Modeling dissolved organic carbon in temperate forest soils: TRIPLEX-DOC model development and validation

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*To "**Geoscientific Model Development**"*

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Abstract

Even though dissolved organic carbon (DOC) is the most active carbon (C) cycling in soil organic carbon (SOC) pools, it receives little attention from the global C budget. DOC fluxes are critical to aquatic ecosystem inputs and contribute to the C balance of terrestrial ecosystems, but few ecosystem models have attempted to integrate DOC dynamics into terrestrial C cycling. This study introduces a new process-based model, TRIPLEX-DOC, that is capable of estimating DOC dynamics in forest soils by incorporating both ecological drivers and biogeochemical processes. TRIPLEX-DOC was developed from Forest-DNDC, a biogeochemical model simulating C and nitrogen (N) dynamics, coupled with a new DOC process module that predicts metabolic transformations, sorption/desorption, and DOC leaching in forest soils. The model was validated against field observations of DOC concentrations and fluxes at white pine forest stands located in southern Ontario, Canada. The model was able to simulate seasonal dynamics of DOC concentrations and the magnitudes observed within different soil layers, as well as DOC leaching in the age-sequence of these forests. Additionally, TRIPLEX-DOC estimated the effect of forest harvesting on DOC leaching, with a significant increase following harvesting, illustrating that land use change is of critical importance in regulating DOC leaching in temperate forests as an important source of C input to aquatic ecosystems.

Keywords: DOC simulation; soil DOC leaching; terrestrial carbon cycle; pine forest; land use change

1. Introduction

Recent climatic change projections have led to a great deal of attention being paid to carbon (C) cycling patterns and controls, particularly those factors that determine whether an ecosystem, from catchment to regional scales, is a net source or sink of atmospheric carbon dioxide (CO_2) (e.g. Jenerette and Lal, 2005; Chapin III et al., 2006; Cole et al., 2007; Buffam et al., 2011). Northern ecosystems have been identified as being especially important for CO_2 exchanges that take place between land and the atmosphere, with temperate forests regarded as a potential C sink (Chapin et al., 2000; Dunn et al., 2007). In contrast to terrestrial ecosystems, temperate aquatic ecosystems are a net C source owing to the mineralization of organic C imported from terrestrial ecosystems and the resultant degassing of inorganic C in lakes and streams (Sobek et al., 2003; Roehm et al., 2009; Humborg et al., 2010; Kosten et al., 2010; Butman and Raymond, 2011; Dennis et al., 2012; Lapierre et al., 2012). Only a handful of studies have attempted to comprehensively integrate terrestrial watershed C balances with their aquatic components. As a result, net ecosystem exchanges (NEE) of temperate terrestrial ecosystems are typically investigated without taking into account C runoff to aquatic ecosystems and the resultant C loss. Therefore, an integrative approach to examine C budgets for both terrestrial and aquatic ecosystems will help us to understand and estimate net C balances on both catchment and regional scales (Grimm et al., 2003; Jenerette and Lal, 2005; Chapin III, 2006; Cole et al., 2007; Buffam et al., 2011).

Understanding the interactive dynamics between terrestrial and aquatic ecosystems has been hampered by uncertainties. Processing DOC is one such uncertainty (Hanson et al., 2004; Chapin III, 2006; Cole et al., 2007; Buffam et al., 2011). DOC plays a key role in the transport of soil nutrients (Qualls et al., 1991; Kaiser et al., 2001; Kaiser and Kalbitz, 2012), leaching from the forest litter layer into mineral soil and then discharged into streams and lakes. Globally, terrestrial ecosystem DOC export to oceans was estimated at approximately 0.17 to 0.36 Pg C yr^{-1} (Aitkenhead and McDowell, 2000; Harrison et al., 2005; Dai et al., 2012). Although DOC exports to water bodies are small relative to other terrestrial C fluxes (Neff and Asner 2001; Cole et al., 2007), they are nonetheless critical to C biogeochemical cycling and budgets in aquatic ecosystems (del Giorgio et al., 1999; Hanson et al., 2004; McCallister and del Giorgio, 2008).

Disturbances in the forested watershed or catchments resulting from forest management activities can alter biogeochemical processes in soils by changing species composition, soil characteristics, soil moisture and soil temperature regimes, soil microbial activity, and water flux, thereby potentially causing extensive alterations to occur to soil DOC dynamics (Kreutzweiser et al., 2008). Little attention has been paid to the question of how DOC concentrations, fluxes, and chemistry vary with land use and forest management practices.

In the past decade, considerable progress has been made in modeling approaches used to estimate DOC flux, such as improvements in soil and watershed C dynamics (Boyer et al., 1996; Currie and Aber, 1997; Band et al., 2001; Raymond et al., 2010; Xu et al., 2012). Models have used a variety of physical and chemical watershed properties to predict DOC concentration or export either regionally or globally, based on empirical relationships between DOC and watershed attributes. Examples are basin size and slope (Clair et al., 1994;

Clair and Ehrman, 1996), soil characteristics (Nelson et al., 1993; Hope et al., 1997; Aitkenhead et al., 1999; Aitkenhead and McDowell, 2000), and land cover type (Eckhardt and Moore, 1990; Dillon and Molot, 1997; Aitkenhead et al., 1999). However, these empirical models often contain numerous environmental variables, some of which may be qualitative in nature, making it impossible to apply to conditions of climate change and human activity over long time spans. To overcome the shortcomings of empirical models, simplistic, process-based mechanistic models that couple hydrological, biological, and geochemical processes have been developed to predict DOC dynamics (Band et al., 2001; Xu et al., 2012).

A handful of more complex process-based soil DOC models have recently been developed. Neff and Asner (2001), for example, have proposed a model related to DOC transport for terrestrial ecosystems, involving rates of production of DOC by vegetation and organic soil compounds, soil profile transport, mineral soil horizon adsorption, and the eventual export from a system. Michalzik et al. (2003) relied on ^{14}C data to determine the age of soil organic matter. Lumsdon et al. (2005) simulated changing organic matter solubility as a function of competitive cation adsorption and hydrophobicity in a single soil horizon. Although these DOC models reasonably simulate soil DOC dynamics, they are currently incapable of investigating the potential impacts of land use change on the fate of DOC, such as forest management practices.

The broad aim in this study is to develop a general and quantitative approach at the landscape scale to simulate changes in soil DOC concentration and flux resulting primarily from successional changes in forest type, productivity, aboveground biomass, litterfall, and forest floor biomass accumulation through stand development. The specific objectives are: (a) to introduce the development of TRIPLEX-DOC, a new DOC process-based model was used in conjunction with the forest soil C model to simulate seasonal and annual DOC concentration and flux patterns from precipitation to subsoil seepage; and (b) to assess land use impacts on dynamics and temporal changes in DOC soil leaching.

2. Model description and methods

DOC concentrations and fluxes were assigned for a vertical profile for a given forest ecosystem as follows (see Fig. 1): input through precipitation and throughfall; forest floor biological production and leaching; subsequent transfer to soil A, B, and C layers, including physical sorption/desorption processes; and the eventual export from a given forest ecosystem.

Fig. 1 provides an overall structure and framework of TRIPLEX-DOC which includes forest growth, soil carbon, hydrological and thermal conditions, and DOC dynamics simulation. This model is primarily based on Forest-DNDC (Li et al., 2000), a process-based biogeochemical model that simulates C and N dynamics and trace gas emissions in upland forest ecosystems.

The forest growth submodel (Li et al., 2000) was adopted from the PnET model (Aber and Federer, 1992), a forest physiology model developed to predict forest photosynthesis, respiration, organic C production and allocation, and litter production. This submodel is driven by solar radiation, temperature, water and N availability, and transfers litter production, water and N demands, and root respiration data to the soil climate submodel or the decomposition submodel.

Soil C is divided into three organic matter pools (Li et al., 2000): residues (primary plant residues), microbial biomass, and humads. Each pool has both a labile and resistant component (Fig. 1). Soil organic matter (SOM) content is related to litter quantity and quality. The forest growth submodel predicts litter production and the litter C/N ratio. After litterfall, the decomposition submodel allocates fresh litter to the very labile, labile, and resistant litter pools based on the litter C/N ratio; then quantifies the decomposition of organic matter resulting in DOC substrate concentrations, ammonium (NH_4^+), nitrate (NO_3^-), and CO_2, based on decay rates (k-values) that are dependent on organic matter quality and soil environmental conditions (e.g., soil temperature, soil moisture, and clay content in soil).

The soil climate submodel converts daily climate data into soil temperature and moisture profiles and is used to calculate soil oxygen availability within the forest soil profile. The hydrological submodel (Li et al., 2000) simulates soil water flux. The soil profile is divided into layers exhibiting different characteristics (e.g., organic soils and mineral soils). This submodel takes into account water input (e.g., precipitation, surface inflow, snow and ice melt), output (evaporation and transpiration), runoff, and water transfer within the unsaturated zone (infiltration, gravity drainage, and matrix redistribution).

Forest-DNDC has previously been used to successfully predict trace gas emissions in regional studies (Kesik et al., 2005; Kiese et al., 2005) and effects of forest management practices on soil environmental factors (Sun et al., 2006; Dai et al., 2012). Additionally, the model is currently parameterized for 12 forest ecosystem tree species/genera: pine, spruce, hemlock, fir, hardwoods, oak, birch, beech, slash pine, larch, cypress, and evergreen oak (Li et al., 2000). It is particularly useful when investigating DOC dynamics for different forest types at a landscape level.

Although Forest-DNDC was developed to competently administer the production of DOC by microorganisms associated with litter C, microbial biomass, and humads decomposition (Li et al., 2000), the model does not include throughfall DOC production. Because mean annual concentrations of DOC in throughfall are between 3 and 35 mg l^{-1} in temperate forests, and the fluxes of DOC range from 40 to 160 kg DOC ha^{-1} y^{-1} (Michalzik et al., 2001), it is an important source that derives as rainfall passes through forest canopies. Moreover, Forest-DNDC also does not adequately estimate DOC consumption and does not include the capacity to simulate sorption/desorption, two key processes that determine DOC decomposition and stabilization in soils (Neff and Asner, 2001). As a result, Forest-DNDC overestimates DOC concentrations in different soil layers (Fig. 2) and makes it impossible to reliably simulate DOC leaching from soils. To overcome these shortcomings, the DOC dynamics submodel incorporates a more precise algorithm describing contributions of throughfall, DOC consumption, and DOC sorption/desorption was integrated into Forest-DNDC. The new model is named as TRIPLEX-DOC, which is more suitable in predicting forest soil DOC metabolic transformations, sorption/desorption, and leaching in changing environmental conditions.

Soil C pools and decomposition processes, forest growth, and hydrological dynamics have been well documented and are described in detail in the DNDC (Li et al., 1992), PnET (Aber and Federer, 1992), and Forest-DNDC models (Li et al., 2000). However, the scope of this study was only to describe DOC processes and the newly redesigned TRIPLEX-DOC, including DOC production and consumption as well as sorption/desorption.

2.1 DOC production and consumption submodel

The biological production and consumption of DOC play an important role in the regulation of soil DOC flux. DOC production *via* throughfall was calculated as follows:

$$DOC_{Interception} = R_i \times [DOC] \tag{1}$$

where $DOC_{Interception}$ is DOC production via throughfall; DOC is the concentration in throughfall; and R_i is interception, a highly simplified function based on the Leaf Area Index (LAI) by Rutter et al. (1971). The other production processes of DOC by microorganisms associated with litter C, root exudates and humified organic matter were adopted from Forest-DNDC (Li et al., 2000).

The major factors affecting DOC biodegradation and the size of these pools included its molecular size, chemical composition (e.g. quantities of carbohydrates, lignin, etc.), polarity and acidity, as well as the chemical characteristics of the solution itself, such as pH, nutrient content, oxygen and metal concentrations (Marschner and Kalbitz, 2003). Because the estimates of decomposition rates are difficult to model by a simple approach considering all the above-mentioned factors, numerous studies have focused on DOC fractions that decompose over a range of time spans (Dahm, 1981; Zsolnay and Steindl, 1991; Qualls and Haines, 1992; Jandl and Sollins, 1997; Yano et al., 1998; Kalbitz et al. 2003). Two kinetically distinct pools of biodegradable DOC have been recognized as fast and slow, and a double exponential equation for two distinct DOC pools with different mineralization rate constants fitted well to the measured data (Qualls and Haines 1992; Kalbitz et al. 2003; Kiikkila et al., 2006; McDowell et al., 2006).

$$DOC_{remain}(\%) = (100 - b) \times 10^{-k_1 t} + b \times 10^{-k_2 t} \tag{2}$$

where t is time (units of day); 100-b and b are the initial percentages of rapidly and slowly decaying components, respectively; and k_1 and k_2 are the rate constants of the two components determined from a range of litters and soils in Canadian forests (Turgeon, 2008).

2.2 DOC sorption/desorption submodel

Sorption and desorption are two key processes related to soil DOC stabilization and production. Because DOC continuously moves in and out of solutions in soil, the Initial Mass (IM) isotherm best represents DOC sorption reactions (Nodvin et al., 1986; Kaiser et al., 1996). This is described by the following linear isotherm:

$$RE = mX_i - b \tag{3}$$

where RE is the amount of DOC released into or removed from a solution; m is the dimensionless regression parameter; X_i is the initial concentration of DOC (mg g soil^{-1}); and b is the intercept (mg DOC released per gram of soil when $X_i = 0$). Functionally, m and b can be viewed as measures of the tendency of soil to adsorb and release DOC. This linear sorption isotherm model is the most widely used by researchers and successfully describes the dissolved organic matter (DOM) sorption phenomena in soil horizons with low sorption capacity or cases that occur within a narrow concentration range (Vandenbruwane et al., 2007).

For DOC, the affinity of soils is closely linked to a number of soil properties. Generally, there are positive correlations between *m* and soil clay content, dithionite extractable iron, and oxalate extractable aluminum (Moore et al., 1992; Nelson et al., 1993; Kaiser et al., 1996; Kaiser and Zech, 1998; Kothawala et al., 2009). Pedotransfer functions (PTF) used in estimating the two parameters (*m* and *b*) were developed by Moore et al. (1992):

$$m_o = 0.451 + 0.02\log(Fe_{cbd}) + 0.032\sqrt{Al_{ox}} + 0.064\log(OC) \tag{4}$$

$$b_o = 0.145 + 0.103\log(OC) - 0.055\sqrt{Al_{ox}} - 0.045\log(Fe_{cbd}) \tag{5}$$

where OC, Al_{ox}, and Fe_{cbd} denote the contents (in mass %) of organic C, oxalate extractable aluminum, and dithionite-citrate-bicarbonate extractable iron; soil properties of Al_{ox} and Fe_{cbd}. were established from Canadian soils (Kothawala et al., 2009). Parameters *m* and *b* are given as a fraction and in units of g kg^{-1}, respectively.

Hydrologic conditions influence the leaching and apparent reactivity of DOC. Within soils, factors such as hydraulic conductivity and bypass flow capacity affect the concentration and flux of inorganic elements in a solution (Prendergast, 1995) and it is likely that DOC behaves in a similar manner (Radulivich et al., 1992). Weigand and Totshe (1998) have provided strong evidence that water flow rates through soil layers affect the fate of DOC. A recent analysis of stream discharge and DOM measurements from 30 forested watersheds in the eastern United States revealed the importance of hydrologic events in regulating the transport of DOC to downstream ecosystems (Raymond and Saiers, 2010).

Sorption affinity m is reduced by a modifier (H_m) that scales with the rate of movement of a solution through soil:

$$m = m_o - H_m \tag{6}$$

This parameterization denotes a kinetic aspect of sorption reaction and a maximum flow rate induced variation in m of 20% for soils with a 100% clay content:

$$H_m = m_o \times 0.2 \times \left(\frac{v}{v_s} \right) \times \left(\frac{\%Clay}{100} \right) \tag{7}$$

where v is the actual pore water velocity, and v_s is the pore water velocity in saturated conditions (a soil-specific parameter). These parameters were established from Forest-DNDC (Li et al., 2000). The equation scales with clay content because the rate of sorption does not appear to be affected by hydrologic flux rates in sandy soils (Weigand and Totsche, 1998).

In contrast to sorption flux, desorption flux appears to be driven by concentration gradients that increase with solution flow (Weigand and Tosche, 1998). Thus, b is increased and calculated as follows:

$$b = b_o + H_b \tag{8}$$

$$H_b = b_o \times 0.2 \times \left(\frac{v}{v_s} \right) \times \left(\frac{\%Clay}{100} \right) \tag{9}$$

As it is with the down-regulating H_m modifier, H_b scales with flow velocity and clay content; however, in contrast to how flow affects m, b is incremented by H_b, establishing a flow-dependent desorption coefficient.

The above DOC submodel was incorporated into Forest-DNDC to simulate DOC flux in temperate forest soils. The program of DOC submodel was developed using the C^{++} language as used in the Forest-DNDC. The Forest-DNDC model is available at http//www.dndc.sr.unh.edu, and its program code is not changed in this study. For simulations, the soil profile (1.0 m) was divided into horizontal layers with a typical thickness of 4 cm. Each layer was assumed to have uniform properties (e.g., temperature, moisture, substrate and microbe concentrations, etc.), and all decomposition calculations were carried out layer by layer. The model was run in a daily time step.

3. Model input and validation data

TRIPLEX-DOC inputs and file format are same as Forest-DNDC model, including daily climate data (maximum and minimum temperature, and precipitation), soil properties (soil type, soil texture, and pH), and forest characteristics and management (forest type, stand age, and percentage of trees removed or harvested).

DOC data used to test and validate our model were measured at the Turkey Point Flux Station and have been reported in Peichl et al. (2007). These data provided an opportunity to quantify the role of DOC in upland forest ecosystems and through comparisons between sites to identify critical controls as well as to test model performance. Turkey Point Flux Station is located on the northern shore of Lake Erie in southern Ontario, Canada (Arain and Restrepo-Coupe, 2005; Peichl et al., 2010). It consists of four eastern white pine (Pinus *strobus* L.) forests that were planted in 2002 (2 year-old), 1989 (15 year-old), 1974 (30 year-old), and 1939 (65 year-old), respectively. All four stands are located within a 20 km radius of each other. The average altitude of the sites is 220 m, the 30 year mean annual temperature is 7.8°C and annual precipitation is 1010 mm, of which 438 mm falls from May to September (Environment Canada norms from 1971 to 2000 taken at Delhi, Ontario). Mean annual snowfall is 133 cm, the mean annual frost-free period is 160 days and the mean growing season length is approximately 212 days (Presant and Acton, 1984). Turkey Point sites are situated on lacustrine sandy plains with Brunisolic Luvisol and Gleyed Brunisolic Luvisol sandy soils (about 98% sand, 1% silt, 1% clay) which are well drained and have low-to-moderate water holding capacity. Meteorological and soil temperature and soil moisture (at several depths at two locations at each site) data were collected at all four age-sequence sites using automatic weather stations. Further site and instrumentation details are given in Table 1 and Peichl and Arain (2006) and Peichl et al. (2010).

DOC data used in our study were collected at monthly intervals from the end of May to the end of November 2004 and at biweekly intervals from early April to November 2005 and from April to mid-May 2006. Throughfall DOC was collected in plastic buckets equipped with a 10 cm radius funnel with necks fitted with glass wool. Leachates from beneath the forest floor and the organic-rich Ah-horizon were sampled using zero-tension lysimeters. Porous cup suction lysimeters at 25, 50, and 100 cm depth were used to sample mineral soils. A detailed description of DOC measurements is given in Peichl et al. (2007).

To mimic forest harvesting, a model simulation was performed for a 80 year-old stand where 50% of the trees were excluded, while biomass was left on the forest floor.

4. Model validation

4.1 Carbon density at different forest ages

The model was run along a series of different forest ages, applying default forest parameter settings of pine (Li et al., 2000) for temperate forest growth. Fig. 3 shows simulation results for 2, 15, 30, and 65 year-old white pine stands compared to observed C density in foliage, wood, forest floor, and soil. Values approximate to 1:1 indicating that the forest growth submodel performed well and therefore has the potential to predict temperate pine forest growth for different stand ages.

4.2 DOC concentrations and leaching in different soil layers

Temporal variation in soil water DOC concentrations and fluxes were simulated and the model was able to capture reasonably well the temporal variations (maximum in summer and minimum in winter) in DOC concentrations in the forest floor or litter layer compared to observations at the 65 and 30 year-old forests (Fig. 4). However, model simulations yielded less temporal variation in DOC concentrations than observed in summer for a 15 year-old forest stand. Model simulations showed good agreement with field observations of DOC in the Ah layer with respect to seasonality and magnitude for the 65 and 15 year-old forest stands but yielded lower DOC concentrations in summer than observed in the 30 year-old forest stand (Fig. 4).

Model simulations showed that DOC concentrations throughout a one year period clearly decreased from the litter layer, to the A horizon and the B mineral horizon, reasonably consistent with observations for both the 65 and 15 year-old forest stands which data had been previously measured (Fig. 5).

Simulated DOC leaching from forests of 2, 15, 30, and 65 year-old stands (Fig. 6) showed a deceasing trend with increasing stand age, in good agreement with field observations throughout the age-sequence investigation. Overall performance indicated that the model was able to capture the primary mechanisms responsible for the variability and dynamics in observed DOC concentrations and leaching in these white pine forest soils.

4.3 Sensitivity analysis

A variety of equations have been used within TRIPLEX-DOC to numerically describe processes involved in C cycle and DOC leaching in forest ecosystems and to quantify their sensitivity to environmental factors. A sensitivity analysis examined the impact of changes in environmental conditions (daily maximum and minimum temperature, and precipitation) on eight model predictions (net primary productivity (NPP), total biomass, floor carbon, soil carbon, annual mean DOC concentration in floor layer, annual mean DOC concentration in Ah layer, annual mean DOC concentration in mineral 50cm, and DOC leaching), that are considered to be the most important variables for overall forest C dynamics and DOC processes in soil at different age forests (Table 2). It provides an opportunity to test the basic behavior of the new model. The sensitivity was tested for model drivers by varying one factor and keeping all others constant, applying a 1℃ increase/decrease in daily maximum and minimum temperature, and a 10% increase/decrease in precipitation to baseline scenarios.

As expected, NPP and total biomass for all age forests responded positively to increases in both daily minimum temperature and precipitation (Table 2). A 1℃ increase in minimum temperature resulted in the increases of 1.9 to 7.5% and 2.8 to 9.2% in NPP and total biomass, respectively, with more response for the young forests. The responses of NPP and total biomass to a 10% increase in precipitation were less pronounced (only 0.1 to 3.1% increase). On the other hand, the NPP and total biomass responded negatively to increases in the maximum temperature. The model predictions of positive soil carbon responses with decreasing temperature and precipitation were also observed (Table 2).

The annual mean DOC concentrations in the forest floor layer, Ah layer, and in mineral soil responded negatively to changes in the minimum temperature and precipitation. However, this relationship was reversed to changes in the maximum temperature (except the 2 year-old forest). The DOC leaching responded positively to the increase of precipitation for all four age forests. The response of DOC leaching to precipitation change (-22.8 to 35.7%) was more significant than the response to temperature (-4.5 to 4.8%).

5. Discussion

5.1 Comparison to previous models

The aim of this study was to introduce TRIPLEX-DOC, a newly redesigned process-based model developed to investigate soil DOC processes. It incorporates many of the best features of existing C processing models, including DOC production and decomposition, sorption/desorption into soil solids, and transport by water percolation. It extends

Forest-DNDC in predicting C cycles by including detailed model representations of soil DOC dynamics and leaching.

The key innovations compared to previous DOC models (Neff and Asner, 2001; Michalzik et al., 2003; Lumsdon et al., 2005) are that TRIPLEX-DOC is the first DOC cycling model to explicitly include land cover type effects for different forest stand ages, soil C biogeochemistry, and hydrological flow on DOC dynamics. TRIPLEX-DOC was validated using observed data, showing that the model can successfully simulate soil DOC concentrations and leaching for different aged forest stands.

The TRIPLEX-DOC modeled DOC production includes fresh litter, root exudates, and humified organic matter, all of which contribute substantial amounts of belowground DOC (Li et al., 1992; Guggenberger, 1994) whereas DOC was produced only from litter in the DocMod model (Currie and Aber, 1997) and only from humified organic matter in the DyDoc model (Michalzik et al., 2003). TRIPLEX-DOC shares similar features to the DOC model (Neff and Asner, 2001) in that both models generate DOC from both litter and soil organic matter. However, estimates from litter in the DOC model (Neff and Asner, 2001) are based on statistical relationships between DOC production and the ratio of lignin to N in incoming litter, whereas estimates from TRIPLEX-DOC are based on Forest-DNDC (Li et al., 2000), a process-based model. In this case, fresh litter is partitioned into very labile, labile, and resistant litter pools based on the input litter C/N ratio, after which each litter pool produces DOC based on its specific decomposition rate, temperature, and soil moisture.

TRIPLEX-DOC adopted a two-fold DOC pool approach to DOC decomposition, with labile and recalcitrant fractions and based on the two-component exponential decay model (Qualls and Haines, 1992; Kalbitz et al. 2003; Kiikkila et al., 2006; McDowell et al., 2006). In contrast, the DyDoc model (Michalzik et al., 2003) is composed of three humic fractions corresponding approximately to hydrophilic (Hum-1), hydrophobic acids (Hum-2), and humic acid and aged humin (Hum-3) for which metabolic transformations are described with first-order decay. The DOC model (Neff and Asner, 2001) only comprises a DOC pool, recycling into soil microbial biomass. Another difference between the models is that DyDOC tracks ^{14}C through a plant-soil-water system, thereby providing additional timescale information but TRIPLEX-DOC confines itself to an overall daily DOC leaching flux.

5.2 Environmental controls on DOC production and transport

Knowledge of factors and processes that regulate DOC production and transport in forest soils is important for the prediction of soil C cycles under a varying climate. Production of DOC in the forest litter layer is thought to be primarily controlled by biological processes (e.g., decomposition of litter, humus, and root exudation), suggesting a high sensitivity to changes in soil temperature and moisture (Kalbitz et al., 2000). Simulations carried out for this study showed a seasonal pattern, the highest DOC concentration occurring in summer in the litter layer and in the Ah layers (Fig. 4). These predications are consistent with results from field observations (Michalzik and Matzner, 1999; Solinger et al., 2001; Kaiser et al., 2002) and laboratory studies (Clark and Gilmour, 1983; Christ and David, 1996; Gödde et al., 1996; Moore et al., 2008), which documented a generally increasing DOC production with increasing soil temperature and moisture. DOC concentrations are higher in the growing season than in non-growing seasons mainly because of the greater microbial activity in response to higher temperatures and moisture of the forest floor (Kalbitz et al., 2000; Yano et al., 2000; Kaiser et al., 2001).

Our results revealed a strong relationship between water flux and DOC flux in all soil layers, exhibiting linear relationships when summed to weekly fluxes (Fig. 7). These results are to be expected since DOC and water move in unison, but they imply that hydrologic flux rather than production mechanisms are the limiting factors of DOC flux. Results were similar to the conclusions based on DOC model simulations (Neff and Asner, 2001) and confirmed by a plot scale experiment carried out in the field (Tipping et al., 1999), reporting an increase in DOC flux with increasing amounts of water passing through the soil.

5.3 Impact of land use on DOC leachate

Understanding the effects of land use change on DOC concentrations and export is imperative when attempting to predict large-scale C dynamics and changes in landscape C budgets. Large areas have undergone land use change through forest regeneration and more recently through afforestation on marginal agricultural land, affecting ecosystem C dynamics (Quideau and Bockheim, 1997; Khomutova et al., 2000; Mattson et al., 2005). TRIPLEX-DOC successfully simulated increases in DOC concentrations in solutions obtained from the litter floor and Ah layer with the increasing age of forest stands (Fig. 4) accompanied with an increasing accumulation of tree and forest floor biomass. Despite higher DOC concentrations found in soil solutions of older stands, results suggest that soil

DOC leaching may be decreased by up to 4-fold for the 65 year-old stand (Fig. 6) compared to a recently established forest stand (2 year-old). This decrease in DOC leaching was mainly attributable to a decline in water loss due to increased water uptake by forest evapotranspiration, indicating the importance of hydrological controls on DOC processes.

TRIPLEX-DOC predicted a significant increase (approximately 4-fold) in DOC leaching from soil following removal of 50% trees compared pre-removal conditions (Fig. 8). This result is in general agreement with results from a number of studies that measured increased DOC export or concentrations (by 2 to 5 fold) in watershed soil water shortly after logging (Plamondon et al., 1982; Hinton et al., 1997; Startsev et al., 1998). This increase in DOC leaching may be attributable to the quantity of biomass (leaves, stem, and roots) left on the ground and soil, which is considered to be a primary source of increased DOC concentration and flux (Qualls et al., 2000; Piirainen et al., 2002). On the other hand, an increase in microbial activity could also be responsible for increased forest DOC concentrations and flux after forest harvesting. This is because temperature and moisture, critical factors for microbial activity, generally increases after harvesting due to more open canopy and reduction in evapotranspiration from the root zone (Londo et al., 1999) and may result in an increased production of DOC (Kaiser et al., 2001; Kalbitz et al., 2000; Neff and Asner, 2001). Water flux also contributes to the release of soil DOC (Kalbitz et al., 2000; Judd and Kling, 2002). It is important to note that forest canopy interception of precipitation and evapotranspiration would decrease after harvesting, increasing water flux to soils and thus resulting in an increase in soil DOC leaching.

6. Conclusion and future improvements

TRIPLEX-DOC is a useful tool when quantifying DOC concentrations and leaching in temperate forest soils as well as in predicting how changes in land use may impact DOC. It is compatible with most ecosystem models related to soil C dynamics and forest growth, and provides an effective way to integrate forest management effects and DOC leaching in forest soils at an ecosystem level. Validation and sensitivity tests demonstrated that TRIPLEX-DOC is capable of simulating DOC processes for forest stands of different ages to a reasonable accuracy. The model provides an insight into the mechanisms that control soil DOC concentrations and export, and may be useful in scaling up DOC leaching from landscape to regional scales. Furthermore, this process-based model can be used to project DOC concentrations and leaching under future climate scenarios.

DOC simulation in this study includes the DOC production from throughfall. Although the interception simulation (Rutter, 1971) represents the physically-based process by a running water balance of rainfall input, storage and output in the form of drainage and evaporation, the interception loss depends strongly on the timing and intensity of rainfall, the vegetation structure and the meteorological conditions controlling evaporation during and after rainfall (Rutter et al., 1975; Dingman, 2002; Brutsaert, 2005). As the Rutter model (1971) used in this study was only treated as a simplified process based on a single-layer vertical vegetation structure and a constant storage capacity, further improvements need to involve more detailed interception processes in the future.

TRIPLEX-DOC recognizes the role of DOC consumption and sorption/desorption as two key mechanisms that regulate DOC concentrations and export rates. Although our simulations do not provide a more detailed validation of the DOC submodel for different forest types, results indicate that DOC consumption and sorption/desorption-based soil submodels can reasonably capture general patterns in DOC concentration and flux rates related to soil depth, at least for temperate pine forests that we studied and where observed DOC flux data were available. Results also underscore the need for more detailed field experiment studies related to different types of forest ecosystems in major climatic regions and DOC sorption/desorption results from TRIPLEX-DOC are limited due to its use of an equilibrium distribution constant rather than using a time-dependent dynamical process (Qualls, 2000). This last point reflects the fact that TRIPLEX-DOC is in its early stage of model development as it pertains to DOC sorption/desorption and improvements could be made by incorporating more dynamic DOC sorption/desorption processes in more realistic ways.

With the future coupling of TRIPLEX-DOC and Geographic Information Systems (GIS) which would contribute a detailed database of regional soil distribution, climate characteristics, and land use patterns, it is anticipated the new model could be a useful tool in improving not only estimations of net C flux and greenhouse gas (GHG) emissions from forest soils on a regional scale, but also DOC export from soils. As the DOC from terrestrial ecosystem is critical to C budgets in the aquatic ecosystems, this estimate of DOC export will improve our understanding of the connectivity between terrestrial and aquatic C cycles, reducing the uncertainty in C fluxes of entire lake-watershed systems. TRIPLEX-DOC would take advantage of the TRIPLEX-GHG simulator (Peng et al., 2013) as well as important C loss pathways entering into aquatic ecosystems (TRIPLEX-Aquatic model) as described in an accompanying paper by Wu et al. (2013). Coupling the two efforts would be a strong contribution to understanding the processing and partitioning of organic C across both terrestrial and aquatic C cycles, resulting in a full regional integration between terrestrial and aquatic ecosystems.

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Figure Captions

Figure 1: Modular structure of TRIPLEX-DOC. The model is composed of four submodels that predict forest growth, soil hydrologic and thermal conditions, C decomposition, and DOC dynamics. The simulations of forest growth, soil carbon, hydrological and thermal conditions were adopted from the Forest-DNDC model, the DOC dynamics simulation is the newly redesigned submodel.

Figure 2: Comparison of annual mean DOC concentrations in different soil layers between Forest-DNDC simulations (Li et al., 2000) and field measurements in a 15 year-old temperate pine forest in southern Ontario

Figure 3: Observed versus predicted C densities in foliage (green), wood (blue), forest floor (dark yellow), soil (orange), and the summed total (black) in an age-sequence of temperate pine forests in southern Ontario.

Figure 4: Time series of measured DOC concentrations versus simulated daily values in litter layer and Ah soils layer in an age-sequence of temperate pine forests in southern Ontario.

Figure 5: Measured versus simulated annual mean DOC concentrations in soils in 65 and 15 year-old temperate pine forests in southern Ontario. Error bars denote standard deviations.

Figure 6: Comparison between measurements and simulations of annual DOC leaching in an age-sequence of temperate pine forests in southern Ontario. Error bars denote standard deviations.

Figure 7: Relationship between weekly soil DOC flux and water flux in litter layer and mineral soil.

Figure 8: Sensitivity analysis on the effects of land use on annual DOC leaching before and after 50% forest harvesting**.**

Table 1 Soil and stand characteristics of an age-sequence of temperate pine forests in southern Ontario.

Characteristics	**65 year old**	**30 year old**	**15 year old**	**2 year old**
Location	42.7098N, 80.3574W	42.7068N, 80.3483W	42.7742N, 80.4588W	42.6609N, 80.5595W
Dominant tree species	White pine (*Pinus strobes*)	White pine (*Pinus strobes*)	White pine (*Pinus strobes*)	White pine (*Pinus strobes*)
Major understory vegetation species	*Quercus vultina, Abies balsamifera, Prunus serotina*	*Quercus vultina*	*Quercus vultina*	none
Max. LAI (m^2 m^{-2})	8.0	5.9	12.8	1.0
Mean tree height (m)	22	12	9	1
Mean tree diameter at DBH (cm)	35	16	16	2.5 (tree base)
Stem density (trees ha^{-1})	429	1492	1242	1683
Aboveground tree biomass (g C m^{-2})	8416	4488	3236	22
Forest floor (g C m^{-2})	1211	545	745	83
Forest floor thickness (cm)	2.5	2.0	3.0	0.5
Tree roots (>2 mm)	1920	923	502	5
Litterfall throughout 2004–2005 (g C m^{-2} $year^{-1}$)	340–400	220–290	440–520	no data
Soil type	Brunisolic Luvisol	Brunisolic Luvisol	Gleyed Brunisolic Luvisol	Brunisolic Luvisol
Soil texture	Fine sandy	Fine sandy	Fine sandy loam	Fine sandy
Soil pH (upper 20 cm)	5.5	5.5	6.2	7.4
Soil C (g C m^{-2})	3700	3000	3400	3700

Data from Peichl and Arain (2006) and Peichl et al. (2007).

Table 2 Results of sensitivity of key variables to changes in climatic variables for different age temperate pine stands used in this study

Pine stands	**Minimum Temperature**		**Maximum Temperature**		**Precipitation**	
	+1℃	**-1℃**	**+1℃**	**-1℃**	**+10%**	**-10%**
2 yr						
NPP	+7.5	-4.1	+0.5	+0.7	+0.1	-0.2
Total biomass	+9.2	-5.3	0.0	+1.1	+0.1	-0.2
Floor carbon	-2.1	+1.4	-2.2	+1.5	-0.2	+0.3
Soil Carbon	-2.3	+2.3	-1.3	+1.1	-1.9	+2.3
DOC concentration in floor layer	-3.2	+2.9	-3.1	+2.8	-1.4	+1.7
DOC concentration in Ah layer	-3.7	+4.4	-1.6	+1.8	-4.6	+5.1
DOC concentration in mineral 50cm	-3.8	+9.1	+0.2	+4.8	-1.0	+4.4
DOC leaching	-2.8	+4.8	-1.4	+3.6	+15.7	-9.7
15 yr						
NPP	+2.4	-2.0	-2.2	+2.0	+2.0	-2.1
Total biomass	+3.3	-2.8	-2.9	+2.4	+2.4	-2.6
Floor carbon	+0.2	+0.3	0.0	+0.6	+0.9	-1.0
Soil Carbon	-3.1	+3.1	-1.6	+1.3	-2.7	+3.5
DOC concentration in floor layer	-1.4	+1.3	-0.5	+0.5	-2.1	+3.0
DOC concentration in Ah layer	-1.7	+1.8	+0.3	-0.4	-3.8	+4.6
DOC concentration in mineral 50cm	-5.2	+8.3	+2.7	-0.1	-5.5	+8.7
DOC leaching	-0.1	+3.2	-4.3	+2.8	+19.6	-20.2
30 yr						
NPP	+2.3	-1.7	-2.9	+2.7	+2.3	-2.4
Total biomass	+3.0	-2.5	-3.5	+3.0	+2.7	-2.6
Floor carbon	+0.6	0.0	+0.4	+0.2	+1.0	-1.2
Soil Carbon	-3.0	+3.2	-0.8	+0.7	-3.0	+3.8
DOC concentration in floor layer	-0.1	+0.6	+1.4	-1.0	-2.8	+3.1
DOC concentration in Ah layer	-1.7	+1.7	+1.1	-1.3	-4.6	+5.5
DOC concentration in mineral 50cm	-3.8	+5.9	+3.9	-2.2	-6.6	+8.1
DOC leaching	-0.9	-0.7	-4.5	-0.4	+35.7	-9.0
65 yr						
NPP	+1.9	-1.3	-4.9	+4.5	+2.9	-3.4
Total biomass	+2.8	-2.3	-5.1	+4.4	+3.1	-3.3
Floor carbon	+0.6	0.0	+0.5	+0.2	+0.9	-1.0
Soil Carbon	-2.1	+2.6	0.0	+0.4	-2.1	+2.8
DOC concentration in floor layer	-0.3	+0.5	+1.6	-1.4	-3.0	+3.9
DOC concentration in Ah layer	-1.0	+1.3	+2.8	-2.4	-4.6	+5.7
DOC concentration in mineral 50cm	-3.1	+4.8	+5.0	-2.9	-6.1	+8.8
DOC leaching	-0.3	-4.9	-3.6	-4.4	+26.1	-22.8

Values given represent percent of change compared to the baseline scenario.

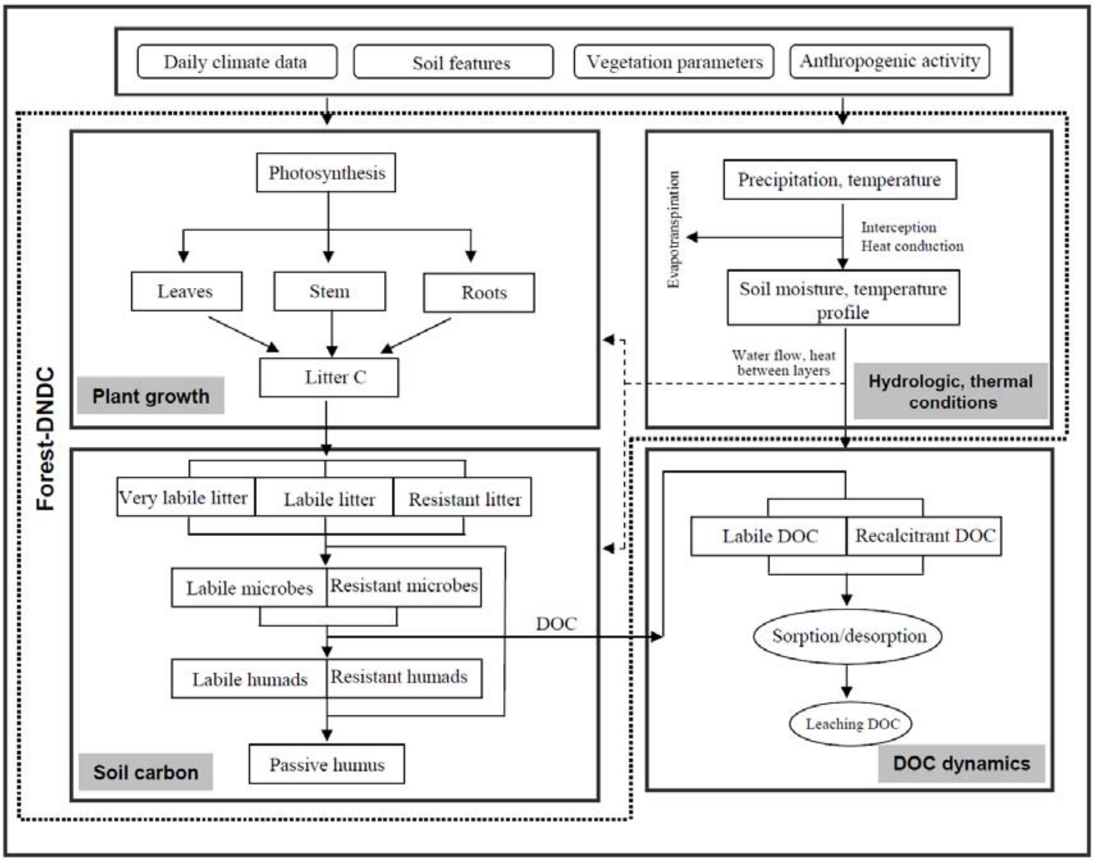

Figure 1: Modular structure of TRIPLEX-DOC. The model is composed of four submodels that predict forest growth, soil hydrologic and thermal conditions, C decomposition, and DOC dynamics. The simulations of forest growth, soil carbon, hydrological and thermal conditions were adopted from the Forest-DNDC model, the DOC dynamics simulation is the newly redesigned submodel.

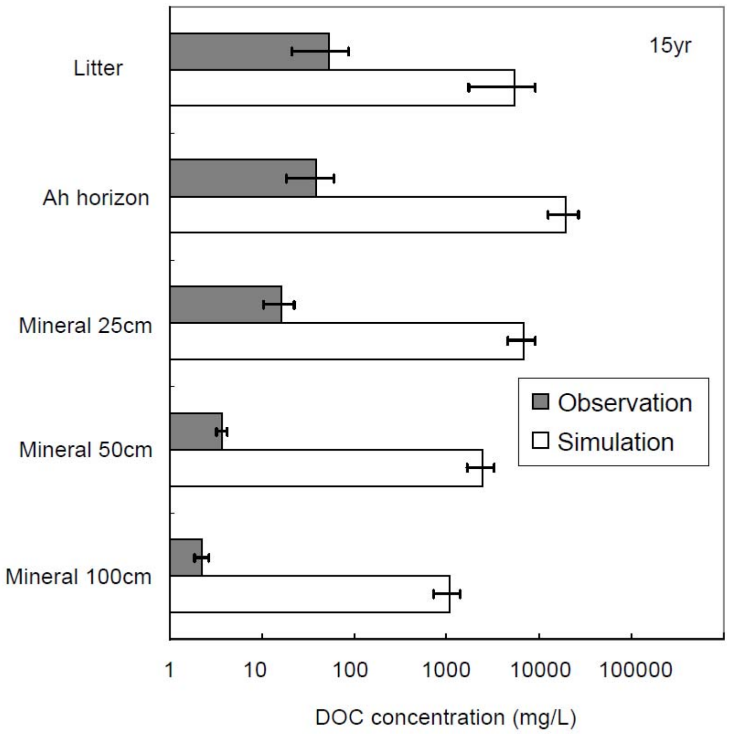

Figure 2: Comparison of annual mean DOC concentrations in different soil layers between Forest-DNDC simulations (Li et al., 2000) and field measurements in a 15 year-old temperate pine forest in southern Ontario.

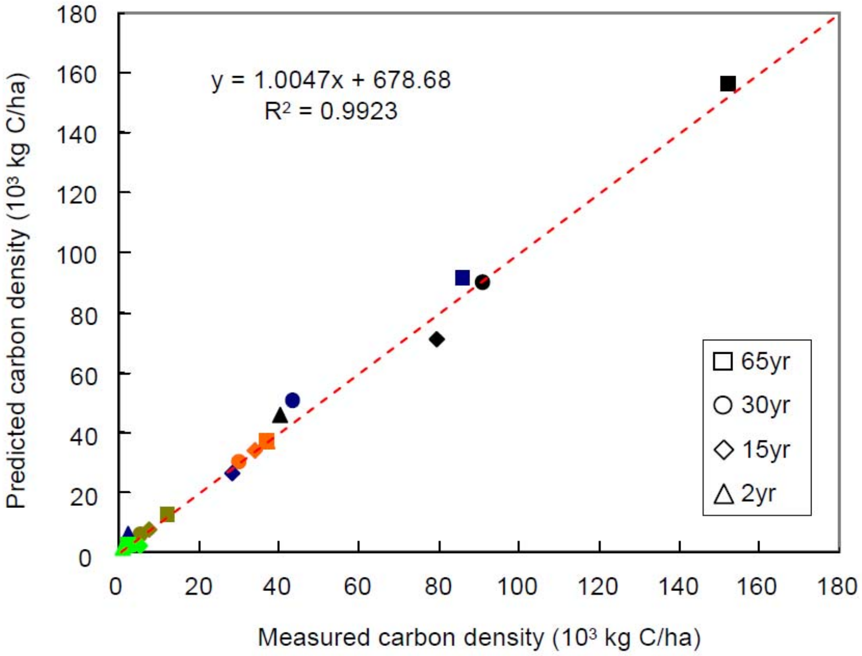

Figure 3: Observed versus predicted C densities in foliage (green), wood (blue), forest floor (dark yellow), soil (orange), and the summed total (black) in an age-sequence of temperate pine forests in southern Ontario.

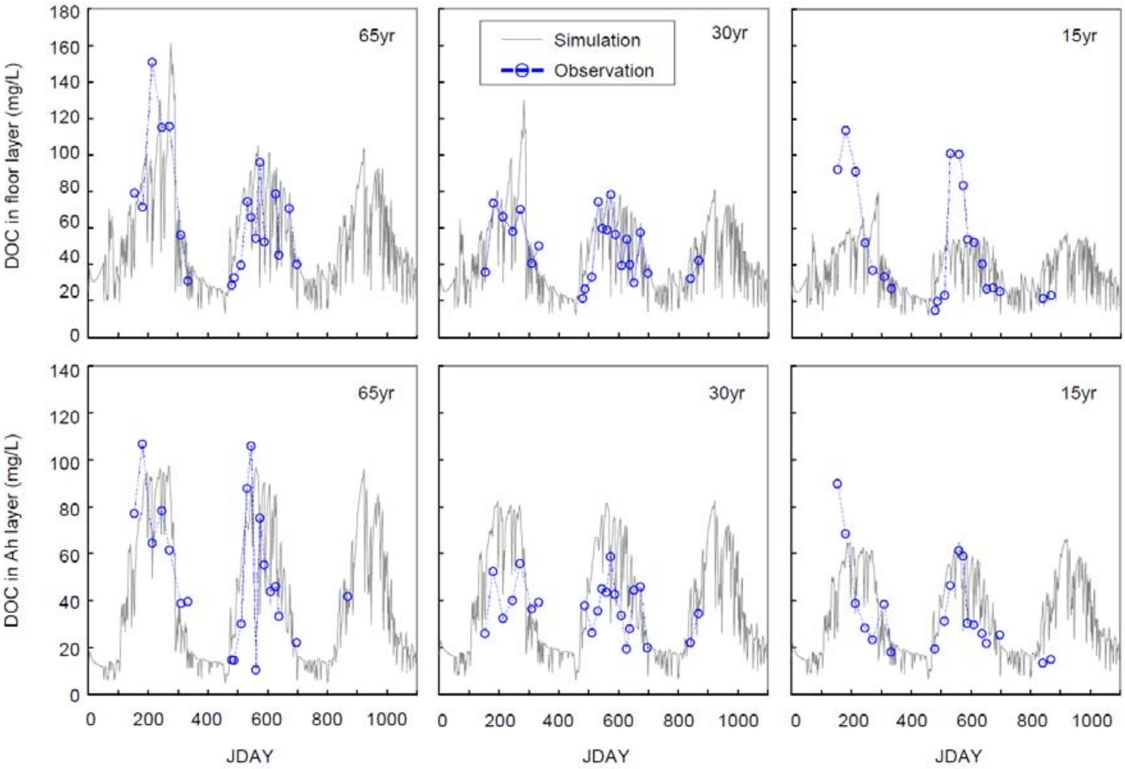

Figure 4: Time series of measured daily DOC concentrations versus simulated values in litter layer and Ah soils layer in an age-sequence of temperate pine forests in southern Ontario.

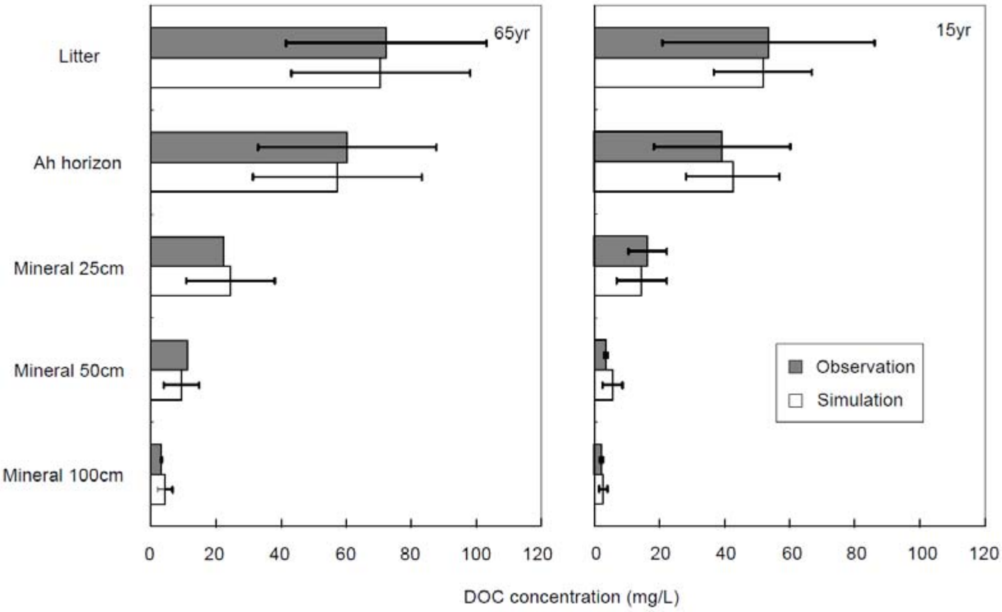

Figure 5: Measured versus simulated annual mean DOC concentrations in soils in 65 and 15 year-old temperate pine forests in southern Ontario. Error bars denote standard deviations.

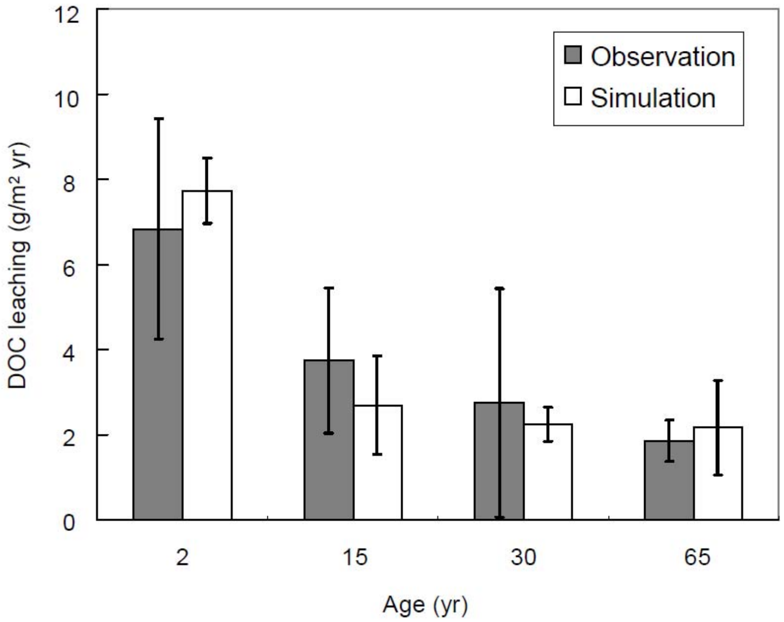

Figure 6: Comparison between measured and simulated annual DOC leaching in an age-sequence of temperate pine forests in southern Ontario. Error bars denote standard deviations.

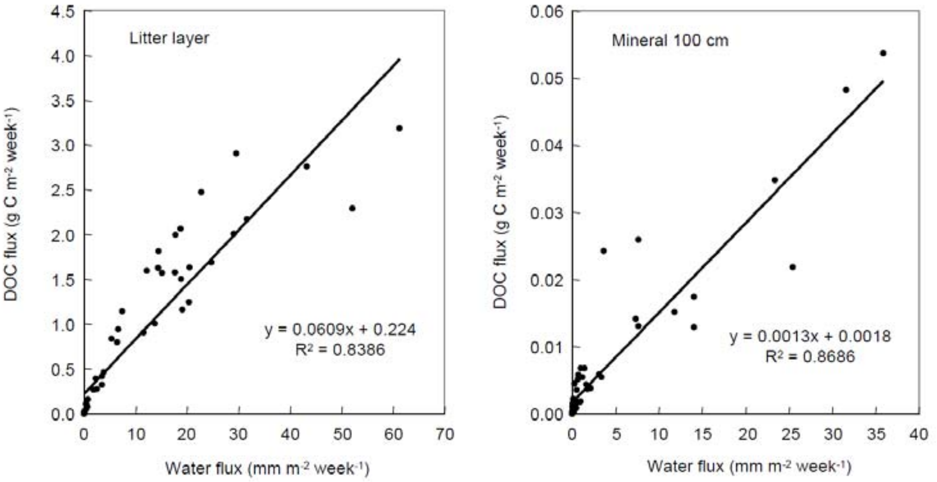

Figure 7: Relationship between weekly soil DOC flux and water flux in litter layer and mineral soil.

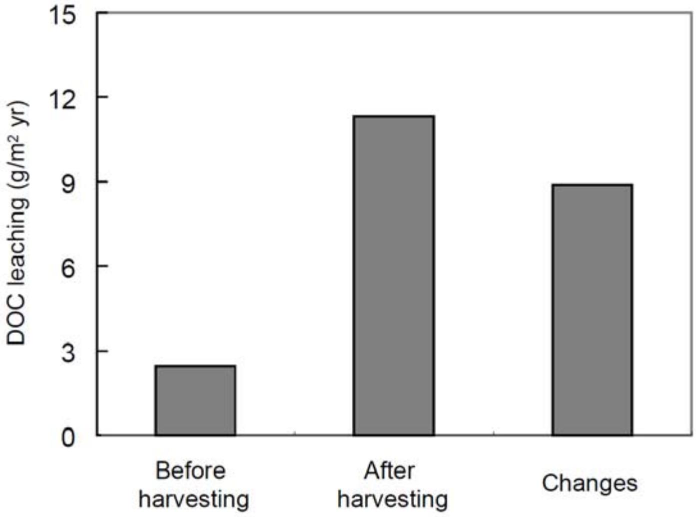

Figure 8: Sensitivity analysis on the effects of land use on annual DOC leaching before and after 50% forest harvesting**.**