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ORIGINAL PAPER

DOC and DIC in flowpaths of Amazonian headwater catchments with hydrologically contrasting soils

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Abstract Organic and inorganic carbon (C) fluxes transported by water were evaluated for dominant hydrologic flowpaths on two adjacent headwater catchments in the Brazilian Amazon with distinct soils and hydrologic responses from September 2003 through April 2005. The Ultisol-dominated catchment produced 30% greater volume of storm-related quickflow (overland flow and shallow subsurface flow) compared to the Oxisol-dominated catchment. Quickflow fluxes were equivalent to 3.2 ± 0.2% of event precipitation for the Ultisol catchment, compared to 2.5 ± 0.3% for the Oxisol-dominated watershed (mean response ±1 SE, $n = 27$ storms for each watershed). Hydrologic responses were also faster on the Ultisol watershed, with time to peak flow occurring 10 min earlier on average as compared to the runoff response on the Oxisol watershed. These different hydrologic responses are attributed primarily to large differences in saturated hydraulic conductivity (K_s). Overland flow was found to be an important feature on both watersheds. This was evidenced by the response rates of overland flow detectors (OFDs) during the rainy season, with overland flow intercepted by 54 ± 0.5% and 65 ± 0.5% of OFDs for the Oxisol and Ultisol watersheds respectively during bi-weekly periods. Small volumes of quickflow correspond to large fluxes of dissolved organic C (DOC); DOC concentrations of the hydrologic flowpaths that comprise quickflow are an order of magnitude higher than groundwater flowpaths fueling base flow (19.6 ± 1.7 mg l^{-1} DOC for overland flow and 8.8 ± 0.7 mg l^{-1} DOC for shallow subsurface flow versus 0.50 ± 0.04,mg l^{-1} DOC in emergent groundwater). Concentrations of dissolved inorganic C (DIC, as dissolved CO_2–C plus HCO_3^-–C) in groundwater were found to be an order of magnitude greater than quickflow DIC concentrations (21.5 mg l^{-1} DIC in emergent groundwater versus 1.1 mg l^{-1} DIC in overland flow). The importance of deeper flowpaths in the transport of inorganic C to streams is indicated by the 40:1 ratio of DIC:DOC for emergent groundwater. Dissolved CO_2–C represented 92% of DIC in emergent groundwater. Results from this study illustrate a highly dynamic and tightly coupled linkage between the C cycle and the hydrologic cycle for both Ultisol and Oxisol

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landscapes: organic C fluxes strongly tied to flowpaths associated with quickflow, and inorganic C (particularly dissolved CO_2) transported via deeper flowpaths.

Keywords Dissolved carbon dioxide · Dissolved organic carbon · Groundwater · Overland flow · Quickflow · Stormflow

Introduction

Biogeochemical cycling within terrestrial ecosystems and across the terrestrial–aquatic interface is dynamically linked with the water cycle. Not only is the movement of carbon (C) and nutrients controlled in large part by the movement of water, but also processes of transformations between biogeochemical forms (e.g. inorganic and organic) are strongly influenced by the rate at which water cycles through the landscape (McClain and Elsenbeer 2001), exerting a primary control on biotic factors controlling C mineralization and humification (Zech et al. 1997).

Recent advances in hydrologic research have refined the conceptualization of hydrologic flowpaths and their contributions to stream flow (McDonnell 2003). Broadly, these include rapid flowpaths occurring at or near the soil surface, and slower flowpaths occurring deeper in the soil profile. A useful corollary to the distinction of rapidity between different flowpaths is their temporal continuity: punctuated versus continuous. The concept of quickflow versus deeper flowpaths encompasses this distinction. Quickflow consists of laterally-oriented overland flow and shallow subsurface storm flow, in addition to direct precipitation of throughfall onto stream channels. Deeper flowpaths follow vertically-oriented percolation in the upper soil horizons prior to their routing through deeper soil horizons and emergence as groundwater-derived base flow.

The biogeochemical distinction between overland flow and shallow subsurface storm flow can become blurred as a result of exfiltration of return flow (Walter et al. 2005), emergence of pipe-flow on upland soils (Elsenbeer and Vertessy 2000), and even the ejection of soil solutes due to raindrop impact (Gao et al. 2005). However, surficial and near-surface flowpaths strongly contrast biogeochemically with hydrologic flowpaths that interact with deeper soil horizons as a result of adsorption and mineralization of organic nutrients (Qualls et al. 2002).

The quantification of carbon fluxes transported by water from terrestrial to aquatic environments is fundamental to resolving the C balance at scales ranging from catchment (Billett et al. 2004) to continental (Siemens 2003). Headwater catchments provide the scale at which stream water exhibits the strongest connection with terrestrial flowpaths (Hope et al. 2004). Because much of what is transported by storm-event driven quickflow is not captured in weekly streamwater sampling strategies, a detailed consideration of C fluxes of hydrologic flowpaths is needed to refine determinations of terrestrial C transport to streams.

Elsenbeer (2001) advanced the concept of hydrologic end-members for tropical soils as comprised of Acrisols (Ultisols in the USDA classification), which are dominated by rapid and laterally-oriented flowpaths, and Ferralsols (Oxisols) that exhibit slower responses as a result of more vertically-oriented flowpaths. Both Oxisols and Ultisols are highly weathered soils typical of humid tropical regions, with Ultisols characterized by a greater increase in clay content with depth. Here, we present results from our Amazonian site with the useful features (from a research perspective) of adjacent catchments under the same climatic conditions and forested ecosystem, but with hydrologically contrasting soils. The only other published study in which these end-member soil formations are found in close proximity was conducted in Panama (Godsey et al. 2004).

In this paper, we use paired-watersheds with hydrologically contrasting soils to evaluate: (1) the role of soil properties in controlling the activation of rapid versus slow flowpaths, and (2) the relative importance of these hydrologic flowpaths on controlling C fluxes at the terrestrial–aquatic interface for upland forested catchments in the Amazon.

Methods

Study site

Research was conducted in the southern Amazon near Juruena, Mato Grosso, Brazil (10°28′ S, 58°28′ W) in a region characterized by rolling topography and strong seasonality. The study catchments are located at about 250 m above sea level on the Brazilian shield, and comprise sequential tributaries to a stream flowing into the Juruena River. Soils in the region overlie the Precambrian gneisses of the Xingu Complex (Ministry of Mines and Energy (Brazil) 1980), and have pH values ca. 5 (Novães Filho 2005), precluding the presence of carbonate minerals. Mean annual temperature in the region is 24 °C, with annual precipitation of 2200 mm distributed in a unimodal pattern with a five month dry season from May–September (Nunes 2003).

Two adjacent, forested headwater catchments with contrasting soil physical characteristics were selected based on an initial recognizance field campaign that used soil color and degree of incisement as distinguishing and readily observable criteria. Each catchment consists of a toposequence of hillslope landscape positions and a perennial first-order stream that originates from a spring. The results presented in this paper comprise monitoring and sampling conducted between September 1, 2003 and April 1, 2005.

Topographic and soil characterization

A topographic survey was conducted using standard surveying techniques, with transects established across each watershed at 20 m intervals perpendicular to the predominant hillslope direction. Elevation was determined every 5 m along transects. GPS was used to adjust the field grid to UTM coordinates. Elevation data from ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) on the Terra satellite was used to offset the field datum to meters above sea level (Fig. 1).

Soil samples were collected at two depths every 20 m along transects by auger, comprising 43 samples at each depth for the Oxisol watershed and 65 samples at each depth for the Ultisol watershed. Composite samples were taken from 5 sub-samples obtained within 1 m^2 at 10 cm depth, and a single sample was collected at 50 cm. The sample design allowed a robust determination of the spatial variability of changes in soil texture and other parameters across the landscape and with depth. Following the initial soil survey, a soil pit was dug for each watershed on the representative soil immediately adjacent to the watersheds but outside of areas contributing to the catchments. Increases in clay content with depth across the landscape were determined from comparison of 10 cm and 50 cm depths at each sample point, and were found to be greater for the Ultisol-dominated watershed than for the Oxisol-dominated watershed (61 ± 2% increase versus 45 ± 2%, mean ± 1 SE, $P < 0.001$ for two-sample T-test). This feature coupled with more detailed investigation of soil diagnostic horizons shows the predominant soil of the Ultisol watershed to be a Plinthic Kandiustult in the USDA classification (Soil Survey Staff 1999), and a Plinthic Acrisol in the FAO classification (FAO-UNESCO 1987). The predominant soil of the Oxisol watershed is a Typic Haplustox in USDA classification (Rhodic Ferralsol in the FAO classification).

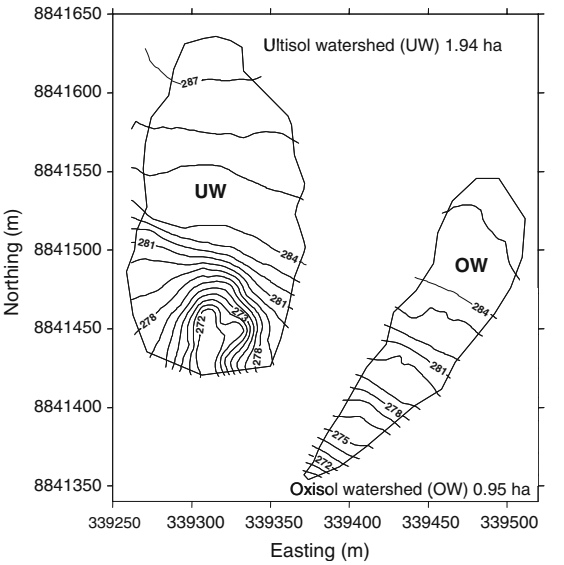

Fig. 1 Location map for the Oxisol watershed (OW) and the Ultisol watershed (UW) in UTM zone 21S coordinates, and 1 m contour intervals with elevation in meters above sea level. The Ultisol watershed shows a higher degree of incisement than the Oxisol watershed

Soil hydraulic conductivity was evaluated in situ for each soil pit using mini-disk infiltrometers (Zhang 1997) with 0.5 cm suction (Decagon Devices, Pullman, WA, USA) with four replicate measurements at each depth: 0, 10, 25, 50 and 100 cm. Since the matrix potential equivalent to 0.5 cm of suction, 0.05 kPa, is indistinguishable from saturation on soil water characteristic curves (cf., Saxton 2005), we report the soil hydraulic conductivity determined in-situ as K_s.

Hydrologic instrumentation

Each watershed was instrumented with devices for recording throughfall and streamflow at 5 minute intervals. A water-level recording device adjacent to a 90° V-notch weir at each watershed outlet was used for determining stream discharge. Initially we used pressure transducers (Telog Instruments, Victor, NY, USA) which were subsequently replaced by water height data loggers with thermisters for measuring water and air temperatures (TruTrack, Christchurch New Zealand). At the time of water sample collection, stream height at the weir was measured directly and leaves occasionally found trapped in the V-notch of the weir were removed, allowing correction of the logged record of stream height. Throughfall was determined from four 200 cm^2 data-logged rain gauges installed 1 m above the forest floor (Pronamic, Silkeborg Denmark) connected to event data loggers (Onset Computer Corp., Bourne MA, USA).

The presence of overland flow was determined spatially using 15 non-recording overland flow detectors (OFDs) per watershed (Elsenbeer and Vertessy 2000; Kirkby et al. 1976). These passive OFDs are made from 20 mm ID PVC pipe and consist of a detector section and a reservoir section connected by a tee. The collector section is perforated along one side by three rows of 1 mm holes, which are perforated at 1 cm intervals along the 20 cm section with 5 mm between rows. The reservoir section is inserted into an installation hole in the soil such that some of the detector holes are in contact with the soil surface; ponding of overland flow will result in water being collected in the reservoir. Determination of the presence of overland flow consists of uncapping the detector, tipping out any collected water, and noting the presence or absence of overland flow. The unit is then redeployed. For the present study, the OFDs were arranged in a semi-randomized fashion, with 5 OFDs installed in each of three landscape positions per watershed: plateau (<2% slope), shoulder slope (2–10% slope) and midslope (>10% slope) for a total of 15 OFDs per watershed. The presence or absence of overland flow was checked biweekly.

Sample collection and analysis

Water samples were collected by hand weekly from groundwater springs. Samples of throughfall, overland flow and leaching water were collected weekly during the rainy season. Spring water was collected directly from tubing inserted horizontally into the spring such that emergent groundwater could be collected prior to interaction with the riparian zone or the atmosphere. Samples were collected monthly from ground water wells in each watershed. These 8 m wells were constructed of 5 cm diameter PVC pipe slotted over the lower 1.5 m, and were located at upper and mid-slope positions in each watershed.

Throughfall was collected in PETG bottles attached to stakes and topped with a 10 cm diameter funnel. A plug of glass wool was placed in the base of the funnel to strain litterfall, which was removed from the funnel. Overland flow samples for analysis were collected from one large PVC tube in each watershed placed on the soil surface at locations of concentrated flowpaths. A zero-tension lysimeter installed at 10 cm depth in each watershed funneled gravity-flow water to PETG collection bottles. These free-draining lysimeters served as a proxy for shallow subsurface storm flow.

Water samples were filtered (Whatman GF/F glass fiber filters, 0.7 μ m, Middlesex, UK), treated ($HgCl_2$) and stored at 3°C until analysis in pre-muffled glass vials with Teflon-lined tops. DOC was determined chromatographically after combustion in a TOC analyzer (Multi N/C 3000, Analytik Jena, Jena Germany).

Dissolved inorganic carbon (DIC) components were determined individually for HCO_3^-–C and

dissolved CO_2–C. HCO_3^-–C was measured by titration with 0.01N H_2SO_4 to pH 4.5 (Neal 2001). Dissolved CO_2–C was measured in the field using an approach for the in situ deployment of an infrared gas analyzer (IRGA) in aquatic systems modified from Tang et al. (2003) and Jassal et al. (2004). The IRGA used was designed to measure CO_2 in harsh and humid environments using a single-beam dual-wavelength, non-dispersive infra-red (NDIR) silicon-based sensor (Vaisala GMT221, Vantaa, Finland). The IRGA was further protected within a high porosity PTFE sleeve that is highly permeable to CO_2 but impermeable to water, allowing dissolved CO_2 from solution to equilibrate with the headspace of the gas bench within the IRGA.

Dissolved CO_2 concentration of spring water was determined by placing the PTFE-sheathed IRGA within a PVC housing connected at the point of groundwater discharge prior to its emergence and subsequent outgassing to the atmosphere. For determination of CO_2 in stream water, the PTFE-sheathed IRGA was submerged in the main channel upstream of the weir. In both cases, the gas bench was allowed to equilibrate in situ for 10 min prior to recording the pCO_2 concentration, which was adjusted to mg l^{-1} via Henry's Law.

Measurement accuracy of this instrument is ±200 ppm CO_2 (±0.08 mg l^{-1} as dissolved CO_2–C), while precision of the method as indicated by standard deviations of replicate samples is ±545 ppm (±0.22 mg l^{-1} dissolved CO_2–C).

Hydrologic and statistical analysis

Storm hydrographs were normalized by corresponding watershed areas (Fig. 1) to allow comparison between responses for the two watersheds. The quickflow component of storm hydrographs was determined by separating the base flow component from total stream flow response to rainfall using a hydrograph line separation technique after Hewlett and Hibbert (1967). A line connecting the beginning of stream flow response to event precipitation with the point at which the change in discharge on the recession limb stabilized at a value greater than $0.95(\frac{Q_t}{Q_{t-1}} > 0.95)$ was used to facilitate calculations of quickflow. Throughfall was calculated as the average response per 5-min interval for the four throughfall gauges. Comparisons between watersheds for hydrologic parameters were made using paired *T*-tests as no series correlation (e.g. autocorrelation) was found for the storm events (Wilks 1995).

Results and discussion

Activation of rapid flowpaths

Runoff responses to rainfall generally began within 10 min in both watersheds, but the storm hydrographs were more rapid for the Ultisol watershed. An analysis of rainy-season stormflow hydrographs for the two watersheds for 27 storms found the average time to peak (T_p) from the beginning of throughfall for the Oxisol watershed to lag the Ultisol watershed (Fig. 2). T_p for the Oxisol (52 ± 6 min) was greater than T_p for the Ultisol (42 ±5 min) ($P = 0.001$).

Quickflow fluxes from the Ultisol were larger than on the Oxisol ($P = 0.017$), while the quickflow component of the rainfall-runoff responses of both watersheds increased linearly for

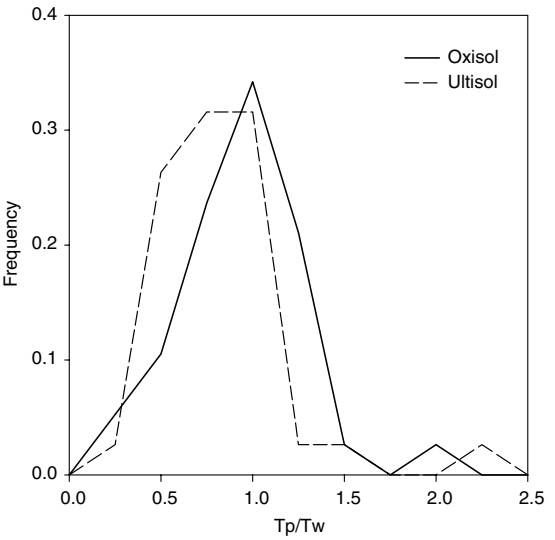

Fig. 2 Frequency distributions of times to peak flow (T_p) normalized by storm duration (T_w). The hydrograph peak frequently occurs before rainfall has ended ($T_p/T_w < 1$) for the Ultisol watershed

increasing rainfall volumes (r^2 = 0.93 for Ultisol and r^2 = 0.57 for Oxisol). The average quickflow runoff volume per event was found to be 3.2 ± 0.2% of event precipitation in the Ultisol-dominated watershed, compared to 2.5 ± 0.3% for the Oxisol-dominated watershed (mean response ±1 SE, n = 27 storms for each watershed). Lesack (1993) determined that the annual mean storm runoff as a percentage of rainfall was 2.8% for a 23 ha watershed in the Central Amazon, a value similar to those of this study. Quickflow was less than 4% of total streamflow for each watershed on an annual basis.

Saturated conductivity (K_s) differed between the Ultisol and the Oxisol. The Ultisol exhibited an initial decrease in K_s with depth from the soil surface to 50 cm, while K_s of the Oxisol increased with depth from the soil surface (Fig. 3). Declining K_s with depth is likely an important factor contributing to more rapid responses with larger quickflow runoff volumes for the Ultisol watershed, though topographic differences between the watersheds would also contribute. K_s at the soil surface was not significantly different between the two soils ($P > 0.05$). There is a feedback between soil hydrologic characteristics, hydrologic responses to precipitation events and catchment geomorphology (Gomi et al. 2002; Robinson et al. 1995), which appears to have resulted in topographic differences between the catchments (Fig. 1). For example, larger volumes of shallow subsurface stormflow could have resulted in erosion and eventual over-steepening

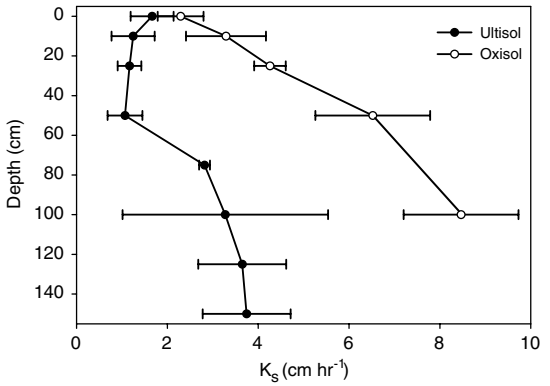

Fig. 3 Saturated hydraulic conductivity (K_s) in the soil profile. Error bars are ±1 SE (n = 4)

and mass wasting of channel banks for the Ultisol catchment.

The K_s values presented in Fig. 3 are within the range found for Ultisols (Acrisols) and Oxisols (Ferralsols) in the humid tropics (Elsenbeer 2001). However, the differences in hydraulic conductivities between the soils in the present study are not as dramatic as those between other Amazonian soils at La Cuenca (Acrisol) and Reserva Ducke (Ferralsol) (reviewed by Elsenbeer 2001).

The Rancho Grande site, also located on the Brazilian shield and comprised of both Ultisols (Godsey and Elsenbeer 2002) and Oxisols (Elsenbeer et al. 1999), is the Amazonian research site most directly comparable with the Juruena site. Increased K_s with depth from the surface was also observed for an Oxisol soil at Rancho Grande (Elsenbeer et al. 1999). In addition, our surface layer K_s values were quite similar to the Rancho Grande forest soil of Elsenbeer et al. (1999), though lower than most studies reviewed by Elsenbeer (2001).

Elsenbeer (2001) presents a runoff response continuum that is useful for understanding our observation that runoff responses did not differ greatly between the two watersheds in the present study. Of the studies considered in that review, it appears as though the Juruena Ultisol and Oxisol watersheds best correspond with the Danum Acrisol (Ultisol) and the Rancho Grande Ferralsol (Oxisol), respectively. These sites lie together in the intermediary group characterized by a modest lateral subsurface component (Elsenbeer 2001). The Juruena Ultisol of this study presented an anisotropy in K_s similar to that of the Danum (Borneo) site, where an increase in K_s between 50 and 75 cm was also observed (Chappell et al. 1998, reviewed by Elsenbeer 2001).

Overland flow was frequently observed on both Juruena watersheds, and was evaluated over the surface of the watersheds by the responses of overland flow detectors (OFDs). The percentage of OFDs indicating overland flow varied over the course of the rainy season, but in a surprisingly consistent fashion for both the Ultisol and the Oxisol watersheds (Fig. 4, r^2 = 0.73). The intercept of the linear regression line relative to the 1:1 line (Fig. 4) indicates that overland flow was in

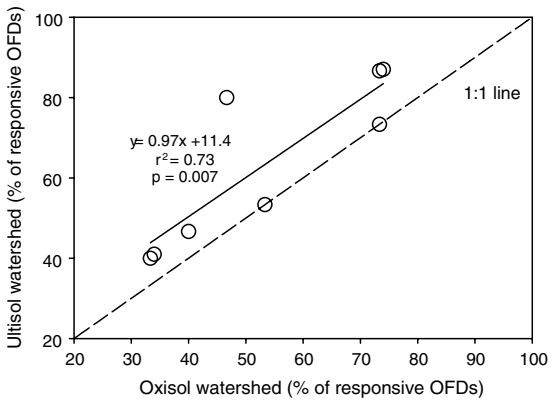

Fig. 4 Percentages of overland flow detectors (OFDs) that were responsive in the Oxisol and Ultisol watersheds for each collection. The 1:1 line indicates when overland flow was generated equally for the two watersheds. That the percentage of responsive OFDs is always at or above the 1:1 line indicates that the spatial extent of overland flow was greater for the Ultisol watershed than for the Oxisol watershed

general more pervasive on the Ultisol watershed. The Ultisol watershed produced 11.4% more overland flow than the Oxisol, as determined from the intercept of the linear relationship of runoff responses for the two watersheds. Nevertheless, the response rate for OFDs on the Oxisol dominated watershed generally differed by less than 20% of the response rate of the Ultisol watershed. This indicates that overland flow is a feature of both Oxisol and Ultisol soils in the Amazon, but was more prevalent for the Ultisol catchment. Among landscape positions, the OFDs placed in the plateau and shoulder slope positions exhibited responses that were not statistically different between the two catchments, while the OFDs in the midslope position consistently indicated more overland flow for the Ultisol watershed than for the Oxisol watershed ($P < 0.01$). Overland flow has now been observed on Oxisol soils in the Amazon (present study) and in Panama (Godsey et al. 2004), which suggests a need to reconsider the hypothesis that overland flow is not an important runoff producing mechanism for Ferrasol (e.g. Oxisol) landscapes (Elsenbeer 2001).

A frequency analysis of the 5 min throughfall record over the course of 2004 indicated that rainfall intensity is frequently sufficient to produce Hortonian runoff across the landscape. Intensities greater than 20 mm h^{-1} were recorded during more than 35% of the 1024 5-min time intervals during 2004 for which precipitation intensity was more than a drizzle (>5 mm h^{-1}), compared to average K_s of surface soil of 19.8 mm h^{-1}. More than 70% of rain events contained at least one 5-minute interval which exceeded 20.0 mm h^{-1} during 2004. These data are illustrative that Hortonian runoff need not be considered a rare occurrence for this tropical forested system.

Carbon biogeochemistry of hydrologic flowpaths

Quickflow and groundwater flow intersect soil horizons with very different C characteristics (Table 1), imparting distinctive C signatures to these hydrologic flowpaths. Mean DOC concentrations were found to vary by an order of magnitude between quickflow-related flowpaths and groundwater-related flowpaths, with DOC transported by overland flow having the highest average concentration (19.6 ± 1.7 mg l^{-1} DOC, mean ±1 SE for combined Ultisol and Oxisol watersheds data, $n = 70$) and emergent groundwater the lowest (0.50 ± 0.04 mg l^{-1} DOC, $n = 83$). DOC concentrations in shallow subsurface flow

Table 1 Soil pH in water with soil to solution ratio of 1:2.5 and organic carbon at discrete depths. $n = 43$ for Oxisol and $n = 65$ for Ultisol at <1 m depths; $n = 3$ at depths >1 m

Depth	pH		Organic C (g kg^{-1})	
	Oxisol	Ultisol	Oxisol	Ultisol
0–20 cm	4.74 ± 0.05	4.72 ± 0.06	9.8 ± 0.2	10.0 ± 0.3
40–60 cm	4.70 ± 0.04	4.76 ± 0.04	5.0 ± 0.2	5.3 ± 0.2
2 m	5.25 ± 0.09	5.53 ± 0.14	2.0 ± 0.5	1.6 ± 0.2
4 m	5.21 ± 0.05	5.72 ± 0.10	0.4 ± 0.1	0.5 ± 0.1
8 m	5.04 ± 0.02	5.47 ± 0.08	0.6 ± 0.1	0.3 ± 0.0

averaged 8.8 ± 0.7 mg l^{-1} for the two watersheds (n = 28).

Significant differences (P < 0.05) between the two watersheds were found for DOC concentrations in overland flow and shallow subsurface flow (Fig. 5, Table 2). The DOC concentrations in the surface and near-surface fluxes that correspond to quickflow were higher for the Ultisol catchment, where more quickflow was also observed. That the DOC concentrations of these fluxes can increase as the volumetric flux of the flowpaths increases is perhaps best considered from the perspective of the C content along the flow path. The travel distance through and mean residence time within the C-rich environment of the litter layer is greater for horizontally-oriented flowpaths than where flowpaths are more vertically-oriented, which could provide conditions allowing for increased extraction of DOC. The more laterally-oriented flowpaths typical of Ultisols (Elsenbeer 2001) could result in increased DOC concentration of shallow subsurface stormflow as this flowpath also passes through a relatively C-rich environment with less sorption opportunities than in the deeper soil (Qualls et al. 2002). Significant differences in DOC concentrations of flowpaths were not found for other measured fluxes.

A general gradient is observed in DOC concentrations for both soils, decreasing with depth from the soil surface. Soil C of the surface horizon (0–20 cm) was not found to be significantly different between watersheds (9.8 ± 0.2 g C kg^{-1} soil for the Oxisol (n = 42) versus 10.0 ± 0.3 g C kg^{-1} soil for the Ultisol (n = 64), P = 0.38), nor between the locations of overland flow and subsurface stormflow collection.

The lower DOC concentrations of deeper flowpaths result from numerous biogeochemical processes occurring within the soil matrix, including sorption and decomposition of DOC (Kalbitz et al. 2003; Qualls et al. 2002; Schwesig et al. 2003). As such, groundwater-derived DOC has already undergone substantial processing compared to quickflow derived DOC that is flushed from the soil surface and upper soil horizons. Terrestrial DOC fluxes sporadically transported by quickflow are almost on par with DOC transported by base flow on an annual basis.

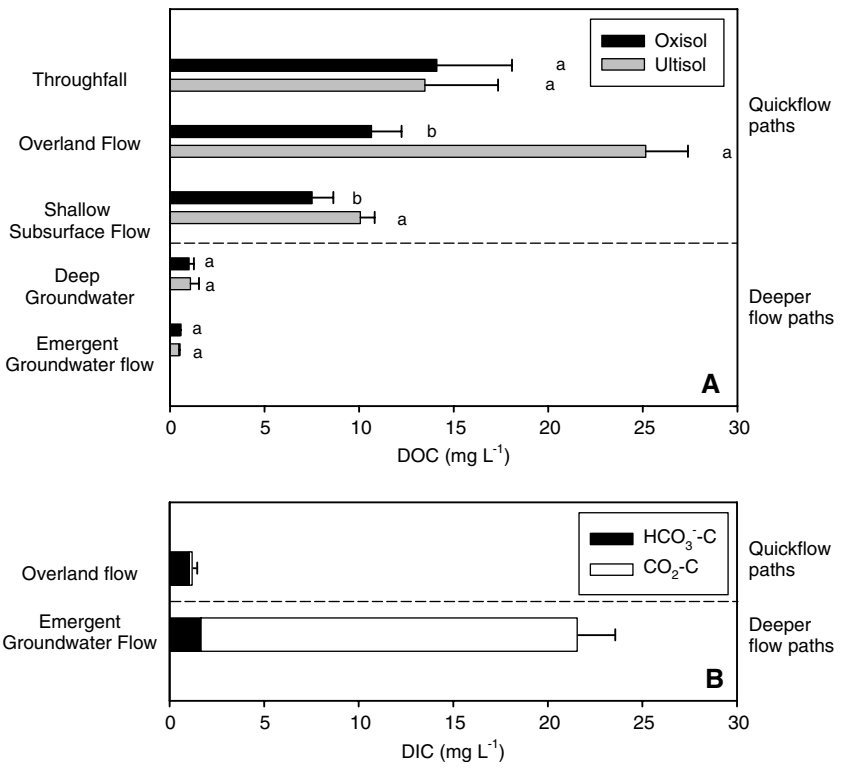

Fig. 5 Average (non-flow weighted) DOC concentrations ±1 SE for hydrologic flowpaths on the Ultisol and Oxisol watersheds, Juruena Brazil for September 2003–April 2005 (Fig. 5A). Different letters indicate where DOC concentrations were significantly different between watersheds (P < 0.05 for two-sample T-test). Average concentrations ±1 SE for DIC constituents HCO_3^-–C and dissolved CO_2–C are presented as pooled data between the two watersheds (Fig. 5B)

Table 2 Hydrologic fluxes and dissolved carbon concentrations of quickflow and deeper flowpaths for forested Juruena headwater catchments, September 2003–April 2005

Parameter*	Oxisol	Ultisol
Stream discharge (l s^{-1})		
Avg.	0.42	1.08
Min. daily	0.12	0.2
Max. instantaneous	39	48
Quickflow (%)	2.5 ± 0.34	3.2 ± 0.3
Baseflow (%)	97.5 ± 0.3	96.8 ± 0.3
DOC (mg l^{-1})		
TF	14.1 ± 4.0	13.5 ± 3.9
OLF	10.7 ± 1.6	25.2 ± 2.2
SSF	7.5 ± 1.1	10.1 ± 0.8
DGW	1.0 ± 0.2	1.1 ± 0.5
EGW	0.51 ± 0.05	0.47 ± 0.05
CO_2-C (mg l^{-1})		
EGW	20.5 ± 1.4	19.0 ± 1.3

*Quickflow and baseflow fluxes expressed as percentage of event precipitation, TF = throughfall, OLF = overland flow, SSF = subsurface stormflow, DGW = deep groundwater, EGW = emergent groundwater at springs

Quickflow DOC concentrations on the order of 10 mg l^{-1} are transported by approximately 4% of streamflow, while the remaining 96% of streamflow originates as low-DOC (~0.5 mg l^{-1}) base flow. Mayorga et al. (2005) showed that much of the CO_2 lost to outgassing from large rivers and wetlands in the Amazon is mineralized from a rapidly cycling pool of young terrestrial organic C, with an older, more recalcitrant pool of DOC comprising an additional component of riverine DOC. The results of the present study suggest that the punctuated input of DOC via quickflow flowpaths is a likely mechanism for the transfer of young, allochthonous C from the landscape to the Amazon River system.

Deeper hydrologic flowpaths were found to be important C pathways, but for inorganic C rather than DOC. Dissolved CO_2 in the groundwater that supplies base flow was found to be supersaturated with respect to the atmosphere (Table 2), and did not vary significantly between watersheds, averaging 19.9 ± 1.8 mg l^{-1} CO_2–C (mean ±1 SE for combined Ultisol and Oxisol watersheds data, $n = 27$, equivalent to 48,700 ppmv pCO_2). CO_2 derived from root and microbial respiration builds up in deeper soil horizons as a result of increasing diffusional distance with depth (Davidson and Trumbore 1995), which can then be dissolved by percolating water (Caron et al. 1998). While the relative magnitude of soil CO_2 derived from root respiration versus that derived from microbial respiration remains unresolved (Davidson and Trumbore 1995; Turpin 1920), the soil atmosphere in the Amazon reaches values for pCO_2 of over 60,000 ppmv at depth (Davidson and Trumbore 1995), resulting in large concentrations of dissolved CO_2 in groundwater (Richey et al. 2002).

The measured CO_2 concentrations were compared with theoretical CO_2 concentrations calculated from pH and alkalinity determinations, as:

$$[CO_2(aq)] = [HCO_3^-][H^+]/K_1 \quad \text{where} \quad K_1 = 10^{-6.3}$$

Dissolution of CO_2 in water results in hydration of CO_2 as $CO_2(aq)$, as well as true H_2CO_3 via protolysis (Stumm and Morgan 1981). We may ignore H_2CO_3 for the purposes of comparing in situ determinations of CO_2 with calculated values since the ratio of $CO_2(aq)$ to H_2CO_3 is 650 at 25°C (Butler 1982).

Measured and calculated values for dissolved CO_2 were found to show good agreement, with calculated concentrations generally slightly higher than the measured values, reflecting the tendency for slight overestimation of alkalinity inherent to endpoint titrations (Mackereth et al. 1978). The mean of the absolute value of the

residual (expressed as [CO_2–$C_{calculated}$/CO_2–$C_{measured}$]) was found to be 0.17 ± 0.05 (mean ±1 SE). A sensitivity analysis of the measured parameters used to determine CO_2–$C_{calculated}$ showed that varying the pH by ±0.01 resulted in ±2.3% variations in CO_2–$C_{calculated}$, while varying the volume of H_2SO_4 used to determine alkalinity by ±0.05 ml resulted in ±6.3% variability in CO_2–$C_{calculated}$. As such, the 17% mean residual between measured and calculated CO_2–C is on par within the analytical sensitivity of the methods employed, given that the tolerances of the variables used for CO_2–$C_{calculated}$ are multiplicative.

CO_2 concentrations in stream water at watershed outlets were found to be substantially less than that of springs. CO_2–C in the stream draining the Oxisol catchment averaged 33% of the CO_2–C concentration in the Oxisol spring. CO_2–C in the stream draining the Ultisol catchment averaged 12% of the CO_2–C concentration in the Ultisol spring. While this indicates substantial outgassing of CO_2 from emergent groundwater occurring in the upper reaches of both headwater streams (Johnson et al. in prep.), the differences in CO_2 concentrations between the two streams may be due to physical differences in the streams themselves rather than differences in water quality. The stream draining the Ultisol catchment was sampled 50 m below its source, while the stream draining the Oxisol catchment was sampled 20 m below its source, which resulted from geomorphological characteristics (e.g. stream constrictions) that favored construction of weirs at different distances below springs. It should be noted that the outgassing occurring in the headwater reaches of streams is driven by concentration gradients between groundwater and the atmosphere, which is enhanced by the turbulent mixing within shallow headwater streams. This process occurs upstream of, and is in addition to, the mineralization of terrestrial C that Richey et al. (2002) found to drive outgassing from large Amazonian rivers and wetlands, and should be considered as an additional C flux to the atmosphere beyond that computed for the central Amazon River system (J. Richey, Pers. Comm.).

Decreases in CO_2 concentration with longitudinal stream distance in headwater streams have also been shown by Palmer et al. (2001), who noted a large decline in free CO_2 between upper and lower sampling sites, and Finlay (2003) who observed dissolved CO_2 concentrations to decrease rapidly downstream from a spring in a forested catchment. The landscape organization of headwater catchments results in focused groundwater discharge at springs, with diffuse groundwater discharge across streambeds along the stream network (National Research Council 2004). As a consequence, the relative contribution of groundwater discharge to total stream discharge decreases as the distance from stream source increases. The CO_2 concentration at each point in a stream represents the balance of inputs, losses to the atmosphere, and CO_2 generated in-stream via mineralization of DOC (Jones and Mulholland 1998).

Dissolved CO_2 concentrations in throughfall and overland flow are at or near atmospheric concentration (~370 ppm; 0.15 mg l^{-1} CO_2–C) and therefore two orders of magnitude lower than in groundwater. An additional difference between the quickflow and deeper flowpaths was that of HCO_3^-–C, which was found to be greater in emergent groundwater than in overland flow (1.6 ± 0.1 vs. 1.0 ± 0.1 mg l^{-1} HCO_3^-–C, means ±1 SE with $n = 70$ and $n = 40$ respectively). DIC transported by groundwater flow was found to be predominantly in the dissolved CO_2–C form (92%) for these acidic, highly-weathered catchments, while quickflow DIC is largely comprised of the HCO_3^-–C form (87%). Geogenic DIC resulting from carbonate weathering is negligible in these highly weathered and acidic soils, whereas the bicarbonate that is present results from buffering of dissolved CO_2 derived from root and microbial respiration.

In synthesizing the contrasting depth versus concentration relationships for DOC and CO_2 in the soil profile, we see conceptually that quickflow flowpaths intersect the zone of relatively high DOC concentrations, while slower and deeper flowpaths intersect with zones of high CO_2 concentrations (Fig. 6). Since streamflow in the study catchments is predominantly derived from

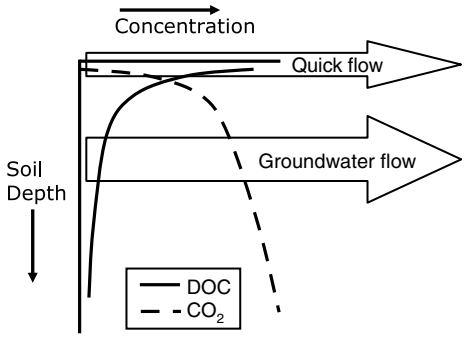

Fig. 6 Conceptual diagram of the intersection of hydrologic flowpaths (quickflow and groundwater flow) with soil enriched in DOC in surface horizons and enriched in CO_2 in deeper horizons

deeper flowpaths, dissolved CO_2 is the dominant form of the fluvial C flux at the terrestrial–aquatic interface in both Oxisol and Ultisol catchments, though much of this CO_2 is lost to outgassing in the upper reaches of streams.

Conclusions

Runoff responses to rainfall were found to be more rapid and with greater quickflow volumes for the Ultisol watershed than for the Oxisol watershed. For the Ultisol, the lower K_s at 50 cm depth compared to the upper soil horizons leads to a stronger lateral flow component, while increasing K_s with depth for the Oxisol allows for increased subsurface percolation.

Overland flow was found to be a frequent occurrence for both watersheds, although the response rate of overland flow detectors was higher on the Ultisol. Measured throughfall intensities were often higher than K_s at the soil surface, indicating that Hortonian runoff could be important overland flow mechanism for the study watersheds. Quickflow was found to represent a relatively minor fraction of total stream flow for both the Oxisol and the Ultisol catchments studied, though there was 30% more quickflow for the Ultisol catchment.

Quickflow is an important mechanism by which relatively unprocessed DOC is transported from the terrestrial to the aquatic environment, since the surface and near surface flowpaths that comprise quickflow are highly enriched in DOC compared to the slower and deeper flowpaths that contribute to base flow. High concentrations of DIC measured for deeper flowpaths in this study indicate that groundwater flow in the form of base flow is a continuous C conduit from the landscape to streams.

A picture emerges of C dynamics at the terrestrial–aquatic interface where precipitation events activate rapid flowpaths associated with large fluxes of organic C, while infiltration and percolation sets the stage for sorption and decomposition of organic C and subsequent groundwater transport of large amounts of biogenic CO_2. Differentiating between the flowpaths and quantifying their fluxes is necessary to resolve the carbon budget at scales ranging from catchment to continental. Further research is also needed in order to quantify the source components and production dynamics of soil CO_2.

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