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Key Points:
- Extremely variable riverine DOC concentration ranging from 10.6 to 114 mg/L
- iDOM accounts for 4-89% of the DOM pool
- Large variability of riverine DOM source and composition

Supporting Information:
- Readme
- Table S1–S5
- Figure S1

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Mobilization of optically invisible dissolved organic matter in response to rainstorm events in a tropical forest headwater river

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Abstract This study emphasizes the importance of rainstorm events in mobilizing carbon at the soil-stream interface from tropical rainforests. Half-hourly geochemical/isotopic records over a 13.5 h period from a 20 km^2 tropical rainforest headwater in Guyana show an order of magnitude increase in dissolved organic carbon (DOC) concentration in less than 30 mins (10.6–114 mg/L). The composition of DOC varies significantly and includes optically invisible dissolved organic matter (iDOM) that accounts for a large proportion (4–89%) of the total DOC, quantified using size exclusion chromatography (SEC). SEC suggests that iDOM is comprised of low molecular weight organic moieties, which are likely sourced from fresh leaf litter and/or topsoil, as shown in soils from the surrounding environment. Although poorly constrained at present, the presence of iDOM further downstream during the wet season suggests that this organic matter fraction may represent an unquantified source of riverine CO_2 outgassing in tropical headwaters, requiring further consideration.

1. Introduction

Inland hydrological processes are fundamental to interactions between the land and ocean that impact global carbon (C) and nutrient balances [*Aufdenkampe et al.*, 2011]. Global river networks annually receive an estimated 2.9 Petagrams (Pg) of organic and inorganic C from the terrestrial environment but only deliver around one third of this C to the World's oceans [*Tranvik et al.*, 2009]. Consequently, rivers are considered highly active processors that temporarily store C in riverbed sediments and recycle C to the atmosphere as CO_2 [*Battin et al.*, 2009; *Cole et al.*, 2007]. Tropical rivers are particularly important in this global context, estimated to transport a total of 0.53 Pg C yr^{-1} to the ocean [*Huang et al.*, 2012] while 0.9 Pg of CO_2 yr^{-1} is released back to the atmosphere [*Richey et al.*, 2002]. Surprisingly, although headwaters ($< 30\ km^2$) typically account for 70–80% of worldwide river networks [*Gomi et al.*, 2002], their role in the mobilizing, transporting, and recycling C is understudied. Our current understanding of C dynamics mainly comes from the main channel of very large ($> 10{,}000\ km^2$) rivers, such as those in the Amazon or Congo watersheds [*Richey et al.*, 1990; *Spencer et al.*, 2012], which integrate the biological and chemical signatures of vast watersheds and consequently do not provide information on the fundamental DOM transformations that are operating over the majority of the channel network in the numerous small streams [e.g., *Rasera et al.*, 2008]. It is at this small scale where the impact of soil, vegetation, and land use is strongest, directly linking dynamic hydrological and climatic processes with the cycling of C and nutrients in the river [e.g., *Dalzell et al.*, 2007]. The few studies available from small tropical headwater forest rivers show large concentrations and unit area flux of dissolved organic carbon (DOC) [e.g., *Johnson et al.*, 2006b; *Mayorga et al.*, 2005; *Waterloo et al.*, 2006] compared to downstream rivers [*Rasera et al.*, 2008; *Richey et al.*, 2002]. However, our limited knowledge of the temporal variability of C cycling at the small headwater scale limits our understanding of how weather variability at the local scale affects the functioning of tropical forest ecosystems as C sinks or sources, i.e., changes in the frequency and/or intensity of rain storm events [*Wohl et al.*, 2012].

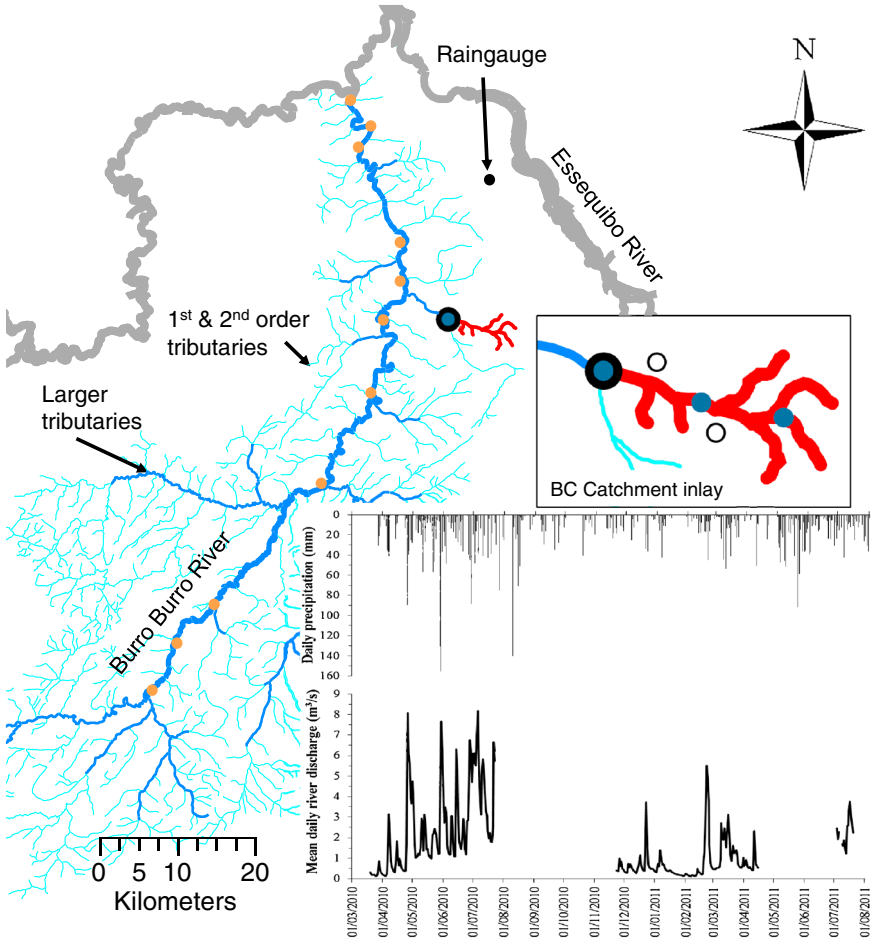

Figure 1. The Burro Burro watershed bounded by the Essequibo River and its tributaries to the north, east, and west (in grey). Orange dots are sampling locations from the BBR survey in March and July 2010 (note that some locations obscured). BC inlay: blue dots show sample locations in March and June/July 2010 and 2011. The black dot shows rainstorm sample location and the river stage transducer. Black circles show soil profiles. Bottom right inlay shows BC average daily discharge and daily precipitation total (March 2010 to August 2011).

Globally, the concentration of DOC in most river waters has a strong relationship with chromophoric, i.e., colored DOM (CDOM) from humic substances [*Carter et al.*, 2012; *Weishaar et al.*, 2003]. When calibrated for individual channels of large rivers in all climate zones, UV-visible absorbance serves as a robust proxy for DOC concentration [*Griffin et al.*, 2011; *Jeong et al.*, 2012], including some large tropical rivers [*Spencer et al.*, 2010; *Yamashita et al.*, 2010]. However, little is known about the overall contribution of CDOM to the total riverine DOM pool at the small headwater scale where soil-water generates the streamflow. To better understand this relationship, we generated field and laboratory data from a pristine tropical rainforest headwater system, documenting variations in riverine DOC quantity and composition with a focus on rainstorm events and peak wet and dry seasons.

2. Material and Methods

In 2010 a field sampling program investigated the seasonal variability of DOC of the Burro Burro River (BBR), a 3200 km^2 headwater watershed situated in the lowland tropical rainforest of central Guyana (Figure 1). Surface water samples (0.5 m) were collected along the main channel from the source to the watershed outlet at 24 and 21 locations during peak dry and wet seasons (March/July after *Bovolo et al.* [2012]; $n = 45$), respectively. To investigate seasonal variability at the small scale, a second-order tributary of the BBR, Blackwater Creek (BC, 20 km^2 watershed; Figure 1), was sampled at three locations along a 5 km transect from the

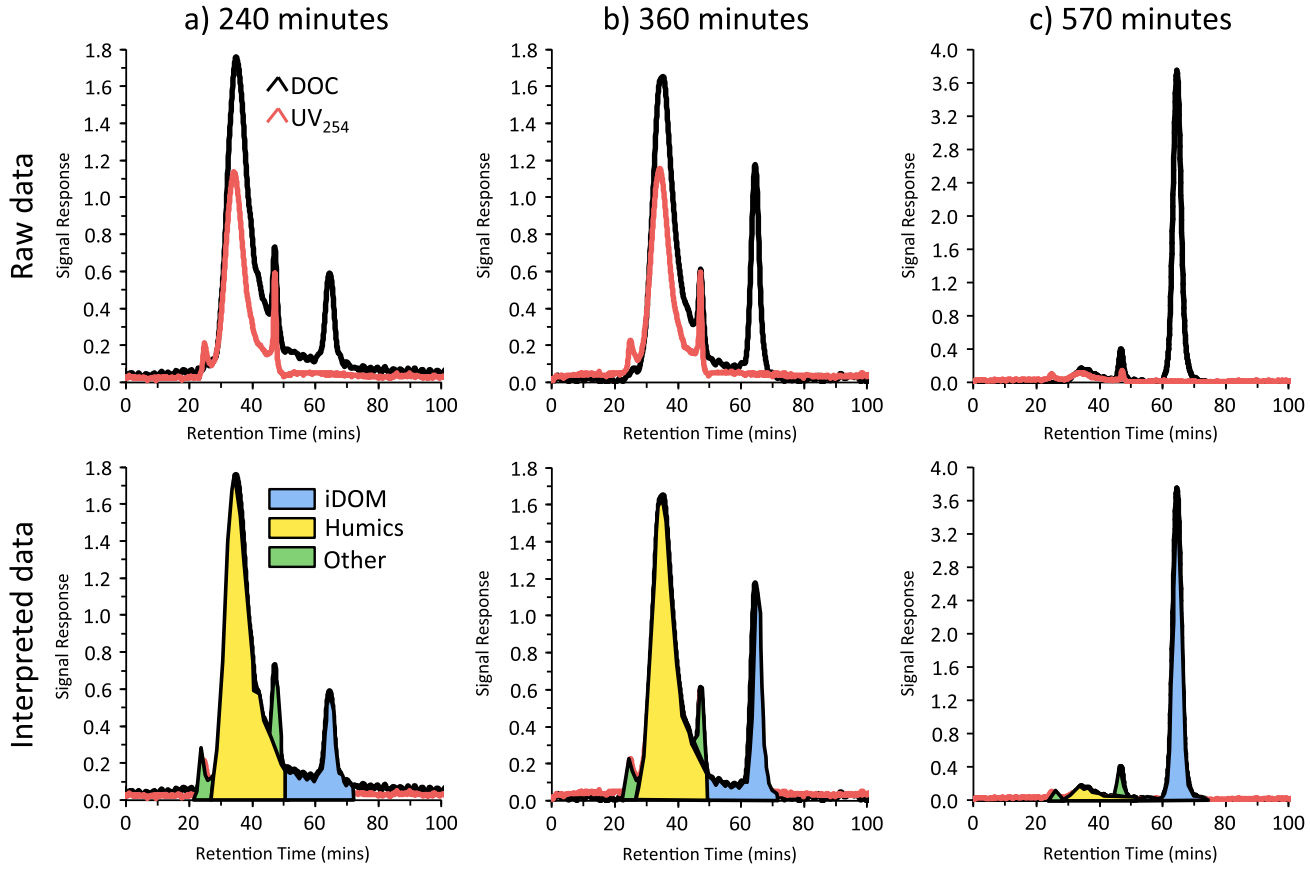

Figure 2. SEC chromatograms of BC water samples at 240, 360, and 570 min encompassing a tropical rain event. Data shown as raw chromatograms with DOC- and UV-detector response and interpreted groups of iDOM, humics, and other compounds.

stream source down to the outlet. Seventy percent of the BBR watershed is occupied by sub-catchments of similar size to the BC watershed, emphasizing the potential relevance of headwater streams to C cycling at this location or elsewhere [*Gomi et al.*, 2002]. Three samples were collected from BC during March and July of 2010 and 2011 ($n = 12$). To ascertain the role of rain events, river samples were collected from a single location on the 7 July 2011, 14 July 2013, 15 July 2013, and 18 July 2013, for a period of ~13 h. All samples were filtered (0.45 μm) and measured in situ for spectral absorbance (200–800 nm) using a UV-visible spectrophotometer and subsequently kept frozen in the dark. All filtered water samples were analyzed in the laboratory for DOC and DOM composition by size exclusion chromatography (SEC) with the 2011 data set analyzed for δ^{13}C-DOC, lignin phenol biomarkers, and iron (Fe).

DOM composition was determined using SEC, which separates DOM into different size fractions based on compound group retention behavior, reference materials, and the amount of OC compared to UV absorbance [*Huber et al.*, 2011]. Briefly, five DOM groups were separated using a SEC column (Figure 2), assigned by the retention times of DOM size which were further grouped in to three classifications: humic substances and its breakdown products ("humics"), low molecular weight neutrals ("iDOM," defined below), and low molecular weight acids, biopolymers (including polysaccharides, amino sugars, and polypeptides), and proteins ("other"). For a full description of field installation and analytical details, see supporting information.

3. Results and Discussion

The globally well-established relationship between DOC and CDOM is observed in the larger BBR during the dry season, but notably this relationship breaks down in the wet season of 2010 (Figure S1 in the supporting information) suggesting a temporary decoupling of both riverine C components. Using UV absorbance at 254 nm

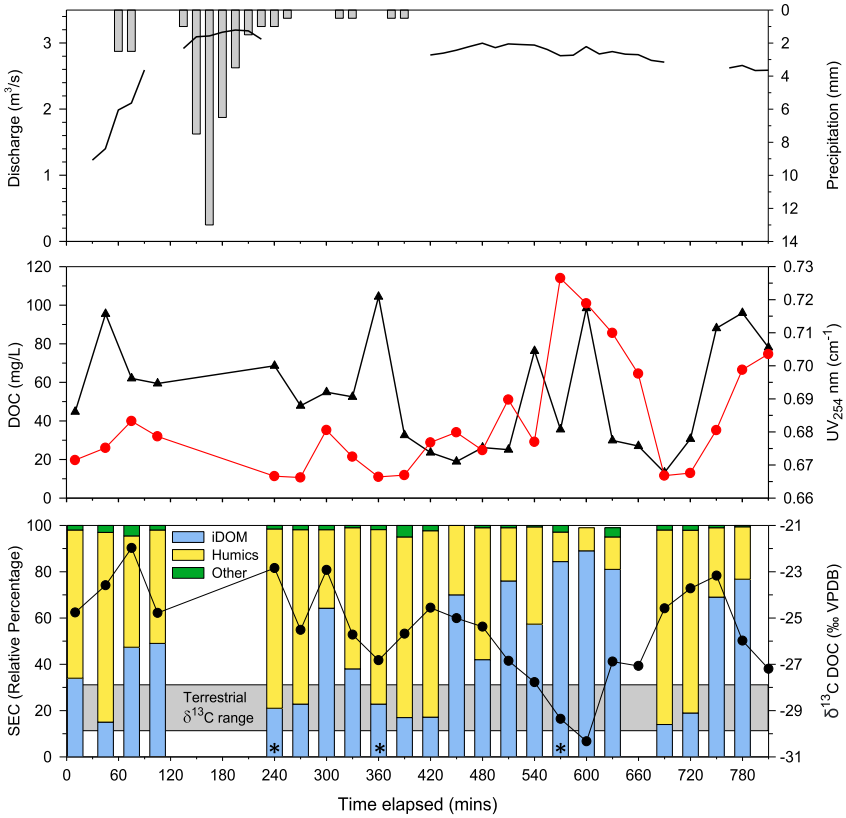

Figure 3. Data collected from BC over 13.5 h encompassing a rain event. (Top) River discharge (line) and precipitation (bars) measured nearby (~15 km) at 5 min intervals (total rainfall 42.5 mm). (Middle) UV absorbance at 254 nm (black line and triangles) and DOC (red line and dots). (Bottom) SEC-derived DOM composition as relative percentage bar of humic organic matter (yellow), iDOM (blue), and other minor compounds (green). The black line is $\delta^{13}C$ of DOC with the grey box displaying the $\delta^{13}C$ range observed in BC forest litter and soils indicating a predominantly terrestrial C3 carbon fixation pathway. Asterisk denotes samples presented in Figure 2.

(UV_{254}) [*Weishaar et al.*, 2003], we observe a linear relationship (R^2) of 0.82 ($p < 0.001$) in the dry season (DOC = 4.0–18.9 mg/L and UV_{254} = 0.011–0.682) but only 0.04 ($p = 0.23$) in the wet season (DOC = 12.1–27.3 mg/L and UV_{254} = 0.183–0.704). This decoupling was observed at other wavelengths (e.g., 270 and 350 nm); and when utilized in a global model (see supporting information), we observe that measured DOC is always greater than DOC modeled using UV absorbance. This suggests that the BBR always contains a component of riverine DOM that is nonchromophoric, nonhumic, and thus optically invisible to UV absorbance spectroscopy but is increased in the wet season (Figure S1). We therefore define the term "invisible" DOM ("iDOM") as the non-chromophoric counterpart of CDOM that contributes to the total DOC pool.

We further studied the relationship between CDOM, iDOM, and DOC during the 2010 and 2011 wet and dry seasons in BC. However, no clear seasonal pattern was evident in the relationship between DOC and UV_{254} (Table S2). Exploring the hydrological regime further, the daily rainfall measured at the Iwokrama field station (~7 km from BC) and the BC discharge record from March 2010 to August 2011 demonstrated a strong response to a series of short rainstorm events (< 24 h), each potentially affecting the relative supply and composition of the two DOC components (Figure 1). To resolve these relationships at the event time scale, BC was sampled at near half-hour resolution encompassing BC's response to a rainstorm event. The 2011 time series (Figure 3 and Tables S3 and S4) captured river discharges ranging from 1.2 to 3.2 m^3/s and an order of magnitude increase in DOC (10.6 to 114.0 mg/L). These values by far exceed the range observed during peak dry and wet seasons recorded in BC, in the larger BBR in 2010 (4.0–27.3 mg/L; Tables S1 and S2) and the ranges reported for Amazonian headwaters during similar storm events [*Johnson et al.*, 2006a; *Waterloo et al.*, 2006]. Notably, the 2013 rain event time series display much lower discharge regimes ranging from 0.79 to 1.68 m^3/s with near stable DOC concentrations (10.6 to 17.7 mg/L). This contrast may represent a hydrological threshold, recognizing

that the 2011 time series captured a period of rainfall totaling 42.5 mm, compared to an order of magnitude lower (1.6 to 2.8 mm) during the 2013 time series (Table S3).

The 2011 time series emphasizes the importance of short-term (subhourly) interactions between organic matter (OM) sources (throughfall, surface, and soil) and riverine DOC transport suggesting a currently unconstrained hydrological threshold behavior. The δ^{13}C-DOC record shows that C sources changed substantially during the event, ranging from −22.0‰ at low-DOC to −30.3‰ at high-DOC supply (Figure 3). More negative δ^{13}C-DOC signatures are consistent with supply from surrounding leaf litter and surface soils below C_3 vegetation (−28.8 to −29.4‰ 0–1 m below ground; Figure 3 and Tables S4 and S5), whereas higher δ^{13}C at low DOC argue for enhanced contribution of autochthonous C, e.g., from microbial or macrophytic sources, in the absence of C_4 vegetation in the study region [e.g., *Baskaran*, 2011]. Alternatively, or in addition, the δ^{13}C shift may represent compositional changes in the total OM pool from biodegradation processes at the surface or during transport, where bulk signatures of OM can be up to 6‰ higher compared to "fresh" OM [e.g., *Wynn*, 2007].

Our study shows that UV absorbance data from BC do not respond to changes in DOC during any of the 2011 and 2013 rainstorm time series ($R^2 < 0.08$; Table S4), consistent with the observations from the larger BBR in the wet season. Lignin phenols (Σ_8; Table S4) measured in the 2011 time series confirm that humic material is present throughout, which should respond to UV absorbance. One possible explanation for the poor relationship between absorbance, DOC, and presence of lignin phenols may be due to interferences of UV absorbance with dissolved Fe^{3+} [*Doane and Horwáth*, 2010]. We confirmed the presence of iron in the 2011 samples from BC (Table S4; Fe = 0.21–0.40 mg/L). However, the observed pH range of 4–6 and redox range between 0.6 and 4.8 pe in the BC indicates the presence of dissolved Fe^{2+}, in the water column, which has been shown to cause minimal interference with UV absorbance [*Doane and Horwáth*, 2010]. Consequently, there must be an additional OM component in our river system explaining the poor relationships described above, i.e., iDOM.

The identification of DOM composition using SEC revealed dominant humic (CDOM) and iDOM components in BC, with relative contributions of iDOM and CDOM between 4.1 and 89.1% and 10.5–91.9%, respectively. The highest iDOM fractions were observed for the 2011 rainstorm at maximum DOC levels with the most depleted δ^{13}C-DOC values (Figure 3) and a river discharge that was ~twofold higher than measured during 2013. SEC calibration suggests that iDOM is composed of low molecular weight compounds [*Huber et al*., 2011] that are potential degradation products of carbohydrate plant OM sources. The variation in riverine DOM composition indicated by δ^{13}C-DOC and SEC results suggest changes in the dominant hydrological pathway. For example, during high rainfall and discharge DOM pools from the upper soil and litter layers are preferentially mobilized, rather than DOM from the deeper subsurface, consistent with observations elsewhere in the tropics [*Johnson et al*., 2006a, 2006b]. We tested whether a surface flow path could selectively mobilize iDOM from the litter layer by conducting water extractable DOM experiments from two soil profiles within the BC catchment (Figure 1 and Table S5). The results demonstrated a maximum potential of 217 mg of DOC leachate per gram litter compared to 38 mg DOC/g in topsoil (0–0.1 m) and 1 mg DOC/g in deeper soil (0.5–1.0 m). Notably, SEC analyses on all litter/soil samples show that ~25% of DOM is iDOM, with a general decrease with depth. This evidence confirms a reservoir of iDOM in the surrounding environment that is available for mobilization to the river, depending on the dominant hydrological flow path. Consequently, during the 2011 rainstorm event a dominant surficial flow path could have preferentially mobilized iDOM from the litter/surface soil pool explaining the simultaneous maxima in riverine DOC and iDOM. Conversely, lower contributions of iDOM during the 2013 time series would represent a stronger geochemical signature from deeper soils (Table S4). Whether this deeper flow path allows for greater OM mineral and microbiological interactions within the subsurface [e.g., *Kaiser and Guggenberger*, 2000; *Kalbitz et al*., 2005] is currently unknown. If so, these subsurface processes could reduce the abundance of iDOM relative to CDOM signature in the river, consistent with our SEC observations during periods of lower discharge in BC. The wider spatial significance of shallow versus deeper mobilization of iDOM to the river is currently unknown. However, the observed decoupling between DOC and UV absorbance in the larger BBR during the 2010 wet season supports the concept of a greater supply of iDOM via near-surface flow paths during rainstorm and seasonal wet periods.

4. Implications

Time series measurements encompassing rainstorm events in small streams (BC) and seasonal patterns in larger rivers (BBR) of Guyanese headwaters demonstrate substantial and short-term mobilization of iDOM

once a hydrological threshold of at least 3.2 m^3/s is passed. This threshold behavior emphasizes the importance of the terrestrial aquatic interface as a hot spot of biogeochemical cycling during hot moments [*McClain et al*., 2003]. The major contribution of iDOM in Guyanese headwaters stands out when compared to global models [*Carter et al*., 2012], which accurately predict DOC in ~1700 rivers from middle to high latitudes, where CDOM represents the main component of riverine DOC and an assumed constant iDOM contribution of 0.8 mg/L. The exploratory nature of this study from Guyana and its remote location inevitably resulted in limitations in data density and spatial coverage that cannot easily be overcome. Further research is required to better constrain the presence, sources, and dynamics of iDOM in other tropical headwater systems and its link to hydrological flow paths and threshold conditions. Furthermore, to assess the spatial distribution and resilience of iDOM as part of the terrestrial C cycle, the interrelationships between headwaters and larger downstream rivers and the role of microbial turnover (either directly or through priming of higher molecular weight material [e.g., *Bianchi*, 2011]) and photooxidation of iDOM need investigation in a catchment-wide context, as this could potentially provide a substantial but currently unconstrained component of riverine CO_2 outgassing [*Mayorga et al*., 2005; *Richey et al*., 2002; *Davidson et al*., 2010].

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