

---

# Simulation of DOM fluxes in a seasonal floodplain of the Okavango Delta, Botswana

N. Mladenov<sup>a,\*</sup>, D.M. McKnight<sup>a</sup>, P. Wolski<sup>b</sup>, M. Murray-Hudson<sup>b</sup>

<sup>a</sup> INSTAAR, University of Colorado, 1560 30th Street, 450 UCB, Boulder, CO 80309-0450, United States

<sup>b</sup> Harry Oppenheimer Okavango Research Centre, Private Bag 285, Maun, Botswana

---

## ABSTRACT

In order to examine dissolved organic matter (DOM) fluxes in seasonal wetland systems that expand and contract seasonally, a time-variable model of dissolved organic carbon (DOC) was developed for a seasonal floodplain in the Okavango Delta of Botswana. The model simulates DOC concentrations from March 2001 to November 2002, during which time DOC concentrations varied between 8 and 31 mg C L<sup>-1</sup>. The model uses a continuously stirred tank reactor (CSTR) approach to describe the hydrologic and biogeochemical controls on DOC leached from litter within the floodplain and transported into the floodplain from upstream. In 2002, a fire burned the floodplain and less litter was available for leaching than in 2001. The model was driven by observations of discharge, water temperature, upstream DOC concentrations, and DOC leaching rates from leaching experiments. Leaching experiments with sedges and grasses indicated that on average 23 mg DOC g<sup>-1</sup> were leached during the first day of wetting and 0.6 mg DOC g<sup>-1</sup> d<sup>-1</sup> were continuously leached afterwards. Leaching experiments also showed a decreased amount of DOC released from burned litter and soils than from unburned litter and soils. A two-pool first-order decay model that represents both rapidly (0.14 d<sup>-1</sup> at 22 °C) and slowly (0.045 d<sup>-1</sup>) decaying pools of DOC provided the best representation of observed patterns in DOC concentration in 2001. The decay rate of the first pool decreased by nearly half in 2002, when an estimated 78% of litter was removed by fire.

Upstream DOC transport into the floodplain was the dominant source of DOC (representing approximately 70% and 75% of the DOC input in 2001 and 2002, respectively), followed by DOC leaching from litter and DOC originating from microbial sources. In 2001, decomposition (representing approximately 36% of the DOC loss), outflow to an adjacent floodplain (36%) and infiltration (28%) were the major removal mechanisms for DOM from the study floodplain. The large amount of DOC transported by infiltration implies storage of DOC in the subsurface, which may influence subsurface heterotrophic activity. In light of future climate change anticipated for the region, a scenario using a 2 °C increase in average water temperature and 10% reduction in upstream DOC mass was performed and resulted in significant (11%) reduction in annual DOC mass within the study floodplain.

### Keywords:

DOC  
Model  
CSTR  
Decay  
Leaching  
Degradation  
infiltration  
Floodplain  
Wetland  
Okavango Delta  
Africa  
Fire  
Burning

---

## 1. Introduction

Dissolved organic matter (DOM) plays many roles in aquatic ecosystems, including providing an energy source for heterotrophic microorganisms and a source of nutrients. In

---

\* Corresponding author. Tel.: +1 720 318 1823.  
E-mail address: mladenov@colorado.edu (N. Mladenov).

surface waters with large seasonal changes in flow, the hydrologic cycle dominates organic material fluxes. Junk et al. (1989) showed that flooding events in the Amazon and Mississippi Rivers pulsed DOM and nutrients into the water column. In studies of permanent wetlands, such as the Everglades in Florida, USA, DOM transport was also found to be controlled by hydrologic processes (Moustafa and Hamrick, 2000; Qualls and Richardson, 2003). With respect to seasonal surface waters, studies have mainly examined DOM fluxes in intermittent and ephemeral rivers (Jones et al., 1995; Jacobson et al., 2000). Our understanding of DOM fluxes in seasonal wetlands, in particular, is limited (Qiu et al., 2003). Because seasonal wetlands support diverse biota and can be important sources of potable water, especially in arid regions of the world, understanding the drivers of biogeochemical cycling in these systems is important.

In addition to hydrologic controls on the transport of DOM in seasonal floodplains, the amount of DOM that is introduced to the water column from leaching of the terrestrial compartment (via microbial processing and abiotic release) is also a function of the OM content of the soil, the amount and type of detritus on the soil surface, and temperature (Karlsson et al., 2005). Petersen and Cummins (1974) found that after leaves entered a stream, leaching was responsible for between 10 and 30% of the initial dry mass loss within the first few days. In the case of wetland litter, Pinney et al. (2000) operated wetland microcosms with hydraulic residence times of 1.6–7.4 days and found that 5–8% of the cattail fragments added were leached as dissolved organic carbon (DOC) during that time. O'Connell et al. (2000) described leaching rates for soil, oak stems, and oak leaves and found that soil leached a negligible fraction of DOC relative to leaves.

The mechanisms for DOM degradation include heterotrophic uptake by aerobic and anaerobic bacteria and degradation by UV light. Incubations of DOM derived from algae (Kragh and Sondergaard, 2004), forest vegetation (Kalbitz et al., 2003), Typha wetland plant material (Pinney et al., 2000), and soils (Qualls and Haines, 1992; Kalbitz et al., 2003) revealed the presence of two distinctly different pools of DOM, a labile pool with DOC decay rates as high as  $0.2 \text{ d}^{-1}$  (Kragh and Sondergaard, 2004) and a recalcitrant pool with DOC decay rates up to three orders of magnitude lower than the labile DOM pool (Kalbitz et al., 2003). In addition to the dependence on DOM quality, DOC decay rates are known to increase with increasing temperature (Grieve, 1991).

The combined influences of flushing, leaching, and decay on DOM can be examined by using coupled hydrologic-biogeochemical models to simulate patterns of changing DOC concentrations observed in natural systems. Temporal changes in DOC concentrations have been examined for an alpine stream (Hornberger et al., 1994; Boyer et al., 2000) and in high latitude headwater streams with groundwater and litterfall as major sources of DOC (Karlsson et al., 2006) using a transport model, which included a continuously stirred tank reactor (CSTR) model. In the examination of wetlands, this type of mass balance approach was used by Pinney et al. (2000) to model the leaching and decay of DOC through constructed wetlands receiving lagoon-treated wastewater and by Wang and Mitsch (2000) to model phosphorus dynamics, including inputs from biomass, in constructed wetlands. To the best of

our knowledge, no time-variable model exists that quantifies changes in DOC in ephemeral water bodies. Seasonal wetlands may differ from constructed wetlands or streams in that they expand and contract seasonally, with periods of no flooding that allow for plant growth and senescence. Extensive areal expansion of wetlands is especially important because it influences the amount of floodplain litter available for leaching as well as primary productivity in the system, generally reported on a per area basis.

The Okavango Delta of Botswana (Fig. 1) is a large wetland, consisting of permanently and seasonally flooded zones, the latter of which are representative of seasonal wetlands in arid regions. The Delta is the terminus of the endoreic Okavango River and contains many seasonal floodplains and channels. Both the DOM dynamics and hydrology of the Okavango Delta have been studied extensively. Large scale (Gieske, 1997; McCutley and Elery, 1998; Bauer et al., 2006) and floodplain-specific (Famberg et al., 2006; Wolski and Savenije, 2006) studies provide detailed descriptions of annual flooding and other hydrologic processes occurring in the Okavango Delta. The floodplains and channels of the Seasonal Swamp (Fig. 1) fill annually, when a slow-moving flood inundates the Delta, depositing sediment and transporting dissolved constituents, including DOM, from upstream. Cronberg et al. (1996) performed a detailed spatial characterization of water chemistry in channels and floodplains of the Delta that showed DOC concentrations to be highly variable in seasonally flooded areas. Mladenov et al. (2005) examined temporal variability in DOM sources in a small seasonal floodplain in the Seasonal Swamp and found the highest DOC concentrations occurred during the rising limb of the annual flood.

During the annual flood, DOM is mobilized from aquatic vegetation in the Permanent Swamp and from terrestrial stores within the seasonal floodplains and transported further downstream (Mladenov et al., 2005). Characterization of DOM by absorbance and fluorescence analyses confirmed greater inputs of plant-derived DOM in a seasonal floodplain during the dry season (which coincides with the annual flood) than in the rainy season (Mladenov et al., 2005). The contributions from plant-derived DOM were highest during the rising limb and peak flood periods (typically from June through September) (Mladenov et al., 2005). Murray-Hudson (unpublished) found greater amounts of plant material available for leaching pre-flood ( $1025 \text{ gm}^{-2}$  dead plant material in 2003) than post-flood ( $165 \text{ gm}^{-2}$  of dead material present after the 2003 flood), indicating a large post-flood loss (>80%) of senescent material to free-floating particulate organic matter (POM) and DOM.

During flood recession the DOM pool becomes increasingly dominated by microbial sources, such as algal exudates and bacterial products (Mladenov et al., 2005). The main processes responsible for the removal of DOM are degradation (by bacteria and UV light) and hydrologic processes, which act to move DOM to downstream surface water bodies and into the subsurface. The high permeabilities of predominantly sandy floodplain soils result in a direct hydraulic link between surface water and floodplain groundwater. Further, the high evapotranspirative demand of dryland vegetation induces strong, permanent lateral groundwater flows from floodplains towards drylands, contributing to losses of surface water as the flood moves downstream.

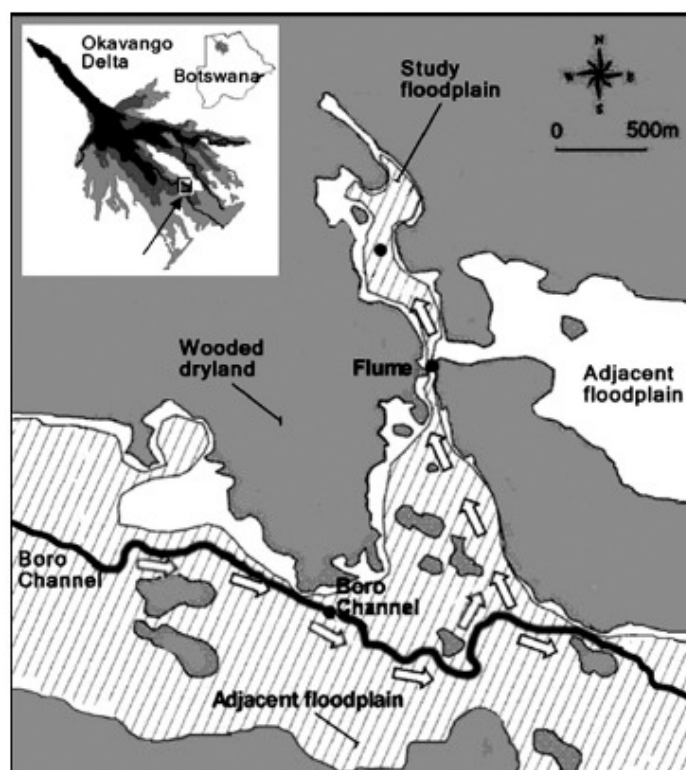


Fig. 1 – Map showing features of the study site, including the Boro channel, flume, study floodplain, and adjacent floodplain which received spillover from the study floodplain in 2001. Hatched lines denote approximate areas of flooding in 2002 and white areas denote approximate areas of flooding in 2001. Inset shows Okavango Delta and Botswana, and the study site is indicated with an arrow.

The dominance of infiltration and lateral transport of surface water with virtual lack of groundwater discharge to surface water in this system allows for a simple representation of floodplain DOM processes (Fig. 2) because groundwater sources of DOM can be neglected. Examination of DOM fluxes in a typical seasonal floodplain of the Okavango Delta is further simplified because the sources of DOM during flooding are generally limited to upstream contributions, leaching of litter from within the floodplain, and autotrophic production. Also, the annual flood arrives during the dry season, when rains are rare, restricting DOM contributions from surface runoff.

The dry season is also a focal period for fire in sub-Saharan Africa, including the Okavango Delta (Heini et al., 2007). Rutz et al. (2004) and Heini et al. (2006) found that burned floodplains of the Okavango Delta experienced a reduction of approximately 78% in dry litter over unburned floodplains. The study floodplain burned in May 2002, and we hypothesize that fire altered the biological and chemical quality of DOM leached from the burned floodplain litter. The decay rates for DOC from burned sources have not been studied. However, it is known that burning can change the structural properties of humic

and fulvic acids in DOC (Fritze et al., 1998) and can produce forms of C that are highly resistant to biological degradation (Gonzalez-Perez et al., 2004). For example, Fritze et al. (1998) showed that DOM extracted from burned humus significantly reduced microbial respiration.

The main objective of this research was to quantify the magnitude and temporal variation of fluxes of DOM into and out of a seasonal wetland in the Okavango Delta. We developed a simple time-variable model (Fig. 2) to represent the dominant hydrologic and biogeochemical controls on DOM in a seasonal floodplain with and without burning. To estimate leaching rates from burned and unburned vegetation in our model, we performed leaching experiments on burned and unburned litter and soil from the Okavango Delta. Then we coupled a hydrologic model (Wolski and Savenije, 2006) with a biogeochemical model of DOC for the study floodplain described above, which incorporates experimentally determined rates of leaching by dominant floodplain plant litter, estimated POM standing stocks, measured autotrophic production in the water column, and measured DOC loadings from upstream. The model was calibrated with observed DOC



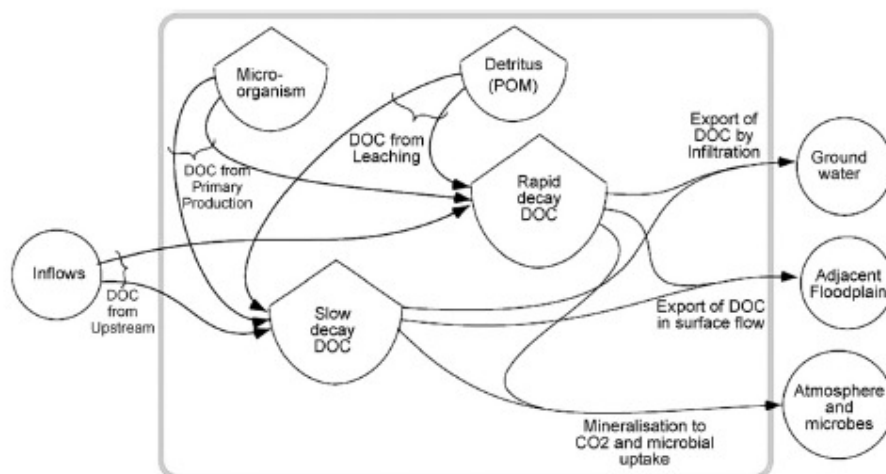


Fig. 2 – Schematic of the floodplain DOC model, showing processes and DOC imports and exports (circles).

concentrations in the study floodplain from March 2001 to November 2002. We conclude that a simple model of DOC leaching and first-order DOC decay, with two DOC pools of differing quality, captured the observed DOC variation over the 2-year period. Model results illustrate the importance of infiltration on DOC removal from the floodplain and of burned litter quality on DOC decay rates.

## 2. Site description

The Okavango Delta is a large, low-gradient wetland in north-western Botswana. The Permanent Swamp region represents about 34% (or 3500 km<sup>2</sup>) of the area of the Okavango Delta (Murray-Hudson et al., 2006) and is permanently flooded and characterized by the sedge, *Cyperus papyrus* and other obligate aquatic plant species. The Seasonal Swamp region represents the remaining 66% (or 6800 km<sup>2</sup>) of the area of the Okavango Delta (Murray-Hudson et al., 2006). An annual flood inundates the Delta during the dry season, from approximately April through September, and it is these floodwaters that supply floodplains of the Seasonal Swamp with most of their water for the year. In addition to the annual flood event, the Delta receives approximately 460 mm year<sup>-1</sup> of rainfall during the rainy season from November to March (Wolski and Savenije, 2006). Evapotranspiration removes approximately 1800 mm year<sup>-1</sup> of water (Wolski and Savenije, 2006). Detailed descriptions of the hydrology of the Okavango Delta are found in Bauer et al. (2006). Water flow during the annual flood is predominantly overland.

### 2.1. Floodplain hydrology in 2001 and 2002

The field research presented here was conducted at a seasonal floodplain, referred to as the “study floodplain,” located in the Seasonal Swamp near the Nxaraga site on the Boro River

(Fig. 1), which is representative of seasonal floodplains in the Delta. It has been a site of ecological monitoring by the Harry Oppenheimer Okavango Research Centre (HOORC) since 1996. With a maximum flooded area of approximately 300,000 m<sup>2</sup> in 2001 and 200,000 m<sup>2</sup> in 2002, the study floodplain has one surface water inflow at the flume (Fig. 1), a small outflow to an adjacent floodplain (that was active only in 2001), and seepage to the groundwater (infiltration). Subsurface flow is from the floodplains toward the neighboring dry lands (termed islands) and is driven by high evapotranspiration by island vegetation. This forms a cone of depression beneath the islands, where solutes become concentrated and groundwater is most saline.

During the modeling period of 2001 and 2002, the flood arrived at the floodplain in the beginning of June. The data shown in Fig. 3 are taken from a hydrologic model of the study floodplain was developed by Wolski and Savenije (2006) that is used to drive the DOC biogeochemical model of this study (see Section 3.3.1). Fig. 3A shows that the water level, inflow rate, and flooded area of the floodplain, peaked in mid-July. Outflow to the adjacent floodplain, which is controlled by a topographic threshold, occurred only during July–November 2001 (Fig. 3A). Inflow to the floodplain displayed different dynamics than water levels. Inflow increased strongly at flood onset and declined rapidly after the flood had reached its peak. This results from inflow being controlled by upstream infiltration and groundwater flow, which decline as the available groundwater storage fills up (Fig. 3B). These patterns can be seen in comparisons of infiltration (modeled) and inflow (measured) rates shown in Fig. 3A and B.

### 2.2. DOM in the study floodplain in 2001 and 2002

As floodwaters spread across the Delta along various flow paths, the water mobilized organic matter from aquatic macrophytes, terrestrial plant litter, and soils, and this plant-derived DOM dominated the DOC pool (Mladenov et al., 2005)

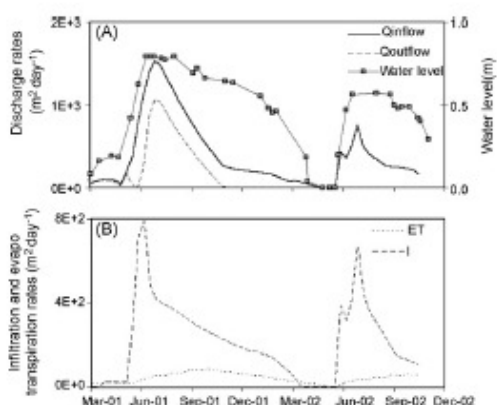


Fig. 3 - Temporal changes in (A) discharge (inflow and outflow) rates and water level and (B) infiltration and evapotranspiration rates from the hydrologic model of Wolski and Savenije (2006). In 2001, high flooding caused spillover into the adjacent floodplain to the east.

and resulted in an increase in DOC concentrations with the rising limb of the flood (Fig. 4A). Analyses of fluorescence, absorbance, and chlorophyll *a* in the study floodplain in 2001 and 2002 (Mladenov et al., 2005) show that DOM derived from aquatic and terrestrial plants dominated the DOM pool, especially during the flood. High specific UV absorbance (SUVA), ranging from 0.02 to 0.03  $L \text{ mg}^{-1}$ , and low fluorescence index (FI) values, ranging from 1.38 to 1.45 (Fig. 4B), during the flood period indicate dominance by plant-derived sources of DOM, in the wetland (Mladenov et al., 2005). Additional contributions from algal and bacterial sources occurred both during and after the flood period. Hoberg et al. (2002) found that, during the flood, primary production (PP) ranged from 0.06 to 0.26  $g \text{ C m}^{-2} \text{ d}^{-1}$  and chlorophyll *a* concentrations ranged from

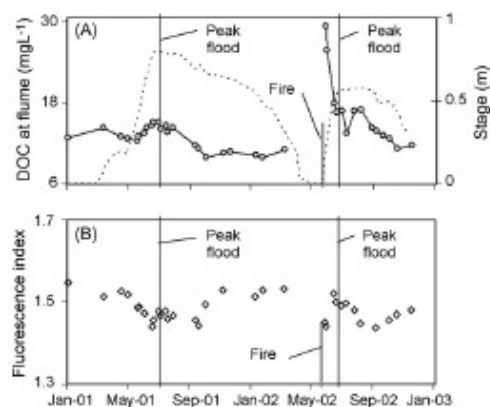


Fig. 4 - Temporal changes in (A) DOC concentrations (circles) and stage (dotted line) and (B) fluorescence index (diamonds) at the flume. Solid lines indicate the time of peak flood and fire (source: Mladenov et al., 2005).

5 to 25  $\mu\text{g L}^{-1}$  in the study floodplain in 1998. Mladenov et al. (2005) found chlorophyll *a* concentrations also ranging from 5 to 20  $\mu\text{g L}^{-1}$  at the flume entrance to the study floodplain during and after the flood of 2001.

Vegetation of the study floodplain was dominated by emergent grasses and sedges, with a small proportion of floating-leaved and submerged aquatics in the topographically lowest portions. The emergent vegetation showed a well-defined zonation with slope (Bonyongo et al., 2000). The sedges *C. articulatus* and *Schoenoplectus corymbosus* dominated the lowest portions. The intermediate zone was dominated by *Panicum repens*, a highly nutritious perennial grass. The zone closest to the dryland-floodplain boundary was a community dominated by the grasses *Setaria sphacelata* and *Eragrostis inamoena*.

### 2.3. Effects of 2002 fire on DOM sources

In early June 2002 large amounts of charred detritus were observed in the water column after the fire and high SUVA values (over 0.03  $L \text{ mg}^{-1}$  measured at 280 nm; Mladenov et al., 2005) were measured in the study floodplain. As UV absorbance is a measure of aromatic carbons in a water sample and fire tends to create aromatic carbon rings, the high SUVA measurements implied that burned organic matter remaining after fire was flushed into the floodplain by floodwaters. The fire affected approximately 270,000  $m^2$  of riverine and floodplain zones upstream of the study floodplain (Heinl et al., 2006), which represent some of the upstream DOC source areas for the study floodplain. As a result, DOC concentrations on 4 June 2002 were approximately 20  $mg \text{ CL}^{-1}$  higher than baseline concentrations throughout 2001 and 2002 and 16  $mg \text{ CL}^{-1}$  higher than the 2001 peak DOC concentrations (Fig. 4A).

## 3. Methods

### 3.1. Field methods

Field sampling techniques and laboratory procedures are described in detail in Mladenov et al. (2005). DOC concentrations of filtered and acidified surface water samples, collected from the study floodplain and flume on March 2001 to November 2002, were measured at the University of Colorado using a Shimadzu TOC 5050 Total Organic Carbon Analyzer.

### 3.2. DOC leaching experiments

Leaching experiments were performed in triplicate on samples of mixed senescent grasses and sedges (*Setaria sphacelata*, *C. articulatus*, *P. repens*, and *E. inamoena*), referred to as "litter" or "POM standing stock," and in duplicate for unburned soil samples (from the top 5 cm). Due to insufficient amounts of burned litter and burned soil samples, no replicate leaching experiments were conducted on those samples. Soil and vegetation samples were collected from the burned study floodplain or a neighboring unburned floodplain in 2002. Samples were dried at 100°C for 48 h and then weighed. Approximately 15 g of dried litter samples were leached with 600 mL of DI water

in covered vessels at room temperature (22°C) for approximately 100 h. To quantify potential leaching from floodplain soils, 350 mL of DI water were added to vessels containing soil and leached for three to 15 days.

Because the aim of our leaching experiments was to determine DOC release under natural conditions, and not to inhibit the amount of DOC released during leaching, no microbial growth inhibitors or bactericides/fungicides were added to the vessels. Baldwin (1999) showed that leachate experiments that used microbial growth inhibitors displayed only abiotic release of DOC and that leachates with no inhibitors had a greater release of DOC.

For each leaching interval, 30–50 mL of leachate was removed from the vessels for DOC analysis and replaced with an equal volume of DI water to reproduce the continuous arrival of new, less organic-rich water into floodplain areas. Resulting DOC concentrations were corrected for this dilution effect by the following equation:

$$C_{\text{corr}} = C_{\text{measured}} \frac{V_{\text{total}} + V_{\text{removed}}}{V_{\text{total}}} \quad (1)$$

where  $C_{\text{corr}}$  is the DOC concentration corrected for dilution,  $C_{\text{measured}}$  the measured DOC concentration before correction,  $V_{\text{total}}$  the total volume of DI water that the plant litter or soil was leached with (600 mL for litter and 350 mL for soil), and  $V_{\text{removed}}$  is the volume that was both removed and replaced as DI water (30–50 mL). Subsequently, DOC concentrations were normalized to both the initial dry mass (DM) of litter and volume of solution to provide a measurement of DOC mass leached ( $\text{mg DOC g}^{-1} \text{ DM}$ ).

### 3.3. Model development

#### 3.3.1. Floodplain hydrology

The floodplain is represented by a CSTR of time-varying volume, with one inlet (surface water inflow at the floodplain inlet), and two outlets (outflow to an adjacent floodplain in 2001, and an outflow via infiltration). The hydrologic model described in Wolski and Savenije (2006) provided values needed to drive the biogeochemical DOC model, namely volume and area of the study floodplain, flow into the adjacent floodplain, and infiltration (Fig. 3). For clarity, the hydrologic model is briefly reviewed here.

The water balance for the floodplain is derived from:

$$\frac{dV}{dt} = Q_{\text{in}} - E - I - Q_{\text{adj}} \quad (2)$$

The hydrologic model of Wolski and Savenije (2006) uses an Euler method to solve Eq. (2) as follows:

$$V_{t+1} = V_t + Q_{\text{in}} dt - E_t dt - I_t dt - Q_{\text{adj}} dt, \quad (3)$$

where  $V_{t+1}$  is the volume ( $\text{m}^3$ ) in the floodplain at time  $t+1$ ,  $V_t$  the volume ( $\text{m}^3$ ) at time  $t$ ,  $Q_{\text{in}}$  the discharge into the floodplain through the flume ( $\text{m}^3 \text{ h}^{-1}$ ),  $E$ , the evaporation rate from flooded area ( $\text{m}^3 \text{ h}^{-1}$ ),  $I$ , the infiltration ( $\text{m}^3 \text{ h}^{-1}$ ), and  $Q_{\text{adj}}$  is the outflow into the adjacent floodplain ( $\text{m}^3 \text{ h}^{-1}$ ).  $Q_{\text{in}}$  and water levels at the flume, located at the floodplain inlet (Fig. 2), were measured weekly for the entire period analyzed here.

Specifically,  $V_t$  was determined by calculating the inundated area ( $A_t$ ) from a GIS digital elevation map of the floodplain at flume water levels corresponding to each time step. The model (Wolski and Savenije, 2006) was calibrated so that the measured inflow to the floodplain was balanced by evaporation and infiltration, and the modeled groundwater behavior in a network of piezometers corresponded to the observed one. Infiltration in the model was dependent on the depth of aeration zone at the flood onset, and subsequently on the lateral groundwater flow from floodplain towards the surrounding drylands. Since the flow into the adjacent floodplain occurring during peak flood of 2001 was not measured, it was calculated as residual flux from measured inflow, evaporation from flooded area and model-derived infiltration.

#### 3.3.2. Time-variable DOC model description

The basic components of the DOC model are illustrated in Fig. 2 and state variables, forcing functions, and parameters found by calibration are listed in Table 1. The model simulations were run from 22 March 2001 (2 months before the start of the 2001 flood period) to 20 November 2002 (when data collection ended). The model has two distinct flood periods, from approximately 17 May to 30 September 2001 and from approximately 29 May to 30 September 2002. A time step  $dt$  of 1 h was used to improve resolution and minimize numerical artifacts. To compare with other studies, rates are reported here as “per day” instead of “per hour.”

Inherent in the CSTR model is the assumption that the floodplain is a completely mixed reactor with DOC concentrations consistent throughout. Yet Mladenov (2004) observed that DOC concentrations at the floodplain edge and center varied by as much as  $2 \text{ mg L}^{-1}$ , indicating that the system is not a truly mixed reactor. Nevertheless, this assumption is necessary for model simplification.

The basic mass balance equations used to calculate change in the amount of DOC in the floodplain,  $dM$ , during the time interval  $dt$  are given below

$$dM = W_{\text{in}} + W_{\text{cont}} + W_{\text{inst}} + W_{\text{pp}} - W_{\text{f}} - W_{\text{adj}} - W_{\text{dec}} \quad (4)$$

$$\frac{dM}{dt} = c_{\text{in}} Q_{\text{in}} + M_{\text{cont}} A + M_{\text{inst}} dA + M_{\text{pp}} A - d - c Q_{\text{adj}} - \lambda_{\text{DOC}} CV, \quad (5)$$

and terms are defined as follows:

- $W_{\text{in}}$  (g), inflowing DOC from upstream—calculated as the product of DOC concentration measured at the flume,  $c_{\text{in}}$  ( $\text{g m}^{-3}$ ), flow rate measured at the flume,  $Q_{\text{in}}$  ( $\text{m}^3 \text{ d}^{-1}$ ), and time,  $t$ .
- $W_{\text{cont}}$  (g), DOC from continuous leaching of detritus—calculated as the product of the experimentally determined continuous flux of DOC from detritus,  $M_{\text{cont}}$  ( $\text{g d}^{-1} \text{ m}^{-2}$ ), and floodplain area,  $A$  ( $\text{m}^2$ ) from Wolski and Savenije (2006), and time,  $t$ .
- $W_{\text{inst}}$  (g), DOC from instantaneous leaching of detritus—calculated as the product of the experimentally determined instantaneous flux of DOC from detritus,  $M_{\text{inst}}$  ( $\text{g d}^{-1} \text{ m}^{-2}$ ), the newly wetted floodplain area,  $dA$  ( $\text{m}^2$ ), and time,  $t$ .



**Table 1 - State variables, forcing functions and parameters used in floodplain DOC model**

State variables, forcing functions and parameters	Units	Source	Value
<b>State variables</b>			
POM, areal POM standing stock	g DM m <sup>-2</sup>	Initial value estimated from field measurements	1025 at start of each flood season
W <sub>inst.</sub> , DOC mass instantaneously released from POC	g DM	Described in Section 3.3.2	Varies
W <sub>cont.</sub> , DOC mass continuously released from POC	g DM	Described in Section 3.3.2	Varies
W <sub>microb.</sub> , DOC from microbial sources	g DM	Described in Section 3.3.2	Varies
<b>Forcing functions</b>			
Q <sub>f</sub> , discharge at flume	m <sup>3</sup> d <sup>-1</sup>	Wolski and Savenije, 2006	1432 at t = 0
Q <sub>adj.</sub> , export to adjacent floodplain	m <sup>3</sup> d <sup>-1</sup>	Wolski and Savenije (2006)	Varies
Q <sub>inf.</sub> , export via infiltration	m <sup>3</sup> d <sup>-1</sup>	Wolski and Savenije (2006)	Varies
T, water temperature	°C	Measured in the field	23.7 at t = 0
C <sub>in.</sub> , DOC concentration at flume	g m <sup>-3</sup>	Measured in the field	14.8 at t = 0
<b>Parameters</b>			
A <sub>f</sub> , area of floodplain	m <sup>2</sup>	Wolski and Savenije (2006)	Varies
V <sub>f</sub> , volume of floodplain	m <sup>3</sup>	Wolski and Savenije (2006)	11807 at t = 0
C <sub>f</sub> , floodplain DOC concentration	g m <sup>-3</sup>	Measured in the field	14.8 at t = 0
λ <sub>POM</sub> , decay rate of POM	d <sup>-1</sup>	Found by calibration in year 1	0.055
L <sub>inst.</sub> , instantaneous rate of DOC release from POC	g C g <sup>-1</sup> DM d <sup>-1</sup>	Experimentally derived	0.023
L <sub>cont.</sub> , continuous rate of DOC release from POC	g C g <sup>-1</sup> DM d <sup>-1</sup>	Experimentally derived	0.0006
m <sub>microb.</sub> , continuous areal flux of DOC microbial mass	g m <sup>-2</sup> d <sup>-1</sup>	Estimated from field measurements (Hoberg et al., 2002)	0.16
λ <sub>DOC1</sub> , decay rate of DOC pool 1	d <sup>-1</sup>	Found by calibration in year 1	0.14
λ <sub>DOC2</sub> , decay rate of DOC pool 2	d <sup>-1</sup>	Found by calibration in year 1	0.045
λ <sub>DOC1</sub> , decay rate of DOC pool 1 during a fire year	d <sup>-1</sup>	Found by calibration in year 2	0.085
λ <sub>DOC2</sub> , decay rate of DOC pool 2 during a fire year	d <sup>-1</sup>	Found by calibration in year 2	0.067

- W<sub>pp</sub> (g), DOC from primary production—calculated as the product of primary productivity (from the literature), M<sub>pp</sub> (g d<sup>-1</sup> m<sup>-2</sup>), floodplain area, A (m<sup>2</sup>) from Wolski and Savenije (2006), and time, t.
- W<sub>adj</sub> (g), export of DOC to the adjacent floodplain—calculated as the product of DOC concentration in the floodplain, c (g m<sup>-3</sup>), model-derived outflow flow rate, Q<sub>adj</sub> (m<sup>3</sup> d<sup>-1</sup>) from Wolski and Savenije (2006), and time, t.
- W<sub>f</sub> (g), export of DOC by infiltration—calculated as the product of DOC concentration in the floodplain, c (g m<sup>-3</sup>), model-derived infiltration rate, I (m<sup>3</sup> d<sup>-1</sup>) from Wolski and Savenije (2006), and time, t.
- W<sub>dec</sub> (g), loss of DOC from decomposition—calculated as the product of DOC concentration in the floodplain, c (g m<sup>-3</sup>), measured floodplain volume, V (m<sup>3</sup>) from Wolski and Savenije (2006), first-order DOC decay rate, λ<sub>DOC</sub> (d<sup>-1</sup>), and time, t.

The decay rate of DOC (λ<sub>DOC</sub>) was adjusted according to water temperatures recorded in the floodplain from March 2001 to December 2002, according to the following expression (after Chapra, 1997, for BOD decomposition):

$$\lambda_{DOC} = 1.047^{T-T_r} \lambda_r \tag{6}$$

where T is the water temperature and λ<sub>r</sub> the decay rate at room temperature, T<sub>r</sub>, or 22°C. It was assumed that the decay rate encompasses degradation from microbial activity and UV light. Loss of DOC to coagulation was not considered here.

This study did not determine DOC decomposition experimentally. Instead, decay rates from the literature were used for the initial run and then optimized during subsequent stages of model calibration (see Section 3.3.4).

An Euler's forward difference approach was used to calculate floodplain DOC mass in each time step, according to the following equation:

$$M_{t+1} = c_t V_t + c_{in} Q_{in} \Delta t + M_{cont} \Delta t + M_{inst} (A_{t+1} - A_t) \Delta t + M_{pp} \Delta t - c_t \Delta t - c_t Q_{adj} \Delta t - \lambda_{DOC} c_t V_t \Delta t \tag{7}$$

where the initial concentration c<sub>t</sub> and initial volume V<sub>t</sub> were the average DOC concentration in the floodplain and measured floodplain volume on 22 March 2001, respectively (Table 1). The concentration in subsequent time steps, c<sub>t+1</sub>, is represented by dividing M<sub>t+1</sub> from Eq. (7) by V<sub>t+1</sub> (Wolski and Savenije, 2006).

The continuous flux of DOC from detritus, M<sub>cont</sub>, is given by

$$M_{cont} = L_{cont} POM \tag{8}$$

where L<sub>cont</sub> is the continuous leaching rate (g DOC g<sup>-1</sup> POM d<sup>-1</sup>) determined from our leaching experiment and POM is the empirically measured areal dry mass content (g dry mass m<sup>-2</sup>) of soil or vegetation. Based upon field observations, each square meter of floodplain was estimated to have approximately 1025 g of litter prior to flood (Murray-Everson, unpublished; Table 1), and this value represents POM at the start of the flood period.

The instantaneous flux of DOC from detritus,  $M_{inst}$ , is given by

$$M_{inst} = L_{inst}POM, \quad (9)$$

where  $L_{inst}$  is the instantaneous leaching rate ( $\text{g DOC g}^{-1} \text{POM d}^{-1}$ ) determined from our leaching experiment. Whereas  $M_{inst}$  contributes to the equation only in the first time step during which a parcel of land becomes wetted,  $M_{cont}$  is continuously leached into solution while the floodplain area remains inundated.

Murray-Hudson (unpublished) measured that  $1025 \text{ g POM m}^{-2}$  was available in the study floodplain prior to flood and that approximately 20% of the POM standing stock remained in the floodplain after flood. The decomposition of litter by leaching, invertebrate activity, and microbial decomposition ( $\lambda_{POM}$ ) was assumed to take the form of first order exponential decay as follows:

$$\lambda_{POM}(^{\circ}\text{C}) = A_0 e^{kT}. \quad (10)$$

The value of the POM decay rate,  $k$  (0.148) was taken from Richardson et al. (2004) for leaf decomposition in a temperate rainforest stream. The decay coefficient,  $A_0$ , was calibrated so that the amount of POC remaining the floodplain was 20% of the initial  $1025 \text{ g POM m}^{-2}$  by 30 September 2001 (Fig. 6). Because of a lack of data on coarse, fine, and ultra-fine particulate matter, POM was not partitioned into its size fractions. POM contributions from upstream (as inputs of suspended particles) were also not known and were assumed to be negligible.

### 3.3.3. Sources of DOC for model

Sources of DOM were affected by flood and non-flood periods and by floodplain burning. During the 2002 flood and post-flood periods, the average POM standing stock was reduced because the study floodplain experienced burning prior to the flood (Fig. 6). A 78% reduction in available litter was applied to the amount of available POM standing stock from 29 May to 20 November 2002 because Heintz et al. (2006) and Rutz et al. (2004) found that burned floodplains experienced a 78% reduction in dry litter over unburned floodplains.

In addition to upstream DOM sources and instantaneous and continuous litter leaching sources, the total microbial contribution to the DOM pool,  $m_{microb}$ , was taken to be the net primary productivity (PP) rate for the study floodplain, or  $0.16 \text{ g d}^{-1} \text{ m}^{-2}$  (Hoberg et al., 2002) (Table 1). Although PP is likely to vary seasonally in a system such as this, long-term measurements of PP were not available and the PP rate was assumed to be constant under all floodplain conditions (fire, flood) and seasons. Also, DOM is an important, if not dominant, energy source for heterotrophic bacteria and, therefore, bacterial DOM sources are also likely to vary seasonally. However, the rates of DOM uptake were not measured and not included as feedbacks to the model.

Some amount of DOM may derive from wet and dry atmospheric deposition, potentially generated by fires elsewhere in the region, but deposition measurements were not available for this study and this source was not included.

### 3.3.4. Treatment of DOC decomposition

Because the decomposition of DOC by microbes and UV light was not measured, the DOC model was developed in three stages, with each subsequent stage providing more information about DOC decomposition for the system. First, because the wetland environment of this study is similar to that studied by Pinney et al. (2000), we used their average decomposition rate of  $0.067 \text{ d}^{-1}$  for DOC from the wetland plant, *Typha capensis* as a starting point for running the model (Table 1). In order to obtain a simulation that was a better match with the observed DOC data, the decay rate was optimized in subsequent stages of the model using a solver (with a maximum run time of 1000s and a maximum of 1000 iterations). This solver was used to minimize the root mean squared error (RMSE) between observed and simulated DOC concentrations for the full length of the model (from March 2001 to December 2002).

In the second stage, the DOC decay rate was calibrated in both years to optimize DOC concentrations by minimizing the RMSE for each year. In Stage 3, a two-pool DOC model, as described in Qualls and Haines (1992), was tested to see if the RMSE could be further minimized. Also fluorescence data measured in Mladenov et al. (2005) indicated differences in DOM quality before and after flooding that support the presence of two different pools of DOC. Lower fluorescence index values and higher DOC concentrations measured during the flood (Fig. 4A) indicate that fresh plant litter was flushed into the floodplain during flood. Therefore, flood periods may contain DOC of higher nutritional value for heterotrophs and may be represented with a rapidly decaying pool of DOC, while the non-flood periods may be better described by a slowly decaying DOC pool (Fig. 5). In the two-pool model of Stage 3, we solved for two decay rates that minimized the RMSE between modeled and measured DOC. Because the transition in dominance from pool 1 (dominant during the flood period) to pool 2 (dominant during the non-flood period) is not expected to be abrupt, we used exponential increase and decrease to transition between pools after the flood period (Fig. 5). At all times both pools sum to 100% and Eq. (7) can be written as

$$\begin{aligned} M_{t+1} = & c_t V_t + c_{in} Q_{in} dt + M_{cont} A_t dt + M_{inst}(A_{t+1} - A_t) dt \\ & + M_{pp} A_t dt - c_t V_t dt - c_t Q_{adj} dt \\ & - (\lambda_{DOC1} c_t V_t dt + \lambda_{DOC2} c_t V_t dt). \end{aligned} \quad (11)$$

When the floodplain was dry (during May 2002), there was no DOC in the water column and, therefore, no decay. After the arrival of new floodwater in June 2002, the rapidly decaying pool was assumed to dominate (Fig. 5).

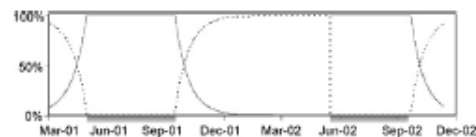


Fig. 5 – Distribution of two pools of DOC. Rapidly decaying pool dominates during flood periods and slowly decaying pool dominates after flood. Both pools sum to 100%.



## 4. Results

### 4.1. DOC leaching from vegetation and soils

During leaching experiments, the highest release of DOC occurred during the first 24 h (Fig. 6A) with 2–3% of the initial C instantaneously leached or “pulsed” as DOC (Table 3). This rapid release was followed by a slower continuous release of DOC (Fig. 6A). Based on initial and final measurements from the burned litter leaching experiment, we found that leaching from unburned litter was slightly greater than from burned litter after 4 days (Fig. 6A). Leaching rates of DOC from unburned soil were also greater than from burned soil (Fig. 6B). The continuous DOC leaching rate for unburned soil was three orders of magnitude lower than that for unburned plant litter (Fig. 6B).

For the time-variable DOC model, we partitioned the rates of leaching into the portion leached in the first day, or  $L_{inst}$ , and the portion leached continuously while the litter was inundated,  $L_{cont}$  (Table 1). After the initial pulse, DOC concentrations increased logarithmically rather than linearly, possibly due to some microbial activity in the leachate. A first-order exponential fit of the data produced a leaching rate ( $7 \times 10^{-5} s^{-1}$ ) that was approximately double that determined in a study by O’Connell et al. (2000) for leached leaves ( $3 \times 10^{-5} s^{-1}$ ). Because a linear rate was employed in the DOC model, we evaluated the data using a linear relationship through the points to obtain  $L_{cont}$  (Fig. 6A). The DOC leach-

ing rate from burned litter could not be determined because of limited temporal data from the experiment (i.e. only initial and final DOC concentrations were measured). Therefore, the model utilized the same leaching rate for burned litter as for unburned litter. Soil leaching was excluded from the model because the rates were much lower than from litter leaching.

### 4.2. Dissolved organic carbon fluxes in 2001 and 2002

In the first stage of model development using a first-order decay rate from Pinney et al. (2000), DOC concentrations during flood were substantially overpredicted, producing a RMSE of modeled to observed data of 4.97 in 2001 and 2.54 in 2002. Model calibration to observed data in Stage 2 generated higher first-order decay rates of  $0.081 d^{-1}$  for 2001 and  $0.082 d^{-1}$  for 2002 (Fig. 8A). This iteration of the model produced much lower RMSE values for 2001 (2.40) and 2002 (0.86; Fig. 8A). In the two-pool model of Stage 3, model calibration resulted in a more rapid decay rate for pool 1 ( $0.14 d^{-1}$ ) in 2001 and similar decay rates for pool 2 in 2001 and 2002 (Fig. 8B). In 2002, the decay rate of pool 1 ( $0.085 d^{-1}$ ) was much lower than in 2001. The use of two pools significantly reduced the RMSE in 2001 from 2.40 to 0.82 (Fig. 8B), which is within 10% of the DOC concentrations measured during the full simulation.

To compare results between 2001 and 2002, we restrict calculations of total mass and % of DOC budget in Table 2 to similar periods for each year, namely from the first day of flood to the last day of model simulation (17 May–20 November 2001 and 28 May–20 November 2002). A plot of DOC sources from the final stage of model development (Fig. 9A) shows that DOC contributions from upstream, entering the floodplain via the flume, were the dominant source of DOC to the floodplain during the flood period, representing 70% in 2001 and 75% in 2002 (Table 2). While the relative contribution of DOC from upstream sources is slightly greater in 2002 than in 2001, the inflowing mass of DOC in 2002 is more than twice as low in 2002 than in 2001 (Table 2). DOC from leaching of plant litter was more significant in 2001 than after the floodplain burned in 2002. The amount of DOC pulsed in the first day of wetting was generally two orders of magnitude smaller than the diffuse leaching (Table 2). In 2002, DOC from microbial sources represented a greater proportion of total DOC inputs (Table 2). Microbial sources of DOC were also slightly higher than contributions from litter within the floodplain during non-flood periods (Fig. 9A).

The amount of DOC lost through decomposition processes and via outflow to the adjacent floodplain represented the greatest sinks of carbon in 2001 (Table 2). In 2002, the volume of the study floodplain was not enough to overflow into the adjacent floodplain and infiltration dominated DOC outputs, transporting large amounts of DOM into the subsurface (Table 2). The peak outflow loss lagged the peak infiltrative loss by approximately one month (Fig. 9B).

### 4.3. Sensitivity analyses and scenarios

In order to determine the sensitivity of the model to changes in model parameters, a sensitivity analysis was performed by adjusting one of the main state variables, forcing functions, or parameters, while keeping all other parameters constant. An

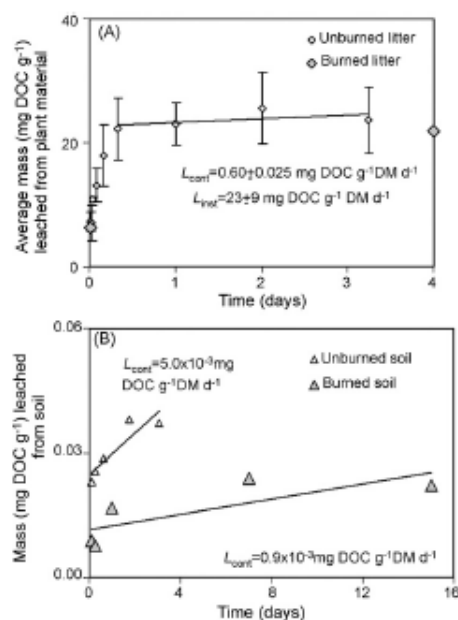


Fig. 6 – DOC mass leached from (A) unburned and burned litter (mixed sedges and grasses) and (B) unburned and burned soils in laboratory leaching experiments. Only samples from initial (15 min) and final (4 days) leaching were available for the burned litter experiment.

**Table 2 – Contribution of input and output processes to total DOC budget in each year**

Input/output processes	Percentage of DOC budget		Total DOC mass (kg C)		Areal DOC mass (g m <sup>-2</sup> d <sup>-1</sup> )
	2001	2002	2001	2002	
<b>DOC inputs</b>					
$W_{in}$ , inflow at flume	70	75	48,908	20,900	–
$W_{inst}$ , instantaneous leaching of floodplain litter	0.3	0.7	195	196	23
$W_{cont}$ , continuous leaching of floodplain litter	19	7	13,552	1,979	0.62
$W_{microb}$ , microbial production	11	17	7,557	4,755	0.16
Total DOC inputs	100	100	70,212	27,830	–
<b>DOC outputs</b>					
$W_{inf}$ , infiltration	28	62	20,158	17,686	–
$W_{dec}$ , decay	36	38	25,293	10,951	–
$W_{adj}$ , outflow to adjacent floodplain	36	0	25,285	0	–
Total DOC outputs	100	100	70,736	28,637	–

Periods examined were 16 May 2001 (first day of flood) to 20 November 2001 and 28 May 2002 (first day of flood) to 20 November 2002. Areal DOC mass values for  $W_{inst}$  and  $W_{cont}$  given at start of flood season, when maximum CPOM is available (1025 g m<sup>-2</sup>). Other values are not reported on a per area basis (shown with a dash).

**Table 3 – Sensitivity analysis of a ±10% change in state variable, forcing function, or parameter values**

State variable/forcing function/parameter	Original value in Stage 3	Percentage change in RMSE after value changed by ±10%
$\lambda_{DOC1}$ 2001 (d <sup>-1</sup> )	0.18	5–6 <sup>a</sup>
$\lambda_{DOC2}$ 2001 (d <sup>-1</sup> )	0.08	4–6 <sup>a</sup>
$\lambda_{DOC1}$ in 2002 (d <sup>-1</sup> )	0.09	8–10 <sup>a</sup>
$\lambda_{DOC2}$ in 2002 (d <sup>-1</sup> )	0.09	1
T (°C) <sup>b</sup>	Range from 14 to 26	20–23
$L_{inst}$ (g C g <sup>-1</sup> CPOM d <sup>-1</sup> )	0.023	0
$L_{cont}$ (g C g <sup>-1</sup> CPOM d <sup>-1</sup> )	0.0016	0–7
$m_{microb}$ (g m <sup>-2</sup> d <sup>-1</sup> )	0.16	1–7
$M_{in}$ , DOC mass loading at flume (g C d <sup>-1</sup> )	Varies	49–57
POM (g C m <sup>-2</sup> )	1025	0–7
$A_{dec}$ , decay coefficient of POM (d <sup>-1</sup> )	20	0–2
Amount of POM standing stock remaining after fire (%)	22	0

<sup>a</sup> Change in RMSE caused by a 10% decrease in values.

<sup>b</sup> The 10% increase and decrease were applied to temperatures at each time step.

adjustment of ±10% was applied to each parameter and the resulting change in RMSE was recorded (Table 3). Results of the sensitivity analysis showed that the model was most sensitive to changes in DOC mass from upstream, with a change of ±10% increasing the RMSE by 49–57%. A 10% decrease in DOC mass loading from upstream ( $m_{in}$ ) resulted in a reduction of between 5 and 7% of total DOC mass per year. The model was also sensitive to water temperature, with a change of ±10% increasing the RMSE by more than 20% (Table 3). A 10% increase in water temperatures resulted in greater DOC decomposition and a 4% decrease in total DOC mass per year. A scenario run with both a 10% increase in temperatures and a 10% decrease in DOC mass loading from upstream resulted in an 11% decrease in total DOC mass in the study floodplain in 2001. The model was least sensitive to changes in decay of pool 2 in 2002, instantaneous leaching, the POM decay coefficient, and the amount of POM standing stock after fire (Table 3).

## 5. Discussion

### 5.1. DOC mass flux due to leaching

Our findings of an initial “pulse” of DOC, followed by continuous leaching of DOC from litter is consistent with the results of Axmanova and Rulik (2005), who showed that DOC release from catkins of alder was highest in the first 2 days of decomposition, with approximately 11% of the initial C leached as DOC. Our pulsed DOC rates for vegetation (0.023 g OC g<sup>-1</sup> dry mass (DM)) were slightly below the range of the O’Connell et al. (2000), where the maximum amount of DOC leached from leaves was 0.045–0.084 g OC g<sup>-1</sup> DM. At an average rate of 0.6 mg DOC g<sup>-1</sup> DM d<sup>-1</sup>, the continuous DOC leaching rate from mixed grasses and sedges in this study was consistent with the rates found for DOC release from leaves, which

ranged from 0.26 to 2.16 mgDOC g<sup>-1</sup>DM d<sup>-1</sup> (O'Connell et al., 2000).

Instantaneous and continuous DOC rates from the soil leaching experiments (Table 1) were also consistent with those of O'Connell et al. (2000), who found that soil leached a negligible fraction of DOC relative to organic matter in leaf, bark, or twig litter. These results are also a function of the limited importance of soil porewaters in this low-gradient, infiltration-dominated floodplain. The study floodplain is a "losing" system and our leaching experiments were designed to reflect this condition. In contrast to our results of negligible soil DOC contributions, studies of rivers that drain soils and receive significant discharge from groundwater (Doyer et al., 1997; Karlsson et al., 2006) show greater DOC contributions from soils.

## 5.2. Dissolved organic carbon fluxes

By simulating DOC concentrations in a seasonal floodplain, this model provides a new understanding of the dominant processes for organic matter input and removal in wetlands that expand and contract over time. This model advances the approaches used in other DOM models, such as the model of DOC decay in wetland microcosms with different hydraulic residence times (Finney et al., 2000), by focusing on a natural seasonal wetland and using a time-variable scope. Karlsson et al. (2006) used a similar, but more detailed approach in their study of total OM (DOM, particulate organic matter (POM), and fine particulate organic matter (FPOM)) in headwater streams, but were additionally equipped with a year of data for model validation.

One of the new approaches of this study that has not been applied in the other modeling studies mentioned above is the utilization of two differently decaying pools of DOC in simulating DOC fluxes. Our simulations demonstrated that a two-pool model provided the best representation of observed patterns in DOC concentration in the study floodplain. The good fit of a two-pool model is consistent with the seasonality of the study floodplain and the potential formation of more recalcitrant DOM over time. Calibration of decay rates (so that the lowest RMSE was produced) assigned the faster decaying pool to the flood season. This is expected because first-order decay is a function of the DOC mass in the system, and, therefore, a higher decay rate occurs when there is a larger concentration of DOC mass. It is also consistent with the assumption that labile portions of the leached DOM and DOM from upstream and microbial sources are consumed preferentially, leaving behind more recalcitrant DOM towards the end of the flood period and in stagnant water after the flood period. Simulations using two pools of DOC also may be worthwhile in studies of DOM decomposition in lotic systems, where seasonal changes in DOM quality may be a function of seasonal changes in DOC sources, for example from groundwater flow to litterfall (as in Karlsson et al., 2006).

In general, the calibrated first-order decay rate of the rapidly decaying pool of DOC in 2001 (0.14 d<sup>-1</sup> at 22 °C) is well within the range observed for labile DOC pools in other studies (0.04–0.07 d<sup>-1</sup> at 22–24 °C from Qualls and Haines, 1992; 0.046–0.067 d<sup>-1</sup> from Pinney et al., 2000; 0.05–0.26 d<sup>-1</sup> at 23 °C

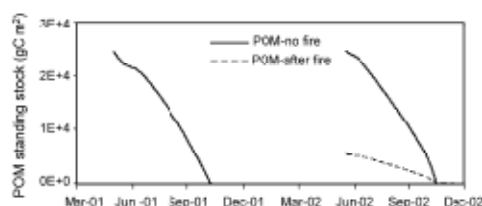


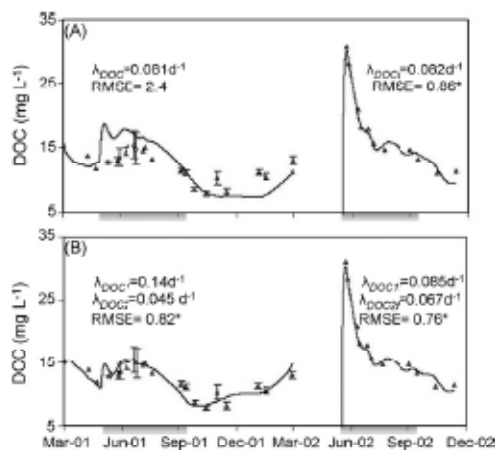
Fig. 7 – Temporal variability in POM standing stock per area. Dashed line shows POM standing stock reduced to 22% of original values due to fire. Only sources from within the floodplain are included (upstream POM inputs not known).

from Strauss and Lamberti, 2002; 0.1–0.31 d<sup>-1</sup> at 23 °C from Kalbitz et al., 2003). Meanwhile, the decay rates of the more recalcitrant second pool of DOC in our study in 2001 and 2002 were an order of magnitude higher than those reported in Kalbitz et al. (2003). Differences in decay rates may be attributed in part to the expansion of the study floodplain, which results in inundation of new POM standing stock and continued leaching of labile DOC throughout the flood period, and not just at the start flood.

The sources of DOC in this simulation are well-represented and indicate that DOC transported into the floodplain from upstream was the dominant source, accounting for 58% of the DOC mass in 2001. It is important to note that upstream DOC sources are affected by DOC release and removal mechanisms that are similar to those we modeled in the study floodplain. DOC inputs to the floodplain from upstream sources are derived from a combination of terrestrial vegetation, microbial products, and aquatic vegetation from the Permanent Swamp. Isotopic and chemical evidence from Mladenov et al. (in press) indicate that plant-derived DOM in the Boro River, at a sampling site just upstream of the study floodplain, has an almost equal contribution of C3 (grasses) and C4 (papyrus, other sedges, and grasses) vegetation.

Within the floodplain, POM standing stock was several orders of magnitude greater than POM from primary production. Yet the DOC produced by litter leaching was only slightly higher than microbial DOC production during the flood of 2001 because the areal DOC flux from the microbial pool remained steady (at 0.16 g m<sup>-2</sup> d<sup>-1</sup>) while the rate of areal DOC flux from POM standing stock quickly declined (from 0.61 at peak flood) due to depletion of litter over time. During the period after flood (October 2001–April 2002), when water was still present in the floodplain, the contribution from autochthonous microbial sources was greater than from continuous leaching of floodplain litter (Fig. 9). By the end of October in both years, the POM standing stock was completely depleted due to removal by chemical, microbial and detritivorous activity. This is consistent with fluorescence results (Fig. 4; Mladenov et al., 2005) that show a slight shift to more microbial DOM sources after the flood period in both years. Also, during the flood of 2002, litter leaching contributed significantly less to the DOM pool because POM standing stock was reduced due to burning (Fig. 7).

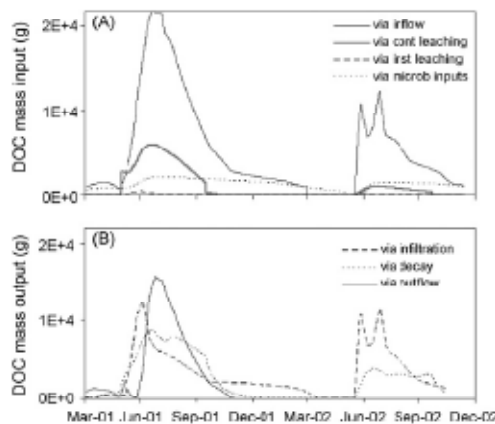




**Fig. 8** – Comparison of observed and simulated DOC concentrations from the floodplain DOC model using (A) only one pool of DOC and (B) two pools of DOC with different decay rates as in Fig. 7. Shading denotes the flood period (approximately May–September). Also shown are the root mean squared errors (RMSE) between measured and modeled DOC concentrations ( $\text{mg L}^{-1}$ ) in 2001 and 2002. An asterisk (\*) indicates that the RMSE is within 10% of measured DOC concentrations.

### 5.3. Model sensitivity and scenarios

DOC mass from upstream sources and water temperature were the most influential model parameters, as illustrated by sensitivity analyses (Table 3). DOC leached in the first day of wetting represented a very minor input of DOC into the sys-



**Fig. 9** – Plots of (A) DOC mass sources, including upstream sources (inflow), continuous leaching, instantaneous leaching, and microbial sources, and (B) DOC mass loss terms, including mass lost to infiltration, decay, and export to the adjacent floodplain from the Stage 3 simulation.

tem. Future modeling efforts could be simplified by combining the instantaneous DOC leaching term with the continuous leaching term.

The effects of increasing temperature on DOM mass in the study floodplain include many complex hydrologic and biogeochemical feedbacks that could not be modeled here, but we expect that floodplain carbon sources and DOC mass would decrease due to increased microbial decomposition in both aquatic and terrestrial compartments. Our evaluation of a scenario with a  $2^\circ\text{C}$  increase in temperature, which is expected for this region due to climate warming (Tyson et al., 2002), resulted in a 4% decrease in DOC mass in the floodplain. Rising water temperature can be expected to have the same effects upon upstream DOC sources. In a scenario with both an increase in water temperatures and a 10% decrease in upstream DOC mass loadings, this compounded effect resulted in significant removal (11%) of total DOC mass per year in the study floodplain. More thorough inverse modeling techniques would reveal more about model sensitivity and could provide temporal sensitivity as well (e.g., the importance of data collected during peak flood versus data collected during flood recession), which could further inform predictions of DOC mass in seasonal floodplains under different climatic regimes.

### 5.4. Effects of fire

Fire was an important control on DOM fluxes in the study floodplain in 2002. For instance, lower decay rates of 2002 likely reflect the more recalcitrant qualities of DOC leached from burned litter. Greater aromatic content and higher molecular weight of DOC derived from burned material makes burned OM more difficult to degrade (Czimczik et al., 2002; Gonzalez-Perez et al., 2004) and may result in slower decay. This more recalcitrant character of burned OM was illustrated in the lower DOC leaching rates from burned soil and plant litter than from unburned material in our leaching experiments.

Calculations of DOC mass in the inflow revealed that less than a third of the DOC mass was transported into the floodplain in 2002 than in 2001. Although this is due in part to lower discharge in 2002, the decline in DOC mass from upstream sources is also the result of burning of litter in upstream areas prior to flood. The marked effect of fire on the amount of POM standing stock available for leaching, and, in turn, on the decay rate of DOC is important because of the high DOC inputs associated with floodplain litter. This result may be relevant for similar systems, such as the Pantanal in Brazil and Kafue Flats in Zambia and other large arid-zone wetlands in which fires are common. Also, given that more frequent and larger fires associated with warmer, drier regimes are expected to affect aquatic ecosystems globally as a result of climate change (Whitlock et al., 2003; IPCC 2007), our results may be important for estimating future carbon budgets in any aquatic ecosystem.

### 5.5. Implications for the Okavango Delta and other seasonal wetlands

In both 2001 and 2002, the infiltrative transport of large amounts of DOM into the subsurface occurred during the

flood period (28% in 2001 and 62% in 2002) and these findings may be especially relevant for biogeochemistry of Okavango Delta groundwater. DOM transport by infiltration may mean substantial storage of DOM of unknown residence time in the groundwater beneath islands. Observations of high DOC concentrations in shallow piezometers in the study floodplain during the floods of 2001 and 2002 (in the range of 10–20 mg C L<sup>-1</sup>; Mladenov, 2004) support model indications of substantial organic carbon storage in the groundwater. Furthermore, an analysis of spectroscopic properties of the groundwater DOC (Mladenov, 2004) indicated that the organic material was mainly plant-derived, but that microbial sources of DOC were also present. This suggests that there may also be significant organic matter cycling in the subsurface and that the organic matter could be involved in microbially mediated redox processes.

In addition to the high groundwater DOC concentrations, Wolski et al. (2005) measured high total N and P concentrations in the groundwater near the study floodplain and other seasonal floodplains, increasing with distance from the edge of the floodplain to the center of the neighboring island. In combination with the carbonaceous energy sources being funneled into the subsurface, the simultaneous infiltration of nutrients may fuel microbial activity in the subsurface.

Groundwater recharge by seasonal wetlands has been noted as a major hydrologic mechanism in several arid wetland studies (Goes, 1999; Holland et al., 2006) and infiltration of dissolved constituents such as DOM may have implications for human and/or ecosystem health. For example, the seasonal floodplains of the Hadejia–Nguru Wetlands of Nigeria also receive a dry season flood and groundwater in this locale, recharged by the floodplains, is relied upon heavily for potable water supply and irrigation (Goes, 1999). This study may also have implications for studies of seasonal prairie wetlands in the northern glaciated plains of North America that are characterized by high infiltration rates and groundwater recharge (Parsons et al., 2004) and very high DOC concentrations (Arts et al., 2000).

High latitude seasonal wetlands, including northern prairie wetlands and thermokarst wetlands, are highly sensitive to climatic variability (Conly and van der Kamp, 2001) and DOC concentrations are expected to increase even further in these systems under increased temperature scenarios (Guo et al., 2004). Yet, warmer temperatures are expected to result in increased microbial utilization of DOC and greater photolytic degradation of DOC in arctic waters (Schindler et al., 1997). Our finding of reduced DOC mass loading in the study floodplain in a model scenario run with higher water temperatures may represent an important consideration for estimating changing carbon budgets in seasonal arctic wetlands.

## 6. Conclusion

This study presents a simulation of DOC fluxes in seasonal floodplain using a simple model calibrated to a 2-year data set of DOC concentrations, in which only the major DOC inputs (litter leaching, autotrophic production, and upstream inputs)

and outputs (decay, infiltration, and outflow) were modeled. The model provides insight into seasonal variations in DOC concentrations and highlights these major findings:

- (1) the seasonality of DOC decomposition is best described by two pools of DOC decaying at different rates
- (2) in both years, upstream DOC sources, subject to the same DOC transformations we modeled in the study, were the primary source of DOC to the study floodplain;
- (3) during flood periods not influenced by fire, organic C derived from vegetation/litter sources within the floodplain represents a greater input of DOC to this seasonal floodplain than does organic C from microbial sources within the floodplain;
- (4) infiltrative losses of DOC were significant and have implications for groundwater quality.

The results of this modeling study are useful for better understanding the processes that control the amount of DOC in the water column of seasonal floodplains. Given the limited studies that evaluate seasonal changes in DOC release and decay in surface waters, the finding of two pools of DOC may be useful for understanding DOC dynamics in wetlands, lakes, and other water bodies for which a mass balance approach is applicable.

## Acknowledgments

We thank G. Hornberger and S. Mehl for constructive review of this manuscript. The original idea for the floodplain model was provided by P. Bauer. We are grateful to the Harry Oppenheimer Okavango Research Centre and the Institute for Arctic and Alpine Research for field and laboratory support. We also would like to thank the Government of Botswana for permitting this field-based research. Special thanks to M. Heintz for fire data and S. Mehl and P. Bauer for modeling insights. This research was supported by the American Association of University Women Scholarship, the Achievement Rewards for College Scientists Endowment, an NSF IGERT Fellowship DGE 9987607, and an INT supplement to the NSF IGERT Grant # 1534588.

## REFERENCES

- Arts, M.T., Roberts, R.D., Kassai, E., Waiser, M., Tumber, V., Plante, A.J., Rai, H., de Lange, H.J., 2000. The attenuation of ultraviolet radiation in high dissolved organic carbon waters of wetlands and lakes on the northern Great Plains. *Limnol. Oceanogr.* 45, 292–299.
- Azmanova, S., Rajlik, M., 2005. DOC release from alder leaves and catkins during decomposition in a small lowland stream. *Int. Rev. Hydrobiol.* 1, 33–41.
- Baldwin, D.S., 1969. Dissolved organic matter and phosphorus leached from fresh and 'terrestrially' aged river red gum leaves: implications for assessing river-floodplain interactions. *Freshw. Biol.* 41, 675–685.
- Bauer, P., Gumbrecht, T., Kinzelbach, W., 2006. A regional coupled surface water/groundwater model of the Okavango Delta, Botswana. *Water Resour. Res.* 42 (4) (Art. No. W04403).

- Bonyongo, M.C., Bredenkamp, G.J., Veenendaal, E., 2000. Floodplain Vegetation in the Nxaraga Lagoon area, Okavango Delta, Botswana. *S. Afr. J. Bot.* 66 (3), 15–21.
- Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1997. Response characteristics of DOC flushing in an alpine catchment. *Hydrol. Process.* 11, 1635–1647.
- Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 2000. Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach. *Hydrol. Process.* 14, 3291–3308.
- Chapra, S.C., 1997. *Surface Water Quality Modeling*. McGraw-Hill, Inc., New York, pp 27–28.
- Conly, F.M., van der Kamp, G., 2001. Monitoring the hydrology of Canadian Prairie wetlands to detect the effects of climate change and land use changes. *Environ. Monit. Assess.* 67, 195–215.
- Cronberg, G., Gieske, A., Martins, E., Prince Nengu, J., Stenstrom, I.M., 1996. Major ion chemistry, plankton, and bacterial assemblages of the Jao/Boro River, Okavango Delta, Botswana: the swamps and flood plains. *Arch. Hydrobiol. Suppl.* 107, 335–407.
- Czuczaj, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Org. Geochem.* 33, 1203–1222.
- Frize, H., Pennanen, T., Kitunen, V., 1998. Characterization of dissolved organic carbon from burned humus and its effects on microbial activity and community structure. *Soil Biol. Biochem.* 30, 687–693.
- Gieske, A., 1997. Modelling outflow from the Jao/Boro River system in the Okavango Delta, Botswana. *J. Hydrol.* 193, 214–229.
- Goes, B.J.M., 1999. Estimate of shallow groundwater recharge in the Hadejia-Nguru Wetlands, semi-arid northeastern Nigeria. *Hydrogeol. J.* 7, 294–304.
- Gonzalez-Perez, J.A., Gonzalez-Vila, F.J., Almendros, G., Knicker, H., 2004. The effect of fire on soil organic matter—a review. *Environ. Int.* 30, 855–870.
- Grieva, I.C., 1991. A model of dissolved organic carbon concentrations in soil and stream waters. *Hydrol. Process.* 5, 301–307.
- Guo, L., Semiletov, I., Gustafsson, O., Ingi, J., Andersson, P., Dudarev, O., and White, D., 2004. Characterization of Siberian Arctic coastal sediments: Implications for terrestrial organic carbon export. *Global Biogeochemical Cycles*, vol. 18. GB1036, doi:10.1029/2002GB002087.
- Heini, M., Neuenschwander, A., Sliva, J., Vanderpost, C., 2006. Interactions between fire and flooding in a Southern African floodplain system (Okavango Delta, Botswana). *Landscape Ecol.* 21, 699–709.
- Heini, M.P., Frost, P., Vanderpost, C., Sliva, J., 2007. Fire activity on drylands and floodplains in the southern Okavango Delta, Botswana. *J. Arid Environ.* 60, 77–87.
- Hoberg, P., Lindholm, M., Ramberg, L., Hessen, D.O., 2002. Aquatic food web dynamics on a floodplain in the Okavango delta, Botswana. *Hydrobiologia* 473, 23–30.
- Holland, K.L., Tyerman, S.D., Mensforth, L.J., Walker, G.R., 2006. Tree water sources over shallow, saline groundwater in the lower River Murray, South-eastern Australia: implications for groundwater recharge mechanisms. *Aust. J. Bot.* 54, 193–205.
- Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry* 25, 147–165.
- Jacobson, P.J., Jacobson, K.M., Angermeier, P.L., Cherry, D.S., 2000. Variation in material transport and water chemistry along a large ephemeral river in the Namib Desert. *Freshw. Biol.* 44, 481–491.
- Jones, J.B., Fisher, S.G., Grimm, N.B., 1995. Vertical hydrologic exchange and ecosystem metabolism in a Sonoran Desert Stream. *Ecology* 76 (3), 942–952.
- Junk, W., Bayley, R.B., Sparks, R.E., 1989. The flood pulse concept in river-floodplain systems. In: Dodge, D.F. (Ed.), *International Large River Symposium*. Can. Spe. Publ. Fish. Aquat. Sci., pp. 110–127.
- Kalbitz, K., Schmerwitz, J., Schwesig, D., Matzner, E., 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113, 273–291.
- Karlsson, C.M., Richardson, J.S., Kiffney, P.M., 2006. Modelling organic matter dynamics in headwater streams of south-western British Columbia, Canada. *Ecol. Model.* 183, 463–476.
- Kragh, T., Sondergaard, M., 2004. Production and bioavailability of autochthonous dissolved organic carbon: effects of mesozooplankton. *Aquat. Microbial Ecol.* 36 (1), 61–71.
- McCarthy, Ellery, 1998. *The Okavango Delta*. Trans. R. Soc. S. Afr. 53, 157–182.
- Mladenc, N., 2004. Evaluation of the effects of hydrologic change in the Okavango Delta of Botswana: analyses of aquatic organic matter transport and ecosystem economics. PhD Dissertation. University of Colorado, Boulder, CO, USA.
- Mladenc, N., McKnight, D.M., Wolke, P., Ramberg, L., 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta of Botswana. *Wetlands* 25 (3), 622–638.
- Mladenc, N., McKnight, D.M., Macko, S.A., Ramberg, L., Cory, R.M., Norris, M., in press. Chemical characterization of DOM in channels of a seasonal wetland. *Aquat. Sci.*
- Moustafa, M.Z., Hamrick, J.M., 2000. Calibration of the wetland hydrodynamic model to the everglades nutrient removal project. *Water Qual. Ecosyst. Model.* 1, 141–167.
- Murray-Judson, M., Wolke, P., Ringrose, S., 2006. Scenarios of the impact of local and upstream changes in climate and water use on hydro-ecology in the Okavango Delta, Botswana. *J. Hydrol.* 331, 73–84.
- O'Connell, M., Baldwin, D.S., Robertson, A.I., Rees, G., 2000. Release and bioavailability of dissolved organic matter from floodplain litter: influence of origin and oxygen levels. *Freshw. Biol.* 45, 333–342.
- Parsons, Hayashi, van der Kamp, 2004. Infiltration and solute transport under a seasonal wetland: bromide tracer experiments in Saskatoon, Canada. *Hydrol. Process.* 18, 2011–2027.
- Petersen, R.C., Cummins, K.W., 1974. Leaf processing in a woodland stream. *Freshw. Biol.* 4, 343–363.
- Pinney, M.L., Westerhoff, P.K., Baker, L., 2000. Transformations in dissolved organic carbon through constructed wetlands. *Water Res.* 6, 1897–1911.
- Qiu, S., McComb, A.J., Bell, E.W., Davis, J.A., 2003. Nutrient response to soil and litter metabolic activity in a transect across a seasonal wetland. *Mar. Freshw. Res.* 54, 242–252.
- Qualls, I.G., Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. *Soil Sci. Soc. Am. J.* 56, 578–586.
- Qualls, I.G., Richardson, C.J., 2003. Factors controlling concentration, export, and decomposition of dissolved organic nutrients in the Everglades of Florida. *Biogeochemistry* 62, 197–229.
- Ramberg, L., Wolke, P., Kragh, M., 2006. Water balance and infiltration in a seasonal floodplain in the Okavango Delta, Botswana. *Wetlands* 26 (3), 677–680.
- Richardson, J.S., Shaughnessy, C.R., Harrison, F.G., 2004. Litter breakdown and invertebrate association with three types of leaves in a temperate rainforest stream. *Arch. Hydrobiol.* 159 (3), 309–325.



- Rutz, D., Heini, M., Silva, J., 2004. The influence of flood and fire on biomass and soil properties of floodplains in Southern Africa. Master's Thesis. Technische Universität München (TUM), Freising-Weihenstephan, Germany.
- Schindler, D.W., Curtis, P.J., Bayley, S.E., Parker, B.R., Beaty, K.G., Stainton, M.R., 1997. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry* 36, 9–28.
- Strauss, E.A., Lamberti, G.A., 2002. Effect of dissolved organic carbon quality on microbial decomposition and nitrification rates in stream sediments. *Freshw. Biol.* 47, 65–74.
- Tyson, P.D., Cooper, G.R.J., McCarthy, T.S., 2002. Millennial to multi-decadal variability in the climate of southern Africa. In: *J. Climatol.* 22, 1105–1117.
- Wang, N., Mitsch, W.J., 2000. A detailed ecosystem model of phosphorus dynamics in created riparian wetlands. *Ecol. Model.* 125, 101–130.
- Whitlock, C., Shafer, S.L., Marlon, J., 2003. The role of climate and vegetation change in shaping past and future fire regimes in the northwestern US and the implications for ecosystem management. *For. Ecol. Manage.* 178, 6–21.
- Wolski, P., Murray-Hudson, M., Fernkvist, P., Lidén, A., Huntsman-Mapila, P., Ramberg, I., 2005. Islands in the Okavango Delta as sinks of water-borne nutrients. *Botswana Notes Records* 37, 253–263.
- Wolski, P., Savenije, H., 2006. Dynamics of surface and groundwater interactions in the floodplain system of the Okavango Delta, Botswana. *J. Hydrol.* 320, 283–301.