that unlike many headwater systems, the alluvial aquifer was well connected to groundwater outside the riparian zone and the mapped seepage area was a focused discharge point for the catchment-scale groundwater flow system.
Introduction

The hydrological controls on chemostatic behavior in headwater streams are poorly understood. The streamwater concentration-discharge relation is said to be chemostatic when stream concentrations of weathering products, e.g. silica, magnesium and sodium, vary little - factors of 3 to 20 (Godsey et al., 2009) - while discharge varies by several orders of magnitude. Several studies have now observed this behavior across diverse catchments (Herndon et al., 2015), in headwaters (Clow and Drever, 1996; Benettin et al., 2015) and at inter-annual time scales (Godsey et al., 2009). Such behavior implies that solute concentrations in stream water are not determined by simple dilution; that is, dilution of a particular solute flux by a particular variable flux of water. In other words, the rates of solute mobilization are (nearly) proportional to water fluxes.

The mechanisms that control chemostatic behavior have not yet been clearly identified. Work thus far suggests that subsurface transit time strongly affects streamflow geochemical composition (Burns et al., 2003; Benettin et al., 2015). Early concentration-discharge analysis at the Hubbard Brook Experimental Forest showed common dilution of weathered minerals (Johnson et al., 1969). Most work in headwater catchments suggest that streamwater concentration-discharge relationships are controlled by mixing between hillslope and aquifer endmembers, where rapid hillslope runoff dilutes alluvial aquifer streamflow sources (Peters and Driscoll, 1987; Hooper, 2001). Intercomparison of sites has shown that the expression of hillslope chemistry in the channel is affected by the ratio of the mobile hillslope volume to the volume of the alluvial aquifer (Hooper, 2001). At some sites, like the Panola catchment in Georgia USA, hillslopes rare contribute to stream (Burns et al., 1999) while at others like the Maimai catchment in New Zealand, hillslope chemistry is expressed regularly in channel stormflow (McGlynn and McDonnell, 2003). However, the role of groundwater exfiltration and mixing within the riparian aquifer and its link to overland flow dynamics on stream geochemical composition is still poorly understood.

Here we examine a groundwater-dominated headwater catchment (Frentress et al., this thesis) that has an intensively monitored and sampled near-stream zone to explore the first order controls on streamwater chemostasis. Past work at our site has shown large runoff responses (Pfister et al., 2002), delayed streamflow (Wrede et al., 2015), and increased groundwater inputs during wet
antecedent conditions (Martínez-Carreras et al., 2015). We build on this work and report a 1-month, intensive, high-frequency sampling period to ask:

What mechanisms are responsible for chemostatic behavior?

What is the role of groundwater exfiltration through the near-stream variably saturated zone?

How does rainfall on the expanded saturated area affect chemostasis?

Study Site

The 0.46-km² Weierbach catchment in Luxembourg (Figure 4.1) is ideally suited to investigate interaction and mixing between surface and subsurface sources because of a strong groundwater response and documented surface saturation expansion at the headwater scale (Frentress et al., this thesis). The Weierbach catchment is 85% forested and underlain by hard, schist bedrock. Catchment elevation ranges from 422 to 512 m above sea level with a mean slope of 5.25° (Martínez-Carreras et al., 2010). Pleistocene periglacial slope deposits (PPSD) define the development of the Leptic Cambic soils, with a biologically active layer occurring within 0.5 m of the soil surface. The silty loamy soils have large (> 40%) quantities of gravels and coarse materials, with fine-textured soils becoming a small portion of soil volume at depths greater than 0.5 m. The porous, weathered PPSD extend to the fractured schist bedrock, and are thought to supply much of the delayed, groundwater flow runoff (Krein et al., 2006; Juilleret et al., 2011). Mean annual precipitation is 845 mm with little seasonality (Pfister et al., 2005). Catchment discharge peaks (0.5 – 1.5 mm/h) between December and February when evapotranspiration (ET) is low (Salvia-Castellví et al., 2005).

Within the Weierbach catchment, a 37-m headwater reach draining the upper 6 ha (Figure 4.2) was selected due to the responsive surface saturation dynamics previously documented with panoramic infrared imagery (Frentress et al., this thesis). Vegetation within this study reach is comprised of herbaceous plants (Impatiens noli-tangere L., Chrysosplenium oppositifolium L. and Oxalis acetosella L.) as well as common fern (Dryopteris carthusiana (Vill.) H. P. Fuchs) (Martínez-Carreras et al., 2015). Organic riparian soils, 0.2 – 0.5 m thick, overly the fractured schist bedrock throughout the area. The entire 184-m² riparian study area was saturated, or nearly saturated, much of the year.
Streamflow from a 2-ha sub-watershed was monitored (starting May 2013) using two, sequential weirs, one at each outlet (4 and 6 ha). The 184-m² near-stream saturated zone was between the two weirs. Within the 2-ha sub-watershed was The lower weir was in a naturally-constricted area of the channel, downstream of the 184-m² saturated area and 37 m downstream from the upper weir. Thus, flow generated within the 2-ha sub-watershed (containing the 184-m² near-stream saturated zone) was quantified by subtracting the 4-ha weir from the 6-ha weir. Uncertainty in the discharge measurements were estimated following (Graham et al., 2010; McMillan et al., 2010).

**Methods**

*Infrared Imagery Collection and Analysis*

A FLIR™ AC250 was used to capture thermal infrared imagery (TIR) of a 25-m² plot within the 184-m² monitored near-stream saturated area. TIR imagery were collected every 15 minutes between December 16, 2013 and January 17, 2014. The saturated proportion in each image was determined using temperature differences between surface water and surrounding soils, vegetation, woody detritus etc. During much of the year, there was a measurable difference between the temperature of superficial water within the saturated zone (including streamflow, exfiltrating groundwater and puddled water) and that of the surrounding soil and vegetation. During winter months, streamflow and exfiltrating groundwater in the Weierbach were often warmer than surrounding vegetation and were easily distinguished. Thus, temperature was a useful proxy for determining the spatial extent of saturation.

Atmospheric temperature and relative humidity parameters for the infrared camera were adjusted according to the image date and time. Trial and error showed that these parameters did not have a large effect on temperature differences; only absolute temperatures. We used an emissivity parameter of 0.95, appropriate for saturated soil, green vegetation, and liquid water and within the range (0.95 – 0.99) applied by others (Robinson and Davies, 1972; Deitchman and Loheide II, 2009; Schuetz et al., 2012; Cardenas et al., 2014). FLIR imagery were exported as temperature matrices using FLIR ResearchIR™. Imagery were then analyzed to determine the number of pixels with the temperature of water, using the temperature range of a known saturated area to classify pixels. A network of known saturated patches were used to define the temperature of saturation for that
image. Low temperature contrasts between water, soil and vegetation can diminish accuracy in differentiating saturated from non-saturated areas. For images when the temperature of the known saturated patches was within 0.5 °C of known non-saturated areas (vegetated hillslopes, woody debris etc.), the image was omitted from the time-series. The FLIR™ AC250 was able to differentiate temperatures as small as 0.1 °C therefore this was a conservative estimate of saturation.

Clustering analysis of the TIR imagery was completed using the link function within Matlab 2014a™. Linkages reflecting the geometric distance between pixel behavior across time were created for subsequent clustering. A pre-defined number of clusters was used to aggregate pixels with similar linkage profiles. Pixels within a cluster tended to behave similarly across the time-series relative to pixels within other clusters. The number of cluster groups selected affected the interpretation of clusters. We used 10 clusters as more led to unnecessary differentiation amongst pixels.

**Rainfall, Streamflow and Groundwater**

Rainfall was measured within the Weierbach catchment (Figure 4.1) using a tipping bucket gauge (0.1-mm increments, Model 52203 rain gauge and CR200X series datalogger – Young, Campbell Scientific Ltd). A rainfall auto-sampler was installed to collect rainfall from the tipping bucket rain gauge in 2-mm increments. Rainfall samples were stored at 4 °C until isotopic analysis. Water stage was recorded on 15-minute intervals at the 4 and 6-ha outlets with ISCO™ 4120 flow loggers. The upstream, 4-ha weir was a box-flume with a 27° v-notch. The downstream, 6-ha weir constricted streamflow using two long planks, forcing flow over a small impoundment. Rating curves for each weir were developed using salt-tracer dilution techniques (Dingman, 1994); volumetric calibration by timing and filling a graduated cylinder was used at the upstream weir whenever possible.

Water table and hydraulic head gradients were monitored at two locations within the riparian zone. Each location consisted of a well at 0.4-m depth, with a screen covering the bottom 0.15 m, paired with a piezometer, open only to the bottom, at 0.15-m depth. Water levels within piezometers were recorded by Diver™ pressure transducers and calibrated using an above-ground Diver™ barometric pressure sensor. Differences in water stage between the piezometer and well at each nest was used to calculate local hydraulic head and hydraulic head gradients.
Electrical Resistivity Tomography

An electrical resistivity tomography (ERT) survey was done in March 2013. ERT is a rapid method for determining subsurface variations in electrical resistivity linked to variation in the clay content, porosity, saturation and the concentration of dissolved electrolytes in soils and bedrock (Reynolds, 2011). Five ERT profiles were carried out within the 2-ha sub-watershed. Two ERT profiles paralleled the stream channel and three profiles were perpendicular to stream. The same acquisition methods were used for all profiles. A Syscal Pro (10 channel, IRIS Instruments) resistivity meter with 120 electrodes was used. Electrodes were spaced every 0.5 m, resulting in a total profile length of 59.5 m. The topography of each line were derived from the LiDAR DEM.

A Wenner-Schlumberger quadripole-array configuration was used for the resistivity measurements. This configuration was chosen due to preferred depth determination and spatial resolution (Dahlin and Zhou, 2004). Inverse solution reconstruction of the resistivity distribution from the apparent resistivity measurements was conducted using the Boundless Electrical Resistivity Tomography (BERT) code, based on the finite element-forward modelling and inversion method described in Rucker et al. (2006) and Günther et al. (2006). Inversions were performed using a smooth inversion optimization method (L2-norm), an anisotropic factor wz of 1 and a regularization parameter, λ, of 20. Before inversion, obvious outliers and low quality data were suppressed by visual inspection and filtering (thresholds applied on measured voltage, injected current intensity and standard deviation of the measurements). For all profiles, acceptable convergence was achieved after five iterations as indicated by a root mean square misfit error in the range 1.90 – 3.02%.

Results

Chemostatic behavior at the headwater reach

A total of 161-mm of rain fell between 13th December 2013 and 17th of January 2014, resulting in a total of 59, 133 and 124 mm of baseflow-adjusted runoff at the 4, 6 and 46-ha scales (Tables 4.1 and 4.2). Stream geochemical concentrations were low and varied little at the 6-ha scale throughout the event; resultant geochemical export was highly correlated to discharge (Figure 4.2). Within the
saturated zone, the geochemical composition of overland flow, groundwater, riparian soil water and streamflow were similar to each other throughout the 34-day observation period (Figure 4.3). While geochemical concentrations decreased somewhat with increased discharge, the change was slight (< 0.5 mg/L), though discharge increased from 0.2 to 4-L/s. The overall geochemical response of streamflow sources within the saturated zone was largely chemostatic, and responded little to increased discharge.

Streamflow dynamics at 4, 6 and 46-ha scales

While this paper focuses on event dynamics starting late 2013, discharge at the 4, and 6 and 46-ha scales was monitored between May of 2013 and August of 2014 and resulted in 6 observed storm events. Four of the six events are reported here, the other two events had very high initial baseflow and long recession limbs which led to erroneous baseflow-adjusted runoff calculations. Pre-event flow was subtracted from total runoff to account for baseflow inputs. Baseflow-adjusted runoff ratios at the 6 and 46-ha outlets were quite high, and ranged from 0.09 to 0.77 and from 0.06 to 0.82 at the 46 and 6-ha scales, respectively (Tables 4.1, 4.2, 4.3). Baseflow-adjusted runoff ratios at the 4-ha scale were much lower, between 0.08 and 0.37, while baseflow-adjusted runoff ratios at the 2-ha scale were very high, between 0.78 and 1.96. The 2-ha sub-watershed was calculated from the difference in flows at the 4 and 6-ha weirs so sub-gauge losses at the 4-ha v-notch weir could have contributed to increased discharges observed at the 6-ha weir, and subsequent 2-ha runoff estimates (see discussion).

Streamflow response at the 6-ha outlet preceded that of the 4 and 46-ha weirs. Streamflow generated within the saturated zone - between 4 and 6-ha weirs – was consistently quickest to respond, particularly during rainfall events during wet antecedent conditions (winter). Discharge produced within the saturated zone was attributed to the 2-ha difference in watershed area. On a per-area basis then, streamflow generated within the saturated zone was 2-3x greater than discharge produced at the 4, 6 and 46-ha scales (Table 4.1).

Groundwater dynamics within the saturated zone

Riparian groundwater levels and streamflow generated within the 184-m² reach increased after an initial 24 mm of rainfall (Figure 4.4). Less than 7 mm of rain fell in the catchment in the two weeks
prior to the December 2013 event. Riparian groundwater levels - measured within piezometers at depths of 0.135, 0.15, 0.4 and 0.415 m – increased and remained elevated throughout the 30-day observation period. In piezometer nest 1, water levels increased from within 0.05 m of the surface to 0.01 to 0.05 m above the surface of the soil (Figure 4.4). In piezometer nest 2, water levels increased from 0.1 m below the surface to between 0.05 m and at the soil surface.

Hydraulic gradients were estimated from differences in water levels between piezometers within each nest. Hydraulic gradients at each nest responded differently during the event period. In piezometer nest 1, the increase in hydraulic head within the 0.415 m piezometer was greater than within the 0.135 m piezometer, which resulted in negative gradients, indicating upwelling (Figure 4). At the second nest, water levels increased more within the 0.15-m deep piezometer than at 0.4 m, which led to positive hydraulic gradients (down-welling). The overall magnitude of down-welling at the second nest was smaller than upwelling at the first nest (Figure 4.4). Given the opposing hydraulic gradient dynamics between piezometer nests extrapolation of the hydraulic gradients to the 184-m² saturated zone was estimated using an average gradient, which indicated net upwelling throughout the event. Saturated hydrologic conductivity values measured and calibrated during the application of a HydroGeoSphere model at this site suggested $K_{sat}$ values of 17 m/day, (Glaser et al., Submitted). Extrapolation of total runoff generated by groundwater gradients within the riparian zone was calculated using the average hydraulic gradient, saturated hydraulic conductivity and area of the saturated zone. This extrapolation required the bold assumption that the average gradient determined from two piezometer nests was representative of the groundwater dynamics throughout the 184-m² zone. Nevertheless, total runoff from the 2-ha sub-watershed was 6,300 m³ while average flux estimated from average gradients were in close agreement, 5,775 m³.

Application of TIR to quantify saturation, groundwater inputs

A total of 2,138 TIR images of a 25-m² contributing zone within the 184-m² monitored riparian zone were collected between December 16, 2013 and January 17, 2014 (Figure 4.5). Imagery was collected at 15-minute intervals. Surface saturation increased at the beginning of the rainfall series but remained variable, though elevated, relative to pre-event saturation levels after its initial increase between the 24th and 28th of December (Figure 4.6). Saturation was only included during periods when average imagery temperatures were at least 0.5 °C different from known areas of
surface saturation; this, combined with battery and camera software issues due to inclement weather, periodically interrupted continuous observation and resulted in periods without saturation observations (Figure 4.6). Clustering analysis of the TIR imagery was used to group pixels of similar behavior within the image (Figure 4.5). Figure 4.7 shows that average temperatures from saturated pixels, which corresponded to areas of cluster 1, responded differently to air temperature than mean TIR image temperatures. Temperature relationships amongst streamflow flow sources were plotted against air temperature. Temperature measured within the 0.135 m deep piezometer within the riparian responded the least to increases in air temperature while streamflow temperature and mean temperature from TIR pixels classified as saturated responded similarly, and increased somewhat with increasing air temperatures. Mean TIR imagery temperatures (including saturated and non-saturated areas) responded almost linearly to increased air temperatures (Figure 4.7).

**Electrical resistivity tomography and subsurface sources of streamflow**

A total of 5 ERT profile measurements were made in March 2013 across the saturated zone within the 2-ha sub-watershed, between the 4 and 6-ha weirs. Inversion results of the five profiles are presented under the form of a pseudo 3D view (Figure 4.8). An interpretation of a cross-sectional profile crossing the riparian (Figure 4.9) was supported by point-scale observations (soil pits, drillings and outcrops) made within or close to the study catchment (Juilleret et al., 2011; Wrede et al., 2015). ERT cross-sectional profile interpretations suggested hard, unfractured bedrock occurred at depths greater than 3 m below the surface, though this was highly variable, deeper, connected fractures could occur (Figure 9). Moderate to weakly fractured bedrock occurs between 1.5 and 3 m deep while heavily weathered and fractured bedrock occurred between 0.4 and 1.5 m deep. A silty-gravelly soil layer occurred between 0 and 0.4 m deep. Hard, unfractured bedrock was found between 0 to 0.4 m below the stream channel, which was largely covered with organic soils.

**Discussion**

While near-stream zones have been studied extensively in past experiments (Lyon et al., 2006; Dahlke et al., 2012; Godsey and Kirchner, 2014) and incorporated into modeling efforts (Birkel et al., 2010; Weill et al., 2013), surface and subsurface sources of flow from these zones contributing
to the stream have not generally been separated. Our work shows that one term in saturation excess overland flow dominates above all others—return flow of groundwater. The near-stream zone is often viewed as an initial source of streamflow during events (McGlynn and McDonnell, 2003; Frei et al., 2010; Nippgen et al., 2015; van Meerveld et al., 2015), but then upon activation of the hillslope zone, this riparian flow source may diminish or be flushed and replaced by hillslope inputs (Burns et al., 2003; McGlynn and McDonnell, 2003). Of course, this depends on the relative volume of the mobile hillslope input and the volume of the alluvial aquifer (Hooper, 2001). The Weierbach catchment appears to be a hydrogeomorphic endmember in this regard where the hillslope was never activated throughout our 1-month sampling period and did not express itself geochemically in the streamwater. Furthermore, the geochemical composition of streamflow, groundwater, riparian soils and overland flow were generally low concentration with little variability. These streamflow sources behaved chemostatically, exhibiting little evidence of dilution nor flushing effects.

The chemostatic nature of geochemistry and discharge at the 6-ha sub-watershed

During the 30-day observation period, a total of 161-mm of rain contributed to a 0.82 runoff ratio at the 6-ha outlet. Stream geochemistry composition was remarkably flat, with major cation, anion and geochemical concentrations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, Silica, SO$_4^{2-}$, K$^+$, Cl$^-$ and NO$_3^-$) varying little across the observation period. All cations showed a slight dilution effect, decreasing after the onset of rainfall. However, this difference was generally quite small, e.g. mean calcium concentrations fell from pre-discharge concentrations of 1.11 mg/L to 0.88 mg/L (s.d. 0.07 and 0.04, respectively), with no rebound in concentration after cessation of rainfall. The chemostatic, or nearly chemostatic, nature of stream geochemical response was well-documented by Godsey et al (2009), who considered 59 catchments of varying geology and size (6 to 2500–km$^2$) and found that discharge varied by multiple orders of magnitude though cation concentrations varied by factors of 3-20. Though Clow and Drever (1996) simulated rainfall experiments found only moderate decreases in solute release rates at the plot scale (49 m$^2$), such chemostatic behavior has not yet been well-documented at small watershed scales (< 1-km$^2$), nor do we have a good understanding of controls on chemostatic response at event-scales within small watersheds.

Specific discharge and runoff ratios at the 6 and 46-ha outlets were quite high, 0.82 and 0.77 for the event starting December, 2013. The runoff ratio at the 2-ha outlet for the same event was
exceptionally high, 1.96. This may be somewhat attributed to weir losses at the 4-ha outlet. These losses would need to be very high, with as much as 56% of the total runoff passing underneath or around the weir, to reduce the 2-ha runoff ratio to 0.82, the ratio observed at the 6-ha outlet. Care was taken during weir installation to prevent lateral and subsurface losses: the v-notch weir was placed directly on the surface of the bedrock within the channel and sealed with clays and other natural materials to prevent sub or side-weir passage of flow; two long steel sheets were inserted to the bedrock and extended out and away from the v-notch weir to help focus concentrate toward the bedrock channel. Furthermore, while the estimate of groundwater exfiltration within this near-stream zone was uncertain, having been extrapolated from only two sets of piezometers, the estimated total exfiltration throughout the event period within the zone, 5,775 m$^3$, was in close agreement with the total runoff measured during the event period, 6,300 m$^3$. While there were certainly losses beneath or around around the weir, it is unlikely these were large enough to fully explain the high ratios. Other sources of runoff ratio error – due to anomalous precipitation records or poor rating curves have likewise been eliminated.

The similarity in runoff response between the 6 and 46-ha suggests that the runoff ratios observed here are unlikely to be attributed to simple gauge error. It is quite possible that there are inter-basin transfers of water through the subsurface. This would explain the high runoff ratios, delayed peak flows, long recession limbs and high baseflows observed in the Weierbach (Martínez-Carreras et al., 2015; Wrede et al., 2015). ERT results indicate large potential subsurface storage however, linking the subsurface dynamics observed at the near-stream zone to subsurface properties along the watershed boundary is not possible with the data we present here. Despite this, inter-basin transfer of water remains a likely candidate for explaining the large runoff ratios - and potentially the geochemical patterns - observed here.

*The groundwater origins of streamwater chemostasis*

Groundwater, soil lysimeter water and overland flow samples from within the saturated riparian zone had similar geochemical concentrations as those measured at the 4 and 6-ha outlets. Differences in temperature within the surface of the saturated zone did indicated the groundwater exfiltration zones. TIR imagery has been used previously to identify groundwater hotspots (Chen et al., 2009), as well as estimate groundwater inputs via changes in stream temperatures at small reach scales (Schuetz and Weiler, 2011) and at larger scales through incorporation of an energy
balance (Loheide and Gorelick, 2006; Cardenas et al., 2014; Ala-aho et al., 2015). Here, we used ground-based TIR to detect exfiltrating groundwater within a saturated zone and validated the TIR with in situ measurements of groundwater temperature from nearby wells and stream temperature.

TIR imagery taken of the 25-m² contributing area was used to quantify saturation throughout the event. Pixels identified as saturated exhibited similar temperature dynamics to piezometer and streamflow temperature. At the same time, air temperature and the non-saturated portion of the TIR imagery were well-correlated with one another. Temperatures within the TIR saturation cluster were lower on average than piezometer temperatures but exhibited similar dynamics during the event. Piezometer, stream and saturated zone groundwater temperatures remained largely flat in response to daily air temperature fluctuations. This suggests that TIR-identified exfiltration areas transmit enough subsurface flow to maintain a heat signature similar to groundwater despite heat withdrawals from the surrounding environment. TIR-identified exfiltration areas tended to be cooler than stream temperature (measured 25 m downstream within the channel), suggesting that these areas reflect greater mixing between cooler, surface or subsurface water stored in the riparian.

Geochemical composition of riparian soil lysimeter and overland flow samples suggested extensive mixing, and largely reflected groundwater geochemistry. Groundwater exfiltration dominated riparian and stream geochemical composition, with only a tiny fraction of flow entering as rain on saturated areas or via lateral flow. This interpretation was supported by large net exfiltration within the 184-m² saturated zone that was similar to total runoff generated. The resulting streamflow at the 4 and 6-ha outlets reflected well-mixed sources that varied little in time and space. The absence of other source endmembers is striking; Hooper (2001) and Burns et al. (2001) used geochemistry to differentiate sources into near-stream, groundwater and upslope or soil end members, while Kendall et al. (1999) found that two end members largely explained streamflow geochemical composition. Flow from this headwater reach of the Weierbach during winter conditions appears to exhibit only one, well-mixed streamflow source. Previous endmember mixing model analysis contrasting runoff dynamics between wet and dry antecedent conditions within the 46-ha Weierbach catchment found that as antecedent wetness conditions became wetter, streamflow reflected more the groundwater component composition (Martínez-Carreras et al.,
The uniformity of geochemical and isotopic composition of streamflow at the 6-ha outlet suggests a large groundwater storage with significantly long flowpaths to facilitate mixing. Event-scale chemostatic response observed here appears to be largely driven by the size, connectedness, and hydraulic conductivity of subsurface layers, identified via ERT, that directly connect the channel to upslope areas.

Our work focused largely on the dynamics within a 6-ha watershed, where streamflow produced within the saturated headwater reach appeared to be in intimate connection with groundwater. This work, focused at the headwater scale during wet, winter conditions, emphasizes groundwater contribution to streamflow and its influence on the chemostatic nature of event-scale geochemical response.

**Riparian streamflow generation**

Mechanistically, it appears that in the Weierbach catchment, all water contributing to the stream is forced through the near-stream zone. Surface saturation extent did increase during the event though its effect on streamflow generation (via rain falling onto it and moving as saturation excess overland flow) was minimal compared to the massively dominant groundwater input to the channel. The geochemical uniformity of riparian water (soil lysimeter, overland flow) as well as the large runoff ratios generated within the saturated zone suggested a continuous, sustained movement of groundwater through the near-stream zone, which is sourced via a continuous water table and unconfined aquifer back into the hillslope and catchment. Surface temperatures within the saturated zone reflected this continuous groundwater exfiltration and its mixing with cooler sources of riparian water (likely stored at the surface in disconnected puddle areas) throughout the event.

Unlike Detty and McGuire (2010), who found that the near-stream aquifer was a primary streamflow source during small events while larger events were sourced by the catchment-scale groundwater aquifer, our site suggests constant communication between the near-stream and a catchment-scale aquifer. Streamflow generated within the riparian zone is suggestive of a continuous flow of groundwater which passes through the relatively homogenous geology of the Weierbach to reflect near-constant geochemical composition. This interpretation is supported by piezometric water levels within the near-stream saturated zone that suggest net exfiltration of
groundwater comparable to total runoff produced between the 4 and 6-ha weirs. The threshold-like response to rainfall and chemostatic response support a catchment-wide fill-and-spill mechanism whose catchment interface is the near-stream zone, where well-mixed waters respond in a threshold-like manner to rainfall.

**Conclusion**

We show that chemostatic behavior in this headwater system is likely due to exfiltration of well-mixed groundwater sources within the near-stream zone. Large groundwater storage and long flowpaths, supported by ERT results, are likely due to large, connected networks of fractured schist layers underlying the Weierbach. Our work shows clearly that groundwater generates streamflow and supplies a steady, well-mixed geochemical solution to riparian soils. The simultaneous, threshold responses of groundwater levels and discharge to rainfall inputs suggests large-scale mobilization of subsurface water to the stream network via the near-stream riparian. This groundwater pathway is supported by TIR imagery and high frequency sampling throughout the near stream zone. The lack of other, common streamflow generation controls (threshold-driven subsurface stormflow, rain falling onto extensive saturated area and contributing to flow, etc) is corroborated through high-frequency sampling of geochemical composition throughout the near-stream zone as well as near-continuous hotspots, imaged using TIR, of exfiltrating groundwater at the surface of the saturated zone. Mechanistically, all water appears to be forced through the narrow near stream zone. This site represents represents perhaps a clear archetype for how near-stream zones can function as highly-connected aquifer networks that expand the traditional alluvial aquifer volume to the catchment-scale.
References


Frentress J, Pfister L, McDonnell JJ. this thesis. Unraveling hydrological controls on stream water chemistry in a headwater catchment (Weierbach, Luxembourg)

Frentress J, Pfister L, McDonnell JJ, Martínez-Carreras N. this thesis. A mechanistic assessment of near-stream saturated area dynamics


Figure 4.1 Stream gauge and groundwater well locations within the 46-ha Weierbach catchment (Luxembourg). Inset: LIDAR DEM of the saturated riparian area found along a headwater reach with TIR-imaged area (yellow).
Figure 4.2 Concentration and export of calcium, magnesium, sodium and silica, as well as net discharge produced from the saturated zone between the 6-ha and 4-ha weirs during a series of rainfall events between December 17, 2013 and January 20, 2014. Concentration (mg/L) and solute export (mg/s) values are shown on the right y-axis.
Figure 4.3 Concentration – discharge relationships amongst streamflow (6-ha and 4-ha), groundwater (GW), riparian soil lysimeters (SS), as well as the TIR-imaged saturated zone (Satz). Geochemical composition units are in mg/L. Note, silica and sulfate plots have different y-scales. All samples were taken between December 17, 2013 and January 20, 2014.
Figure 4.4 Depth from soil to water level within two piezometer nests (blue and black) located in the saturated zone between the 6 and 4-ha weirs, as well as hydraulic gradients the two (red). Rainfall and discharge during the same time period included in upper plot for reference. Soil level (black line) and no-flow zero gradient (red line) are indicated as well. Right-axis corresponds to hydraulic gradient (dimensionless) and has been reversed for ease in interpretation, negative hydraulic gradients indicate upwelling. Individual piezometer depths are noted in figure legends. Vertical red lines indicate sampling times when water columns within piezometers were manually withdrawn and sampled for geochemistry.
Figure 4.5 Top: Digital image of saturated zone between 4 and 6-ha weirs (above). Note that digital imagery was taken from the ground-level and TIR imagery from 5 m above. Bottom-left: TIR imagery of the same saturated area at 15:00 on January 13th, 2014. Image extent is 25 m². Liquid water appears warmest (>5 °C). Bottom-right: Identified clusters (n = 10) across the TIR time-series.
Figure 4.6 Rainfall-runoff (above) and thermal dynamics time-series (below). Proportion of saturation within TIR imagery plotted on y-axis (below) with endmember temperatures plotted on left-axis: piezometers (41.5 and 13.5-cm depths, red and cyan), mean of classified saturated TIR pixels (blue), mean of pixels throughout TIR (green), and air temperature (magenta).
Figure 4.7 Relationships between saturated zone component temperatures and air temperature measured shown above. Shallow piezometer (13.5-cm depth, green), stream temperature measured at the 6-ha outlet (cyan), mean temperatures of pixels classified as saturated via the TIR imagery (red), and mean temperatures of TIR image extent – including saturated areas (black) – were all plotted against air temperature measured at the same time within the Weierbach catchment. Overlap, within 0.5 °C, between TIR saturation pixels (red) and TIR total image pixels (black) would have been excluded from the estimated saturation response. A reference line is plotted with a 1:1 slope (black).
Figure 4.8 ERT profile locations at the 2-ha sub-watershed. Flow direction and location of stream channel is indicated by the black arrow.
Figure 4.9 ERT profile interpretation of cross-section that intersected the near-stream saturated zone.
Table 4.1 Rainfall (mm) and specific discharge (mm) between June 2013 and January 2014

<table>
<thead>
<tr>
<th>Date</th>
<th>Rainfall</th>
<th>46 ha</th>
<th>6 ha</th>
<th>4 ha</th>
<th>2 ha</th>
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</thead>
<tbody>
<tr>
<td>18-Jun - 6-Jul-2013</td>
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<td>8</td>
<td>16</td>
<td>7</td>
<td>64</td>
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<tr>
<td>1-Nov - 22-Nov-2013</td>
<td>114</td>
<td>68</td>
<td>71</td>
<td>17</td>
<td>200</td>
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<tr>
<td>22-Nov - 6-Dec-2013</td>
<td>25</td>
<td>2</td>
<td>1</td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>13-Dec - 17-Jan-2014</td>
<td>161</td>
<td>124</td>
<td>133</td>
<td>59</td>
<td>315</td>
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</tbody>
</table>

Table 4.2 Ratios of total rainfall and runoff between May 2013 and January 2014.

<table>
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<th>6 ha</th>
<th>4 ha</th>
<th>2 ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-Jun - 6-Jul-2013</td>
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<td>0.77</td>
<td>0.82</td>
<td>0.37</td>
<td>1.96</td>
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</tbody>
</table>

Table 4.3 Pre-event discharge (mm/h) between June 2013 and January 2014.

<table>
<thead>
<tr>
<th>Date</th>
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<th>6 ha</th>
<th>4 ha</th>
<th>2 ha</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>1-Nov - 22-Nov-2013</td>
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<td>0.06</td>
<td>0</td>
<td>0.2</td>
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<td>13-Dec - 17-Jan-2014</td>
<td>0.03</td>
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Chapter 5 Conclusion

This thesis has examined mechanistically the role of the near-stream zone in controlling the physical, chemical and isotopic response of a headwater stream. My main findings were that groundwater discharge component during winter events completely overwhelms any effect of rain falling on saturated areas, that the alluvial aquifer behaves as an extension of the catchment groundwater storage and that chemostatic behavior at the headwater scale is controlled by subsurface mixing.

In chapter 1, I found that groundwater sources appeared largely responsible for general trends in the observed stream geochemistry response during low-flow periods of the FDC. Mixing of groundwater and soil water endmembers explained stream geochemical response at high-flows. There were also strong similarities between the FDC and GWDC at high flows, which suggested groundwater and discharge responses were directly coupled. The proportion of saturated area, quantified via panoramic TIR imagery, increased with both discharge and groundwater levels. Stream geochemical signatures were variable and unrelated to discharge throughout the high-flow period. At the temporal and spatial resolution implemented, groundwater drove stream geochemical and flow behavior across the FDC.

In the second chapter, I found that although high-frequency surface saturation measurements via TIR imagery responded visibly and dynamically to input precipitation, they were poorly correlated to discharge dynamics, and they did not affect event water composition in the channel. The unchanging isotopic composition of streamflow suggested that exfiltrating groundwater within the saturated riparian zone appeared to be the sole source of streamflow and surface saturation. This was further supported by near-simultaneous response of riparian groundwater dynamics and well-response 200-m distant from the stream channel. This mechanistic assessment of near-stream saturated area dynamics suggested that groundwater, and not the visible surface saturation dynamics, was the real driver of storm runoff and headwater streamflow generation at this site.

In the third and final chapter, I showed that chemostatic behavior in this headwater system was due to exfiltration of well-mixed groundwater sources within the near-stream zone. Layers of fractured schist beneath the catchment were likely the groundwater storage unit of the catchment.
This supported the conclusion that long flowpaths and large storage were responsible for the well-mixed geochemical composition of groundwater and ultimately, the chemostatic response observed at the headwater and event-scale. The lack of other common streamflow generation controls (threshold-driven subsurface stormflow, rain falling onto extensive saturated area and contributing to flow, etc.) was corroborated through high-frequency sampling of geochemical composition throughout the near-stream zone as well as near-continuous hotspots, imaged using TIR, of exfiltrating groundwater at the surface of the saturated zone. This site represents a clear archetype for how near-stream zones can function as highly-connected aquifer networks that expand beyond the alluvial aquifer to the catchment-scale.

While this work has contributed to a better understanding of catchment storage, more work is yet needed. We still lack a clear understanding of the extent of subsurface storage – within the Weierbach and at catchments worldwide. Moreover, excessively-high rainfall runoff ratios indicate that inter-basin transfer of water occurs at this site. This is likely occurring through the layers of fractured schist but our understanding of the conductivity, connectivity and extent of these layers is severely lacking. The application of ERT here revealed some of the potential that geophysical approaches may have in revealing the extent of potential subsurface storage, the dynamics of its connectedness to the stream channel as well as controls on subsurface storage and release.

Furthermore, understanding of how subsurface dynamics control geochemical solute composition of streamflow remain poorly understood. We have documented chemostatic behavior in the Weierbach at the headwater scale during a series of rainfall events, as well as across multiple years at the catchment scale (through the lens of the flow duration curve). We have not yet looked for chemostatic behavior at seasonal or larger spatial scales. The Weierbach catchment is part of the 240-km² Attert Experimental Network, which contains multiple experimental catchments with varying size, lithology and land cover. In many ways, the chemostatic behavior observed within the Weierbach begs the question of how applicable these chemostatic phenomena are at the larger basin-scale, where differences in catchment storage and runoff dynamics are greater.

We also lack critical knowledge of catchment-scale surface saturation at event and seasonal scales. Work here utilized TIR imagery at the headwater scale in part because of the difficulty in deploying multiple cameras to collect sufficient observations (during and immediately following rainfall) to quantify catchment-scale surface saturation. The upscaling of plot-scale dynamics – either surface
saturation or groundwater exfiltration – has also yet to be addressed. There exists a strong likelihood that surface saturation dynamics and the relative contributions of groundwater to the SEOF component will change at larger scales, particularly during wet or snow-melt conditions when near-stream saturation can expand rapidly. More observations of stream network expansion – at event and seasonal scales, connected with an enhanced understanding of groundwater release dynamics, would help us to better understand catchment-scale storage and release of water. This is particularly important in schist-dominated catchments like the Weierbach, where largely out-of-sight subsurface flowpaths control the output of water and solutes from the catchment.
Bibliography


Frentress J, Pfister L, McDonnell JJ. this thesis. Unraveling hydrological controls on stream water chemistry in a headwater catchment (Weierbach, Luxembourg)

Frentress J, Pfister L, McDonnell JJ. this thesis. The role of near stream groundwater exfiltration of headwater stream chemostasis

Frentress J, Pfister L, McDonnell JJ, Martínez-Carreras N. this thesis. A mechanistic assessment of near-stream saturated area dynamics


Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. *Forest hydrology* 275–290


