Biogeochemistry (2011) 105:149–157
DOI 10.1007/s10533-011-9595-x

Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds

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Received: 14 March 2010 / Accepted: 25 February 2011 / Published online: 17 March 2011

Abstract Over two hundred samples were collected in tropical headwater forested catchments in the lowland Amazon basin near Juruena, Mato Grosso Brazil. These were analyzed for fluorescence characteristics and DOC concentrations, and represented a range of terrestrial hydrologic flowpaths and first-order streams during baseflow and stormflow conditions. The fluorescence index (FI) of McKnight et al. (2001) was found to have a significant relationship with DOC concentrations for stream water at baseflow conditions, but FI values within individual terrestrial flowpaths and stormflow varied little for the range of DOC concentrations observed. FI values were seen to increase for increasing residence time of water within the terrestrial ecosystem, while DOC concentration decreased for increasing hydrologic residence time. The FI of terrestrial flow paths indicated that DOC became increasingly characterized by microbially derived carbon for flow paths with longer residence times, on the order through fall and overland flow < percolating soil water < groundwater. Base flow samples of stream water had a mean FI value of 1.78, compared with 1.51 and 1.44 for through fall and overland flow, respectively, and 1.65 for percolating soil water. The FI values for stream water at base flow were also seen to vary seasonally, and were inversely proportional to DOC concentrations over time.

Keywords Baseflow · Fluorescence index · Emergent groundwater · Overland flow · Stormflow · Throughfall

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Introduction

Dissolved organic matter in soils and streams is comprised of a myriad of carbon-based compounds

that exhibit a wide range of bioavailability and degrees of recalcitrance. As the fluxes of dissolved organic carbon (DOC) are fundamental to the global carbon balance (Cole et al. 2007), characterization of DOC is fundamental to understanding carbon cycling in terrestrial and aquatic ecosystems. Yet DOC is infrequently characterized beyond reporting bulk DOC concentrations and fluxes, even in long term ecological research programs (Jaffé et al. 2008).

Fluorescence characteristics of dissolved organic matter have been suggested as a potentially useful means for characterizing differences in the bioavailability of DOC (McKnight et al. 2001). These differences have enabled researchers to utilize fluorescence spectroscopy as a tool for inferring DOC sources in a diverse range of settings, including sewage outfalls in temperate-zone urbanized watersheds (Carstea et al. 2009), tropical mangrove estuaries (Jaffé et al. 2004), salmon-bearing streams (Hood et al. 2007) and permafrost zones (Balcarczyk et al. 2009). DOC fluorescence characteristics have also been used as hydrological tracers for identifying flowpaths contributing water from the landscape to water bodies (Mariot et al. 2007), including tracing source water contributions to streams from diverse flowpaths during storm events (Katsuyama and Ohte 2002).

A range of approaches have been employed for elucidating DOC characteristics based on spectrofluorometric analyses. These range from the highly detailed excitation-emissions matrices (EEMs) for aqueous samples (derived from a comprehensive matrix of combinations of excitation and emissions wavelengths) to the highly summarized information expressed by a fluorescence index (FI). A commonly employed FI is computed as the ratio of emission intensity at 450 nm to that of 500 nm for a fixed excitation wavelength of 370 nm (McKnight et al. 2001). While EEMs contain additional information relative to an indexed approach, the FI has the advantage of allowing a straightforward comparison across samples of various DOC concentrations and compositions, as well as facilitating comparisons of DOC quality among disparate studies (Jaffé et al. 2008).

Typical FI values for river water samples are in the range of 1.3–1.8 (Brooks and Lemon 2007). High FI values within this range are indicative of DOC consisting of microbially-derived substances, while low FI values for the typical range suggest that water samples contain terrestrially-derived substances (McKnight et al. 2001). Intermediary values suggest contributions from a combination of DOC sources.

In this paper, we present fluorescence data in conjunction with DOC concentrations over a full year for a range of hydrologic flowpaths in four forested headwater catchments of the lowland Brazilian Amazon. Our objectives were to characterize DOC quality in streams at baseflow and stormflow, as well as in various hydrological flowpaths draining the landscape, both over time and across watersheds. The purpose of this was to improve our understanding of organic carbon dynamics at the terrestrial-aquatic interface.

Materials and methods

Site description

Four forested headwater catchments were selected for a range of research questions related to watershed biogeochemistry. The 1–2 ha study catchments are located in the southern Amazon near Juruena, Mato Grosso, Brazil (10°28′ S, 58°28′ W), and are described in more detail in Johnson et al. (2006a, b). Briefly, the study catchments are tributaries to the Juruena River, and are located at about 250 m above sea level on the Brazilian shield. The four catchments are located within an area approximately 250 × 250 m. Soils are classified as Oxisols and Ultisols (Soil Survey Staff 1999) that overlie the Precambrian gneisses of the Xingu Complex (Ministry of Mines and Energy (Brazil) 1980). The climate is classified as Aw in the Köppen-Geiger climate classification (Peel et al. 2007), with seasonality characterized by a 5 month dry season (May–September). Annual precipitation averaged 2100 mm y^{-1} during the study, falling almost entirely within the rainy season.

Each watershed consists of a gently (< 2%) sloping plateau, riparian hillslope and valley bottom, within which flows a perennial stream emerging from a groundwater spring. The spring comprises < 5% of the flow at the watershed outlet, located ca. 50 m below the point of focused groundwater emergence. A V-notch weir was constructed in each watershed to facilitate discharge measurement, which was

calculated from the v-notch equation based on water level data recorded using a capacitance water level sensor and data logger (TruTrack WT-HR 500, Christ Church, New Zealand).

Sample collection and preparation

Water samples were collected weekly during the rainy season and biweekly during the dry season from a range of hydrological flowpaths across a hillslope transect in each catchment. Sampled flowpaths included throughfall, overland flow, percolating soil water collected by zero-tension lysimeters, and emergent groundwater at springs located at the base of hillslopes.

Throughfall collectors were located 1 m above the soil surface, with glass-wool lined funnels preventing detritus from entering sample bottles. Lysimeters were installed at 10 cm depth via a trench that was excavated to provide access to the area beneath the collection area, and consisted of funnels filled with acid-washed sand leading by tube to a sample collection bottle. Trenches were located on the down-slope side of collection areas to minimize their influence on percolation dynamics. Trench faces were lined with plastic sheeting to minimize evaporative losses from the soil profile.

Emergent groundwater and overland flow were collected as described in Johnson et al. (2006b). Briefly, emergent groundwater was collected at groundwater springs from an open PVC pipe inserted into the hillslope. A hose was connected to the pipe to ensure that collected samples did not come into contact with the riparian area or streambed. Sample bottles were filled by gravity flow at collection times. Overland flow collectors consisted of 75 mm diameter PVC pipe fitted with a spigot-type spout that was opened for sample collection. The pipes were oriented downslope and placed in locations that showed signs of slight rill erosion, and were thus indicative of overland flow. The spigots were opened for 5 s to allow sediment accumulated in the collectors to flush before samples were collected. Collectors were drained following sample collection. PVC and plastics were new at installation and conditioned prior to installation for 72 h by submerging them in a flowing stream adjacent to the study catchments (DOC < 1 mg l^{-1}).

Here, overland flow is defined as surficial runoff, which can be due to either saturation excess (e.g. runoff derived from precipitation falling on saturated soils) or Hortonian overland flow (e.g. overland flow resulting from a precipitation intensity that exceeds infiltration capacity). Johnson et al. (2006a) demonstrated that 5-minute precipitation intensity was frequently (e.g. $> 35\%$ of 5-minute rainfall periods recorded) greater than the saturated conductivity of the soil (2 cm h^{-1}), indicating that Hortonian overland flow processes can occur in this well-drained tropical soil.

Stream water samples were collected at baseflow and stormflow conditions. Stormflow samples were collected using passive stormflow samplers adjacent to V-notch weirs located at each watershed outlet (Johnson et al. 2006b). The collectors were deployed in pairs at heights corresponding to 10 and 20 times minimum discharge rates. As rainfall events raised the water level at the weir, the lower stormflow collector filled. A second stormflow collector filled if the water level rose sufficiently. The collection bottles were fitted with vertically oriented ventilation tubes allowing air to be displaced as the bottles filled; the vent tubes were looped over to avoid collection of precipitation. The narrow (5 mm) internal diameter of the ventilation tubes ensured that discrete stormflow samples were collected. For example, doubling the stage height would only cause hydrostatic displacement of 0.6% of the 300 ml storage volume of the stormflow collection bottle. This design, while robust and inexpensive, only provides sample collection on the rising limb of hydrographs. Grab samples collected from the V-notch weirs at the watershed outlets represented baseflow conditions.

All samples were collected in acid washed PETG bottles (Thermo Fisher Scientific, Rochester, NY), filtered (Whatman GF/F filters, 0.7 μm pore size) within 24 h of collection, and preserved (saturated $HgCl_2$ added to adjust sample concentration to 30 μM Hg). Samples were stored at 3°C in glass vials with Teflon-lined caps until analysis. Vials were acid-washed, rinsed in deionized distilled water and dried in a muffle furnace prior to use. Caps were acid-washed, rinsed in deionized distilled water and air-dried. All collection techniques are described in further detail in Johnson et al. (2006a, b).

DOC and fluorescence analysis

The preserved samples were divided into two aliquots, with DOC concentration determined for one aliquot, and spectrometric and fluorescence analysis conducted on the second. DOC was determined via high-temperature combustion and oxidation in a TOC analyzer following acid addition and external sparging to remove inorganic carbon (Multi N/C 3000, Analytik Jena, Jena Germany). Absorbance at 370, 450 and 500 nm was determined by spectrophotometer (Varian UV–Vis Spectrophotometer, Walnut Creek, CA, USA).

Fluorescence intensities were measured at emission wavelengths of 450 and 500 nm for excitation at 370 nm using a spectrofluorometer (Model 430, Turner Corporation, Mountain View, CA, USA). Absorbance and DOC concentrations were used to correct the fluorescence intensities for inner-filter effects following the procedures described in McKnight et al. (2001) and Ohno (2002), and were then blank adjusted to account for Raman scattering (McKnight et al. 2001). The fluorescence index (FI) was then calculated after McKnight et al. (2001), with differences in FI of > 0.1 considered significant. Results are considered internally comparable since all data were collected on a single instrument. Details on FI calculations are presented in the next section.

The Suwanee River fulvic acid (SRFA) standard was obtained from International Humic Substances Society (IHSS) and used to assess instrument performance and to allow comparisons between FI data from the present study with other work. Cory et al. (2010) report that for FI-based interpretation of fulvic acid sources, results are robust independent of instrument used. SRFA dilutions ranging in concentration from 0.125 to 5.6 mg C l^{-1} were prepared to ensure linear responses from the spectrofluorometer ($R^2 > 0.999$ were obtained for each excitation/emission combination). Solutions were also prepared using quinine sulfate (QS) to facilitate comparisons between data obtained in the present study with other investigations. The SRFA and QS standards were evaluated at 1 mg l^{-1} DOC for this purpose. The FI of the standards (after applying correction procedures described above) were found to be 1.32 and 2.11 for SRFA and QS solutions, respectively. For comparison, FI values of 1.3–1.4 are reported in the literature for SRFA (McKnight et al. 2001).

Fluorescence index calculations

There are few if any complete mathematical expressions for the calculation of FI in the literature, one of which (Westerhoff et al. 2001) contains an error.[1] As the Westerhoff et al. (2001) formulation can lead to complications when attempting to compare FI values from different and disparate studies, a mathematical formulation of FI (*sensu* McKnight et al. (2001)) is presented here:

$$FI = \frac{I_{\mathrm{cor}}(370:450)}{I_{\mathrm{cor}}(370:500)} \tag{1}$$

where the florescence index (FI) is given as the ratio of corrected fluorescence intensities at 370:450 and 370:500 (excitation: emission wavelengths in nm). The intensities are corrected for inner-filter effects as:

$$I_{\mathrm{cor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}}) = \frac{I_{\mathrm{uncor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}})}{10^{-[\mathrm{L_{ef}}(\mathrm{A_{ex}}+\mathrm{A_{em}})]}} - I_{\mathrm{bl\_cor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}}) \tag{2}$$

Where $I_{\mathrm{uncor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}})$ are the uncorrected intensities for each pair of excitation: emission wavelengths in nm, and $\mathrm{L_{ef}}(\mathrm{A_{ex}} + \mathrm{A_{em}})$ is the effective pathlength multiplied by the summation of absorbance values for the excitation and emission wavelengths. For a typical 1 cm cuvette, $\mathrm{L_{ef}}$ is equal to 0.5 cm. If absorbance data are recorded as specific absorptivity, it must be multiplied by the DOC concentration before applying to Eq. (2). The second term on the right hand side of Eq. (2) accounts for blank adjustments related to the inner-filter effect. $I_{\mathrm{bl\_cor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}})$ may be determined by using the intercept term obtained from the regression of DOC concentration against fluorescence intensity for each $\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}}$ pair using a series of dilutions of a standard such as the IHSS Suwanee River fulvic acid, provided the relationship is highly linear and the intercept term is highly significant, or can be computed as $\frac{I_{\mathrm{bl\_uncor}}(\lambda_{\mathrm{ex}}:\lambda_{\mathrm{em}})}{10^{-[\mathrm{L_{ef}}(\mathrm{A_{ex}}+\mathrm{A_{em}})]}}$ using Milli-Q deionized water.

[1] Westerhoff et al. (2001) Eq. (1) should read "$10^{-(\mathrm{Aem}+\mathrm{Aex})}$" rather than "$10^{-\mathrm{Aem}} + 10^{-\mathrm{Aex}}$". Also, absorbance values for the inner filter correction are only multiplied by DOC concentration if recorded as specific absorbances.

Statistical analysis

Due to similarities between temporal trends and magnitudes in DOC concentrations, sample results from the four watersheds were pooled by hydrologic flowpath. This approach afforded greater statistical power to comparisons between flowpaths, which were evaluated using analysis of variance and Tukey's 'Honest Significant Difference' method (Tukey HSD). Statistical analyses were implemented in R, a software environment for statistical computing and graphics (R version 2.9.2, R Development Core Team (2009)).

Results

During the May 2005–May 2006 study period for which both DOC and FI values were determined, emergent groundwater was found to have the lowest DOC concentrations and the least variance in DOC. Baseflow was also very dilute in DOC, as it is derived primarily from groundwater discharge (both focused groundwater emerging at the springs and diffuse groundwater discharge leading to increased discharge along the stream channel). Terrestrial flowpaths located higher on the landscape (throughfall, overland flow and percolating soil water) all had high DOC concentrations, which contribute towards the high DOC concentrations in stormflow in the streams (Fig. 1a).

Among terrestrial flowpaths, emergent groundwater had the highest FI values, followed by percolating soil water. Emergent groundwater exhibited the greatest variance of FI (Fig. 1b). Surprisingly, the FI for streamwater at baseflow (BF) was not statistically distinguishable from stormflow (SF) when comparing between BF and SF for all sample dates (Fig. 1, panel B). We found that the means and standard deviations were similar between stormflow and the flowpaths activated by precipitation events (e.g. throughfall and overland flow) for both FI and DOC concentrations (SF, TF and OF flowpaths in Fig. 1).

Streamwater at baseflow exhibited temporal variability in DOC concentration and FI values that were inversely related, as illustrated by the time-series of boxplots in Fig. 2a and c. Stormflow concentrations of DOC exhibited the same temporal variability as

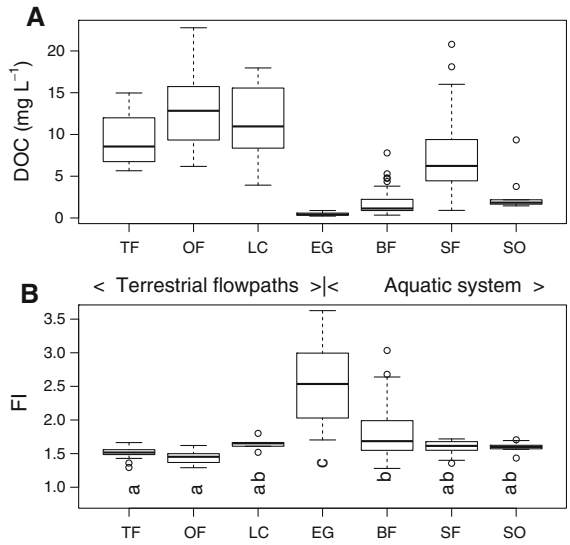

Fig. 1 Dissolved organic carbon (DOC) concentrations (**a**) and fluorescence index (FI, **b**) in terrestrial flowpaths and the aquatic system of four first-order catchments and one second-order catchment near Juruena, Mato Grosso. The data presented by the five horizontal lines of each boxplot summarize the smallest value, the lower quartile, the median value, the upper quartile, and the largest value (from bottom to top). Statistical outliers are indicated by open circles. The abbreviations represent throughfall (TF), overland flow (OF), percolating water intercepted by zero-tension lysimeters (LC), emergent groundwater (EG), baseflowin first-order streams (BF), stormflow in first-order streams (SF), and baseflow in the second-order stream (SO). Different letters below the FI box plots indicate statistically significant differences between flowpaths

baseflow DOC, with peak concentrations about 3–4 times higher in the early wet season compared with the values at the end of the wet season (Fig. 2b). However, FI values for stormflow were relatively consistent throughout the study (Fig. 2d). None of the sampled terrestrial flowpaths demonstrated a coherent temporal pattern for FI.

Considering the aggregate sample set independent of time, a significant relationship between DOC concentration and FI was identified only for baseflow ($r^2 = 0.66$, $P < 0.001$, Fig. 3a). A wide range of FI values was observed across the range of DOC concentrations for emergent groundwater (Fig. 3b), with less variability in FI across the DOC range observed for stormflow samples (Fig. 3c) and terrestrial flowpaths (Fig. 3 d and e). Overall, samples that were very dilute in DOC (e.g. < 1 mg l^{-1}) were characterized by high FI values (Fig. 3a, b, f). However, the high FI values in this case may not

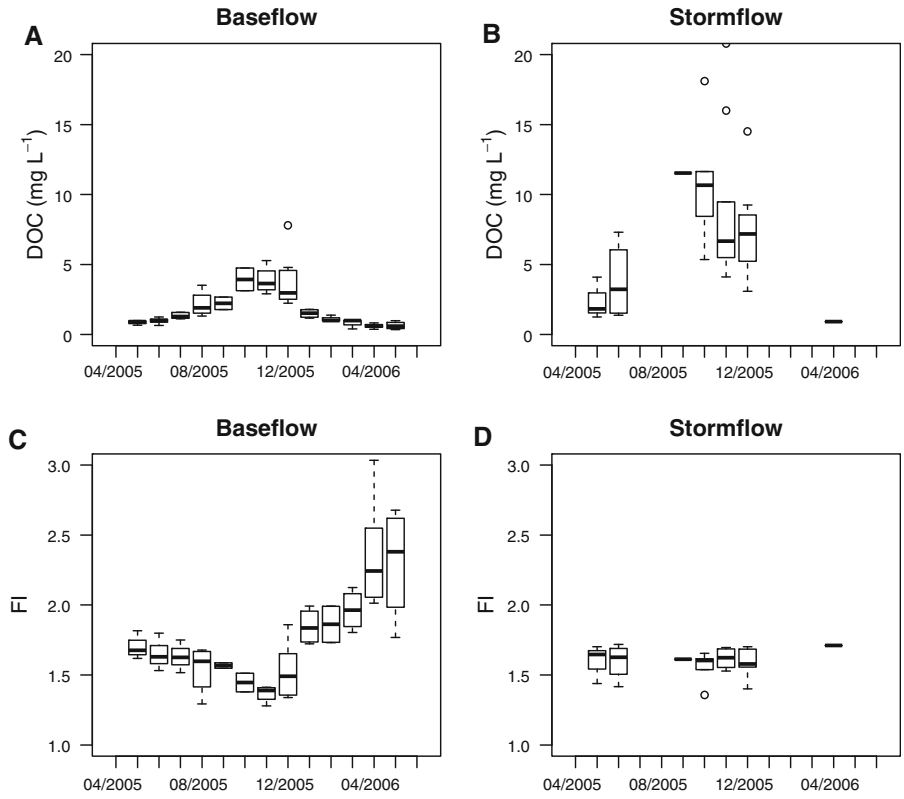

Fig. 2 Monthly boxplots of dissolved organic carbon (DOC) concentrations (**a** and **b**) and fluorescence index (FI, **c** and **d**) in baseflow (**a** and **c**) and stormflow (**b** and **d**) of four first-order streams near Juruena, Mato Grosso, Brazil. Individual box and whiskers are comprised of the independent samples pooled from the four streams for each month

be representative of humic fluorophores, which is discussed further in the following section.

Results from baseflow samples of one watershed (Ultisol watershed of Johnson et al. (2006a), which was further investigated in Johnson et al. (2007)) are presented in Fig. 4 to illustrate the temporal patterns in FI relative to changes in DOC concentrations, stream discharge and seasonality. Data from two years are plotted for all data except FI, for which only the last year is available. Once the rainy season began and streamflow increased, FI was seen to track increases in discharge (Fig. 4) and was inversely related to DOC concentration.

Discussion

The baseflow FI was fairly constant during the dry season of 2005, with values consistently around 1.6. However, DOC concentration increased significantly during the dry season as streamflow decreased. That FI was rather constant during this period is indicative of the consistent source of DOC during the dry season, which is a mix of emergent groundwater and leaching of litterfall deposited into the stream.

Over the course of the year, there was a wide-range of FI values for baseflow samples, with lowest values occurring during the beginning of the rainy season (November–December) as fresh terrestrial carbon sources are mobilized from the landscape into the stream. The high DOC values for this period represent a "first flush" of terrestrially-derived C that builds up during the dry season (e.g. litterfall) and is rapidly leached by the first rains.

Highest FI values for baseflow samples were found at the end of the rainy season, by which point the microbial decomposition of terrestrial litter deposits and soil carbon is clearly evidenced. DOC stream-water concentrations are quite low for this period as the most labile C sources have already been leached

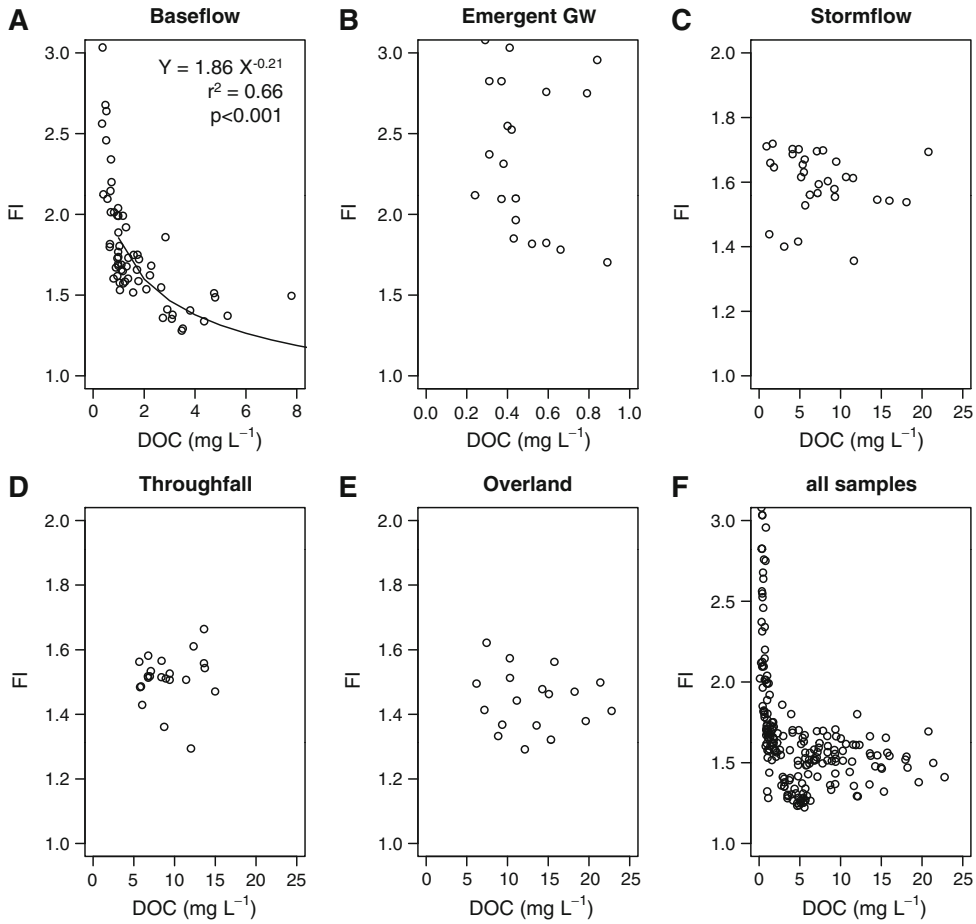

Fig. 3 Relationships between dissolved organic carbon (DOC) concentrations and fluorescence index (FI) in flowpaths of four headwater catchments near Juruena, Mato Grosso. Data is grouped by flowpath in **a–e**, while panel **f** presents data from all flowpaths

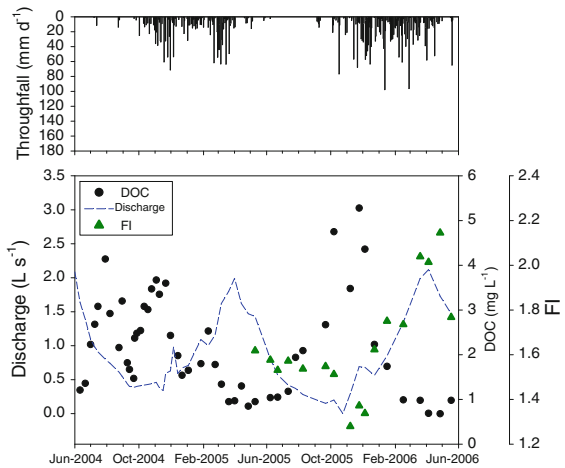

Fig. 4 Precipitation, discharge, dissolved organic carbon (DOC) concentration and fluorescence index (FI) at baseflow for one watershed

and microbially acquired or transported by water to the stream. The microbial character of streamwater DOC late in the rainy season is consistent with other indicators of microbial activity. Johnson et al. (2008) reported soil CO_2 concentrations for 0–8 m depth in the same watershed, with highest CO_2 concentrations occurring during the end of the rainy season, coincident with highest baseflow FI values.

The range of FI values for stormflow was much more narrow than for baseflow. However, stormflow FI values (1.60 ± 0.10, mean ±1 SD) did span much of the continuum from microbial to terrestrial sources indicated by McKnight et al. (2001). FI values for the second order stream had the same mean FI as stormflow, but slightly less variance (1.60 ± 0.08, mean ±1 SD).

The mean FI values of individual flowpaths increased with hydrologic residence time on the

landscape, increasing in the order: throughfall and overland flow (FI of 1.51 and 1.44, respectively, with means not significantly different) <soil leachate (FI = 1.65) <groundwater (FI = 2.52). This increase is consistent with the standard interpretation of FI values, where higher values are representative of more microbially-derived carbon sources (Brooks and Lemon 2007; McKnight et al. 2001). In the case of this study area, the bioavailability of DOC would be expected to decline on the same order as above (throughfall > overland flow > soil leachate > groundwater).

Precipitation interacts with the forest canopy and extracts highly labile carbon from leaves, flowers and epiphytic mats, resulting in throughfall that is enriched in DOC relative to incident precipitation. After reaching the forest floor, further increases in DOC concentration were observed due to interactions with the litter layer and soil surface. However, throughfall resulting in overland flow will also mix with DOC in the litter layer that is more highly microbially processed than that of throughfall due to longer water residence times in the litter layer relative to the forest canopy. Likewise, as water percolates through the upper soil horizons, it becomes stripped of the most labile compounds, with the resulting DOC composition enriched in microbial residues as reflected in the higher values of FI. By the time water has percolated through the vadose zone and into groundwater, it presents very dilute concentrations of DOC, as essentially all bioavailable compounds have been utilized by microbes within the soil profile.

Mean baseflow FI for second order streams is lower (e.g. more "terrestrial") than mean FI values for the first order stream (BF and SO in Fig. 1a). This is consistent with the reduced influence of groundwater inputs on streamwater DOC quality for increasing stream order (Mayorga et al. 2005). Emergent groundwater DOC is highly "microbial", as indicated by the FI values. This focal groundwater emergence in the headwater springs has more influence over streamwater DOC quality for the first order streams than for second order streams, where groundwater inputs are more diffuse and mix with water that has already interacted with benthic organic carbon that is largely litterfall-derived.

The extremely high values for FI observed for emergent groundwater and baseflow samples with low DOC concentrations are anomalous with values reported in the literature. While FI values greater than the microbial end-member range of 1.7–2.0 (McKnight et al. 2001) have been reported, the fluorescence index was developed for characterizing the humic and fulvic acids. The high values observed in the present study for waters very dilute in DOC suggests that non-humic fluorophores may be dominating the fluorescence properties at low DOC concentrations.

Conclusions

In this paper we have focused on the Fluorescence Index as a means of elucidating DOC quality differences among different hydrological flowpaths, and between terrestrial and aquatic components of tropical forested headwater catchments. The fluorescence index of streamwater during baseflow conditions was found to exhibit a significant and inverse relationship with DOC concentration. Within other terrestrial and aquatic flowpaths in the headwater catchments studied, FI was not significantly related to DOC concentration.

In this study, FI values increased for terrestrial flowpaths along a gradient of increasing hydrologic residence time. FI values for baseflow were also found to decrease with increasing stream-order. These results are consistent with the biogeochemical underpinnings of the fluorescence index. At the terrestrial-aquatic interface, emergent groundwater that fuels baseflow presents FI values with a highly microbial signature, suggesting that the DOC in groundwater that finally emerges as streamflow has been stripped of the terrestrial fingerprint exhibited by FI values of throughfall and overland flow. This groundwater-derived streamflow rapidly acquires the DOC characteristics of the stream environment due to turbulent mixing and in-stream decomposition of litterfall delivered from the canopy over the stream, with stormflow FI values showing a more "terrestrial" origin than baseflow due to contributions of DOC from terrestrial flowpaths during storm events. This study demonstrates that a hydrologic flowpath-oriented study utilizing FI to characterize DOC quality can provide process-based information that would not be obtained solely by analyzing DOC concentrations.

Fluorescence characteristics have been demonstrated to be useful for describing DOC precursors and distinguishing between sources of water based on differences in DOC quality (Carstea et al. 2009; Cook et al. 2009). However, as fluorescence characteristics are quite variable in space and time, care should be taken in characterizing the seasonal patterns in potential source waters if FI is to be used as a tool for hydrologic investigation.

Acknowledgments The study was supported by NASA LBA-ECO grant to project group ND-11. The authors greatly appreciate the collaborations of field site hosts Rohden Indústria Lígnea Ltda. and Apolinário Stuhler. We thank Benedito Silveira de Andrade and Elielton Anterio da Souza for field assistance. Discussions with Robert G.M. Spencer and the comments provided by the anonymous reviewers were very useful in revising the manuscript.

References

Balcarczyk KL, Jones JB, Jaffe R, Maie N (2009) Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. Biogeochemistry 94(3):255–270

Brooks PD, Lemon MM (2007) Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. J Geophys Res 112:G03S05. doi:10.1029/2006JG000262

Carstea EM, Baker A, Pavelescu G, Boomer I (2009) Continuous fluorescence assessment of organic matter variability on the Bournbrook River, Birmingham, UK. Hydrol Process 23(13):1937–1946

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, Melack J (2007) Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems 10(1):172–185

Cook RL, Birdwell JE, Lattao C, Lowry M (2009) A multimethod comparison of atchafalaya basin surface water organic matter samples. J Environ Qual 38(2):702–711

Cory RM, Miller MP, McKnight DM, Guerard JJ, Miller PL (2010) Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. Limnol Oceanogr Method 8:67–78

Hood E, Fellman J, Edwards RT (2007) Salmon influences on dissolved organic matter in a coastal temperate brownwater stream: an application of fluorescence spectroscopy. Limnol Oceanogr 52(4):1580–1587

Jaffé R, Boyer JN, Lu X, Maie N, Yang C, Scully NM, Mock S (2004) Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. Mar Chem 84(3–4):195–210

Jaffé R, McKnight D, Maie N, Cory R, McDowell WH, Campbell JL (2008) Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. J Geophys Res Biogeosci 113:G04032

Johnson MS, Lehmann J, Riha SJ, Novães Filho JP, Couto EG (2006a) DOC and DIC in flowpaths of Amazonian headwater catchments with hydrologically contrasting soils. Biogeochemistry 81:45–57

Johnson MS, Lehmann J, Selva EC, Abdo M, Riha SJ, Couto EG (2006b) Organic carbon fluxes within and exports from headwater catchments in the southern Amazon. Hydrol Process 20:2599–2614

Johnson MS, Weiler M, Couto EG, Riha SJ, Lehmann J (2007) Storm pulses of dissolved CO_2 in a forested headwater Amazonian stream explored using hydrograph separation. Water Resour Res 43:W11201

Johnson MS, Lehmann J, Riha SJ, Krusche AV, Richey JE, Ometto JPHB, Couto EG (2008) CO_2 efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. Geophys Res Lett 35:L17401

Katsuyama M, Ohte N (2002) Determining the sources of stormflow from the fluorescence properties of dissolved organic carbon in a forested headwater catchment. J Hydrol 268:192–202

Mariot M, Dudal Y, Furian S, Sakamoto A, Vallès V, Fort M, Barbiero L (2007) Dissolved organic matter fluorescence as a water-flow tracer in the tropical wetland of Pantanal of Nhecolândia, Brazil. Sci Total Environ 388:184–193

Mayorga E, Aufdenkampe AK, Masiello CA, Krusche AV, Hedges JI, Quay PD, Richey JE (2005) Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. Nature 436:538–541

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kulbe T, Andersen DT (2001) Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol Oceanogr 46(1):38–48

Ohno T (2002) Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environ Sci Technol 36(4):742–746

Peel MC, Finlayson BL, McMahon TA (2007) Updated world map of the Köppen–Geiger climate classification. Hydrol Earth Syst Sci 11:1633–1644

R Development Core Team (2009) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna

Soil Survey Staff (1999) Soil taxonomy. USDA Natural resource conservation service, Washington

Westerhoff P, Chen W, Esparza M (2001) Fluorescence analysis of a standard fulvic acid and tertiary treated wastewater. J Environ Qual 30:2037–2046