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Dissolved Organic Carbon in Tropical Watersheds

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Fabien Rizinjirabake

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Dissolved organic carbon in tropical watersheds: Linking field observation and ecohydrological modelling

Abstract

Dissolved organic carbon (DOC) is a general description of the organic material dissolved in water. DOC is an important source of energy, carbon, and nutrient transfers from terrestrial to aquatic ecosystems. The export of DOC into aquatic ecosystems may contribute to the carbon balance of terrestrial ecosystems and to water degradation. Ongoing climate and land cover changes will affect both DOC generation and transport, with implications for both terrestrial and aquatic ecosystems. An assessment of land use land cover and climate variability's impacts on DOC export is needed for better management of ecosystems. Watersheds are fundamental units of ecosystem functioning and are therefore an interesting organizational unit when used to understand the combined effects of land use land cover and climate variability on DOC export. Some studies have been conducted to explore this impact of land cover and climate variability on DOC, but most were conducted in a temperate environment and few in a tropical environment. In this regard, this dissertation focused on the impact of land use land cover and climate variability on DOC mobilization and export in the Rukarara River Watershed (RRW), Rwanda. The main aim is to determine how different carbon input and output processes interact under climate and land cover variability to impact DOC emanating from tropical watersheds.

Data used for this study include land cover maps produced from satellite imagery, daily air temperature and precipitation, digital elevation models (DEMs), water stage, flow, net primary productivity (NPP), soil properties such as total organic carbon (TOC), total nitrogen (TN), cation exchange capacity (CEC), aluminum (Al), iron (Fe), and soil texture within the RRW. Field observations were used to quantify riverine DOC loads, soil water extractable organic carbon (WEOC), DOC in percolation water (pDOC) and leached DOC (LDOC) and to describe their spatial variation and relationships with the aforementioned factors. Statistical models (including simple and quadratic regressions, general linear model, linear mixed effect models) were used to predict DOC within the study area. An eco-hydrological model, the Regional Hydro-Ecological Simulation System (RHESSys), was used to simulate streamflow and link it with stream DOC within the study area. The results of this study show that land use land cover and climate change interact to produce soil WEOC, from which a significant fraction is transported into streams, mainly through overland flow and loaded by the Rukarara River. The riverine DOC loss was low compared to the NPP of the RRW, but may affect the function of both land and water resources with the study area. The RHESSys model detected the response of the watershed to climate variability within the RRW and captured the significant monthly variability in streamflow within the RRW. This result indicates the potential use of RHESSys to estimate streamflow in the RRW and similar tropical watersheds. Stream DOC concentration was explained by simulated streamflow in the natural forest, indicating the potential use of RHESSys model simulated streamflow to predict stream DOC in the study watershed and similar ecosystems. Further studies should evaluate the performance of the RHESSys model to simulate other hydroecological processes in the tropical environment.

Key words
Dissolved Organic Carbon (DOC), watershed, climate variability, land use land cover variability, field observations, ecohydrological modelling

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“The Earth will not continue to offer its harvest, except with faithful stewardship. We cannot say we love the land and then take steps to destroy it for use by future generations”.

Saint John Paul II

Contents

List of Papers

This thesis is based on the following papers, which are referred to their Roman numerals:

I. Rizinjirabake, F., Abdi, A. M., Tenenbaum, D. E., & Pilesjö, P. (2018). Riverine dissolved organic carbon in Rukarara River Watershed, Rwanda. *Science of the Total Environment*, *643*, 793-806. https://doi.org/10.1016/j.scitotenv.2018.06.194.

II. Rizinjirabake, F., Pilesjö, P. & Tenenbaum, D. E.. Sources of soil dissolved organic carbon in a mixed agricultural and forested watershed in Rwanda (Submitted revised version under review in the Catena journal).

III. Rizinjirabake, F., Pilesjö, P. & Tenenbaum, D. E.. Dissolved organic carbon leaching flux in a mixed agriculture and forest watershed in Rwanda (under review in the Journal of Hydrology – Regional Studies journal).

IV. Rizinjirabake, F., Tenenbaum, D. E., Kharus A. S. E. & Pilesjö, P. Distributed hydroecological modelling of the Rukarara River Watershed, Rwanda (manuscript).

V. Rizinjirabake, F., Abdi, A. M., Tenenbaum, D. E., & Pilesjö, P. (2018). Data for dynamics analysis of riverine dissolved organic in watersheds. *Data in Brief*. https://doi.org/10.1016/j.dib.2018.08.171

Paper contributions

I. Rizinjirabake Fabien was responsible for the design of the subproject, analyzed data and led the manuscript writing.

II. Rizinjirabake Fabien was responsible for the design of the subproject, analyzed data and led the manuscript writing.

III. Rizinjirabake Fabien was responsible for the design of the subproject, analyzed data and led the manuscript writing.

IV. Rizinjirabake Fabien was responsible for the conceptualization; data curation; formal analysis; methodology, and manuscript writing.

V. Rizinjirabake Fabien was responsible for the organization of data and led the manuscript writing.

List of tables

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Abstract

Dissolved organic carbon (DOC) is a general description of the organic material dissolved in water. DOC is an important source of energy, carbon, and nutrient transfers from terrestrial to aquatic ecosystems. The export of DOC into aquatic ecosystems may contribute to the carbon balance of terrestrial ecosystems and to water degradation. Ongoing climate and land cover changes will affect both DOC generation and transport, with implications for both terrestrial and aquatic ecosystems. An assessment of land use land cover and climate variability's impacts on DOC export is needed for better management of ecosystems. Watersheds are fundamental units of ecosystem functioning and are therefore an interesting organizational unit when used to understand the combined effects of land use land cover and climate variability on DOC export. Some studies have been conducted to explore this impact of land cover and climate variability on DOC, but most were conducted in a temperate environment and few in a tropical environment. In this regard, this dissertation focused on the impact of land use land cover and climate variability on DOC mobilization and export in the Rukarara River Watershed (RRW), Rwanda. The main aim is to determine how different carbon input and output processes interact under climate and land cover variability to impact DOC emanating from tropical watersheds.

Data used for this study include land cover maps produced from satellite imagery, daily air temperature and precipitation, digital elevation models (DEMs), water stage, flow, net primary productivity (NPP), soil properties such as total organic carbon (TOC), total nitrogen (TN), cation exchange capacity (CEC), aluminum (Al), iron (Fe), and soil texture within the RRW. Field observations were used to quantify riverine DOC loads, soil water extractable organic carbon (WEOC), DOC in percolation water (pDOC) and leached DOC (LDOC) and to describe their spatial variation and relationships with the aforementioned factors. Statistical models (including simple and quadratic regressions, general linear model, linear mixed effect models) were used to predict DOC within the study area. An eco-hydrological model, the Regional Hydro-Ecological Simulation System (RHESSys), was used to simulate streamflow and link it with stream DOC within the study area. The results of this study show that land use land cover and climate change interact to produce soil WEOC, from which a significant fraction is transported into streams, mainly through overland flow and loaded by the Rukarara River. The riverine DOC loss was low compared to the NPP of the RRW, but may affect the function of both land and water resources with the study area. The RHESSys model detected the response of the watershed to climate variability within the RRW and captured the significant monthly variability in streamflow within the RRW. This result indicates the potential use of RHESSys to estimate streamflow in the RRW and similar tropical watersheds. Stream DOC

concentration was explained by simulated streamflow in the natural forest, indicating the potential use of RHESSys model simulated streamflow to predict stream DOC in the study watershed and similar ecosystems. Further studies should evaluate the performance of the RHESSys model to simulate other hydroecological processes in the tropical environment.

Sammanfattning

Löst organiskt kol (DOC) är en allmän beteckning på organiskt material upplöst i vatten. DOC är en viktig källa för energi, kol och näring som överförs från markbundna till akvatiska ekosystem. Exporten av DOC till akvatiska ekosystem kan bidra till kolbalansen i markbundna ekosystem och till försämrad vattenkvalitet. Pågående klimat- och markförändringar kommer att påverka både genereringen och transporten av DOC, med implikationer för både markbundna och akvatiska ekosystem. En bedömning av markanvändning och klimatvariationers inverkan på exporten av DOC behöver göras för att bättre kunna hantera ekosystemen. Avrinningsområden är fundamentala för ekosystemets funktion och är därför intressanta för förståelsen för hur de kombinerade effekterna av markanvändning, gröngödsling och klimatvariationer påverkar exporten av DOC. Ett mindre antal studier har utförts för att undersöka hur marktäckning och klimatvariation påverkar DOC men de flesta har genomförts i tempererat klimat och endast få i tropiskt klimat. I denna avhandling har jag fokuserat på hur markanvändning, marktäckning och klimatvariationer har påverkat mobiliseringen och exporten av DOC i Rukarara River Watershed (RRW), Rwanda. Huvudsyftet är att bestämma hur DOC i tropiska avrinningsområden påverkas av växelverkan mellan olika processer för in- och utflöde av kol under varierade klimat- och marktäckningsförhållanden.

Data som har används för denna studie innefattar marktäckningskartor som skapats med utgångspunkt från satellitbilder, daglig temperatur i luft, nederbörd, DEMs, flodens vattennivå och flöde, nettoprimärproduktion (NPP), jordegenskaper som totalt organiskt kol (TOC), total kvävemängd (TN), katjonbyteskapacitet (CEC), aluminium (Al), järn (Fe) samt jordstruktur inom RRW. Fältobservationer har använts för att kvantifiera flodbaserat DOC, extraherbart organiskt kol i markvatten (WEOC), DOC i perkolationsvatten (pDOC) samt urlakat DOC (LDOC) för att beskriva deras rumsliga variation och relationer till ovannämnda faktorer. Statistiska modeller (inklusive linjär och kvadratisk regression, generell linjär modell samt modeller för linear mixed effect) har använts för att förutse DOC inom det studerade området. En ekohydrologisk modell, Regional Hydro-Ecological Simulation System (RHESSys), har använts för att simulera DOC-flöden inom det studerade området. Resultaten från denna studie visar att markanvändning och klimatförändring växelverkar för att skapa jord-WEOC, av vilket en signifikant del har transporterats till bäckar, huvudsakligen genom att rinna över marken, som leder till Rukararafloden. Förlusten av DOC till floden var låg jämfört med NPP i RRW, men kan tänkas påverka funktionen av både mark- och vattenresurser i det studerade området.

Abbreviations

A.D:	Anno Domini (“in the year of the Lord”)
AAS:	Atomic Absorption Spectroscopy
AIC:	Akaike Information Criterion
Al:	Aluminum
ANOVA:	Analysis Of Variance
API:	Antecedent precipitation index
BEPS-terrainLab:	Boreal Ecosystem Productivity Simulator (BEPS) model coupled to terrainLab model
BIOME-BGC:	Biome BioGeochemical Cycles model
CEC:	Cation Exchange Capacity
CGIS-UR:	Centre of Geographic Information and Remote Sensing of the University of Rwanda
CN:	Curve Number
CO_2:	Carbon dioxide
CS:	Centre Site
DEM:	Digital Elevation Model
DHSVM:	Distributed Hydrology Soil Vegetation Model
DOC:	Dissolved Organic Carbon
DOM:	Dissolved Organic Matter
EcoHAT:	Eco-Hydrological Assessment Tool
ES:	Eastern Site
Fe:	Iron
FB:	Farm basin
GLM:	Generalized Linear Models
GPS:	Global Positioning System
HSD:	Honest Significant Difference
HSG:	Hydrologic Soil Groups
IPCC:	Intergovernmental Panel on Climate Change
LDOC:	Leached Dissolved Organic Carbon
LM:	Linear Model
LME:	Linear Mixed Effect model
LOI:	Loss On Ignition
LULC:	Land Use Land Cover
MASL:	Meter above sea level
MAT:	Mean Antecedent Temperature

MODIS:	Moderate Resolution Imaging Spectro-radiometer
MT-CLIM:	Mountain Climate Simulator
NF:	Natural forest basin
NPP:	Net Primary Productivity
ORNL DAAC:	Oak Ridge National Laboratory Distributed Active Archive Center
pDOC:	percolation water DOC
pH:	hydrogen potential
Qi:	water flow
Ra:	Rainfall amount
REML:	Restricted Maximum Likelihood
RHESSys:	Regional Hydro-Ecological Simulation System
Ri:	Rainfall intensity
RRW:	Rukarara River Watershed
RWFA:	Rwanda Water and Forest Authority
SI:	Spatial Index
SOC:	Soil Organic Carbon
SOM:	Soil Organic Carbon
SP:	Slope position
SSR:	Sum of Squared Residuals
SWAT:	Soil and Water Assessment Tool
TB:	Tea basin
TN:	Total Nitrogen
TOC:	Total Organic Carbon
TOPOG:	Terrain analysis-based hydrologic modelling package
TPI:	Topographic Position Index
VIC:	Variable Infiltration Capacity
WEOC:	Water Extractable Organic Carbon
WS:	Western site

Introduction

What is DOC and why do we care about it?

Dissolved organic carbon (DOC) is the fraction of total organic carbon that can pass through a filter below 0.45 µm in size. DOC may contain amino acids, simple carbohydrates, a fraction of microbial biomass, and other simple organic compounds, fractions of humic acids of low molecular weight, as well as other numerous simple organic compounds (Gonet and Debska, 2006; Zou et al., 2005). DOC is a broad practical classification for organic molecules of varied composition within soils (soil DOC) and aquatic systems (water DOC). Soil DOC is a labile natural part of soil solution (Schwalm and Zeitz, 2014); it is the chemical and microbial degradable carbon that is physically accessible by soil microbes (Zou et al., 2005). Water DOC originates from within a body of water from aquatic plants or algae (autochthonous DOC) and from the external environment to a body of water from land areas (allochthonous DOC).

Soil DOC is linked with its capacity to supply nutrients (Sucker and Krause, 2010); its export to water may cause both land and water degradation. Land degradation is an environmental problem that threatens food and energy security (Lobell et al., 2008, biodiversity (Maitima et al., 2009), resilience to climate change (Neely et al., 2009) and induces migration (Mélanie, 2008), offsite problems such as sedimentation and carbon emissions affecting climate change (Mupenzi et al., 2011). Soil DOC plays also a role in soil aggregation and erosion control, acid-base balance and exchange capacity in the soil, mobilization and export of nutrients, bioavailability and ecotoxicology of heavy metals, transformation and transport of organic contaminants (Arnold et al., 2010). In addition, it plays an important role in carbon cycling in watersheds: It causes 25% - 50% of the annual loss of carbon in forest-floor (Kalbitz et al., 2000). As the mobile fraction of soil organic matter (SOM), DOC represents a key vehicle for the translocation and loss of soil nutrients (Hagedorn et al., 2004). Regarding natural water degradation, high DOC concentrations can result in brown water, with a negative impact on drinking water purification and water recreational value. Also, high DOC concentrations reduce light penetration in water, and this affects the aquatic productivity and thereby aquatic food chain (Erlandsson et al., 2011). Additionally, high DOC in water affects predator-prey interactions (Stasko et al.,

2012) and, coupled to nitrogen and phosphorus, induces eutrophication processes (Aparicio et al., 2016). However, a reasonable amount of water DOC plays a key role in aquatic ecosystem function: It is a potential source of carbon and energy for heterotrophic organisms and thus contributes significantly to aquatic ecosystem metabolism. Understanding the dynamics of soil and water DOC is, therefore, important for better management of land and water resources.

Over the past two decades, a significant amount of allochthonous DOC has been exported into natural waters and, therefore, increased water DOC concentrations across large parts of the world. This increase of DOC in natural waters can increase CO_2 production in aquatic ecosystems, exacerbating global warming. Increased water DOC input may stimulate heterotrophic metabolism and thus CO_2 production. Also, increased water DOC affects water color with, eventually, a shading effect that negatively impacts on water primary production by decreasing atmospheric CO_2 uptake by water primary producers, thus increasing CO_2. The increased DOC may acidify the water and, consequently, decrease water pH with a subsequent increase in CO_2. Understanding water and soil DOC dynamics is therefore important for implementing effective global warming mitigation.

Soil DOC production and climate change

Soil DOC is the outcome of processes that depend on climate: soil organic matter (SOM) production, decomposition, mineralization and sorption (Kalbitz et al., 2000). The CO_2:DOC production ratio increases with warming, meaning that DOC production increases with temperature due to enhanced photosynthesis under higher CO_2 conditions (Cox et al., 2013). But Moore et al. (2008) indicated that DOC mineralization is even more temperature sensitive, especially in the tropics. Thus, high DOC production is offset by high decomposition of old soil carbon, induced by the microbial priming effect. This microbial priming effect is an extra decomposition of organic carbon after the addition of easily decomposable organic substances to the soil (Kuzyakov, 2010; Dalenberg and Jager, 1989) or nutrients such as, for example, nitrogen (Léon et al., 1995; Jenkinson et al., 1985;), phosphorus (Fokin and Radzhabova, 1996), and sulfur (Chapman, 1997; Lefroy et al., 1994; O'Donnell et al., 1994) or other soil treatments such as drying and rewetting (Kuzyakov, 2010). Under climate change, the microbial priming effect is induced by increased photosynthesis consequent to higher CO_2 and precipitation, and this has positive implications for rooting depth and exudates. These exudates increase the activity of soil microorganisms, resulting in acceleration of SOM mineralization or microbial biomass turnover in the rhizosphere (Figure 1). However, this microbial priming effect is not always straightforward (Zimmerman et al., 2011). For example, SOM decomposition increased up to 5-fold or decreased by up to 30% in the presence of plant residues (Nottingham et al., 2009; Bell et al., 2003) or root exudates (Cheng and Lehmann, 2009; Kuzyakov, 2002).

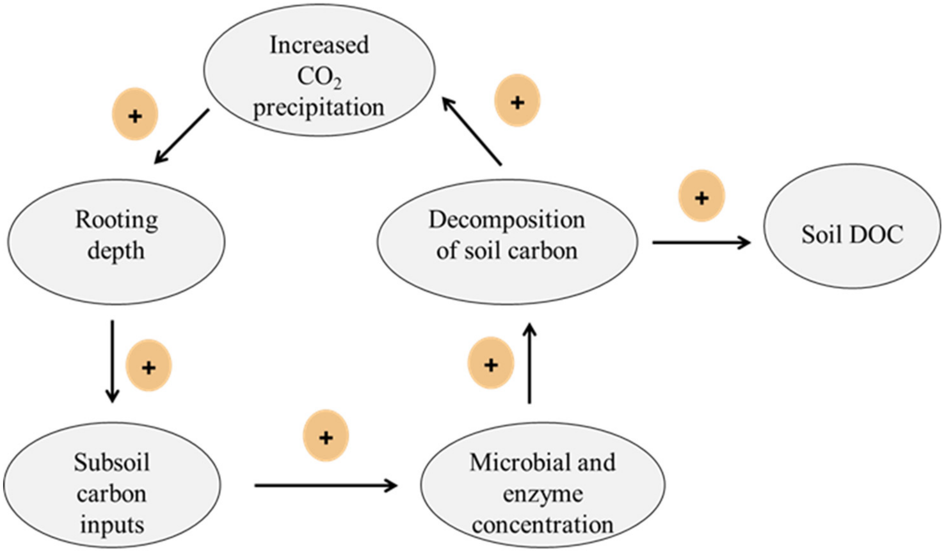

Figure 1 Increased soil DOC production stimulated by high soil old carbon decomposition induced by the microbial priming effect.

Climate change also impacts on soil DOC production through its effects on carbon and nitrogen interactions. Increased photosynthesis under higher CO_2 negatively affects soil nitrogen availability (Figure 2); more soil nitrogen is taken up by plants. Such nitrogen-limited conditions suppress the CO_2 fertilization effect on canopy assimilation (Maaroufi et al., 2015) thus limiting organic matter production and, therefore, soil DOC. Under these conditions of limited soil nitrogen, fungi decompose lignin and the resulting increase of soil nitrogen can cause a shift from fungal to bacterial decomposers, with less SOM decomposition and thus less soil DOC (Maaroufi et al., 2015). The lignin decomposition leads to a positive feedback in response to rising atmospheric CO_2, whereas the shift from fungal to bacterial decomposers leads to a limited CO_2 fertilization effect, and consequently less soil DOC.

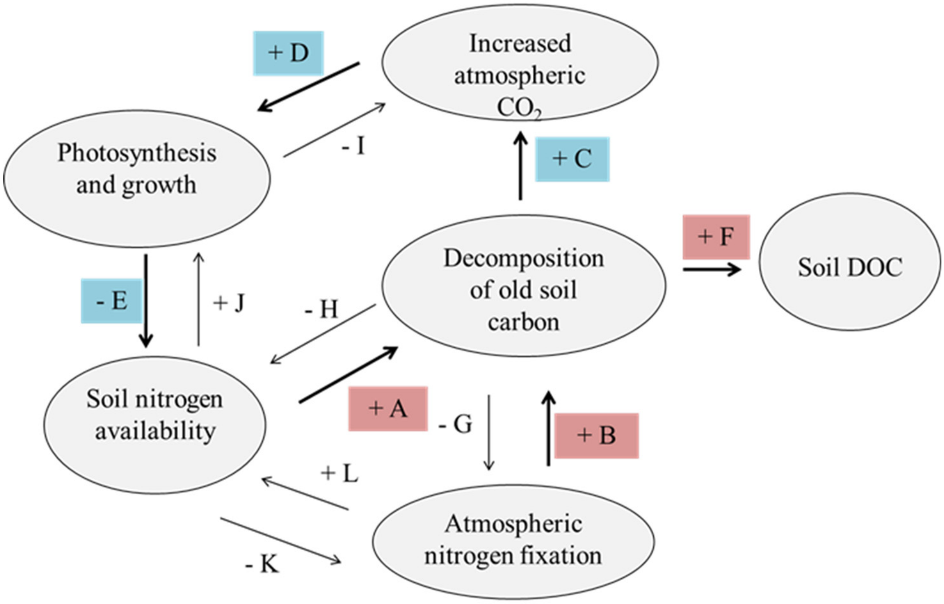

Figure 2 Increased soil DOC production stimulated by high old soil carbon decomposition (arrow +E) induced by the nitrogen priming effect (arrows +A and +B) through a lower carbon to nitrogen ratio. Additionally, the figure shows effect of high old soil carbon decomposition on atmospheric CO_2 (arrow + C), photosynthesis (arrow + D), soil nitrogen availability (arrow + E), and other interrelations within the cycle (arrows G to L).

Soil DOC export into natural waters

The export of soil DOC from the terrestrial system to the aquatic ecosystem is fundamental for the global carbon cycle, because it is an interface between terrestrial and marine carbon cycling (Richey et al., 2004). The soil DOC delivery processes, include leaching, groundwater retention and discharge, floodplain and riparian zone exchange and retention, and waste discharge. The spatial delivery scale is local, whereas the temporal scale varies from days for point sources and surface runoff, to days to weeks or months for riparian zones, and from weeks to years for shallow aquifers, and years to centuries for deep aquifers (Bouwman et al., 2013).

Soil DOC export depends on many factors including hydrology, temperature, land use land cover, mineral soil absorption, hydraulic soil conductivity, dry-wet cycle of hydrological conditions, surface and sub-surface runoff, landscape position, transformations between particulate, dissolved and gaseous phases that may occur during the transport, and DOC redox reactivity (Williams et al., 2010; Mattsson et al., 2009; Blair et al., 2004; Webster et al., 1999). Changes in temperature may influence DOC export from soils by altering decomposition and mineralization of organic matter (Sucker and Krause, 2010). Increased precipitation alters the water budget and discharge, which then increases DOC concentrations (Hongve et al., 2004). Land use changes influence the retention and the export of organic carbon from watersheds (Johnson et al., 2009). Landscape position along a hillslope affects biophysical processes such as infiltration, erosion, sedimentation and insolation that, in turn, affect DOC inputs and losses (Balkcom et al., 2005).

The riparian zone is the main source of DOC entering streams independent of upslope conditions (Strohmeier et al., 2013; Dick et al., 2015; Ledesma et al., 2015). Lateral DOC fluxes from riparian zone to streams are limited to only a fraction of the total riparian zone, with most lateral DOC fluxes occurring within predominant flow paths (Ledesma et al., 2015). Riparian zones have filtering capacity to retain and release nutrient and sediment (Ranalli and Macalady, 2010). The transport of DOC from floodplains to streams dominates during wetter periods, whereas deeper sources dominate during dry periods (Tiwari et al., 2014; Dick et al., 2015). The role of leaching process on soil DOC depends on soil properties and vegetation (Fujii et al., 2011). For example, soil ionic strength and pH influence organic matter solubility, whereas ferric and aluminum oxides or hydroxides and clay determine the sorption process (Chantigny, 2003) where high adsorption reduces DOC leaching (Kalbitz et al., 2000).

DOC simulation in watersheds

Contemporary environmental problems are being approached more and more on the geographic basis of the watershed to understand ecosystem processes and responses to climate change and land-cover (Tetzlaff et al., 2013). From this perspective, process-based models have been developed to simulate soil DOC export into rivers (see Table 1). Some models of this sort focus on soil absorption (Yurova et al., 2008), hydrological rainfall-runoff processes (Xu et al., 2012), DOC production (Wu et al., 2014), some combination of DOC production, soil absorption and leaching functions, or combination of ecological and hydrological processes (Futter et al., 2009). The latter approach is interesting because it can include the effects of climatic, hydrological, biogeochemical and ecological processes and their interrelations in soil and water (Palmer and Bernhardt, 2006; Krysanova et al., 2005). Hydrological processes interact with climate and terrestrial vegetation to determine water availability and flow regimes. These flow regimes and their interaction with soils influence ecological processes such as nutrient cycling. In return, ecological processes and patterns influence water availability (Palmer and Bernhardt, 2006). Hydroecological models are important tools for studying the mechanisms of ecological patterns and processes and for assessing the effects of environmental change on hydrological and ecological processes (Chen et al., 2014).

Table 1
Summary of models used to understand ecosystem hydrological and eco-hydrological processes.

Model types	**Goal**	**Examples**
One-way coupling models	Describe biophysical properties such as canopy interception, rainfall interception, infiltration, and evapotranspiration to simulate hydrological processes without considering the impact of hydrological processes on physiological or biochemical processes of the vegetation.	Distributed Hydrology Soil Vegetation Model (DHSVM) (Wigmosta et al., 1994) Variable Infiltration Capacity (VIC) (Liang et al., 1994).
Mutually coupling models	Simulate hydrological and ecological processes considering vegetation dynamic change in the leaf, root depth and litter, and changes in the soil moisture.	(See examples for below model types)
Conceptual models	Couple hydrological models with parametric models such as light-use efficiency models or empirical crop growth models	Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998) Eco-Hydrological Assessment Tool (EcoHAT) (Liu et al., 2009).
Semi-physical process based models	Discretize the watershed into fully distributed space units and describe interaction between the dynamic growth of the vegetation and hydrology	TOPOG model (o'Loughlin, 1986)
Physical process based models	Describe physiological processes and mechanisms such as photosynthesis, couple vegetation biochemical processes and hydrological processes and characterize finally hydrological processes particularly the effects of soil moisture on the vegetation biochemical process.	Regional Hydro-Ecological Simulation System (RHESSys) model (Band et al., 1993) BEPS-TerrainLab (Govind et al., 2009)

Problem statement

The Earth's climate is changing in both temperature and precipitation patterns due to the emission of carbon greenhouse gases to the atmosphere, altering its heat-trapping capacity (IPCC, 2007). This changing climate can have both immediate and long lasting effects on primary production, accumulation and export of soil organic carbon into natural waters, and therefore on carbon balance. There is debate about the amount of carbon stored in, and emitted from, terrestrial ecosystems (Le Quéré et al., 2016). Quantifying this carbon balance is a challenge, as the interactions between climate change and land use land cover (LULC) on carbon export into natural waters are not well understood (Moss et al., 2011; Matthews and Caldeira, 2008). Sources and destinations of carbon fluxes from the land to water, especially for dissolved organic carbon (DOC), are still unclear (Yang et al., 2013). There is a need to understand how changing climate and other disturbance regimes, such as land use land cover change, combine to give a particular signature to DOC export.

DOC export to waters may cause both soil and natural water degradation. Land degradation is a global problem that affects at least a quarter of the global land area (Lal et al., 2012), seriously undermining the livelihoods in all agro-ecologies across the world (Nkonya et al., 2011). Land degradation reduces biological products, including food, and carbon sequestration services of the land ecosystem (Le Quéré et al., 2016). Also, soil DOC export threatens soils' potential to mitigate climate change (Neely et al., 2009; Stockmann et al., 2013). Development activities such as agriculture, urbanization, forestry and industries often lead to more intensive land use, which increases runoff, and consequent transport of pollutants directly into the natural waters. Land and water degradation results in decreasing ecosystem resilience and provision of environmental services (Costanza et al., 1997). Land and water degradation threaten food security for many of the poorest and most food insecure living in Asia, Africa and Latin America (Kaiser, 2004). Land and water degradation is a challenge that must then be tackled to preserve ecosystem resilience and provision of environmental services and meet poverty alleviation goals. As it is ubiquitous in terrestrial ecosystems, DOC can serve as a sensitive indicator of land and water natural water degradation through shifting in ecological processes (Bolan et al., 2011; Srinivasarao et al., 2014).

Watersheds are fundamental units of ecosystem functioning, and thus can help us to better understand combined effects of changing climate and land use land cover on DOC export. This is important in order to identify mitigation strategies for healthy watersheds that maintain their balanced nutrient cycling, energy, and services such as water quality and food for people and wildlife. Some studies on DOC export dynamics have been conducted, but most of them are focused on temperate watersheds, and very few on tropical watersheds. There is a need for such studies in tropical watersheds, where coupled climate–carbon-cycle models indicate that carbon storage on land will increase due to the simultaneous enhancement of plant photosynthesis and water use efficiency under higher atmospheric CO2 concentrations, or will decrease due to higher soil and plant respiration rates associated with warming temperatures (Cox et al., 2013).

Aims and objectives

The aim of this research is to determine how different carbon input and output processes interact under climate and land cover variability to impact DOC from tropical watersheds. A key uncertainty is the degree to which tropical watersheds respond to climate driven changes in hydrology and DOC export. Understanding this could help to develop effective integrated watershed policies that can build resilience to the impacts of climate and land cover changes and protect watershed services. This research is focused on soil water DOC mobilization and transfers, to better understand their dynamics (Figure 3). Within the study area, the specific objectives of the research are the following:

1. Quantifying water DOC loads to estimate to what extent riverine DOC affects the carbon budget in the study area (Papers I and V);
2. Investigating soil WEOC concentration and quantifying the effect of topography, land cover, rainfall amount and intensity, mean average temperature and soil properties on its variation (Paper II);
3. Investigating leached DOC flux and factors controlling its variation in the study area (Paper III);
4. Simulating water flow and linking it with stream DOC contents in the Rukarara River basin using the Regional Hydroecological Simulation System (RHESSys) model (Paper IV).

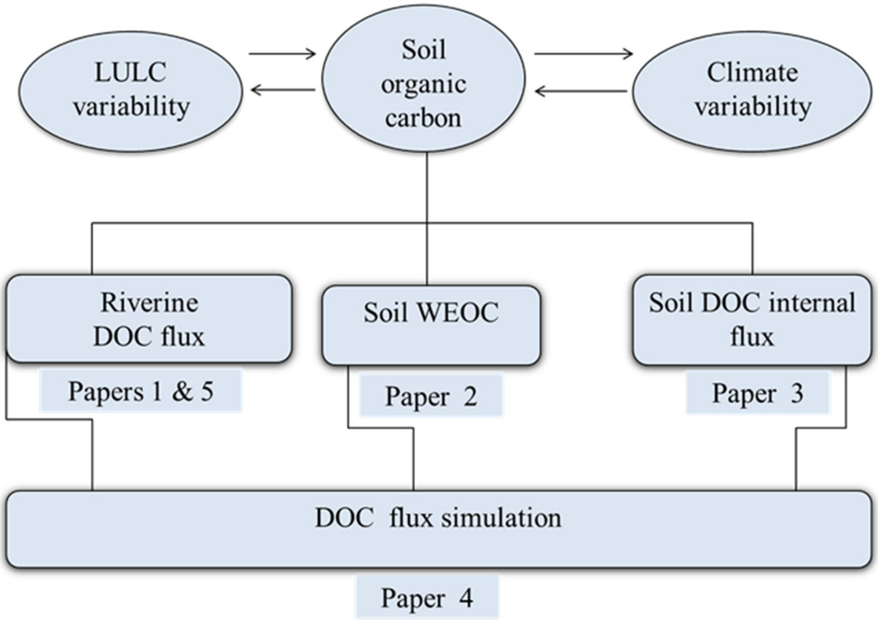

Figure 3 Overview of the thesis.

Materials and Methods

Study sites

The research presented here includes field studies (Papers 1, 2, 3, and 5) and a simulation study (Paper 4). All studies were carried out in the Rukarara River Watershed, a mixed agriculture and forest watershed in Southwestern Rwanda. Three sites were selected in the watershed: The Eastern site (ES), the Centre site (CS) and the Western site (WS) (Figure 4). The ES and CS sites were located areas dominated, respectively, by small crops and tea plantations. The WS was located in the Nyungwe National Park, a primary mountainous rainforest forest. The watershed drains an area of 493.5km^2 and its landscape is composed of mountainous terrain with elevations from 1,541 to 2,924 MASL and slopes from 0° to 68°. More detailed information on the study watershed was provided in the following papers.

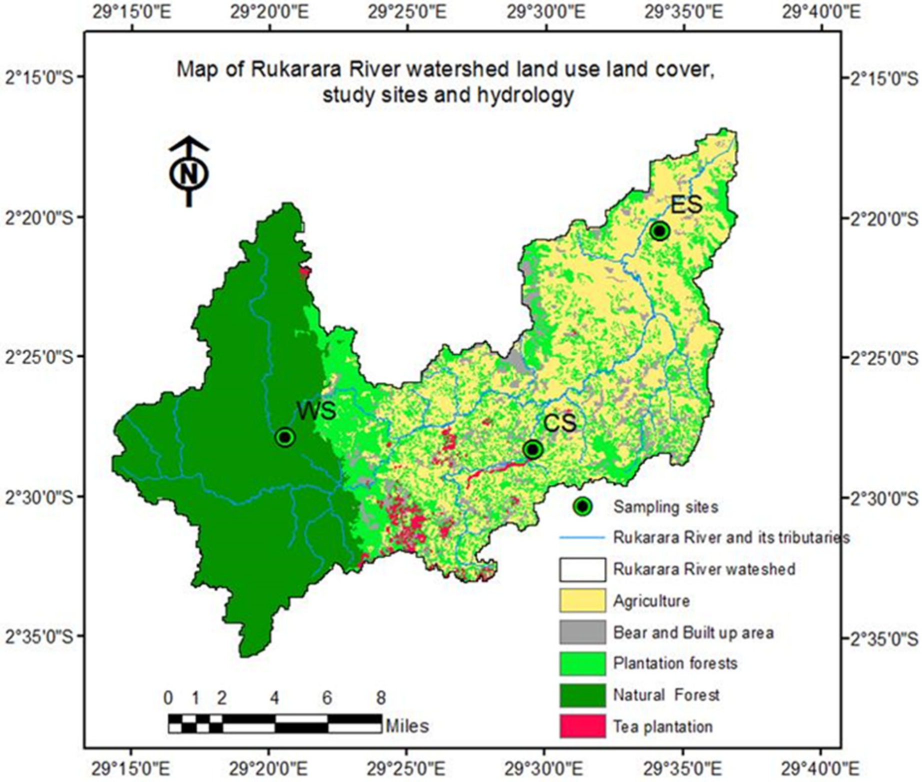

Figure 4 Map showing study sites within the study area, the Rukarara River Watershed.

Data used in this thesis

This project used various kinds of data, including field measurements, laboratory analysis data, spatial data, historical data, and literature-based data. Field measurements include rainfall, air temperature, and water stage data. Rainfall data were recorded using tipping bucket rain gauges with integrated data loggers (OMC-210-2). Air temperature data were recorded using temperature sensors (automatic pressure transducer stage gauges with integrated data logger PT2X and mini-divers). Water stage data were measured at the three small river sites and at the Rukarara River outlet using current meters (small and medium size) and the aforementioned automatic pressure transducers.

Laboratory analysis data included samples of soil collected in topsoil (0–20cm depth), stream water, percolation water, and leached water. Soil samples were used to analyze soil water extractable organic carbon (WEOC) and physico-chemical soil properties including total organic carbon (TOC), total nitrogen (TN), iron (Fe ppm), aluminum (Al ppm), and cation Exchange Capacity (CEC), clay content, sand content, and silt content. WEOC was analyzed using a modified version of the Zhang et al. (2011) method, whereas stream DOC, percolation water (pDOC), and leached waters (LDOC) was analyzed on a TOC analyzer. Soil texture elements were analyzed using the improved Bouyoucos method (Bouyoucos, 1962); TOC (%) by the Loss On Ignition (LOI) method (Davies, 1974); TN (%) by the micro-Kjeldahl digestion - distillation method (Bremner, 1996); Fe and Al (ppm) by the Sodium tetraborate method followed by the atomic absorption spectroscopy (AAS) method, and the CEC (mEq/100g) by the Sodium acetate method (Taiwan, 1994).

Regarding spatial data, this research project utilized land use land cover maps derived from remote sensing imagery (for the years 2008 and 2015), a 10m digital elevation model (DEM), net primary productivity (NPP) derived from remote sensing imagery, soil depth, and GPS data. The land use land cover map for the year 2008 was obtained from Wasige et al. (2014), whereas the land use land cover map for the year 2015 was developed based on a 6.5 m ground resolution RapidEye satellite image of the study area. The 10 m DEM was provided by the Centre of Geographic Information and Remote Sensing of the University of Rwanda (CGIS-UR). Soil depth and soil texture data were provided by CGIS-UR. NPP data were Moderate Resolution Imaging Spectroradiometer (MODIS) (MOD17A3: 500 m × 500 m) data (ORNL DAAC, 2018; Running and Zhao, 2015). GPS data were collected during sampling campaigns.

Historical rainfall and temperature data were provided by Meteo Rwanda, whereas historical flow data were provided by the Rwanda Water and Forest Agency (RWFA) and the Rukarara Hydropower Station. Curve number (CN) values were selected according to the Mockus (1969) handbook, whereas HSGs data were retrieved from the ORNL DAAC (HYSOGs250m) (Ross et al., 2018). Vegetation physiological parameters and soil parameters, required to run the RHESSys model, were derived from Peng et al. (2016). The use of all of the above data in their respective papers is summarized in the following Table 2.

Table 2
Summary of data used in this thesis and their use in different papers

Data type	Use	Paper number
Rainfall	To determine relationship between WEOC and rainfall through antecedent precipitation index (API).	Paper 2
	Data in brief	Paper 5
	As input data for running RHESSys model	Paper 4
Air temperature	To determine relationship between WEOC and temperature through mean antecedent temperature (MAT).	Paper 2
	Data in brief	Paper 5
	As input data for running RHESSys model.	Paper 4
Water stage	To produce rating curves necessary to predict non-measured flow data that have been used in estimation of annual DOC load.	Paper1
Soil properties	To determine responses of DOC to soil properties within the study area.	Paper 2
WEOC	To quantify soil DOC and its relationship with LULC, soil properties, and landscape attributes.	Paper 2
sDOC	To calculate DOC loadings	Paper 1
pDOC	To determine the effect of climate variability on soil DOC.	Paper 2
LDOC	To quantify the effect of leaching process on soil DOC.	Paper 3
Land cover	To calculate spatial distribution index (SI) used in turn to describe the influence of LULC on DOC loading.	Paper 2
	To calculate curve number (CN), area and mean slope for each LULC class	Paper 3
	As input data to run the RHESSys model	Paper 4
DEM	To calculate topographic position index (TPI) used to identify slope position (SP)	Paper 2
	To calculate Topographic Wetness Index (TWI) used to describe the topography of different LULC classes and to quantify overland flow and therefore the combined effects of LULC and topography on DOC loading.	Paper 1
	To delineate watershed boundary, to calculate slope, identify elevation data	Papers 1- 4
Soil depth	As input data to run the RHESSys model	Paper 4
NPP	To calculate daily NPP and to estimate the impact of stream DOC loading on the carbon sequestration within the study area.	Paper 1
	Data in brief	Paper 5
GPS data	To map sampling sites and points, and rain gauge and sensors locations	Papers 1- 4
Historical rainfall	To fill in missing data	Paper 2
Historical flow	To calibrate the RHESSys model simulated flow	Paper 4

A series of statistical techniques and models were used in this thesis to compare DOC values, to evaluate the controlling effects on DOC, to predict DOC values, or to determine relationships between DOC and climate variability, soil properties, LULC and landscape attributes. A t-test was used to test the statistical difference between two DOC values. A one-way ANOVA with the post hoc Tukey honest significant difference approach (Tukey HSD) and the Spearman's rank correlation were used to evaluate the effects of, respectively, LULC and slope position (SP) on WEOC (Paper 1).

Various predictions were performed in this thesis using simple linear models (LM), quadratic models, power function, generalized linear models (GLM) and linear mixed-effects models (LME). LMs that summarize and study relationships between two continuous variables were used to predict WEOC as a function of soil properties (Paper 1), and LDOC flux as a function of rainfall amount (Ra) and intensity (Ri), on the one hand, and Q and F on the other hand (Paper 3). GLMs that analyze fixed effects were used to estimate the fixed effects of soil properties including TOC, TN, Al, CEC, Fe, and soil texture elements on WEOC (Paper 1). GLMs that analyze both fixed and random effects were used to model WEOC and LDOC. Fixed effects are defined as the effects of covariates, whereas random effects are effects of factors whose levels are sampled from a larger population (Bolker et al., 2009). LMEs assume normal distributed residuals and are appropriately applied to repeated data that are likely to be correlated. Fitted to repeatedly-measured data, LMEs involve the estimation of covariance parameters to capture this correlation. In the Paper 1, LMEs analyzed fixed effects of soil properties and random effects of sites (East, Center and West) and LULC (natural forest, plantation forest, tea plantation, and cropland) on WEOC. In Paper 3, LMEs analyzed fixed effects with respect to LULC (forests and cropland) for Q and F and in respect with site (WS, CS, ES) on LDOC. The quadratic model was used to determine the relationships between pDOC, precipitation and temperature via API and MAT (Paper 1), whereas the power function was used to determine the relationship between stage and flow on one hand, and between DOC and flow on other hand (Paper 2).

LME models were fitted by the restricted maximum likelihood (REML) method, which has the advantage of producing unbiased estimates of variance and covariance parameters (Liu et al., 2017). LMEs were evaluated by using the Akaike Information Criterion (AIC), which was found optimal by Yang (2005) for selecting a model with the optimal balance between minimal mean squared error and minimal complexity.

Hydroecological simulation

Apart from statistical models, the Regional Hydro-Ecological Simulation System (RHESSys) model was applied in this thesis to simulate DOC concentration and flux in the study area. The RHESSys model has already been successfully applied to many watersheds to simulate DOC flux (e.g.: Yang et al., 2013; Rouhani et al., 2014). The carbon cycling in the RHESSys model includes the estimation of photosynthesis, vegetation respiration, vegetation allocation and turnover rates, organic matter decomposition rate. Photosynthesis is estimated by the Farquhar photosynthesis model (Farquhar and von Caemmerer, 1982), vegetation respiration by the Ryan model (Ryan, 1991), and the vegetation allocation processes by the 3-PG model (Landsberg and Waring, 1997) or the Dickenson et al. (1998) model. The vegetation turnover rate is determined by vegetation specific parameters that are scaled by environmental factors. Soil and decomposition rates are based on the work of Thornton (1998). Both soil and litter pools are associated with C:N ratios and a potential decay rate, including carbon lost and carbon transferred to soil or litter pools. Soil and litter respiration are computed as percentage of decomposition rates. Details about sub-models and corresponding mathematical equations used in the RHESSys model can be found in Tague and Band (2004).

During carbon cycling in RHESSys model, plants fix carbon from atmospheric CO2 through photosynthesis, whose rate depends on nutrient availability, water availability, incoming radiation, and temperature. A portion of fixed carbon is used for plant respiration; another portion is allocated to the various parts of plants for their respiration, growth and maintenance (first carbon pool). Within RHESSys modeling, the Landsberg and Waring (1997) partitioning strategy is used in RHESSys model to estimate species-specific allocation ratios. Nutrient availability affects the amount of carbon allocated to roots, with a greater proportion going to roots on infertile sites than those on fertile sites. The remaining fixed carbon continuously gives rise to litter and soil organic carbon (secondary carbon pools). DOC in soil solutions is produced from theses secondary pools via decomposition processes (Figure 5). The decomposition rate is calculated using base decomposition rates for the litter and soil pools before it is scaled by soil temperature, nutrient availability and soil water content.

The RHESSys model simulates hydrological processes, including lateral and vertical flows and, thus, the DOC flux associated with these flows. The rainfall that reaches the soil surface after being intercepted by the canopy strata infiltrates into soil layers following Philip's infiltration equation (Philip, 1957). The RHESSys model uses a three layer model (root zone, unsaturated zone, and saturated zone) to simulate vertical rainfall water fluxes. The vertical movement of water through the soil profile is based on hydraulic conductivity and pressure gradient at the boundary of the saturated and unsaturated zones. When the soil layers are saturated, the lateral flow carries the DOC out from the soil. The DOC transport depends on soil porosity, decay rate of soil porosity, soil depth at defined layers (root zone, unsaturated and saturated zones), soil DOC availability, DOC distribution with depth, DOM production rate, DOC absorption rate, and soil water content.

All rainfall water exceeding the soil storage capacity is routed to one or more downslope patches within one time step, whereas only a portion of the patch's subsurface water store is routed to the downslope patches following an exponential transmissivity decay model. Lateral drainage of saturated water is routed to streams via surface flow, shallow subsurface flow, or groundwater depending on topography and soil characteristics.

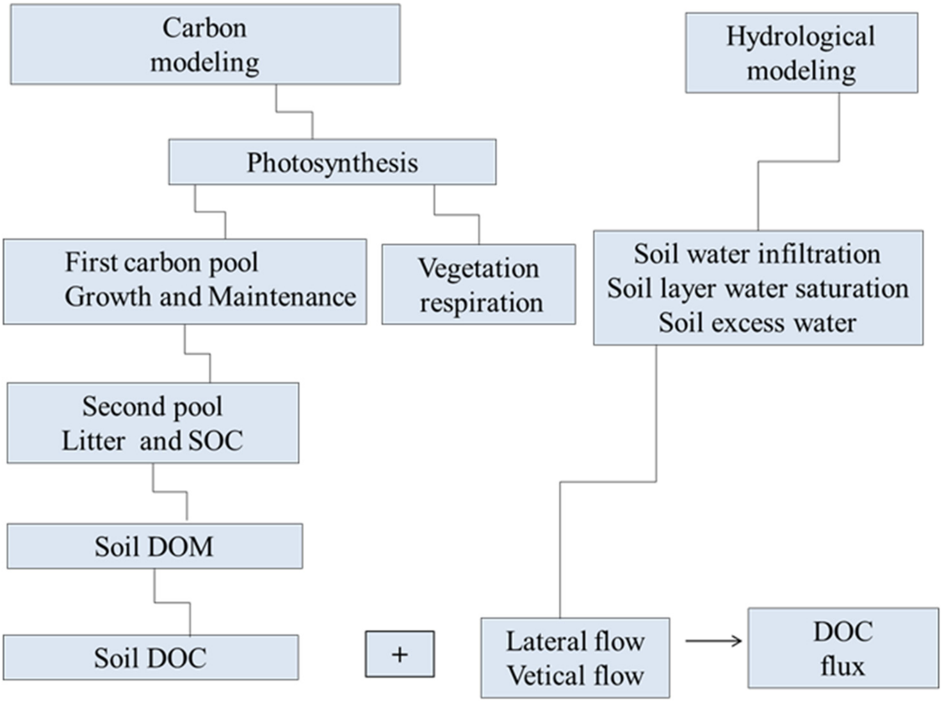

Figure 5 Simplified framework of DOC simulation in the RHESSys model.

A text document called a worldfile was used to reference input maps with landscape, soil and land cover characteristics, and vegetation physiological traits of the study area for RHESSys initialization state variables. Soil physical characteristics and vegetation physiological traits of the study area characteristics were all defined in default files (soil and vegetation default files). Remote sensing and in situ data can both be used as inputs to simulate watershed dynamics using the Regional Hydro-Ecological Simulation System (RHESSys) (Nemani et al., 2009; Tague and Band 2004). A flow table was used to describe the connectivity between the patch objects. Patch objects were created from the 10m DEM, the soil map, and the land use/land cover map. The RHESSys model, through its hydrological models, used this information to model subsurface and overland flow routing. The MT-CLIM sub-model (Running et al., 1987) used topography and climate satiation variables to model the spatial distribution of climate variables over the study area. An ecophysiological model based on BIOME-BGC (Running and Coughlan, 1988; Running and Hunt, 1993) in conjunction with a hillslope hydrology model based on DHSVM (Wigmosta et. al, 1994) was used to estimate carbon, water and nutrient fluxes.

Results and discussion

Impact of LULC variability on DOC within the RRW

Stream DOC, WEOC, pDOC and LDOC decrease from natural forest to cropland sites within the RRW. Our results are consistent with Camino-Serrano et al. (2014) and Were et al. (2015), who both found that natural forests have higher DOC than other types of vegetation due to their higher inputs of detritus to the soils (Eclesia et al., 2012). The higher DOC in the natural forest within the RRW is due to the important accumulation of TOC, from which DOC is mobilized. Within the RRW, Wasige et al. (2014) found higher organic carbon stock in the natural forest compared to other LULC classes. TOC is the raw material from which DOC is produced, and positively affects the rates, extent, and pathways of microbial degradation. This preponderant role of TOC on DOC mobilization was confirmed by results that show TOC to have the highest correlation coefficient (0.60) with WEOC compared to other soil properties (TN, CEC, and Al) whose relationships with WEOC are statistically strong at significance level of 5% within the study area (Figure 6).

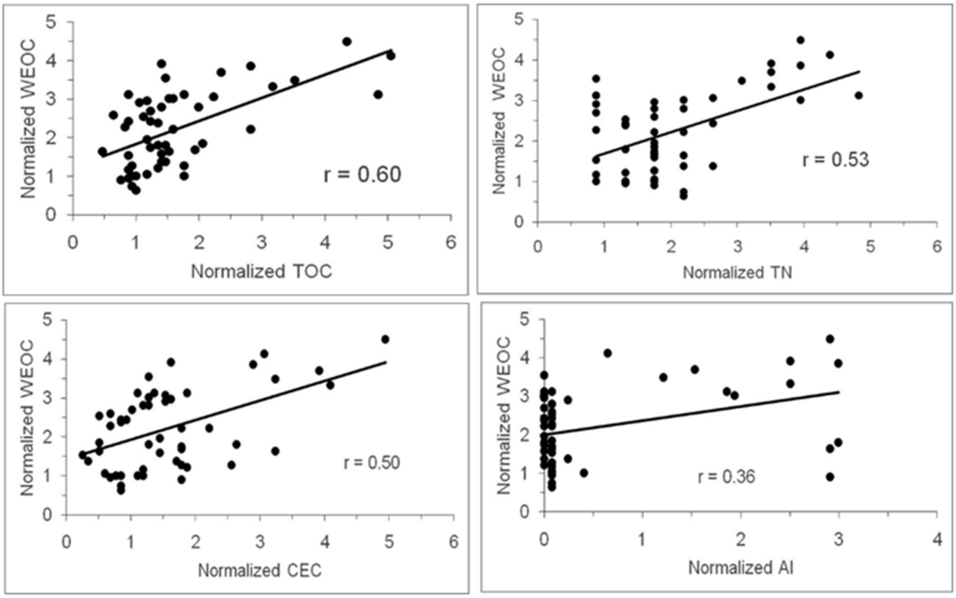

Figure 6 Relationship between normalized soil properties and WEOC and the corresponding correlation coefficients in the RRW. Figure from Paper 2.

The lowest stream DOC, soil WEOC, pDOC and LDOC in cropland sites is explained by the loss of SOM that followed the conversion of the natural forest to croplands. Oslo (1996) indicated that the soil of Rwanda has been farmed since at least 300 A.D. The conversion from forest to agriculture lands decreased soil organic carbon (SOC) stocks via soil structure degradation by increased water erosion rates, and SOC export from fields (Grimaldi et al., 2003; Don et al., 2011). Also, the conversion from natural forest to cropland greatly influenced the characteristics of soil carbon and nitrogen and impacted on the amount and quality of litter input, the litter decomposition rates and the processes of SOM stabilization in soils, and the quantity and quality of soil microorganisms (Soosaar et al., 2011; Zhang et al., 2007).

Impact of climate variability on DOC within the RRW

Antecedent precipitation, rainfall intensity and WEOC within the RRW

High pDOC was observed when the values of the antecedent precipitation index (API) were at their optima and the natural forest showed the highest R2 (Table 3). Additionally, LDOC flux increases with both the rainfall amount (Ra) and mean rainfall intensity (Ri) in the RRW (Figure 8). The effect of API on pDOC is consistent with the results of Wen et al. (2006), Saidy (2013) and Sierra et al., (2015), that all observed an increase in carbon decomposition with increased soil water content. Optimal API causes high soil water content and consequently high diffusion of soil DOC (Taggard et al., 2012). Optimal API represents optimal antecedent wetness that is important for SOM dissolution, microbial activity and DOC lateral and vertical fluxes. A decrease of pDOC after it reaches its optimum can be explained by excess of soil moisture that dilutes microbial enzymes and affects substrate concentration and oxygen diffusion at the enzyme reaction site (Wen at al. 2006) reducing SOM decomposition rate into DOC.

Table 3
Quadratic regression models of percolation water DOC (pDOC) as a function of APIs, their coefficients of determination and squared errors within the RRW. Table adapted from Annexes A-C, Paper 2.

Sites	NAD	Quadratic regression models	R^2	SSR
NF	21	$pDOC=-5E\text{-}04API^2+0.07API+3.72$***	0.17*	137.79**
TP	7	$pDOC=-16E\text{-}04API^2+0.13API+4.21$***	0.14*	165.92**
CL	56	$pDOC=-11E\text{-}04API^2+0.10API+2.10$***	0.12*	224.99**

NAD: number of antecedent days with the highest R^2; NF: Natural forest site; TP: Tea plantation site; CL: Cropland site; pDOC: percolation water DOC; API: antecedent precipitation index of the corresponding number of antecedent days; *: the highest squared R; **: the least SSR; ***: the best quadratic regression model.

Antecedent wetness was found to be negatively correlated with the soil capacity to store rainwater in the RRW (Figure 7). The study showed an inverse relationship between LDOC flux and rainwater soil storage capacity on LDOC in the RRW. This inverse relationship could be associated with soil infiltrability (Eigel and Moore, 1983). As soils store rainwater, the infiltration water and, therefore, LDOC flux decreased. With increased rainfall storage, fine particles moved down in the soil profile to 0.1–0.5 mm depth and accumulated, clogging conducting pores, decreasing infiltration water volume but generating more overland flows (Agassi et al., 1981). When these overland flows were initiated, subsequent raindrop impacts lifted organic carbon particles into the flows and increased the turbulence of these flows, which in turn enhanced the erosive power of overland flows (Bradford et al., 1987). This lift of organic carbon particles into overland flows progressively decreased DOC concentration in infiltration water and therefore LDOC flux. This decrease of LDOC flux is probably exacerbated by high slopes (mean slope = 44.27%) within the RRW.

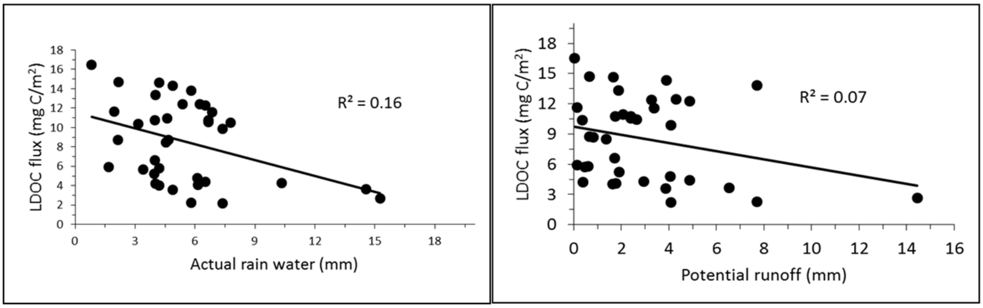

Figure 7 Trend lines between LDOC flux, actual rainfall storage and potential runoff in the RRW. Figure from Paper 3.

Rainfall intensity (Ri) was found to be in a direct relationship with LDOC flux. The direct relationship between LDOC and Ri could be associated with shortened initial breakthrough of percolation and increased percolate volume under high intensity rainfall. The latter has been found to be more effective in detaching soil (Morgan, 1978, Van Dijk, et al., 2002). Under high rainfall intensities, significant portions of rainfall water likely moved through macropores and produced most of the percolation (Ma et al., 2014; Edwards et al., 1992). Also, physical protection of soil organic carbon (SOC) was removed by water erosion and when raindrop-impacted aggregates were broken down, DOC was released. High rainfall intensities can move great amount of DOC and therefore increase LDOC flux.

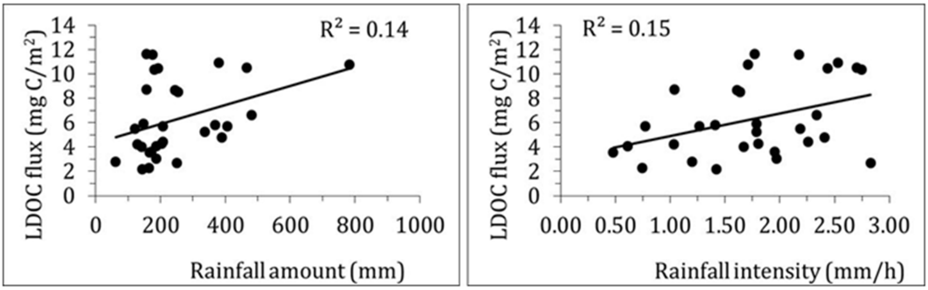

Figure 8 Trend lines between leached DOC (LDOC), rainfall and rainfall intensity in the RRW. Figure from Paper 3.

Mean average temperature and DOC within the RRW

The highest pDOC was observed at the natural forest site with the lowest temperature (13.99^{0}C) and the highest WEOC (0.69g/L) compared to other sites (Tea: 18.54 ^{0}C; 0.42g/L; Farm: 20.33^{0}C and 0.29 g/L respectively). This result can be explained by high SOM that may be intrinsically sensitive to temperature and, therefore, may need low activation energy to initiate the decomposition process and mobilize DOC at the site. The low activation energy effect combines with SOM of high quality at the site to mobilize more DOC as compared to tea plantations and croplands sites. Mean TN at the natural forest site is 0.08%, exactly double the mean TN at tea and cropland sites. High TN favors soil carbon-decomposing microorganisms in terms of amount and quality. These microorganisms, under favorable conditions of temperature and soil moisture, decompose and produce more pDOC in soil solution at the natural forest site as compared to the other sites.

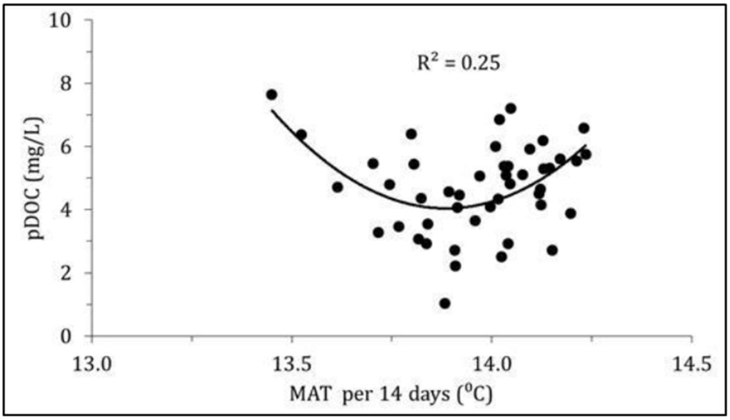

Figure 9 Quadratic trend line of percolation water DOC as a function of MAT in natural forest. Figure from Paper 2.

The convex up relationship between pDOC and MAT (Figure 9) indicating high pDOC at lower temperatures, can be explained by low utilization of soil DOC by microorganisms. The relative decrease of the pDOC with intermediate temperatures can be due to the decline of soil DOC as it was utilized by microorganisms. As the temperatures increase, microorganisms increase their physiological and metabolic processes rates such as enzyme production (A'Bear et al., 2014). The higher pDOC at higher temperatures is then explained by microbial activity on both easily decomposable and/or highly stable organic carbon (A'Bear et al., 2012; Deressa, 2015). pDOC is probably enhanced by increased projected temperature and precipitation in the study area (Paeth et al., 2009). Temperature increase will then positively influence terrestrial organic carbon production, its decomposition to DOC, leaching and, therefore, transport into streams.

Impact of surface, subsurface and groundwater flows on riverine DOC within the RRW

Flow duration curve analysis revealed that the quick flow component is a very important stream flow component within the RRW (Figure 10).

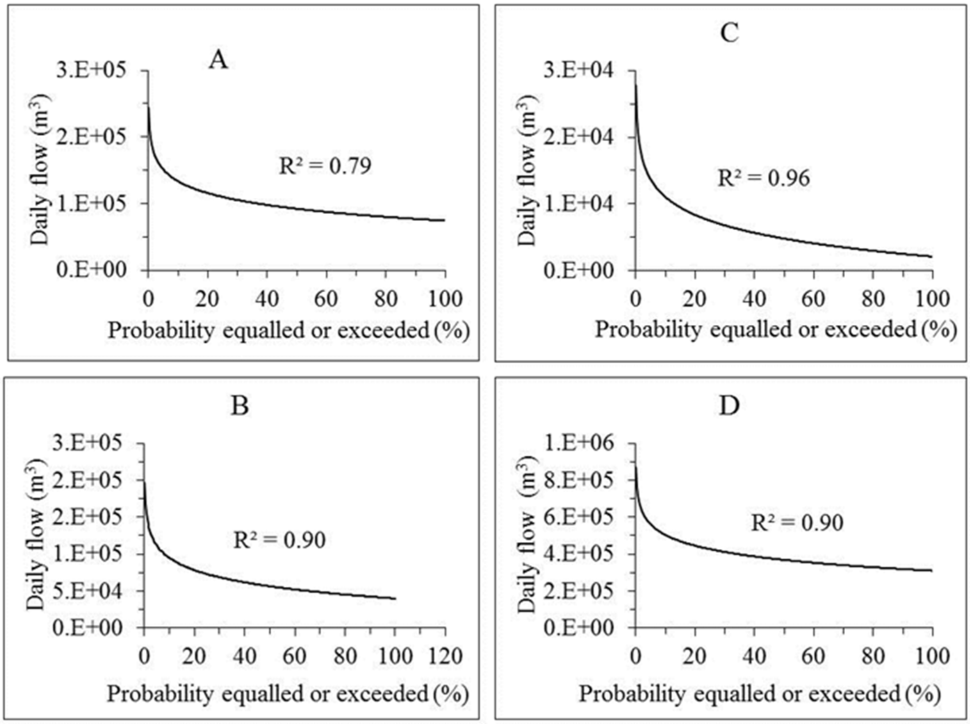

Figure 10 Probability - flow relationships within the RRW for a two-year period from March 2015 to February 2017. Letters A, B, C and D represent the relationship for the stream in natural forest, tea, farm and outlet. Figure from Paper 1.

Our results indicated groundwater contributions ranging from 1.20 to 2.73%, meaning quick flow contributions of 97.27 to 98%. Quick flow includes runoff, interflow and direct precipitation; all of which mobilize and transport DOC into streams and rivers. This result is confirmed by the observation of high riverine DOC during high flow periods (Figure 11) and the low impact of leaching on topsoil carbon. Topsoil LDOC flux to deeper soil layers represents 0.5% of the annual NPP and 0.02% of the soil carbon stock in the RRW. The quick flow role in riverine DOC can be associated with the steeper slopes found in the RRW (mean slopes =44.27%), which favor runoff and not leaching.

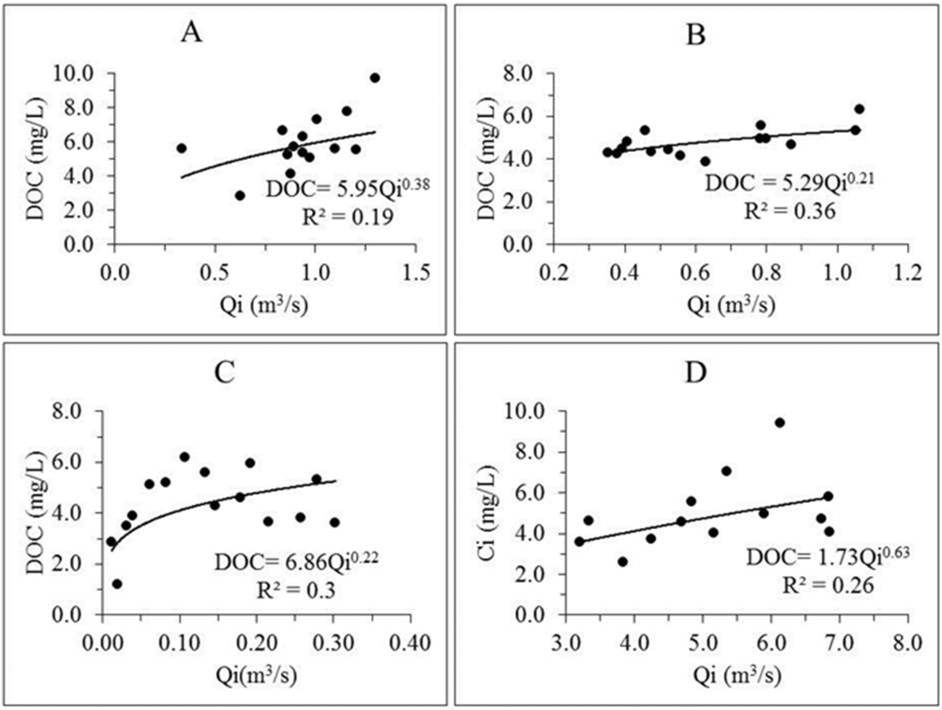

Figure 11 Relationship between stream flow and DOC in the RRW. Letters A, B, C and D correspond to the streams at natural forest, tea, farm and outlet stations. Equations represent the power function of the relationship between discharge and stream DOC at the sites and the corresponding coefficient of determination (R^2). Figure from Paper 1.

Impact of riverine DOC loss on carbon budget in the RRW

DOC riverine loading is 8.44% of the daily NPP of the RRW (Paper 1). This riverine DOC is low compared to its NPP, but is higher than global riverine DOC loss (5%) (Lal et al., 2013). DOC loss through riverine loading is low, but could have direct consequences for the net carbon balance in the watershed, and can constrain its productivity, as long as soil DOC is linked with a soil's capacity to supply nutrients (Sucker and Krause, 2010). Soil DOC loss is associated with the loss of soil nutrients and this may exacerbate soil degradation in the study area and therefore reduce crop production with direct consequences on food security. A drastic decline in soil organic matter can degrade soil structure, lead to erosion, and reduce agricultural productivity (Stocking, 2003). In terms of ecosystem function, DOC riverine loss can cause shifts in primary productivity, decomposition, leaching/discharges, and/or transport in both terrestrial and aquatic ecosystems (Clark et al., 2010).

Streamflow hydroecological modelling

Our results indicated less than satisfactory performance of RHESSys model in simulating stream flow and low explained variation of stream DOC by simulated streamflow in the farm basin (Paper 4). Possible inaccuracies in landscape representation may have come in estimates of climate, soil, vegetation, and landscape attributes and from fine-scale heterogeneity in soil drainage characteristics. Additionally, streamflow calibration does not completely resolve errors in soil parameter estimates (Beven and Freer, 2001). These types of errors in model input data may explain unsatisfactory performance of our implementation of the RHESSys model to simulate stream flow of the farm basin. It may also be that our representation of this landscape simply does not include the significant anthropogenic influences on this landscape that are exerted in terms of cropping and water management practices.

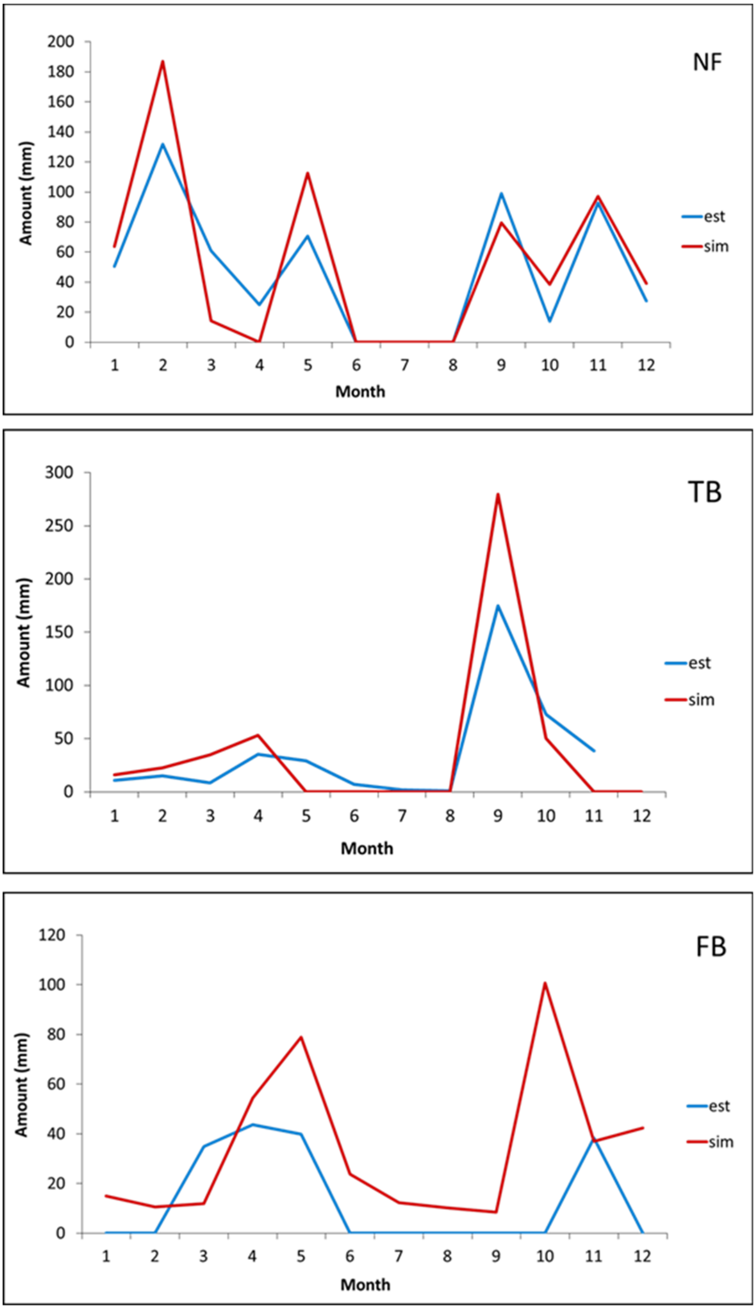

Figure 12 Variation of monthly streamflow within the RRW. Figure parts NF, TB, and FB show the natural forest, tea and farm basins, respectively; “sim” indicates RHESSys simulated streamflow and “obs” indicates simulated Thornthwaite streamflow.

Simulated streamflow and DOC in the natural forest basin

RHESSys simulated streamflow explained 85% of the variance of monthly stream DOC in the natural forest (Figure 5 from Paper 4). The poor prediction of stream DOC by simulated flow data in the farm and tea basins could be due to high variance of stream DOC in these locations, as compared to that found in the natural forest basin. This is likely mainly due to human activities, and their insufficient representation in our simulations. For example, we realized during sampling campaigns that some parts of buffer zone were cultivated. This could have had a significant impact on the export of organic matter in the farm and tea basins, and could only have been effectively simulated and quantified with detailed information about cultivation practices, describing precisely when and how they were applied.

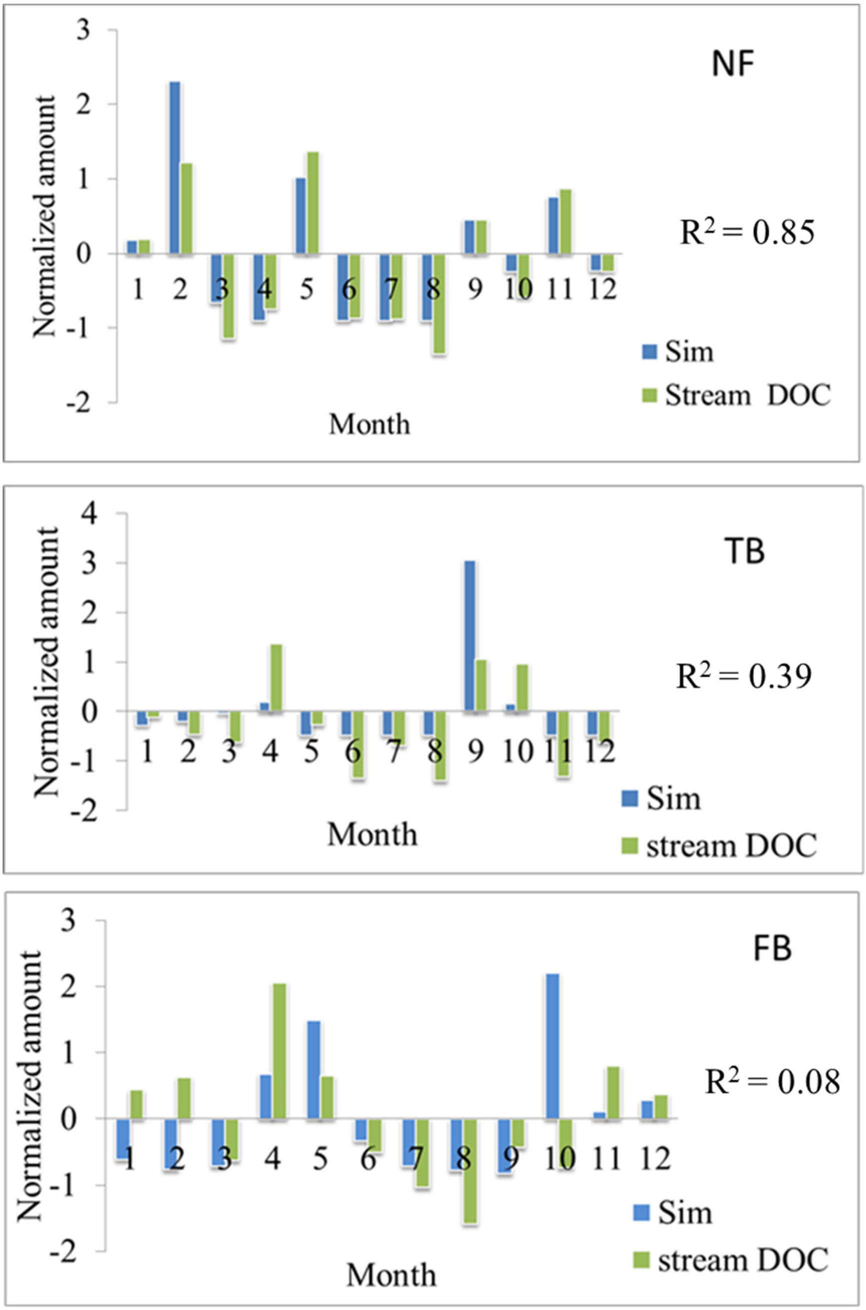

Figure 13 Monthly distribution of RHESSys simulated stream flow and observed stream DOC within the RRW. NF, TB, and FB stand, respectively, for the natural forest, tea, and farm basins.

Conclusion and outlook

This dissertation has investigated the dynamics of DOC in a mixed agriculture and forest watershed, focusing on its mobilization and export. The following are the main conclusions linked to the main aims:

1. Riverine DOC loading from the study watershed is low compared to its NPP, but is higher than global average riverine DOC loss, and may measurably affect the carbon budget in the study area.
2. The land use land cover, through its control on soil total organic carbon (TOC), is the overarching factor explaining soil WEOC dynamics within the study area. In return, TOC can be sufficiently predicted by WEOC in the study watershed. Land use cover change from forest to land crop will decrease soil DOC and, therefore, exacerbate land degradation within the studied watershed.
3. The annual LDOC flux from topsoil was 2% of the net primary productivity (NPP), and LULC was the main controlling factor, with the highest LDOC flux within plantation forest. Land cover change from cropland to plantation forest will increase LDOC within the RRW with implications on groundwater quality.
4. The RHESSys model detected the response of the watershed to climate variability within the natural forest basin and captured the significant monthly variability in streamflow within the basin. This result indicates the potential use of RHESSys to estimate streamflow in forest basin and similar tropical watersheds.
5. Hydrological and stream dissolved organic carbon data for a three-year period in a tropical watershed were produced. The data are useful in water resource management, ecosystem restoration and conservation.

This dissertation has studied DOC mobilization and export using field observations, and statistical and eco-hydrological modelling approaches. The acquired knowledge and data can be used for further research and management of watersheds. For example, most riverine DOC was found to be transported by overland flow. This information is useful for watershed managers, who can choose to enhance existing anti-erosive practices. Some DOC and associated nutrients, such as nitrogen, can leach from soils into adjacent streams (Lal et al., 2013). An excess of DOC and nitrogen has impacts on groundwater quality (Jahangir et al., 2012). To give some insights into the impact of landscape DOC and nitrogen on groundwater quality within the studied watershed or similar watersheds, further research can use our methodology and data. The majority of DOC in terrestrial and aquatic environments is ultimately returned to the atmosphere as CO_2 (Bolan et al., 2011) CH_4. Our results for DOC within different LULC classes can be used in such research on CO_2 and CH_4 dynamics within the study area. Our results can be also used in future research into soil nutrients deletion and metal transport into stream waters, given that DOC is known to act as a key vehicle for the translocation and loss of soil nutrients into waters (Hagedorn et al., 2004). Streamflow simulation was successfully calibrated and validated at the monthly scale in the RRW using the RHESSys model. This result indicates the potential use of RHESSys to estimate hydroecological processes in the forest basin and similar tropical watersheds.

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