Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics

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[1] The spatial sources and delivery mechanisms of dissolved organic carbon (DOC) to streams are poorly understood. We examined the relationship between storm DOC dynamics, catchment landscape units, and catchment scale to elucidate controls on DOC export dynamics at the Maimai watersheds, a group of highly responsive, steep, wet catchments located on the west coast of the South Island of New Zealand. Specifically, we address the controls on the characteristic hysteresis in DOC export dynamics (i.e., DOC concentrations higher on the rising than falling limb of the discharge hydrograph) previously ascribed to a flushing mechanism. We found that during the storm event, the proportion of riparian runoff was larger on the rising than falling limb of the hydrograph, while the proportion of hillslope runoff was smaller on the rising than falling limb of the hydrograph. The delayed response of hillslope runoff resulted in a disconnection between hillslope and riparian areas early in the event and higher DOC concentrations on the rising limb than the falling limb of the event hydrograph. Later in the event, hillslope and riparian areas became connected once the hillslope soil moisture deficits were satisfied. We suggest that the relative timing of riparian and hillslope source contributions and the connections and disconnections of dominant runoff contributing areas are the first-order catchment controls on stream DOC concentrations and mass export. *INDEX TERMS:* 1806 Hydrology: Chemistry of fresh water; 1871 Hydrology: Surface water quality; 1890 Hydrology: Wetlands; 1860 Hydrology: Runoff and streamflow; *KEYWORDS:* dissolved organic carbon (DOC), headwater, scale, runoff sources, riparian zone, hillslope, catchment hydrology

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1. Introduction

[2] Dissolved organic carbon (DOC) is an important water quality constituent. DOC can make a significant contribution to the acidity of natural waters through formation of organic acids [*Eschleman and Hemond*, 1985] and affects biological activity through light adsorption [*Davies-Colley and Vant*, 1987]. Through the formation of organic complexes, DOC can influence nutrient availability [*Stewart and Wetzel*, 1981] and control the solubility, transport, and toxicity of metals [*Reuter and Perdue*, 1977]. Although much is known about DOC export dynamics as measured at catchment outlets [*Kaplan and Newbold*, 1993; *Boyer et al.*, 2000], little is known about internal catchment source fluxes and pathways of shallow groundwater DOC in response to storm rainfall. Few studies [e.g., *Easthouse et al.*, 1992; *Hinton et al.*, 1998] have related stream DOC dynamics to groundwater flow paths and sources.

[3] Recent literature has indicated that N and DOC flushing during storm events is an important mechanism in the export of DOC and N in small catchments [*Creed et al.*, 1996; *Boyer et al.*, 1997]. DOC flushing has been proposed as a response mechanism in a wide range of catchments and under varied conditions [*Foster and Grieve*, 1982; *McDowell and Likens*, 1988; *Moore*, 1989; *Hornberger et al.*, 1994]. DOC flushing, in the context of this work, is the mechanism whereby DOC built up in organic soil is flushed by rising water tables or infiltrating rainfall, resulting in diminished or limited supplies of labile DOC for latter periods of storm events or subsequent rain storms [*Boyer et al.*, 1997; *Brooks et al.*, 1999]. While flushing behavior is well studied, the geographic sources of DOC are less understood in upland catchments such as Maimai. Wetlands have been shown to be a major source of DOC where present [*Gorham et al.*, 1986; *Urban et al.*, 1989; *Koprivnjak and Moore*, 1992; *Kortelainen*, 1993]. *Dosskey and Bertsch* [1994] showed that 90% of the DOC for a watershed in the Atlantic coastal plain originated in riparian wetlands that comprised only 6% of the watershed area. Although uplands often dominate total watershed area in most instances, they are thought to contribute a small portion of the DOC exported, due to DOC sorption to mineral soils prior to reaching the stream [*Fieberg et al.*,

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1990]. However, recent research indicates that preferential flow in some hillslopes may allow transmission of hillslope runoff and labile nutrients with little matrix interaction [*Hill et al.*, 1999; *Buttle et al.*, 2001], enabling rainfall-driven organic horizon DOC transmission downslope. Therefore riparian and hillslope sources of DOC are difficult to separate based on catchment outlet observations. The dominant sources and flow paths of water may differ between catchments or within a single catchment during storms and this may have a strong influence on resulting stream DOC dynamics [*Hinton et al.*, 1998]. Therefore DOC sources and water flow paths cannot be easily inferred from catchment outflow concentrations alone. Study of DOC dynamics where sources can be isolated and flow paths delineated is a necessary next step in this area of research.

[4] To date, no study has systematically discretized a catchment into its major landscape units to determine the spatial sources of DOC contributions and to define the controls on temporal DOC dynamics in catchment runoff. The main hindrance to doing this has been the logistical constraint of through flow trench construction and isolation of dominant watershed features through either direct or indirect measurement. We report on new work from the Maimai experimental catchment where we were able to separate riparian and hillslope contributions to catchment DOC export to determine the spatial and temporal sources of DOC export. This was made possible by the relatively simple hydrology of the site (reviewed recently by *McGlynn et al.* [2002]) and the previous installation of a large hillslope trench system that effectively sampled direct hillslope runoff prior to entry into the riparian zone.

[5] Our study builds upon a wealth of previous hydrological and DOC research, most notably, previous catchment-based DOC investigations at Maimai by *Moore* [1989] which showed: (1) a significant positive correlation between DOC and discharge, (2) concentrations of DOC that were higher on the rising limb than the falling limb of the stream hydrograph, and (3) concentrations of DOC that decreased down the soil profile from 50 mg/L at the surface to 12 mg/L in the subsoil horizons. We hypothesize that the sources of streamflow shift during storm events from near-stream riparian zones to hillslope zones as events progress and that differences in DOC concentrations associated with source waters controls temporal DOC dynamics observed at the catchment outlet.

[6] Hydrologic processes at Maimai can explain some of the observed DOC discharge patterns described by *Moore* [1989]. The rapid movement of water through subsoil horizons via macropores, found by *Mosley* [1979] and *McDonnell* [1990], could allow DOC-rich water to circumvent adsorption by the subsoil horizons, leading to the input of relatively DOC-rich water to the stream. Alternatively, part of the storm flow would be generated by saturated overland flow on the lower slopes and riparian zones [*Pearce et al.*, 1986; *McDonnell*, 1990] early in the event, and this may explain higher concentrations of DOC on the rising limb. Each or both of these mechanisms could be responsible for the observed DOC patterns reported (higher on the rising limb of hydrographs) [*Moore*, 1989].

[7] To test this hypothesis we need to isolate the main DOC sources and sinks and then quantify their connections and disconnections during rainfall events. Unfortunately, this is a significant challenge. Previously, at best, we could measure and sample stream discharge and perhaps wells and suction lysimeters in different catchment positions. However, the Maimai catchment and a few others like it around the world that have been trenched (e.g., Plastic Lake, Ontario [*Hill et al.*, 1999], Panola Mt., Georgia [*Burns et al.*, 2001], and Kyru, Japan [*Ohte et al.*, 2001]) offer new potential for quantifying hillslope runoff timing, quantity, and quality. In addition, isolating hillslope dynamics allows us to quantify the role of this dominant portion of the landscape and isolate the response of the riparian zones by a difference approach. Riparian response is characterized by point measurements (i.e., wells, lysimeters, and water content probes) and quantified by a difference approach whereby riparian runoff is the residual in the catchment runoff response minus the hillslope runoff response (B. L. McGlynn and J. J. McDonnell, Quantifying the relative contributions of riparian and hillslope zones to catchment runoff and composition, submitted to *Water Resources Research*, 2002) (hereinafter referred to as McGlynn and McDonnell, submitted manuscript, 2002). Our nested landscape units include gauged divergent, planar, and convergent hillslope sections comprising a characteristic hillslope unit, a first-order catchment (collection of hillslopes with a narrow riparian zone), and a second-order catchment (collection of first-order catchments, hillslopes, and riparian zones widening toward the catchment outlet. By monitoring multiple nested catchment scales, including a trenched hillslope section, and riparian zones at each catchment scale, we can bracket and isolate landscape units and hydrological processes that are often otherwise obscured in catchment runoff–DOC relations. This residual approach enables quantification of the relative roles of different landscape units in controlling catchment runoff DOC concentrations and mass export. With a guiding philosophy that processes should be observed at the scale in which they occur [*Blöschl and Sivapalan*, 1995], we address the following questions to develop a greater understanding of DOC transport, mixing, and export timing: (1) Do hillslopes or riparian zones exhibit evidence of DOC flushing or hysteresis in the runoff–DOC relationship? (2) What are the sources of runoff and DOC at the first and second order catchment scales? (3) How do landscape units connect and disconnect hydrologically during and between events and how does this influence DOC export?

2. Study Site

[8] Maimai is a long-term hydrological research site with many published hydrological research investigations [*McGlynn et al.*, 2002]. The Maimai study area consists of multiple research catchments that form the headwaters of the Grey River and are located to the east of the Paparoa mountain range on the West Coast of the South Island of New Zealand (Figure 1a). Much of the hydrological research to date has been directed toward adjacent, remarkably similar catchments (<10 ha), sharing similar topographic, geologic, and soil characteristics [*Mosley*, 1979; *Pearce et al.*, 1986; *Rowe et al.*, 1994]. Slopes are short (<300 m) and steep (average 34°), with local relief of 100–150 m. The research described in this paper was conducted within the M15 catchment (2.6 ha) (Figure 1b), the newly

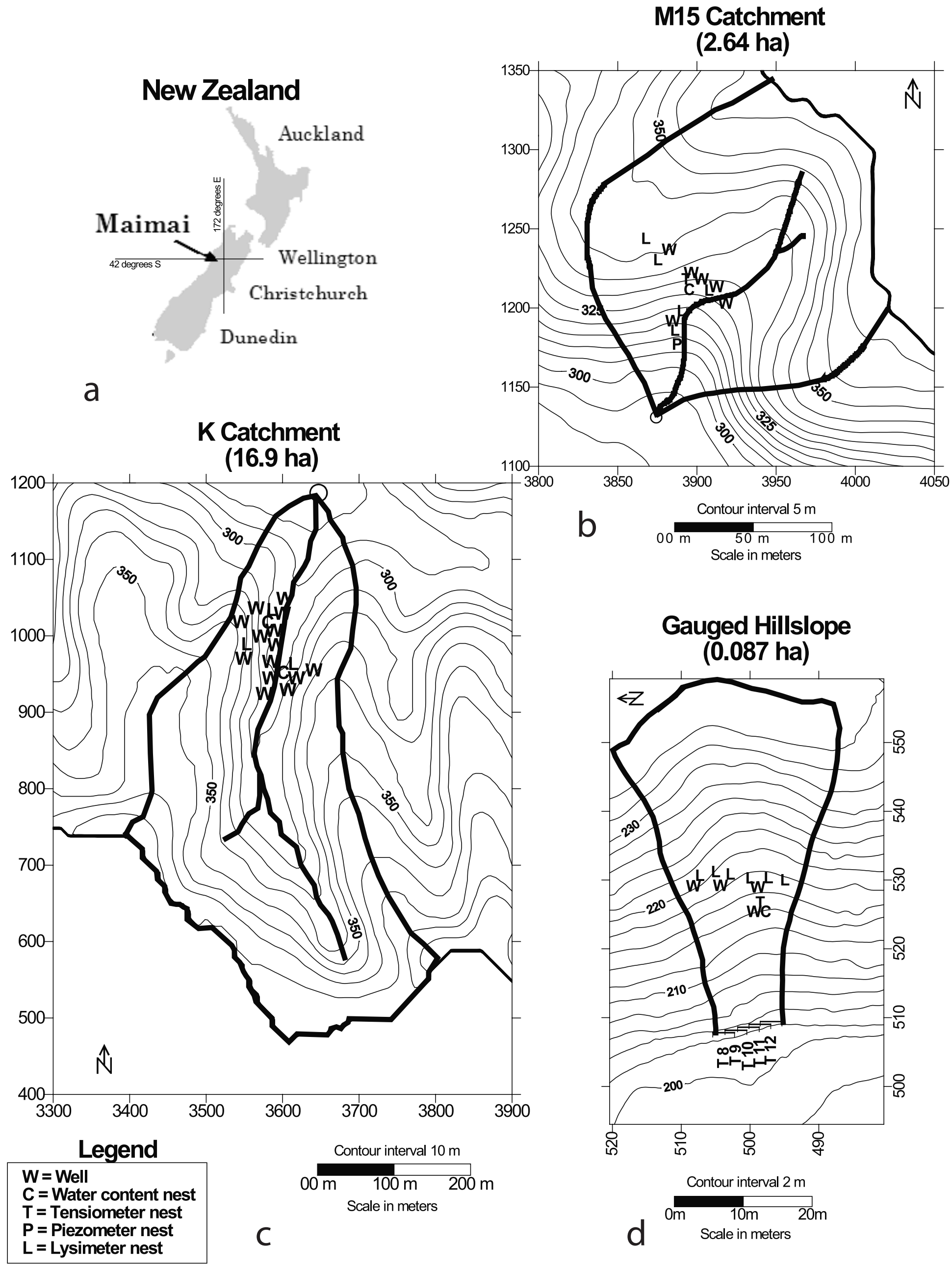

Figure 1. (a) Location of study area on the west coast of the South Island of New Zealand. Detailed map of topography and instrumentation locations on the (b) M15 catchment, (c) K catchment, and (d) gauged hillslope. Grid coordinates on x and y axes refer to local datum and are not consistent between maps.

gauged K catchment (16.9 ha) (Figure 1c), and at an adjacent (<2 km down valley) gauged hillslope (0.087 ha) (Figure 1d). Riparian zones in each catchment (2.6 ha and 16.9 ha catchment scales) were instrumented, mapped, and isolated by a difference approach (e.g., McGlynn and McDonnell, submitted manuscript, 2002), treating the riparian zone as a residual between monitored hillslope runoff and total catchment runoff in the catchment runoff balance calculation.

[9] Frequent, and sometimes prolonged periods of rainfall result from the passage of frontal systems originating in the Tasman Sea, across the Paparoa Range (from westerly and northerly directions). Mean annual rainfall is approximately 2600 mm, producing an estimated 1550 mm of runoff. The site shows minimal seasonality but summer months are the driest; rainfall from December to February averages 165 mm per month and between 190 and 270 mm for the rest of the year. Typically, there are 156 rain days per year, moderate temperatures, and about two snow days per year [*Rowe et al.*, 1994]. Climatic conditions during this study (1999) were consistent with those reported by *Rowe et al.* [1994].

[10] The Maimai catchments are highly responsive to storm rainfall. Quickflow (QF as defined by *Hewlett and Hibbert* [1967]) comprises 65% of the mean annual runoff and 39% of annual total rainfall (P) [*Pearce et al.*, 1986].

The quickflow response ratio (R index = QF/P) is roughly double that of the most responsive basins documented in the eastern United States [*Hewlett and Hibbert*, 1967] and comparable to that observed at the H.J. Andrews Experimental Forest in the western Cascade Mountains of Oregon [*Harr*, 1977]. The vegetation is an evergreen mixed beech–podocarp–hardwood forest that is multistoried with a canopy 20–36 m high, a dense fern and shrub understory, and a fern and moss ground cover [*Rowe and Pearce*, 1994]. Annual interception losses were estimated by *Rowe* [1979] to be 26% of precipitation for undisturbed mixed evergreen forest. Mean evaporation rates for the Maimai M8 catchment have been estimated as 0.46 and 0.28 mm/hr for summer and winter respectively [*Pearce and Rowe*, 1981].

[11] The Maimai catchments are underlain by a firmly compacted, moderately weathered, early Pleistocene conglomerate known as the Old Man Gravels. The conglomerate is comprised of clasts of sandstone, granite, and schist in a clay-sand matrix. It has been described as poorly permeable with seepage losses to deep groundwater estimated at 100 mm/yr [*O'Loughlin et al.*, 1978; *Pearce and Rowe*, 1979]. The overlying soils are classified as Blackball Hill soils and were developed from weathered conglomerate and colluvium. The typical soil horizon has a thick, well-developed organic horizon (average 17 cm) with DOC in solution averaging 56 mg/L. A thin slightly stony, dark grayish brown A horizon, and a moderately thick, highly friable mineral layer of podsolized, stony, yellow-brown earth subsoils (average 60 cm) with solution DOC concentrations of 12 mg/L were observed at 30–40 cm depth [*Moore*, 1989]. Silty loam/clay loam textures dominate the Maimai soils. Study profiles examined by *Webster* [1977] showed that the organic humus layer had an infiltration rate of 6100 mm/hr and mean total porosity and macroporosity of 86% and 39% by volume. The organic humus layer is the major source of labile DOC [*Moore*, 1989]. The mineral soils are highly permeable (K_{sat} = 250 mm/hr) and promote rapid translocation of materials in suspension or solution [*Rowe et al.*, 1994]. The soils are strongly weathered, leached, and have low natural fertility. The total porosity averaged 70% by volume, with average bulk densities of 0.8 g/cm^3. The soils typically remain within 10% of saturation by volume during much of the year [*Mosley*, 1979], but are not typically anoxic due to frequent rainfall and steep well-drained slopes.

[12] Maimai soils are thin and promote the lateral development of root networks and channels. Soil profiles at vertical pit faces in the Maimai M8 catchment revealed extensive macropores and preferential flow pathways which form along cracks and holes in the soil and along live and dead root channels [*Mosley*, 1979, 1982]. Significant organic staining of preferential flow paths (horizontal and vertical cracks, macropores, and the soil bedrock interface) has also been observed [*McDonnell*, 1990], indicating transmission of DOC-rich water along these pathways. Soil pits excavated on the gauged hillslope, in the 2.6 ha, and in the 16.9 ha catchments that were used for this study were consistent with prior published observations of macropores and organic staining of preferential flow pathways (described above). Lateral root channel networks were evident in the numerous tree throws that exist throughout the catchments. Preferential flow was also observed along soil horizon planes and at the soil-bedrock (Old Man Gravels) interface.

3. Methods

3.1. Water Inputs and Outputs

[13] Rainfall was measured in 0.2 mm increments with a tipping bucket rain gauge located at the base of the excavated and trenched hillslope (Figure 1a). We reactivated the hillslope trench excavated by *Woods and Rowe* [1996] [*McGlynn et al.*, 2002]. A subset of the original trench flow troughs (T8–T12) was instrumented and gauged at 5-min intervals (Figure 1d). Runoff from each 1.7-meter trench section was collected with 1 liter tipping buckets from gutters sealed to the bedrock surface at the trench face (see *Woods and Rowe* [1996] for a detailed description). Flow proportional sampling of hillslope runoff was accomplished by subsampling (diverting) 6 ml from each one-liter tipping bucket from high flow trough T11 (hollow position) and low flow trough T8 (planar position). Subsampled flow was routed downslope to sequential samplers with 10–1.5 liter collection bottles. Sequential samples represented 250 liters of runoff. Calibration checks of sequential samplers were made throughout each event. The time period associated with each sequential sample was flow rate dependent and determined based on the number of tips recorded and the number of sequential sample bottles filled.

[14] We instrumented the gauged hillslope and hillslopes and riparian zones in the first-order M15 catchment and second-order K catchment with nests of porous cup suction lysimeters, wells, and nests of water content probes. Suction lysimeters were 57 mm diameter and typically installed at 2 depths per nest; one at the A/B horizon boundary and the second near the middle of the mineral soil profile. Lysimeters were evacuated to −35 kPa and sampled prior to, during, and following rain events. Groundwater wells were fully screened 90 mm PVC completed to the soil bedrock interface and instrumented with TruTrack, Inc. recording capacitance rods. Water level was recorded at 5-min intervals. Water samples were collected from wells with stage activated in situ samplers as the water tables rose and manually sampled with a peristaltic pump as water tables receded. Campbell CS-615 water content probes were installed at 3 depths in each nest. Water content probe nests were located in the K (16.9 ha catchment) riparian zone, M15 (2.6 ha catchment) riparian zone, and upslope of the gauged hillslope trench. Water content data was recorded at 5-min intervals with Campbell CR510 data loggers. Streamflow was computed from stage measured with TruTrack, Inc. recording capacitance rods at 90° V notch weirs located at each catchment outlet.

[15] The gauged hillslope was instrumented with four wells, six lysimeter nests, one nest of water content probes 10–15 meters upslope of the excavated trench perpendicular to the fall line and distributed over a hollow, planar, divergent hillslope transect. The first-order Maimai M15 catchment (2.6 ha) was instrumented with seven wells, a nest of recording piezometers, a nest of three recording water content probes, and three nests of suction lysimeters (Figure 1b). The second-order Maimai

Table 1. M15 Catchment and Gauged Hillslope Physical Characteristics

	Site	Area, m^2	Soil Depth Mean, m	Soil Depth Range, m	Mean Slope
Zero order	gauged hillslope	870	0.6	0.15–2	40%
First order	M15 catchment	26,400	0.6	0.15–2	38%
First order	M15 riparian zone	575	0.55	0.13–1	16.7% (streambed)
Second order	K catchment	169,000	0.6	0.15–2	<38% (estimated)
Second order	K riparian zone	5,186	0.68	0–0.81	7.1% (streambed)

K catchment (16.9 ha) was instrumented with 16 wells, 2 nests of 3 recording water content probes, 3 nests of suction lysimeters, and a recording Campbell Scientific CS-247 electrical conductivity probe at the catchment outlet (Figure 1c). Instrumentation in the 2.6 ha M15 catchment and the 16.9 ha K catchment was located primarily in riparian and lower hillslope positions. However, additional wells and lysimeters were located in mid-slope positions for corroboration of observations from the instrumented and trenched hillslope.

3.2. DOC Sampling

[16] Runoff was gauged at 6 through flow troughs that drained the trenched hillslope (Figure 1a), the 2.6 ha catchment (Figure 1b), and the 16.9 ha catchment (Figure 1c). Event DOC sampling included a high flow trough (hollow position) and a low flow trough (planar position) at the trenched hillslope, and both catchment outlets. The twenty wells distributed throughout the study hillslope and catchments were event sampled for DOC, resulting in 3–5 samples from each well. Lysimeters were sampled for DOC in the riparian and hillslope zones at each catchment and at the gauged hillslope for preevent water, mid-event water, and post-event water DOC concentrations.

3.3. Analytical Methods

[17] Samples for chemical analysis, including DOC, were collected in 250 ml high-density polyethylene bottles. Subsamples for chemical analysis were passed through 0.45 μm glass fiber syringe filters. Cation samples were acidified to a pH of 1.0 to 1.5 with HCl prior to analysis for H_4SiO_4 concentration by direct-coupled plasma emission spectroscopy. Analytical precision for H_4SiO_4 was 0.8 μmoles/L. DOC concentrations were determined with a persulfate oxidation method. Electrical conductivity was collected with a Campbell Scientific, Inc. model CS-247 probe at 5-min intervals at the K (16.9 ha) catchment outlet.

3.3.1. Landscape Discretization

[18] Riparian area estimates were made by integrating 42 surveyed riparian widths measured at 10 m intervals perpendicular to the stream channel from the weir to the point of channel initiation in the 2.6 ha and 16.9 ha catchments, respectively. Riparian hillslope boundaries were determined with sampling for riparian soil characteristics (i.e., gleying), terrain characteristics (i.e., valley bottoms between stream and abrupt break in slope), and corroborated with water table, soil moisture, and solute dynamics at instrumentation sites. Riparian zone volumes were computed based on soil depth measurements at 6–12 points across the same transects. Total hillslope area in each catchment was computed as the residual of total catchment area and mapped riparian area. Mean soil depths for the hillslope areas were based upon detailed measurements across numerous sub-4 ha catchments by *McKie* [1977] and on our hillslope trench site as measured by *Brammer* [1996].

[19] Our gauged hillslope was selected based on previous research [*Woods and Rowe*, 1996; *Woods and Sivapalan*, 1997; *McDonnell et al.*, 1998; *McGlynn et al.*, 2002]. We instrumented this hillslope and used it as a surrogate for hillslope units in the M15 (2.6 ha) and K (16.9 ha) catchments. We tested the validity of using the gauged hillslope as a surrogate for all hillslopes in the M15 catchment (McGlynn and McDonnell, submitted manuscript, 2002) and found that the gauged hillslope was representative of the catchment wide hillslope runoff response and solute signature. The nature of the trenched hillslope response and runoff solute composition was characteristic of hillslope water table response and solute characteristics measured on other hillslopes in the M15 and K catchments as will be shown in the results section. Topographic analysis of the gauged hillslope and hillslopes comprising a Maimai headwater catchment demonstrated comparable mean, median, and frequency distributions of the topographic index ln (a/tanβ) (McGlynn and McDonnell, submitted manuscript, 2002), supporting the assumption that the gauged hillslope was characteristic of hillslopes in Maimai headwater catchments (based on surface topography). The gauged hillslope unit consisted of troughs T8–T12 that represented a cross section of hillslope conditions typical of the M15 and K catchments, including discernable hollow, planar, and divergent slope sections. Gauged hillslope runoff from the trench reported in this paper represents individually gauged but amalgamated hillslope sections. Table 1 lists the landscape component area estimates and volumes for all of our monitored sites.

3.3.2. Landscape Analysis

[20] We performed topographic analyses of landscape organization on 20 m DEMs of the M15 and K catchments [*McGlynn and Seibert*, 2003] and found that area was accumulated at comparable rates in the headwaters portions of the K catchment and in the whole M15 catchment. We computed the catchment area for each stream pixel from the headwaters to the catchment outlet to determine the rates of catchment area accumulation. In the 16.9 ha K catchment, we subdivided the area accumulation along the stream network, from the headwaters to the catchment outlet, into riparian and hillslope contributions based on field mapping of riparian zones and development of a relationship between catchment area and riparian width [*McGlynn and Seibert*, 2003]. These analyses allowed for distributed evaluation of local riparian to hillslope area ratios at each point along the stream network, evaluation of the nature of landscape unit

scaling, and assessment of potential landscape unit contributions to runoff in both catchments.

3.3.3. Hydrograph Separation

[21] Following the flow-based hydrograph separation procedure outlined and tested by McGlynn and McDonnell (submitted manuscript, 2002), we applied the area-normalized runoff calculated from the gauged hillslope to the hillslopes in the M15 (2.6 ha) and K (16.9 ha) catchments to determine the runoff originating in hillslope positions versus riparian positions. We assumed no time lag between hillslope runoff and catchment runoff because the hillslope trench was located at the base of the hillslope and thus closely connected to catchment runoff timing. The difference between runoff observed at the catchment outlet and that derived from hillslope runoff estimates was attributed to nonhillslope runoff (i.e., riparian runoff). Catchment runoff was then a function of riparian runoff (including direct channel rainfall) and hillslope runoff. Thus separation of catchment runoff into its two major spatial components (hillslope water and riparian water) provided a framework for investigation of the spatial and temporal sources of DOC in catchment runoff and the relative roles of riparian and hillslope positions in DOC export.

4. Results

4.1. Catchment Physical Attributes

[22] Hillslopes and riparian zones often exhibit distinct hydrological characteristics due to their location in the landscape, antecedent moisture status, and proximity of the local water table to the soil surface [*Seibert et al.*, 2002]. Our results indicate that riparian zones react (water tables develop or rise) more quickly in response to rainfall inputs than do hillslope areas, as evidenced by data from wells, piezometers, tensiometers, and soil water content probes over 15 months of record (McGlynn and McDonnell, submitted manuscript, 2002; B. L. McGlynn et al., The effects of catchment scale and landscape organization on streamflow generation, submitted to *Water Resources Research*, 2002 (hereinafter referred to as McGlynn et al., submitted manuscript, 2002). This is partially indicative of higher antecedent soil moisture and more persistent water tables in near stream positions. Hillslope positions drained more fully between events and built higher soil moisture deficits. The hillslope troughs provided quantification of hillslope runoff initiation, rates, and dynamics (McGlynn and McDonnell, submitted manuscript, 2002). The headwater portions of the Maimai catchments, including M15 (2.6 ha) and K (16.9 ha), have short steep slopes, abrupt breaks in slope at the hillslope-riparian zone interface, and narrow riparian zones with riparian widths increasing down valley (Figures 1 and 2). Typically, riparian zones exhibited soil characteristics indicative of higher average soil moisture status and prolonged periods of saturation, resulting in soil gleying, and the accumulation of fine sediments, as well as increased weathering and deposition [*McKie*, 1977]. Due to the topographic, hydrologic, and soils differences between hillslope and riparian areas, isolation and mapping based on solute signatures, soils, landform, topography, proximity to stream, moisture status, and response to storm rainfall was possible (McGlynn and McDonnell, submitted manuscript, 2002).

[23] Catchment physical attributes including catchment component landscape units are summarized in Tables 1 and 2. The M15 catchment consisted of a collection of hillslope units similar to the gauged hillslope plus a narrow valley bottom riparian zone. Riparian zones in the M15 catchment comprised 575 m^2 or 2% of the catchment area (and 2% by soil volume). The channel had a mean slope of 16.7%. The channel was well scoured with little to no accumulation of large woody debris and organic matter. The riparian zone in the K catchment was 5,186 m^2 and was 3% of the total catchment area. Riparian widths increased with catchment area and were largest toward the catchment outlet. The K stream channel had a mean slope of 7.1%, significantly lower than the mean slope in the M15 catchment stream channel. The channel was well scoured at the headwaters (similar to the M15 catchment); however, the lower 3/4 of the stream channel contained numerous debris dams, large woody debris, and significant organic accumulation, in contrast to the M15 stream channel.

4.2. Antecedent Conditions

[24] Antecedent rainfall conditions prior to the 6/12/99 event were high; 30-day antecedent rainfall index (API_{30}) was 237.6 mm, API_{14} was 116.2 mm, and API_7 was 31.4 mm (where API_X = the sum of all rain in the previous X days). As a result, soils in hillslope and riparian positions were within 0–20% of saturation by volume prior to the event. Prestorm base flow was 0.12 mm/hr in the M15 catchment and 0.7 mm/hr in the K catchment, due to rainfall inputs shortly before the 6/12 event. During the 15 months of hydrological monitoring at our sites for this study, 48 runoff events were recorded with peak runoff rates in excess of 0.5 mm/hr, 26 events in excess of 2 mm/hr, and 8 events in excess of 4 mm/hr. The event reported on here had a peak runoff rate of 3 mm/hr. Therefore the storm reported on here was a relatively common event under high antecedent moisture conditions.

4.3. DOC Response

[25] DOC response to rainfall was temporally variable from the soil block to the hillslope to the catchment scale. DOC concentrations in hillslope soils showed strong stratification with depth that persisted throughout the storm event. Shallow soil water DOC concentrations sampled with suction lysimeters ranged from 23 to 53 mg/L (Figure 2a). Deep soil suction lysimeters and groundwater wells had DOC concentrations that ranged from 1.3 to 5.3 mg/L (Figure 2a). DOC in a hillslope hollow (T11) through flow sample prior to the event was 2.8 mg/L, suggesting that deep soil matrix water was draining to the trench face prior to the first rainfall. DOC concentrations sampled in rainfall-driven hillslope runoff from the convergent hillslope section (T11) showed DOC concentrations ranging from 18–20 mg/L during the initial phase of storm through flow, which were intermediate between shallow and deep soil water DOC concentrations (Figure 2a). Once T11 (hillslope hollow) runoff rates reached 20 liters/5 min, DOC concentrations rapidly decreased to 1.3–6.3 mg/L, similar to deep soil DOC concentrations. They remained at this level through the rest of the event. Runoff from the planar hillslope trench section (T8) showed a similar DOC concentration pattern through time. T8 DOC was 19 mg/L in initial runoff and decreased to 2.5–3.8 mg/L, similar to T11, but lagged by 2 hours (Figures 2a and 2b). DOC concentrations from troughs T11

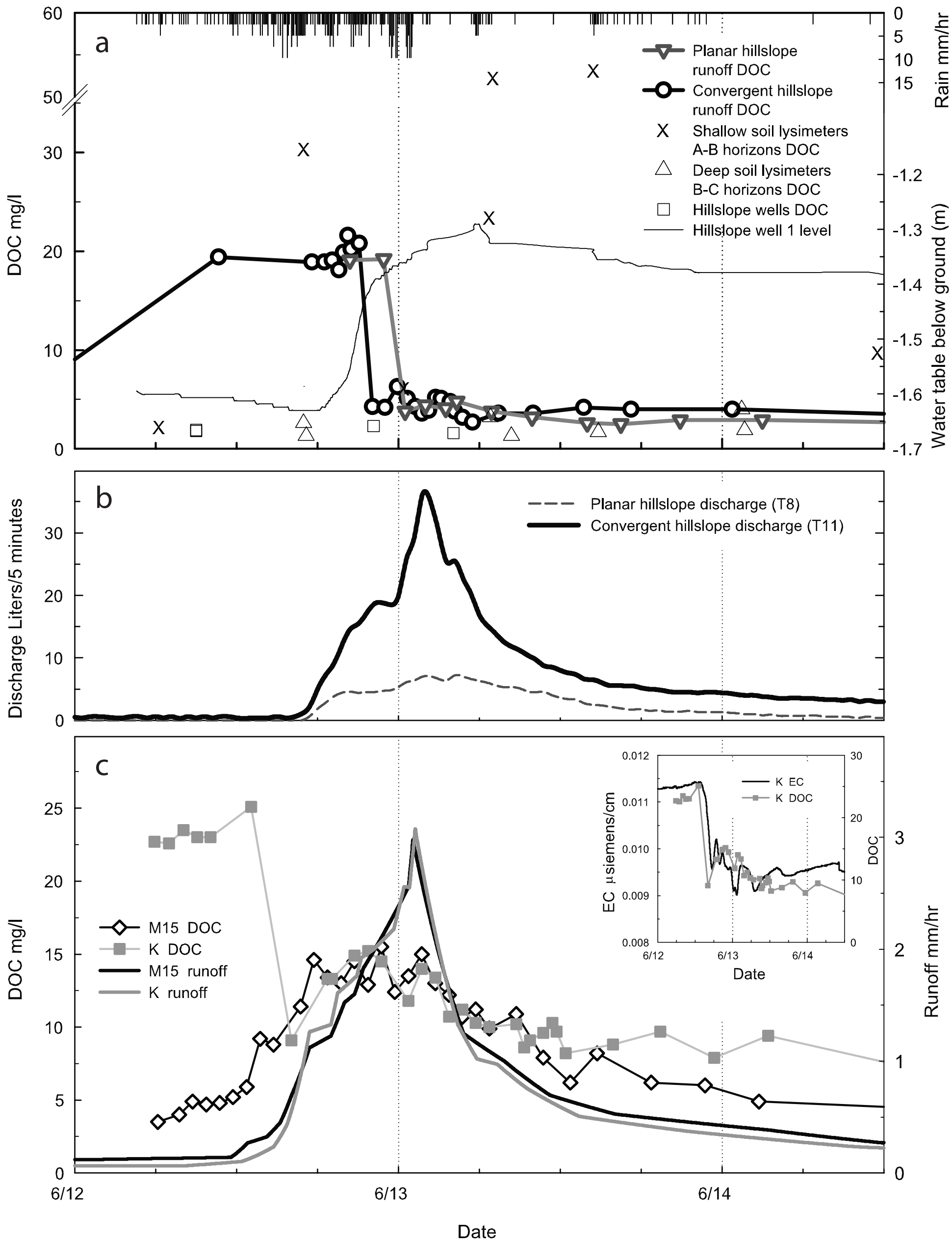

Figure 2. (a) Gauged hillslope runoff, soil profile DOC concentrations, and hillslope well 1 water table dynamics through time. (b) Planar (T8) and convergent (T11) hillslope trench section runoff dynamics through time. (c) M15 and K catchment DOC concentrations and runoff through time.

and T8 suggested a shift in relative proportions of shallow soil source water (high DOC) to deep soil source water (low DOC) on the rising limb of the hillslope through flow hydrograph.

[26] DOC concentrations in riparian zone water in the M15 catchment (2.6 ha) ranged from 2.2 to 17 mg/L. These waters were sampled from wells and lysimeters over the course of the event (Figure 3a). Preevent riparian matrix water was 4 mg/L, increasing to 12 mg/L with the onset of rainfall. Concentrations decreased and remained steady at 8–9 mg/L as water tables rose, hillslope runoff continued, and the event progressed. Preevent DOC streamflow concentration was 3.5 mg/L and increased to a peak of 15.5 mg/L more than 2 hours ahead of the runoff peak, and decreased to 4.5 mg/L as streamflow receded (Figure 3a). Overall, M15 runoff DOC concentrations were well correlated to discharge, although concentrations were greater on the rising than falling limbs of the hydrograph.

[27] DOC concentrations and water table dynamics measured at lower hillslope positions in the K catchment (16.9 ha) (Figure 3b) and the M15 catchment (2.6 ha) were comparable to DOC concentration and runoff patterns observed at the gauged hillslope (Figure 2a), corroborating the representativeness of the gauged hillslope measurements. Hillslope water DOC concentrations entering the riparian zone were initially high, with a mean of 21.4 mg/L decreasing to less than 12 mg/L as water tables rose (coincident with gauged hillslope runoff increases) (Figure 3b). In lower K catchment riparian positions, DOC concentrations were significantly higher: means ranged from 18 to 38 mg/L over the

Table 2. Discretized Landscape Unit and Catchment Areas, Volumes, and Ratios[a]

Variable	Second-Order K – 16.9 ha Catchment	First-Order M15 – 2.6 ha Catchment
Catchment area m^2	169,000	26,400
Catchment volume m^3	101,540	15,699
Channel area m^2	1,159	183
Channel area/riparian area	0.22	0.32
Channel area/catchment area	0.01	0.01
Hillslope area m^2	162,627	25,642
Hillslope volume m^3	97,603	15,385
Riparian area m^2	5,168	575
Riparian volume m^3	3,936	314
Riparian area/hillslope area	0.03	0.02
Riparian area/catchment area	0.03	0.02
Riparian and channel area/catchment area	0.04	0.03
Riparian volume/hillslope volume	0.04	0.02

[a]Volume refers to total soil reservoir and does not include porosity estimates.

event (Figure 3b). DOC concentrations in riparian positions increased with rainfall, peaking as water tables rose to the ground surface.

[28] Preevent DOC concentrations in the K catchment stream water were 22–23 mg/L and remained constant until 17 mm of rain fell, streamflow increased from 0.07 to 0.54 mm/hr, and hillslope runoff began (Figures 2a–2c and Table 3). Once these thresholds were achieved, K catchment runoff DOC concentrations decreased rapidly to values coincident with the M15 catchment. Following this point, both M15 and K streamflow DOC concentrations were comparable through the rest of the rising limb, peak, and falling limb of the storm hydrograph. However, late in the recession period, K catchment (16.9 ha) runoff DOC remained elevated while M15 catchment (2.6 ha) runoff DOC concentrations continued to decrease (Figure 2). DOC concentrations in the K catchment runoff were well correlated ($R^2 = 0.78$) with 5-min recording electrical conductivity at the catchment outlet, especially during the rapid decrease in DOC concentration on the rising limb of the event hydrograph (inset in Figure 2c), corroborating the temporal pattern observed in the K catchment runoff DOC concentrations.

[29] Total event driven DOC export from the 16.9 ha K catchment was 4.65 kg/ha, 0.25 kg/ha greater than the 2.6 ha M15 catchment export (Table 4). Hillslope DOC export accounted for 22–36% of the total K catchment DOC export while the remaining 64–78% originated in riparian and channel zones. Hillslope DOC export formed 25–41% of M15 catchment export with riparian and channel areas contributing 59–75%. We observed patterns in DOC concentrations in time and space; however, DOC concentrations alone were inadequate for resolving our core hypotheses because multiple flow paths and combinations of source waters could result in similar DOC dynamics at the base of the trenched hillslope at each catchment outlet. This motivated us to examine DOC juxtaposed with a more conservative tracer.

4.4. Runoff Source Water Mixing Analysis

[30] Bivariate mixing plots of DOC versus silica revealed the spatial source components contributing to hillslope runoff (Figure 4a), M15 catchment runoff (Figure 4b), and K catchment runoff (Figure 4c). Hillslope runoff began as predominantly shallow soil water mixed with smaller amounts of deeper matrix water and shifted rapidly to predominantly deeper soil water on the rising limb of the hydrograph. M15 catchment runoff base flow was a mixture of deep riparian soil water sampled from just above the Old Man Gravels in the riparian zone and shallower riparian zone soil water. As the event progressed and runoff increased, the proportion of riparian water contributing to total streamflow decreased. Streamflow silica signatures moved from riparian zone signatures toward initial hillslope runoff signatures, then peak hillslope runoff signatures, and then finally back toward riparian source signatures as streamflow receded. This sequencing of catchment runoff sources based on silica and DOC compositions of streamflow end-members corresponded to the timing of hydrological response of each end-member. The K catchment runoff DOC-silica concentrations follow a trajectory similar to the M15 catchment, aside from preevent and initial storm flow runoff, where the mixing diagram suggests that higher DOC concentrations in the lower K catchment riparian zone and stream channel controlled elevated base flow and initial storm runoff concentrations (Figure 4c).

4.5. Hydrological Dynamics at the Gauged Hillslope, M15 Catchment, and K Catchment

[31] In order to further elucidate controls on observed DOC concentrations in space and time, we investigated hydrological response from the soil block, to the hillslope, to the catchment scale. Soil moisture conditions in deep, mid profile, and shallow profile soil positions on the gauged hillslope were within 10% of saturation by volume at the onset of the 6/12 event (Figure 5a). Hillslope runoff, upslope soil moisture, and upslope water table development were well correlated in response to rainfall (Figures 2a and 2b). Gauged hillslope runoff peaked 20.7 hours after the onset of rainfall, increasing rapidly once initiated (Table 3 and Figure 2b). Soil profile moisture response to rainfall on the hillslope and lateral hillslope through flow were coincident and lagged rainfall initiation by 11–12 hours (Table 3 and Figures 3b and 4a). Soil saturation was observed at a depth of 1 m, 16 hours following the onset of rainfall. Mid and shallow soil water content probe positions responded more slowly to storm rainfall and peaked 21 hours and 21.3 hours after rainfall initiation (but without any observed saturation).

[32] Hillslope runoff exhibited a pronounced threshold response to rainfall (Figure 2b). This threshold response was due to unsaturated conditions though the soil profile on the hillslope prior to the event (Figure 5a), aside from water ponded in a monitored bedrock depression (see hillslope well 1 in Figure 2a). Through flow was recorded ~6 hours before matrix saturation was measured at the deep hillslope water content probe position. However, once saturation was achieved in the lower soil matrix, DOC concentrations in through flow decreased nearly instantaneously. Hillslope through flow entering the riparian zones therefore was characterized by a temporal step shift decrease in DOC concentrations on the rising limb of the discharge hydrograph.

[33] Riparian soil moisture conditions in the M15 catchment, as represented by a nest of recording water content probes and riparian wells (reflecting the range of riparian

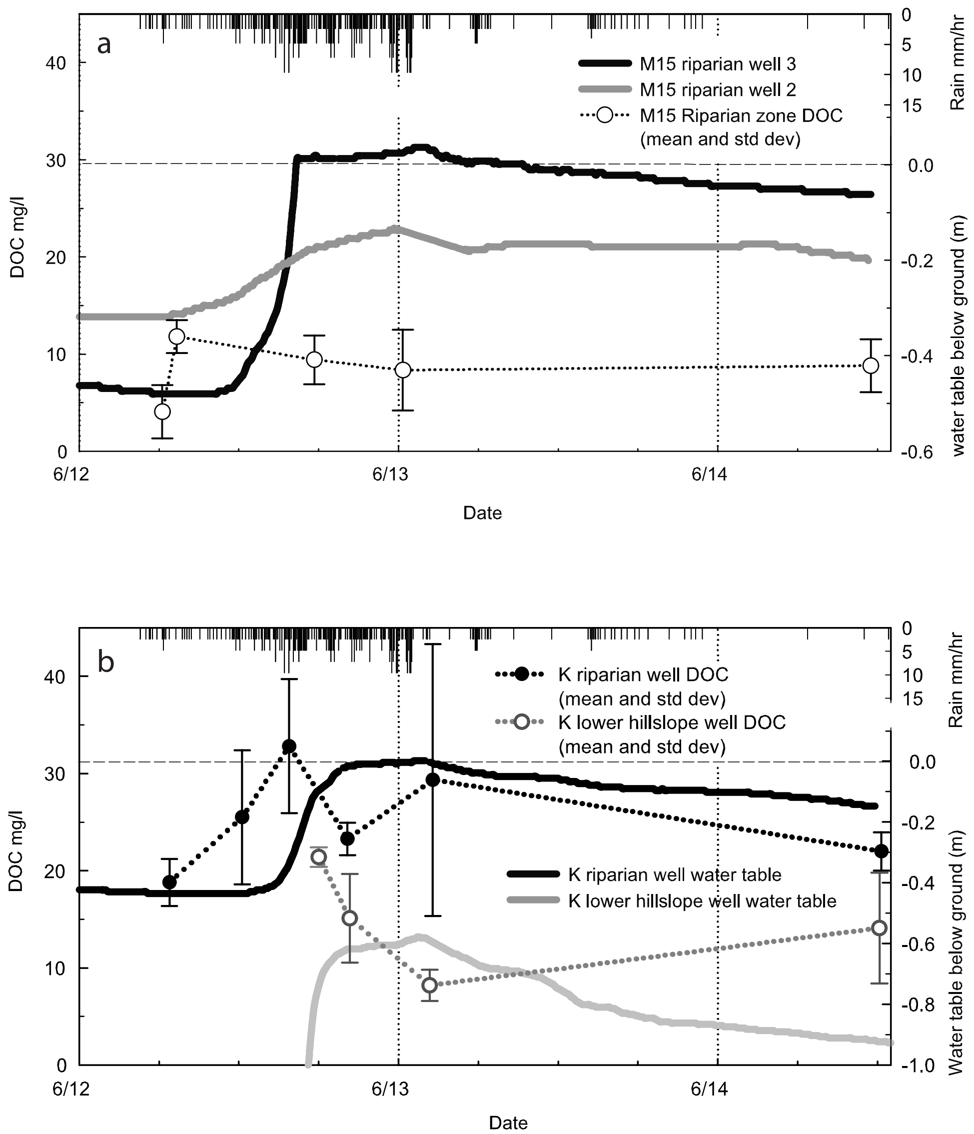

Figure 3. (a) M15 catchment riparian zone water table dynamics and well and lysimeter DOC concentrations through time (note location of ground surface and surface saturation in M15 well 3). (b) K catchment riparian and lower hillslope water table dynamics and associated DOC concentrations sampled from wells and lysimeters (note location of ground surface and surface saturation in the representative K riparian well).

well dynamics), are shown in Figures 4b and 5a. The deep soil water content probe position showed volumetric water content within 5% of saturation and mid-profile and shallow profile positions within 20% of saturation. Vertical wetting front movement from shallow to deep positions was evident with response lags to rainfall of 3.2 hours, 6.7 hours, and 7.8 hours respectively. Saturation developed at deep to shallow positions 10.7 hours, 11.8 hours, and 20.6 hours following rainfall initiation (Table 3). M15 riparian well response to rainfall was variable with initiation lags of 2 to 6 hours and lags-to-peak of 12 to 19 hours (Figure 3a and Table 3). Hillslope wells located in the M15 catchment reflected temporal dynamics observed at the gauged hillslope. M15 catchment runoff response to rainfall was rapid (initiation within 1.7 hours) and peaked 20.1 hours following rainfall initiation. Riparian positions in the M15 (2.6 ha)

Table 3. Hydrological Response Timing[a]

Site	Lag From First Rainfall, hours	Lag to Peak Response, hours
M15 WC1 (deep)	6.8	10.7*
M15 WC2 (middle)	11.7	11.8*
M15 WC3 (shallow)	3.2	20.6*
M15 catchment runoff	1.7	20.1
K WC1 (deep)	*	*
K WC2 (middle)	7.0	11.5*
K WC3 (shallow)	7.0	15.6*
K catchment runoff	3.4	20.3
HSLP WC1 (deep)	11.0	11.0*
HSLP WC2 (middle)	12.0	21.3
HSLP WC3 (shallow)	12.0	21.0
Gauged hillslope runoff	12.3	20.7

[a]Asterisk indicates saturation.

Table 4. DOC Export and Runoff Ratios[a]

Location	Area, ha	Runoff, mm	Hillslope Area, ha	Riparian Area, ha	Runoff Ratio	DOC Export, kg/ha (Kilograms Total)	Hillslope DOC Export, kg/ha (Kilograms Total)	Riparian DOC Export, kg/ha (Kilograms Total)
First-order M15 catchment	2.64	41.8	2.58	0.06	0.57	4.4 (11.64)	1.14–1.86 (2.94–4.8)	114–145 (6.84–8.7)
Second-order K catchment	16.9	39.4	16.38	0.52	0.55	4.65 (78.59)	1.1–1.7 (17.44–28.14)	97–118.2 (50.45–1.15)
Hillslope T11-hollow	0.0285	28.06			0.5	1.86 (0.053)		
Hillslope T8-planar	0.0055	18.31			0.33	1.14 (0.0063)		

[a]Ranges of observed hillslope DOC export included in calculations. Note that individual trough runoff ratios are suspect due to difficulties in upslope area determination on relatively planar hillslopes as described by *Woods and Rowe* [1996], *McDonnell* [1997], and *McGlynn et al.* [2002].

catchment exhibited persistent water tables (Figure 3a) and high preevent moisture conditions in the unsaturated zone of the soil profile (Figure 5b). As a result, riparian zone response to rainfall and subsequently catchment runoff was rapid (Table 3 and Figures 4b and 5a), although still lagging rainfall slightly.

[34] In the 16.9 ha K catchment, riparian moisture conditions were monitored with 2 nests of recording water content probes and 9 riparian wells (Figure 1c). In addition, wells were located in hillslope positions for corroboration with gauged hillslope runoff dynamics (Figure 3b). Deep soil positions in the K riparian zone were saturated prior to the onset of rainfall. Middle and shallow riparian soil profile positions were within 10% of saturation (Figure 5c). Middle and shallow water content probes responded coincidentally to rainfall with lags of 7 hours. The middle profile position exhibited saturation with a lag of 11.9 hours and the shallow profile position was saturated after 15.6 hours. Once saturation was achieved throughout the K riparian soil profile, it persisted throughout the event study period (Figure 5c). The K catchment storm runoff initiation lagged rainfall by 3.4 hours and peak runoff was lagged 20.3 hours (Figure 2c and Table 3).

[35] M15 catchment (2.6 ha) riparian positions and runoff responded most quickly to rainfall, followed by riparian positions and runoff in the K catchment (16.9 ha), and later followed by hillslope positions and runoff (Figure 2 and Table 3). This suggests a riparian and channel control of early portions of the event hydrograph in both catchments as a result of 1-D infiltration of direct rainfall and through flow initiation in riparian zones and direct channel precipitation (Figure 5). Once soil moisture deficits were satisfied on the hillslope, water tables developed, and runoff from hillslope zones into riparian zones and directly into the channel in both catchments was initiated (Figures 2, 3, and 5 and Table 3). The timing of riparian zone and hillslope zone responses and contributions to catchment runoff is revealed in the hysteretic nature of hillslope runoff to catchment runoff (Figure 6, top inset), riparian zone runoff to catchment runoff (Figure 6, bottom inset), and most clearly in riparian zone to hillslope zone runoff (Figure 6). The hysteresis plots were derived from flow-based hydrograph separations as described in the methods section and by McGlynn and McDonnell (submitted manuscript, 2002) (Figure 7). Monitored hydrological response at multiple spatial scales suggested that threshold runoff responses, temporally variable DOC sources, and hysteresis in catchment runoff sources might partially explain observed catchment DOC dynamics. However, questions remained about the relative distribution of hillslopes and riparian zones and the nature of catchment area accumulation. Landscape analysis was therefore necessary to further constrain the causal factors of DOC export patterns.

4.6. Landscape Analysis

[36] Both the M15 and K catchments show comparable distributions of local hillslope area inputs to the stream network [*McGlynn and Seibert*, 2003]. However, the K catchment is more than 6 times larger than the M15 catchment. In the headwater M15 catchment and in headwater portions of all Maimai catchments, hillslope area accumulation is maximized, due to convergent topography, while riparian area at the channel heads is minimal, due to steep side slopes and steep channel bed slopes. This means that in headwater reaches, hillslope area is focused through narrow near stream riparian zones, as shown in Figure 8, where near the origin of the figure, hillslope area is accumulated rapidly in sub-2.5 ha headwaters where riparian area is accumulated more slowly. Riparian area is concentrated toward the K (16.9 ha) catchment outlet, where the catchment valley bottom widens (Figures 1 and 2). The transition to a higher rate of riparian area accumulation occurs at a catchment scale of 10–12 ha. In these lower catchment reaches (>12 ha), hillslope area continues to be accumulated at a constant rate, following the higher rate of accumulation in the channel head regions. This results in a greater riparian to hillslope area ratio in the K catchment with locally higher ratios concentrated in lower stream reaches, even though headwater reaches in the K catchment and the M15 catchment show similar ratios. Landscape analysis of hillslope area inputs and local riparian area along the stream network in the K catchment suggests that although the total riparian area in the K catchment is relatively large (compared to the M15 catchment), 30% of the catchment area is accumulated in sub-3 ha catchments. 60–70% of the K catchment area accumulation occurs along stream reaches with greater local riparian to hillslope area ratios. The physical attributes of the two catchments suggest that runoff DOC variability between the catchments may be attributable partially to landscape morphology, structure, and the distribution of these hillslopes and riparian zones.

5. Discussion

[37] The solute dynamics (especially DOC) observed at catchment outlets have typically been ascribed to 1-D water table dynamics across the entire catchment. We suggest that mixing of spatial sources of catchment runoff might provide an alternative hypothesis to 1-D water table control of catchment runoff solute dynamics, especially DOC [*Horn-*

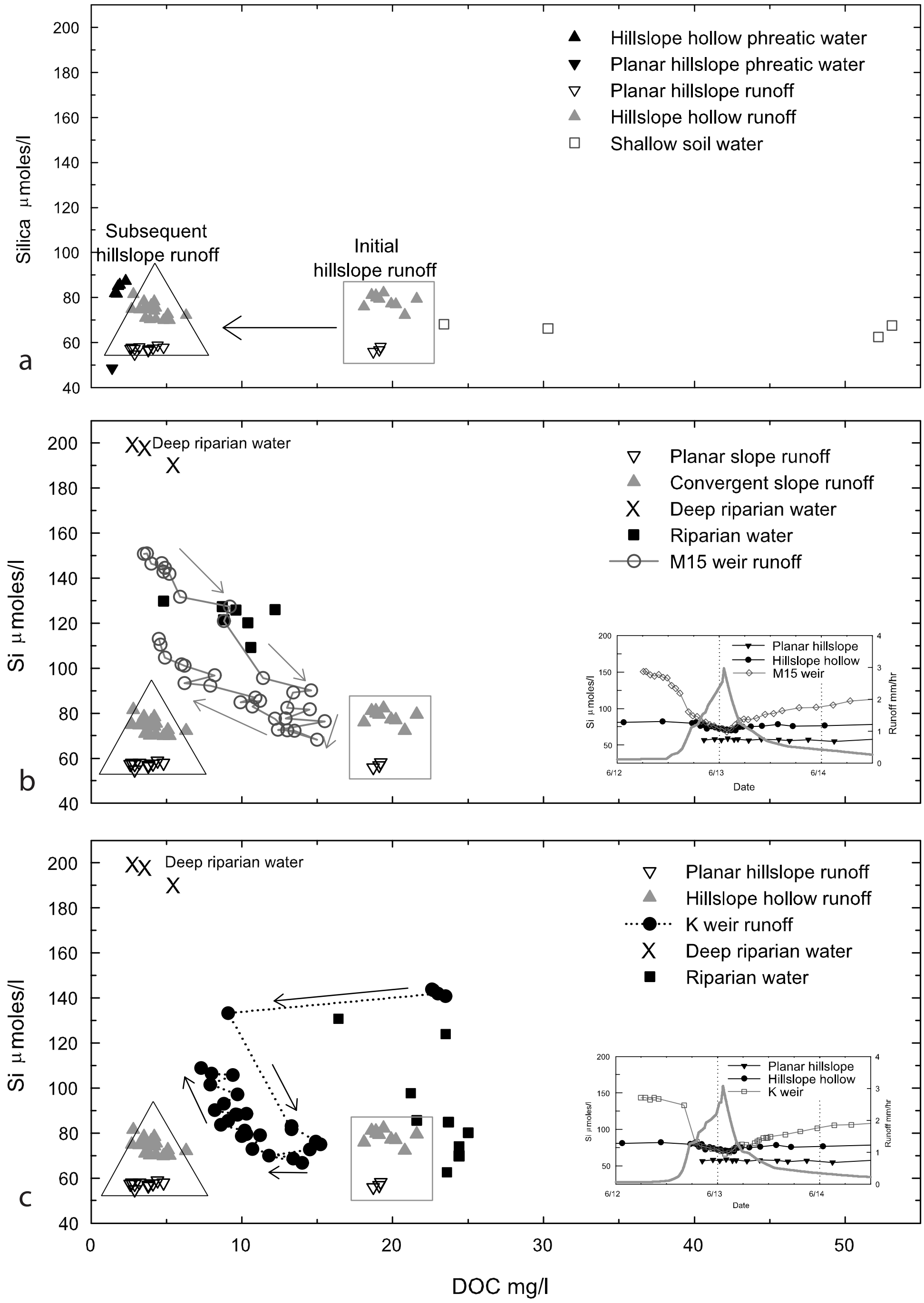

Figure 4. (a) Bivariate mixing plot of gauged hillslope runoff and end-member DOC concentrations. Note decrease in runoff DOC concentrations through the rainfall event (arrows). (b) Bivariate mixing diagram of M15 catchment runoff and end-member DOC concentrations through time (arrows). Inset chart shows the M15 catchment runoff signature convergence on hillslope runoff silica concentrations. (c) Bivariate mixing diagram of K catchment runoff and end-member DOC concentrations through time (arrows). Note high initial K catchment runoff DOC and rapid shift toward M15 catchment riparian water and runoff signatures and subsequent coincident tracking of M15 catchment runoff DOC. Inset chart demonstrates K catchment runoff signature convergence on hillslope runoff silica concentrations.

berger et al., 1994; *Boyer et al.*, 1996], nitrate [*Creed et al.*, 1996], and silica [*Hornberger et al.*, 2001; *Scanlon et al.*, 2001]. In areas where landscape unit response to precipitation is variable [*Boyer et al.*, 1997], or landscape organization results in travel time variability among areas with distinct solute signatures, or where connections/disconnections between landscape units occurs, the mixing of distinct source waters might explain solute dynamics observed at the catchment outlet.

[38] Our findings suggest that sequencing of spatial sources of runoff explains DOC and silica solute dynamics at the Maimai catchments. We found riparian runoff dom-

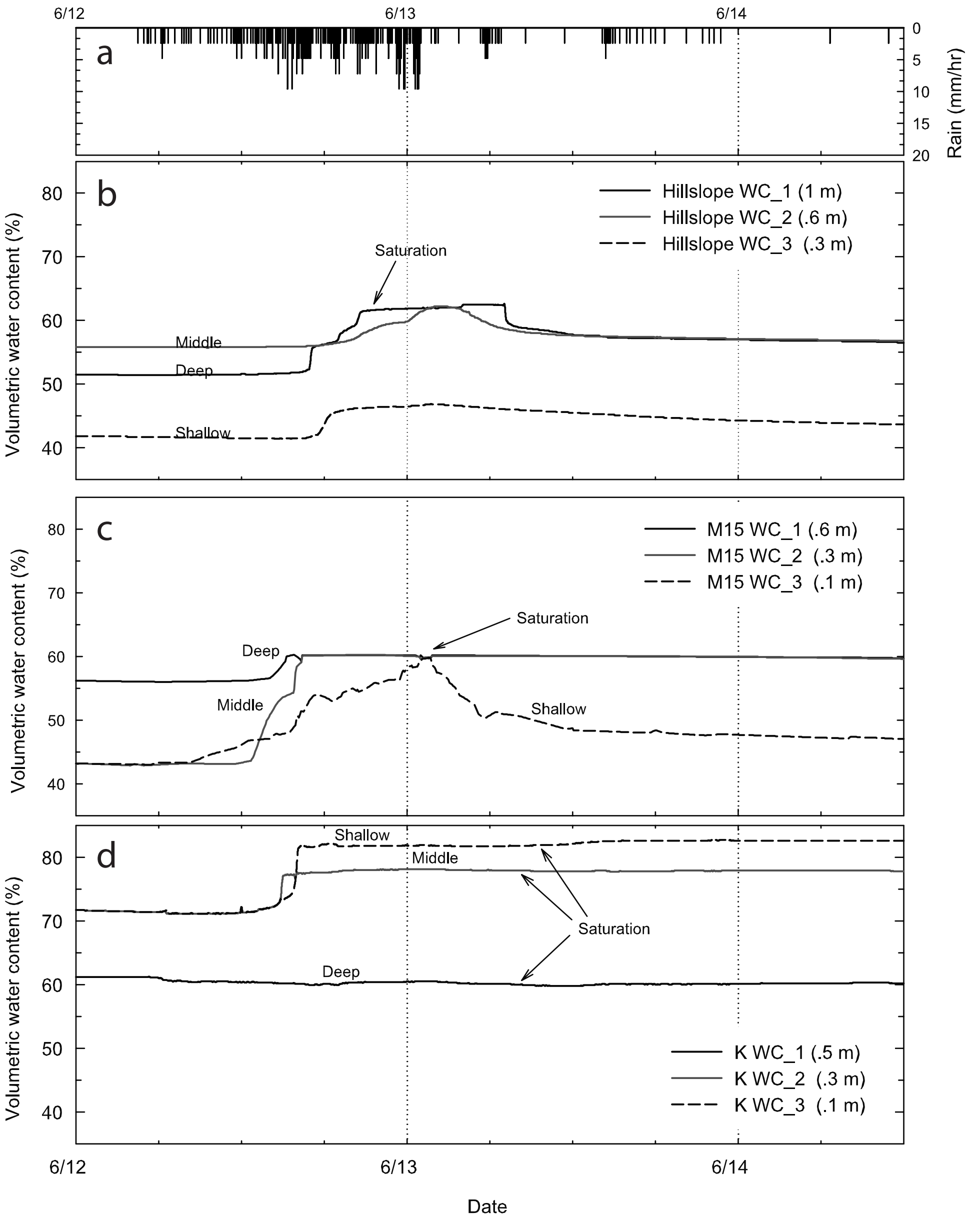

Figure 5. (a) Event rainfall, (b) water content response at the gauged hillslope nest, (c) M15 riparian zone nest, and (d) the K catchment riparian zone nest.

inance of early portions of the event hydrograph. Once hillslope runoff began, initial hillslope runoff, a second source of high DOC, contributed to the rising limb of the storm hydrograph. Falling limb catchment runoff was dominated by low DOC hillslope runoff. Our results help explain the higher concentrations of DOC on the rising limb than falling limb of storm hydrographs across Maimai catchments observed by *Moore* [1989]. We did not find evidence to suggest that 1-D water table dynamics over the entire watershed might control solute dynamics and hysteresis observed at each catchment outlet. Furthermore, we did not find evidence of DOC flushing at the hillslope scale; rather, organic horizon - deeper matrix water mixing proportions and preferential/bypass flow appeared to control DOC dynamics. Hillslope through flow DOC dynamics were not positively correlated to upslope water table height. On the event timescale, the labile organic horizon DOC supply was infinite (not exhausted), as demonstrated by temporally consistent shallow lysimeter DOC concentrations measured on the hillslope and in the riparian zone throughout the event. We cannot rule out DOC flushing as a mechanism that operates through successive large storm events or at seasonal timescales, however, we found no evidence at the event timescale.

5.1. Mechanisms of DOC Transport and Sources of Catchment Runoff DOC

[39] The initial rainfall driven runoff from the gauged hillslope consisted mostly of O-horizon water until a water table developed on the hillslope; we then observed a step shift decrease in DOC concentrations and a greater proportion of deep matrix water. The step shift in hillslope runoff DOC concentrations can be explained by one of two mechanisms. The first mechanism is the hydrological

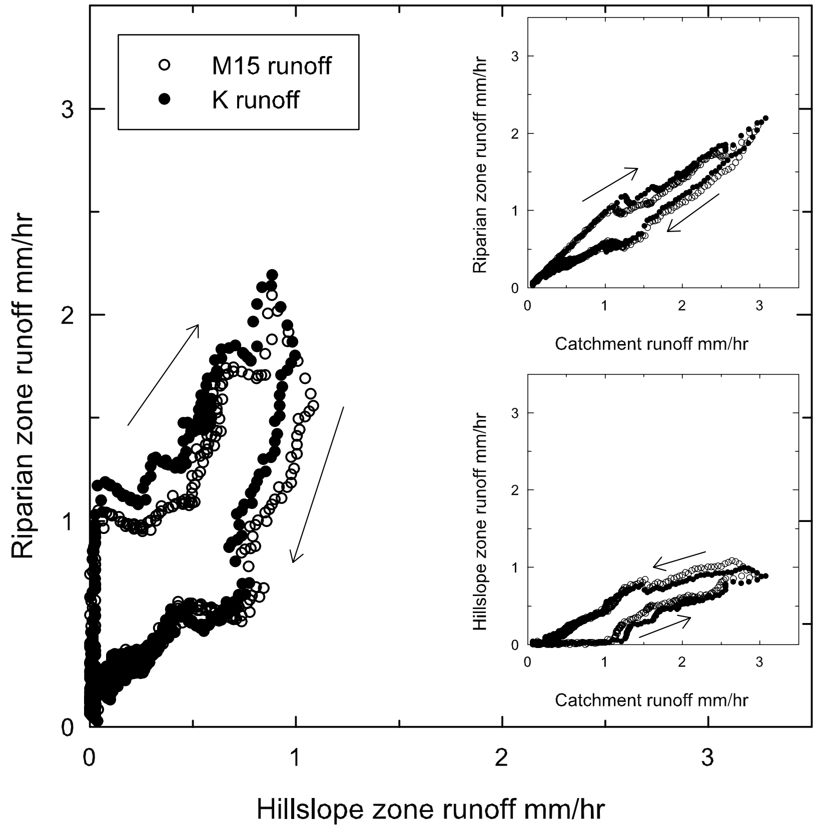

Figure 6. Bivariate plots of riparian zone versus hillslope zone runoff, hillslope zone versus catchment runoff (top inset), riparian zone versus catchment runoff (bottom inset) for catchments M15 and K based on hydrological hydrograph separations (Figure 7).

mechanism postulated by *McDonnell* [1990], whereby infiltrating rainfall flows through the O-horizon and perches at the B-horizon interface, exploits vertical cracks and root channels, and moves vertically to the base of the soil profile and then laterally downslope along the soil-bedrock interface. This mechanism has been observed since 1990 in Canada [*Peters et al.*, 1995], Japan [*Tani*, 1997], and the USA [*Freer et al.*, 2002]. This mechanism suggests that preferential flow could have supplied DOC-rich water to the base of the soil profile. Eluviated zones and root channels at the soil-bedrock interface could have promoted rapid lateral transmission of DOC-rich water to the trench face with little matrix interaction. Once the supply of water to the soil-bedrock interface exceeded lateral transmissivity, a water table would have developed (backed up into the soil profile) on the hillslope and the proportion of matrix water in hillslope runoff would have increased markedly, resulting in the observed step shift in DOC concentrations.

[40] A second mechanism could also explain the observed hillslope through flow DOC pattern. Flushing of a finite source of labile DOC from the organic 0.17 m of the upper soil profile could result in the same DOC concen-

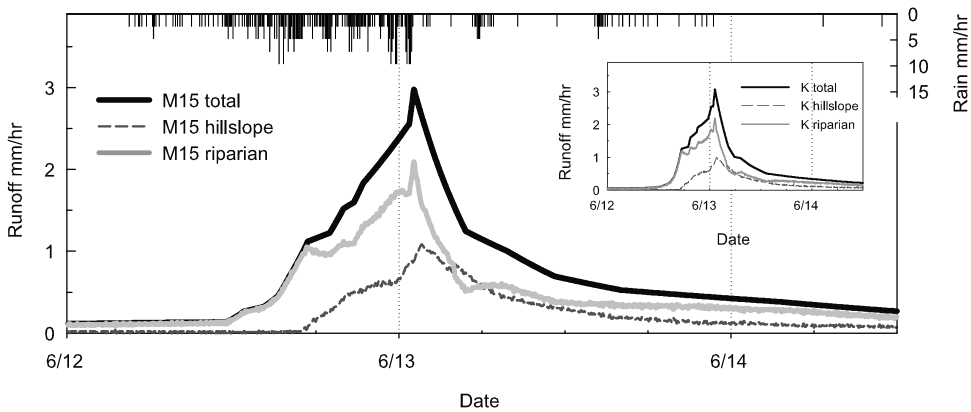

Figure 7. Hydrological hydrograph separations of M15 and K (inset) catchment runoff into hillslope zone and riparian zone components based on gauged hillslope runoff rates.

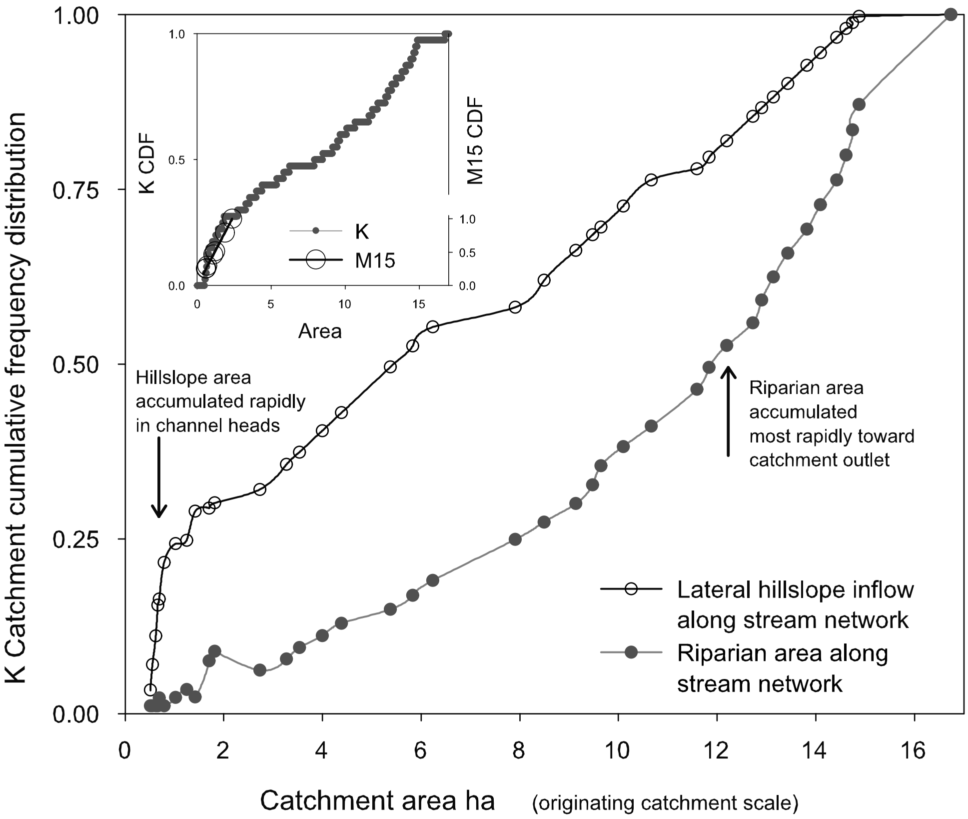

Figure 8. Cumulative frequency distributions (CDFs) of hillslope and riparian areas as a function of originating catchment scale in the K catchment. Note rapid hillslope area accumulation in upper headwaters and most rapid riparian area accumulation toward the catchment outlet. Inset graph compares rates of area accumulation in the M15 and K catchments. Note that they are nearly identical at comparable catchment scales.

tration pattern observed at the trench face. The supply of DOC would have to be finite to produce the observed step shift in hillslope runoff DOC concentrations. However, consistently high shallow lysimeter DOC concentrations observed throughout the event would preclude flushing of a finite shallow DOC source mechanism. A related mechanism sometimes referred to as flushing, whereby a rising hillslope water table intersects high DOC in shallow soils, would result in a positive relationship between hillslope runoff, hillslope water tables, and DOC concentrations. Our results, however, do not support this alternative flushing mechanism. DOC was not positively correlated with hillslope runoff nor was it positively correlated to rising water tables.

[41] Research by *Moore* [1989] supports both the infinite shallow DOC source conclusion and the mechanism postulated by *McDonnell* [1990]. The δ^{18}O data collected for this event showed only minor isotopic separation between old and new water. Notwithstanding, *McDonnell et al.* [1998], *McGlynn et al.* [2002], McGlynn et al. (submitted manuscript, 2002), McGlynn and McDonnell (submitted manuscript, 2002), all found little (<10%) new water in hillslope runoff. Therefore it is unlikely that dilution of soil water by rainfall could account for the observed pattern in DOC concentrations.

[42] Two flow paths might account for the delivery of high DOC water source to the trench face: perched lateral flow in the organic/litter layer of the soil profile and preferential/bypass flow vertically to the bedrock interface and then laterally downslope. Flow though the soil matrix alone cannot explain the volume of high DOC water in initial hillslope runoff due to high adsorption rates and capacities in the mineral soil matrix [*Moore*, 1989]. We cannot rule out either perched shallow flow or preferential flow; however, we present the available data and postulate a likely flow regime (described below) based on this data, historical research at Maimai (reviewed by *McGlynn et al.* [2002]), and observations at other research sites around the world [*Peters et al.*, 1995; *Tani*, 1997; *Newman et al.*, 1998; *Hill et al.*, 1999; *Buttle et al.*, 2001].

[43] Soil water content probe data from the hillslope nest upslope of T11 suggested bypass flow of water to depth in the soil profile (Figure 5a). The deepest water content probe located near the soil-bedrock interface responded ahead of shallow and mid-profile water content probes, indicating bypass flow of water past the upper and mid-soil matrix to deep soil positions. The shallow water content probe responded after the deepest probe, indicating downward matrix wetting front propagation concurrent with preferential/bypass flow to depth. The delayed and damped mid profile water content probe response further indicated bypass of the soil matrix by a portion of the wetting front via preferential flow and the slower movement of the matrix wetting front. Furthermore, previous research by *McDonnell* [1990] supports the bypass flow to depth mechanism in Maimai hillslopes where water was found to be transmitted

vertically by macropores and vertical cracks, and then laterally along eluviated zones at the soil-bedrock interface. Numerous studies on the Canadian Shield area of Ontario, Canada have observed and described bypass flow to depth and lateral flow downslope at the soil-bedrock interface [*Peters et al.*, 1995; *Hill et al.*, 1999; *Buttle et al.*, 2001]. In this study, as the water table backed up into the soil matrix with increasing soil profile wetness, as described by *McDonnell* [1990], bypass flow of high DOC shallow soil source water would be diluted by low DOC water from the lower soil profile matrix. This occurred as water tables developed on the hillslope and runoff rates increased. Our observations indicate that early hillslope runoff contained high concentrations of DOC. DOC concentrations rapidly shifted toward more dilute concentrations (Figure 2a) as saturation was achieved in the soil profile, water tables developed on the hillslope, runoff rates became elevated, and total runoff volume increased.

[44] These DOC findings at the hillslope scale help resolve the hillslope runoff process by corroborating the observed hydrology. The proportions of shallow soil water and deep soil water in hillslope runoff shift through the event. Shallow soil water contributes proportionately more water early in the runoff hydrograph while deeper matrix soil water contributes proportionately more as water tables build and the event progresses. Without the DOC tracer, we could not have observed the interplay between shallow soil water and deeper matrix water during a storm event. The hillslope does not exhibit DOC flushing; rather, shifting proportions of source water and early preferential flow vertically and laterally along the soil bedrock interface appear to control the observed runoff concentration patterns.

[45] We found no evidence that riparian zones exhibit DOC flushing. Riparian zone lysimeters showed relatively stable DOC concentrations. Flushing is a term used to describe two often-related mechanisms. One refers to the flushing of a limited supply of DOC resulting in decreased DOC concentrations through single or successive events [*Boyer et al.*, 1997] and a second to rising water tables intersecting with DOC or N-rich shallow soils [*Creed et al.*, 1996]. The occurrence of either type of flushing can result in increased concentrations on the rising limb and peak of the discharge hydrograph and lower concentrations on the falling limb. Our evidence from intensive hillslope soil water and through flow monitoring and riparian observations do not demonstrate either flushing mechanism. If one considered catchment outflow DOC concentrations alone, it would not be possible to differentiate between causal mechanisms of DOC dynamics. DOC flushing was not the mechanism responsible for observed DOC dynamics in this study; rather, the temporally dynamic mixing of spatial sources of runoff controlled the observed DOC patterns in runoff at the hillslope scale and at the 2.6 ha and 16.9 ha catchment scales.

5.2. Sources of Catchment Runoff

[46] The 2.6 ha M15 catchment is comprised of a collection of hillslope units (comparable to the gauged hillslope), a narrow riparian zone (2% of catchment area), and a well-scoured high-gradient stream channel (Tables 1 and 2). The high runoff ratio (0.57) indicates that areas outside of the narrow riparian zone contributed sizable amounts of runoff to the hydrograph due to the small relative volume of water stored in the riparian zone (2% of the catchment soil volume) and the limited area capable of generating saturation excess overland flow.

[47] The 16.9 ha K catchment is a collection of M15-like catchments with additional wider valley bottom riparian zones, increasing in width toward the catchment outlet. The headwaters of the K catchment contain high gradient scoured stream channels similar to those in the M15 catchment; however, longitudinal gradients decrease downstream toward the catchment outlet, where debris dams and in-channel organic accumulation become more common. Overall, the riparian zone in the K catchment comprises 3% of the catchment area, with greater proportions in lower catchment sections. Despite the slightly larger riparian zone in the K catchment, the runoff ratio (0.55) was similar to M15 and also indicates that areas outside of the riparian zone contributed sizable amounts of runoff to the hydrograph due to the small relative volume of water stored in the riparian zone (4% of the total catchment soil volume) and limited area for generation of saturation excess overland flow. Thus hillslope runoff was a significant contributor to catchment runoff in both catchments with slightly greater proportions of riparian runoff in the larger K catchment despite a slightly lower total runoff ratio (0.55 compared to 0.57). The runoff ratio disparity suggests slightly greater unfilled storage in the K catchment, possibly concentrated in the large riparian zone volume in the K catchment.

[48] Runoff rates from the gauged hillslope on a per unit area basis were in excess of riparian zone storage in both catchments. The M15 riparian zone was flushed with 7 pore volumes and the K catchment riparian zone was flushed with 3.4 pore volumes. Pore volume flushing rates assume volumetric water content of 50% for the riparian zone in each catchment, mapped riparian volumes for each catchment, and average hillslope area inputs along the channel network. Based on work by *McGlynn and Seibert* [2003], however, we know that hillslope inputs to the channel network are highly variable and a distributed measure of riparian to hillslope area or volume ratios along the channel network are more informative than bulk catchment ratios and likely control hillslope water expression in catchment runoff. The relative proportions of riparian zone and hillslope zone runoff in total catchment runoff were estimated using a flow-based hydrograph separation technique (McGlynn and McDonnell, submitted manuscript, 2002) and indicated that riparian zones formed the majority of catchment runoff throughout the event, with highest riparian proportions early in the event hydrograph and in late recession periods (Figure 7). Hysteresis in the relationship between hillslope zone runoff and catchment runoff was counterclockwise demonstrating greater hillslope contributions on the falling than on the rising limb of the catchment hydrographs (Figure 6). Riparian runoff hysteresis was opposite (clockwise), with greater riparian zone runoff on the rising than falling limb of the catchment hydrographs (Figure 6, top inset). The relationship between riparian zone runoff and hillslope zone runoff (Figure 6, bottom inset) shows the relative proportions of riparian and hillslope runoff over the event and the greater proportion of riparian

zone runoff throughout most of the event (except for a short period on the falling limb). Riparian runoff was most dominant in both catchments on the rising limb of the storm hydrograph. The high DOC in the wide K riparian zone and the low DOC in the narrow M15 riparian zone controlled differences in base flow and rising limb catchment DOC concentrations.

[49] The K catchment shows a step shift in runoff DOC concentrations (Figure 2c) because the initial catchment runoff is comprised primarily of lower catchment riparian and stored channel water rich in DOC where differences between the catchments are most pronounced. The M15 catchment lacks the greater riparian zone development and organic accumulation present at larger catchment scales. Once greater proportions of the K catchment contributed to runoff directly (headwaters), DOC concentrations between the catchments became coincident, highlighting the temporally limited role of lower valley riparian zones in the K catchment.

5.3. Landscape Unit Hydrologic Connections and Disconnections

[50] Our observations of a delayed threshold response in hillslope runoff in addition to near-stream and in-channel dominance of the tails of the storm hydrograph suggest that there is a disconnection between riparian zones and hillslopes between events and during early portions of large events. There was a tighter connection between hillslope runoff and catchment runoff and greater expression of nonriparian water once hillslope soil moisture deficits were satisfied. Hillslope water then contributed to catchment runoff directly, resulting in increased DOC on the rising limb due to initially high hillslope runoff DOC, and lower concentrations at peak runoff and on the falling limb of the catchment hydrograph due to decreased hillslope runoff DOC.

[51] We observed the effect of the sequencing of landscape unit contributions to runoff (Figures 7 and 8) on DOC dynamics. Runoff source areas shift through the event and their associated DOC concentrations control outflow DOC dynamics through time. The impact of the disparity between the riparian zone extent in the M15 and K catchments was most pronounced early and late in the storm flow period when riparian zone runoff was proportionately greatest. At Maimai, catchment scale and landscape organization are tightly coupled [*McGlynn and Seibert*, 2003; McGlynn et al., submitted manuscript, 2002]. The nature of catchment area accumulation shifts in a downstream direction. Hillslope inputs to the stream are relatively constant in space in the M15 and K catchments; however riparian widths increase downstream. For example, the M15 and K catchment headwaters are both characterized by highly convergent topography, high hillslope inputs to the channel network, and narrow riparian zones. In a downstream direction as catchment scale increases, hillslope inputs are consistent (albeit variable), while riparian widths increase linearly with scale [*McGlynn and Seibert*, 2002]. As a result, the relative role of the riparian zone increased with catchment size. However, the impact of the larger riparian zone toward the K catchment outlet was limited to base flow and early portions of the storm hydrograph. Once greater proportions of each catchment were contributing to runoff, including headwater areas and hillslopes, runoff from headwater positions and hillslopes dominated the runoff response and signature of both catchments.

5.4. A Method for Constraining Equifinality in Catchment Outflow Observations With Internal Catchment Dynamics

[52] Convergence of conclusions based on local hydrometric dynamics, flow-based hydrograph separation results, and solute mixing diagram approaches is a powerful way to constrain a conceptual model of DOC dynamics. These data show unambiguously that the sources of runoff and associated solutes changed over the course of the storm event. The isolation of runoff from different landscape units and characterization of associated solute export was necessary to distinguish between spatial sources of storm flow. As a result, we were able to observe that hillslope runoff concentrations were temporally variable, despite relatively consistent well and lysimeter concentrations through time. We were also able to produce runoff and DOC export budgets for the M15 and K catchments, quantifying the amount of DOC contributed by riparian zones and hillslope zones in each catchment (Table 4). Differences in the size and organic composition of riparian zones controlled the disparity in the catchment DOC budgets. Differences in riparian zone characteristics between the catchments were most apparent on the rising and later recession portions of the storm hydrograph—when proportions of catchment runoff contributed by near stream areas were greatest. When hillslope runoff was observed, DOC, silica, and runoff responses in both catchments were coincident, due to the large proportion of hillslope area in both catchments and the limited riparian reservoirs.

[53] Landscape analysis and discretization provide valuable insight into the relative roles of dominant landscape units in controlling catchment hydrology and solute export. The first step toward evaluation of the roles of landscape units in catchment runoff is recognition that dominant landscape units exist and that governing hydrological and geochemical processes may vary between different units. Incorporating this newfound understanding into a model structure that takes advantage of this landscape similarity provides a possible way forward for performing plot scale research in a landscape context and for scaling-up plot scale research to the catchment or mesoscale.

6. Conclusions

[54] We found markedly higher preevent and early hydrograph rising limb DOC concentrations in the 16.9 ha K catchment than in the 2.6 ha M15 catchment. We suggest that differences in landscape organization, stream gradient, channel organic accumulation, riparian zone extent, and riparian zone to hillslope area and volume ratios between the two catchments accounted for higher DOC concentrations in the larger 16.9 ha K catchment on the tails of the hydrograph, especially at preevent base flow and on the rising limb of the event hydrograph. Once hillslope runoff was a major contributor to storm runoff, both catchments responded with coincident DOC concentrations, reflecting the influence of the major landscape unit in both catchments (hillslope zones). Hillslope runoff was a mix-

ture of shallow high DOC organic soil water and deep low DOC mineral soil water. A rapid shift in source proportions from shallow to deep soil water on the rising limb of the hillslope through flow hydrograph was evident in both convergent and planar hillslope sections, and resulted in nearly 4-fold dilution of DOC concentrations. We found that hillslope runoff did not exhibit hysteresis in the runoff-DOC relationship, nor did a positive relationship exist between DOC concentration and runoff. Our results indicate that catchment DOC dynamics reflect the mixing of geographic streamflow source waters at the catchment outlet. At the Maimai catchments, changing proportions of riparian and hillslope water contributions to catchment runoff can explain DOC concentration patterns in catchment storm runoff. Initially elevated DOC concentrations in hillslope runoff and the higher proportion of riparian water on the rising limb of the hydrograph partially explain the positive correlation between DOC and catchment runoff as well as the hysteresis in the catchment runoff-DOC relationship. We suggest that the relative timing of riparian and hillslope source contributions, connections and disconnections of dominant runoff contributing areas, as well as the internal dynamics of these zones, are a first order control on catchment DOC concentrations and mass export at Maimai and perhaps other watersheds.

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