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Conversion of Forest to Agriculture Increases Colored Dissolved Organic Matter in a Subtropical Catchment and Adjacent Coastal Environment

Stacey L. Felgate[1,2], Christopher D. G. Barry[3], Daniel J. Mayor[2], Richard Sanders[2,4], Abel Carrias[5], Arlene Young[6], Alice Fitch[3], Claudia G. Mayorga-Adame[7], Gilbert Andrews[6], Hannah Brittain[2], Sarah E. Cryer[1], Chris D. Evans[3], Millie Goddard-Dwyer[2,8], Jason T. Holt[7], Bethany K. Hughes[9], Dan J. Lapworth[10], Adam Pinder[3], David M. Price[1], Samir Rosado[6], and Claire Evans[2]

[1]Ocean and Earth Sciences, University of Southampton, Southampton, UK, [2]Ocean Biogeosciences, National Oceanography Center, Southampton, UK, [3]UK Center for Ecology and Hydrology, Bangor, UK, [4]Norwegian Research Centre, Bjerknes Centre for Climate Research, Bergen, Norway, [5]Faculty of Science and Technology, University of Belize, Belmopan, Belize, [6]Coastal Zone Management Authority and Institute, Belize City, Belize, [7]Marine Systems Modelling, National Oceanography Centre, Liverpool, UK, [8]Department of Earth, Ocean, and Ecological Sciences, University of Liverpool, Liverpool, UK, [9]Natural Sciences, University of Southampton, Southampton, UK, [10]British Geological Survey, Wallingford, UK

Key Points:

- A shift from broadleaf forest to agri-urban land increased colored dissolved organic matter in the Belize River watershed
- Humic-like material increased in transit downstream and behaved conservatively in coastal waters, indicative of its recalcitrance
- Land-use change has increased terrigenous dissolved organic matter concentrations overlying Belize's coral reefs

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

S. L. Felgate,
stacey.felgate@soton.ac.uk

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Author Contributions:

Conceptualization: Richard Sanders, Chris D. Evans, Claire Evans
Data curation: Stacey L. Felgate
Formal analysis: Stacey L. Felgate, Christopher D. G. Barry, Claudia G. Mayorga-Adame, Jason T. Holt, Adam Pinder
Funding acquisition: Claire Evans
Investigation: Stacey L. Felgate, Christopher D. G. Barry, Abel Carrias, Alice Fitch, Gilbert Andrews, Hannah Brittain, Sarah E. Cryer, Millie

Abstract

Land-ocean dissolved organic matter (DOM) transport is a significant and changing term in global biogeochemical cycles which is increasing as a result of human perturbation, including land-use change. Knowledge of the behavior and fate of transported DOM is lacking, particularly in the tropics and subtropics where land-use change is occurring rapidly. We used Parallel Factor (PARAFAC) Analysis to investigate how land-use influenced the composition of the DOM pool along a subtropical land-use gradient (from near-pristine broadleaf forest to agri-urban settings) in Belize, Central America. Three humic-like and two protein-like components were identified, each of which was present across land uses and environments. Land-use mapping identified a strong ($R^2 = 0.81$) negative correlation between broadleaf forest and agri-urban land. All PARAFAC components were positively associated with agri-urban land-use classes (cropland, grassland, and/or urban land), indicating that land-use change from forested to agri-urban exerts influence on the composition of the DOM pool. Humic-like DOM exhibited linear accumulation with distance downstream and behaved conservatively in the coastal zone whilst protein-like DOM exhibited nonlinear accumulation within the main river and nonconservative mixing in coastal waters, indicative of differences in reactivity. We used a hydrodynamic model to explore the potential of conservative humics to reach the region's environmentally and economically valuable coral reefs. We find that offshore corals experience short exposures (10 ± 11 days yr^{-1}) to large (~120%) terrigenous DOM increases, whilst nearshore corals experience prolonged exposure (113 ± 24 days yr^{-1}) to relatively small (~30%) terrigenous DOM increases.

Plain Language Summary

The transport of land-derived dissolved organic matter into the oceans plays a substantial and important role in the global carbon and nutrient cycles. Land-use change can alter the type and amount of material being transported, with widespread implications for downstream ecosystems. This is particularly true in the tropics and subtropics where land-use change is occurring most rapidly, and where research into its effects is often lacking. We investigated whether land-use had an effect on the type and amount of land-derived material found in a subtropical river system that is experiencing a rapid conversion from forest to agricultural and urban land-use. We found that streams draining agricultural and urban land contained more land-derived material than those draining forested land, and that a substantial fraction of this material reached the coastal environment. We estimated the frequency with which this land-derived material reached the region's environmentally and economically valuable coral reefs, and suggest that land-use-derived material reaches nearshore corals often and offshore corals rarely.

Goddard-Dwyer, Bethany K. Hughes, David M. Price, Samir Rosado
Methodology: Stacey L. Felgate, Christopher D. G. Barry
Project Administration: Stacey L. Felgate
Resources: Abel Carrias, Arlene Young, Dan J. Lapworth, Claire Evans
Software: Claudia G. Mayorga-Adame
Supervision: Daniel J. Mayor, Richard Sanders, Chris D. Evans
Validation: Stacey L. Felgate, Christopher D. G. Barry
Visualization: Stacey L. Felgate, Alice Fitch, Claudia G. Mayorga-Adame
Writing – original draft: Stacey L. Felgate
Writing – review & editing: Stacey L. Felgate, Christopher D. G. Barry, Daniel J. Mayor, Richard Sanders, Abel Carrias, Arlene Young, Alice Fitch, Claudia G. Mayorga-Adame, Gilbert Andrews, Hannah Brittain, Sarah E. Cryer, Chris D. Evans, Millie Goddard-Dwyer, Jason T. Holt, Bethany K. Hughes, Dan J. Lapworth, Adam Pinder, David M. Price, Samir Rosado, Claire Evans

1. Introduction

The land-ocean aquatic continuum is a complex network of environments that include streams, lakes, reservoirs, wetlands, estuaries, and coastal seas. The lateral transport of terrigenous dissolved organic matter (DOM) through this continuum is a significant and changing biogeochemical term with widespread implications for global carbon and nutrient cycling (Drake, Raymond, & Spencer, 2018). Anthropogenic perturbations including climate change and land-use change are major contributors to altered terrigenous DOM transport, and are estimated to have doubled the amount of land-derived carbon entering the continuum since the start of the industrial revolution, increasing it by ∼1 Pg (Regnier et al., 2013). Despite this scale of change, we know relatively little about what happens to terrigenous DOM in transit, how much of it reaches the open ocean, or what effects it has therein. This lack of understanding hinders our ability to quantify the role of aquatic DOM in global biogeochemical cycles, including the potential contribution of land-use change derived DOM to anthropogenic CO_2 emissions.

Studies of terrigenous DOM in tropical and subtropical catchments are sparse, yet climate change effects are disproportionately high in these regions and they are commonly subject to high rates of land-use change resulting from ongoing development. Between 1980 and 2000, ∼80% of new agricultural land originated from the world's tropical and subtropical forests (Gibbs et al., 2010), and the expansion of cropland and pasture continues to be the principal driver of deforestation in the developing world (Houghton, 2003; Song et al., 2018). Agricultural expansion has been associated with declines in water quality, including those related to shifts in the composition of the DOM pool such as reduced water clarity, eutrophication, and deoxygenation (Mello et al., 2018; Singh et al., 2017; Yang et al., 2012). Shifts in DOM composition are commonly investigated using optical tools (absorbance and fluorescence spectrophotometry; Murphy et al., 2010; Stedmon et al., 2003) which target the chromophoric or "colored" fraction (cDOM). cDOM can also provide a qualitative measure of DOM quantity, with absorbance typically correlating strongly with dissolved organic carbon (DOC) concentration in terrestrially influenced systems (e.g., Carter et al., 2012). Much of the cDOM pool is also fluorescent (fDOM), and methods by which fluorescent properties can be used to investigate cDOM character have been well established (Murphy et al., 2010; Stedmon et al., 2003).

Forests typically accrue relatively aromatic, recalcitrant soil organic matter (SOM) in their surface soils (Inamdar et al., 2012) which is highly colored. Deforestation results in reduced soil stability, leading to increased export of this material which peaks post-felling and reduces gradually over time (West et al., 2004). Conversion of deforested land to agriculture can further enhance SOM export as a result of physical disturbance (tillage), hydrological modification (irrigation), and overgrazing (Condron et al., 2014; Graeber et al., 2015; Klumpp et al., 2009). As a result, agricultural soils are up to 60 times as erosive as forest soils (Renard et al., 2017). Recent work suggests that older, less aromatic, less highly colored DOM may be released as deeper soil horizons become destabilized. This material is more bio-labile and thus, undergoes more rapid remineralization than surface SOM (Drake et al., 2019). At the same time, overuse of fertilizers can increase the export of aliphatic and low-aromaticity, low-colored DOM forms that are also bio-labile (Gücker et al., 2016) whilst anthropogenic DOM of a similar character has been shown to increase in urban settings (Arango et al., 2017; Smith & Kaushal, 2015). This is particularly relevant in areas where sanitation is poor (e.g., Mostofa et al., 2010). Thus, land-use can be the primary explanator of variance in the DOM pool where anthropogenic influence is high (Roebuck et al., 2019), and land-use change from forested to agri-urban can have profound implications for the quantity and composition of DOM entering the land-ocean aquatic continuum. Our understanding of forest SOM cycling is dominated by temperate studies (Kalbitz et al., 2000), but previous research has shown that tropical and subtropical forest soils may exhibit higher turnover rates and contain lower SOM stocks than temperate forest soils do (Trumbore, 1993), and that they may also contain a substantial pool of less recalcitrant DOM which undergoes relatively rapid remineralization once mobilized (Gmach et al., 2020).

Once in the land-ocean continuum, terrigenous DOM undergoes a range of bio-mediated and photo-mediated transformations, driven by a range of biotic and abiotic processes which vary by geographical and climatic setting, water residence time, environmental conditions, and the molecular properties of the DOM (Anderson et al., 2019; Kothawala et al., 2020). Catchment land-use can modify these transformations by altering the environmental conditions, water residence time and/or DOM composition. For example, inorganic nutrient export from agri-urban settings can promote the in-situ growth of microorganisms, resulting in an increase in the amount of autochthonous DOM present (e.g., algal exudates and protein-like material; Evans et al., 2017; Williams et al., 2016) and have been linked with increased DOM diversity (Kamjunke et al., 2019). Altered hydrological conditions and increased residence times associated with watercourse modification (e.g., hydroelectric dams and reservoirs) can enhance autochthonous production and the opportunities for bio-degradation and photo-degradation (Mayorga et al., 2010; Winemiller et al., 2016). The net effect of such transformations across the continuum determines the quantity and composition of DOM exported to the ocean.

Land-ocean DOM fluxes constitute organic carbon subsidies and inputs of bioavailable dissolved organic nutrients into the coastal ocean which influence, for example, microbial community composition and net ecosystem metabolism, carbonate equilibria, and gaseous carbon fluxes, with implications for water quality, productivity, biodiversity, and the global carbon cycle (Lønborg et al., 2020; St. Pierre et al., 2020). While the economic impacts of nutrient and sediment fluxes on coastal ecosystems are well recognized (Fichot & Benner, 2014; Molotoks et al., 2018), increased DOM inputs can also negatively impact ecosystem health and the marine economy, notably through impacts on coral reefs (Butler et al., 2013; Devlin & Schaffelke, 2012; Sharp et al., 2014). This link between land and sea means that the effective co-management of terrestrial and marine ecosystems and the economies which rely upon them requires an understanding of terrigenous DOM transport and transformation within the aquatic continuum.

In this study, we investigate the character and behavior of terrigenous DOM in a subtropical watershed which has been subject to significant deforestation and agricultural expansion, and which drains into an economically and environmentally valuable coastal zone, focusing on the colored and fluorescent fraction. Belize is the most forested country in Central America, but recent estimates place mature forest cover at just 59% compared to 76% in 1980, a 25% loss over 40 years (Cherrington et al., 2010; Voight et al., 2019). Agriculture supports ∼9% of Belize's gross domestic product (GDP), and is expanding (Prouty et al., 2008; Statistical Institute of Belize, 2019). Belize is also home to the Belize Barrier Reef which is a global biodiversity hotspot (Young, 2008) and supports ∼30% of the country's GDP via tourism and fisheries-related activities (Prouty et al., 2008; Statistical Institute of Belize, 2019).

We studied cDOM character in Belize's largest catchment, the Belize River Watershed. We investigated (1) the influence of land-use change on cDOM character using a forested to agri-urban land-use gradient and (2) the behavior of land-use change mediated DOM as it moves from land to sea. Finally, we employed a hydrodynamic model to investigate connectivity between terrigenous cDOM and the environmentally and economically important coral reefs of the Belize Barrier Reef. We hypothesized that (1) subcatchments draining agri-urban land will contain more cDOM than subcatchments draining forested land; (2) humic-like cDOM will be transported downstream and into the coastal environment, whilst protein-like cDOM will be rapidly remineralized; and (3) humic-like cDOM will persist within the Belize River plume, and reach the Belize Barrier Reef.

2. Methods

2.1. Regional Setting

The Belize River watershed covers an area of 8,542 km^2. Air temperatures range from 25°C to 38°C in the wet season (c. May–November), and 16°C to 28 °C in the dry season (c. December–April). Annual precipitation ranges from ∼2,500 mm in upland regions to ∼1,600 mm in lowland regions, ∼80% of which occurs during the wet season. Annual actual evapotranspiration is 56% to 75% precipitation, such that annual runoff in subcatchments ranges from 400 to 1,100 mm. The Maya Mountains (Figure 1) comprise Paleozoic metamorphic and volcanic rocks with granitic intrusions; soils are siliceous, acid, and highly erodible. Surrounding these to the north and west are karstic hill systems where Cretaceous limestones and dolomites underlie calcareous soils with better agricultural stability. Coastal plains account for ∼50 km of the downstream length of the Belize River and are comprised of Pleistocene alluvium deposits. Agriculture is predominantly banana, sugar, and citrus crops, with grazing livestock (Statistical Institute of Belize, 2019; Young, 2008). More detailed descriptions of Belize's physiogeography, soils, geology, land suitability for agriculture, and hydrological characteristics are provided elsewhere (Baillie et al., 1993; Esselman & Boles, 2001; Hartshorn et al., 1984; Heyman & Kjerfve, 1999; King et al., 1993)

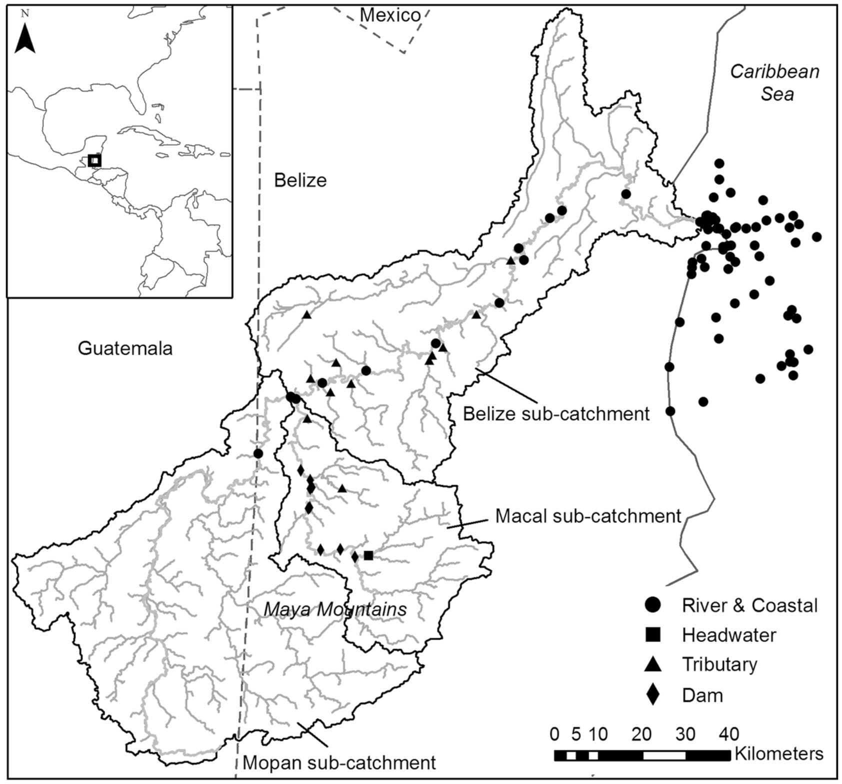

Figure 1. Map of the Belize River watershed, with sampling locations shown. The Mopan and Macal subcatchments are also shown.

The Belize River has two principal subcatchments: the Macal River (1,466 km^2) and the Mopan River (3,690 km^2) (Figure 1). Both drain from relatively pristine forested landscapes above 400 m elevation within the Maya Mountains, but much of the Mopan catchment lies within the Western Uplands region of Guatemala which has been subject to severe deforestation (Karper & Boles, 2004). The main river stem of the Mopan flows ~50 km northeast through agricultural land at ~150 m elevation, before re-entering Belize at the border near Benque. The Macal drains north and passes through a series of three hydroelectric dams (henceforth termed "the dam complex"), which are also intended to serve flood control purposes: the Chalillo (capacity = 120 million m^3; build completed 2005, ~380 m elevation), Mollejon (1.7 million m^3, completed 1995, ~280 m elevation), and Vaca (0.12 million m^3, completed 2010, ~130 m elevation) dams. Physicochemical and ecological impacts of these dams are described elsewhere (Lanza, 2019). The Mopan and Macal merge ~33 km downstream of the border to form the Belize River at an elevation of 60 m. The Belize River then continues ~120 km north-east, gradually declining in elevation toward the coast at Belize City. It is flanked by mandated riparian forest strips and flows through a predominantly agricultural setting, with inputs from agricultural-dominated catchments to the north, and less modified, primarily forested subcatchments to the south. The coastal environment to which the Belize River discharges supports a considerable tourism sector, diverse fisheries, and mangrove cayes (Young, 2008). Notably, the Belize Barrier Reef, a substantial part of the world's second-largest barrier reef system (the Mesoamerican Barrier Reef), lies ~20 km offshore, with some nearshore coral formations as close as ~5 km offshore. Studies have found elevated levels of trace metals, which are indicators of landscape derived sediments, in nearby corals influenced by neighboring catchments which have been subject to significant soil erosion due to forest clearance combined with high slope and runoff (Heyman & Kjerfve, 1999; Prouty et al., 2008).

2.2. Land-Use Mapping

Land-use within the Belize River watershed was derived from random forest classification in *R* (R Core Team, 2019) on composited Sentinel-1 and Sentinel-2 level 2A images captured between November 2018 and February 2019 along with a digital elevation model (DEM) (Lehner et al., 2008). Model validation data were collected in February 2019 using catchment-wide in-person surveys, guided by an existing, coarser resolution country-level land cover map (Meerman, 2015). Classification errors were <1% (Table S1). Subwatersheds were generated for each sampling location using a DEM and the ArcHydro toolbox. Land-use classes were extracted for each subwatershed as a percentage using zonal statistics (Table S2). Eleven distinct classes were identified: submontane broadleaf forest, lowland broadleaf forest, plantation, urban, grassland, cropland, wetland, inland waters, pine savanna, broadleaf savanna, and shrub. Land-use varied significantly (ANOVA; $p \leq 0.05$) between tributary sampling locations, and a strong negative correlation ($R^2 = 0.81$) was observed between % broadleaf forest (lowland and submontane) and % agri-urban (cropland, grassland, plantation, and urban) land-use (Figure S1). Land-use did not vary significantly along the length of the main river (ANOVA; $p > 0.42$; Figure S2), and so was excluded as an explanatory variable within the main river data set. A land cover map of the watershed is given in Figure S3.

2.3. Water Sample Collection

Water samples were collected during three visits between October 2018 and October 2019 at locations shown in Figure 1 (split by sampling visit in Figure S4). The dam complex (October 2019) and tributaries (November 2018, January 2019, and October 2019) were sampled from the riverbank using a plastic bucket. A rigid inflatable boat was used to conduct a sampling transect of the main river trunk (November 2018), and a small research vessel was used in coastal waters (November 2018 and October 2019). Specific conductance, salinity, pH, and water temperature were recorded at each sampling location using a Hach-Lange® handheld Multimeter probe (Hach). Sampling of the main river trunk operated as a single transect from the Belize-Guatemala western border to the limit of the freshwater extent, near Belize City, and water was collected at intervals selected to be approximately equidistant whilst avoiding sampling directly from incoming tributaries. Coastal sampling was conducted as three distinct transects adjacent to the Belize River outflow, covering the inshore region, the mid-section, and the adjacent portion of the Belize Barrier Reef, with samples taken across the full range of observed salinities (0–38 ppt). The boat was allowed to deviate from the planned transect lines to locate and sample the freshwater plume, which was identified according to salinity. Samples for determination of DOC concentration were filtered (0.45 μm Fischer® cellulose acetate) into Nalgene® HDPE bottles and stored cool and dark until their return to the laboratory. Freshwater DOC samples were then stored at 4°C. Saline DOC samples were frozen before analysis in 2018 and chilled in 2019. A comparison of absorbance spectra (see Section 2.4) produced by samples subject to each treatment indicated no statistically significant differences (ANOVA; p value > 0.05) and so the DOC data are considered comparable. Samples for optical measurement were filtered (0.45 μm Fischer® cellulose acetate) into Wheaton® amber borosilicate glass vials bottles and stored cool and dark until their return to the laboratory, then at 4°C in the dark. All sample bottles were acid washed (24 h in 10% v/v Hydrochloric Acid) and Milli-Q® rinsed before use, and were triple rinsed with sample filtrate before use. Cellulose acetate filters were flushed with 100 ml sample water before use.

2.4. Laboratory Analyses

All laboratory analyses were conducted in the United Kingdom. DOC was determined by Pt-catalyzed combustion against glycine and potassium hydrogen phthalate standards using a TOC-VCPN analyzer (Shimadzu). Reproducibility of standards was within 2% in the range 0–50 ppm. Absorbance spectra (200–800 nm) were determined at 1 nm intervals using a Cary 60 UV-Vis dual-beam spectrophotometer (Agilent) against ultrapure water (Milli-Q®). Absorbance at 254 nm (a254) is presented as a measure of cDOM. Fluorescence was measured using a Cary Eclipse scanning fluorescence spectrophotometer (Agilent), corrected for instrument-specific biases following manufacturer protocols, for excitation (Ex) wavelengths of 255–400 nm (5 nm intervals) and emission (Em) wavelengths of 280–500 nm (2 nm intervals). Ex and Em slit widths of 5 nm were employed, with a PMT voltage of 725 V and scan rate of 9,600 nm/min. Blanks were obtained using both ultrapure water in analytical cuvettes, and a sealed pure water standard (Starna®), and comparison of these were not statistically different. No samples were sufficiently optically dense to require dilution to enable robust inner-filter corrections (Kothawala et al., 2013).

2.5. Parallel Factor Modeling

Excitation-Emission Matrices produced via fluorescence spectrophotometry were modeled via parallel factor (PARAFAC) analysis, which is a tool commonly used to decompose the cDOM pool according to its fluorescent properties (Stedmon et al., 2003). Fluorescence data were modeled by in *R* using the StaRdom package (version 1.1.14, Pucher et al., 2019; R Core Team 2019). Non-negativity constraints were applied to normalized data, following standard pre-processing protocols for which blanks specific to each analytical run were used for correction and normalization of Raman peaks (Murphy et al., 2010). Excitation wavelengths <255 nm were discarded due to increased noise at those wavelengths. Identification of PARAFAC components was undertaken using the OpenFluor database of published fluorescence spectra (www.openfluor.org; Accessed July 6, 2020), using a 95% similarity criterion (Murphy et al., 2014). Sample fluorescence was calculated as the sum of peak fluorescence values (F_{max}) associated with each PARAFAC component.

2.6. Theoretical Mixing Lines

Theoretical conservative mixing lines for component fluorescence and DOC were plotted according to a standard two-endmember mixing model (Equation 1) where F_{SW} is the theoretical fraction saline water in the sample, X_{SW} is the endmember concentration for saline water, F_{FW} is the theoretical fraction fresh water in the sample, and X_{FW} is the endmember concentration for fresh water. Conservative mixing indicates that any reduction in fluorescence or concentration within the coastal zone is the result of dilution (i.e., no net addition or removal of fluorescent DOM or bulk DOC). Divergence from the associated theoretical mixing line therefore indicates net addition (data points above the line) or removal (data points below the line) in transit. Endmember salinities were 0 and 36.1 ppt in 2018, and 3.3 and 37.8 ppt in 2019, with the model extrapolated from 0 to 38 ppt as required.

$$Modelled\ Value = \left(F_{FW}\ x\ X_{FW}\right) + \left(F_{SW}\ x\ X_{SW}\right) \tag{1}$$

2.7. Hydrodynamic Model

A coastal hydrodynamic model of 1/60° horizontal resolution was used to investigate the potential for the Belize River plume to influence the local region of the BBRRS, using salinity as a tracer. For this, we used Nucleus of a European Model for the Ocean (NEMO; https://www.nemo-ocean.eu/) following the shelf-sea configuration setup for high-resolution operational forecasting in the NW European continental shelf (Graham et al., 2018; Guihou et al., 2018). The model was run for a 21-year period (1995–2015) and forced by atmospheric fields from the ERA5 reanalysis (European Centre for Medium-Range Weather Forecasts, 2019), hydrography, residual currents, and elevation from a 1/12° (~9 km) global NEMO model, and tides from FES2014 (Lyard et al., 2020). River freshwater inflows from the four major rivers in the region (Hondo, Belize, Motaqua, and Ulua) were taken from GlobalNEWS2 (Mayorga et al., 2010), and modulated by the mean annual flow cycle from the Belize River "Doublerun" flow gauge (data provided by Department of Natural Resources, Belize). Further model description is given in Supporting Information (Text S1).

The Belize Barrier Reef was mapped into georeferenced coral reef polygons obtained from the Global Distribution of Coral Reefs data set (UNEP-WCMC, 2018). Salinity thresholds were selected based on a combination of previous studies (Purdy et al., 1975; Sweetman et al., 2019), field data, and local knowledge of minimum salinity conditions overlying nearshore (~20 ppt) and offshore (~30 ppt) corals. The number of days when salinity went below these thresholds was counted for each reef polygon, and these data were converted to monthly averages across the 21-year model run (Tables S3 and S4).

2.8. Statistics

All statistics were done in *R* (R Core Team, 2019), and all analyses used an alpha of 0.05. Assumptions of normality and heteroscedasticity were met. Analysis of variance (ANOVA) was used to identify differences between sampling trips and environments. No significant difference was observed between sampling year within the tributaries, and so those data were grouped for analysis. Cooks distance was used where appropriate to identify and examine outliers. Relationships between land-use, DOC, and component fluorescence

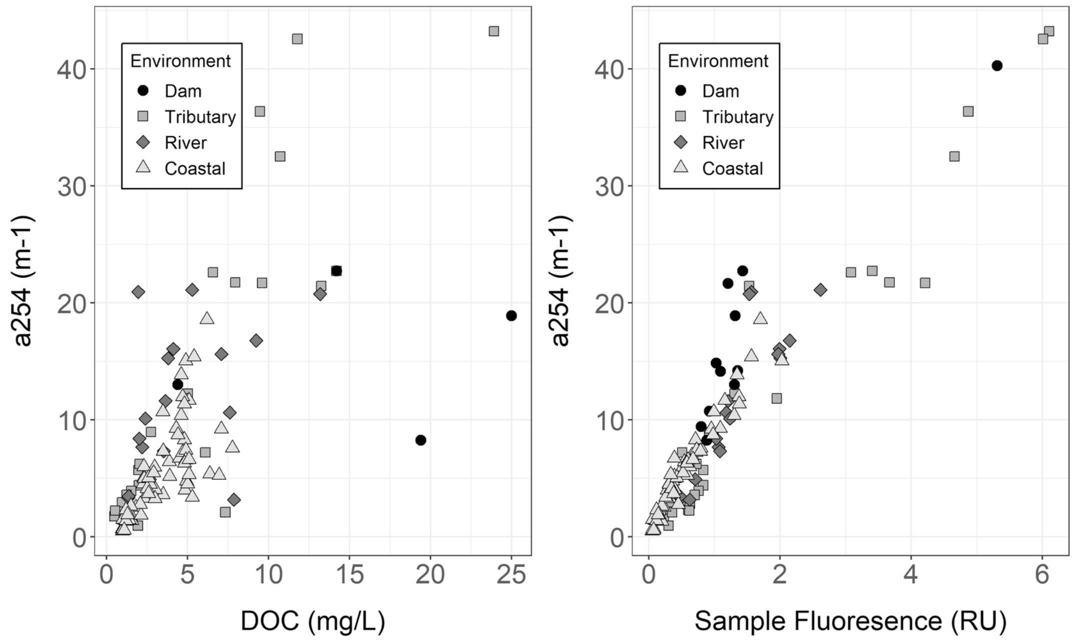

Figure 2. Plots of (left) dissolved organic carbon versus a254 showing a variable decoupling between the two measurements, and (right) sample fluorescence versus a254, indicating a more coupled relationship.

intensities within the tributaries were investigated using stepwise multiple linear regression analysis, with the final model selected by Akaike information criterion (AIC). Collinearity between land-use classes was examined using Variance Inflation Factors (VIF; "car" package, Fox & Weisberg, 2011) and explanatory variables were removed from models in decreasing order of VIF score until all scores were <5. This resulted in the removal of broadleaf forest (collinear with grassland [$R^2 = 0.67$], cropland [$R^2 = 0.66$], urban [$R^2 = 0.54$], and plantation [$R^2 = 0.18$]), broadleaf savanna (collinear with wetland [$R^2 = 0.68$], pine savanna [$R^2 = 0.36$], and grassland [$R^2 = 0.14$]), and shrub (collinear with plantation [$R^2 = 0.61$], cropland [$R^2 = 0.18$], and pine savanna [$R^2 = 0.13$]). The relationship between land-use and the composition of the fluorescent DOM pool was then investigated using redundancy analysis (RDA; "vegan" package, Oksanen et al., 2019), in which the best fit was backward selected using F statistics.

3. Results

3.1. cDOM Versus DOC

We observed a significant positive relationship between DOC and absorbance ($R^2 = 0.52$; $p \leq 2.2 \times 10^{-16}$), but the strength of this relationship varied depending on location. It was stronger in the tributaries ($R^2 = 0.75$; $p = 1.89 \times 10^{-9}$) and coastal zone ($R^2 = 0.52$; $p \leq 2.2 \times 10^{-16}$) and weaker in the main river ($R^2 = 0.15$; $p = 0.07$) and dam complex ($R^2 = -0.47$; $p = 0.87$). This is indicative of a variable decoupling between DOC and cDOM. The system contains a substantial and variable portion of non-colored, non-absorbing DOM. However, we observed a strong positive correlation between a254 and sample fluorescence ($R^2 = 0.89$; $p \leq 2.2 \times 10^{-16}$), indicating that the cDOM pool is highly fluorescent (Figure 2). We, therefore, present DOC data as an indicator of total DOM concentration and characterize the cDOM pool according to its fluorescent characteristics.

3.2. PARAFAC Results

A total of 207 excitation emission matrices were included in the analysis, resulting in a five-component model which explained 98.2% of sample fluorescence, and which was split-half validated for randomized divisions of the data set (Tucker's Congruence Coefficients >0.91 for Ex loadings and >0.96 for Em loadings). The five components identified, henceforth termed C1–C5, were characterized as terrestrial humic-like

Table 1
Characterization of Fluorophores C1–C5 According to Excitation and Emissions Maxima, Coble Peaks (Coble, 1996), a Large Parallel Factor Model (Murphy et al., 2011), and a Study of DOM Composition in a Tropical River Network (Congo; Lambert et al., 2016)

	Ex max (nm)	Em max (nm)	Coble peaks	Murphy et al. (2011)	Lambert et al. (2016)
C1	<255 (355)	470	C Humic-like (350, 420–480)	G1 – Terrestrial humic-like fluorescence	C1 – Terrestrial humic-like. *High aromaticity, high molecular weight (MW), photo sensitive*
C2	<255 (310)	410	M Marine humic-like (312, 380–420)	G2 – Microbial humic-like fluorescence	C2 – Microbial humic-like. *Aliphatic, low MW*
C3	360	438	C Humic-like (350, 420–480)	G3 – Wastewater/nutrient enriched tracer	C5 – Humic-like *Low aromaticity, low MW. photoproduct*
C4	265	314	B Tyrosine-like (275, 310)	G7 – Tyrosine-like	C6 – Protein-like *Aliphatic, low MW, autochthonous, biolabile*
C5	290	352	T Tryptophan-like (275, 340)	G6 – Tryptophan-like	

Note. Lambert et al. (2016) gained supplemental insight using molecular techniques, and that insight is given in italics.

(C1–C3) and protein-like (C4 and C5) through comparison with Coble Peaks (Coble, 1996) and two studies in which all components were also found: a large (~1,500 data point) model of fluorescence in municipal water schemes (Murphy et al., 2011), and a study of the Congo River network (Lambert et al., 2016) (Table 1). This characterization was further verified using the OpenFluor database (Murphy et al., 2014). The humic-like components (C1–C3) have different sources and characteristics. C1 was characterized as highly aromatic material of terrigenous origin (likely SOM), C3 as lightly aromatic material of microbial origin, and C2 lightly aromatic material that may be linked to nutrient pollution and/or wastewater (see Table 1). Previous work indicates that C1 may be susceptible to photodegradation, whilst C3 may be a product of photodegradation (Lambert et al., 2016). The protein-like components (C4 and C5) were both characterized as highly labile material of autochthonous origin, with C4 being tyrosine-like and C5 being tryptophan-like. PARAFAC contour and loadings plots are provided in Figures S5 and S6.

3.3. DOM Composition in the Mopan and Macal Rivers

The Mopan and Macal Rivers both have their headwaters in the Chiquibul Nature Reserve. The remote nature of the reserve made sampling difficult, and we could not gather sufficient samples within it to allow us to test the significance of our result. Given the lack of available data for the region, we present the data we could obtain as indicative only.

In 2018, two headwater samples were taken immediately before and after the confluence of a first-order and second-order stream that feeds the Macal. Sample fluorescence was higher after the confluence (5.31 RU) than it was before it (1.16 RU), but the composition of the fluorescence pool was broadly similar across both samples (mean = 41% C1, 31% C2, 19% C3, 5% C4, and 3% C5). Water originating in the Chiquibul reserve is transported to the Belize River via either the Macal and the dam complex, or the Mopan and Guatemala. Fluorescence in the Macal had dropped to 0.8 RU after transit through the dam complex, whilst fluorescence in the Mopan had dropped to 1.1 RU after transit as it re-entered Belize at the Guatemalan border). Despite this similarity in post-transit fluorescence values, the composition of the fluorescence pools had clearly diverged in transit. In the Macal, we observed a net decrease in the contribution of highly aromatic fluorescence (C1 = −6%) and a net increase in the contribution of protein-like fluorescence (C4 = +3%; C5 = +4%). In the Mopan, we observed a net decrease in the contribution of microbial humic-like fluorescence (C3 = −10%) and a net increase in the % contribution of both highly aromatic (C1 = +3%) and lightly aromatic (C2 = +7%) terrigenous material. In short, cDOM in the Macal became more autochthonous in nature after transit through the dams, and cDOM in the Mopan became more allochthonous in nature after transit through Guatemala's Western Uplands.

Table 2
Multiple Linear Regression Models for Predicting DOM Fluorescence Intensity and DOC Concentration as a Function of % Land-Use

	R^2	Intercept	Grassland	Cropland	Water	Urban
C1	0.79	−0.54 (0.15)	0.02 (0.01, 6.58)	**0.13 (0.02, 69.24)**	1.08 (0.03, 5.13)	–
C2	0.83	−0.43 (0.12)	0.02 (0.01, 11.81)	**0.09 (0.02, 68.35)**	0.89 (0.30, 5.04)	–
C3	0.73	−0.11 (0.05)	0.01 (0.00, 7.58)	**0.03 (0.01, 65.22)**	0.22 (0.11, 3.46)	
C4	0.67	0.03 (0.01)	**0.001 (0.001, 64.00)**	–	–	0.004 (0.002, 5.10)
C5	0.68	−0.03 (0.03)	**0.01 (0.001, 55.56)**	–	0.20 (0.11, 4.26)	0.02 (0.01, 6.94)
DOC	0.56	−1.03 (1.59)	**0.16 (0.06, 51.24)**	0.46 (0.22, 6.22)	–	–

Note. Coefficient standard errors and % variance explained are given in parentheses. For each parameter, the primary land use explanator is highlighted in bold.

3.4. The Influence of Land Use on DOM Composition

Multiple regression analysis identified significant relationships between land use and both cDOM fluorescence and DOC concentration within the tributaries (Table 2). Agricultural land (cropland and grassland) was the primary explanator of both fluorescence and DOC concentration. Cropland was the major explanator of humic-like (C1–C3) fluorescence (69%, 68%, and 65% variance explained, respectively). Grassland was the primary explanator of protein-like (C4 and C5) fluorescence and DOC concentration (64%, 56%, and 51% variance explained, respectively). Urban land was correlated with protein-like (C4 and C5) fluorescence (5% and 7% variance explained, respectively). The extent of inland water upstream of the sampling point explained a consistent portion of humic-like (C1–C3) and C5 protein-like fluorescence (3%–5% variance explained) but was not significant for C4 protein-like fluorescence or DOC concentration.

Redundancy analysis identified broadly similar relationships to multiple linear regression modeling (Figure 3). Grassland (F statistic = 35.11 on 1 and 26 degrees of freedom [DF]), cropland (F = 8.78 on 1 and 25 DF) and inland water (F = 3.39 on 1 and 24 DF) all significantly increased the amount of variance explained for cDOM fluorescence and DOC concentration ($p < 0.05$ in all cases). RDA 1 explained 70% of total variance in DOC and DOM fluorescence and ordinated the data points along a land-use gradient whereby samples from sites with >50% broadleaf forest cover have positive loadings and samples with <40% broadleaf forest cover had negative loadings. RDA two explained a further 3% of variance.

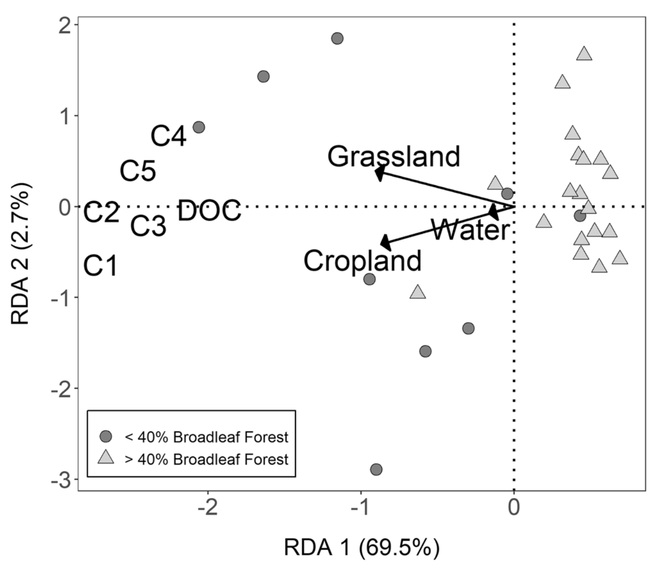

Figure 3. Redundancy analysis plot showing the relationships between land-use, dissolved organic carbon (DOC), and colored dissolved organic matter (cDOM) fluorescence. Data points represent individual samples, and are categorized according to % broadleaf forest. Land-use classes as plotted as arrow vectors, and DOC concentration and cDOM fluorescence are shown as text labels.

Sites draining land with <40% broadleaf forest cover (henceforth termed "agri-urban dominated") had significantly higher sample fluorescence intensities and DOC concentrations than sites draining >40% broadleaf forest (henceforth termed "broadleaf dominated") ($p > 0.002$). Agri-urban dominated sites contained significantly higher proportions of humic-like C1 ($p = 0.03$) and C2 ($p = 0.04$) fluorescence, whilst broadleaf dominated sites contained a significantly higher proportion of protein-like C4 fluorescence ($p = 0.02$). No significant difference was observed for the proportions of humic-like C3 ($p = 0.17$) and protein-like C5 ($p = 0.95$) found in these samples. Mean sample fluorescence was 3.86 ± 1.83 RU for agri-urban dominated sites, and 0.80 ± 0.72 RU for broadleaf dominated sites, with associated mean DOC concentrations of 10.1 ± 5.6 mg L^{-1} 3.2 ± 4.1 mg L^{-1}, respectively. Fluorescence contributions were 42 ± 4% C1, 36 ± 4% C2, 11 ± 2% C3, 3 ± 1% C4, and 7 ± 5% C5 for agri-urban, and 38 ± 5% C1, 33 ± 4% C2, 12 ± 2% C3, 10 ± 8% C4, and 7 ± 3% C5 for broadleaf dominated sites.

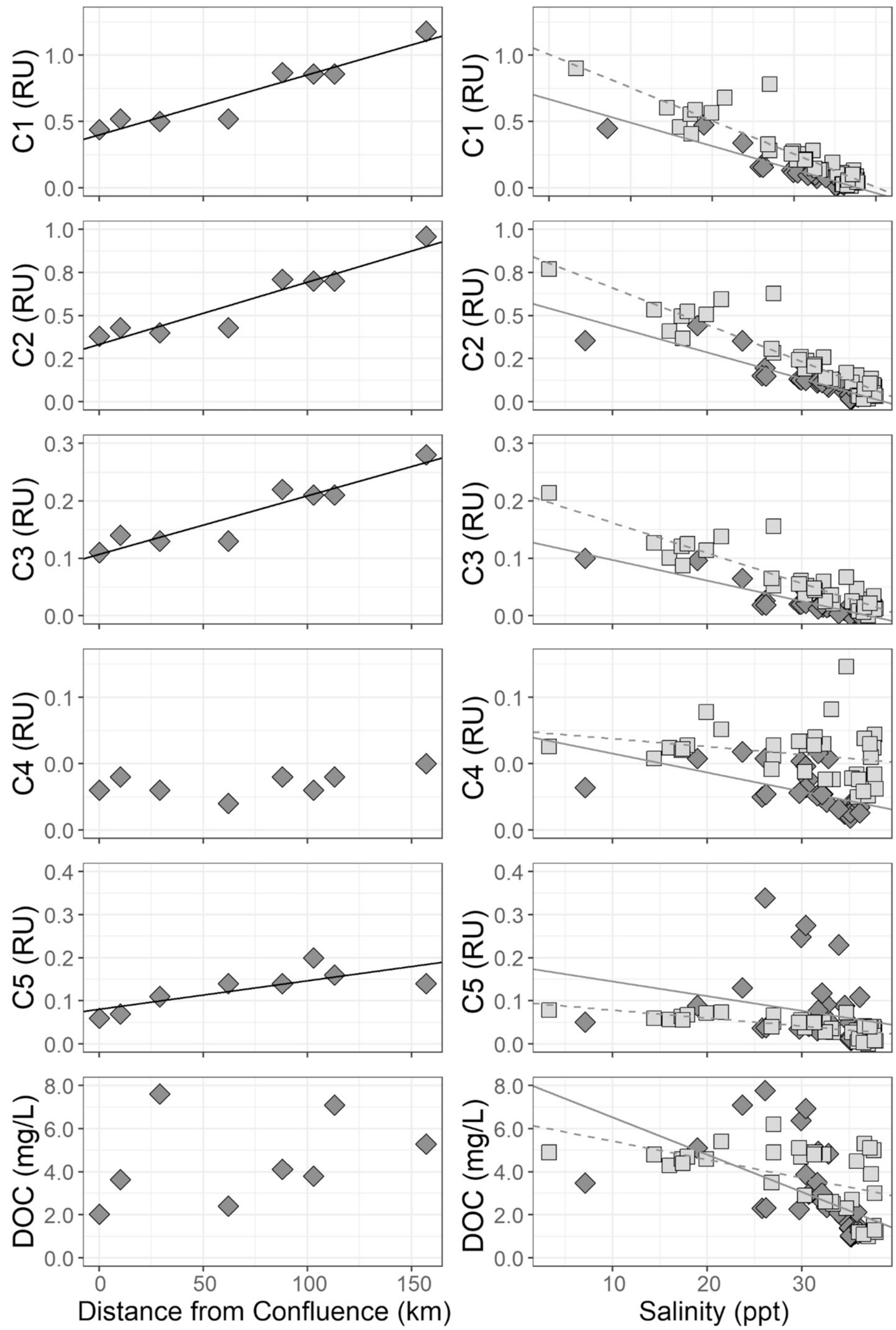

Figure 4. Relationships between colored dissolved organic matter fluorescence and dissolved organic carbon concentration as a function of (left) distance downstream from the start of the Belize River, with solid line black line indicating significant linear relationships ($p < 0.05$) and (right) salinity within the adjacent coastal environment, with theoretical mixing lines indicated by solid (2018) and dashed (2019) dark gray lines. Data from 2018 are shown as dark gray diamonds. Data from 2019 are shown as light gray squares.

3.5. Behavior of cDOM and DOC in Downstream Receiving Waters

In 2018, we found a net increase in DOM fluorescence and DOC concentration between the start of the Belize River (at the confluence of the Mopan and Macal Rivers) and the limit of freshwater extent during the 2018 Belize River transect (Figure 4). This was duplicated during our 2019 coastal sampling trip (Figure 4).

Humic-like DOM components (C1–C3) increased with increasing distance from the confluence in a linear fashion within the main river stem ($R^2 = 0.89$, 0.88, and 0.86) and appeared to decline as a linear function of salinity (i.e., behaved conservatively) within the coastal zone (Figure 4). There is some evidence of the addition of humic-like fluorescence in the mid-salinity range which we attribute to the mixing of waterbodies (e.g., carried south from the outflow from the Rio Hondo) as opposed to in-situ addition.

C4 protein-like DOM fluorescence exhibited a nonlinear increase in the main river stem, and behaved non-conservatively within the coastal zone, with evidence of net addition at higher salinities. DOC concentrations behaved similarly to C4. C5 fluorescence exhibited a linear increase with distance downstream, albeit to a lesser degree than C1–C3 ($R^2 = 0.55$). During 2018, C5 behaved non-conservatively in the coastal zone with evidence of addition at high salinities during the 2018 sampling. In 2019, C5 appeared to behave somewhat conservatively, and was present at much lower intensity than in 2018.

3.6. Does DOM From the Belize River Watershed Reach the Belize Barrier Reef?

The conservative behavior of humic-like (C1–C3) DOM allowed the associated fluorescence values to be statistically modeled across the full salinity range (0–38 ppt) using theoretical mixing lines (Section 2.6). We found no significant difference between modeled fluorescence intensities across years ($p < 0.04$), and so the modeled values were averaged to provide an estimate of DOM fluorescence at any given salinity point.

Modeled salinity over the outer reefs adjacent to the river outflow had a mean value of 34.07 ± 1.16 (SD) ppt (range = 30.60–35.33), with a mean yearly minimum value of 29.1 ± 0.51 ppt (range = 28.2–29.9 ppt). Salinities overlying this portion of the reef dropped below 30 ppt for an average of 10 ± 11 days yr^{-1} (Figure S7), during which time estimate fluorescence intensities in overlying waters were more than double those predicted under "normal" (34 ppt) conditions (C1 = 121%; C2 = 111%; C3 = 108%). Near-shore coral formations in close proximity to the Belize River outflow were subject to low-salinity (<30 ppt) conditions throughout most of the year (356 ± 12 days yr^{-1}), and mean salinity was 24.33 ± 3.08 ppt (range = 18.57–31.01). Salinity dropped below 20 ppt for 113 ± 24 days yr^{-1}, during which time estimated fluorescence intensities in overlying waters were around 30% higher than those predicted at "normal" (24 ppt) conditions (C1 = 30%; C2 = 29%; C3 = 20%), and around 130% higher than those predicted at 30 ppt (C1 = 136%; C2 = 132%; C3 = 130%).

4. Discussion

4.1. The Effect of Land-Use on the DOM Pool

Within the tributaries, we observed a strong positive relationship between agri-urban land and DOM fluorescence. The relationship between DOM fluorescence and cDOM concentration has been well established (Stedmon et al., 2003). A historic regional trend from broadleaf forest to agri-urban has also been established for Belize (Cherrington et al., 2010; Voight et al., 2019), and is predicted to continue (Cherrington et al., 2014). Our findings therefore suggest that conversion of land from forested to agri-urban has, and will continue to, drive an increase in the amount of cDOM entering the Belize River aquatic continuum.

Humic-like, SOM-derived material (C1) was the primary DOM type found within the tributaries. The export of SOM following deforestation has been shown to peak immediately following land-use modification as the historic SOM stock is remobilized, and this peak export period lasts for between 5 to 50 years (West et al., 2004 and references therein). Beyond that period, SOM export will continue at a reduced rate owing to ongoing perturbation relating to crop production and, to a lesser extent, grazing (Fujisaki et al., 2017; West et al., 2004). Much of the agricultural land in Belize is <50 years old and thus within the time window of SOM depletion. These cleared and cultivated lands are likely exporting SOM laid down by the preceding forest at elevated rates relative to farms that have been established for longer, and the associated SOM export can be expected to decline with time. It is possible that SOM exported from deforested tropical landscapes may be less aromatic and more biolabile than SOM exported from the preceding forest (Drake et al., 2019). On average, agri-urban dominated sites contained a higher proportion of highly aromatic C1 and lightly aromatic C2 fluorescence than was observed in broadleaf dominated sites. C1 is a typical humic-like recalcitrant SOM signal, whilst C2 is associated with less humic SOM (Table 1) and may be a signal of this biolabile pool.

This is further supported by our observation that transit through Guatemala resulted in a 10% increase in the contribution of humic-like (C1 and C2) DOM. We could not access the Guatemalan portion of the Mopan, but the increase observed at the border relative to the headwaters may have resulted from the heavily deforested and highly agricultural landscape through which the Mopan flows (visible in Figure S4). In the ∼32 km between the Belize-Guatemala border and the confluence of the Belize River, sample fluorescence in the Mopan increased from 1.1 to 1.6 RU, but the composition of the fluorescence pool shifted away from C1 and C2 type DOM and toward microbially derived (C3) and protein-like (C4 and C5) type DOM. This suggests that the Belizean portion of the Mopan is either more productive than the Guatemalan portion, and/or that the Belizean portion receives less C1 and C2 type SOM from the surrounding landscape than the Guatemalan portion. We cannot say whether this shift occurs at the border, or whether it begins further upstream.

The dominant grassland use was animal pasture. Over-grazing of pasture by cattle and other livestock may be partially responsible for enhanced SOM export (Dlamini et al., 2016). Protein-like fluorescence typically increases with increasing anthropogenic DOM inputs from households (i.e., sewage) and farm wastes (Baker et al., 2004). Protein-like fluorescence was significantly elevated in agri-urban tributaries and anecdotal evidence suggests that animal agriculture (i.e., cattle and chicken rearing) in Belize does result in the dumping of animal waste, including bones and blood, into the river system (Pers. obs. and Carrias et al., 2018). The observed co-occurrence of elevated protein-like fluorescence with grassland may therefore be related, at least in part, to the discharge of agricultural waste associated with livestock farming. This link between protein-like fluorescence and farm wastes, including silage liquor and animal slurry, has been made elsewhere (Baker, 2002), but with much higher ratios of protein-like: fulvic/humic-like fluorescence (0.5–20) than we observed in this study (mean = 0.22 ± 0.24; range = 0.02–1.02).

It is also of note that a high proportion of the population lives in non-urban areas. Due to the resolution of our land cover mapping, stand-alone rural dwellings with a footprint of less than 10 m^2 were not captured. These dwellings are especially prevalent on the edge of grassland where farmers reside near their grazing stock. Whilst Belize's largest population centers benefit from sanitation facilities, these non-urban dwellings typically dispose of waste directly into the river or connecting streams. Therefore, a portion of protein-like DOM fluorescence originating from grassland may relate to rural household waste, and it may have been possible to explain a greater proportion of the variance in these components if we had been able to better resolve all of the urban settlement within our study area. Other population and/or household metrics might prove useful in this regard in future work.

The dam complex was not ascribed as a distinct land-use class, but is nevertheless the result of human activity. Dams increase residence time in the Macal, increasing the opportunity for removal via photodegradation, biodegradation, and flocculation (Evans et al., 2017; Queimaliños et al., 2019; Worrall et al., 2018). We observed a net reduction in sample fluorescence which could indicate either a reduction in the concentration of fluorescent DOM or a shift from highly fluorescent humic-like DOM toward less fluorescent protein-like DOM, for example. Whilst sample fluorescence decreased, indicating DOM removal within the dams, it is of note that the relative proportion of protein-like (C4 and C5) DOM fluorescence increased. This suggests the preferential removal of humic-like material, presumably through photodegradation and/or flocculation, coupled with enhanced microbial activity. This same removal of humic-like DOM does not appear consistent with patterns observed in the main river stem and coastal zone, but residence times in the Belize River are in the order of days whilst the dams have residence times in the order of months (Karper & Boles, 2004). Another factor may be the presence of riparian forest along the Belize River which shades much of the waterbody, whereas the scale of the dams leaves most of the water surface unshielded from incident light.

The relatively consistent positive relationship observed between inland waterbodies and DOM fluorescence (between 3% and 5% of variance explained for C1–C3 and C5 fluorescence) arises due to the fact that a higher density of streams, rivers, drainage ditches, and other channels increases land-water connectivity and may therefore facilitate land-water DOM transfer. The conspicuous absence of a relationship between protein-like C4 fluorescence and inland water suggests it may predominantly originate from point sources (e.g., agri-urban waste) rather than in-situ production. However, given the presence of C4 in the relatively pristine Chiquibul reserve and in broadleaf-dominated sites as well as agri-urban ones, it is more likely that C4 DOM is the product of low-level in-situ production which is added to and/or encouraged by point source inputs of highly bio-labile DOM.

4.2. Downstream Transport of DOM

We observed a net decrease in DOM fluorescence and DOC concentration between land and sea which is consistent with globally observed patterns (Massicotte et al., 2017). However, a range of smaller, ecosystem-scale variations were also apparent. The Belize River is flanked by riparian forest, beyond which lies some of the most agriculturally suitable land in Belize (King et al., 1993). As a result, riparian land use along its length is extremely stable (Figure S2) and can be excluded as a source of variation in the composition of the main river DOM pool. C1–C3 DOM increased linearly within the Belize River (Figure 4), which indicates that (1) these DOM forms are being added or produced faster than they are being removed; and/or (2) their rates of addition, production, and removal do not vary with distance. This is consistent with a terrigenous humic-like characterization (Table 1), whereby relatively recalcitrant DOM is being added from the surrounding environment. One protein-like component (C4) accumulated non-linearly, indicating that rates of addition, production, and removal are unbalanced. This is consistent with a highly labile DOM type which originates from distinct point sources and/or the production of which varies in response to external factors. This behavior was mirrored in the coastal environment (Figure 4), where humic-like components behaved conservatively with salinity whilst C4 protein-like fluorescence behaved non-conservatively, with evidence of significant addition at high salinity. C5 behavior was more mixed: it exhibited a weak linear relationship with distance downstream ($R^2 = 0.53$) and which appeared to behave conservatively during the 2019 coastal sampling period. This likely indicates subdued in-situ production rates relative to 2018, rather than the transport of conservative material from the terrigenous environment.

Our study therefore suggests that (1) land-use change increased the amount of humic-like and protein-like cDOM in receiving waterbodies; (2) humic-like cDOM increased in the river during transit from upland to lowland; and (3) humic-like cDOM behaved conservatively within the coastal zone. Thus, we have demonstrated a link between land-use change and the downstream DOM pool, specifically with regards to agri-urban land and the export of humic-like (C1–C3) material.

4.3. Does Land-Use Change Influence the Belize Barrier Reef?

Frequent and/or chronic exposure to low-salinity, high DOM waters can negatively impact coral species, with effects including extended photosynthetic recovery periods, reduced growth, and increased mortality (Lirman & Manzello, 2009). Our modeling results indicate a substantial (up to 130%) increase in humic-like DOM during periods of Belize River, Belize Barrier Reef connectivity. The number of days per year at which the offshore reef was subject to these conditions was low (10 ± 11 days yr^{-1}). This suggests that any deleterious effect of DOM exposure would manifest as a short-term stress response in near-surface corals which dissipated quickly upon return to normal conditions (Aronson et al., 2000). The nearshore corals which experience these <30 ppt conditions for the majority of the year (356 ± 12 days yr^{-1}) are almost certainly adapted to this, but were exposed to their lower salinity limit (<20 ppt) more frequently (113 ± 24 days yr^{-1}). Whilst the increase in DOM was lower in relative terms (30% increase between 24 and 20 ppt at the nearshore corals relative to 120% increase between 34 and 30 ppt at the outer reef), the length of exposure was much greater. Thus, it is these nearshore corals which we suggest might most be at risk due to increasing DOM as a result of land-use change. Previous, coarser scale modeling work of the Belizean coastal zone supports our findings, reporting that buoyant terrigenous matter was highest (>3 g m^{-3}) over the same nearshore reefs, and that it peaked during periods of high river discharge and under specific current conditions (Burke & Sugg, 2006).

The relationship between land use and protein-like DOM in the coastal zone is less straight forward due to in-situ production and removal for which we do not have a baseline. Table 3 shows fluorescence values for these parameters (and for DOC) under conservative conditions, but we observed significant addition of C4

Table 3
Modeled Fluorescence for Dissolved Organic Matter Components and Dissolved Organic Carbon (DOC) at 20, 24, 30, and 34 ppt in November 2018 and October 2019

Salinity (ppt)	Year	C1 (RU)	C2 (RU)	C3 (RU)	C4 (RU)	C5 (RU)	DOC (mg L^{-1})
20	2018	0.545	0.451	0.131	0.030	0.070	3.13
	2019	0.421	0.361	0.103	0.045	0.039	2.85
	Mean	**0.483**	**0.406**	**0.117**	**0.038**	**0.055**	**2.99**
24	2018	0.418	0.348	0.100	0.027	0.056	2.70
	2019	0.325	0.279	0.080	0.042	0.031	2.44
	Mean	**0.371**	**0.314**	**0.090**	**0.034**	**0.044**	**2.57**
30	2018	0.227	0.194	0.055	0.022	0.035	2.06
	2019	0.181	0.157	0.047	0.036	0.019	1.83
	Mean	**0.204**	**0.175**	**0.051**	**0.029**	**0.027**	**1.94**
34	2018	0.100	0.091	0.024	0.019	0.021	1.63
	2019	0.085	0.075	0.025	0.033	0.011	1.42
	Mean	**0.093**	**0.083**	**0.024**	**0.026**	**0.016**	**1.52**

Note. Values were obtained via theoretical mixing lines. Conservative components (C1–C3) are discussed in the text. Conservative fits for other (non-conservative) components (C4, C5, and DOC) are provided for interest only.

and C5 in the coastal environment (Figure 4). Whilst it is clear that riverine inputs of protein-like DOM and DOC are higher than those observed in more saline waters, we cannot determine the extent to which material of terrigenous origin persists relative to fresh production.

Almost all future climate scenarios for the region result in a significant reduction in precipitation within the watershed, but projected land-use change is predicted to result in increased export of SOM into nearby waterbodies, the combination of which will likely result in increased sediment and SOM export from the catchment (Cherrington et al., 2014). At the same time, the number of heavy rainfall events and storms is predicted to increase in the coming years (Parry et al., 2008). Combined, this could (a) enhance the export of terrigenous DOM into the Belize River watershed, and (b) increase the number of days within a year when the river plume interacts with the barrier reef. Thus, interaction between the terrestrial and marine environments is likely to increase with time, and further study is required to understand the consequences of this.

4.4. Limitations and Future Study

We infer from these results that DOM quantity and character vary along a dominant axis of variation, namely land-use, but land-use in the study catchment at least partially tracks intrinsic site properties such as geology, elevation, and soil type. In the absence of historic baseline data, a future temporal study might allow us to better quantify the degree to which some (if any) observed variation could pre-date land-use change. In this regard, the data produced by this study might provide a suitable baseline, particularly for the less modified, broadleaf-dominated subcatchments.

Seasonality plays an important role in land-ocean DOM transport. In-stream concentrations are typically maximal at the onset of runoff, continuously decreasing after the initial flush (Xenopoulos et al., 2017), and residence time can be considered the dominant control on the fate and reactivity of DOM along a river network, owing to changes in in-stream processing time (Catalán et al., 2016). Our sampling was timed to coincide with wet and dry seasons, yet unpredictable weather resulted in broad-scale similarities in terms of flow, and missed maximal runoff. In the dry season, DOM concentration has been shown to decrease in forested streams, but to increase in highly modified subcatchments (Liu et al., 2019), and other work in a tropical river catchment suggests a strong wet/dry season influence on DOM composition (Hong et al., 2012; Spencer et al., 2010). The lack of sampling during peak wet season may therefore have biased our findings toward agri-urban environments, and full flood sampling is required to elucidate this. Additionally, our hydrodynamic model used mean annual discharge data, with the observed interannual variability in the freshwater plume being mostly driven by variability in ocean currents and surface winds. Future work should aim to include interannual variability in river discharge, which could be achieved through on-going efforts to collect the in-situ hydrology data required to strengthen discharge estimates for the study catchment, or by including some more general forcing, for example precipitation averaged over the river catchment taken from an atmospheric model like the ERA5 reanalysis (European Centre for Medium-Range Weather Forecasts, 2019). Nonetheless, the range of modeled salinity conditions produced by the model are representative of typical conditions over the 21-year model run, and plume penetration is greatest during peak river-discharge months (October and November). Thus, under future climate scenarios, an increase in river discharge can be expected to increase connectivity between the Belize River watershed and the adjacent portion of the reef. This is particularly relevant during peak river discharge months, where connectivity was estimated to reach >40 days yr^{-1} under certain hydrodynamic regimes.

An interesting note is that we did not find a good agreement between DOC and sample fluorescence. This indicates that the DOM pool contained a significant non-colored fraction that was not characterized via PARAFAC analysis. Such material is typically thought to be highly labile autochthonous and/or anthropogenic material that undergoes rapid remineralization (Pereira et al., 2014). Thus, its omission from our study is unlikely to have influenced our overall finding: that recalcitrant humic-like material reaches the coastal environment. However, future studies may wish to employ different techniques such as high-resolution mass spectroscopy to characterize this non-colored fraction.

Finally, we note that cellulose acetate filters can leach DOC, cDOM, and fDOM. We pre-flushed our filters with 100 ml sample water in the field to negate this effect (Karanfil et al., 2003; Khan & Subramania-Pillai, 2007) and used the same batch of filters throughout our sampling campaigns, but did not collect filter blanks and therefore cannot therefore exclude the possibility of filter-based sample contamination. Nevertheless, the clear changes in DOC, and fluorescence that we observed in space and time indicate that any such effects, if apparent, were minor.

5. Summary and Conclusions

In this study, we used PARAFAC analysis to investigate how the composition of the aquatic DOM pool varied across a land-use gradient in a subtropical watershed. Agri-urban land use was negatively correlated with broadleaf forest, a result consistent with the documented regional land-use change trajectory from broadleaf forest to agri-urban land use. Five cDOM components were identified: three humic-like components (C1–C3) and two protein-like components (C4 and C5).

We hypothesized that subcatchments draining agri-urban land would contain more cDOM than subcatchments draining forested land. Agri-urban land use was positively associated with all five cDOM components and measured DOC concentration. Agri-urban samples contained a higher proportion of aromatic, highly colored cDOM than broadleaf forest samples did. It is possible that this finding is an intrinsic outcome of changes in soil type and vegetation from upland to lowland; however, we speculate that it could also be a transient pattern resulting from the relative infancy of Belize's agricultural land and the ongoing loss of SOM laid down by the preceding broadleaf forest.

We also hypothesized that humic-like DOM would be transported downstream and into the coastal environment, whilst protein-like DOM would be rapidly remineralized. Our findings supported this hypothesis, with humic-like (C1–C3) fluorescence exhibiting significant positive relationships with distance downstream and conservative mixing behavior within the coastal zone whilst protein-like (C4 and C5) fluorescence exhibited no relationship with distance downstream and non-conservative mixing behavior in the coastal zone.

Given the conservative nature of C1–C3 DOM, it is likely that this terrigenous material is carried along the main river and into the coastal zone. Our final hypothesis was that humic-like DOM persists within the Belize River plume to reach the adjacent barrier reef, where it may have a deleterious effect. Hydrodynamic modeling of the Belize coastal zone over a period of 21 years found the Belize River plume interacted with the offshore reef infrequently and for short periods of time, and with the nearshore reef more frequently, and for longer periods of time. We suggest that any deleterious effect on the offshore corals is likely to be short-lived and minimal, but that nearshore corals are likely to be influenced more strongly. Interaction between the Belize River plume, the Belize Barrier Reef, and the coastal environment more widely may increase under future climate and land-use scenarios, and whilst it is possible that cDOM at the levels identified here may have little effect on the coastal environment, potential impacts (e.g., darkening) require careful study. This is particularly true in the context of compound stressors, particularly freshening, acidification, warming, and pollution from various compounds which may be bound to and carried with terrigenous DOM. For example, dissolved mercury and pesticides associated with agricultural and urban land use have previously been reported overlying Belizean coral reefs (Alegria, 2009).

In summary, we find a strong link between land-use change and cDOM composition and quantity in receiving waters of the Belize River watershed, including those overlying the economically and environmentally important Belize Barrier Reef. The potential for human activities on land to negatively impact the coastal environment is not unique to Belize, and so our findings are relevant more broadly, particularly for coastal developing nations where agri-mediated deforestation is ongoing and reliance on the marine economy is high.

Data Availability Statement

All data used in this study are available at: 10/f75z (Felgate, Cryer, et al., 2021); 10/f754 (Felgate, Barry, et al., 2021); 10/f75t (Cryer et al., 2021).

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References

Alegria, V. E. (2009). *Land-based sources of pollutants to coastal waters of southern Belize – comparison of predictive model with empirical data*. University of South Florida. Retrieved from https://scholarcommons.usf.edu/etd/1825/

Anderson, T. R., Rowe, E. C., Polimene, L., Tipping, E., Evans, C. D., Barry, C. D. G., et al. (2019). Unified concepts for understanding and modelling turnover of dissolved organic matter from freshwaters to the ocean: The UniDOM model. *Biogeochemistry*, *146*, 105–123. https://doi.org/10.1007/s10533-019-00621-1

Arango, C. P., Beaulieu, J. J., Fritz, K. M., Hill, B. H., Elonen, C. M., Pennino, M. J., et al. (2017). Urban infrastructure influences dissolved organic matter quality and bacterial metabolism in an urban stream network. *Freshwater Biology*, *62*(11), 1917–1928. https://doi.org/10.1111/fwb.13035

Aronson, R. B., Precht, W. F., Macintyre, I. G., & Murdoch, T. J. T. (2000). Coral bleach-out in Belize. *Nature*, *405*, 36. https://doi.org/10.1038/35011132

Baillie, I. C., Wright, A. C. S., Holder, M. A., & Fitzpatrick, E. A. (1993). *Revised classification of the soils of Belize*. Retrieved from https://gala.gre.ac.uk/id/eprint/11109/1/11109_Baillie_Revisedclassificationofthesoils(book)1993.pdf

Baker, A. (2002). Fluorescence properties of some farm wastes: Implications for water quality monitoring. *Water Research*. *36*, 189–195. https://doi.org/10.1016/S0043-1354(01)00210-X

Baker, A., Ward, D., Lieten, S. H., Periera, R., Simpson, E. C., & Slater, M. (2004). Measurement of protein-like fluorescence in river and waste water using a handheld spectrophotometer. *Water Research*, *38*, 2934–2938. https://doi.org/10.1016/j.watres.2004.04.023

Burke, L., & Sugg, Z. (2006). *Hydrologic modeling of watersheds discharging adjacent to the Mesoamerican Reef*. World Resources Institute

Butler, J. R. A., Wong, G. Y., Metcalfe, D. J., Honzák, M., Pert, P. L., Rao, N., et al. (2013). An analysis of trade-offs between multiple ecosystem services and stakeholders linked to land use and water quality management in the Great Barrier Reef, Australia. *Agriculture, Ecosystems & Environment*, *180*, 176–191. https://doi.org/10.1016/j.agee.2011.08.017

Carrias, A., Cano, A., Saqui, P., Ake, J., & Boles, E. (2018). *Management plan for the Belize River watershed. Belize*.

Carter, H. T., Tipping, E., Koprivnjak, J.-F., Miller, M. P., Cookson, B., & Hamilton-Taylor, J. (2012). Freshwater DOM quantity and quality from a two-component model of UV absorbance. *Water Research*, *46*, 4532–4542. https://doi.org/10.1016/j.watres.2012.05.021

Catalán, N., Marcé, R., Kothawala, D. N., & Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geoscience*, *9*, 501–504. https://doi.org/10.1038/ngeo2720

Cherrington, E. A., Ek, E., Cho, P., Howell, B. F., Hernandez, B. E., Anderson, E. R., et al. (2010). *Forest cover and deforestation in Belize: 1980–2010*.

Cherrington, E. A., Kay, E., & Waight-Cho, I. (2014). *Modelling the impacts of climate change and land use change on Belize's water resources: Potential effects on erosion and runoff* (pp. 1–32). https://doi.org/10.13140/RG.2.2.16952.75524

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Marine Chemistry*, *51*(4), 325–346. https://doi.org/10.1016/0304-4203(95)00062-3

Condron, L. M., Hopkins, D. W., Gregorich, E. G., Black, A., & Wakelin, S. A. (2014). Long-term irrigation effects on soil organic matter under temperate grazed pasture. *European Journal of Soil Science*, *65*(5), 741–750. https://doi.org/10.1111/ejss.12164

Cryer, S. E., Felgate, S. L., Goddard-Dwyer, M., Strong, J. A., Andrews, G., Barry, C. D. G., et al. (2021). *Discrete water samples for biogeochemical parameters collected in line with autonomous surface vehicle C-worker 4 sensor data in Belize's coastal zone – October 2019*. British Oceanographic Data Centre - Natural Environment Research Council 10/f75t Discrete biogeochemical data collected in Belize's coastal zone - 2019 (bodc.ac.uk).

Devlin, M., & Schaffelke, B. (2012). Catchment-to-reef continuum: Case studies from the Great Barrier Reef. A special issue – Marine Pollution Bulletin 2012. *Marine Pollution Bulletin*, *65*, 77–80. https://doi.org/10.1016/j.marpolbul.2012.04.013

Dlamini, P., Chivenge, P., & Chaplot, V. (2016). Overgrazing decreases soil organic carbon stocks the most under dry climates and low soil pH: A meta-analysis shows. *Agriculture, Ecosystems & Environment*, *221*, 258–269. https://doi.org/10.1016/j.agee.2016.01.026

Drake, T. W., Raymond, P. A., & Spencer, R. G. M. (2018). Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. *Limnology & Oceanography*, *3*(3), 132–142. https://doi.org/10.1002/lol2.10055

Drake, T. W., Van Oost, K., Barthel, M., Bauters, M., Hoyt, A. M., Podgorski, D. C., et al. (2019). Mobilization of aged and biolabile soil carbon by tropical deforestation. *Nature Geoscience*, *12*, 541–546. https://doi.org/10.1038/s41561-019-0384-9

Esselman, R. E., & Boles, E. (2001). *Status and future needs of limnological in Belize*. International Association for Limnology

European Centre for Medium-Range Weather Forecasts. (2019). *ERA5*. https://doi.org/10.24381/cds.adbb2d47

Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Frogbrook, Z., & Kothawala, D. N. (2017). Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nature Geoscience*, *10*(11), 832–835. https://doi.org/10.1038/NGEO3051

Felgate, S. L., Barry, C. D. G., Cryer, S. E., Mayor, D. J., Carrias, A., Andrews, G., et al. (2021). *Discrete water samples for biogeochemical parameters collected in the Belize River and tributaries – 2019*. British Oceanographic Data Centre - Natural Environment Research Council 10/f754 Discrete biogeochemical data collected in the Belize River and tributaries - 2019 (bodc.ac.uk).

Felgate, S. L., Cryer, S. E., Barry, C. D. G., Mayor, D. J., Carrias, A., Andrews, G., et al. (2021). *Discrete water samples for biogeochemical parameters collected in the Belize River, tributaries, estuary and surrounding coastal ocean – Belize, 2018*. British Oceanographic Data Centre - Natural Environment Research Council 10/f75z Discrete biogeochemical data from the Belize River, tributaries, estuary and surrounding coastal ocean - Belize, 2018 (bodc.ac.uk).

Fichot, C. G., & Benner, R. (2014). The fate of terrigenous dissolved organic carbon in a river-influenced ocean margin. *Global Biogeochemical Cycles*, *28*, 300–318. https://doi.org/10.1002/2013GB004670

Fox, J., & Weisberg, S. (2011). *An {R} companion to applied regression*. Thousand Oaks, CA: Sage.

Fujisaki, K., Perrin, A.-S., Garric, B., Balesdent, J., & Brossard, M. (2017). Soil organic carbon changes after deforestation and agrosystem establishment in Amazonia: An assessment by diachronic approach. *Agriculture, Ecosystems & Environment*, *245*, 63–73. https://doi.org/10.1016/j.agee.2017.05.011

Gücker, B., Silva, R. C. S., Graeber, D., Monteiro, J. A. F., & Boëchat, I. G. (2016). Urbanization and agriculture increase exports and differentially alter elemental stoichiometry of dissolved organic matter (DOM) from tropical catchments. *The Science of the Total Environment*, *550*, 785–792. https://doi.org/10.1016/j.scitotenv.2016.01.158

Gibbs, H. K., Ruesch, A. S., Achard, F., Clayton, M. K., Holmgren, P., Ramankutty, N., & Foley, J. A. (2010). Tropical forests were the primary sources of new agricultural land in the 1980s and 1990s. *Proceedings of the National Academy of Sciences of the United States of America*, *107*(38), 16732–16737. https://doi.org/10.1073/pnas.0910275107

Gmach, M. R., Cherubin, M. R., Kaiser, K., & Cerri, C. E. P. (2020). Processes that influence dissolved organic matter in the soil: A review. *Scientia Agricola*, *77*. https://doi.org/10.1590/1678-992x-2018-0164

Graeber, D., Goyenola, G., Meerhoff, M., Zwirnmann, E., Ovesen, N. B., Glendell, M., et al. (2015). Interacting effects of climate and agriculture on fluvial DOM in temperate and subtropical catchments. *Hydrology and Earth System Sciences*, *19*(5), 2377–2394. https://doi.org/10.5194/hess-19-2377-2015

Graham, J. A., O'Dea, E., Holt, J., Polton, J., Hewitt, H. T., Furner, R., et al. (2018). AMM15: A new high-resolution NEMO configuration for operational simulation of the European north-west shelf. *Geoscientific Model Development*, *11*, 681–696. https://doi.org/10.5194/gmd-11-681-2018

Guihou, K., Polton, J., Harle, J., Wakelin, S., O'Dea, E., & Holt, J. (2018). Kilometric scale modeling of the North West European shelf seas: Exploring the spatial and temporal variability of internal tides. *Journal of Geophysical Research: Oceans*, *123*, 688–707. https://doi.org/10.1002/2017JC012960

Hartshorn, G. S., Nicolait, L., Hartshorn, L., Bevier, G., Brigtman, R., Cal, J., et al. (1984). *Belize country environmental profile: A field study (USAID Contract No. 505-0000-C-00-3001-00)*.

Heyman, W. D., & Kjerfve, B. x. r. (1999). Hydrological and oceanographic considerations for integrated coastal zone management in Southern Belize. *Environmental Management*, *24*, 229–245. https://doi.org/10.1007/s002679900229

Hong, H., Yang, L., Guo, W., Wang, F., & Yu, X. (2012). Characterization of dissolved organic matter under contrasting hydrologic regimes in a subtropical watershed using PARAFAC model. *Biogeochemistry*, *109*, 163–174. https://doi.org/10.1007/s10533-011-9617-8

Houghton, R. A. (2003). Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850-2000. *Tellus B: Chemical and Physical Meteorology*, *55*(2), 378–390. https://doi.org/10.1034/j.1600-0889.2003.01450.x

Inamdar, S., Finger, N., Singh, S., Mitchell, M., Levia, D., Bais, H., et al. (2012). Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. *Biogeochemistry*, *108*, 55–76. https://doi.org/10.1007/s10533-011-9572-4

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., & Matzner, E. (2000). Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Science*, *165*, 277–304. https://doi.org/10.1097/00010694-200004000-00001

Kamjunke, N., Hertkorn, N., Harir, M., Schmitt-Kopplin, P., Griebler, C., Brauns, M., et al. (2019). Molecular change of dissolved organic matter and patterns of bacterial activity in a stream along a land-use gradient. *Water Research*, *164*, 114919. https://doi.org/10.1016/j.watres.2019.114919

Karanfil, T., Erdogan, I., & Schlautman, M. A. (2003). Selecting filter membranes for measuring DOC and UV254. *Journal - American Water Works Association*, *95*, 86–100. https://doi.org/10.1002/j.1551-8833.2003.tb10317.x

Karper, J., & Boles, E. (2004). *Human impact mapping of the Mopan and Chiquibul rivers within Guatemala and Belize with comments on riparian forest ecology, conservation and restoration*.

Khan, E., & Subramania-Pillai, S. (2007). Interferences contributed by leaching from filters on measurements of collective organic constituents. *Water Research*, *41*, 1841–1850. https://doi.org/10.1016/j.watres.2006.12.028

King, I., Pratt, J. H., Warner, M. P., & Zisman, S. A. (1993). Agricultural development prospects in Belize, *NRI Bulletin*, *48*, 175–196.

Klumpp, K., Fontaine, S., Attard, E., Le Roux, X., Gleixner, G., & Soussana, J.-F. (2009). Grazing triggers soil carbon loss by altering plant roots and their control on soil microbial community. *Journal of Ecology*, *97*(5), 876–885. https://doi.org/10.1111/j.1365-2745.2009.01549.x

Kothawala, D. N., Kellerman, A. M., Catalán, N., & Tranvik, L. J. (2020). Organic matter degradation across ecosystem boundaries: The need for a unified conceptualization. *Trends in Ecology & Evolution*, *36*, 113–122. https://doi.org/10.1016/j.tree.2020.10.006

Kothawala, D. N., Murphy, K. R., Stedmon, C. A., Weyhenmeyer, G. A., & Tranvik, L. J. (2013). Inner filter correction of dissolved organic matter fluorescence. *Limnology and Oceanography: Methods*, *11*, 616–630. https://doi.org/10.4319/lom.2013.11.616

Lambert, T., Bouillon, S., Darchambeau, F., Massicotte, P., & Borges, A. V. (2016). Shift in the chemical composition of dissolved organic matter in the Congo River network. *Biogeosciences Discussions*. *13*, 5405–5420. https://doi.org/10.5194/bg-2016-240

Lanza, G. (2019). *Chalillo dam project , Belize Central America: An update on the ecological health of the Macal River watershed*.

Lehner, B., Verdin, K., & Jarvis, A. (2008). New global hydrography derived from spaceborne elevation data. *Eos, Transactions, American Geophysical Union*, *89*, 93. https://doi.org/10.1029/2008EO100001

Lirman, D., & Manzello, D. (2009). Patterns of resistance and resilience of the stress-tolerant coral *Siderastrea radians* (Pallas) to sub-optimal salinity and sediment burial. *Journal of Experimental Marine Biology and Ecology*, *369*, 72–77. https://doi.org/10.1016/j.jembe.2008.10.024

Liu, Q., Jiang, Y., Tian, Y., Hou, Z., He, K., Fu, L., & Xu, H. (2019). Impact of land use on the DOM composition in different seasons in a subtropical river flowing through a region undergoing rapid urbanization. *Journal of Cleaner Production*, *212*, 1224–1231. https://doi.org/10.1016/j.jclepro.2018.12.030

Lønborg, C., Carreira, C., Jickells, T., & Álvarez-Salgado, X. A. (2020). Impacts of global change on ocean dissolved organic carbon (DOC) cycling. *Frontiers in Marine Science*, *7*. https://doi.org/10.3389/fmars.2020.00466

Lyard, F. H., Allain, D. J., Cancet, M., Carrère, L., & Picot, N. (2020). FES2014 global ocean tides atlas: Design and performances. *Ocean Science Discussions*, 1–40. https://doi.org/10.5194/os-2020-96

Massicotte, P., Asmala, E., Stedmon, C., & Markager, S. (2017). Global distribution of dissolved organic matter along the aquatic continuum: Across rivers, lakes and oceans. *The Science of the Total Environment*, *609*, 180–191. https://doi.org/10.1016/j.scitotenv.2017.07.076

Mayorga, E., Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., Bouwman, A. F., et al. (2010). Global Nutrient Export from WaterSheds 2 (NEWS 2): Model development and implementation. *Environmental Modelling & Software*, *25*, 837–853. https://doi.org/10.1016/j.envsoft.2010.01.007

Meerman, J. (2015). *Belize rivers shapefile*. Retrieved from http://www.biodiversity.bz/

Mello, K. D., Valente, R. A., Randhir, T. O., dos Santos, A. C. A., & Vettorazzi, C. A. (2018). Effects of land use and land cover on water quality of low-order streams in Southeastern Brazil: Watershed versus riparian zone. *Catena*, *167*, 130–138. https://doi.org/10.1016/j.catena.2018.04.027

Molotoks, A., Stehfest, E., Doelman, J., Albanito, F., Fitton, N., Dawson, T. P., & Smith, P. (2018). Global projections of future cropland expansion to 2050 and direct impacts on biodiversity and carbon storage. *Global Change Biology*, *24*, 5895–5908. https://doi.org/10.1111/gcb.14459

Mostofa, K. M. G., Wu, F., Liu, C.-Q., Fang, W. L., Yuan, J., Ying, W. L., et al. (2010). Characterization of Nanming River (southwestern China) sewerage-impacted pollution using an excitation-emission matrix and PARAFAC. *Limnology*, *11*(3), 217–231. https://doi.org/10.1007/s10201-009-0306-4

Murphy, K. R., Butler, K. D., Spencer, R. G. M., Stedmon, C. A., Boehme, J. R., & Aiken, G. R. (2010). Measurement of dissolved organic matter fluorescence in aquatic environments: An interlaboratory comparison. *Environmental Science & Technology*, *44*(24), 9405–9412. https://doi.org/10.1021/es102362t

Murphy, K. R., Hambly, A., Singh, S., Henderson, R. K., Baker, A., Stuetz, R., & Khan, S. J. (2011). Organic matter fluorescence in municipal water recycling schemes: Toward a unified PARAFAC model. *Environmental Science & Technology*, *45*, 2909–2916. https://doi.org/10.1021/es103015e

Murphy, K. R., Stedmon, C. A., Wenig, P., & Bro, R. (2014). OpenFluor – An online spectral library of auto-fluorescence by organic compounds in the environment. *Analytical Methods*, *6*(3), 658–661. https://doi.org/10.1039/c3ay41935e

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legrendre, O., McGlinn, D., et al. (2019). *vegan: Community ecology package*. Retrieved from https://cran.r-project.org/package=vegan

Parry, M. L., Canziani, O. F., Palutikof, J. P., van der Linden, P. J., & Hanson, C. E. (2008). Climate Change 2007: Impacts, adaptation and vulnerability. Contribution of Working Group II to the fourth assessment report of the intergovernmental panel on climate change. *Journal of Environmental Quality*, *37*(6). https://doi.org/10.2134/jeq2008.0015br

Pereira, R., Isabella Bovolo, C., Spencer, R. G. M., Hernes, P. J., Tipping, E., Vieth-Hillebrand, A., et al. (2014). Mobilization of optically invisible dissolved organic matter in response to rainstorm events in a tropical forest headwater river. *Geophysical Research Letters*, *41*, 1202–1208. https://doi.org/10.1002/2013GL058658

Prouty, N. G., Hughen, K. A., & Carilli, J. (2008). Geochemical signature of land-based activities in Caribbean coral surface samples. *Coral Reefs*, *27*, 727–742. https://doi.org/10.1007/s00338-008-0413-4

Pucher, M., Graeber, D., Preiner, S., & Pinto, R. (2019). *staRdom*.

Purdy, E. G., Pusey, W. C., & Wantland, K. F. (1975). Continental shelf of Belize: Regional shelf attributes. *Studies in geology*.

Queimaliños, C., Reissig, M., Pérez, G. L., Soto Cárdenas, C., Gerea, M., Garcia, P. E., et al. (2019). Linking landscape heterogeneity with lake dissolved organic matter properties assessed through absorbance and fluorescence spectroscopy: Spatial and seasonal patterns in temperate lakes of Southern Andes (Patagonia, Argentina). *The Science of the Total Environment*, *686*, 223–235. https://doi.org/10.1016/j.scitotenv.2019.05.396

R Core Team. (2019). *R: A language and environment for statistical computing*. Vienna, Austria: R Foundation for Statistical Computing. Retrieved from http://www.r-project.org/

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., et al. (2013). Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience*, *6*(8), 597–607. https://doi.org/10.1038/ngeo1830

Renard, K. G., Laflen, J. M., Foster, G. R., & McCool, D. K. (2017). The revised universal soil loss equation. In *Soil erosion research methods*. https://doi.org/10.1201/9780203739358

Roebuck, J. A., Seidel, M., Dittmar, T., & Jaffé, R. (2019). Controls of land use and the river continuum concept on dissolved organic matter composition in an anthropogenically disturbed subtropical watershed. *Environmental Science & Technology*, *54*(1), 195–206. https://doi.org/10.1021/acs.est.9b04605

Sharp, R., Tallis, H. T., Ricketts, T., Guerry, A. D., Wood, S. A., Chaplin-Kramer, R., et al. (2014). *InVEST user's guide*. The Natural Capital Project.

Singh, S., Dash, P., Silwal, S., Feng, G., Adeli, A., & Moorhead, R. J. (2017). Influence of land use and land cover on the spatial variability of dissolved organic matter in multiple aquatic environments. *Environmental Science & Pollution Research*, *24*(16), 14124–14141. https://doi.org/10.1007/s11356-017-8917-5

Smith, R. M., & Kaushal, S. S. (2015). Carbon cycle of an urban watershed: Exports, sources, and metabolism. *Biogeochemistry*, *126*(1–2), 173–195. https://doi.org/10.1007/s10533-015-0151-y

Song, X.-P., Hansen, M. C., Stehman, S. V., Potapov, P. V., Tyukavina, A., Vermote, E. F., & Townshend, J. R. (2018). Global land change from 1982 to 2016. *Nature*, *560*, 639–643. https://doi.org/10.1038/s41586-018-0411-9

Spencer, R. G. M., Hernes, P. J., Ruf, R., Baker, A., Dyda, R. Y., Stubbins, A., & Six, J. (2010). Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. *Journal of Geophysical Research*, *115*. https://doi.org/10.1029/2009JG001180

Statistical Institute of Belize (2019). *Percent of total GDP by activity (1992–2018)*. Retrieved from http://sib.org.bz/statistics/gross-domestic-product/

Stedmon, C. A., Markager, S., & Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry*, *82*(3–4), 239–254. https://doi.org/10.1016/S0304-4203(03)00072-0

St. Pierre, K. A., Oliver, A. A., Tank, S. E., Hunt, B. P. V., Giesbrecht, I., Kellogg, C. T. E., et al. (2020). Terrestrial exports of dissolved and particulate organic carbon affect nearshore ecosystems of the Pacific coastal temperate rainforest. *Limnology & Oceanography*, *65*, 2657–2675. https://doi.org/10.1002/lno.11538

Sweetman, B. M., Foley, J. R., & Steinberg, M. K. (2019). A baseline analysis of coastal water quality of the port Honduras marine reserve, Belize: A critical habitat for sport fisheries. *Environmental Biology of Fishes*, *102*, 429–442. https://doi.org/10.1007/s10641-018-0811-6

Trumbore, S. E. (1993). Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements. *Global Biogeochemical Cycles*, *7*, 275–290. https://doi.org/10.1029/93GB00468

UNEP-WCMC (2018). *Global distribution of warm-water coral reefs, compiled from multiple sources including the millennium coral reef mapping Project, Version 4.0. Includes contributions from IMArS-USF and IRD (2005)*. Cambridge, UK: UN Environment World Conservation Monitoring Centre. Retrieved from http://data.unep-wcmc.org/datasets/1

Voight, C., Hernandez-Aguilar, K., Garcia, C., & Gutierrez, S. (2019). Predictive modeling of future forest cover change patterns in southern Belize. *Remote Sensing*, *11*(7), 823. https://doi.org/10.3390/rs11070823

West, T. O., Marland, G., King, A. W., Post, W. M., Jain, A. K., & Andrasko, K. (2004). Carbon management response curves: Estimates of temporal soil carbon dynamics. *Environmental Management*, *33*(4), 507–518. https://doi.org/10.1007/s00267-003-9108-3

Williams, C. J., Frost, P. C., Morales-Williams, A. M., Larson, J. H., Richardson, W. B., Chiandet, A. S., & Xenopoulos, M. A. (2016). Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. *Global Change Biology*, *22*(2), 613–626. https://doi.org/10.1111/gcb.13094

Winemiller, K. O., McIntyre, P. B., Castello, L., Fluet-Chouinard, E., Giarrizzo, T., Nam, S., et al. (2016). Balancing hydropower and biodiversity in the Amazon, Congo, and Mekong. *Science*, *351*, 128–129. https://doi.org/10.1126/science.aac7082

Worrall, F., Burt, T. P., Howden, N. J. K., Hancock, G. R., & Wainwright, J. (2018). The fate of suspended sediment and particulate organic carbon in transit through the channels of a river catchment. *Hydrological Processes*, *32*(1), 146–159. https://doi.org/10.1002/hyp.11413

Xenopoulos, M. A., Downing, J. A., Kumar, M. D., Menden-Deuer, S., & Voss, M. (2017). Headwaters to oceans: Ecological and biogeochemical contrasts across the aquatic continuum. *Limnology & Oceanography*, *62*, S3–S14. https://doi.org/10.1002/lno.10721

Yang, L., Hong, H., Guo, W., Huang, J., Li, Q., & Yu, X. (2012). Effects of changing land use on dissolved organic matter in a subtropical river watershed, southeast China. *Regional Environmental Change*, *12*(1), 145–151. https://doi.org/10.1007/s10113-011-0250-9

Young, C. A. (2008). Belize's ecosystems: Threats and challenges to conservation in Belize. *Tropical Conservation Science*, *1*(1), 18–33. https://doi.org/10.1177/194008290800100102