HYDROCHEMICAL MODELING OF DISSOLVED ORGANIC CARBON OF A SMALL, UNDISTURBED, OLD-GROWTH FORESTED WATERSHED IN SOUTHERN CHILE

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ABSTRACT

A simple, mechanistic hydrochemical model for DOC export was developed and tested for a small, old-growth forested watershed on the Chiloé island in southern Chile. Despite the important roles of DOC in both terrestrial and aquatic ecosystems, there are few tested watershed scale DOC models published to date and, in general, they have had modest success in reproducing observed stream DOC fluxes. The model developed here coupled a simple Boussinesq-type hydrological model of lateral subsurface flows from two soil layers and an Arrhenius-type model for DOC production in soil water. One unique aspect of this model is that DOC production is scaled to account for soil saturation. The streamflows were well simulated (r^2=0.86). Simulated stream water DOC concentrations also agreed well with observed values (r^2=0.80). Simulated soil water DOC concentrations were generally underestimated for the shallow soil layer and overestimated for the deep layer compared to observed values. Lysimeter sampling errors, lack of agreement between modeled and actual soil layers and the relative position of the lysimeters in the watershed are discussed as the possible causes of these deviations. In general, the model presented here captured the DOC stream water trends in this old-growth forest better than similar models used in other ecosystems. The simple structure of this DOC model may offer a good platform to gradually and accurately increase its intricacy, providing a better understanding of the inherent complexity of the processes regulating the carbon dynamics in forested ecosystems.

BIOGRAPHICAL SKETCH

Maria Vicenta Valdivia was born in Coquimbo, Chile, in 1973. She graduated in 1996 with a Bachelor of Aquaculture Sciences degree from Universidad Católica de Norte, Chile, and in 1998 she received the professional title of Aquacultural Engineer from the same university. Back in Chile, she worked at the Marine Resources Department of Fundación Chile, a non-profit, private organization, where she developed a deep interest in environmental sciences and the impact of human activities in aquatic ecosystems. In 2003 she started her MS/PhD in Biological and Environmental Engineering at Cornell University.

ACKNOWLEDGMENTS

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LIST OF SYMBOLS

A Watershed area (m^2)

AWC Available water capacity (m)

α_{deep} Linear reservoir coefficient of deep soil layer (d^{-1})

α_i Linear reservoir coefficient of soil layer i (d^{-1})

$\alpha_{shallow}$ Linear reservoir coefficient of shallow soil layer (d^{-1})

b Soil saturation parameter (dimensionless)

C Ratio of DOC production rate at field temperature (T) to DOC production rate at a reference temperature (T_0)

D_i Soil depth (m)

$DOC_{(t)}$ DOC concentration in soil water at day *(t)* (mg L^{-1})

$DOC_{(t-1)}$ DOC concentration in soil water at previous day *(t-1)* (mg L^{-1})

DOC_0 DOC production at a reference temperature (T_0) (mg L^{-1})

DOC_{deep} DOC concentration in soil water in deep soil layer (mg L^{-1})

$DOC_{P(t)}$ DOC production in soil water at day *(t)* (mg L^{-1})

DOC_{rain} DOC concentration in precipitation (0.3 mg L^{-1}, based on average measured rainwater concentrations from the study site, in the two years of study)

$DOC_{shallow}$ DOC concentration in soil water in shallow soil layer (mg L^{-1})

DOC_{stream} Stream DOC concentration at day *(t)* (mg L^{-1})

E_0 Modified activation energy (K)

E_a Activation energy (kJ mol^{-1})

ET Evapotranspiration (m)

f Drainage fraction (dimensionless)

K_{deep} Saturated hydraulic conductivity of deep soil layer (m d^{-1})

K_i	Saturated hydraulic conductivity of soil layer i (m d^{-1})
$K_{shallow}$	Saturated hydraulic conductivity of shallow soil layer (m d^{-1})
L	Total stream length (m)
PET	Potential evapotranspiration (m)
$Q_{(t-1)}$	Interflow of previous day *(t-1)* (L d^{-1})
Q_{10}	Factor by which the reaction rate increases when the temperature increases by 10°C (with respect to a reference temperature)
Q_{deep}	Interflow from deep soil layer (L d^{-1})
Q_i	Interflow from soil layer i (L d^{-1})
Q_{max}	Maximum interflow from a soil layer in the two years of study (L d^{-1})
$Q_{overland}$	Overland flow (L d^{-1})
$Q_{shallow}$	Interflow from shallow soil layer (L d^{-1})
ϕ_i	Drainable porosity (dimensionless)
R	Gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1})
$S_{(t)}$	Water storage in a soil layer at day *(t)* (L)
S_{deep}	Water storage in deep soil layer (L)
S_i	Water storage in soil layer i (L)
S_{max}	Maximum water storage in a soil layer in the two years of study (L)
$S_{shallow}$	Water storage in shallow soil layer (L)
SC_{max}	Maximum storage capacity (m)
T	Field temperature (K)
T_0	Reference temperature (K)
θ	Soil water content (dimensionless)
θ_{fc}	Field capacity (dimensionless)
θ_{sat}	Soil water content at saturation (dimensionless)
θ_{wp}	Wilting point (dimensionless)

CHAPTER 1

HYDROCHEMICAL MODELING OF DISSOLVED ORGANIC CARBON OF A
SMALL, UNDISTURBED, OLD-GROWTH FORESTED WATERSHED IN
SOUTHERN CHILE

1. INTRODUCTION

Dissolved Organic Carbon (DOC) plays several important roles in terrestrial and
aquatic ecosystems. Through the formation of organic complexes, DOC can influence
nutrient availability (*e.g.* Stewart & Wetzel, 1981; Fernandez-Perez *et al.*, 2005),
affect the solubility, mobility, and toxicity of metals (Reuter & Perdue, 1977; Martell
et al., 1988), and control the absorption of pesticides to soils (Senesi, 1992). DOC
also influences aquatic biological activity through light absorption (Davies-Colley &
Vant, 1987; Williamson & Zagarese, 1994) and may contribute significantly to
freshwater acidity through the formation of organic acids (Eshleman & Hemond,
1985). DOC is also linked to the formation of trihalomethanes as by-products of the
disinfection of drinking water with chlorine, which constitutes a potential threat to
human health (Siddiqui *et al.*, 1997). Nevertheless, despite extensive research on the
biogeochemical processes controlling DOC dynamics (see review by Kalbitz *et al.*,
2000), there are curiously few successfully tested predictive DOC models at watershed
scale.

There is a general trend across biogeochemistry and hydrology towards increasing
model complexity, often to the point where individual processes cannot be tested with
meaningful measurements and model parameters cannot be independently determined
(Grayson *et al.* 1992, Baveye & Boast, 1999). Indeed, several modeling efforts for

DOC fluxes in terrestrial ecosystems explicitly simulate complex relationships between DOC production and consumption, sorption reactions, and their spatial relations throughout the soil profile, frequently without testing the model results against field measurements (Parton *et al.*, 1994; Currie & Aber 1997; Neff & Asner, 2001; Michalzik *et al.*, 2003). While this type of approach allows researchers to explore the importance of different processes, as well as the potential interactions among them, it is evident from comparing modeling studies that increased model complexity does not necessarily lead to increased accuracy of the model results (*e.g.* Steenhuis *et al.*, 1999). Complex models are usually subject to over-parameterization, which prevents them from reaching their potential performance level (Perrin *et al.*, 2001). In addition, the knowledge about specific modeled processes is sometimes not accurate enough to support a high model complexity. Thus, the performance of simple models in some cases may be similar, if not better, than that of complex models. Certainly, some of the most cited watershed scale DOC models are parsimonious and their results have been tested against field data (*e.g.* Grieve, 1991; Boyer *et al.,* 1996). Although these models were able to capture the general seasonal patterns of stream DOC, the authors provided no statistical analysis to compare observed and predicted data in order to evaluate the model performance.

This study develops and tests a similarly simple model of watershed hydrology and bulk DOC availability specifically for a small, old-growth, forested watershed in southern Chile that receives very little atmospheric pollution and has no history of major land use change. Attention to such systems offers valuable baseline information for comparisons of nutrient retention, provision, and cycling strategies among forest ecosystems (Matzner & Davis, 1996). Modeling old, minimally impacted systems allows us to neglect complicating anthropogenic influences and, by assuming the

system is in a state of long-term equilibrium (Vitousek & Reiners, 1975), we can ignore net accumulation and loss processes.

The DOC model presented here is built on the general framework used by Grieve (1991) and Boyer *et al.* (1996), based on new evidence about the origin of DOC in forest soils while retaining a similar level of simplicity. This model also incorporates a simpler yet more realistic hydrological model than previously published DOC models at watershed scale.

2. ORIGIN AND FLUXES OF DOC IN FORESTED ECOSYSTEMS

Naturally occurring DOC is a composite of molecules from simple sugars to complex fulvic and humic acids (McDowell & Likens, 1988). Fulvic acids are believed to comprise the bulk of DOC, but it also contains several classes of low molecular weight compounds such as aliphatic and aromatic organic acids, peptides, amino acids, mono- and disaccharides, amino sugars, phenolics and siderophores (McKeague *et al.*, 1986), which account for no more than 5% of the total DOC (Van Hees *et al.*, 2005). DOC in forest soils is produced principally by litterfall decomposition, root exudation, microbial activity, and leaching from humus in the soil (Qualls *et al.*, 1991; Guggenberger & Zech, 1994; Kalbitz *et al.*, 2000; Yano *et al.*, 2000; Kaiser *et al.*, 2001). However, the quantitative contribution of each source is a subject of controversy.

Recent findings support the theory that shallow soil water DOC is relatively old (older than 30 years) (Trumbore *et al.*, 1992; Tegen & Dörr, 1996), and produced during incomplete decomposition of recalcitrant soil carbon (Hagedorn *et al.*, 2002, 2004),

i.e. decomposition of complex humus molecules into smaller, recalcitrant moieties, which become leachable (F. Hagedorn, pers. comm.). This decomposition probably involves microbial as well as chemical and physical processes. The release of DOC from fresh litter, although much larger than that from humified carbon (Moore & Dalva, 2001), has been emphasized as an important source for heterotrophic respiration (Gaudinski *et al.*, 2000; Harrison *et al.*, 2000). Thus, it is rapidly assimilated by the soil microbial biomass prior to leaching, making minor contributions to DOC in soil and stream water (McDowell & Likens, 1988; Qualls & Haines, 1992; Trumbore *et al.*, 1992; Tegen & Dörr, 1996; Zsolnay, 1996; Schiff *et al.*, 1997; Hagedorn *et al.*, 2002, 2004, Van Hees *et al.*, 2005). Based on this evidence, the model presented here relies on the simplification that all DOC in soil and stream water comes from recalcitrant soil carbon, and that biological DOC consumption can be ignored since it exclusively affects tight recycling of labile DOC.

Export of DOC from forested catchments depends on a complex, seasonally and spatially varying interplay of production, sorption, and hydrology (Cronan & Aiken 1985; Schiff *et al.*, 1997). DOC production is strongly regulated by temperature, which is considered the major factor influencing the dynamics of soil organic carbon (Knorr *et al.*, 2005). Indeed, the temperature-dependence of DOC production has been reported in several studies, evidenced by observed DOC summer maxima (Vance & David, 1991; Schindler *et al.,* 1992; Guggenberger & Zech, 1994; Christ & David, 1996). To date, the most commonly used equation for modeling DOC production as a function of temperature is the Q_{10} relationship, *i.e.* the factor by which the reaction rate increases when the temperature increases by 10ºC (with respect to a reference temperature), originally developed by Van´t Hoff (1898):

$$C = Q_{10}^{\left(\frac{T - T_0}{10}\right)} \qquad (1)$$

where C is the ratio of DOC production rate at field temperature (T) to DOC production rate at a reference temperature (T_0). Eq. (1) was recently used by Michalzik *et al.* (2003) to model DOC production in forest soils, and it has been also extensively used for modeling organic matter decomposition (Kätterer *et al.*, 1998). Another model that has a long history is the exponential function proposed by Arrhenius (1889):

$$C = e^{-\left(\frac{E_a}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)} \qquad (2)$$

where E_a is the activation energy (kJ mol^{-1}) and R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}). This equation has been used in several studies to model soil respiration rates (Moore, 1986; Lloyd & Taylor, 1994; Leirós *et al.*, 1999). Lloyd & Taylor (1994) slightly modified the Arrhenius equation (Eq. 2) in order to improve its temperature sensitivity:

$$C = e^{-E_0\left(\frac{1}{T-227} - \frac{1}{T_0-227}\right)} \qquad (3)$$

where E_0 is the modified activation energy (K). This equation provides a similar, and sometimes even better, description of the temperature response at lower temperatures than Eq. (2) (Lomander, 2002).

Soil saturation degree is another important factor influencing DOC production. It has been observed that increasing water content enhance DOC production (Christ & David 1996), as well as soil respiration (Nyhan, 1976; Clark & Gilmour, 1983; Howard & Howard, 1993). It has also been observed that cycles of soil drying and rewetting have been related to large and rapid increases in soil respiration rates (*e.g.* Orchard & Cook, 1983; Bloem *et al.*, 1992). Different models have been proposed to account for the observed effects of soil saturation on soil respiration and organic matter decomposition (*e.g.* Moore, 1986; Stott *et al.*, 1986; Howard & Howard, 1993; Leirós *et al.*, 1999; Lomander, 2002), but in general experimental studies are scarce, particularly for DOC production. Some authors (*e.g.* Leirós *et al.*, 1999; Magid *et al.*, 1999) sustain that increased decomposition rates are probably due to associated increased temperature rather than pure soil saturation effects. In fact, soil temperature and saturation usually covary seasonally in temperate ecosystems, and although soil temperatures are in general highest by late summer, potential evapotranspiration might be strong enough to reduce soil water even in presence of high precipitation. Thus, the development of models describing a combination of effects of temperature and soil saturation is essential in order to realistically represent DOC production in forest soils.

Sorption reactions in the soil profile may also influence DOC fluxes and have, indeed, been taken into consideration in a number of DOC models (*e.g.* Neff & Asner, 2001; Michalzik *et al.*, 2003). Adsorption has been shown to significantly influence the concentrations of organic acids in soil solution (Jones *et al.*, 1996; Jones & Brassington, 1998; Ponizovsky *et al.*, 1999; Hu *et al.*, 2001), and is a central feature in the podzolisation process (Farmer *et al.*, 1980). Adsorption is usually considered to be an irreversible process, since desorption rates are in general very slow, resulting in long residence times of organic carbon in soils (Van Hees *et al.*, 2003). The

mechanism by which complex humus molecules are decomposed into smaller, recalcitrant moieties that become leachable and eventually give origin to DOC in soil and stream water probably involves microbial as well as chemical and physical processes. The specific nature of these processes and their relative significance in DOC formation, however, is a riddle still unresolved, but it is probable that desorption is one of these processes. In fact, desorption increases with temperature (McBride, 1994), which is consistent with the conceptual framework of the DOC model presented in this study. For this reason, however, their effects cannot be analyzed separately. Although DOC adsorption may also be important controlling DOC fluxes, is very unlikely that it plays a role in the case of the study site. In general, affinity for DOC is higher in soils with high clay content and high iron and aluminum oxides (Moore *et al.*, 1992; Kaiser *et al.*, 1996; Kaiser & Zech, 1998), and the clay content in the soils of the study site is low (D.R. Vann, unpubl. data). These soils are also very shallow, which minimize the surface available for DOC adsorption. Finally, old-growth, undisturbed ecosystems, like the study site, are essentially in equilibrium, *i.e.* there is no net long-term (inter-annual) nutrient accumulation or loss (Vitousek & Reiners, 1975), which means that DOC adsorption-desorption should be at steady-state. Therefore, sorption reactions were neglected, at least explicitly, in this modeling study.

The transport of carbon to streams is strongly influenced by catchment hydrology, and fluxes of DOC in stream water are usually linked to discharge and hydrological flow paths. In general, DOC concentrations in stream water show a positive correlation with discharge (Fisher & Likens, 1972; Schlesinger & Melack, 1981; Naiman, 1982; Meyer & Tate, 1983; Grieve, 1984; Edwards & Cresser, 1987; McDowell & Likens, 1988). This relationship is attributed to the flushing of old soil water stored in the

subsoil (Pearce *et al.*, 1986) and previously bare areas of the stream channel (Casey & Farr, 1982). However, this correlation is sometimes weak (Bishop *et al.*, 1990; Grieve, 1991). Hysteresis effects often occur during storms, usually resulting in DOC concentrations that are higher, at a given discharge, on the rising than on the falling limb of the storm hydrograph (McDowell & Fisher, 1976; Moore, 1989; McGlynn & McDonnell, 2003), although the reverse trend has also been reported (Edwards, 1984; Grieve, 1984; Moore & Jackson, 1989). Thus discharge alone rarely explains all of the variation in DOC concentrations in stream water. In fact, several authors have pointed to the importance of the hydrologic flow paths in determining drainage water composition and hence controlling DOC delivery (Cronan & Aiken, 1985). Upper soil horizons of forested catchments are in general highly organic, and the content of organic carbon is lower in deeper mineral soils (*e.g.* Edwards, 1984). Therefore, watershed DOC models need to consider the relative contribution of water flowing though different soil horizons because this largely controls stream DOC concentrations.

3. METHODS

3.1. STUDY AREA

The study area is a small 1.2 ha watershed located in southern Chile, on the western slope of Cordillera de Piuchén in the Chiloé National Park (42º22'S, 74º03'W) (Fig. 1). The Cordillera de Piuchén is the southernmost extension of the Coastal Cordillera, a north-south trending mountain belt that flanks the western edge of Chile's central valley. The watershed was under intensive study between 1994 and 2000 as part of an international research program, the Cordillera de Piuchén Ecosystem Study (CPES).

The elevation ranges from about 650 to almost 690 m above the sea level. The upland region is dominated by flat Magellanic moorland, consisting of tussock-sedge-cushion plant vegetation (Zarin *et al*, 1998), which changes to steep slopes and dense forest to the east (Salmon *et al.*, 2001). The forested portion of the watershed consists of a zone sheltered from direct winds dominated by the conifer Alerce Andino (*Fitzroya cupressoides*), and east-facing slopes occupied by a transitional forest dominated by Ciprés de las Guitecas (*Pilgerodendron uviferum)* and Tepual *(Tepualia stipularis)*.
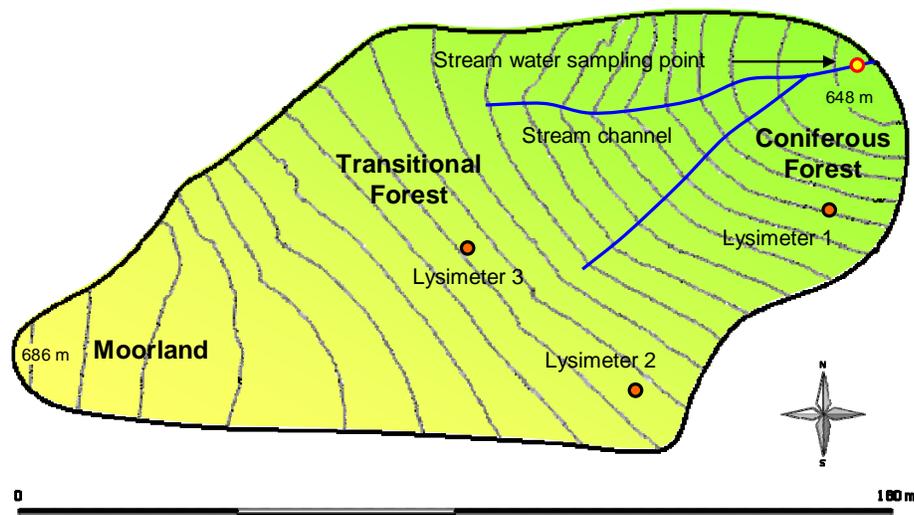
Figure 1. Schematic of the study watershed, showing location of lysimeters used to collect soil water and location of the stream water sampling point.

The climate is humid, with annual average rainfall of 5,804 mm and temperature ranging from 2.6 to 23.5 ºC over the two years of study. The periodic dry-up of the stream during summer periods suggests no significant deep groundwater reservoir, which seems especially valid considering the high annual precipitation.

The soils in this small watershed have been provisionally classified as cryofolists/cryaquents and are shallow ranging from 35 cm in the moorland to 70 cm depth in the forest (D.R. Vann, unpubl. data). There are two identifiable soil layers: a highly organic top layer, which varies in depth from 10 to 30 cm, and a mineral bottom layer. Underlying the soils there is a highly weathered, impermeable bedrock predominantly composed of quartzofeldspathic schists, pre-Cambrian to Paleozoic in age (Zarin *et al.*, 1998). The schists are heterogeneous in composition, containing some chlorite and muscovite, with minor amounts of sphene, apatite, magnetite and tourmaline (Watters & Fleming, 1962).

The physical description of this watershed fits the classic example of Dunne & Leopold (1978) of an area hydrologically controlled by Variable Source Area (VSA) processes with shallow subsurface lateral flow (interflow) dominating the hydrograph.

3.2. WEATHER AND STREAMFLOW DATA COLLECTION

Daily rainfall, temperature and streamflow data were collected over two years, from February 12th, 1997 to February 12th, 1999. Precipitation was continuously measured in a clear contiguous to the watershed using a Belford rain gauge, which was checked and reset approximately every two weeks.

Streamflow was measured using two Parshall flumes (one high and one low capacity) installed in series at the end of the basin. Stage-discharge relationships for each flume were validated using periodic manual stream discharge measurements, and stage measurements were continuously recorded using a Stevens recorder on a 16-day time scale.

3.3. DOC MEASUREMENTS

Precipitation samples were collected for chemical analyses every time the gauge was reset. Stream water samples were collected periodically at 5 m upstream to the flumes for chemical analyses. Three low vacuum suction lysimeter sites in the watershed provided periodically information on soil water chemistry (lysimeter locations in Fig. 1). Shallow (10 cm) and deep (20 cm) soil water samples were collected at each site by applying a 30 cm Hg vacuum over a 1-2 day period.

All water samples were filtered through a pre-rinsed Gelman A/E glass fiber filters (<1 μm nominal pore size), stored in thoroughly rinsed clean HDPE bottles, kept on ice for up to 6 hours, and subsequently refrigerated. Samples were collected in duplicate, with HPLC-grade (High Pressure Liquid Chromatography) chloroform (0.5% of final volume) added as a preservative to one of the two samples. Samples were shipped by refrigerated air express to Cornell University for analysis. Water samples were analyzed for DOC by high-temperature (850ºC) platinum catalyst combustion, using a Shimadzu 5000 analyzer.

Note that as part of this study, a full suite of chemicals was analyzed, including the conservative chemicals chloride and silica, which were used to validate the hydrological model. See Salmon *et al.* (2001) for a full description of chemical analyses.

3.4. MODEL DESCRIPTION

The conceptual model assumes a two-layer system with unique flow and DOC

production rates. DOC production is function of temperature and soil saturation. Transport of DOC from soils to stream water is function of discharge along specific hydrological flow paths. The hydrological response of the catchment was simulated using a simple lumped (*i.e.* non-distributed) model, which routed the discharge through three basic flow paths: deep interflow, shallow interflow, and overland flow (runoff).

3.4.1. HYDROLOGY MODEL

The hydrology model estimates the stream flow contributions discharging from the shallow (< 30 cm) and deep (> 30 cm) soil layers. Based on field investigations (Salmon *et al.,* 2001), the model assumes two soil layers and no deep percolation below the deep soil layer, as previously described. The model is a simple water budget that updates the daily available soil water storages ($S_{shallow}$ and S_{deep}) in the shallow and deep soil layers, respectively (Fig. 2). Precipitation and potential evapotranspiration (*PET*) are the driving meteorological processes. Evapotranspiration (*ET*) is estimated by the Thornthwaite-Mather (1955) soil-water budget, which assumes that *ET* decreases linearly from *PET* for soil water content (θ) above field capacity (θ_{fc}) to zero at the wilting point (θ_{wp}) (Steenhuis & Van der Molen, 1986). *ET* is preferentially drawn from the shallow soil layer. Any water in the shallow soil layer above field capacity is considered excess and may drain vertically into the deep layer; as long as the lower is not at maximum capacity. Shallow soil water in excess of saturation is considered overland flow and routed to the stream during the day.
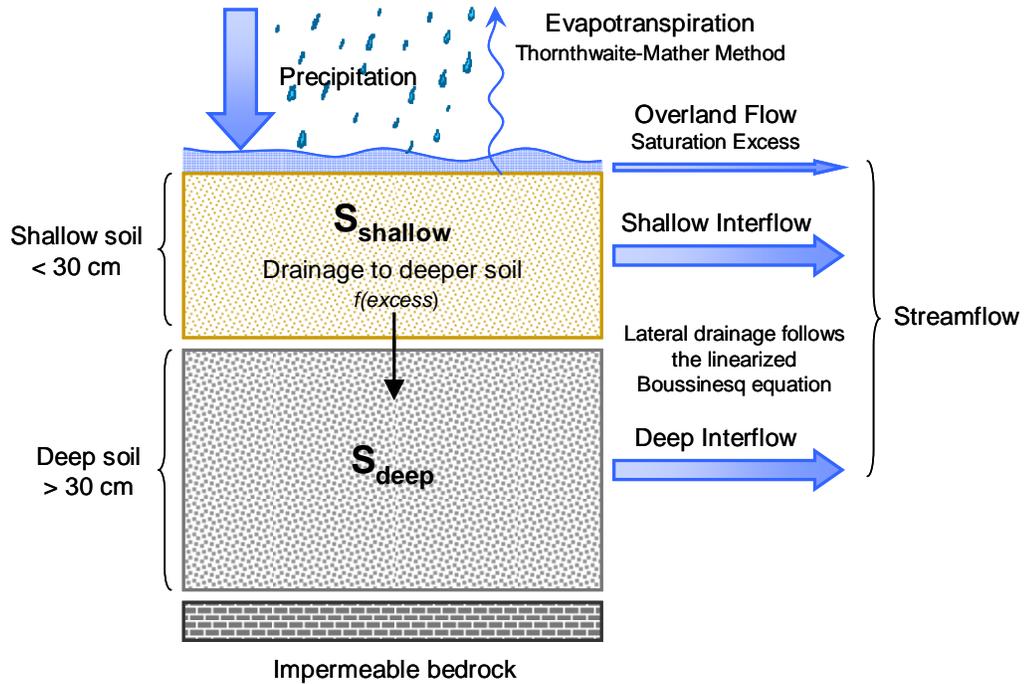
Figure 2. Schematic of the conceptual hydrology model.

Lateral subsurface flow, or interflow, from each layer is calculated using the linearized Boussinesq (1903, 1904) description for lateral drainage (Brutsaert & Neiber, 1977):

$$Q_i = \alpha_i \cdot S_i \qquad (4)$$

where Q_i is the subsurface lateral flow from soil layer i, α_i is the linear reservoir coefficient of soil layer i, and S_i is the water storage in soil layer i. Streamflow is the sum of overland flow and lateral flows from each of the soil layers, *i.e.* shallow and deep interflows. Linear reservoir coefficients were calculated based on a small subset of observed data using a recession analysis (Brutsaert & Neiber, 1977).

3.4.2. DOC MODEL

The modeling approach used here describes the DOC budget in each soil layer discretely expressed for daily time steps, and solved for the DOC concentration in soil water at day (t), $DOC_{(t)}$:

$$DOC_{(t)} = DOC_{P(t)} + DOC_{(t-1)} - DOC_{(t-1)} \cdot f(Q_{(t-1)}) \qquad (5)$$

where $DOC_{P(t)}$ is the DOC production in soil water at day (t), and $DOC_{(t-1)}$ is the DOC concentration in soil water at previous day $(t-1)$. The model assumes that at day (t) a fraction of $DOC_{(t-1)}$ remains in soil water according to how much DOC was flushed out during the previous day $(t-1)$, which is expressed by the term $DOC_{(t-1)} \cdot f(Q_{(t-1)})$ as a function of the interflow from a soil layer at previous day $(t-1)$, $Q_{(t-1)}$.

Eqs. 1-3 were used to predict daily DOC production in soil water for each soil layer. The discussion here, however, will be limited to Lloyd & Taylor (1994) equation since it performed slightly better than Eqs. 1 and 2 (see Appendix). The DOC production in soil water at day (t), $DOC_{P(t)}$, is simulated using:

$$DOC_{P(t)} = DOC_0 \cdot e^{-E_0 \left(\frac{1}{T_{(t)}-227} - \frac{1}{T_0-227} \right)} \left[\frac{1 - e^{\left(-b\frac{S_{(t)}}{S_{max}} \right)}}{1 - e^{(-b)}} \right] \qquad (6)$$

where DOC_0 is the DOC production at a reference temperature (T_0); $S_{(t)}$ is the water storage in a soil layer at day (t), and S_{max} is the maximum water storage in a soil layer in the two years of study. $DOC_{P(t)}$ and DOC_0 are expressed in terms of DOC

concentrations instead of production rates since the time step is constant. The bracketed term on the right-hand-side of Eq. 6 scales DOC production according to how wet the watershed is, *i.e.* a function based on the soil saturation degree, $S_{(t)}/S_{max}$, within a soil layer, ranging from 0 (dry) to 1 (saturated). *b* is a calibration parameter and it determines the curvature of the function. The rest of the terms were defined earlier for Eq. (3).

The function $f(Q_{(t-1)})$ can be intuitively chosen as the ratio $Q_{(t-1)}/Q_{max}$, where Q_{max} is the maximum interflow from a soil layer in the two years of study. This results in a $DOC_{(t-1)}$ flushing that increase linearly with $Q_{(t-1)}$, ranging from 0 (no flow) to 1 (maximum flow). Non-linear functions based on the ratio $Q_{(t-1)}/Q_{max}$ were also explored in order to improve the model fit. The best fit was obtained with the following non-linear function:

$$ f(Q_{(t-1)}) = \left[\frac{1 - e^{\left(\frac{Q_{(t-1)}}{Q_{max}} \right)}}{1 - e} \right] \qquad (7) $$

This term describes an exponential curve, also ranging between 0 and 1, which results in almost a straight line. The theoretical implications of this function are discussed later. Thus, Eq. (5) can be rewritten as:

$$ DOC_{(t)} = DOC_{P(t)} + DOC_{(t-1)} \left[1 - \frac{1 - e^{\left(\frac{Q_{(t-1)}}{Q_{max}} \right)}}{1 - e} \right] \qquad (8) $$

Water storage and interflow values for each soil layer are obtained from the

hydrological model. Although soil temperature would be the most appropriate variable to use here, we followed Boyer *et al.* (1996) and use air temperature as a surrogate.

Finally, the stream DOC concentration at day *(t)*, DOC_{stream}, is calculated as a mixture of waters from overland flow and interflows from the shallow and deep soil layers:

$$DOC_{stream} = \frac{Q_{shallow} \cdot DOC_{shallow} + Q_{deep} \cdot DOC_{deep} + Q_{overland} \cdot DOC_{rain}}{Q_{stream}} \qquad (9)$$

where $Q_{shallow}$ and Q_{deep} are the interflow from shallow and deep soil layers, respectively; $Q_{overland}$ is the overland flow; $DOC_{shallow}$ and DOC_{deep} are DOC concentrations in soil water in shallow and deep soil layers, respectively; and DOC_{rain} is the DOC concentration in precipitation, 0.3 (mg L^{-1}), based on average measured rainwater concentrations from the study site in the two years of study. Overland flow is assumed to be the result of direct precipitation on saturated areas.

4. RESULTS AND DISCUSSION

4.1. HYDROLOGY MODEL

The hydrological model simulated streamflow well (r^2=0.86) (Fig. 3). Although some modeled peak values did not match the data, the model provided a good representation of the observed baseflow, *i.e.* deep interflow. This is not surprising considering that the model simulated shallow and deep interflows using linear reservoir coefficients, which were calculated based on a small subset of observed data using a recession analysis. The hydrological model was parameterized based on field measurements,

and estimates were used when no measurements were available (Table 1). No attempt was made to optimize the model and it showed lack of sensitivity to parameters that were arbitrarily chosen, *i.e.* ± 10% variations in the unknown values resulted in less than 10% changes in the standard error of the observed and simulated streamflow values (data not shown). In spite of the crude approximation resulting from their lumped nature and simple structure, the results demonstrate that lumped models may be sometimes very efficient in predicting an integrated hydrological response. This seems especially valid in the case of the small watershed in this study, which presents low hydrologic heterogeneity.

As an independent verification of the calculated linear reservoir coefficients, they were compared to values estimated using a physical description of the linear reservoir coefficient (*e.g.*, Brutsaert & Neiber, 1977; Mendoza *et al.*, 2003):

$$\alpha_i = \frac{0.3465 \, \pi^2 K_i \, D_i \, L^2}{\phi_i \, A^2} \tag{10}$$

where, for the soil layer i, K_i is the saturated hydraulic conductivity (m d^{-1}), D_i is the soil depth (m), L is the total stream length (m), ϕ_i is the drainable porosity (dimensionless), and A is the watershed area (m^2). There was no replication for measures of some field parameters, especially hydraulic conductivity. Estimations of K at a single point were $K_{shallow} = 5$ and $K_{deep} = 0.1$ (m d^{-1}), based on Hvorslev tests (Freeze & Cherry, 1979). Nevertheless, $\alpha_{shallow}$ calculated with available field data was within 10% of the value obtained from the recession analysis and α_{deep} was 0.01 (d^{-1}), same order of magnitude as the value in Table 1. Thus the linear reservoir coefficients used in this model are within reasonable physical limits.
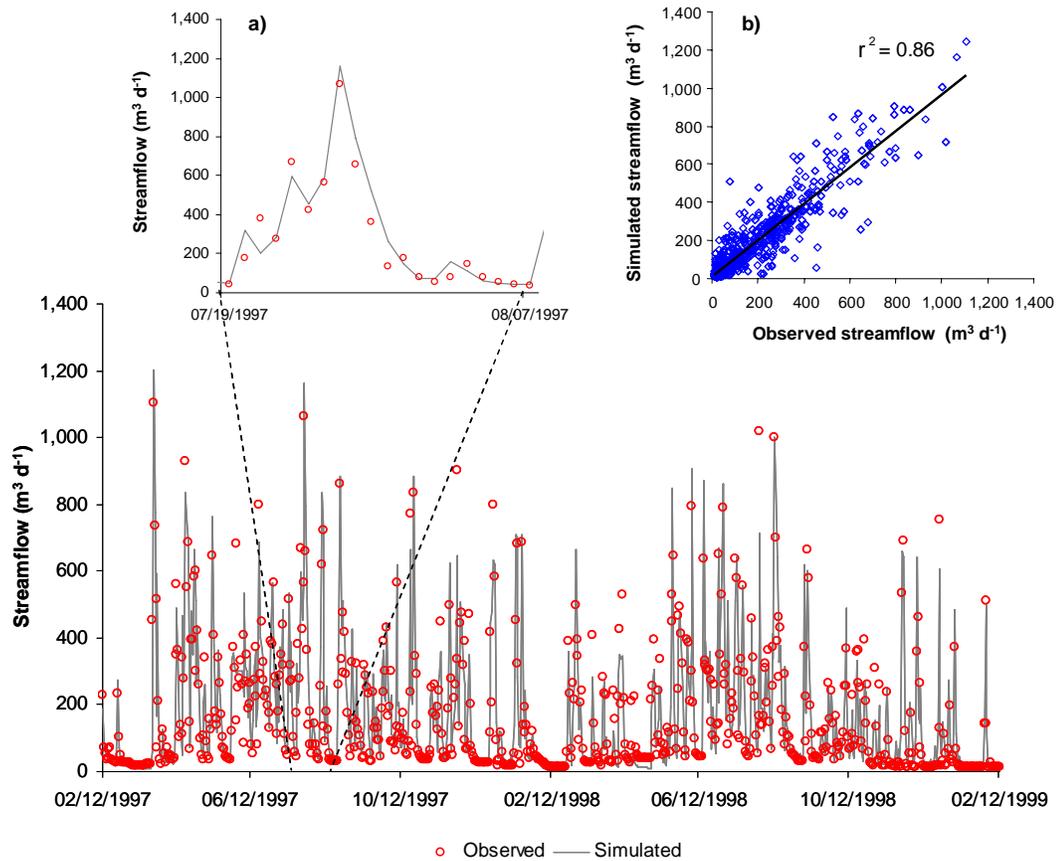
Figure 3. Observed and simulated streamflow for the study period. Insets show a) an example short-period hydrograph and day-to-day level of agreement between the model and observed data, and b) observed vs. simulated daily streamflows.

To check the simulated interflows, stream concentrations of two conservative chemical constituents, chloride and silica, were estimated using the simulated interflows and average measured soil water concentrations for shallow and deep soil layers. Streamflow concentrations were predicted as a simple mixing of the shallow and deep simulated interflows, similarly to Eq. (9). The mixing model average stream concentrations for chloride and silica were 4.4 ± 0.3 and 1.1 ± 0.4 (mg L^{-1}),

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respectively, which were similar to the observed concentrations 4.1 ± 0.9 and 0.9 ± 0.6 (mg L^{-1}), respectively, for the two years of study.

Table 1. Hydrology model parameters.

Parameter	Shallow Soil Layer	Deep Soil Layer
Maximum storage capacity, SC_{max} (m)	0.12[a]	0.06[b]
Available water capacity, AWC (m)	0.04[a]	0.02[b]
Linear reservoir coefficient, α (d^{-1})[c]	0.81	0.04
Drainage fraction, f	0.80[d]	-

[a] The soil storage parameters for the shallow soil layer were calculated from properties estimated in the field: depth = 0.3 m, $\theta_{sat} = 0.8$, $\theta_{fc} = 0.3$, $\theta_{wp} = 0.2$, $SC_{max} = 0.3(0.8-0.2)$, $AWC = 0.3(0.3-0.2)$
[b] Estimated as half the shallow soil layer capacity.
[c] Determined from hydrograph recession analyses; values are averages from seven well defined recession events (data not shown), std. dev. were 0.76 and 0.02 (d^{-1}) for the shallow and deep soil layers, respectively.
[d] Calibration parameter; model is not sensitive to this value for $f = 0.75$ to 1.

4.2. DOC MODEL

4.2.1. STREAM DOC CONCENTRATIONS

The DOC model fits the observed stream water DOC concentrations well, $r^2 = 0.80$ (Fig. 4). Interestingly, the agreement between observed and simulated concentrations in stream water at watershed scale was slightly better than the original Lloyd & Taylor (1994) results for forest soils. Although the discussion has been limited to Lloyd & Taylor (1994) equation, we found that Van't Hoff (1898) and Arrhenius (1889) equations also gave similarly good results ($r^2 = 0.79$) (see Appendix).
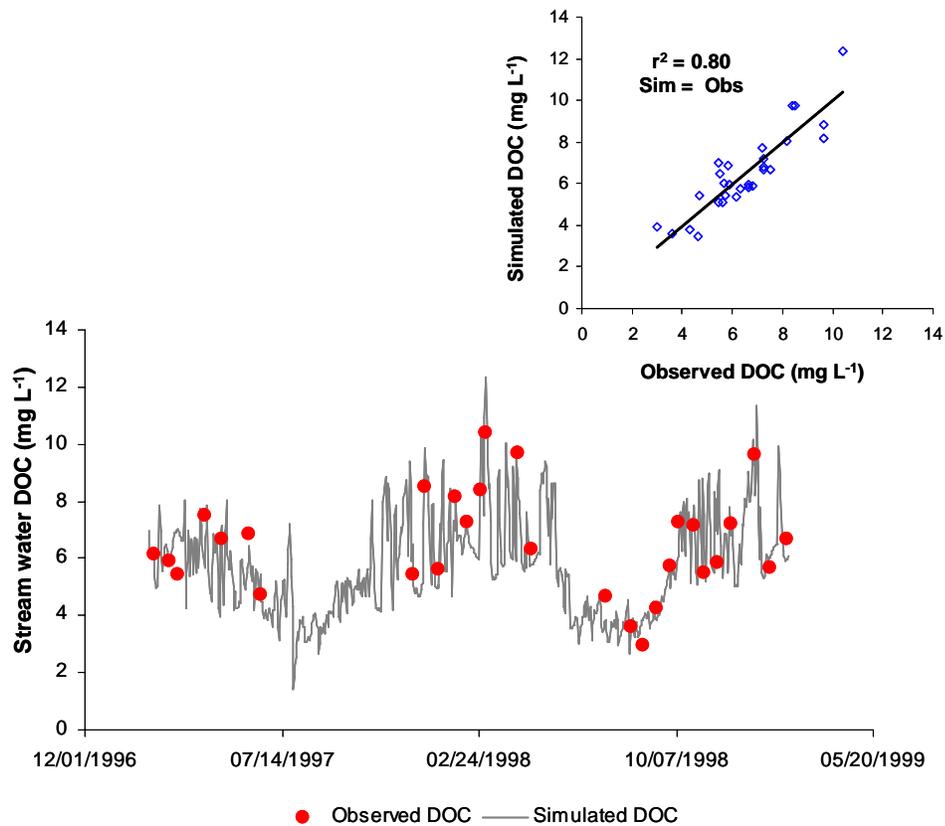
Figure 4. Observed and simulated DOC concentration in streamflow. Inset shows observed vs. simulated values.

Unlike the hydrological model, there were several unknown parameters which were used to calibrate the DOC model, specifically DOC_0, T_0, E_0 and b (Eq. 8) (Table 2). The shallow soil DOC_0 was higher than the deep soil DOC_0, which was anticipated since the shallow soils on the study site are highly organic. Although the values of DOC_0 are in the range of those reported for soil incubation experiments (*e.g.* Christ & David 1996, Chow *et al.*, 2003; Sjöberg *et al.*, 2003; Wehrer & Totsche, 2005), the diversity of incubation conditions, extractants used, and soil types made comparisons to this study difficult. Values of the modified activation energy, E_0, for shallow and

deep soil layers were in the range of values previously reported for soil respiration (Lloyd & Taylor, 1994; Leiros *et al.*, 1999). E_0 was lower for the deep soil layer, *i.e.* the energy barrier that must be overcome for DOC production is lower than in the shallow layer. This is probably compensatory for the use of air temperature instead of soil temperature, which would decrease with depth, particularly during the most active periods of DOC production.

Table 2. DOC model parameters (Eq. 8).

Parameter	Shallow Soil Layer	Deep Soil Layer
DOC_o (mg L^{-1})	10.7	4.8
E_o (K)	389	118
T_o (K)	294	294
Soil saturation parameter, b	1.6	0.4

The reference temperature, T_0, was 294 K (21°C) for both soil layers. The value of b was higher for the shallow than for the deep soil layer, indicating that DOC production in the shallow soils follows a logarithmic trend with respect to soil saturation. More specifically, DOC production in the shallow layer does not begin to drop off due to drought until the soil saturation degree, $S_{(t)}/S_{max}$, is less than half. The DOC production in the lower layer, on the other hand, drops nearly proportionally to soil saturation. This is perhaps not surprising, since the higher content of organic matter in the shallow soil results in an enhanced water holding capacity compared to mineral soil. Further research is needed, however, in order to draw more specific conclusions. The non-linear function used for scaling $DOC_{(t-1)}$ (Eq. 7) describes an exponential curve that increases with $Q_{(t-1)}$, resulting in a slightly reduced DOC flushing relative to the use of the linear flushing function $Q_{(t-1)}/Q_{max}$. This is likely to account for a small

fraction of $DOC_{(t-1)}$ present in tightly bound soil water that is not immediately incorporated into the hydrological flow and delivered to the stream, but until the next day. The curve described by this function is the same for both soil layers, since no calibration parameters were used. It is possible, however, that in fact the flushing response of the two layers is different due to their particular soil characteristics. Nevertheless, no additional fitting using a calibration parameter was attempted in order to avoid increasing the model uncertainty.

4.2.2. SOIL WATER DOC CONCENTRATIONS

Although this DOC model did not provide fully distributed predictions of DOC, simulated soil water DOC concentrations were compared with average observed concentrations sampled using three lysimeters in the study watershed. Simulated DOC concentrations for the shallow layer were slightly lower than observed shallow lysimeter concentrations and simulated deep soil layer concentrations were generally higher than the observed deep lysimeter concentrations ($r^2 < 0.4$) (Fig. 5). The very high lysimeter readings occurred during dry periods and probably represent relatively tightly bound soil water that was not necessarily part of the hydrological flow. Indeed, it is probable that the suction lysimeters sampled portions of the profile that did not contribute substantially to the streamflow, which is not an uncommon problem (Grossmann & Udluft, 1991; Lehmann & Schroth, 2003). It is also possible that the structure of the modeled soil layers does not realistically capture the distribution of DOC in the soil profile. Indeed, the average of both soil layers for the observed (6.0 mg L^{-1}) and simulated soil water DOC concentrations (6.4 mg L^{-1}) are very similar. Finally, the relative position of the lysimeters in the watershed may not be representative of the overall DOC response of the catchment, explaining at least in

part the differences between observed and simulated soil water DOC concentrations. In fact, it is likely that the soil water DOC most strongly influencing stream water concentrations may be that in the riparian area within the coniferous forest, where there were no lysimeters. McGlynn and McDonnell (2003) recently demonstrated that the spatial distribution of soil water DOC plays an important role in stream DOC concentrations and the model used here does not capture spatial variability. The spatially distributed nature of soil DOC in watersheds may be related to the presence of specific plant species, which have positive feedbacks with the soil reinforcing patterns of nutrient availability in natural ecosystems through their uptake and use of nutrients (Vitousek, 1982). Indeed, Aitkenhead & McDowell (2000) found that mean soil C:N (carbon : nitrogen) ratios and consequently DOC exports in coniferous forests are higher than in other forests.
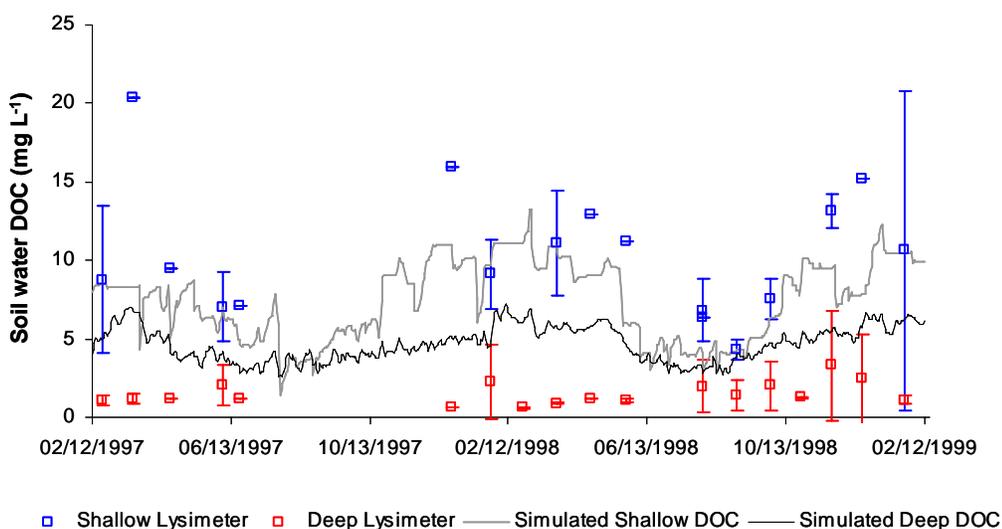

Figure 5. Comparison between observed and simulated DOC concentration in soil water. The error bars are +/- one standard deviation of measurements; symbols with no error bars are based on a single measurement, usually due to insufficient sample volume from the other lysimeters.

One particular aspect of this model is that it does not consider exchange of DOC between the two soil layers, *i.e.* the simulated lower concentration does not include any DOC leached down from the shallow layer, and the shallow layer does not take into account what would have been lost through leaching. However, because recharge to the lower soil layer takes place under fully saturated conditions, it is likely that a substantial portion of the vertically draining water by-passes the bulk of the upper soil layer, traveling primarily through preferential pathways, and thus does not contribute to DOC transfer between the two layers.

4.3. COMPARISON OF DOC MODELS

Comparing the results of the DOC model presented here to those previously published using other similarly simple models, primarily the model of Grieve (1991) later modified and tested by Boyer *et al.* (1996), it is evident that the simulated values obtained in this study agreed better with the observed data. Unfortunately, Grieve (1991) and Boyer *et al.* (1996) did not publish any statistics or other quantifiable criteria to evaluate the accuracy of their models but rather characterized the performance in qualitative terms. Both models relate DOC production with temperature using a power function at a constant rate, which is common (*e.g.* Moore, 1986; Vance & David, 1991; Schindler *et al.,* 1992; Guggenberger & Zech, 1994; Christ & David, 1996). Nevertheless, the reaction rate of processes related to soil carbon dynamics, including DOC production, is not constant but temperature dependent as well, as it is expressed by Eqs. 1-3, which is the reason the DOC model presented here is based in three equations that estimate DOC production based on a reference temperature.

The models of Grieve (1991) and Boyer *et al.*, (1996) also account for DOC consumption as a temperature dependent first-order decay term, an issue that was side-stepped in this study based on evidence supporting that DOC consumption affects only the labile DOC fraction which probably makes little or no contribution to DOC in streams. In fact, the inclusion of DOC decomposition may account for the underestimation of DOC concentrations reported by Grieve (1991). Similarly to Grieve (1991) and Boyer *et al.* (1996), the simulated DOC in soil water in this study only captured the broad patterns and statistical agreement was poor. Interestingly, it appears to be similar to that achieved by Michalzik *et al.* (2003) using a much more comprehensive, although less mechanistic, model. It is important to note that the watershed of this study is substantially different from the wetland and alpine systems studied by Grieve (1991) and Boyer *et al.* (1996), respectively.

4.4. IMPLICATIONS OF THE DOC MODEL

In recent years, several studies have evidenced long-term increases in DOC concentrations in streams and rivers across Europe and the U.S. (*e.g.* Worrall *et al.*, 2003, 2004; Clark *et al.*, 2004). The causes of the observed rises in stream DOC concentrations are attracting considerable debate, being rising temperature due to global warming one of them.

The importance of temperature in influencing decomposition of soil organic carbon has already been stated. Nevertheless, the sensitivity of soil carbon pools to global warming is a major uncertainty. Extensive evidence form experimental studies indicate that decomposition processes are temperature dependent (Kätterer *et al.*, 1998). This tenet, however, was challenged by Giardina & Ryan (2000), who suggested that organic carbon decomposition in soil is not sensitive to temperature.

Using data from field measurements and laboratory incubations to calculate the turnover time of soil organic carbon, *i.e.* is the inverse of the first-order rate constant for the decomposition process, they concluded that turnover time was almost independent of mean annual temperature over the range 5–35 ºC. Their analysis, however, neglected not only the sensitivity of decomposition rates to temperature but also the extreme heterogeneity of soil carbon, which include compounds with intrinsic turnover times ranging from <1 yr to >6 x 10^3 yr (Trumbore *et al.*, 1996; Davidson *et al.*, 2000; Trumbore, 2000).

Recently, Knorr *et al.* (2005) re-analysed Giardina & Ryan (2000) conclusions using a simple three-pool model that partitions soil organic carbon into components with different intrinsic turnover rates. Based on Arrhenius (1889) equation, they analyzed experimental data from soil incubation experiments from an undisturbed site. To explain the results, they found it necessary to have two active pools (one with a much faster turnover time than the other), and a very slow, recalcitrant pool which was effectively inert during the experimental period and accounted for 95% of total soil organic carbon. They concluded that the recalcitrant carbon pool is more sensitive to temperature than labile soil organic carbon, implying that the long-term positive feedback of soil decomposition in a warming world may be even stronger than previously predicted by global models. Arrhenius equation (1889) shows that the higher the activation energy for a soil carbon pool, the higher the sensitivity to decomposition at temperatures above the reference temperature. The opposite trend is observed for temperatures below the reference temperature. This relationship is also true for Lloyd & Taylor (1994) equation, and for Van't Hoff (1898) equation as well with increasing Q_{10} values. This is consistent with the DOC model presented here, which is based in the simplification that, despite of the importance of labile soil carbon

to DOC fluxes in terrestrial ecosystems, only recalcitrant, old carbon is contributing to DOC in streams, and that temperature is a major driving factor of DOC production.

Increasing temperature is only one aspect of the climatic change evidenced by global warming. Alterations of the hydrological cycles are also expected, including changes in the intensity and patterns of precipitation, evapotranspiration and soil moisture. Soil moisture degree is directly simulated by global climate models, albeit over a very coarse spatial resolution, and outputs from these models give an indication of possible trends (McCarthy *et al.*, 2001). Reduced soil moisture in Northern Hemisphere mid-latitude summers is expected as the result of higher winter and spring evapotranspiration, caused by higher temperatures, reduced snow cover, and lower rainfall inputs during summer (Gregory *et al.*, 1997). Nevertheless, local patterns of soil moisture will vary not only with the degree of climate change but also with soil characteristics. Soils with lower water holding capacity will be more sensitive to climate change, and waterlogging or cracking in soils due to changes in the precipitation patterns may affect water storage properties (McCarthy *et al.*, 2001). Similarly, infiltration capacity and water holding capacity of many soils are influenced by the frequency and intensity of freezing (Boix-Fayos *et al.*, 1998). Thus, changes in soil moisture patterns are difficult to estimate, since it is unclear whether regional climate will become more variable. Therefore, streamflow DOC trends based on soil moisture predictions are uncertain.

5. CONCLUSIONS

The simple model presented in this study provided a good representation of the stream DOC response of a small, undisturbed, old-growth watershed, demonstrating the

feasibility of parsimonious DOC modeling. Lloyd & Taylor (1994) equation provided a good foundation for building a DOC model at watershed scale, although Van't Hoff (1898) and Arrhenius (1889) equations could be calibrated to provide reasonably good fits as well. The model results support the assumption that temperature, soil saturation, discharge, and hydrological flow paths are the major factors controlling the DOC response of the study catchment. The simple structure of this mechanistic hydrochemical DOC model may offer a good platform to gradually and accurately incorporate additional processes. Nevertheless, currently there are too many unknown parameters to justify additional conceptual complexity, particularly because it is not obvious how to determine the soil DOC production parameters *a priori*. The next step is to incorporate spatially distributed processes and potential feedbacks arising from the spatial variability of vegetation and soil characteristics.

Table A1.   DOC model parameters based on Van´t Hoff (1898) equation.

| Parameter	Shallow Soil Layer	Deep Soil Layer
DOC_0 (mg L^{-1})	11.2	5.4
Q_{10}	2.9	1.6
T_0 (K)	294	294
Soil saturation parameter, b	1.6	0.4
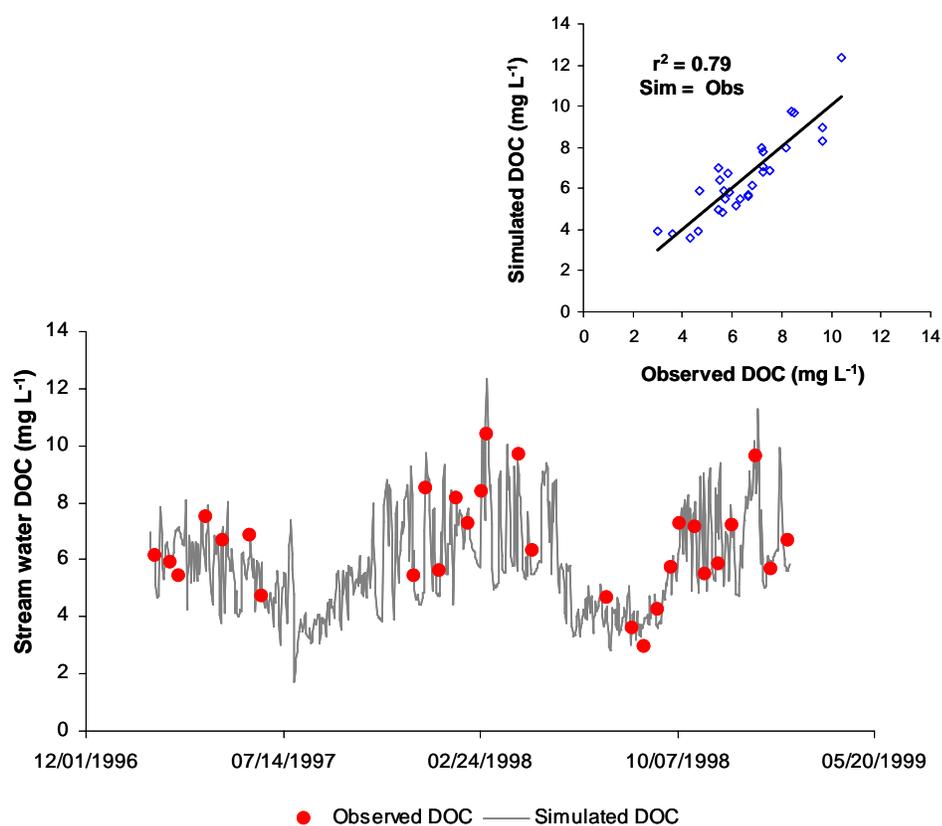
Figure A1.   Observed and simulated DOC concentration in streamflow, using Van´t Hoff (1898) equation. Inset shows observed vs. simulated values.

Table A2. DOC model parameters based on Arrhenius (1889) equation.

| Parameter	Shallow Soil Layer	Deep Soil Layer
DOC_0 (mg L^{-1})	11.7	5.4
E_a (kJ mol^{-1})	79	30
T_0 (K)	294	294
Soil saturation parameter, b	1.6	0.4
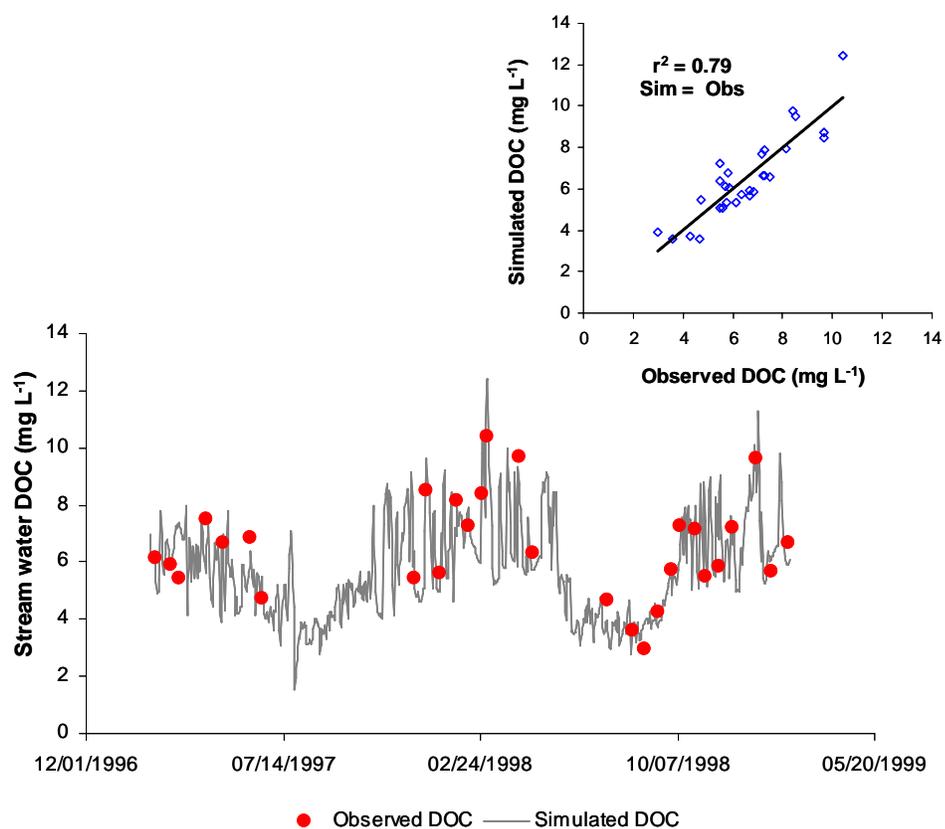
Figure A2. Observed and simulated DOC concentration in streamflow, using Arrhenius (1889) equation. Inset shows observed vs. simulated.

REFERENCES

Aitkenhead, J.A, McDowell, W.H. 2000. Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scale. Global Biogeochemical Cycles, 14 (1): 127-138.

Arrhenius, S., 1889. Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren. Zeitschrift für Physik Chemique, 4: 226-248.

Baveye, P., Boast, C.W., 1999. Physical scales and spatial predictability of transport processes in the environment. In: Corwin, D.L., Loague, K., Ellsworth, T.R. (Eds.), Assessment of Non-Point Source Pollution in the Vadose Zone, Geological Monograph Series 108. American Geophysical Union, Washington, pp. 261-280.

Bishop, K.H., Grip, H., Piggott, E.H., 1990. Spate-specific flow pathways in an episodically acid stream. In: Mason, B.J. (Ed.), The Surface Waters Acidification Programme. Cambridge University Press, Cambridge, pp. 107-119.

Bloem, J., de Ruiter, P.C., Koopman, G.J., Lebbink, G., Brussard, L., 1992. Microbial numbers and activity in dried and rewetted arable soil under integrated and conventional management. Soil Biology and Biochemistry, 24 (7): 655-665.

Boix-Fayos, C., Calvo-Cases, A., Imeson, A.C., Soriano-Soto, M.D., Tiemessen, I.R., 1998. Spatial and short-term temporal variations in runoff, soil aggregation and other soil properties along a Mediterranean climatological gradient. Catena, 33 (2): 123-138.

Boussinesq, J., 1903. Sur le débit, en temps de sécheresse, d'une source alimentée par une nappe d'eaux d'infiltration. C.R. Hebd. Sé-ances Acad. Sci., 136: 1511-1517.

Boussinesq, J., 1904. Recherches theoriques sur l'ecoulement des nappes d'eau infiltrees dans le sol et sur le debit des sources, J. Math. Pures Appl., 10: 5-78.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1996. Overview of a simple model describing variation of dissolved organic carbon in an upland catchment. Ecological Modelling, 86 (2-3): 183-188.

Brutsaert, W., Nieber, J.L., 1977. Regionalized drought flow hydrographs from a mature glaciated plateau. Water Resources Research, 13 (3): 637-643.

Casey, H., Farr, I.S., 1982. The influence of within-stream disturbance on dissolved nutrient levels during spates. Hydrobiologia, 91 (2): 447-462.

Chow, A.T., Tanji, K.K., Gao, S., 2003. Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. Water Research 37 (18): 4475-4485.

Christ, M.J., David, M.B., 1996. Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol. Soil Biology and Biochemistry, 28 (9): 1191-1199.

Clark, M.D., Gilmour, S.T., 1983. The effect of temperature on decomposition at optimum and saturated soil water contents. Soil Science Society of America Journal, 47 (5): 927-929.

Clark, M.J., Cresser, M.S., Smart, R., Chapman, P.J., Edwards, A.C., 2004. The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. Biogeochemistry, 68 (1): 1-19.

Cronan, C.S., Aiken, G.R., 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochimica et Cosmochimica Acta, 49 (8): 1697-1705.

Currie, W.S., Aber, J.D., 1997. Modeling leaching as a decomposition process in humid montane forests. Ecology, 78 (6): 1844-1860.

Davidson, E.A., Trumbore, S.E., Amundson, R., 2000. Biogeochemistry - Soil warming and organic carbon content. Nature, 408 (6814): 789-790.

Davies-Colley, R.J., Vant, W.N., 1987. Absorption of light by yellow substances in freshwater lakes. Limnology and Oceanography, 32 (2): 416-425.

Dunne, T., Leopold, L.B., 1978. Water in Environmental Planning. W.H. Freeman, New York, 818 pp.

Edwards, A.C., 1984. Some factors influencing elemental mobilities in an upland catchment in the Grampian Region. PhD Thesis, University of Aberdeen.

Edwards, A.C., Cresser, M.S., 1987. Relationships between ultraviolet absorbance and total organic carbon in two upland catchments. Water Research, 21 (1): 49-56.

Eshleman, K.N., Hemond, H.F., 1985. The role of organic acids in the acid-base chemistry of surface waters at Bickford watershed, Massachusetts, Water Resources Research, 21 (10): 1503-1510.

Farmer, V.C., Russell, J.D., Berrow, M.L., 1980. Imogolite and protoimogolite allophane in spodic horizons: evidence for a mobile aluminum silicate complex in podzol formation. Journal of Soil Science, 31 (4): 673-684.

Fernandez-Perez, M., Flores-Cespedes, F., Gonzalez-Pradas, E., Urena-Amate, M.D., Villafranca-Sanchez, M., Socias-Viciana, M., Perez-Garcia, S., 2005. Effects of dissolved organic carbon on phosphate retention on two calcareous soils. Journal of Agricultural and Food Chemistry, 53 (1): 84-89.

Fisher, S.G., Likens, G.E., 1972. Stream ecosystem: organic energy budget. BioScience, 22 (1): 33-35.

Freeze, R.A., Cherry, J.A., 1979. Groundwater. Prentice-Hall, Englewood Cliffs, N.J. 604 pp.

Gaudinski, J.B., Trumbore, S.E., Davidson, E.A., Zheng, S., 2000. Soil carbon cycling in a temperate forest: radiocarbon estimates of residence times, sequestration rates and partioning of fluxes. Biogeochemistry, 51 (1): 33-69.

Giardina, C.P., Ryan, M.G., 2000. Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature. Nature, 404 (6780): 858-861.

Grayson, R.B., Moore, I.D., McMahon, T.A., 1992. Physically based hydrologic modeling, 2. Is the concept realistic? Water Resources Research, 28 (10): 2659-2666.

Gregory, J.M., Mitchell, J.F.B., Brady, A.J., 1997. Summer drought in northern midlatitudes in a time-dependent CO_2 climate experiment. Journal of Climate, 10 (4): 662-686.

Grieve, I.C., 1984. Concentrations and annual loading of dissolved organic matter in a small moorland stream. Freshwater Biology, 14 (5): 533-537.

Grieve, I.C., 1991. A model of dissolved organic carbon concentrations in soil and stream waters. Hydrological Processes, 5 (3): 301-307.

Grossmann, J., Udluft, P., 1991. The extraction of soil water by the suction-cup method: A review. Journal of Soil Science, 42 (1): 83-93.

Guggenberger, G., Zech, W., 1994. Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, N.E. Bavaria, Germany. Soil Biology and Biochemistry, 26 (1): 19-27.

Hagedorn, F., Blaser, P., Siegwolf, R., 2002. Elevated atmospheric CO_2 and increased N deposition effects on dissolved organic carbon – clues from ^{13}C signature. Soil Biology and Biochemistry, 34 (3): 355-366.

Hagedorn, F., Saurer, M., Blaser, P., 2004. A ^{13}C tracer study to identify the origin of dissolved organic carbon in forested mineral soils. European Journal of Soil Science, 55 (1): 91-100.

Harrison, A.F., Harkness, D.D., Rowland, A.P., Garnette, J.S., Bacon, P.J., 2000. Annual carbon and nitrogen fluxes in soils along the European forest transect, determined using ^{14}C-bomb. In: Schulze, E.D. (Ed.), Carbon and Nitrogen Cycling in European Forest Ecosystems. Springer, Berlin, pp. 237-256.

Howard, D.M., Howard, P.J.A., 1993. Relationship between CO_2 evolution, moisture content and temperature for a range of soil types. Soil Biology and Biochemistry, 25 (11): 1537-1546.

Hu, H.Q., He, J.Z., Li, X.Y., Liu, F., 2001. Effect of several organic acids on phosphate adsorption by variable charge soils of central China. Environment International, 26 (5-6): 353-358.

Jones, D.L., Brassington, D.S., 1998. Sorption of organic acids in acid soils and its implications in the rhizosphere. European Journal of Soil Science, 49 (3): 447-455.

Jones, D.L., Prabowo, A.M., Kochian, L.V., 1996. Aluminium-organic acid interactions in acid soils II. Influence of solid phase sorption on organic acid-Al complexation and Al rhizotoxicity. Plant and Soil, 182 (2): 229-237.

Kaiser, K., Zech, W., 1998. Soil dissolved organic matter sorption as influenced by organic and sesquioxide coating and sorbed sulfate. Soil Science Society of America Journal, 62 (1): 129-136.

Kaiser, K., Guggenberger, G., Zech, W., 1996. Sorption of DOM and DOM fractions to forest soils. Geoderma, 74 (3-4): 281-303.

Kaiser, K., Guggenberger, G., Haumaier, L., Zech, W., 2001. Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) stands in northeastern Bavaria, Germany. Biogeochemistry, 55 (2): 103-143.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Science, 165 (4): 277-304.

Kätterer, T., Reichstein, M., Andrén, O., Lomander, A., 1998. Temperature dependence of organic matter decomposition: a critical review using literature data analyzed with different models. Biology and Fertility of Soils, 27 (3): 258-262.

Knorr, W., Prentice, I.C., House, J.I., Holland, E.A., 2005. Long-term sensitivity of soil carbon turnover to warming. Nature, 433 (7023): 298-301.

Lehmann, J., Schroth, G., 2003. Nutrient Leaching. In: Schroth, G., Sinclair, F.L. (Eds.), Trees, Crops and Soil fertility - Concepts and Research methods. CAB International, Wallingford, UK. pp. 151-166.

Leirós, M.C., Trasar-Cepeda, C., Seoane, S., Gil-Sotres, F., 1999. Dependence of mineralization of soil organic matter on temperature and moisture. Soil Biology and Biochemistry, 31 (3): 327-335.

Lloyd, J., Taylor, J.A., 1994. On the temperature dependence of soil respiration. Functional Ecology, 8 (3): 315-323.

Lomander, A., 2002. Organic Matter Turnover in Forest and Arable Land: Temperature and Moisture Effects and Dynamics of Heavy Metals. Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala.

Magid, J., Kjaergaard, C., Gorissen, A., Kuikman, P.J., 1999. Drying and rewetting of a loamy sand did not increase the turnover of native organic matter, but retarded the decomposition of added ^{14}C-labelled plant material. Soil Biology and Biochemistry, 31 (4): 595-602.

Martell, A.E., Motekaitis, R.J., Smith, R.M., 1988. Structure stability relationships of metal-complexes and metal speciation in environmental aqueous-solutions. Environmental Toxicology and Chemistry, 7 (6): 417-434.

Matzner, E., Davis, M., 1996. Chemical soil conditions in pristine *Nothofagus* forests of New Zealand as compared to German forests. Plant and Soil, 186 (2): 285-291.

McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press New York, 406 pp.

McCarthy, J.J., Canziani, O.F., Leary, N.A., Dokken, D.J., White, K.S., 2001. Climate Change 2001: Impacts, Adaptation, and Vulnerability. Cambridge University Press. 1032 pp.

McDowell, W.H., Fisher, S.G., 1976. Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecology, 57 (3): 561-569.

McDowell, W.H., Likens, G.E., 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs, 58 (3): 177-195.

McGlynn, B.L., McDonnell, J.J., 2003. The role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. Water Resources Research, 39 (4): 3-1 - 3-18.

McKeague, J.A., Chesire, M.V., Andreux, F., Berthelin, J., 1986. Organomineral complexes in relation to pedogenesis. In: Huang, P.M., Schnitzer, M. (Eds.), Interaction of Soil Minerals with Natural Organics and Microbes. SSSA, Madison, WI, pp. 549-592.

Mendoza, G.F., Steenhuis, T.S., Walter, M.T., Parlange, J-Y., 2003. Estimating basin-wide hydraulic parameters of a semi-arid mountainous watershed by recession-flow analysis. Journal of Hydrology, 279 (1-4): 57-69.

Meyer, J.L., Tate, C.M., 1983. The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecology, 64 (1): 33-44.

Michalzik, B., Tipping, E., Mulder, J., Gallardo Lancho, J.F., Matzner, E., Bryant, C.L., Clarke, N., Lofts, S., Vicente Esteban, M.A., 2003. Modelling the production and transport of dissolved organic carbon in forest soils. Biogeochemistry, 66 (3): 241-264.

Moore, A.M., 1986. Temperature and moisture dependence of decomposition rates of hardwood and coniferous leaf litter. Soil Biology and Biochemistry, 18 (4): 427-435.

Moore, T.R., 1989. Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand, 1. Maimai. Water Resources Research, 25 (6): 1321-1330.

Moore, T.R., Dalva, M., 2001. Some control on the release of dissolved organic carbon by plant tissues and soils. Soil Science, 166 (1): 38-47.

Moore, T.R., Jackson, K.J., 1989. Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand, 2. Larry River. Water Resources Research, 25 (6): 1331-1339.

Moore T.R., de Souza, W., Koprivnjak, J.F., 1992. Controls on the sorption of dissolved organic carbon by soils. Soil Science, 154 (2): 120-129.

Naiman, R.J., 1982. Characteristics of sediment and organic carbon export from pristine boreal forest watersheds. Canadian Journal of Fisheries and Aquatic Sciences, 39 (12): 1699-1718.

Neff, J.C., Asner, G.P., 2001. Dissolved Organic Carbon in Terrestrial Ecosystems: Synthesis and a Model. Ecosystems, 4 (1): 29-48.

Nyhan, J.W., 1976. Influence of soil temperature and water tension on the decomposition rate of carbon-14 labelled herbage. Soil Science, 121 (5): 288-293.

Orchard, V.A., Cook, F.J., 1983. Relationship between soil respiration and soil moisture. Soil Biology and Biochemistry, 15 (4): 447-453.

Parton, W.J., Ojima, D.S., Cole, D.V., Schimel, D.S., 1994. A general model for soil organic matter dynamics: sensitivity to litter chemistry, texture and management. In: Bryant, R.B., Arnold, R.W. (Eds.), Quantitative modeling of soil forming processes. SSA Special Publication 39. Soil Science Society of America. pp 147-167.

Pearce, A.J., Stewart, M.K., Sklash, M.G., 1986. Storm runoff in humid headwater catchments, 1. Where does the water come from?. Water Resources Research, 22 (8): 1263-1272.

Perrin, C., Michel, C., Andréassian, V., 2001. Does a large number of parameters enhance model performance? Comparative assessment of common catchment model structures on 429 catchments. Journal of Hydrology, 242 (3-4): 275-301.

Ponizovsky, A.A., Mironenko, E.V., Studenikina, T.A., 1999. Tartrate retention by a typic Haplustoll. Communications in Soil Science and Plant Analysis, 30 (1-2): 21-30.

Qualls, R.G., Haines, B.L., 1992. Biodegradability of dissolved organic carbon in forest throughfall, soil solution, and stream water. Soil Science Society of America Journal, 56 (2): 578-586.

Qualls, R.G., Haines, B.L., Swank, W.T., 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology, 72 (1): 254-266.

Reuter, J.H., Perdue, E.M., 1977. Importance of heavy metal - organic matter interactions in natural waters. Geochimica et Cosmochimica Acta, 41 (2): 325-334.

Salmon, C.D., Walter, M.T., Hedin, L.O., Brown, M.G., 2001. Hydrological controls on chemical export from a pristine old-growth forest in Chile. Journal of Hydrology, 253 (1-4): 69-80.

Schiff, S.L., Aravena, R., Trumbore, S.E., Hinton, M.J., Elgood, R., Dillon, P.J., 1997. Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ^{13}C and ^{14}C. Biogeochemistry, 36 (1): 43-65.

Schindler, D.W., Bayley, S.E., Curtis, P.J., Parker, B.R., Stainton, M.P., Kelly, C.A., 1992. Natural and man-caused factors affecting the abundance and cycling of

dissolve organic substances in Precambrian shield lakes. Hydrobiologia, 229: 1-21.

Schlesinger, W.H., Melack, J.M., 1981. Transport of organic-carbon in the world rivers. Tellus, 33 (2): 172-187.

Senesi, N., 1992. Binding mechanisms of pesticides to soil humic substances. Science of the Total Environment, 123/124: 63-76.

Siddiqui, M.S., Amy, G.L., Murphy, B.D., 1997. Ozone enhanced removal of natural organic matter from drinking water source. Water Research, 31 (12): 3098-3106.

Sjöberg, G., Bergkvist, B., Berggren, D., Nilsson, S.I., 2003. Long-term N addition effects on the C mineralization and DOC production in mor humus under spruce. Soil Biology and Biochemistry, 35 (10): 1305-1315.

Steenhuis, T.S., Van der Molen, W.H., 1986. The Thornthwaite-Mather procedure as a simple engineering method to predict recharge. Journal of Hydrology, 84 (3-4): 221-229.

Steenhuis, T.S., Parlange, J-Y., Sanford, W.E., Heilig, A., Stagnitti, F., Walter, M.F., 1999. Can we distinguish Richard's and Boussinesq's equations for hillslopes?: The Coweeta experiment revisited. Water Resources Research, 35 (2): 589-594.

Stewart, A.J., Wetzel, R.G., 1981. Dissolved humic materials: Photodegradation, sediment effects, and reactivity with phosphate and calcium carbonate precipitation. Archiv für Hydrobiologie, 92 (3): 265-286.

Stott, D.E., Elliott, L.F., Papendick, R.I., Campbell, G.S., 1986. Low temperature or low water potential effects on the microbial decomposition of wheat residue. Soil Biology and Biochemistry, 18 (6): 577-582.

Tegen, I., Dörr, H., 1996. ^{14}C measurements of soil organic matter, soil CO_2 and dissolved organic carbon (1987-1992). Radiocarbon, 38 (2): 247-251.

Thornthwaite, C.W., Mather, J.R., 1955. The water balance. Publications in Climatology, 8 (1): 1-104.

Trumbore, S., 2000. Age of soil organic matter and soil respiration: Radiocarbon constraints on belowground C dynamics. Ecological Applications, 10 (2): 399-411.

Trumbore, S.E., Chadwick, O.A., Amundson, R., 1996. Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change. Science, 272 (5260): 393-396.

Trumbore, S.E., Schiff, S.L., Aravena, R., Elgood, R., 1992. Sources and transformation of dissolved organic carbon in the Harp Lake forested catchment: the role of soils. Radiocarbon, 34 (3): 626-635.

Vance, G.F., David, M.B., 1991. Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest floor, central Maine, U.S.A. Geochimica et Cosmochimica Acta, 55 (12): 3611-3625.

Van Hees, P.A.W., Jones, D.L., Finlay, R., Godbold, D.L., Lundström, U.S., 2005. The carbon we do not see—the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review. Soil Biology and Biochemistry, 37 (1): 1-13.

Van Hees, P.A.W., Vinogradoff, S.I., Edwards, A.C., Godbold, D.L., Jones, D.L., 2003. Low molecular weight organic acid adsorption in forest soils: effects on soil solution concentrations and biodegradation rates. Soil Biology and Biochemistry, 35 (8): 1015-1026.

Van't Hoff, J.H., 1898. Lectures on Theoretical and Physical Chemistry. Part 1. Chemical Dynamics. Edward Arnold, London, pp 224-229.

Vitousek, P.M., 1982. Nutrient cycling and nutrient-use efficiency. American Naturalist, 119 (4): 553-572.

Vitousek, P.M., Reiners, W.A., 1975. Ecosystem succession and nutrient retention: Hypothesis. BioScience, 25 (6): 376-381.

Watters, W.A., Fleming, C.A., 1962. Contributions to the geology and palaeontology of Chiloe Island, Southern Chile. Philosophical Transactions of the Royal Society of London, Series B, Biological Sciences, 263 (853): 369-408.

Wehrer, M., Totsche, K.U., 2005. Determination of effective release rates of polycyclic aromatic hydrocarbons and dissolved organic carbon by column outflow experiments. European Journal of Soil Science, 56 (6): 803-813.

Williamson, C.E., Zagarese, H.E., 1994. The impact of UV-B radiation on pelagic freshwater ecosystems. Ergebnisse der Limnologie, 43. 225 pp.

Worrall, F., Burt, T., Shedden, R., 2003. Long term records of riverine dissolved organic matter. Biogeochemistry, 64 (2): 165-178.

Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P., 2004. Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry, 70 (3): 369-402.

Yano, Y., McDowell, W.H., Aber, J.D., 2000. Biodegradable dissolved organic carbon

in forest soil solution and effects of chronic nitrogen deposition. Soil Biology and Biochemistry, 32 (11-12): 1743-1751.

Zarin, D.J., Johnson, A.H., Thomas, S.M., 1998. Soil organic carbon and nutrient status in old-growth montane coniferous forest watersheds, Isla Chiloé, Chile. Plant Soil, 201 (2): 251-258.

Zsolnay, A., 1996. Dissolved humus in soil waters. In: Piccolo, A. (Ed.), Humic Substances in Terrestrial Ecosystems. Elsevier Science, Amsterdam, pp. 171-223.