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Storm pulses of dissolved CO_2 in a forested headwater Amazonian stream explored using hydrograph separation

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[1] Dissolved CO_2 dynamics in stormflow and event water versus preevent water contributions to storm hydrographs were assessed in a forested headwater catchment of the Brazilian Amazon using high-frequency data. We applied the transfer function hydrograph separation model (TRANSEP) using specific conductance as a conservative tracer, finding preevent water to average 0.79 ± 0.03 of storm discharge (mean $\pm$ 1 SE for $n = 14$ storms). In situ, direct measurements of dissolved CO_2 were able to capture new hydrobiogeochemical processes in real time, including CO_2 pulses observed on the falling limb of storm hydrographs, the magnitudes of which were inversely related to preevent water fractions ($r = -0.97$, $p < 0.0001$).

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1. Introduction

[2] Stormflow in a range of small temperate zone catchments has been shown to be predominantly composed of preevent water that is stored in catchments prior to precipitation events [*Buttle*, 1994; *Genereux and Hooper*, 1998; *Kirchner*, 2003]. Also referred to as ''old'' water, this preevent water exhibits a chemical or isotopic signature that is similar to water stored in a catchment prior to a precipitation event. In temperate zone hydrology, differences between $\delta^{18}O$ values in preevent and event water have frequently been used as a conservative tracer of hydrologic flow paths for hydrograph separation [*Genereux and Hooper*, 1998; *Weiler et al.*, 2003].

[3] The preevent water contribution to stormflow in the lowland tropics has received relatively little attention relative to temperate watersheds [*Burns*, 2002], in part due to physical constraints to the applicability of ^{18}O. That is, storm trajectories in lowland tropical systems may not result in a $\delta^{18}O$ signal for event water that differs significantly from preevent water because recycling of soil water via evapotranspiration supplies a substantial portion of rainfall (cf. more than 50% of precipitation originates via soil water recycling in the Amazon [*Nobre et al.*, 1991]), thus limiting the applicability of isotopic hydrograph separation (IHS) for these systems. Nevertheless, the possibility that rapid catchment responses to precipitation in tropical lowland watersheds also convey ''old'' water to streams has been noted as a knowledge gap for hydrology [*Buttle and McDonnell*, 2005] and merits exploration.

[4] We have observed pulses of dissolved CO_2 in stormflow of forested headwater streams in the Amazon basin (Figure 1) using a novel method involving in situ deployment of an infrared gas analyzer (IRGA) in streams. As the CO_2 concentration of soil water is greatly in excess of the atmospheric CO_2 concentration equivalent for precipitation (e.g., event water), we hypothesized that increases in stream water CO_2 during a storm to concentrations above base flow concentrations prior to the storm demonstrate a preevent water contribution to stormflow. Direct use of dissolved CO_2 concentrations for hydrograph separation into event and preevent components however, is complicated by CO_2 dynamics within streams and within the watershed. Losses of CO_2 from the stream surface to the atmosphere due to outgassing [*Richey et al.*, 2002], as well as in-stream CO_2 production from organic matter processing via respiration [*Mayorga et al.*, 2005] and photo-oxidation [*Anesio et al.*, 1999] violate the mass balance requirements for the use of CO_2 in hydrograph separation.

[5] Small streams are intimately connected with their catchments, and are significant conduits for the export of terrestrial carbon [*Hope et al.*, 2004]. As the quantity of CO_2 delivered to small streams is difficult to quantify and represents a major unknown in regional carbon budgets [*Cole et al.*, 2007], assessing terrestrial carbon fluxes to streams when they are at their most highly connected stage (e.g., during storm events) is of practical importance.

[6] There is growing consensus in the hydrologic community that effective hydrograph separation is incumbent on the use of detailed hydrochemical data in conjunction with hydrometric data [*Burns*, 2002; *Buttle*, 2001]. This approach has proven useful in the lowland humid tropics as

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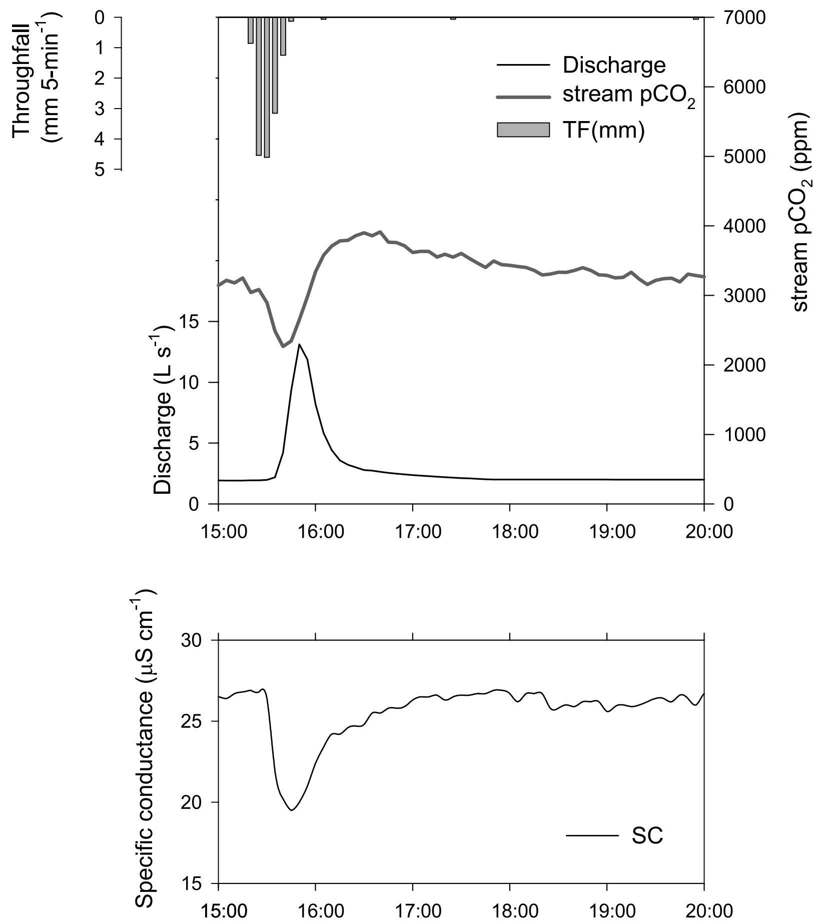

Figure 1. (top) Measured throughfall, stream discharge, and dissolved CO_2 and (bottom) specific conductance (SC) for 31 March 2005 storm. Hydrometrics and water quality parameters were measured at 5-min intervals in forested headwater catchment, Juruena, Brazil.

well. For example, *Elsenbeer and Lack* [1996] present combined hydrometric and hydrochemical data demonstrating a significant event water contribution to stormflow for a lowland forested tropical headwater catchment.

[7] In this paper we describe preevent water contributions to lowland tropical storm hydrographs employing the transfer function hydrograph separation model (TRANSEP) using specific conductance as a conservative tracer. We then use this information to explore CO_2 pulses observed in stormflow and the relationships of the CO_2 pulses to storm characteristics.

2. Methods

2.1. Study Site

[8] The 2 ha study watershed is located in the seasonally dry southern Amazon near Juruena, Mato Grosso, Brazil (10°28′S, 58°28′W) at an elevation of about 250 m above sea level (m above sea level (a.s.l.)) on the Brazilian shield. The forested headwater catchment is organized as a series of landscape units from a nearly flat (<2% slope) upper plateau located above a steeper hillslope (20–40% slope), which gives rise to emergent groundwater and a perennial stream flowing through a narrow (<10 m) riparian zone with a closed canopy. Soils in the watershed are highly weathered and acidic, overlay Precambrian gneisses of the Xingu Complex [*Novaes Filho et al.*, 2007], and classify as a Plinthic Kandiustult in the USDA classification [*Soil Survey Staff*, 1999]. The mean annual precipitation (2200 mm a^{-1}) falls primarily during the 7-month rainy season (October–April); mean annual temperature in the region is 24°C [*Johnson et al.*, 2006].

2.2. Hydrometrics and Water Quality Data

[9] Stream discharge was measured using a recording capacitance probe upstream from a 90°V notch weir located at the watershed outlet. Rainfall and throughfall were measured using data logging tipping buckets. All parameters were recorded at 5 min intervals, and are described in more detail by *Johnson et al.* [2006]. Rainfall measurements were made in a clearing 2 km from the study watershed, but highly localized precipitation events resulting from convective precipitation forming over the nearby Juruena River precluded using the rainfall gauge to model rainfall-runoff behavior in the catchment. As such, throughfall data was utilized for assessing runoff responses to storm events in this study.

[10] We deployed a multiparameter sensor (Hydrolab DataSonde 4, Hach Environmental, Loveland, Colorado, USA) in the well-mixed zone upstream from the weir and

adjacent to the water level recorder, and recorded pH, dissolved oxygen, specific conductance and temperature at 5 min intervals. The sensor was deployed for 2-week periods on four occasions, and included deployments early in the rainy season, during the heaviest rains, and early in the dry season when storm frequency is low but stream responses remain rapid. The sensor was calibrated in the Juruena field lab prior to deployments, and was checked for sensor drift and changes in offsets following field deployments.

[11] Dissolved CO_2 was measured continuously in situ using an infrared gas analyzer (IRGA) modified for deployment in aquatic systems as described in *Johnson et al.* [2006], and submerged in the main channel upstream of the weir. Briefly, the IRGA uses a single-beam dual-wavelength, nondispersive infrared (NDIR) silicon-based sensor (Vaisala GMT221, Vantaa, Finland), and was protected within a high-porosity PTFE sleeve (International Polymer Engineering, Tempe, Arizona, USA). The sleeve, which is highly permeable to CO_2 but impermeable to water, allows dissolved CO_2 to equilibrate with the headspace of the IRGA. Response time of the IRGA is 30 s (Vaisala GMT220 series user guide, Vantaa, Finland).

[12] Dissolved CO_2 concentrations in stream water were recorded at 5 min intervals. We assessed the measurement accuracy for this method in comparison to dissolved CO_2 determined by gas chromatography following headspace equilibration [*Billett et al.*, 2004; *Kling et al.*, 1991], and found it to fall within the manufacturer stated accuracy for this IRGA (±280 ppm CO_2 for dissolved CO_2 concentrations in present study).

2.3. Transfer Function and Hydrograph Separation Model (TRANSEP) Application

[13] TRANSEP is a quantitative approach to analyze the temporal variability in stormflow components of event water and preevent water by describing the residence time of solute transport and the transmittance of hydraulic behavior of catchments [*Weiler et al.*, 2003]. The model was designed to be usable for a range of tracers, and includes a nonlinear module to simulate an effective precipitation time series on the basis of the approach of *Jakeman and Hornberger* [1993], and a linear module that incorporates the effective precipitation and a runoff transfer function to produce the rainfall-induced runoff response of the catchment [*Weiler et al.*, 2003]. Several transfer functions can be implemented within TRANSEP, though the two linear parallel reservoirs (TLPR) transfer function was found to perform best in previous applications of TRANSEP [*Weiler et al.*, 2003]. In the present example we also utilized the TLPR transfer function.

[14] Specific conductance in precipitation has been shown to be relatively constant at seasonal scales in the Amazon [*Nepstad et al.*, 2002; *Williams and Fisher*, 1997]. We used it as a tracer that can be considered conservative for the very short event duration in application of the TRANSEP model. At base flow in the study catchment, specific conductance increased approximately fourfold within the headwater stream in all seasons, from 12 ± 1 $\mu S\ cm^{-1}$ in emergent groundwater to 53 ± 3 $\mu S\ cm^{-1}$ at the watershed outlet (means ± 1 SE). In stormflow however, specific conductance varied systematically at the watershed outlet, becoming more dilute on the rising limb of the hydrograph and returning to near–base flow concentrations on the falling limb of the hydrograph (Figure 1, bottom plot).

[15] We applied TRANSEP to 14 storms occurring during wet and dry seasons in the Brazilian Amazon for storm events ranging in size from 2.4 to 30.7 mm (mean event size = 13 mm), and ranging in duration from 15 to 135 min (mean storm duration = 60 min). Model output was evaluated against measured parameters using Nash-Sutcliffe efficiency, eff_{NS}, [*Nash and Sutcliffe*, 1970], where an eff_{NS} value of 1 indicates a perfect model fit to measured values.

3. Results

3.1. TRANSEP-Based Hydrograph Separation

[16] We analyzed 14 storms (11 rainy season and 3 dry season storms) for preevent water and event water contributions to stormflow using TRANSEP. The model performed well for the tropical headwater catchment studied, with average eff_{NS} model efficiency of 0.91 for simulated discharge relative to observed, and eff_{NS} = 0.61 for simulated concentration relative to observed (Table 1).

[17] Preevent water accounted for 0.79 ± 0.03 as a fraction of stormflow (mean ± 1 SE for n = 14 storms). The preevent water fraction was also found to decrease linearly with event size ($r = -0.59$, $p = 0.02$). The smallest storm analyzed, 2.4 mm, corresponded to a storm hydrograph almost entirely composed of preevent water (preevent water fraction of 0.95, the highest of all analyzed storms). The storm hydrograph with the smallest preevent water fraction, 0.52, was produced by a large (28 mm) event characterized by average intensity but long duration (135 min).

[18] Within-storm measured and modeled results are presented in Figure 2 for a representative (31 March 2005) storm. Simulated stormflow and stream water values for specific conductance showed good agreement with measured values throughout the event. The amount of throughfall that corresponded to stormflow discharge represents a minor fraction of measured throughfall (Figure 2), as reflected in the runoff coefficient for this storm (Table 1). The event water component of stormflow was found to be greatest on the rising limb of the hydrograph, and at peak flow represented nearly half of the storm discharge. Over the course of this storm, event water represented 25% of total stormflow, with preevent water comprising the remainder.

3.2. CO_2 Dynamics in Stormflow

[19] The dissolved CO_2 concentration in stream water was observed to increase on the falling limb of all storm hydrographs. These CO_2 pulses were always found to lag the peak storm discharge. The majority of storms analyzed also presented a decline in dissolved CO_2 concentration in stream water on the rising limb (cf. Figure 1). Taken together, these features of the dissolved CO_2 chemograph indicate (1) contributions early in the events from quick flow pathways that are low in CO_2 including direct precipitation/throughfall and overland flow, indicative of rapid event water contributions, and (2) later contributions from flow paths with larger CO_2 concentrations.

[20] The within-storm dynamics of the preevent water fraction was found to be in good agreement with the dissolved CO_2 dynamics in stormflow (Figure 3). Initially,

Table 1. Storm Parameters and TRANSEP Model Results for 14 Events in Forested Headwater Catchment Near Juruena, Brazil[a]

Event Date	TF, mm	Maximum Intensity, mm 5-min^{-1}	Duration, min	Runoff Coefficient, % Measured	Runoff Coefficient, % Simulated	Discharge eff_{NS}	Concentration eff_{NS}	Preevent Fraction, %	CO_2 Pulse,[b] %
28 Apr 2004	30.7	13.6	30	4.8	4.8	0.87	0.82	83	120
30 May 2004	20.0	5.5	45	3.7	3.7	0.85	0.63	90	108
26 Dec 2004	16.8	2.9	105	3.3	3.3	0.94	0.28	68	127
26 Dec 2004	5.0	0.4	80	3.2	3.2	0.98	0.69	92	102
27 Dec 2004	3.6	3.2	15	4.2	4.2	0.78	0.41	85	113
2 Jan 2005	27.8	3.7	135	5.9	5.9	0.89	0.84	52	143
2 Jan 2005	2.4	0.9	25	2.4	2.4	0.97	0.27	95	103
4 Jan 2005	10.7	3.5	35	4.2	4.2	0.87	0.57	70	124
6 Jan 2005	6.1	0.4	120	4.1	4.0	0.95	0.83	86	109
11 Jan 2005	14.6	4.4	45	4.0	4.0	0.88	0.59	74	126
12 Jan 2005	3.0	0.5	45	3.6	3.6	0.96	0.65	96	104
14 Jan 2005	11.1	3.4	50	4.6	4.6	0.88	0.48	74	121
17 Jan 2005	15.7	2.5	75	5.9	5.9	0.98	0.69	73	126
31 Mar 2005	14.5	4.6	25	5.9	5.8	0.94	0.82	75	125
Average	12.9	3.5	59	4.3	4.2	0.91	0.61	79	118
SD	8.9	3.3	38	1.1	1.1	0.06	0.19	12	12
SE	2.4	0.9	10	0.3	0.3	0.02	0.05	3	3

[a]TF, Throughfall; eff_{NS}, Nash-Sutcliffe efficiency.
[b]CO_2 pulse given as maximum concentration of dissolved CO_2 in stormflow as percentage of base flow concentration prior to event.

the preevent water contribution to streamflow declined as quick flow was delivered to the stream, which also diluted the concentration of dissolved CO_2 in the stream. As the preevent fraction of streamflow increased later in the event, the dissolved CO_2 concentration was seen to recover.

[21] Additionally, the dissolved CO_2 concentration on the falling limb of hydrographs was found to become augmented relative to prestorm base flow levels (Figures 1 and 3) as a pulse of CO_2 contributed to streamflow from different flow paths. Regression analysis found that the preevent water fraction of stormflow is strongly, though negatively, correlated with the magnitude of CO_2 pulses, which was calculated for each event as the maximum dissolved CO_2 concentration in stormflow as a percentage of prestorm CO_2 concentration in base flow (r = 0.97, p < 0.0001). This result was unexpected and is discussed later in the paper.

4. Discussion

4.1. Preevent Water in Tropical Stormflow

[22] The preevent water fraction of storm runoff averaged about 79% of total storm runoff (Table 1), which is similar to the fractions determined in small catchments in other climatic settings. For example, the preevent water fraction averaged 79% for two storms in a forested 17 ha catchment in New Zealand [*Weiler et al.*, 2003], and 77% for a 19 mm event in a forested 3 ha catchment on the Canadian shield of southern Ontario [*Buttle and Peters*, 1997], typical of small forested catchment responses in the temperate zone [*Kendall and McDonnell*, 1998; *Uchida et al.*, 2006].

[23] The preevent water component of tropical stormflow is less established, and results to date are mixed, presumably due to site characteristics and the low number of storms analyzed. In comparing the responses of different catchments to a single large event in steep headwater catchments using $\delta^{18}O$ as a tracer in Ecuador (~2000 m a.s.l.), *Goller et al.* [2005] found responses for one cultivated and one forested catchment to be event water dominated, while a second forested catchment showed an opposite response. Working in a forested lowland tropical headwater catchment, *Schellekens et al.* [2004] also reported mixed results for the two storms for which hydrograph separation was performed using a range of solute pairs, with preevent water contributing the bulk of stormflow for a small storm (14 mm; 1 standard deviation less than mean storm size). However, event water was found to contribute the majority of stormflow for a very large storm (228 mm; more than 14 standard deviations greater than the mean storm size reported) [*Schellekens et al.*, 2004]. The present study demonstrates preevent water dominance of stormflow for a range of storms in a forested headwater catchment in the Amazon. Nevertheless, it is possible that event water could comprise a larger fraction of stormflow for an unusually large event, as was found by *Schellekens et al.* [2004] in Puerto Rico.

[24] *Hornberger et al.* [1994] proposed that the preevent contribution to stormflow increases as a function of antecedent soil moisture, with wetter soils expected to have larger preevent components. This was demonstrated in the present study, and is illustrated by an increasingly positive relationship between antecedent precipitation indices (API) and preevent components of stormflow (e.g., wetter conditions at the time of the storm corresponded to larger preevent contributions): r = 0.03 for API_{14}, r = 0.40 for API_7, and r = 0.46 for API_2, where the subscripts note the days prior to storm events for each API.

[25] The results of the fourteen storms analyzed in the present study suggest that lowland forested catchments in the humid tropics may exhibit a preevent water dominance in stormflow that is typical of small forested catchments in the temperate zone. This does not negate the importance of fast flow paths in delivering significant biogeochemical fluxes from landscapes to tropical streams. Previous work in the study area identified quick flow flow paths as the delivery mechanism of approximately half the annual dissolved organic carbon (DOC) that is mobilized from catchment to streams, which is transported by shallow subsurface stormflow and overland flow [*Johnson et al.*, 2006]. Both saturation excess overland flow and Hortonian (e.g., infil-

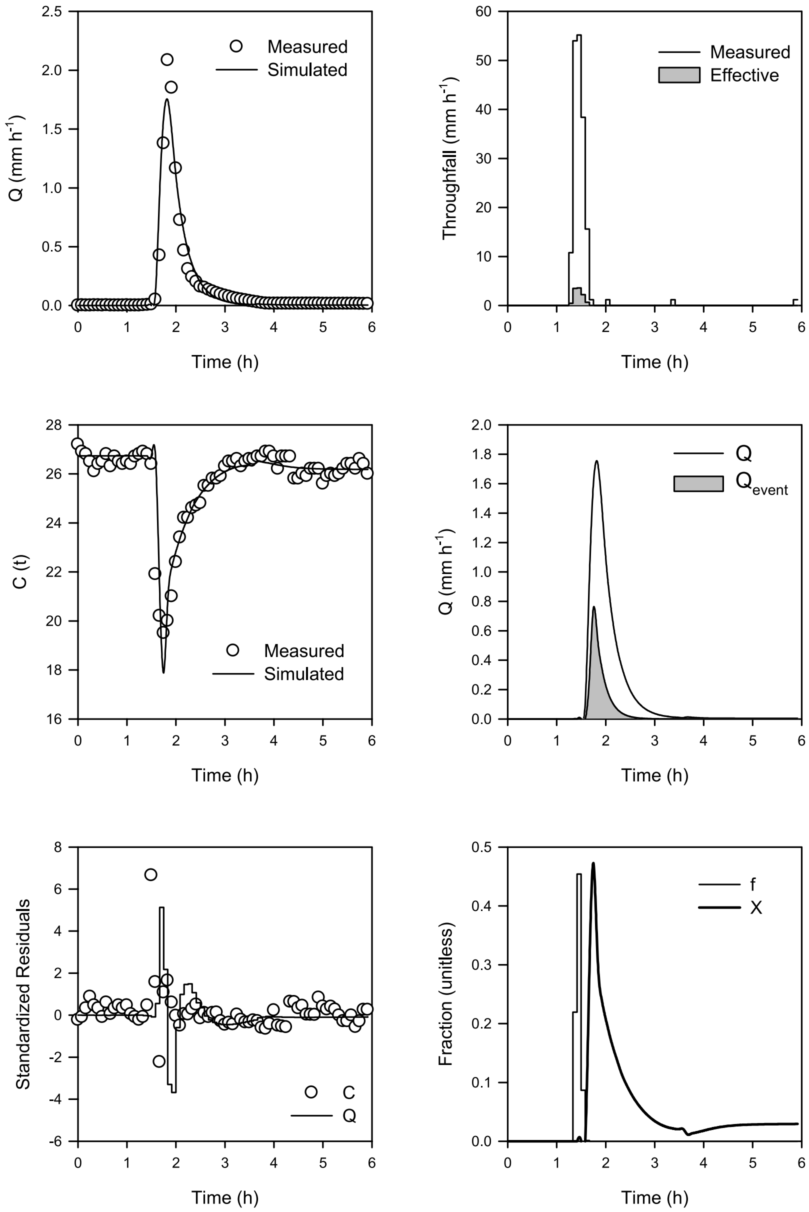

Figure 2. Measured and TRANSEP-optimized results for 31 March 2005 event. Subplots on left present (from top to bottom) stormflow discharge *Q*, specific conductance in stream water *C*, and standardized residuals for stormflow and concentration. Subplots on right present measured (from top to bottom) throughfall and effective throughfall that produces runoff, simulated storm discharge and event water discharge, and the fraction of event water in effective throughfall *f* and the fraction of event water in storm discharge *X*.

tration excess) overland flow have been observed in the study catchment, with the latter form due to high precipitation intensities rather than low infiltration capacities [*Johnson et al.*, 2006]. These quick flow flow paths are also relevant in stormflow CO_2 dynamics.

4.2. CO_2 Pulses in Stormflow

[26] The within-storm dynamics of dissolved CO_2 in storm water are indicative of contributions from both fast and slow flow paths (Figures 1 and 3). Previous work has demonstrated that several of the flow paths contributing to quick flow (overland flow and direct precipitation) are low in dissolved CO_2, while deeper flow paths deliver water with high concentrations of dissolved CO_2 to streams [*Johnson et al.*, 2006]. We found concentration-discharge patterns in storm events to exhibit counterclockwise hysteresis loops when plotting stormflow discharge (*x* axis) against dissolved CO_2 concentrations (*y* axis, data not shown). This hysteresis behavior, with declining concentrations on the rising limb and counterclockwise loops, is more typical of conservative solutes [*Andrea et al.*, 2006], rather than for what must be considered nonconservative behavior of dissolved CO_2.

[27] Also interesting is the pulse of CO_2 on the falling limbs of storm hydrographs that exceeded pre-storm base flow concentrations for each of the fourteen storms ana-

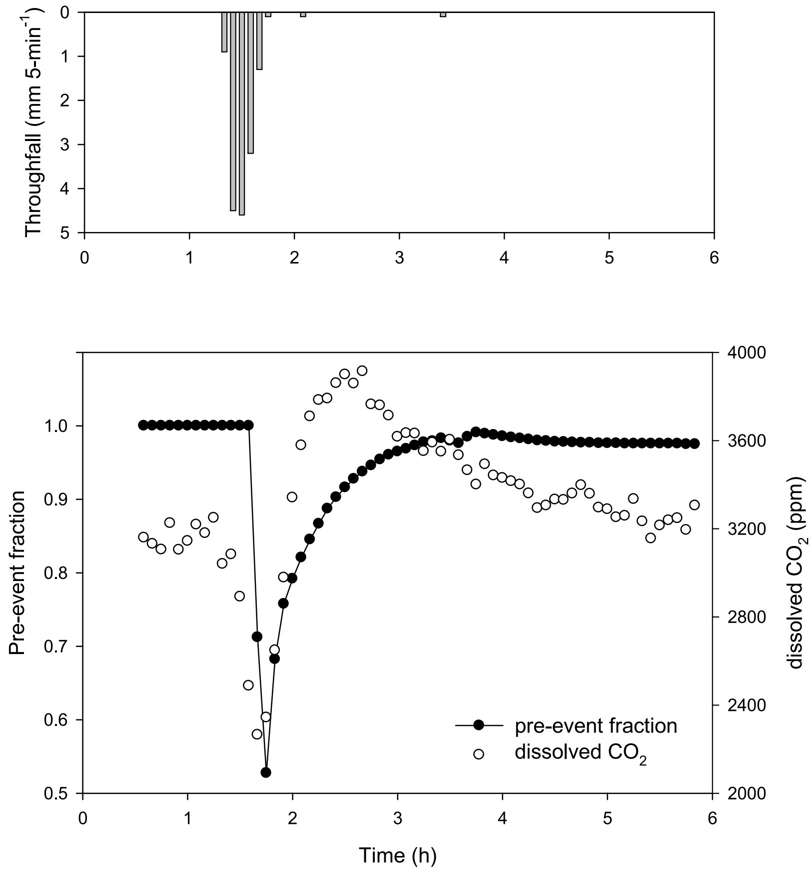

Figure 3. Preevent fraction of stormflow discharge determined from TRANSEP model plotted against measured dissolved CO_2 dynamics for 31 March 2005 storm in forested headwater catchment, Juruena, Brazil. Measured throughfall is presented in the top plot for reference.

lyzed. The implication of these pulses is that there is either a change in the rate at which CO_2 evades from the stream surface, or there is delivery of additional CO_2 from a flow path that is slower than overland flow. The contribution of additional CO_2 from a late arriving flow path is a more probable mechanism since the timing of the dissolved CO_2 pulse occurs on the falling limb of hydrographs when the ratio between discharge and wetted perimeter is declining. This is when we would expect to observe declining dissolved CO_2 concentrations in concert with increasing importance of streambed roughness and the turbulent mixing which drives CO_2 evasion in small streams [*Billett et al.*, 2006].

[28] Shallow subsurface stormflow arriving from upgradient is a likely pathway for delivery of additional CO_2 during catchment responses to storm events. This can occur via dissolution of terrestrially respired CO_2 within soils as subsurface stormflow traverses the soil environment, which is greatly enriched in CO_2 relative to the aboveground atmosphere, or as displacement of soil water that has already equilibrated with the high-CO_2 soil environment. The strongly negative and highly significant relationship between the magnitude of CO_2 pulses and the preevent water fraction of stormflow runoff ($r = -0.97$, $p < 0.0001$) suggests that additional CO_2 is contributed to the stream during storm events via dissolution of gaseous soil CO_2 by an event water flow path arriving after peak discharge (Figure 3).

[29] In addition, the CO_2 concentration of the event water component of stormflow can be estimated at each time step from the event water fraction at the time step computed in the hydrograph separation (e.g., X in the bottom subplot on the right-hand side of Figure 2) together with the CO_2 concentration in preevent water, assuming that the CO_2 concentration in preevent fraction of stormflow is constant throughout the storm and equivalent to base flow values. Accepting these assumptions as a first approximation of event water CO_2 concentration as a function of time shows that (1) peak event water CO_2 concentration is an order of magnitude higher than base flow CO_2 concentration in the stream and that (2) the peak event water CO_2 concentration also arrives on the falling limb of the storm hydrograph and after the CO_2 pulse has passed. Several aspects of this feature merit discussion, as the event water CO_2 peak is obscured within the overall stream water CO_2 flux by the minor contribution of event water late on the falling limb of the storm hydrograph.

[30] The calculated peak event water CO_2 concentration (~25,000 ppm) is consistent with soil CO_2 concentrations in the upper 50 cm of soil (M. Johnson, unpublished data, 2006), although it is only about half the concentration of CO_2 in emergent groundwater [*Johnson et al.*, 2006]. Previous research on soil-stream CO_2 linkages by *Hope et al.* [2004] has suggested that soil-respired sources of CO_2 more distant to the stream channel become depleted during rainfall events as macropore flow transports CO_2 to the

stream channel. Taken together, the CO_2 pulse observed on the falling limb of storm hydrographs and the event water CO_2 concentration peak following the stormflow CO_2 pulse indicate that at least some "preevent CO_2" is flushed from soils into streams by event water. Thus our hypothesis that the CO_2 pulse is indicative of preevent water is only partly satisfied. That is, in addition to preevent water that is high in CO_2 contributing to the CO_2 pulse, it is joined by "preevent CO_2" dissolved by event water and transported to the stream.

[31] The relationship between the magnitude of CO_2 pulses in stormflow and the API indices was found to be increasingly negative in response to higher precipitation inputs in the days prior to the storms analyzed (e.g., wetter antecedent conditions corresponded to smaller CO_2 pulses): $r = 0.06$ for API_{14}, $r = -0.23$ for API_7, and $r = -0.47$ for API_2. Clearly there is a relationship between API and soil CO_2 concentrations [cf. *Davidson et al.*, 2004] that would impact the quantity of CO_2 available to dissolution by percolating event water, but present understanding of the relationship between soil moisture and soil CO_2 is incomplete [*Welsch et al.*, 2006]. Research in Amazonian rain forest soils has demonstrated a parabolic relationship between gaseous soil CO_2 efflux and soil moisture content, with soil CO_2 efflux highest at intermediary soil moisture contents [*Sotta et al.*, 2006]. This relationship is due to the influence of soil moisture on both CO_2 production and gaseous CO_2 transport. While dissolution of CO_2 and its aqueous transport within soils and into streams following rainfall will also vary as a function of soil moisture, further research into CO_2 production and transport dynamics at the subhourly timescale that is relevant to rainfall-runoff relationships in tropical forests is still needed.

4.3. Application of TRANSEP to Tropical Catchments

[32] TRANSEP was able to capture many of the within-storm nuances of discharge and concentration dynamics, resulting in very reasonable values for eff_{NS} (Table 1). The average runoff coefficient (4.3%) in the present study compares well with a prior approach using recession analysis in conjunction with the hydrograph line separation technique of *Hewlett and Hibbert* [1967] that resulted in an average runoff coefficient of 3.2% [*Johnson et al.*, 2006]. Relatively small runoff coefficients are typical for small Amazonian catchments that respond rapidly to intense precipitation, even following deforestation [*Williams et al.*, 1997]. In addition, while originally developed for use with isotope data, TRANSEP was found to be robust when applied using specific conductance.

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