MERCURY EXPORT FROM SMALL FORESTED WATERSHEDS IN WESTCENTRAL NOVA SCOTIA, CANADA: DEVELOPMENT OF AN ECOLOGICAL MODEL

by

Chengfu Zhang

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The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "MERCURY EXPORT FROM SMALL FORESTED WATERSHEDS IN WESTCENTRAL NOVA SCOTIA, CANADA: DEVELOPMENT OF AN ECOLOGICAL MODEL" by Chengfu Zhang in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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External Examiner: _____

Research Supervisor: _____

Examining Committee: _____

_____

Departmental Representative: _____

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ABSTRACT

As an efficient filter of airborne Hg compounds, forests retain a significant portion of the Hg deposited to the land. Forested watersheds have been identified as major sources of low-concentration Hg compounds to surrounding streams and lakes. Mercury export from forests is highly variable in both space and time. It is difficult to use field surveys alone to capture the spatiotemporal variation inherent in this variable. Mathematical models are required for improved representation.

The objective of this Thesis is to develop and test a monthly dynamic model that can be used to estimate seasonal Hg export from forested watersheds to low-ordered forest streams. The fully developed model consists of four model components: (i) a forest hydrology component, to simulate variation in soil temperature, soil moisture, and stream discharge for input to the other model components; (ii) a forest nutrient cycling and biomass growth component, to simulate forest growth and litter production; (iii) a forest litter decomposition component, to simulate seasonal production of dissolved organic carbon (DOC); and (iv) a monthly DOC and Hg export component to simulate the translocation of DOC and Hg from forested watersheds to low-ordered streams. The Hg-export component incorporates an Hg-to-DOC binding coefficient estimated from a one-time stream survey of Hg and DOC concentrations.

Simulations of in-stream Hg concentrations show two main trends: (i) an annual trend, associated with the seasonal (monthly) dynamics of forest litter production, decomposition, and DOC production and export, and (ii) a multiple-year trend, associated with forest harvesting and re-growth patterns of regenerating forests. This study demonstrates that (i) wetland- and conifer-dominated watersheds release a greater amount of Hg to aquatic ecosystems than upland- and deciduous species-dominated watersheds, and (ii) forests nearing maturity, export more Hg than young forests.

Keywords: dissolved organic carbon, environmental mercury, forest management, forest growing cycle, forested watersheds, stream-water quality, systems modelling

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CHAPTER 1 INTRODUCTION

1.1 Introduction

The impact of mercury (Hg) on human health was initially discovered in 1956 in Minamata City, Japan, with the diagnosis of a patient suffering from neurological symptoms. The neurological disorder was traced to the ingestion of methyl Hg (MeHg or CH_3Hg^+), which was discharged to community water supplies by a local factory (Chisso Corporation) when producing acetaldehyde using Hg as a catalyst (Harada, 1995). Since then, it has been found that Hg can affect the immune system, alter genetic and enzymatic systems, and damage the nervous system. The toxicity of Hg is greatly enhanced when converted to MeHg (Hamada and Osame, 1996; Wiener et al., 2003; Wagner et al., 2007). Methyl Hg is particularly harmful to developing embryos, which are 5-10 times more sensitive than adults (Cordier et al., 1991).

Mercury is a heavy metal (200.59 g $mole^{-1}$), with a melting and boiling point of -38.9^oC and 357.3^oC, respectively; Hg is the only metal to occur in liquid form at room temperature (20^oC). Mercury is a poor conductor of heat, but a reasonable conductor of electricity. With these unique characteristics, Hg is widely used in the measurement of atmospheric temperature and pressure. Chemically, Hg has three valence states: i.e., elemental Hg^0 and two positively-charged states, Hg^{+1} and Hg^{+2}. Hg^{+2} is very stable and bonds to both inorganic and organic molecules.

In terrestrial ecosystems, microorganisms and vegetation take up Hg by either wet or dry deposition and convert it into MeHg (Grigal, 2002). Mercury, particularly MeHg, is

highly bioaccumulative (Downs et al., 1998; Bowles et al., 2001). In some parts of Canada, Hg content in hair was found to exceed the tentative safety criterion of 50 parts per million by volume (ppm_v; Takeuchi et al., 1977). In some cases, mild neurological symptoms were evident (Harada et al., 1977). The objective of this Chapter is to review the processes involved in the circulation of Hg in the environment.

1.2 Hg Transfer, Bioaccumulation, and Amplification

1.2.1 Hg Transfer

Mercury is released to the environment by both natural and anthropogenic means. After entering into the atmosphere, the Hg is transported downwind and depending on the level of atmospheric mixing (associated with atmospheric stability and turbulence), some or all of the airborne Hg is deposited. Deposition provides a means for the direct transfer of Hg from the atmosphere to terrestrial and aquatic ecosystems. Following the biogeochemical cycle, Hg remains in the ecosystem until it is finally sequestered (stored) in soils and in lake- and ocean-bottom sediments (Donald, 1994).

Hg emissions to the atmosphere - As much as 2.5 million kg $year^{-1}$ of Hg enters the environment naturally through (i) weathering of rocks, (ii) volcanic eruptions, (iii) forest fires, and (iv) emissions of organic gases from terrestrial and aquatic vegetation (Nriagu, 1989). Since the beginning of the industrial revolution, Hg emissions have been continuously increasing through mining and burning of fossil fuels. It has been estimated that anthropogenic activities have increased global atmospheric Hg emissions by a factor of about three relative to natural emissions (Andren and Nriagu, 1979; Mason and Sheu, 2002). Current Hg depositions are 4-6 times higher than their levels in 1900 in

northeastern North America (Perry et al., 2005). The air now contains 3-6 times more Hg than it did prior the 19th century (Edelson et al., 1995).

Hg transport and deposition - In the atmosphere, Hg is present as elemental Hg or as particulates (Morel et al., 1998). If Hg is emitted as elemental Hg, it will reside in the atmosphere for about 1-2 years, until it is converted to either particulate or soluble form. Final deposition of airborne elemental Hg can occur at very far distances from the emission source. If Hg is emitted as a soluble compound, its final deposition can occur in vicinity of the source (Mason et al., 1994), especially when raining. Observations and modelling studies revealed that dry deposition of Hg contributes about the same as or more than wet deposition (Grigal, 2002; Cohen et al., 2004). Topographic relief and vegetation types encountered along the dispersion track of Hg have been shown to have a strong influence on the total Hg transferred to terrestrial ecosystems (Miller et al., 2005).

Spatially, atmospheric circulation determines where airborne Hg is eventually deposited. At the global scale, Hg has been shown to relocate from warm to cold places and from coastal to inland places (Ryan et al., 2003; Vanarsdale et al., 2005). Hg deposition at any location results from the cumulative effects of global, regional, and local sources (Driscoll et al., 2007; Paulson and Norton, 2008).

Long-term trends show that deposition of atmospheric Hg increased from the end of the 19th century to about 1990, and stabilised in the early 2000's (Perry et al., 2005). Seasonally, Hg deposition is typically low in winter and high in summer (Miller et al., 2005; Vanarsdale et al., 2005). This seasonal variation arises, as snow is less efficient at scavenging Hg, and Hg^0 oxidises to Hg^{+2} more efficiently in summer (Glass and Sorensen, 1999; Mason et al., 2000; Guentzel et al., 2001).

Sequestration in sediments - Following atmospheric transport and ecosystem assimilation, Hg is eventually transferred to soils or sediments at the bottom of lakes and oceans. The rate at which this happens is closely related to atmospheric Hg concentrations. For example, Hg in sediments in North American lakes and bogs has been steadily increasing for more than a century (starting in the late 1800's), peaking in the 1960's and 1970's, and decreasing during the last two decades (Lorey and Driscoll, 1999; Kamman and Engstrom, 2002).

1.2.2 Bioaccumulation and Amplification

Once Hg is deposited, microorganisms and vegetation on land or in water absorb the Hg and convert it to MeHg. Hg bioaccumulation in organisms depends on topography (defining deposition patterns), vegetation, waterbody characteristics, and the longevity of the living organisms involved. For example, bioaccumulation in organisms in freshwater lakes is shown to be different from that of organisms in rapidly moving water (Evers and Clair, 2005; Evers et al., 2007). Mercury content in organisms increases from marine, estuarine, riverine, to lacustrine systems (Evers et al., 2005; Yates et al., 2005). Species, such as the belted kingfisher (*Ceryle alcyon*), bald eagle (*Haliaeetus leucocephalus*), mink (*Mustela vison*), and river otter (*Lutra canadensis*) are good indicators of Hg-contamination of the environment. High-trophic level species of fish, birds, and mammals are extremely vulnerable to neurological and reproductive damage, as a result of Hg biomagnification (Evers and Clair, 2005).

1.3 Role of Forest Ecosystems in Hg Circulation

Forests filter much more airborne Hg than other vegetation types (Hurley et al., 1995). Also, differences exist in the rate coniferous and deciduous forests absorb and accumulate Hg (Rea et al., 1996). As a result of their ability to accumulate deposited Hg, forests serve as important sources of Hg to adjacent waterbodies (Allan et al., 2001).

Atmospheric deposition of Hg to forest ecosystems occurs (i) with the direct absorption of the pollutant by the leaves (dry deposition) or (ii) with the pollutant's incorporation in precipitation and direct delivery to soils (wet deposition; Lindberg et al., 1995). Direct deposition to leaf and branch surfaces can elevate Hg concentrations in rainwater as it trickles down through the canopy (Iverfeldt, 1991). Mercury held by leaves during the growing season reaches the forest floor with the autumn leaf drop. Mercury on the forest floor may be absorbed by plant roots, reside in the soil unaltered, or be exported to aquatic ecosystems with the pollutant's interaction with dissolved organic carbon (DOC; Rea et al., 1996; Allan et al., 2001) and surface water flow.

Various studies show strong correlation between in-stream Hg and DOC concentrations (Watras and Huckabee, 1994; Dennis et al., 2005; Meng et al., 2005; Reddy et al., 2007). Topography, soil and vegetation types, surface discharge, and soil reduction-oxidisation reaction (redox) environment suitable for DOC production, elevate Hg concentrations in surface waters (Mierle and Ingram, 1991; Kamman et al., 2004; Shanley et al., 2005). Of all vegetation covers, forests contribute the greatest amount of DOC to aquatic ecosystems (Hurley et al., 1995). As a result, DOC serves as an important link between forest-management (tree-removal) activities and Hg export in forest-dominated watersheds.

1.4 Systems Models

Field experiments provide (i) a basis for discovering the fundamental mechanisms controlling natural systems, and (ii) data for testing of models. In general, the development and application of mathematical models can provide a framework to (i) test hypotheses, (ii) integrate experimental results, (iii) provide understanding of relationships among different components of systems, and (iv) reproduce processes under the influence of environmental factors (Tiktak and van Grinsven, 1995). Models can also provide a means to fill gaps in experimental data (Xing et al., 2007, 2008a, 2008b; Zhang et al., 2010). While field and laboratory experiments can help establish the discrete nature of biological and ecological events, numerical models can help delineate the continuous nature of these same events and be used to predict the impact of natural and anthropogenic disturbance on these events. Based on various levels of spatial application, Hg-circulation models can be classed into three main groups, i.e., (i) global, (ii) regional, and (iii) watershed-scale (site-level) models.

1.4.1 Global- and Regional-Scale Models

The GRAHM (Global-Regional Atmospheric Heavy Metals model; Dastoor and Larocque, 2004) and DEHM models (Danish Eulerian Hemispheric Model; Christensen et al., 2004) are examples of models developed for global and hemispheric-scale Hg circulation. The ADOM (Acid Deposition and Oxidant Model; Petersen et al., 2001), CMAQ (Community Multiscale Air Quality model; Bullock and Brehme, 2002), and HYSPLIT models (Hybrid Single Particle Lagrangian Integrated Trajectory model;

Cohen et al., 2004) are models developed for the simulation of regional-scale Hg circulation.

All of these models require meteorological input for their operation. For example, the GRAHM and DEHM models use Canada's operational Global Environmental Multiscale (GEM) model with meteorological variables estimated with the PSU/NCAR Mesoscale Model v. 5 (MM5). Model complexity varies with respect to their treatment of Hg transfer to the atmosphere. For example, the GRAHM model simulates both Hg emissions and re-emissions, but some of the other models only simulate emissions. In practice, global- and hemispheric-circulation models can be used to define the boundary conditions for regional-to-watershed-level models, in an attempt to account for Hg sources outside these models' computational domain.

All of these models consider the three forms of Hg in their treatment of Hg circulation, i.e., (i) gaseous elemental Hg, (ii) total particulate Hg, and (iii) reactive-gaseous Hg. Common attributes of these models is that they tend to simulate (i) gaseous-elemental-Hg better than the other Hg species, and (ii) the long-lived Hg species better than the short-lived species. While the global-scale Hg circulation models can simulate the impact of global sources on a particular location, the regional models provide better definition (i.e., variation in Hg concentrations) at receptor locations (Ryaboshapko et al., 2007).

1.4.2 Watershed-Level Models

To better understand the fate of atmospheric Hg deposition at the watershed scale, many models have been developed to simulate the processes of (i) atmospheric

deposition, (ii) Hg transformation in terrestrial ecosystems, and (iii) export from terrestrial to aquatic ecosystems. In the scientific literature there are three types of watershed-scale Hg models: (i) empirical models, (ii) steady-state models, and (iii) process-based models. Meng et al. (2005) developed an empirical model to clarify the relationship between Hg concentrations and in-stream DOC and the surrounding environment. It was found that in-stream DOC and Hg concentrations were reasonably correlated to (i) stream and lake dimensions, (ii) water origin, and (iii) water acidity. Models by Hope et al. (2005) and Ambrose et al. (2005) are steady-state models developed to simulate watershed Hg cycling and accumulation. The models reproduced Hg transport related to atmospheric deposition and volatilisation to and from terrestrial surfaces and accumulation in lake-bottom sediments. IEM-2M (United States Environmental Protection Agency, 1997) is a process-based model that simulates the annual processes associated with the transformation of Hg in watersheds, in particular Hg^0 to Hg^{2+} and MeHg. Because of its internal structure, IEM-2M is inherently unable to simulate seasonal Hg-export dynamics in waterways. Also, IEM-2M simulates Hg export from watersheds through soil erosion, which is recognised as a less important pathway for environmental Hg.

1.5 Problem Domain and Thesis Objectives

As watersheds form natural land-management units, their management affects downstream water quality. To address Hg issues in low-ordered forest streams, Hg export should be investigated at the watershed scale.

Research in Hg circulation at the global to regional scales has been ongoing for a very long time with many successes. However, Hg-circulation studies at the watershed-ecosystem level are particularly few. As a result, further research is needed, in particular as it pertains to the circulation of Hg in ecosystems. At the watershed scale, empirical and steady-state models because of their internal structure are inherently incapable to simulate seasonal trends in Hg-export dynamics. Available process-based models, like IEM-2M, are also unsuitable for this work because of their coarse temporal resolution (i.e., annual). The **objective of this Thesis** is to develop a monthly Hg-export model to estimate (i) seasonal trends in in-stream concentrations of total Hg (THg), and (ii) the impact of forest management and re-growth patterns on watershed Hg dynamics. Development of this process model has the potential to augment our understanding of small-scale processes involved in the re-distribution of Hg in forested watersheds, once deposited to the land.

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CHAPTER 2 MODEL CONCEPTUALISATION AND FRAMEWORK

2.1 Process Conceptualisation

Movement of Hg from atmospheric deposition to aquatic ecosystems by interacting with DOC is well documented in the scientific literature, e.g., Mierle and Ingram (1991), Allan and Heyes (1998), and Shanley et al. (2005). In this study, Hg export from forested watersheds is based on the observation that total Hg (THg) and in-stream DOC concentrations are linearly correlated (Meng et al., 2005).

2.2 Model Components and Integration Structure

The monthly Hg-export model is based on the integration of four modelling components, namely (i) a forest hydrology component (**ForHyM2**; Meng et al., 1995; Balland, 2003), (ii) a forest nutrient cycling and biomass growth component (**ForNBM**; Zhu et al., 2003), (iii) a monthly forest litter decomposition component (**FLDM**; Zhang et al., 2007; Zhang et al., 2010), and (iv) a **monthly DOC production and DOC and Hg export** component (Figure 2.1). To differentiate organic matter-absorption capabilities between wetland and upland soils of watersheds, the wetland-to-total-watershed-area ratio is introduced. Determination of this area ratio is based on a wetland-area delineation obtained with the Wetted Areas Mapping (WAM) technology of Meng et al. (2004). Fundamental to estimating this ratio is (i) a Digital Elevation Model (DEM) and hydrology layer of the study area, and (ii) Geographic Information System (GIS) capabilities in watershed-area delineation and calculation.

ForHyM2 is used to simulate variation in soil temperature, soil moisture, and stream discharge for input in the other model components (Figure 2.1). With appropriate input from ForHyM2, ForNBM is used to simulate forest growth and litter production and FLDM, seasonal litter decomposition. Output from FLDM is used as input to the DOC model to estimate the level of DOC produced by forests, and stream discharge is used in the calculation of DOC export from source areas to streams.

The integrated model (Figure 2.1) is a point model with a refined temporal resolution. Because of its aspatial nature, individual watershed attributes relevant to the export of DOC and THg, in particular forest cover (i.e., coniferous, deciduous, or mixedwood cover) and wetland-to-total-watershed-area ratio are treated as weighing factors in the calculation of DOC production and export. Figure 2.1 gives the various model components and their relationships among each other.

2.3 Spatial and Temporal Scale

Model scale is determined by the resolution and scope of the problem (Wu et al., 2005) and the need to capture the range in natural variation (Landres et al., 1999). For highly variable systems, the resolution should ideally be high. Choice of proper spatial

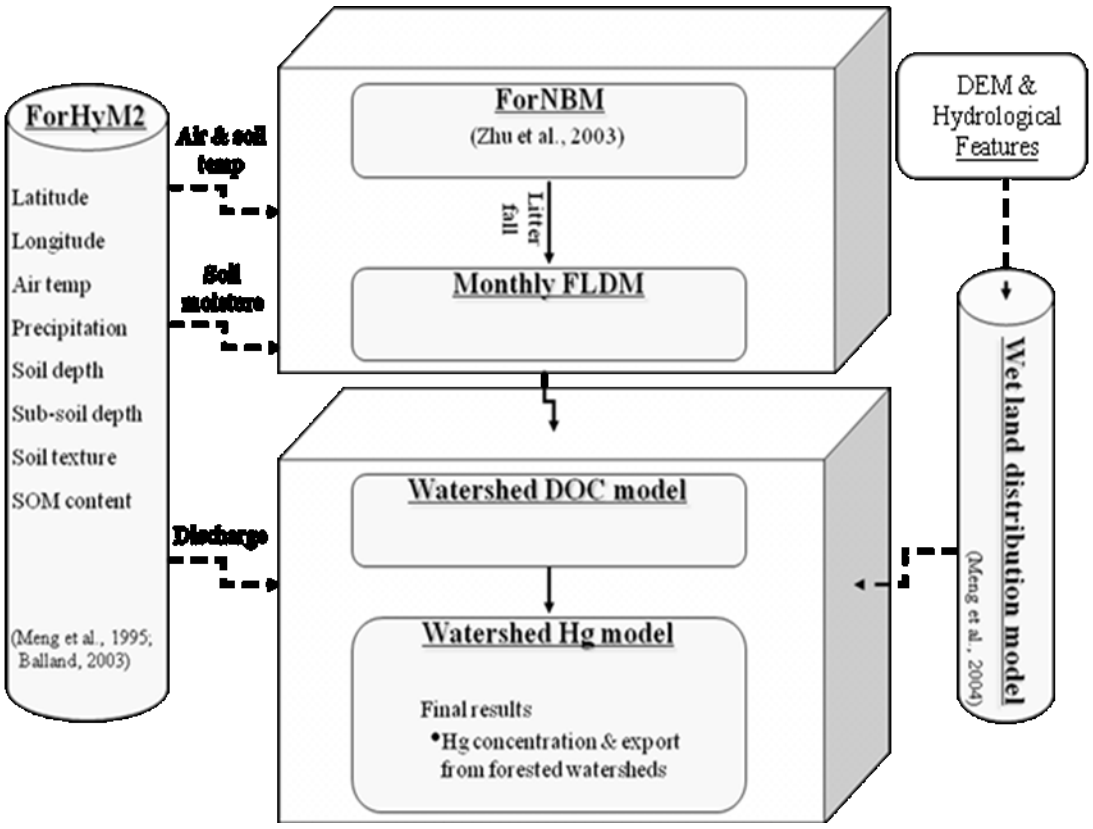

Figure 2.1 Overall model structure of the integrated DOC and Hg export model.

Table 2.1 Model input and output variables.

Variables	Units	Temporal representation
INPUT		
Site location		
Latitude	Degree	
Longitude	Degree	
Vegetation coverage		
Vegetation composition	Unitless	
Forest-floor litter stock	tonne ha^{-1}	
Soil specification		
Soil depth	cm	
Subsoil depth	cm	
Soil texture (sand, silt, and clay)	%	
Soil organic matter content	%	
Forcing variables		
Daily air temperature	^{o}C	Daily average
Daily precipitation	mm	Daily total
OUTPUT		
Biomass		
Total stem wood and foliage	tonne ha^{-1}	
Litter fall	$month^{-1}$	
Forest floor biomass	tonne ha^{-1}	
Stream DOC and Hg concentration		
DOC concentration	mg L^{-1}	Monthly average
Hg concentration	ng L^{-1}	Monthly average

and temporal scales can result in more efficient representation and improved accuracy of results. For this Thesis, the spatial scale is defined as a small watershed (< 2000 ha) at a forest-stand resolution (> several ha); and the temporal scale, as a complete forest-growing cycle of 75 years (i.e., a forest rotation).

Even though annual average concentrations of Hg and DOC may meet water-quality standards, seasonal concentrations may actually exceed these standards. To address the seasonal Hg and DOC concentration dynamics, I used a monthly timestep.

2.4 Model Operation

Required input information for running the model, such as site conditions, data for forcing variables, such as air temperature and precipitation, and the output of the model are summarised in Table 2.1.

2.5 Thesis Outline

The main body of the Thesis is organised as a series of four scientific manuscripts. These manuscripts are assembled as Chapters 3-6. Chapter 1 provides the context for the research by giving (i) an introduction and literature review related to the regional-to-local pathways and contamination of the environment by Hg, and (ii) a discussion of the inherent relationship between within-watershed DOC production and export and outlet Hg concentrations. Chapter 2 provides an overview of the integrated DOC-THg export model used in the simulation of seasonal Hg-

export dynamics in two forested-watersheds in Kejimkujik National Park, westcentral Nova Scotia (NS). Since FLDM is the basis for assessing the impacts of forest management on seasonal streamwater quality (with respect to DOC and THg loading), and since annual models by definition are not designed to simulate seasonal variation, Chapter 3 provides modification of an annual version of FLDM to a monthly revised form, which is subsequently validated by comparing its results to **litterbag residual mass** data collected as part of the Canadian Inter-site Decomposition Experiment (CIDET; Trofymow and the CIDET Working Group, 1998). In Chapter 4, results of a one-pool litter decomposition formulation are compared to those of the revised monthly FLDM (based on a three-pool formulation) and *in-situ* measurements of **forest-floor residual litter mass** associated with the Boreal Forest Transect Case Study (BFTCS; Bhatti et al., 2003). In Chapter 5, the monthly DOC production and export model is described. Model simulations are subsequently compared against field-based DOC-concentration measurements associated with the two NS watersheds. Based on model parameterisation and simulations from work appearing in Chapters 3 through 5, Chapter 6 provides short- (seasonal) to long-term (150-year) simulations of within-watershed export of THg from the NS watersheds, integrating the processes of forest clearcutting and re-growth in its treatment of DOC production and export. Lastly, Chapter 7 provides a summary of research results and major contributions to the science of Hg-circulation in small-forested watersheds.

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CHAPTER 3 LITTER DECOMPOSITION AND NITROGEN MINERALISATION FROM AN ANNUAL TO A MONTHLY MODEL

Chengfu Zhang[a,c], John A. Trofymow[b], Rob C. Jamieson[c], Fan-Rui Meng[a], Robert Gordon[d], Charles P.-A. Bourque[a,*]

[a] *Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada*

[b] *Pacific Forestry Centre, 506 West Burnside Road, Victoria, British Columbia, V8Z 1M5, Canada*

[c] *Department of Process Engineering and Applied Science, Dalhousie University, Halifax, NS, B3J 1Z1, Canada*

[d] *Ontario Agricultural College, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

[*] Corresponding author at: Faculty of Forestry and Environmental Management, 28 Dineen Drive, PO Box 4400, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada. Tel.: 1-506-453-4509; Fax.: 1-506-453-3538.

E-mail address: cbourque@unb.ca (C. P.-A. Bourque)

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3.1 Abstract

The forest litter decomposition model (FLDM) described in this Chapter provides an important basis for assessing the impacts of forest management on seasonal streamwater quality and export of dissolved organic carbon (DOC). By definition, models with annual timesteps are incapable to capture seasonal, within-year variation. In order to simulate seasonal variation in litter decomposition and DOC production and export, an existing annual FLDM has been modified to account for monthly dynamics of decomposition and residual mass in experimental litterbags placed in 21 different forest types across Canada.

The original annual FLDM was formulated with three main litter pools (fast, slow, and very slow decomposing litter) to address the fact that forest litter is naturally composed of a mixture of organic components that decompose at different rates. The annual FLDM was shown to provide better simulations than more complex models, like CENTURY and SOMM.

The revised monthly model retains the original structure of the annual FLDM, but decouples litter decomposition from nitrogen (N) mineralisation. In the model, monthly soil temperature, soil moisture, and mean January soil temperature are shown to be the most important controlling variables of within-year variation in decomposition. Use of the three variables in a process-based definition of litter decomposition is a significant departure from the empirical definition used in the annual model. The revised model is shown to give similar calculations of residual mass and N concentrations as the annual model (R^2= 0.91, 0.78), despite producing

very different timeseries of decomposition over a 6-year simulation period. It is shown from a modelling perspective that (i) forest litter decomposition is independent of N mineralisation, whereas N mineralisation is dependent on litter decomposition, and (ii) mean January soil temperature defines litter decomposition in the summer because of winter-temperatures' role in modifying forest-floor microorganism community composition and functioning in the following summer.

Keywords: CIDET data, decomposition, dissolved organic carbon, forest residual litter mass, organic matter, model simulation

3.2 Introduction

Litter decomposition is a key process that facilitates the cycling of carbon (C) and nutrients in forest ecosystems. Litter decomposition is largely controlled by litter quality (Heal et al., 1997), dominant weather features (Fierer and Schimel, 2002; Borken et al., 2003), and composition and activity of microorganisms in the soil and forest floor (Jenkinson et al., 1991; Berg and Matzner, 1997; Gillon et al., 1999). Dead organic matter (DOM) is known to influence the properties of forest ecosystems, including those of soils, such as soil structure, moisture content, nutrient retention, and thermal insulation (Meyer and Arp, 1994; Prescott et al., 2000; Balland, 2003). Carbon dioxide (CO_2) released from the decomposing litter affects (i) the rate C returns to the atmosphere (Jenkinson et al., 1991) and (ii) the rate soils undergo weathering, by raising in-soil CO_2 concentrations and soil acidity. During decomposition, part of DOM is converted to dissolved organic carbon (DOC) that is eventually transported to aquatic ecosystems downstream. DOC is not only an important source of energy to aquatic ecosystems, but also serves as an important carrier of toxic metals in watersheds (Thurman, 1985; Bryant et al., 1998; Eatherall et al., 1998; Alberts et al., 1994; Zhu et al., 2003; Ravchandran, 2004). As a result, modelling forest litter decomposition is fundamental to understanding the seasonal processes associated with nutrient cycling (including C) and soil and streamwater quality evolution in both managed and unmanaged forest ecosystems (Kimmins, 1977; Zhu et al., 2003).

Existing forest litter decomposition models are based on one of two main hypotheses, namely (1) decomposing organic matter gradually alters its chemical composition from fresh litter to fermented litter to humus (Berg et al., 1993; Berg, 2000; Chertov and Komarov, 1997), or (2) organic matter consists of a mixture of chemical components that decompose at different rates (Trofymow et al., 1995; Knorr et al., 2005 a; Preston et al., 2009 a, b). Models such as SOMM (Chertov and Komarov, 1997), CANDY (Franko et al., 1995), and CENTURY (Parton et al., 1987; CENTURY, 2000) are based on the first hypothesis, and models like DOCMOD (Currie and Aber, 1997), MBL_GEN (Rastetter et al., 1991), GEN_DEC (Moorhead, 1999), and the annual Forest Litter Decomposition Model (FLDM; Zhang et al., 2007) are based on the second. This Chapter focuses on the use and modification of FLDM.

The annual FLDM is first used to derive annual timeseries of residual litter mass and nitrogen (N) for 21 Canadian Inter-site Litter Decomposition Experiment (CIDET) sites (Zhang et al., 2007). The model calculates mass reduction and N-concentration dynamics in litterbags according to three litter pools (i.e., fast, slow, and very slow decomposing litter) and two N pools (slow and very slow mineralising N pools). Initial mass and N pools are established according to the original chemical composition of the litter. Primary weather input to the model includes mean (1) January and (2) July air temperatures and (3) annual precipitation. The original FLDM has a very simple structure, possessing fewer model variables

and parameters than most decomposition models in the scientific literature (Zhang et al., 2008).

Models are normally developed with an aim to solve specific problems, such as bridge data gaps. In this Chapter, the annual model is revised to a monthly model, so that the impact of seasonal litter decomposition on (i) downstream export of DOC and Hg (Levin, 1992; Dumanski et al., 1998) and (ii) streamwater quality may be addressed at a later stage (via Chapters 4 through 6). Given that annual concentrations obscure seasonal dynamics, monthly models are needed to undertake such studies.

The objective of this Chapter is to modify the original annual FLDM, so that it can generate monthly timeseries of residual litter mass and N for enhanced simulation of within-year litter decomposition. In this work, CIDET data are used to estimate parameters for the revised monthly model. Results generated with the model are subsequently compared against results generated with several other decomposition models.

3.3 Monthly Model

3.3.1 Model Structure

The monthly forest litter decomposition model is developed from the annual FLDM (Zhang et al, 2007). Data for monthly forcing variables in FLDM (i.e., soil temperature and soil moisture) are derived from the forest hydrology model, ForHyM2 (Arp and Yin, 1992; Yin and Arp, 1993; Meng et al., 1995).

In the monthly model, the litter mass decomposition and N mineralisation components are decoupled, such that litter mass decomposition is made independent of N mineralisation; N mineralisation, although, retains its dependence on litter decomposition. This reformulation of FLDM (Zhang et al., 2007) renders the revised model even simpler than the original, annual model.

3.3.2 Revised FLDM

3.3.2.1 Mass Decomposition and Model Initialisation

Litter decomposition in three litter pools is simulated by

$$M(t) = \sum_{i=1}^{3} M(t)_i \text{ , and} \tag{3.1}$$

where

$$\frac{\partial M(t)_1}{\partial t} = - k_1 \cdot f_{climate}\, M(t)_1 , \tag{3.2}$$

$$\frac{\partial M(t)_2}{\partial t} = - f_{climate}\, M(t)_2 , \tag{3.3}$$

$$\frac{\partial M(t)_3}{\partial t} = - k_3\, f_{climate}\, M(t)_3 , \tag{3.4}$$

where M(t) is the total mass remaining at time t (in grams); i=1,2,3 denotes the fast, slow and very slow decomposing litter pools; and k_1 and k_3 are litter pool-specific decomposition rate ratios between the fast and the slow and between the very slow and slow decomposing litter pools, respectively; $f_{climate}$ is a climate factor, which

addresses the impact of climate on litter decomposition through soil temperature and soil moisture.

Initialisation of mass in the three litter pools is based on the following

$$M(0)_1 = M(0)\, g\,, \tag{3.5}$$

$$M(0)_2 = M(0)\, e\, (1 - g)\,, \text{ and} \tag{3.6}$$

$$M(0)_3 = M(0)\, (1 - e)\, (1 - g)\,, \tag{3.7}$$

where $M(0)_1$, $M(0)_2$, and $M(0)_3$ are the initial mass content in the fast, slow, and very slow decomposing litter pools (in grams); e and g are mass partitioning coefficients; g defines the mass fraction between the fast decomposing litter pool (g) and the slow and very slow decomposing litter pools (1-g); e gives the mass fraction between the slow (e) and the very slow decomposing litter pools (1-g); g and e are estimated from

$$g = \exp(a_0 + a_1 \alpha + a_2 \beta)\ , \text{ and} \tag{3.8}$$

$$e = \exp(- a_3 \gamma)\,, \tag{3.9}$$

where α, β, and γ are the initial water-extractable material (%), acid-hydrolysable material (%), and ash content (%) of the original leaf litter, respectively; a_0, a_1, a_2, and a_3 are equation parameters that determine the distribution of organic matter in the three litter pools. Based on Eq. (3.8) and (3.9), the greater the initial water-

extractable and acid-hydrolysable content of the original leaf litter, the greater is the amount of litter partitioned to the fast decomposing litter pool. The greater the ash content, the greater is the amount of litter partitioned to the very slow decomposing litter pool.

3.3.2.2 N Mineralisation and Model Initialisation

For N mineralisation, it is assumed that the N mass corresponding to the fast and slow mineralising pools is mineralised at the same rate as the decomposition of the litter in the slow decomposing litter pool and the remaining N is mineralised at the same rate as the decomposition of the litter in the very slow decomposing litter pool, i.e.,

$$N(t) = \sum_{i=2}^{3} N(t)_i \,, \quad \text{and} \tag{3.10}$$

where N(t) (in grams) is N mass remaining at time t; i= 2 and 3 represent the slow and very slow mineralising N pools;

$$\frac{\partial N(t)_2}{\partial t} = - f_{climate} N(t)_2 \left(\frac{[N(t)_2] - [N(0)]}{NM_{final} - [N(0)]} \right), \text{ and} \tag{3.11}$$

$$\frac{\partial N(t)_3}{\partial t} = - k_3 f_{climate} N(t)_3 \left(\frac{[N(t)_3] - [N(0)]}{NM_{final} - [N(0)]} \right). \tag{3.12}$$

where i= 2,3 represent the slow and very slow mineralising N pools; NM_{final}, a parameter, is the assumed N concentration in well-humified litter (unitless) and [N(0)] is the initial N concentration of the litter (unitless).

The N concentration of the litter at time t is given by

$$[N(t)] = \frac{N(t)}{M(t)}. \tag{3.13}$$

Equations to initialise the two N pools are given by

$$N(0)_2 = N(0)[g + e(1-g)], \text{ and} \tag{3.14}$$

$$N(0)_3 = N(0)(1-e)(1-g). \tag{3.15}$$

3.3.3 Forest Hydrology Model

The forest hydrology model (ForHyM2), originally developed by Arp and Yin (1992) and Yin and Arp (1993), and later verified and updated by Balland (2003), is used to generate the required monthly soil temperature and soil moisture input (in A layer) to the revised FLDM. The ForHyM2 model is composed of a heat transfer and a water flow sub-model. The heat sub-model simulates heat input to the forest as a function of energy transfer from the top of the forest canopy to the forest floor and its eventual conduction through the soil. ForHyM2 simulates water flow as a function of (i) precipitation input, either as rain or snow, (ii) evapotranspiration, (iii) interception, (iv) stemflow and throughfall, (v) deep percolation, and (vi) surface

and subsurface flow through the forest floor and soil sub-layers. Figure 3.1 provides a schematic of ForHyM2. The current version of ForHyM2 (Balland, 2003) simulates water fluxes at a daily time resolution using inputs of daily accumulated precipitation and average air temperature. Papers by Arp and Yin (1992), Yin and Arp (1993), Meng et al. (1995) and Balland and Arp (2005) provide further detail concerning ForHyM2.

3.3.4 Incorporation of Weather Effects

The climate factor is addressed in the revised FLDM by means of

$$f_{climate} = k_2 f_T . f_W , \tag{3.16}$$

where f_T and f_W are soil temperature and moisture-related factors, and k_2 is an equation parameter (unitless). The temperature factor is given by an Arrhenius-type equation,

$$f_T = exp\left(-\left(\frac{Ea}{R}\right)\left(\left(\frac{1}{T_{soil}+273}\right)-\left(\frac{1}{288}\right)\right)\right), \tag{3.17a}$$

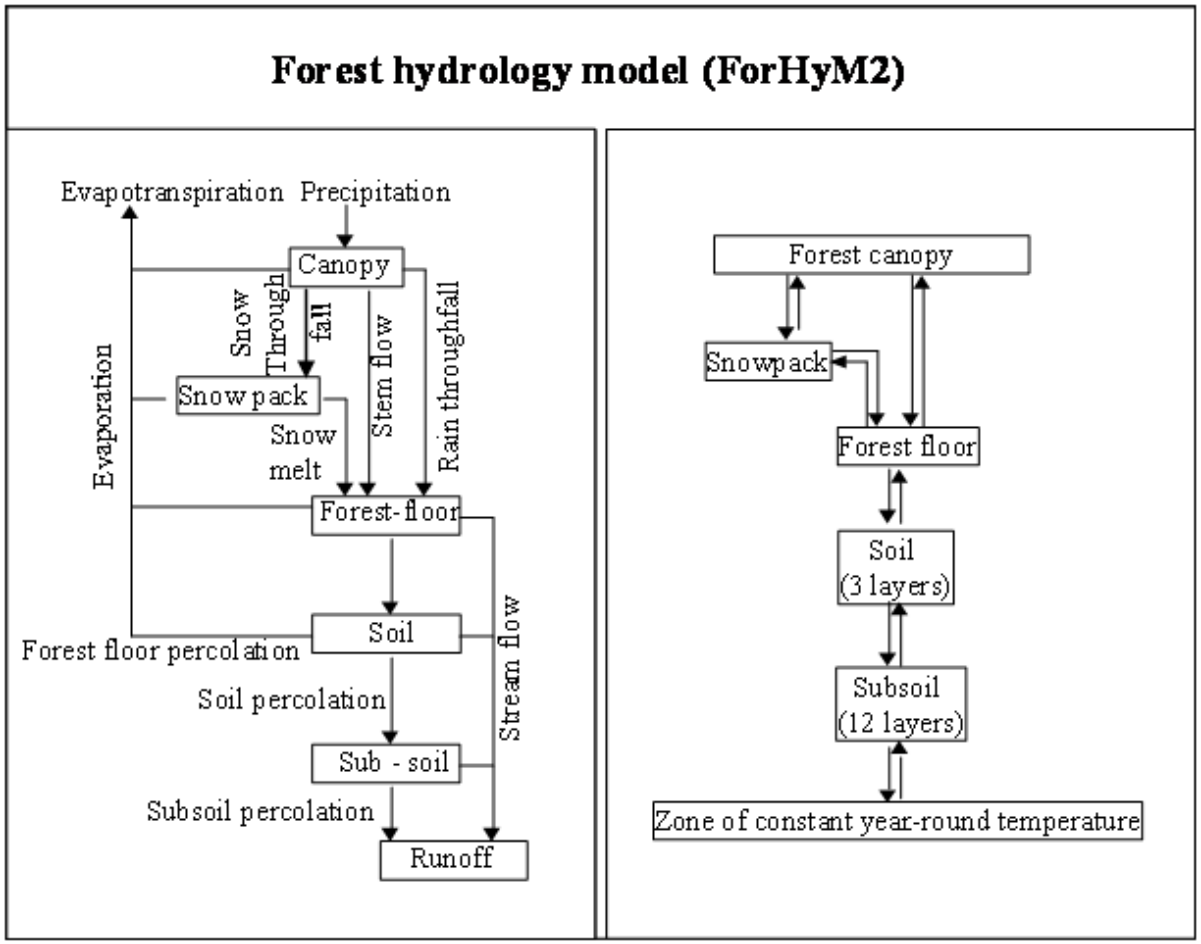

Figure 3.1 Schematic diagram of ForHyM2 (after Arp and Yin, 1992; Yin and Arp, 1993; Meng et al., 1995).

where T_{soil} (^{o}C) is the soil temperature, Ea is the active energy (J mol^{-1}), and R is the universal gas constant (=8.31 J mole^{-1} C^{-1}). Parameters Ea and R in Eq. (3.17a) define the energy required for litter decomposition.

It was found during model calibration that the performance of the revised FLDM could be greatly enhanced by incorporating mean January soil temperature in the formulation of f_T. Incorporating mean January soil temperature (T_{Jan}) modifies f_T, such that

$$f_T = \left(T_{Jan} + p_{TJan}\right)\exp\left(-\frac{Ea}{R}\right)\left(\left(\frac{1}{T_{soil}+273}\right)-\left(\frac{1}{288}\right)\right), \qquad (3.17b)$$

where p_{TJan} is an equation parameter (^{o}C). The impact of adding mean January soil temperature to the definition of f_T is investigated later.

The soil moisture factor (f_w) is based on work by Bourque et al. (2000), whereby

$$f_w = \max(0, \kappa\xi^{\alpha}(1-\xi)^{1/\alpha}) \qquad (3.18)$$

and

$$\xi = \begin{cases} 0 & ;\text{if} \quad sm < sm_{min} \\ \left(\dfrac{sm - sm_{min}}{sm_{max} - sm_{min}} \right) & ;\text{if} \quad sm_{min} < sm < sm_{max} \\ 1 & ;\text{if} \quad sm > sm_{max} \end{cases}$$

$$\alpha = \sqrt{\frac{\chi}{1-\chi}},$$

$$\kappa = \frac{1}{\chi^{\alpha}(1-\chi)^{1/\alpha}}$$

and

$$\chi = \frac{sm_{opt} - sm_{min}}{sm_{max} - sm_{min}} .$$

Equation terms sm_{min}, sm_{max}, and sm_{opt} represent minimum, maximum, and optimal soil moisture (% volume) needed for forest litter decomposition; κ, ξ, α, and χ are intermediate variables.

3.3.5 Summary of Modifications to the Annual Model

1) In the annual model, the equation of litter decomposition in the very slow decomposing litter pool is given by

$$\frac{\partial M(t)_3}{\partial t} = -k_3 \, f_{climate} \, M(t)_3 \{1 - MNfinal[N_3(t)](1 - a_4[N(0)])\} \qquad (3.19)$$

where a_4 is a parameter for N mineralisation (unitless). In the monthly model, Eq. (3.3) is a simplification of Eq. (3.19), as a result of the fact that litter decomposition is made independent of N mineralisation.

2) In the annual model, N mineralisation is simulated with

$$\frac{\partial N(t)_2}{\partial t} = - a_4 \, f_{climate} \, M(t)_2 \, [N(0)], \text{ and} \tag{3.20}$$

$$\frac{\partial N(t)_3}{\partial t} = - a_4 \, k_3 \, f_{climate} \, [N(0)] \, M(t)_3 \left\{ 1 - \frac{[N3(t)](1 - a_4[N(0)]}{NM_{final}}) \right\}. \tag{3.21}$$

In the monthly model, the original equations [i.e., Eq. (3.20) and (3.21)] are replaced with simpler equations, i.e., Eq. (3.11) and (3.12). With these modifications, the monthly model formalises the concept that litter decomposition is independent of N mineralisation, whereas N mineralisation is contingent on litter decomposition.

3) In the annual model, the climate factor is formulated as

$$f_{climate} = \left\{ \left(\min\left(1, \frac{Ppt}{p_1}\right) + \frac{T_{Jan}}{p_2} \right) \exp\left(-\left(\frac{Ea}{R}\right)\left(\frac{1}{T_{July} + 273} - \frac{1}{288}\right)\right)\right\}, \tag{3.22}$$

where Ppt, T_{Jan}, and T_{July} are the annual total precipitation (mm), average January air temperature (^oC), and average July air temperature (^oC), respectively; p_1 (mm) and p_2 (^oC) are equation parameters. In the monthly model, the January temperature is retained (in the form of soil temperature) to address the state of litter decomposition in the following summer. Monthly soil temperatures and soil moisture replace July air temperature and annual precipitation in the annual model.

Conversion of an annual model to a monthly model is not a straight forward process; it may mean significant changes need to be made to capture detail not

addressed in the annual model (e.g., seasonal dynamics). In the annual model, climate is related to litter decomposition empirically; while in the monthly model climate is related to decomposition mechanistically. This change is a significant departure, as it generalises the monthly model and permits its use across a wider range of site conditions. Empirical approaches limit the use of models to the range in the data used in generating the empirical relationship.

3.4 Data processing and Model Parameterisation

3.4.1 CIDET Field Experiments

The CIDET experiment was designed to characterise forest litter decomposition and N mineralisation by placing a series of litterbags at 21 different forest sites across Canada. The sites consisted of 18 upland (well-drained) and three wetland sites. The sites were selected as representative of the major eco-climatic regions of Canada (Table 3.1; Figure 3.2; Trofymow et al., 2002). The litter species in the decomposition bags involved 12 litter types (10 foliage types and 2 wood blocks) representative of the main forests and forest floor vegetation in Canada.

Each site was divided into four 5 × 11 m plots within a 4-ha area, each roughly 20 m apart. Each litterbag contained 10 g of dry litter from one litter species or 20-g wood block. Ten litterbags and 2 bags of wood blocks were tied to form one string. Ten strings were placed in each plot with 10 replications.

Table 3.1 CIDET litterbag site location, climate, and vegetation characteristics (Trofymow and the CIDT Working Group, 1998).

Code	Site name	Eco-climatic region	Dominant forest cover	Latitude (N)	Longitude (W)	Altitude (m)	Temperature			Ppt.
							Jan. (°C)	July (°C)	Ann. (°C)	Ann. (mm)
BAT	Batoche	Transitional Grassland	none	52°43'	106°7'	472	-21.5	17.4	0.1	398
CBR	CB Rocky Harbour	Maritime Low Boreal	fir-birch-spruce	49°32'	57°50'	50	-5.7	15.7	4.2	1200
CHA	Chapleau	Humid Low Boreal	pine-spruce	47°38'	83°14'	460	-16.9	16.8	1.1	834
GAN	Gander	Maritime Mid-Boreal	spruce-fir-birch	48°55'	54°34'	115	-6.2	16.5	4.3	1130
GI1	Gillam	Low Subarctic	spruce-larch	56°19'	94°51'	140	-28	15	-5.2	485
GI2	Gillam	Low Subarctic	none	56°19'	94°51'	125	-28	15	-5.2	485
HID	Hidden Lake	Moist Montane Southern cordilleran	hemlock-cedar-birch	50°33'	118°50'	650	-5.7	18.1	6.3	547
INU	Inuvik	High Subarctic	spruce-birch-spruce	68°19'	133°32'	73	-29.6	13.6	-9.8	266
KAN	Kananaskis	Montane Southern Cordilleran	pine-spruce-poplar	51°00'	115°00'	1530	-10.2	14.1	2.8	657
MAR	Morgan Arboretum	Humid Mid-Cool Temperate	beech-maple	45°25'	73°57'	48	-10.6	21	6.1	863
MON	Montmorency	Perhumid Low Boreal	fir-birch-spruce	47°19'	71°8'	670	-14.7	12.6	0.6	1494
NH1	Nelson House	Subhumid High Boreal	pine	55°55'	98°37'	280	-26.6	15.6	-3.9	542
NH2	Nelson House	Subhumid High Boreal	none	55°55'	98°37'	260	-26.6	15.6	-3.9	542
PAL	Prince Albert	Subhumid Low Boreal	pine	53°13'	105°58'	476	-21.5	17.4	0.1	398
PET	Petawawa	Humid High Cool Temperate	pine	45°55'	77°35'	173	-12.9	16.6	4.3	822
PMC	Port McNeill	Maritime South Pacific Cordilleran	hemlock-fir	50°36'	127°20'	100	2.4	13.6	7.9	1783
SCH	Schefferville	Low Subarctic	spruce-larch	54°52'	66°39'	500	-22.8	12.6	-4.8	769
SHL	Shawnigan Lake	Coastal South Pacific Cordilleran	douglas-fir	48°38'	123°42'	355	1.8	17.1	9.3	1215
TER	Termundee	Transitional Grassland	aspen	51°50'	104°55'	536.5	-19.1	18.4	1.8	371
TOP	Topley	Boreal Southern Cordilleran	pine-fir-spruce	54°36'	126°18'	1100	-12.3	14.1	2.5	513
WHI	Whitehorse	Boreal Northern Cordilleran	pine-spruce-aspen	60°51'	135°12'	667	-20.7	14.1	-1.2	261

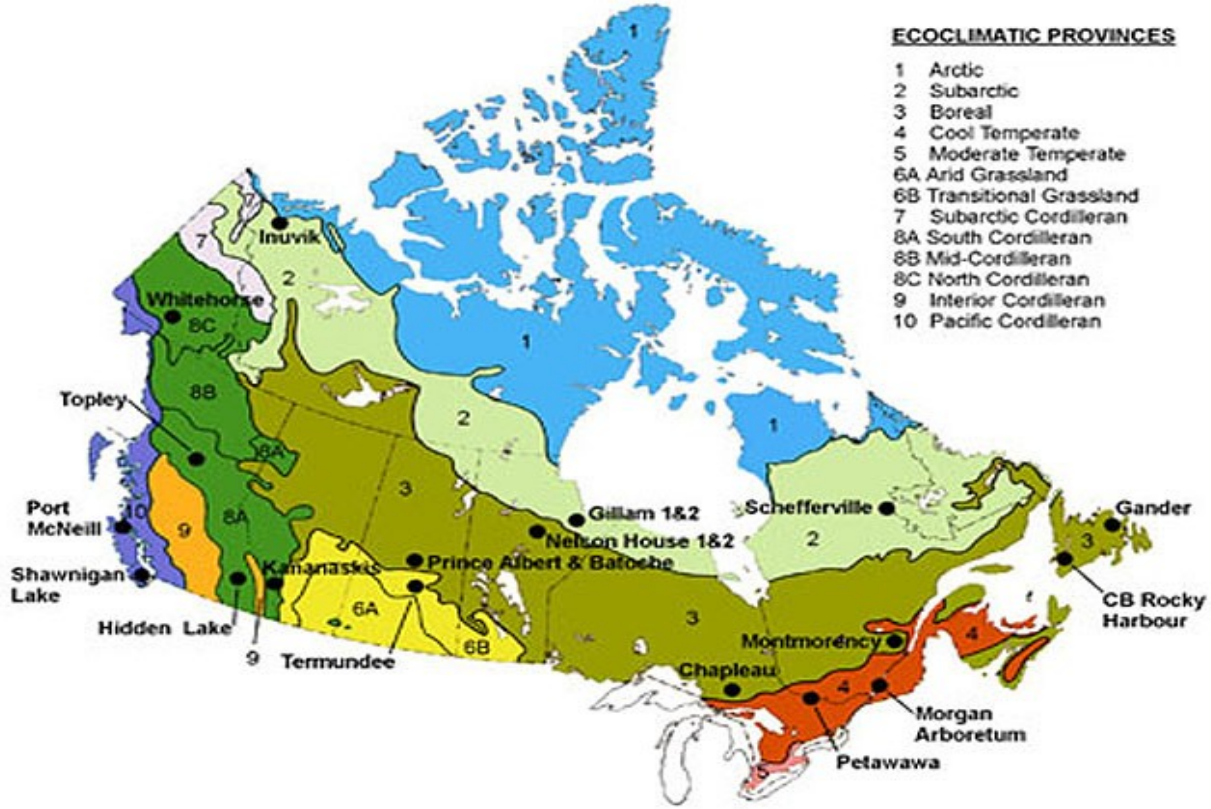

Figure 3.2 Distribution of CIDET sites within the eco-climatic provinces of Canada (Ecoregions Working Group and Canadian Committee on Ecological Land Classification, 1989; Trofymow et al., 2002).

About 11,000 litterbags (i.e., 12 litterbags on one string, 10 strings in one plot, 4 plots at one site, and 21 sites in all) were placed on top of the forest floor in the fall of 1992. In every subsequent fall, a sub-sample of litterbags was collected at each plot for laboratory analysis.

Initial chemical composition of each litter species were analysed before being placed in the litterbags (Table 3.2). Residual mass and elemental concentrations of C, N, and phosphorous (P) were measured after each annual collection (Trofymow and the CIDET Working Group, 1998).

3.4.2 CIDET and Weather Data Collection

In this work, daily weather input into ForHyM2 was collected from Meteorological Service of Canada weather stations nearest each site. Daily soil temperature and moisture derived with ForHyM2 were then summarised into monthly averages for input into FLDM. Annual averages of the daily input for ForHyM2-model initialisation and parameter optimisation are given in Table 3.1. CIDET data used in this study related to the initial (1992) and subsequent litterbag content from 1993 through to 1998. Residual mass and N remaining in each litterbag were averaged according to species and site (Moore et al., 1999; Trofymow et al., 2002). Table 3.2 gives initial elemental concentrations, water- and non-polar extractables, acid-hydrolysable and unhydrolysable residues, and ash content (Trofymow et al., 1995; Trofymow and the CIDET Working Group, 1998).

Table 3.2 CIDET litterbag litter type and initial chemical composition in % (Trofymow and the CIDET Working Group, 1998).

Litter type	C	N	P	S	Ca	Mg	K	Proximate chemical fractions				
								Ash	Non-polar extractable	Water-soluble	Acid-hydrolysable	AUR
Trembling aspen	46.8	0.67	0.13	0.16	2.05	0.16	1.23	8.38	8.75	35.42	33.7	14.4
American beech	47.0	0.71	0.04	0.2	0.99	0.25	0.08	7.05	7.25	12.90	45.3	28.0
White birch	48.0	0.72	0.04	0.1	0.85	0.24	0.26	3.38	6.52	35.94	30.3	24.0
Western red cedar	49.7	0.64	0.05	0.12	1.68	0.09	0.11	7.2	10.72	10.51	36.5	35.6
Bracken fern	46.3	0.88	0.07	0.12	0.77	0.31	0.43	7.21	2.26	9.04	49.1	32.9
Plains rough fescue	43.8	0.71	0.06	0.15	0.37	0.13	0.5	9.22	9.06	12.86	58.5	11.2
Douglas fir	49.6	0.7	0.11	0.27	1.28	0.11	0.16	6.74	10.27	11.48	41.6	30.3
Jack pine	49.7	1.28	0.13	0.14	0.46	0.12	0.27	2.65	6.97	15.24	42.4	32.8
Black spruce	49.5	0.73	0.08	0.28	0.66	0.09	0.22	4.16	10.92	19.85	37.0	28.3
Tamarack	48.8	0.59	0.02	0.32	0.66	0.25	0.31	5.89	9.35	31.10	30.1	24.0

Note: All of the fractions are based on total dry litter weight; AUR, acid-unhydrolysable residue (identified as lignin).

3.4.3 Model Implementation and Parameter Optimisation

The modelling work was implemented in ModelMaker™, visual-programming software for systems modelling (ModelMaker, 1999). This software can realise the mathematical functions visually and integrate the differential equations with numerical methods, such as Euler's, midpoint, or a 5^{th}-order Runge-Kutta method. The software optimises the model parameters automatically by minimising the Chi-square function (χ^2), i.e.,

$$\chi^2 = \sum \frac{(P_j - O_j)^2}{err^2},$$

either with the Levenberg-Marquardt or Nelder-Mead simplex method. In the minimising function, P_j and O_j are the individual modelled and field-based data values; err is the level of uncertainty in the data predetermined by the user.

3.5 Results and Discussion

3.5.1 Model Parameterisation

Table 3.3 gives the values and ranges of parameter values for the two monthly FLDM [one using Eq. (3.17a) in its definition of $f_{climate}$, and one using Eq. (3.17b)] and the original annual FLDM. Parameter values in Eq. (3.17b) are nearly similar to those of the annual FLDM, which means that the input variables and the model time resolution have little effect on (i) the distribution of chemical elements in the three

Table 3.3 Parameter values for the monthly FLDM using Eq. (3.17a) (A), monthly model using Eq. (3.17b) (B), and the original annual model (C).

Parameters	A		B		C	
	Value	Range(±)	Value	Range(±)	Value	Range(±)
k_1	13.27	1.62	17.92	1.82	19.8	2
k_2	0.153	0.011	0.082	0.005	0.377	0.014
k_3	0.31	0.03	0.35	0.03	0.292	0.023
Ea	72104	2633	103879	2726	61690	2312
NM_{final}	0.0176	0.006	0.0176	0.006	0.0194	0.006
a_0	-10.6	0.4	-10.9	0.32	-6.6	0.2
a_1	0.14	0.004	0.14	0	0.116	0.003
a_2	0.127	0.005	0.131	0.005	0.104	0.003
a_3	0.139	0.018	0.119	0.014	0.155	0.015
a_4					55.5	1.5
sm_{Max}	1	0	1	0		
sm_{Opt}	0.97	0	0.95	0		
p_{TJan}			20.7	0.5		

litter pools; (ii) the ratio between N mineralisation and litter decomposition; (iii) the relative decomposition in the fast, slow, and very slow decomposing litter pools; and (iv) the assumed C and N concentrations in the well-humified litter mass.

The parameter, Ea, varies from 62 000 with the annual FLDM to 103 879 with the monthly model based on Eq. (3.17b). Values of Ea in the two models are consistent with values reported in the literature, e.g., 73 700 (Borken et al., 2003).

Theoretically, litter decomposition increases when soil moisture is within [sm_{min}, sm_{opt}], and decreases when $sm>sm_{opt}$. In this study, sm_{opt} is found to be very close to sm_{max}, which suggests that soil moisture is best for aerobic respiration under prevailing site conditions ($sm<sm_{opt}$).

3.5.2 Model versus Measurements

The revised monthly model with Eq. (3.17b), provides nearly similar estimates of residual mass and N concentrations as the original, annual-based FLDM, giving a coefficient of determination (R^2) of 0.91 (vs. 0.92 for the original model) and 0.78 (vs. 0.80) when modelled results are compared against CIDET field measurements (Table 3.4). As in the annual FLDM, the revised monthly model captures the year-to-year impact of species and climate on litter decomposition (Table 3.5, Figure 3.3). Species with higher water extractable materials are shown to undergo rapid decomposition within their first year (e.g., plains rough fescue), while species with

Table 3.4 Model comparison, coefficient of determination (R^2), and error values (average and range) for residual mass and N concentration by species and CIDET sites.

	Residual mass					N concentration				
	A	B	C	D	E	A	B	C	D	E
R^2										
Species										
Average (range ±)	0.90 (0.31)	0.92 (0.04)	0.92 (0.04)	0.79 (0.12)	0.87 (0.08)	0.72 (0.09)	0.72 (0.09)	0.76 (0.10)	0.64 (0.12)	0.71 (0.11)
Sites										
Average (range ±)	0.90 (0.08)	0.91 (0.08)	0.93 (0.05)	0.88 (0.12)	0.89 (0.10)	0.80 (0.14)	0.80 (0.12)	0.85 (0.12)	0.79 (0.14)	0.80 (0.12)
All	0.90	0.91	0.92	0.80	0.87	0.77	0.78	0.80	0.72	0.76
Confidence interval										
Y-intercept, a	(-0.22,0.02)	(-0.19,0.06)	(-0.11,0.10)	(-0.42,-0.07)	(-0.47,-0.19)	(-0.06,0.01)	(-0.05,0.02)	(-0.05,0.01)	(-0.13,-0.04)	(-0.13,-0.05)
Slope, b	(0.10,1.03)	(1.0,1.03)	(0.99,1.03)	(1.01,1.06)	(1.03,1.07)	(1.04,1.10)	(1.03,1.09)	(1.03,1.08)	(1.10,1.18)	(1.11,1.17)
Errors										
Species										
Average (range ±)	-0.59 (2.94)	-0.02 (0.41)	-0.03 (0.04)	0.02 (0.41)	0.00 (0.41)	0.68 (3.39)	-0.05 (0.18)	-0.04 (0.11)	-0.07 (0.19)	-0.07 (0.18)
Site										
Average (range ±)	0.00 (0.76)	-0.02 (0.59)	-0.03 (0.52)	0.02 (1.23)	0.00 (0.94)	-0.06 (0.17)	-0.05 (0.16)	-0.04 (0.14)	-0.07 (0.26)	-0.07 (0.19)
All										
Average (range ±)	0.00 (4.38)	0.02 (4.73)	-0.05 (4.42)	-0.02 (6.12)	-0.01 (5.49)	0.06 (1.66)	0.05 (1.69)	-0.04 (1.56)	0.07 (1.82)	0.07 (1.72)

Note: A, Revised FLDM using Eq. (3.17a), B, Revised FLDM using Eq. (3.17b), C, Annual FLDM, D=SOMM model, E, CENTURY model. The 95% confidence interval is defined for both regression intercept and slope.

Table 3.5 Comparison of measured and simulated data; coefficient of determination (R^2) is associated with the residual mass and N concentration over a 6-year period (1992-1998).

Years	Mass remaining					N concentration				
	A	B	C	D	E	A	B	C	D	E
1	0.75	0.78	0.79	0.63	0.71	0.72	0.70	0.72	0.64	0.68
2	0.76	0.79	0.80	0.62	0.74	0.63	0.64	0.63	0.52	0.57
3	0.78	0.83	0.82	0.58	0.75	0.75	0.76	0.78	0.65	0.72
4	0.76	0.82	0.81	0.58	0.73	0.70	0.71	0.73	0.62	0.69
5	0.76	0.79	0.82	0.53	0.72	0.61	0.61	0.68	0.53	0.60
6	0.76	0.80	0.82	0.53	0.72	0.65	0.66	0.72	0.60	0.67
Average	0.76	0.80	0.81	0.58	0.73	0.68	0.68	0.71	0.59	0.66
Range	0.04	0.05	0.02	0.11	0.05	0.14	0.15	0.15	0.14	0.15

Note: A, Revised FLDM using Eq. (3.17a), B, Revised FLDM using Eq. (3.17b), C, Annual FLDM, D, SOMM model, E, CENTURY model.

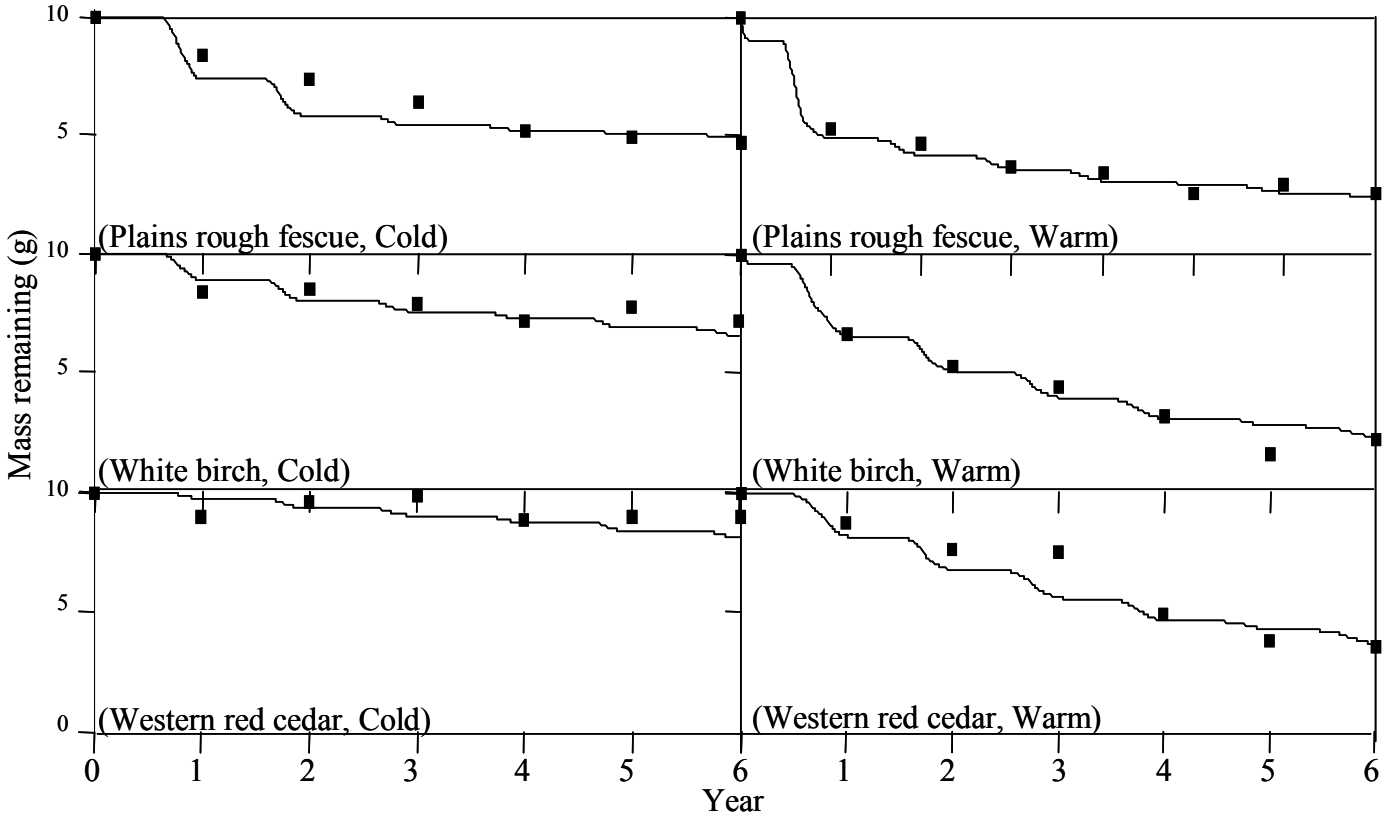

Figure 3.3 Comparison of measured (squares) and model-simulated (lines) residual mass as a function of time and species for both a warm (Petawawa) and a cold site (Inuvik).

higher acid extractable materials undergo greatest decomposition within the first four years (e.g., white birch). Species with high ash content are shown to resist decomposition and typically undergo the slowest decomposition among the species considered (e.g., western red cedar). Litter decomposition is shown to be sensitive to climatic differences. Litter decomposition at the colder and dryer sites (e.g., Inuvik) is shown to be slower than at the warmer and wetter sites of Canada (e.g., Petawawa).

N concentration is shown to increase as litter decomposes; its build-up rate is shown to be positively correlated to the rate of litter decomposition (Figure 3.4).

3.5.3 Mean January Soil Temperature

The revised monthly model with Eq. (3.17b) is shown to capture litter decomposition better than the monthly model with Eq. (3.17a); see Tables 3.4 and 3.6. When winter soil temperatures are high, litter decomposition rates in subsequent summers is expected to be fast; in cold winters, summer decomposition is suppressed. This property is suspected to be directly related to the extent organisms in the soil and forest floor (insects, earthworms, and soil bacteria) can survive winter conditions to contribute to the decomposition of litter matter in the following summer. Ground-dwelling insects have been observed to survive moderately-warm winters and perish in cold winters (Crozier, 2004), affecting the makeup of soil and forest-floor community of decomposers.

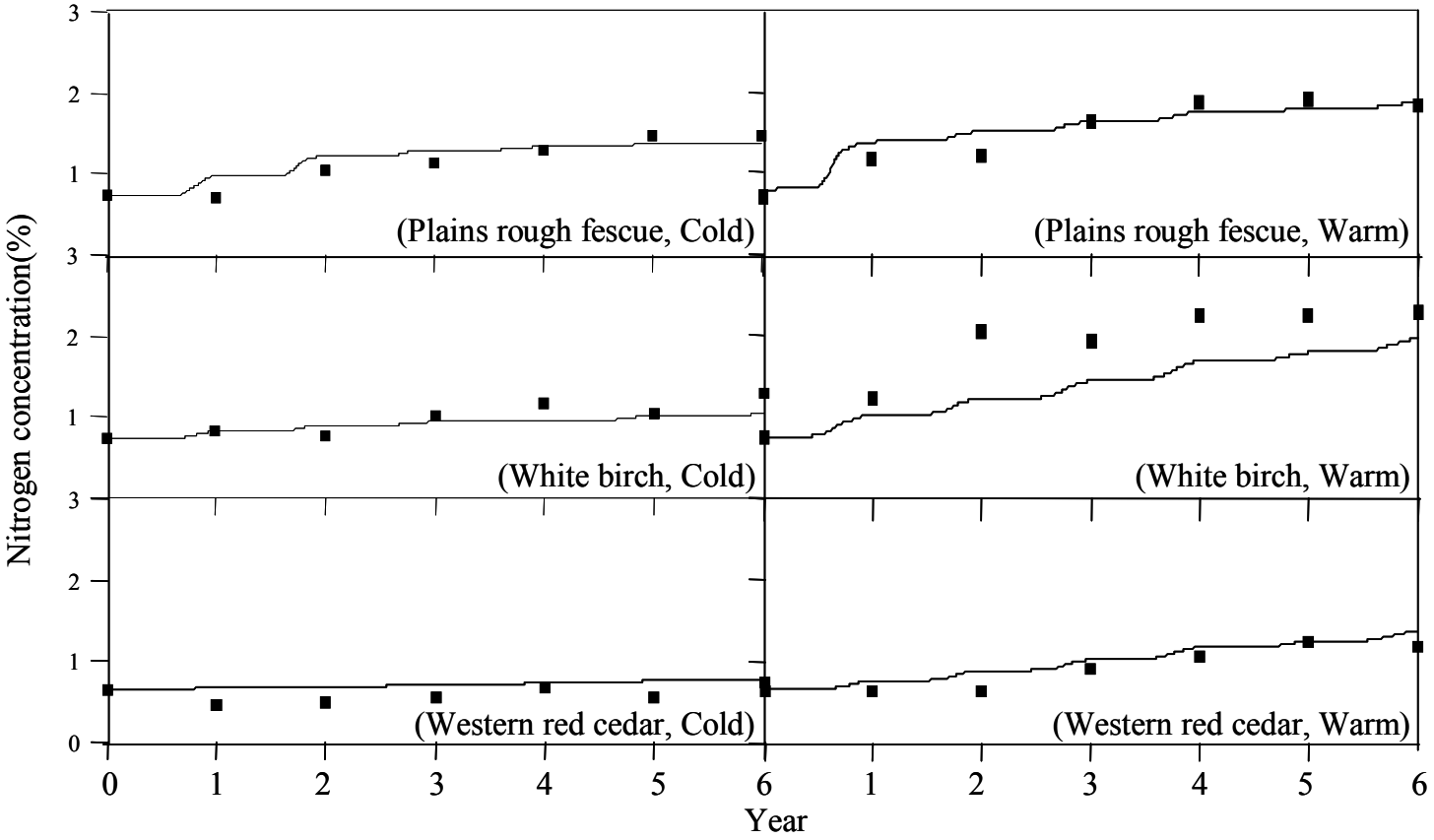

Figure 3.4 Comparison of measured (squares) and model-simulated (lines) N concentrations as a function of time and species for both a warm (Petawawa) and a cold site (Inuvik).

3.5.4 Litter Decomposition and N Mineralisation

In the monthly model, litter decomposition is made independent of N mineralisation, whereas N mineralisation is affected by decomposition. Decoupling litter decomposition from N mineralisation is well supported by field experimentation. For example, (1) McClaugherty et al. (1985) found that N mineralisation did not affect leaf and wood litter mass decomposition; (2) Murphy et al. (1998) demonstrated that the rate of litter decomposition was only limited by available C and not by N content; (3) Prescott (1995) found that N accessibility alone, either exogenous or endogenous, did not control the rate of litter decomposition; and (4) Knorr et al. (2005b) found N content affected litter decomposition only when N content exceeded normal field conditions.

3.5.5 Model Comparison

SOMM (Chertov and Komarov, 1997) and CENTURY (2000) are both monthly litter decomposition models. The SOMM model consists of three C pools and three N pools, seven C flows and seven N flows and 61 parameters (Zhang et al., 2008). The CENTURY model has five C pools and five N pools, 13 C flows and 13 N flows and 25 parameters. Compared to FLDM, the SOMM and CENTURY models are much more complex (Zhang et al., 2008). Tables 3.4-3.5 and Figures 3.5-3.6 provide results from a comparison of the FLDM (two revised monthly and annual versions), SOMM, and CENTURY models. CIDET data-vs.-model prediction data pairs for the SOMM and CENTURY models give R^2-values of 0.80 and 0.87 for the

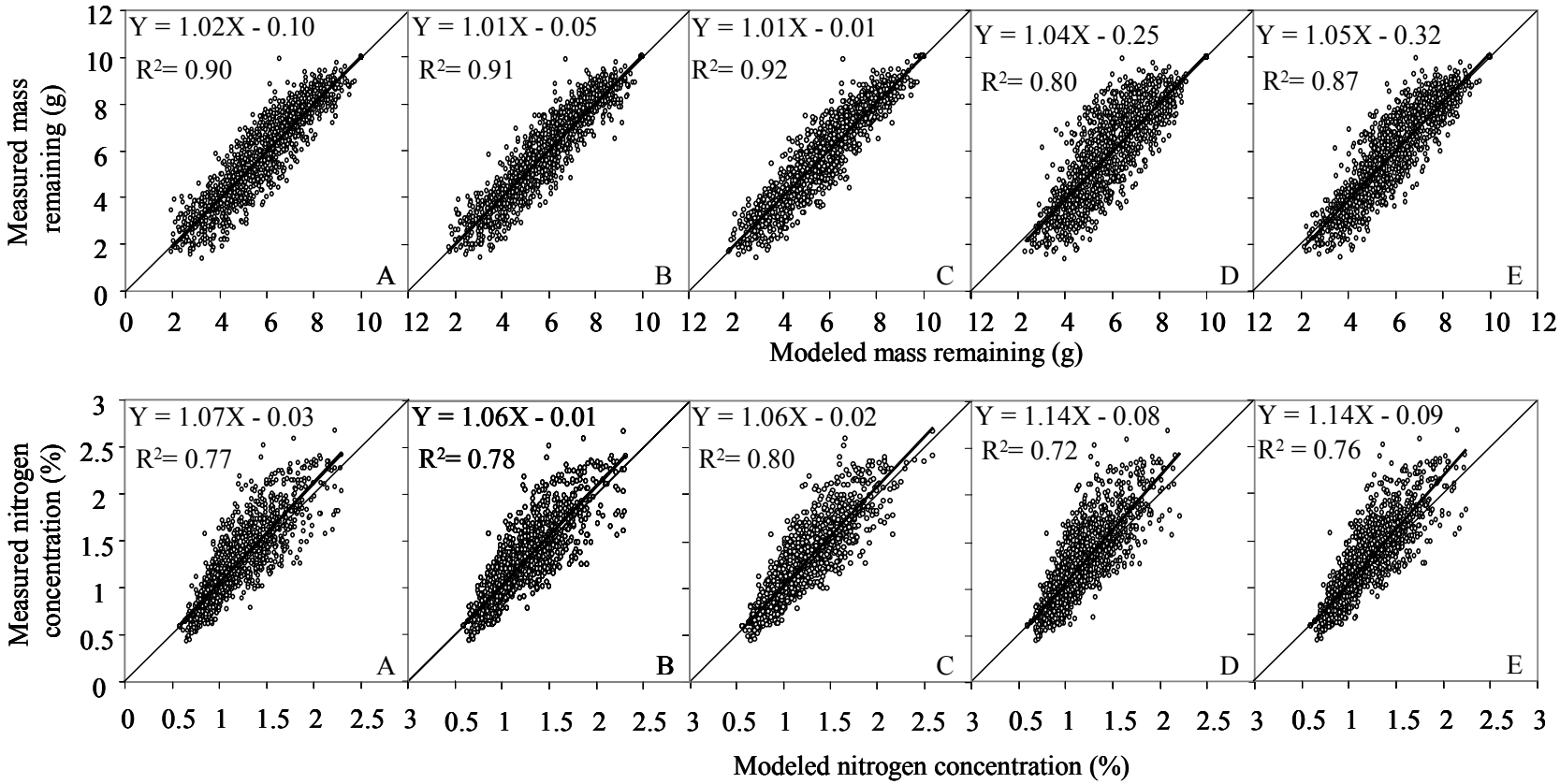

Figure 3.5 Comparison of CIDET litterbag and model-simulated residual mass and N concentrations for each consecutive year from 1992 through 1998. Model simulations are based on A, Revised FLDM using Eq. (3.17a), B, Revised FLDM using Eq. (3.17b), C, Annual FLDM, D, SOMM model, E, CENTURY model.

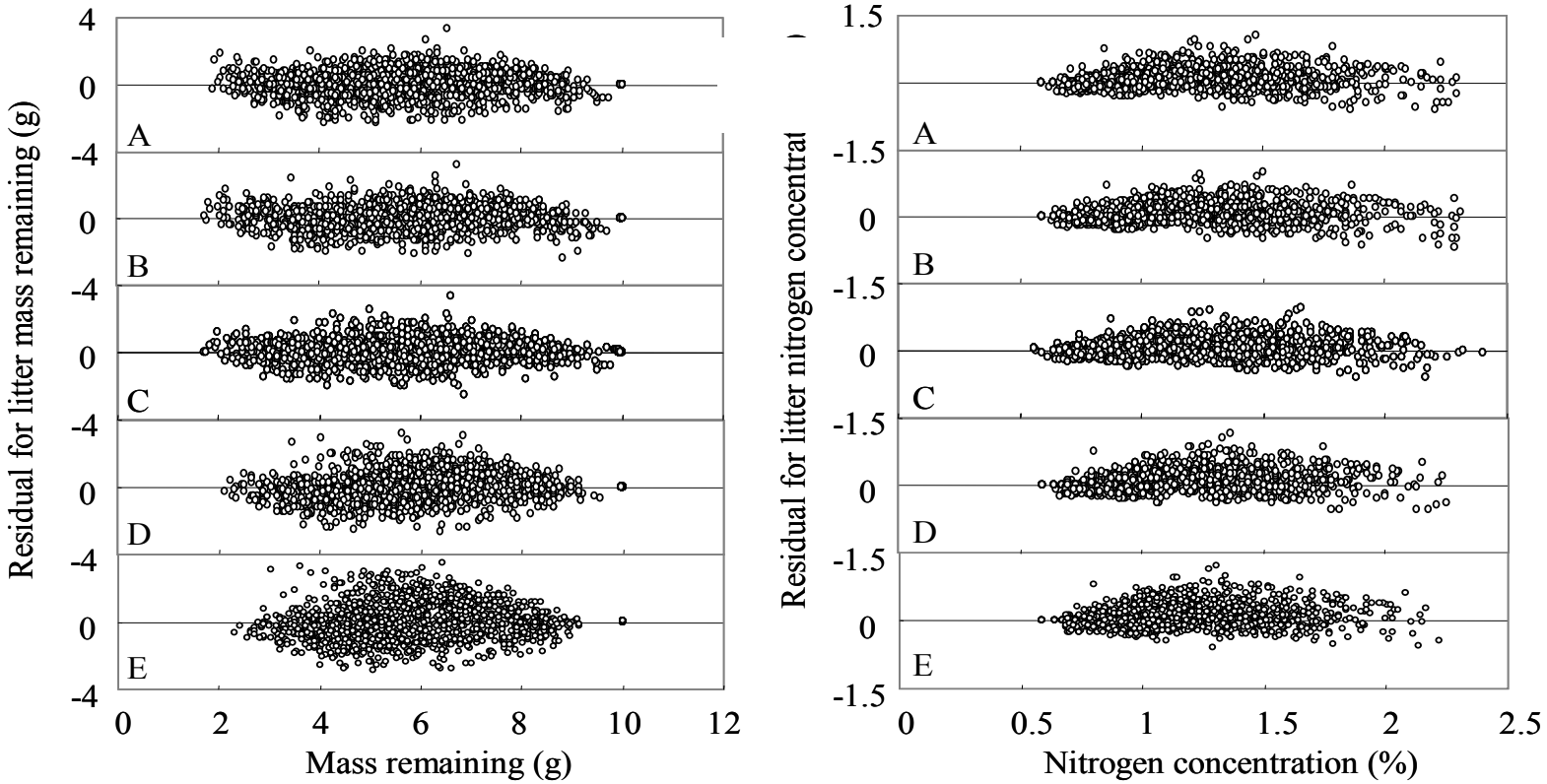

Figure 3.6 Residuals for measured vs. model-fitted residual litter mass and N concentrations in CIDET litterbags filled with aspen litter. Figures A-E are associated with model results from the revised monthly FLDM using Eq. (3.17a), monthly model using Eq. (3.17b), the original annual model, the SOMM model, and the CENTURY model, respectively.

residual mass and 0.72 and 0.76 for mineralised N. The revised monthly FLDM with Eq. (3.17b) shows less bias in litter decomposition and N mineralisation, than what is observed with the SOMM and CENTURY models. Clearly, the simpler revised FLDM is more effective at modelling litter decomposition. The comparison provided shows that overly complex models do not necessarily outperform simpler models. A common risk associated with complex models is increased model error and incorrect output (Larocque, et al., 2008).

3.5.6 Performance of Revised FLDM

While the annual FLDM can capture litter decomposition and mineralised N concentrations trends fairly well, the revised model, unlike the annual model, can capture the seasonal variation in litter decomposition. Figure 3.7 gives the projected monthly litter decomposition of aspen at the CBR site (CB Rocky Harbour) from 1992-1998. Trends in litter decomposition increase in spring from inactivity in winter, and reach a maximum in the summer. Decomposition drops in the fall with decreasing temperatures and discontinues in winter.

3.6 Concluding Remarks

The monthly model developed in this Chapter and the original, annual forest litter decomposition model (FLDM) show no significant difference in the prediction of residual mass. The greatest difference arises in their prediction of decomposition. Decomposition in the new model varies as a function of seasonal weather, while the

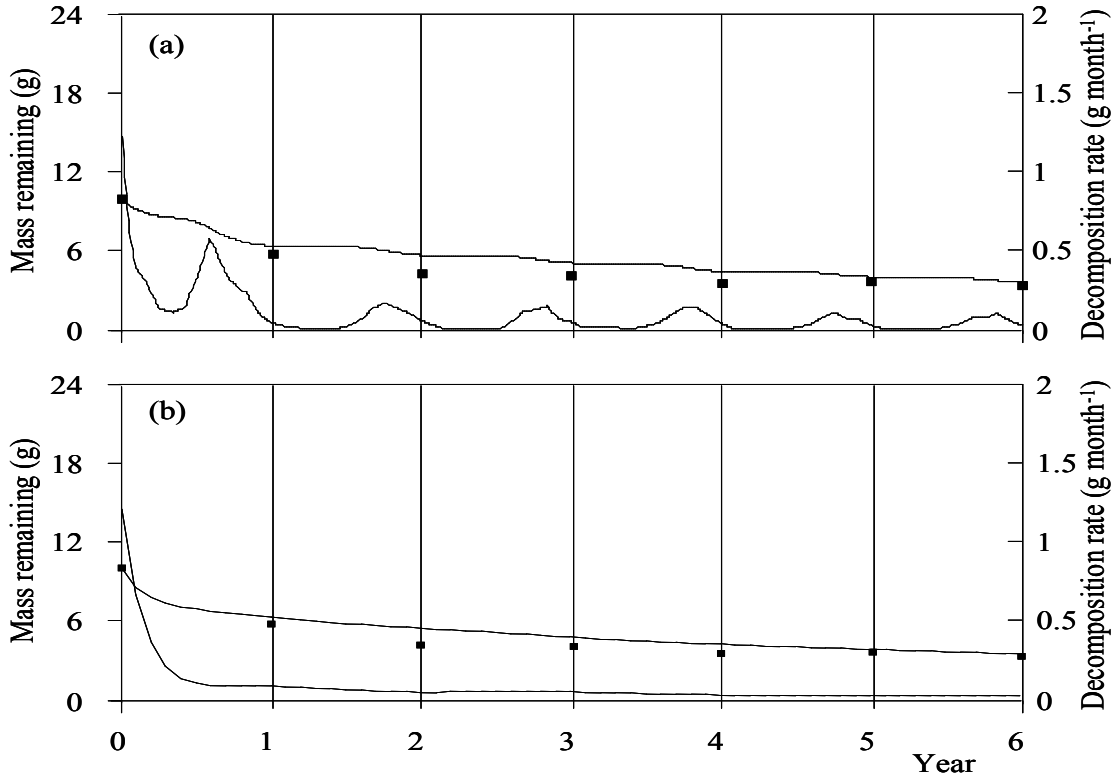

Figure 3.7 Comparison of simulated residual litter mass (lines) with the monthly FLDM using Eq. (3.17b) (upper figure) and original, annual FLDM (bottom figure) against corresponding CIDET data (squares). Superimposed are the corresponding modelled decomposition rates (lower lines).

annual model assumes an average decomposition rate throughout the year. The added requirements for soil temperature and moisture as input to the new model require that the model rely on output from a forest hydrology model. The forest hydrology model used in this work is simple and calculates water fluxes according to inputs of daily mean air temperature and precipitation measured at first-order weather stations in vicinity to the sites. The revised model, incorporating the effect of mean January soil temperature by way of Eq. (3.17b), outperformed more complex forest litter decomposition models, like SOMM and CENTURY. This is particularly emphasised when model results are compared to litterbag decomposition data from the CIDET project.

From a modelling standpoint, two important facts are uncovered not previously reported: (i) litter decomposition is independent of N mineralisation, whereas N mineralisation is dependent on litter decomposition; and (ii) mean January soil temperature is shown to define litter decomposition in the following summer; a feature not addressed in the annual FLDM, CENTURY, or SOMM models. This fact is particularly important when studying the effects of climate warming on forest litter decomposition.

3.7 Acknowledgements

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CHAPTER 4 LONG-TERM FOREST-FLOOR LITTER DYNAMICS IN CANADA'S BOREAL FOREST: COMPARISON OF TWO MODEL FORMULATIONS

Chengfu Zhang[a,b], Rob C. Jamieson[b], Fan-Rui Meng[a], Robert J. Gordon[c], Jagtar Bhatti[d], Charles P.-A. Bourque[a,*]

[a] *Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada*
[b] *Department of Process Engineering and Applied Science, Dalhousie University, Halifax, NS, B3J 1Z1, Canada*
[c] *Ontario Agricultural College, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*
[d] *Northern Forestry Centre, Canadian Forest Service, 5320 - 122nd Street, Edmonton, Alberta, T6H 3S5, Canada*

Running title: Forest-floor litter dynamics

[*] Corresponding author at: Faculty of Forestry and Environmental Management, 28 Dineen Drive, PO Box 4400, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada. Tel.: 1-506-453-4509; Fax.: 1-506-453-3538.
E-mail address: cbourque@unb.ca (C. P.-A. Bourque)

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4.1 Abstract

Dissolved organic carbon (DOC) and nutrients exported from forest ecosystems are the main source of energy and nutrients to aquatic ecosystems in small watersheds. DOC and nutrients from forests are released with the decomposition of the organic litter. In this study, comparison is made between simulations of long-term forest-floor litter dynamics generated with a monthly forest nutrient cycling and biomass growth model (ForNBM) initially coupled with (i) a one-pool decomposition formulation, and (ii) a revised three-pool formulation (i.e., FLDM, Chapter 3) consisting of three decomposing litter pools representing fast, slow and very slow decomposing litter matter (Zhang et al., 2010, Ecological Modelling 221, 1944-1953). Modelled forest-floor litter dynamics are compared against field measurements collected at several northern jack pine (*Pinus banksiana*) stands along a SW-NE oriented transect (climate gradient) associated with the Boreal Forest Transect Case Study. The comparison shows that the single-pool formulation underpredicts residual litter when forests are < 65 years old. This underprediction is resolved when the three-pool formulation (i.e., FLDM) is used. From a ecosystems-response point of view, the three-pool formulation demonstrates that (i) forest-floor litter initially increases with forest development and reaches a plateau once the forest matures; (ii) the forest floor stores more carbon (C) at the southern and warmer sites than at the northern and colder sites; and (iii) in a similar climate regime, the forest floor stores more C (and potentially more DOC) at productive sites than at nutrient-poor sites.

Keywords: boreal forest, climate change, ecosystems modelling, forest-floor carbon stock

4.2 Introduction

Nutrients and dissolved organic carbon (DOC) leached from forest ecosystems are important sources of nutrients and energy to aquatic ecosystems in small watersheds (Wetzel et al., 1972; Wetzel, 1983; Pace, 1993; Kim et al., 2010). Transport of DOC from terrestrial ecosystems to streams is an important component of the terrestrial carbon (C) cycle (Ludwig et al., 1996; Warnken and Santschi, 2004; Battin et al., 2009). DOC is released with (i) the decomposition of the organic litter and release of C (this Chapter's focus), and (ii) interaction of the decomposing litter with flowing water.

To address forest-floor litter decomposition, a nutrient cycling and biomass growth model is integrated (i.e., **ForNBM**; Zhu et al., 2003a, 2003b) with (i) a forest hydrology and (ii) a forest-litter decomposition sub-module (Figure 4.1). Currently, ForNBM simulates the effects of forest growth and management on streamwater quality with a simple one-pool litter decomposition formulation (Zhu et al., 2003a, 2003b). Given that forest litter is composed of a mixture of organic compounds that decompose at different rates (Trofymow and the CIDET Working Group, 1998), a single-pool formulation may be unsuitable in the long-term simulation of forest-ecosystem litter dynamics.

Complexity of forest litter decomposition models in the scientific literature varies in the number of pools (state variables), process equations and input variables employed (Powlson et al., 1996; Zhang et al, 2008). For example, (i) CENTURY (Parton et al., 1987) has 26 pools and 25 equation parameters, (ii) SOMM (Chertov and Komarov, 1997) has 14 pools and 61 parameters, (iii) Candy (Franko et al., 1995) has 6 pools and 8 parameters, and (iv) DOCMOD (Currie and Aber, 1997) has 21 pools and 21 parameters.

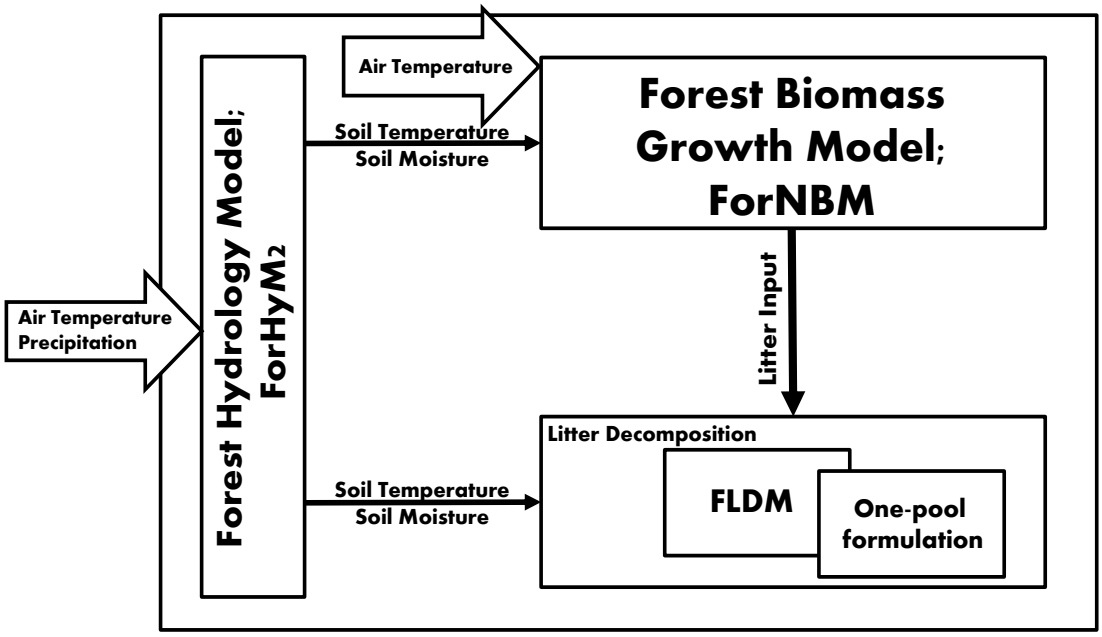

Figure 4.1 Integrated monthly forest-floor litter decomposition model. In the integrated model, (1) ForNBM (Zhu et al., 2003a) is used in the calculation of annual litter fall, (2) one-pool litter decomposition or three-pool FLDM formulation (Zhang et al., 2007 and 2010) in the calculation of forest-floor litter decomposition, and (3) ForHyM2 (Meng et al., 1995; Balland, 2003) in the calculation of soil temperature and soil moisture for input to ForNBM and litter decomposition formulation (i.e., either the single-pool or FLDM formulation). Air temperature input to ForHyM2 and ForNBM and precipitation to ForHyM2 are obtained from first-order climate stations nearest BFTCS sites.

In CANDY and SOMM, leaf litter decomposition follows a sequential process from a biologically-active state to a humified state. In CENTURY, the initially separate pools are transferred to intermediate active, microbe-dominated, and slow pools to passive humus pools.

The seasonal forest litter decomposition model (FLDM, three-pool formulation) is based on three litter pools representing fast, slow, and very slow decomposing litter matter (Zhang et al., 2007 and 2010). In FLDM, litter decomposition is specified independent of N mineralisation (Zhang et al., 2010). In general, FLDM is shown to provide better simulations than the more complex models, such as SOMM, CENTURY, DOCMOD, or CANDY (Zhang et al., 2008, 2010).

The objective of this study is to compare the results generated with a single-pool and a three-pool litter decomposition formulation in the long-term simulation of forest-ecosystem litter dynamics (Figure 4.1). Results of modelled (i) forest growth and litter production with ForNBM, and (ii) forest-floor residual litter mass with either the single- or three-pool formulation (i.e., FLDM) are compared against field measurements taken at several northern jack pine (jP; *Pinus banksiana*) stands along a SW-NE oriented transect (climate gradient) in the boreal forest of northwest Canada (i.e., from northern Saskatchewan to northern Manitoba). The effect of stand age, local climate, and site quality on simulated jP-stand forest-floor C (and DOC-production) dynamics is investigated as a function of litter decomposition formulation.

4.3 Study Area and Field Data Collection

4.3.1 Study Area

Field data used in this Chapter are derived from the Boreal Forest Transect Case Study (BFTCS; Bhatti et al., 2003). BFTCS is an extensive field experiment designed to investigate C dynamics as a function of climate change over the next 50-100 years. The study area measures about 850 km × 100 km; an area extending from the prairie grassland-forest transition zone (low boreal forests), south at Prince Albert, Saskatchewan (SK; 53° 13' N 105° 41' W), through to the mid- and high-boreal forests of Thompson, Manitoba (MB; 55° 48' N 97° 52' W), and low subarctic tundra, north at Gilliam, MB (56° 21' N 94° 42' W; Figure 4.2). Climate along the BFTCS transect varies from "warm and dry" at its southern end to "cold and wet" at its northern end. Ten jP-dominated sites were selected for this study; eight along the southern portion of the study-transect near Prince Albert, SK, and two near Thompson, MB (Figure 4.2).

4.3.2 Site Selection in 'Space Trade for Time' Experiments

The BFTCS experiment is designed with the assumption that spatial variation in C dynamics along a climate gradient can be used to represent C-stock evolution under a climate-change regime (i.e., a 'space trade for time' scheme; Pickett, 1989). Long-term field experiments (> 50 years) are risky to implement because of the possibility of unanticipated disturbance disrupting the research, e.g., by events of fire, windthrow, and insect-disease infestation, to some or all of the study sites (Taylor and MacLean, 2005; Jeffries et al., 2006; Evans, et al., 2007). To satisfy the experimental requirement of

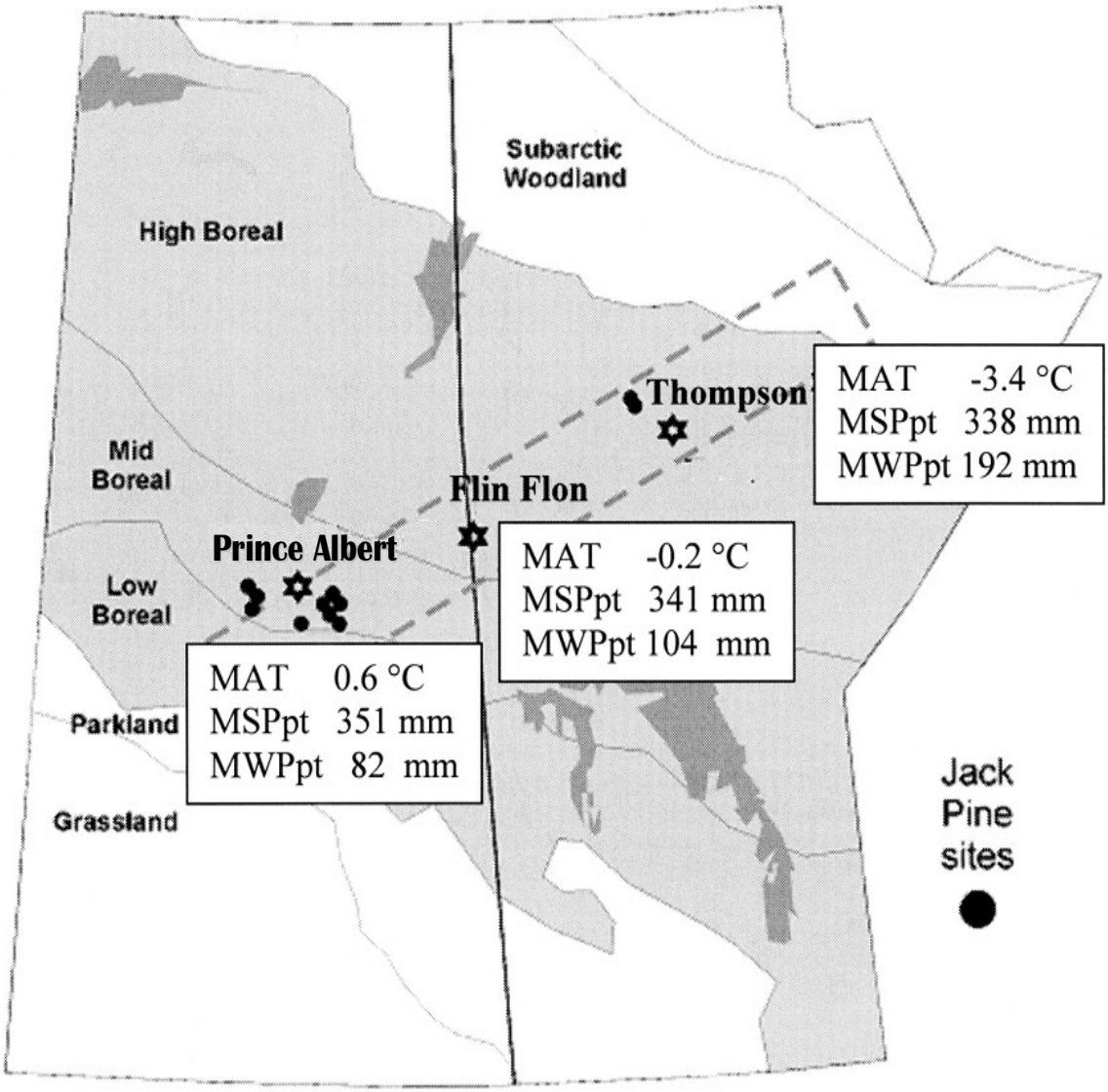

Figure 4.2 Location and orientation of the Boreal Forest Transect Case Study (BFTCS) and field sites (after Shaw et al., 2006); MAT=mean annual temperature, MSPpt=mean summer precipitation, and MWPpt= mean winter precipitation.

comparable sites across the transect (Pickett, 1989), sites were selected according to their (i) stand-initiation disturbance regime (i.e., fire); (ii) location (i.e., flat terrain); and (iii) species composition (i.e., predominantly jP).

4.3.3 Field data Collection

Field data collected as part of the BFTCS study included (i) living biomass, (ii) foliage litter fall, and (iii) total forest-floor C. In addition to the BFTCS field data, forest growth and forest-floor residual litter mass from Nalder and Wein (1999) were also used.

At each site (Figure 4.2), three 20 m × 20 m inventory plots were established. Plot-level tree measurements recorded in June 2001 included tree height and diameter at breast height (DBH). Aboveground tree biomass was calculated with allometric equations from Alban and Laidly (1982). Plot-level biomass was determined by summing the biomass of individual trees within each plot. Biomass at each site was, in turn, calculated by averaging the biomass estimated for the three inventory plots (Table 4.1). Stand age was estimated by counting tree rings of 10-15 trees at each site.

Forest litter fall in each plot was determined with the assistance of 36 plastic buckets (27.3-cm diameter and 30.0-cm deep) with mesh bottoms to retain foliage, twigs, bark, and cones (Table 4.2). Litter traps were installed in June 2000 and samples were collected in both 2001 and 2002.

Forest-floor samples were collected by separating the leaf (L), fibric (F), and humic (H) layers using 15 cm × 15 cm templates with three replicates. All forest-floor samples,

Table 4.1 Living forest biomass in ten jack pine-dominated sites, eight near Prince Albert, Saskatchewan, and two near Thompson, Manitoba.

Name	Climate region[a]	Latitude (degree)	Longitude (degree)	Age (year)	Branches (kg m^{-2})	Foliage (kg m^{-2})	Stem bark (kg m^{-2})	Stem wood (kg m^{-2})	Total tree (kg m^{-2})
SHAR75	Prince Albert	53.8757	-104.6453	28	0.76	0.41	0.53	2.46	4.16
SHAR94	Prince Albert	53.9080	-104.6560	9	0.00	0.11	0.00	0.21	0.32
STOJP	Prince Albert	53.9147	-104.6902	90	0.96	0.53	0.97	7.86	10.31
SF77	Prince Albert	54.4848	-105.8174	26	0.66	0.39	0.49	2.45	3.99
PJM2	Prince Albert	53.2257	-105.9780	80	0.87	0.48	0.85	6.61	8.81
SJDM8	Prince Albert	53.9672	-104.6387	38	0.51	0.27	0.39	1.44	2.61
SJIH4	Prince Albert	53.8616	-105.1079	60	0.70	0.53	0.69	4.41	6.32
GJM1	Prince Albert	53.2257	-105.9780	80	0.66	0.39	0.60	4.08	5.73
NTOJP	Thompson	54.8400	-102.5127	74	0.60	0.33	0.51	3.43	4.87
NJIL1	Thompson	55.9283	-98.6218	83	0.56	0.30	0.44	3.02	4.32

[a] Prince Albert represents the southern climate regime of the BFTCS transect and Thompson, the northern climate regime.

Table 4.2 Foliage litter fall and forest-floor carbon (C) mass in ten jack pine-dominated stands associated with BFTCS.

Site code	Years	Litter fall mass ($g\ m^{-2}\ year^{-1}$)			Forest floor C ($kg\ m^{-2}$)
		Jack pine	Black spruce	Trembling aspen	
SHAR75	2003-05	105.82	0.00	3.17	0.9
SHAR94	2003-05	13.59	0.00	6.57	0.1
STOJP	2000-05	83.04	0.00	1.49	0.5
SF77	2003-05	72.67	2.17	7.27	1.7
PJM2	2002-05	91.59	0.00	0.21	0.6
SJDM8	2000-05	94.03	0.00	28.03	0.7
SJIH4	2000-05	60.24	28.44	0.18	1.4
GJM1	2001-05	60.45	1.45	6.97	0.9
NTOJP	2000-05	69.41	0.00	11.63	0.5
NJIL1	2000-05	71.84	0.00	0.03	0.3

excluding live vegetation and large branches and roots, were oven-dried at 70^{o}C, weighed, and finely grounded. Carbon content of the samples were analysed by dry combustion using a LECO Carbon Determination System (Model CR 12). Resulting C content were then averaged for each site. Because the forest floor is composed of a blend of organic matter and soil, the density of the forest floor can vary considerably over very small distances and, as a result, deriving an accurate estimate of residual mass of organic matter directly is fairly difficult to do. As an alternate, it is assumed that the forest-floor residual organic-matter mass is equal to two times the forest-floor C content (CIDET data and Xing et al., 2005). Forest-floor C content for individual sites is summarised in Table 4.2.

4.3.4 Climate Data

Daily average air temperature and precipitation sums (rain and snow) from 1968 to 2003 were collected from first-order climate stations at Prince Albert, SK, and Thompson, MB. Consecutive 25 years of data were cycled 6 times to generate area-specific timeseries of 150 years of daily weather data to simulate forest-floor litter dynamics across BFTCS-study sites.

4.4 Model Integration

Forest litter input to each of the litter decomposition formulations is simulated with ForNBM; soil temperature and soil moisture input to ForNBM and decomposition formulations (including FLDM) are generated with the forest hydrology model, ForHyM2 (Meng et al., 1995; Balland, 2003; see Figure 4.1). Air temperature input to

ForNBM and ForHyM2 and precipitation to ForHyM2 are from climate stations nearest the BFTCS sites.

4.4.1 ForNBM

ForNBM was developed to simulate net primary productivity (NPP) and nutrient cycling based on mean monthly air temperature, soil temperature, soil moisture, forest site conditions, and forest-management prescriptions. Past uses of the model, include (i) simulating forest growth and C cycling; (ii) determining nutrient sustainability of forests based on nutrient cycling and soil-geochemical balances; and (iii) evaluating the effects of forest management on the environment, including streamwater quality. For detailed description of ForNBM, refer to Zhu et al. (2003a).

In this study, foliage-litter fall in ForNBM (Zhu et al., 2003a) was reformulated as

$$M_{lf} = \mathrm{F_{lf1}} \mathrm{M_{wd}}^{\mathrm{F_{lf2}}} \quad \text{, with} \tag{4.1}$$

$$F_{ltr} = \mathrm{F_{lf3}} \mathrm{M_{lf}} \text{ ; if } \varepsilon_{\mathrm{W}} \varepsilon_{\mathrm{T}} \varepsilon_{Age} < 0, \tag{4.2}$$

where M_{wd} and M_{lf} are the living stem and leaf biomass (tonne ha^{-1}), F_{ltr} is the annual litter fall mass (tonne ha^{-1}), and F_{lf1}, F_{lf2}, and F_{lf3} are equation parameters (non-dimensional); $\varepsilon_{\mathrm{W}}, \varepsilon_{\mathrm{T}}$, and ε_{Age} are soil moisture-, soil temperature-, and stand age-related variables; see Zhu et al. (2003a) for equation formulations.

ForNBM is developed based on the principle that (i) living foliage biomass and living stem mass can be adequately represented by allometric equations, such as those of Alban and Laidly (1982), and (ii) foliage fall can be represented as a constant ratio of

foliage biomass production (Zhu et al., 2003a). Foliage litter fall is initiated in the autumn, when tree productivity is essentially zero (Aber and Federer, 1992).

4.4.2 Litter Decomposition Formulations

4.4.2.1 One Pool

In the one-pool litter decomposition formulation, changes in forest-floor litter mass is modelled according to

$$dML_{lf}/dt = - k_0 \, f_{climate}(ML_{lf} + F_{Ltr}), \quad (4.3)$$

where ML_{lf} is the total residual litter mass in the forest floor (tonne ha^{-1}), $f_{climate}$ is a climate factor, and k_0 is an equation parameter.

4.4.2.2 Three Pools

FLDM (three-pool formulation) is based on the assumption that foliage litter is composed of three organic compounds that decompose at different rates (Figure 4.3; LIDET, 1995; Trofymow and the CIDET Working Group, 1998; Minderman, 2005). During each autumn, litter is distributed among the fast, slow and very slow decomposing litter pools based on the litter's initial water-extractable, acid-hydrolysable, and ash content (Zhang et al., 2007 and 2010). Litter distribution in the three litter pools and their decomposition rates are defined by:

$$dML_1/dt = - k_1 \, f_{climate}(ML_1 + g \, F_{Ltr}) \quad (4.4)$$

$$dML_2/dt = - f_{climate} (ML_2 + (1 - g) e F_{Ltr}) \quad (4.5)$$

$$dML_3/dt = - k_3 f_{climate} (ML_3 + (1 - g) (1 - e) F_{Ltr}) \quad (4.6)$$

$$ML_{lf} = ML_1 + ML_2 + ML_3 \quad (4.7)$$

where ML_1, ML_2, and ML_3 are the residual mass in the three litter pools (tonne ha^{-1}; ML_{if} is the total residual litter mass), k_1 and k_3 are equation parameters (non-dimensional), and e and g are litter-mass partitioning coefficients:

$$g = \exp(a_0 + a_1 \alpha + a_2 \gamma) \text{ , and} \quad (4.8)$$

$$e = \exp(- a_3 \beta) , \quad (4.9)$$

where a_0, a_1, a_2, and a_3 are equation coefficients (non-dimensional), and γ and α are the water- and acid-extractable content of the litter and β, the ash content (all in % volume).

The climate factor, $f_{climate}$, is expressed as:

$$f_{climate} = k_2 f_T . f_W , \quad (4.10)$$

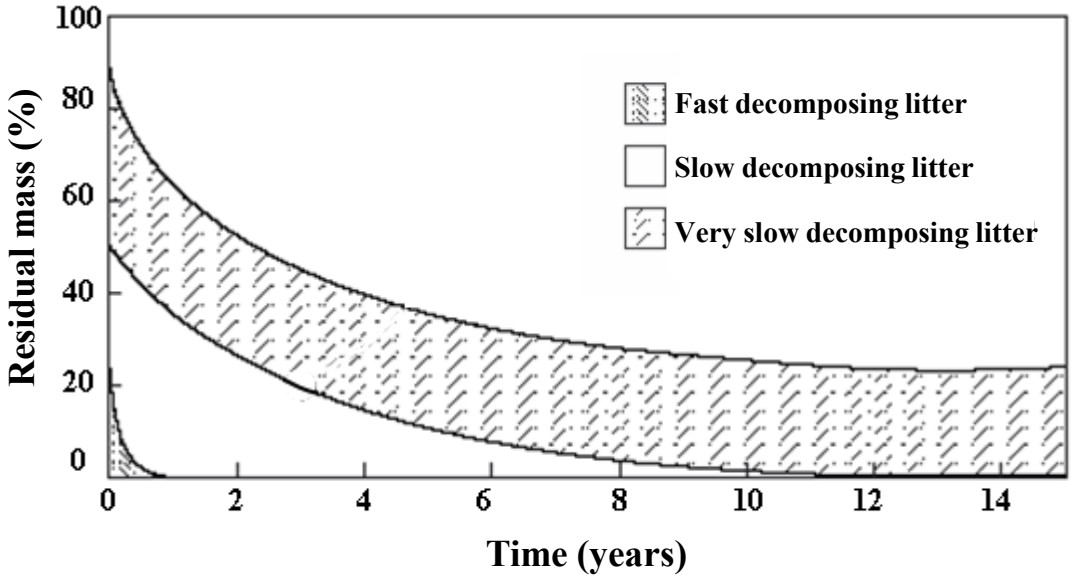

Figure 4.3 Litter-chemical compounds and associated decomposition rates (after LIDET, 1995). Partitioning to the different litter pools each autumn is based on the litter's initial water-extractable, acid-hydrolysable, and ash content (Zhang et al., 2010).

where f_T and f_W are temperature and moisture-related factors, and k_2 is an equation parameter (non-dimensional; Zhang et al., 2010). Environmental-forcing variables of FLDM are mean January soil temperature and mean monthly soil temperature and soil moisture. Mean January soil temperature is used to address the effect of previous winter temperatures on decomposer-communities winter survival and overall performance in the following summer (Zhang et al., 2010).

4.4.3 ForHyM2

ForHyM2 was originally developed by Meng et al. (1995) and Balland (2003). Figure 4.1 gives the water and heat flux components of ForHyM2. The current version of ForHyM2 simulates heat and water fluxes at a daily timestep using inputs of daily accumulated precipitation and average air temperature obtained from first-order weather stations nearby. For model input to ForNBM and litter decomposition formulations, simulated weather is averaged monthly.

4.5 Model Realisation and Parameterisation

ForHyM2 is formulated in the STELLA™ environment (1998) and ForNBM and litter decomposition formulations in ModelMaker™ (1999), both visual-programming software. To make the simulation simple and comparable between sites, stand biomass, leaf litter fall, and forest-floor litter are all expressed as per hectare (ha) quantities.

Given lack of direct measurements, it is assumed that the chemical composition of jP (jack pine) foliage and fine-root litter in the three-pool litter decomposition calculations is the same as that of jP foliage from the CIDET experiment (Trofymow and the CIDET

Working Group, 1998) and as reported in Zhang et al. (2010). Based on observations that (i) fine-root biomass is nearly the same as that of living foliage, and (ii) about ½ of the fine roots are distributed aboveground (Currie and Aber, 1997), it can be safely assumed that the annual input of fine roots to the forest floor is about ½ of that of foliage. Post-disturbance quantity of litter matter in the fast, slow, and very slow decomposing litter pools is estimated by the calculated litter masses [with Eq. (4.4)-(4.6)] prior to stand initiation. This is a reasonable approach providing that fire during stand initiation is limited to the crowns.

Parameters in the integrated model (Figure 4.1) are calibrated in part based on (i) field measurements of biomass growth and litter fall from the Prince Albert-area sites, and (ii) decomposition-related parameter values derived from the CIDET-litterbag experiment (Zhang et al., 2010) and other studies (e.g., Xing et al., 2005). Calibration of biomass growth and litter fall-related parameters are optimised by minimising the differences between the modelled and field-measurements of biomass growth and litter fall with numerical-optimisation methods available in ModelMaker™ (1999). Forest-floor residual litter mass is only used to re-define the decomposition rate in the single- and three-pool litter decomposition formulations for the current sites (i.e., by changing k_0 and k_2, respectively; Table 4.3); the CIDET data (Zhang et al., 2010) generally indicated a faster decomposition rate (180% greater) than what was observed for the Prince Albert-area sites. Once calibrated, the integrated model (Figure 4.1) is used to simulate forest-floor litter dynamics for both the Prince Albert- and Thompson-area sites. Model parameter values and their calibration-data sources are summarised in Table 4.3.

Table 4.3 Values for forest growth and litter decomposition parameters in ForNBM and in the one-pool and three-pool (FLDM) litter decomposition formulations. Field calibration data (i.e., biomass, litter fall, and forest-floor litter) comes from the Prince Albert-area sites.

Forest process	Unit	Value	Derived from	Data source
Living biomass increment				
M_{max} [a]	tonne	(0.79-1.91)	Calibration	Biomass
P_{age0}	unitless	0.016	Calibration	Biomass
P_{age1}	unitless	2.390	Calibration	Biomass
P_{age2}	unitless	0.083	Calibration	Biomass
T_{max}	^oC	40	Calibration	Biomass
T_{opt}	^oC	20	Calibration	Biomass
T_{min}	^oC	5	Calibration	Biomass
sm_{max} [b]	% volume	1	Calibration	Biomass
sm_{opt}	% volume	0.80	Calibration	Biomass
sm_{min}	% volume	0.16	Calibration	Biomass
F_{lf1}	unitless	0.25	Calibration	Biomass
F_{lf2}	unitless	0.67	Calibration	Biomass
Litter fall				
F_{lf3}	unitless	0.20	Calibration	Litter fall
Litter decomposition				
a_0	unitless	-10.9	Zhang et al. (2010)	CIDET
a_1	unitless	0.14	Zhang et al. (2010)	CIDET
a_2	unitless	0.131	Zhang et al. (2010)	CIDET
a_3	unitless	0.119	Zhang et al. (2010)	CIDET
E_a	J $mole^{-1}$	103879	Zhang et al. (2010)	CIDET
k_1	unitless	17.92	Zhang et al. (2010)	CIDET
k_2 (three-pool)	$month^{-1}$	0.015	Calibration	Forest-floor litter
k_3	unitless	0.35	Zhang et al. (2010)	CIDET
p_{TJan}	^oC	20.70	Zhang et al. (2010)	CIDET
sm'_{max} [b]	% volume	1	Zhang et al. (2010)	CIDET
sm'_{opt}	% volume	0.95	Zhang et al. (2010)	CIDET
sm'_{min}	% volume	0.00	Zhang et al. (2010)	CIDET
R	J $mole^{-1}$ $^oC^{-1}$	8.31	Constant, Zhang et al. (2010)	Theory
k_0 (one-pool)	unitless	0.58	Calibration	Forest-floor litter
C : OM [c]	unitless	0.50	Xing et al., 2005	Stem and litter analysis

[a] M_{max} correspond to the average, minimum, and maximum soil productivity for the BFTCS sites; [b] sm'_{min}, sm'_{max}, and sm'_{opt} for litter decomposition differ from sm_{min}, sm_{max}, and sm_{opt} for photosynthesis; [c] Carbon (C) to organic matter (OM) ratio.

From field measurements, forest-stand growth varies significantly from site to site, even on low-relief to flat terrain. It is hypothesised that this variation results from differences in soil quality. To capture this variability, the M_{max} parameter (i.e., maximum biomass a site potentially can support) is adjusted in ForNBM (Zhu et al., 2003a), while keeping all other model parameters unchanged (Table 4.3).

For comparison, the measured and modelled values are classified into three age classes, i.e., (i) 0-25, (ii) 25-65, and (iii) > 65 years old. Modelled maximum, average, and minimum values for stem growth, litter fall, and forest-floor residual litter mass are calculated as a function of M_{max}, stand age, and climate regime (i.e., warm-dry vs. cold-wet). Indication of goodness-of-fit between the field measurements and modelled results is determined with the ratio of the root mean square error (RMSE) to RMSE at 95% confidence level (i.e., $RMSE_{95\%}$; Smith et al., 1997). When $RMSE/RMSE_{95\%}$ is < 1, it denotes that the modelled values fall within the 95% confidence interval of the field measurements and that the modelled values are in reasonably good agreement with the measurements (Smith et al., 1997; Shaw et al., 2006). As there are limited number of sites and measurement types, $RMSE/RMSE_{95\%}$ calculations are applied only to stem growth and forest-floor residual litter mass evaluations.

4.6 Results and Discussion

4.6.1 Living Biomass Growth and Foliage Litter Fall

Modelled stem growth is nearly similar to the field measurements for the three age classes and climatic regions (Table 4.4; Figure 4.4a). Accounting for differences in soil

Table 4.4 Model-accuracy analysis for stem growth, litter fall, and residual forest-floor litter mass as a function of stand age and climate regime (Prince Albert, SK, and Thompson, MB).

		M_{wd}[a] (tonne ha^{-1})		**Leaf fall** (tonne ha^{-1} $year^{-1}$)		**ML_{lf}**[b] (tonne ha^{-1})		
Sites	**Age**	**Measured**	**Modelled**	**Measured**	**Modelled**	**Measured**	**FLDM**	**One-pool**
Prince Albert								
Average	14.7	11.7	11.2	0.2	0.2	12.0	20.3	17.5
Range	0-25	3.2-16	5.8-16.1		0.2-0.3	2-18	14.5-28.1	
Average	44.6	66.3	72.9	1.0	0.9	25.8	20.1	17.3
Range	25-65	26.1-140	38.2-105	0.8-1.2	0.6-1.1	16-42	13.5-26.3	
Average	87.5	106.6	113.5	0.8	1.2	22.7	27.0	25.9
Range	>65	82.0-144	59.5-163.6	0.7-0.9	0.8-1.5	12.4-36	17.4-34.1	
Thompson								
Average	52.1	60.3	61.7		0.8	26.0	17.0	15.0
Range	25-65	42-74	32.1-64.2		0.5-1.0	20-36	11.2-17.7	
Average	75.7	56.8	71.3	0.8	1.0	21.6	20.1	19.1
Range	>65	41.1-78	42.3-84.6	0.7-0.8	0.6-1.3	6.8-36	13-20.6	

[a] M_{wd} is the living total tree biomass; [b] ML_{lf} is the residual forest-floor litter mass.

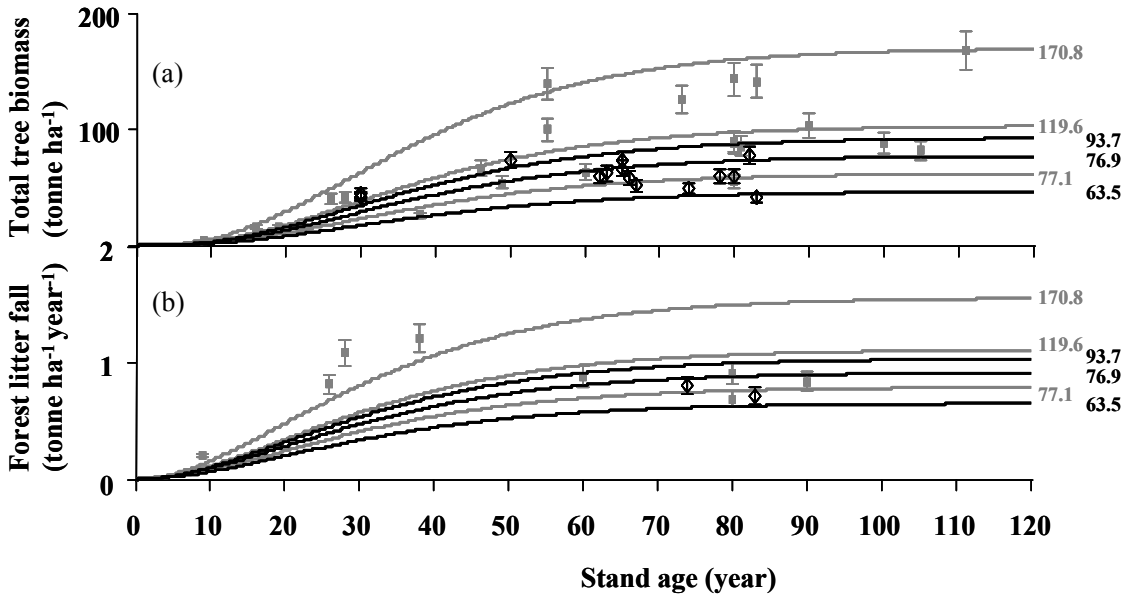

Figure 4.4 Forest-stand total tree biomass growth (a) and foliage-litter production (b). Square (gray) and diamond (open) symbols represent the mean of field measurements from Prince Albert, SK (warm-dry climate), and Thompson, MB (cold-wet climate); the vertical bars give the first standard deviation from the mean. Gray and black lines represent model simulations for the same climate regions (Prince Albert, SK, and Thompson, MB, respectively). Forest stand biomass growth is calculated with ForNBM; foliage-litter production in ForNBM is based on Eq. (4.1). Range of biomass growth and foliage-litter production are calculated by adjusting the M_{max} parameter (indicator of site productivity) in the biomass-production equation of ForNBM; maximum biomass for various model simulations are grouped according to climate regions (associated with gray and black values, to the right of the figures).

productivity, the average RMSE/RMSE$_{95\%}$ for the two regions is 0.44, indicating reasonable agreement between modelled and field measurements of biomass.

Modelled and measured leaf litter fall for the two climatic regions also exhibit strong agreement (Table 4.4; Figure 4.4b), particularly when the forests are young (0-25 year old class). For the southern sites, the integrated model slightly underpredicts foliage litter fall when the forest is < 65 years old, and overpredicts when the forest is > 65 years old. For the northern sites, modelled foliage litter fall provides better agreement.

Modelled stem growth increases when the forest is young and reaches a maximum at about 30 years, at which point it begins to decrease. Field measurements and modelled results show that stem biomass growth decreases northward from the Prince Albert to the Thompson sites (Figure 4.2). Foliage litter fall follows a similar trend that is consistent with the output from both the CENTURY and EFIMOD2 models (Peng et al., 1998; Shaw et al., 2006).

4.6.2 Comparison of the Two Litter Decomposition Formulations

When the forest stands are < 65 years old, RMSE/RMSE$_{95\%}$ for the three-pool and the single-pool litter decomposition formulations are 0.56 and 0.66 for the Prince Albert-area sites and 0.89 and 1.02 for the Thompson-area sites, indicating that the three-pool formulation (FLDM) gives on average better predictions of residual litter mass than the single-pool formulation (see also Figure 4.5a). Model results for the three-pool and single-pool formulations converge at around 65-70 years subsequent to stand initiation (Figure 4.5a; Table 4.4), producing RMSE/RMSE$_{95\%}$ of 0.41 and 0.49 for Prince Albert- and Thompson-area stands > 65 years old. The observed underprediction with the single-

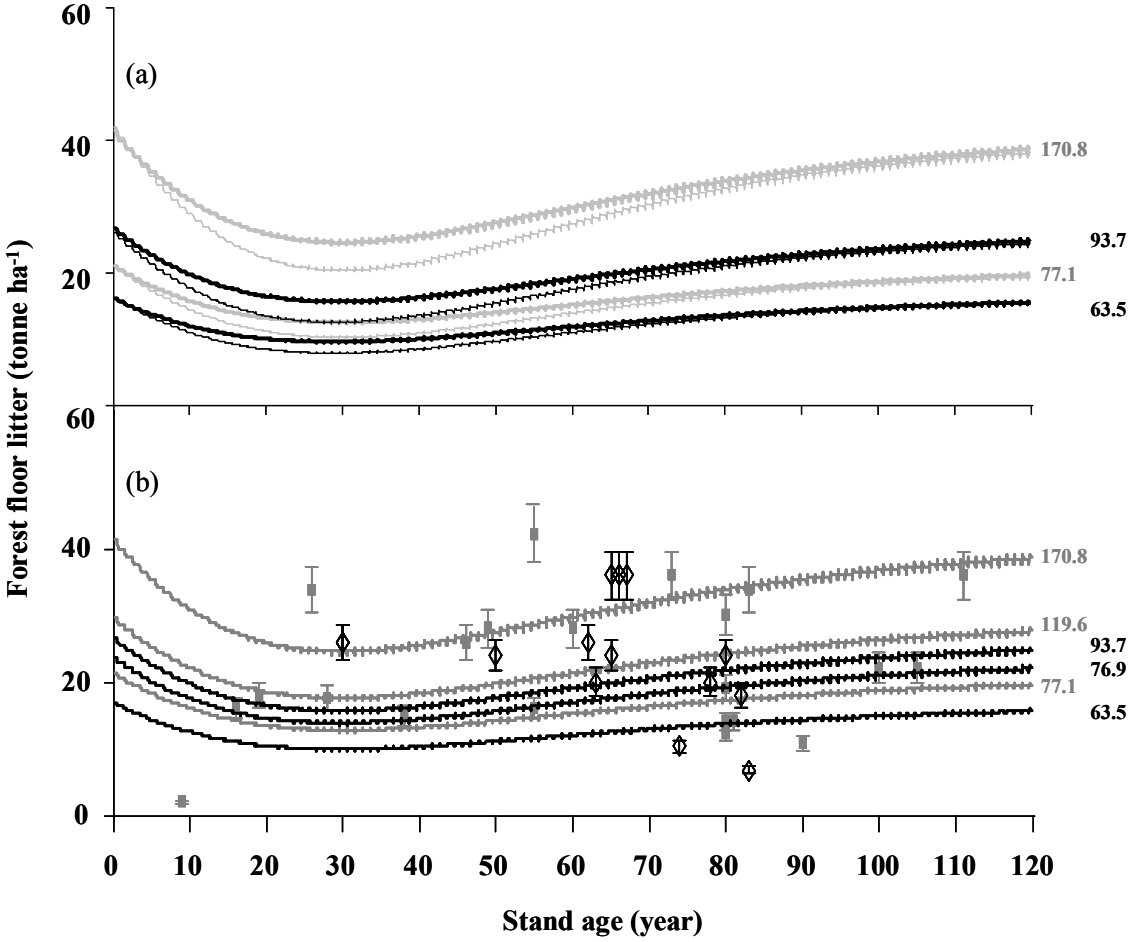

Figure 4.5 Forest-floor residual litter mass**.** In (a), the thin and bold lines represent simulations with the one- and three-pool litter decomposition formulations (e.g., FLDM) as a function of variable M_{max} (indicator of site productivity); gray and black lines represent simulations according to climate regions (i.e., Prince Albert, SK, and Thompson, MB). In (b), the range of forest-floor residual litter mass is calculated with the three-pool FLDM formulation by adjusting M_{max} as a function of site productivity and climate region (associated with gray and black lines; values to the far right of the figures represent the maximum biomass for the various model simulations). Square (gray) and diamond (open) symbols represent the mean of field measurements from the Prince Albert- and Thompson-area sites, respectively; the vertical bars give the first standard deviation from the mean.

pool formulation (Figure 4.5a) is largely due to improper simulation of the very slow decomposing litter matter.

Attributes of FLDM results are quite similar to those generated with the EFIMOD2 model (Shaw et al., 2006). After an initial decline in the first 25 years (a feature also reported by Aber et al., 1978), the forest-floor litter gradually increases with continued growth of the forest. In general, FLDM provides slightly better agreement to the measured forest-floor residual litter mass than EFIMOD2 for all of the stands, leading to $RMSE/RMSE_{95\%} = 0.57$ and 0.68, independent of climate regime.

4.6.3 Impact of Forest Age and Climate on Residual Forest Litter

Influence of forest age on forest-floor residual litter mass continues to be controversial. For example, Nalder and Wein (1999 and 2006) and MacLean and Wein (1977) found forest-floor litter dynamics were virtually unaffected by stand age, whereas Foster et al. (1995) found the exact opposite. In this Chapter, forest-floor litter mass is shown to vary as a function of stand age (see Figure 4.5). The EFIMOD2 and work by Aber et al. (1978) support the conclusion of this analysis.

Inspection of BFTCS-field data, forest-floor litter is observed to increase as a function of stand age at the southern sites. At the northern sites, an initial increase is followed with a small decrease when the forests are old. Impact of climate variation on forest-floor residual litter mass also varies across studies. For example with the CENTURY model, Peng et al. (1998) shows that residual litter in the forest floor is greatest at the northern sites of the BFTCS experiment. With the EFIMOD2 model, Shaw et al. (2006) shows that residual litter is nearly the same across all sites, regardless of

location. Results with FLDM, show that residual litter is greatest at the southern sites (Figure 4.5b), which is consistent with the findings of Nalder and Wein (1999) for jP and trembling aspen (*Populus tremuloides*) stands from the same area. These disagreements stress the importance of developing accurate ecosystem models for the long-term simulation of forest-floor litter dynamics.

4.6.4 Impact of Soil Productivity on Forest-Floor Litter Dynamics

Based on maximum-minimum stem growth (Figure 4.4a), the integrated model (Figure 4.1) captures most of the variation in leaf litter fall (Figure 4.4b) and associated forest-floor residual litter mass (Table 4.5; Figure 4.5b). Results from the integrated model indicate that soil quality, along with soil temperature and soil moisture, are important variables in simulating the long-term response of forest-floor litter.

From Figures 4.4b and 4.5b, forest-litter fall and residual litter on the forest floor are generally greatest when forest growth is greatest, particularly on productive sites. Nutrient-poor sites exhibit an overall reduction in forest growth and associated litter production and, as a result, promote an inferior accumulation of organic debris on the forest floor. This result is consistent with Huang and Schoenau (1996), where they observed greater litter accumulation on lower, high productivity slopes than on higher, low productivity slopes. From this study, variation in forest biomass production, foliage litter fall, and forest-floor residual litter mass for specific climate zones is largely controlled by site quality and, as a result M_{max}. For improved implementation of "space trade for time" experiments, one should consider the effects of site quality (and potentially, site index) on forest-growth response. Evaluation of site quality spatially is

vital to scaling up forest growth and litter-production processes and forest-floor C-content (and DOC-production) dynamics to the landscape.

4.6.5 Impact of Climate Change on Forest-Floor Litter Storage

In recent decades, air temperatures have been increasing in Canada's northern boreal forests, which are expected to result in significant changes in C stocks in northern forests (Chapman and Walsh, 1993; Jones, 1994). With climate warming, this integrated model predicts that forest-stem growth will decrease in the southern limit of the BFTCS transect and increase in the north, as long as increases in air temperature are uniform across the transect (Nalder and Wein, 1999). With reductions in net litter production induced by decreasing stem growth and increasing litter decomposition, forest-floor residual litter is expected to decrease at the southern limit of the transect with climate warming. At the northern limit, stem growth, and litter production are expected to increase with increases in air temperature, causing a greater accumulation of litter matter on the forest floor than what is currently taking place.

4.7 Concluding Remarks

The single-pool litter decomposition formulation underpredicts forest-floor residual litter mass when forests are < 65 years old. The underprediction is largely due to the inaccurate simulation of the very slow decomposing litter matter.

The integrated model with the three litter-pool formulation (i.e., FLDM), like EFIMOD2, provided reasonable simulation of (i) forest growth, (ii) foliage litter fall, and (iii) forest-floor residual litter mass for two climate regions in Canada's northern boreal

forest. The integrated model shows that forest growth and forest-floor C storage are largely controlled by stand age, climate, and soil quality at individual sites. With increasing stand age, forest-floor C storage is increased. In general, more C (and potentially more DOC) is stored in the forest floor on nutrient-rich and unconstrained soils than on poor-quality soils. Indications exist that forest management by removing trees has the potential to alter forest-floor C stocks. On average, forest-floor C storage is highest at the forest sites at the southern limit of the BFTCS transect and least, at its northern limit. With increases in air temperature, forest growth, foliage litter fall, and forest-floor residual litter mass are expected to decrease in the southern boreal forest and increase in the north.

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CHAPTER 5 MODEL SIMULATION OF MONTHLY DISSOLVED ORGANIC CARBON CONCENTRATIONS IN SMALL FORESTED WATERSHEDS

Chengfu Zhang[a,b], Rob C. Jamieson[b], Fan-Rui Meng[a], Robert Gordon[c], Charles P.-A. Bourque[a,*]

[a] *Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada*
[b] *Department of Process Engineering and Applied Science, Dalhousie University, Halifax, NS, B3J 1Z1, Canada*
[c] *Ontario Agricultural College, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

Running title: Monthly DOC export

[*] Corresponding author at: Faculty of Forestry and Environmental Management, 28 Dineen Drive, PO Box 4400, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada. Tel.: 1-506-453-4509; Fax.: 1-506-453-3538.
E-mail address: cbourque@unb.ca (C. P.-A. Bourque)

This Chapter is in review as a scientific article with Ecological Modelling.

5.1 Abstract

Dissolved organic carbon (DOC) plays an important role in both terrestrial and aquatic ecosystems. In-stream DOC concentration is an important indicator of water-quality because high DOC concentrations naturally lead to reductions in oxygen in streamwater. Recent studies also indicate that DOC is also responsible in transferring toxic metals (e.g., mercury, Hg) from terrestrial sources to aquatic ecosystems. However, assessing DOC or Hg dynamics is fairly challenging as a result of extreme spatiotemporal variation. Typically, process-based models with short-to-medium term temporal resolutions are required to model DOC and Hg dynamics. The objective of this research is to develop a watershed-based monthly DOC production and export model that integrates the processes of (i) forest litter decomposition (DOC production), (ii) wetland-to-watershed area ratio (DOC storage), and (iii) relevant hydrological (DOC-export) processes in the calculation of in-stream concentrations. Model results are compared against DOC concentrations collected at the stream outlets of two separate forested watersheds in Kejimkujik National Park, Atlantic Canada. Comparisons for the two watersheds show that predicted monthly DOC concentrations are generally in good agreement with field-based concentrations, giving R^2-values of 0.61 and 0.63 for Pine Marten Brook watershed and 0.72 and 0.75 for Moose Pit Brook watershed for model calibration and validation, respectively.

Keywords: DOC production, export, forest watersheds, hydrology, litter decomposition, model simulation, seasonal dynamics, stream discharge

5.2 Introduction

Dissolved organic carbon (DOC) leached from terrestrial ecosystems is an important source of energy for aquatic ecosystems in small watersheds (Wetzel et al., 1972; Wetzel, 1983; Pace, 1993; Kim et al., 2010). In aquatic ecosystems, DOC can be utilised by bacteria and other microorganisms as food substance (Wetzel, 2006). Transport of terrestrial C to streams is an important component of the C cycle of ecosystems (Ludwig et al., 1996; Warnken and Santschi, 2004; Battin et al., 2009). DOC concentration is an important water-quality indicator as high in-stream DOC concentrations and acute microbial activity naturally lead to depletion of oxygen in streamwater (Yano et al., 2000; Moore et al., 2003). Furthermore, DOC serves as an effective carrier of toxic metals (e.g., mercury, Hg), facilitating the transfer of these metals from terrestrial sources (e.g., forests) to aquatic ecosystems (Driscoll et al., 1995; Krabbenhoft et al., 1995; Scherbatskoy et al., 1998; Driscoll et al., 2007). In-stream Hg concentrations are difficult to model directly, as they are highly variable in both space and time. A number of field studies have shown the presence of strong correlation between in-stream DOC and Hg concentrations (Dennis et al., 2005; Meng et al., 2005; Reddy et al., 2007). As a result, opportunity exists to model in-stream Hg concentrations from predictions of DOC concentrations.

In the scientific literature there are three types of DOC-production models: (i) process-based models, (ii) steady-state models, and (iii) data-based (statistical) models, all with their distinct focus and application. One of these models is the process-based model of Neff and Asner (2001). This model is designed to simulate DOC-concentration dynamics in the soil. The model accounts for the processes of DOC production and DOC absorption and desorption in mineral soils. The model simulates in-soil DOC-

concentration dynamics fairly well. The INCA-C model by Futter et al. (2007) is designed to simulate soil- and streamwater DOC dynamics. The model considers the processes of (i) litter decomposition, (ii) solid organic C and DOC transformations in soils associated with forest, peatland, and wetland systems, and (iii) DOC transformations in streams. The model has been tested against measurements of in-stream DOC concentrations, but not for soil water. Lumsdon et al. (2005) modelled soil DOC-concentration dynamics by simulating organic matter (OM) solubility as a function of soil-particle surface electrical charge and soil temperature. Clark et al. (2005) modelled in-stream DOC concentrations seasonally as a function of soil temperature and soil sulphate (SO_4^{2-}) content.

Models by Neff and Asner (2001), Futter et al. (2007), and Lumsdon et al. (2005) all have built-in functions for in-soil DOC processes, but all are modelled differently. In Neff and Asner's (2001) model, (i) DOC absorption is modelled as a function of in-soil DOC concentration, actual pore-water velocity, and soil-clay content, and (ii) DOC desorption is modelled as a function of soil organic C content and actual pore-water velocity. In INCA-C (Futter et al., 2007), DOC absorption and desorption are modelled according to the size of non-dissolvable organic C content and DOC pools in the mineral soil and as a function of soil temperature and water content. The models by Lumsdon et al. (2005) and Clark et al. (2005) exclude the processes of DOC production and absorption in their formulation.

Canham et al. (2004) used a steady-state model to simulate DOC concentrations in lakes. The model addressed (i) DOC input from upstream lakes and the surrounding catchment area, and (ii) the internal, in-lake production of DOC and its eventual export.

The model takes into account the contributions of DOC from various catchment land-cover types (e.g., farmland, forests), but not in-soil DOC processes. The model is fairly accurate in capturing between-lake variation in DOC concentrations. DOCMOD developed by Currie and Aber (1997), simulates DOC production based on a three litter pool conceptualisation. The model successfully reproduces measured forest-floor DOC content for different vegetation covers. DOCMOD currently does not account for (i) the effects of watershed hydrology, and (ii) DOC absorption by mineral soil in its formulation. As a result, the model is not suitable for simulating DOC export from forested watersheds. Meng et al. (2005) developed a regression model to elucidate the relationship between upstream DOC concentrations and the surrounding environment. It was found that in-stream DOC concentrations were reasonably correlated to stream and lake dimensions (e.g., width of streams, diameter of lake), water source (surface or ground water), and water acidity (pH).

All model types have their limitations. For instance, process-based models rarely address the impact of topography and vegetation cover on within-watershed DOC production and export processes and steady-state and empirical models are incapable of simulating temporal (seasonal) dynamics due to their internal structure and assumptions.

In instances when annual average concentrations of Hg and DOC may meet water-quality standards, individual concentrations used in the calculation of the annual average may actually exceed the standard. Therefore it would be useful to produce a model which can predict concentrations of DOC, and associated contaminants, on shorter time scales. The objective of this research is to develop a watershed-based DOC production and export model that integrates the processes of (i) forest litter decomposition (and DOC

production), (ii) wetland-to-watershed area ratio (DOC storage), and (iii) relevant hydrological (DOC-export) processes in the calculation of monthly in-stream DOC concentrations. In doing so, the functionality of DOCMOD is extended by incorporating a variable DOC storage and export component. The calibrated model is validated by comparing model predictions of monthly DOC concentrations at the outlet of two forested watersheds with stream-based concentrations. The integrated DOC model presented here provides a strategic basis for the simulation of seasonal dynamics of Hg concentrations in small forest streams to be considered in Chapter 6.

5.3 Conceptual Model

DOC production and export in this integrated model is controlled by three main factors, i.e., (i) litter decomposition, (ii) ratio of wetland-to-watershed area, and (iii) water flow through the decomposing litter. Figure 5.1 gives the overall structure of the integrated DOC production and export model.

A series of DOC sources, sinks, and fluxes can be identified as DOC moves from terrestrial to aquatic ecosystems, all of which are mediated by local hydrology (Moore, 1997). In forest ecosystems, DOC production is largely controlled by forest litter decomposition and to a lesser extent, by forest throughfall and root exudates (McDowell and Likens, 1988; Qualls et al., 1991; Currie and Aber, 1997; Moore, 1997; Müller et al., 2009). Rate of litter decomposition and DOC production depends on the chemical composition of the decomposing OM and the internal environment of the substrate, particularly its core temperature and liquid water content (Godde et al., 1996; Currie and Aber, 1997; Hongve, 1999). When OM decomposes, the partly decomposed material

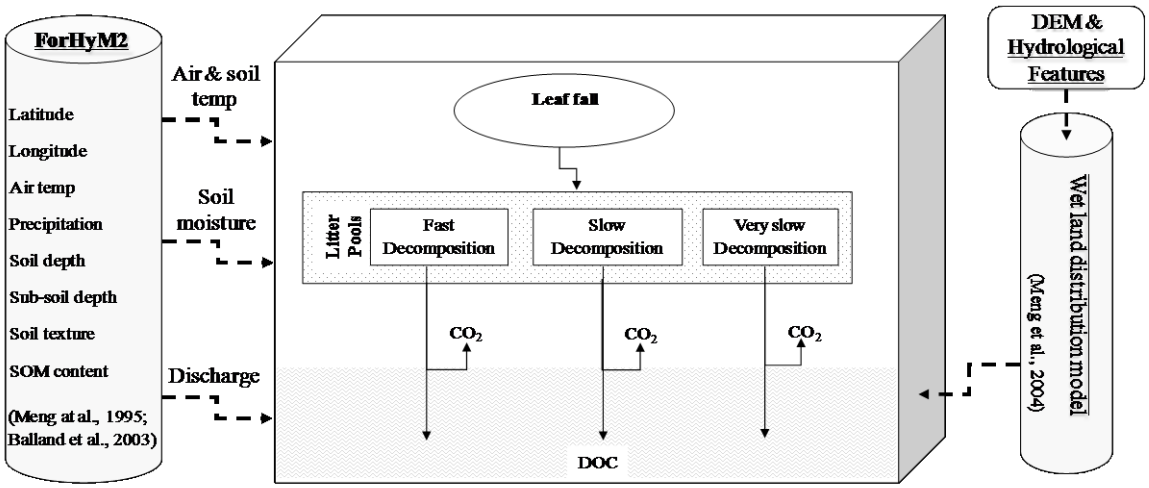

Figure 5.1 Structure of the DOC production and export (in-stream concentration) simulation model. ForHyM2 is used to simulate variation in soil temperature and moisture, and stream discharge. Monthly FLDM is used to simulate monthly litter decomposition. Output from FLDM is used as input to the DOC model in estimating DOC export from decomposing litter. Wetland-to-watershed area ratio derived from the wetland distribution model is used to calculate within-watershed DOC export from upland and wetland areas of the watersheds.

becomes water soluble and is flushed out as water flows through the decomposing litter (Gosz et al., 1973; Yavitt and Fahey, 1985; Thurman, 1985; Stevenson, 1994; David et al., 1995; Zsolnay, 1996).

Litter decomposition in the integrated DOC model (Figure 5.1) is simulated with the Forest Litter Decomposition Model (FLDM; Zhang et al., 2007; Zhang et al., 2010a). FLDM is based on the hypothesis that forest litter decomposition proceeds at different rates as determined by the chemical composition of the decomposing litter. In FLDM, as in DOCMOD (Currie and Aber, 1997), litter is partitioned in three litter pools, i.e., fast, slow, to very slow decomposing litter pool (Zhang et al., 2007; Zhang et al., 2010a). A comparison of model results with field-based measurements have shown the model to perform reasonably well (Zhang et al., 2008; Zhang et al., 2010a). As in DOCMOD the production of DOC is assumed to be mostly associated with decomposing leaf and root litter and to a lesser extent decomposing coarse woody debris (Currie and Aber, 1997).

DOC absorption by the mineral soil is modelled as a proportion of DOC production from litter decomposition based on the fact that over time DOC absorption is in equilibrium with DOC input (Nodvin et al., 1986). DOC export is expected to increase with an increase in surface water flowing through the decomposing litter layer (Eckhardt and Moore, 1990; Trofymow et al., 2002).

Input to the integrated DOC production and export model includes (i) soil temperature and soil moisture to simulate forest litter decomposition with FLDM (Figure 5.1) and (ii) water discharge, to simulate DOC export. Timeseries for these variables are generated with an existing Forest Hydrology Model (ForHyM2; Meng et al., 1995; Balland, 2003; Figure 5.2).

5.4 Model Specifics

5.4.1 Forest hydrology model

ForHyM2 is site-specific and simulates within-forest environmental conditions at a daily timestep. Results from model simulations with ForHyM2 have been previously used as input in ecosystem nutrient cycling (Zhu et al., 2003) and forest litter decomposition (Zhang et al., 2008 and 2010a) modelling. ForHyM2 is composed of a heat-conduction and water-flow component. The heat-conduction component simulates forward and backward heat transfer between the forest canopy, the forest floor, the upper soil, and lower soil. The water-flow component addresses the processes of (i) precipitation, either in the form of rain or snow, (ii) forest interception, (iii) evapotranspiration, (iv) throughfall, (v) stemflow, (vi) deep percolation, and (vii) surface and subsurface runoff. Based on daily air temperature and precipitation collected at local weather stations, ForHyM2 simulates evapotranspiration from forests, melting of ice and snow, and freezing of water. Simulated soil moisture and ice content of the soil are used in the calculation of heat conductivity and latent heat exchange in soils. Figure 5.2 provides the schematics of the heat-conduction and water-flow components of ForHyM2.

5.4.2. Wetland Mapping

A ratio of wetland-to-total-watershed-area is used as a measure of OM-absorption partitioning between dry and wet areas of the watershed. Upland and wetland zone classification is based on the distribution of depth to water table (DWT).

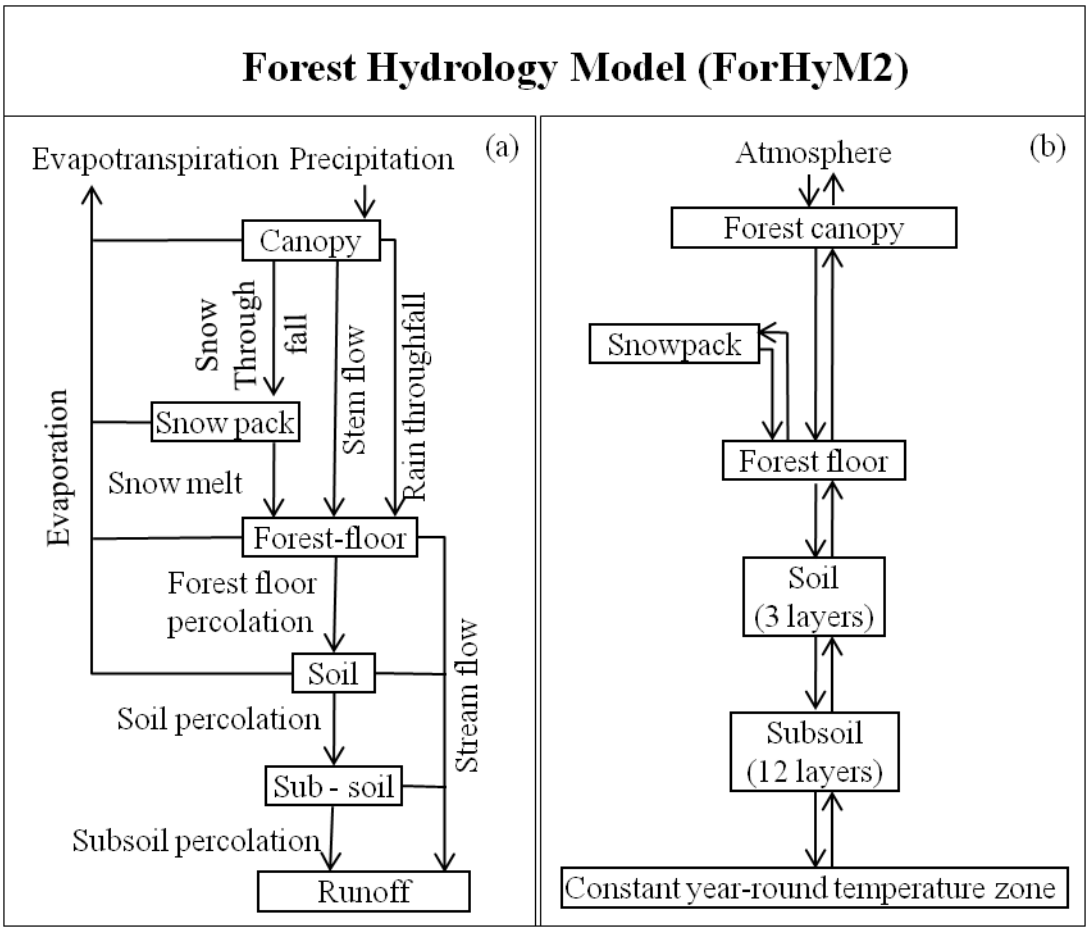

Figure 5.2 Water (a) and heat flux (b) components of the Forest Hydrology Model v. 2 (ForHyM2; Meng et al., 1995).

DWT distribution is estimated with the notion that its value increases from open water (0 m) to higher elevations (Meng et al., 2004). Watershed areas with DWT values below a critical threshold (< 1 m) are classified as being part of wetland systems and the remaining watershed area, as upland zones (Meng et al., 2004). Wetland distribution mapping with the DWT-mapping technology has been applied and tested with reasonable success for the Canadian Provinces of New Brunswick, Nova Scotia, and Alberta, and the northern state of Maine, USA.

5.4.3 Forest Litter Decomposition and Potential DOC Production

5.4.3.1 Litter Decomposition

In the monthly version of FLDM (Zhang et al. 2010a), the litter pools are supplied forest leaf and root litter during each autumn, and their rates of decomposition are estimated according to first-order reaction kinetics. Litter decomposition in the three litter pools is simulated by

$$\frac{\partial M_1(t)}{\partial t} = -k_1 f_{climate}(M_1(t) + ML_1), \text{ and} \quad (5.1)$$

$$\frac{\partial M_2(t)}{\partial t} = - f_{climate}(M_2(t) + ML_2), \text{ and} \quad (5.2)$$

$$\frac{\partial M_3(t)}{\partial t} = -k_3 f_{climate}(M_3(t) + ML_3), \quad (5.3)$$

where $M_1(t)$, $M_2(t)$, $M_3(t)$ are the litter masses in the three forest litter pools at time "t"; ML_1, ML_2 and ML_3 are the litter fall distribution in the three litter pools (in tonne year^{-1});

k_1 and k_3 are litter pool-specific ratios between the fast and slow and between the very slow and slow decomposition litter pools, respectively; and $f_{climate}$ is a climate factor.

Addition of leaf litter to the fast, slow, and very slow decomposing litter pools is estimated from

$$ML_1 = MLg, \tag{5.4}$$

$$ML_2 = ML(1-g)\,e, \text{ and} \tag{5.5}$$

$$g = \exp(a_0 + a_1\alpha + a_2\gamma), \tag{5.6}$$

where ML is the total litter fall (tonne ha^{-1} $year^{-1}$) at the start of the leaf and fine-root fall period (T_{Lf}); and e and g are mass partitioning coefficients, given by

$$g = \exp(a_0 + a_1\alpha + a_2\gamma), \text{ and} \tag{5.7}$$

$$e = \exp(-a_3\beta), \tag{5.8}$$

where α, γ, and β are the initial water-extractable (%), acid-hydrolysable (%), and ash content (%) of the original litter; a_0, a_1, a_2, and a_3 are calibration parameters.

Impact of climate on litter decomposition is addressed by:

$$f_{climate} = k_2 f_T . f_W, \tag{5.9}$$

where f_T and f_W are soil temperature and soil moisture-related factors, and k_2 is an equation parameter. The temperature factor is given by

$$f_T = (T_{Jan} + P_{TJan}) \exp(-(Ea/R)(1/(T_{soil} + 273) - 1/288)), \quad (5.10)$$

where T_{Jan} is the mean January soil temperature, T_{soil} (^oC) the monthly average soil temperature, Ea the active energy (J mol^{-1}), and R the universal gas constant (= 8.31 J $mole^{-1}$ C^{-1}); P_{TJan} is an equation parameter.

The soil moisture factor (f_w) is based on Bourque et al. (2000), whereby

$$f_w = \max(0, \kappa \xi^{\alpha} (1-\xi)^{1/\alpha}) \quad (5.11)$$

and

$$\xi = \begin{cases} 0 & ; if \quad sm < sm_{\min} \\ \left(\dfrac{sm - sm_{\min}}{sm_{\max} - sm_{\min}} \right) & ; if \quad sm_{\min} < sm < sm_{\max} \\ 1 & ; if \quad sm > sm_{\max} \end{cases}$$

$$\alpha = \sqrt{\frac{\chi}{1-\chi}},$$

$$\kappa = \frac{1}{\chi^{\alpha}(1-\chi)^{1/\alpha}}$$

and

$$\chi = \frac{sm_{opt} - sm_{\min}}{sm_{\max} - sm_{\min}}.$$

Here, sm_{min}, sm_{max}, and sm_{opt} are equation parameters representing minimum, maximum, and optimal soil moisture needed for forest litter decomposition.

5.4.3.2 Potential DOC Production

As in DOCMOD (Currie and Aber, 1997), the integrated model with FLDM (Figure 5.1) is based on the hypothesis that DOC production in the three decomposing litter pools is proportional to the rate of decomposition in each litter pool. Potential DOC production in the three pools is given by

$$\frac{\partial \mathrm{DOCP(t)}}{\partial \mathrm{t}} = \sum_{\mathrm{i=I}}^{3} \mathrm{p_{DOCi}} \frac{\partial \mathrm{M_i(t)}}{\partial \mathrm{t}} \ , \qquad (5.12)$$

where $\frac{\partial \mathrm{DOC_P(t)}}{\partial \mathrm{t}}$ is the potential solvable C from decomposing litter (mg month^{-1}) and $\mathrm{P_{DOCi}}$ is an equation parameter.

5.4.4 DOC Export from Terrestrial Sources

Impact of water flow on DOC transport from the decomposing litter to streams is based on work by Eckhardt and Moore (1990). Integrating the potential DOC-production equation (Eq. 5.12) with the two DOC-export functions (Eckhardt and Moore, 1990), the fate of DOC is defined by

$$\frac{\partial \mathrm{DOC(t)}}{\partial \mathrm{t}} = b_{DOCu}(1-\mathrm{R_{wet}}) \frac{\partial \mathrm{DOC_{PU}(t)}}{\partial \mathrm{t}} ((1-\mathrm{R_{wet}}) \frac{\partial Q}{\partial t})^{\mathrm{b_Q}} + b_{DOCw} \frac{\partial \mathrm{DOC_{PW}(t)}}{\partial \mathrm{t}} \mathrm{R_{wet}} (\frac{\partial Q}{\partial t})^{\mathrm{b_Q}} \ , \qquad (5.13)$$

where $\frac{\partial DOC(t}{\partial t}$ denotes total DOC production (mg month^{-1}) at time "t", $\frac{\partial DOC_{PU}(t)}{\partial t}$ and $\frac{\partial DOC_{PW}(t)}{\partial t}$ are the potential production of DOC at either upland or wetland sites at time "t", $\frac{\partial Q}{\partial t}$ is the surface-water flow rate (tonne month^{-1}), R_{wet} is the portion of wetland area to total watershed area, and b_Q, b_{DOCu} and b_{DOCw}, and P_{wet} are equation parameters.

In-stream DOC concentrations are modelled according to

$$[DOC(t)] = \frac{\frac{\partial DOC(t)}{\partial t}}{\frac{\partial Q}{\partial t}} \quad , \tag{5.14}$$

where [DOC(t)] denotes the in-stream DOC concentration at time "t" (in mg L^{-1}). Variables and parameters in Eq. (5.1)-(5.14) are summarised in Table 5.1.

5.5 Study Area and Field-data Collection and Analysis

The study area consists of two forested watersheds (i.e., Pine Marten and Moose Pit Brook watersheds) situated in Kejimkujik National Park, westcentral Nova Scotia, Canada (Figure 5.3). The soil in KMP is a brown sandy-loam from the Bridgewater series with a soil profile characterised by a relatively thin organic horizon of 5-10 cm, an A-horizon of 1-15 cm thick, and a B-horizon of approximately 50 cm thick (Eastern Ecological Services Ltd, 1976). With the influence of coastal and continental weather, the climate in the area is mostly humid and cool in winter and temperate in summer. The

Table 5.1 Equation state variables and parameters, units, and equation number.

Symbol	Meaning	Unit	Eq.
$f_{climate}$	Climate factor	unitless	2
α	Initial water-extractable material content	%	7
γ	Initial acid-hydrolysable material content	%	7
β	Initial ash content	%	8
f_T	Temperature factor for litter decomposition	unitless	9
f_W	Soil moisture factor for litter decomposition	unitless	9
T_{Jan}	Monthly average January soil temperature	^oC	10
T_{soil}	Monthly average soil temperature	^oC	10
sm	Monthly average soil moisture	% volume	11
$DOC(t)_P$	Potential solvable C from decomposing litter	mg $month^{-1}$	12
R_{wet}	Ratio of wetland versus whole watershed	unitless	13
[DOC(t)]	DOC concentration in stream at time t	mg L^{-1}	14
k_1	Decomposition ratio between the fast and slow decomposition litter pools	unitless	1
k_2	Parameter for the slow decomposition litter pool	$month^{-1}$	2
k_3	Decomposition ratio between the very slow and slow decomposition litter pool	unitless	3
T_{Lf}	Beginning of leaf fall	month	4
ML	Average total leaf fall mass per year	tonne ha^{-1} $year^{-1}$	4
a_0	Parameter for initialisation of litter decomposition	unitless	7
a_1	Parameter for initialisation of litter decomposition	unitless	7
a_2	Parameter for initialisation of litter decomposition	unitless	7
a_3	Parameter for initialisation of litter decomposition	unitless	8
Ea	Constant, representing activation energy	J $mole^{-1}$	10
P_{TJan}	Parameter for litter decomposition	^oC	10
R	Universal gas constant	J $mole^{-1}$ C^{-1}	10
sm_{max}	Parameter for the response of soil moisture on litter decomposition	% volume	11
sm_{opt}	Parameter for the response of soil moisture on litter decomposition	% volume	11
sm_{min}	Parameter for the response of soil moisture on litter decomposition, set to zero	% volume	11
P_{DOC1}	Parameter for DOC release from the fast decomposing litter pool	mg $tonne^{-1}$	12
P_{DOC2}	Parameter for DOC release from the slow decomposing litter pool	mg $tonne^{-1}$	12
P_{DOC3}	Parameter for DOC release from the very slow litter decomposing pool	mg $tonne^{-1}$	12
b_Q	Parameter for DOC release	unitless	13
b_{DOCu}	Parameter for DOC release from unpland soil	unitless	13
b_{DOCu}	Parameter for DOC release from wetland soil	unitless	13

mean annual precipitation is 1403 mm, of which 57% falls during the November-April (winter) period. The mean annual temperature is 6.3^{o}C and the average temperature for the growing season is 15.1^{o}C (Allen et al., 1992).

Surficial area of the Pine Marten and Moose Pit Brook watersheds is 130 and 1730 ha, respectively. Forest is the main vegetation cover in the two watersheds (Allen et al., 1992). The main deciduous species are red maple (*Acer rubrum*), American beech (*Fugus grandifolia*), and several birches (*Betula spp*), amounting to 44, 38, and 18% of the total hardwood basal area of the area. The main coniferous species are balsam fir (*Abies balsamea*), spruce (*Picea spp*), eastern white pine (*Pinus strobus*), and eastern hemlock (*Tsuga canadensis*), amounting to 35, 33, 15, and 13% of the softwood basal area. Wetlands occur on 31 ha (accounting for 23.9% of the total watershed area) and 616 ha (35.6%) of the Pine Marten and Moose Pit Brook watersheds, respectively. Vegetation cover and wetland predominance in the two watersheds are provided in Table 5.2.

Daily air temperature and precipitation for the 1995-2005 period were collected from a weather station in Kejimkujik National Park (Figure 5.4) and several Environment Canada weather stations located nearby (data not shown). Stream discharge was collected at the outlet of Moose Pit Brook watershed by Environment Canada personnel. Water samples were collected on a weekly basis from both Pine Marten and Moose Pit Brook watersheds. DOC concentrations in water samples were determined with a Shimadzu high-temperature combustion instrument (Clair et al., 2008).

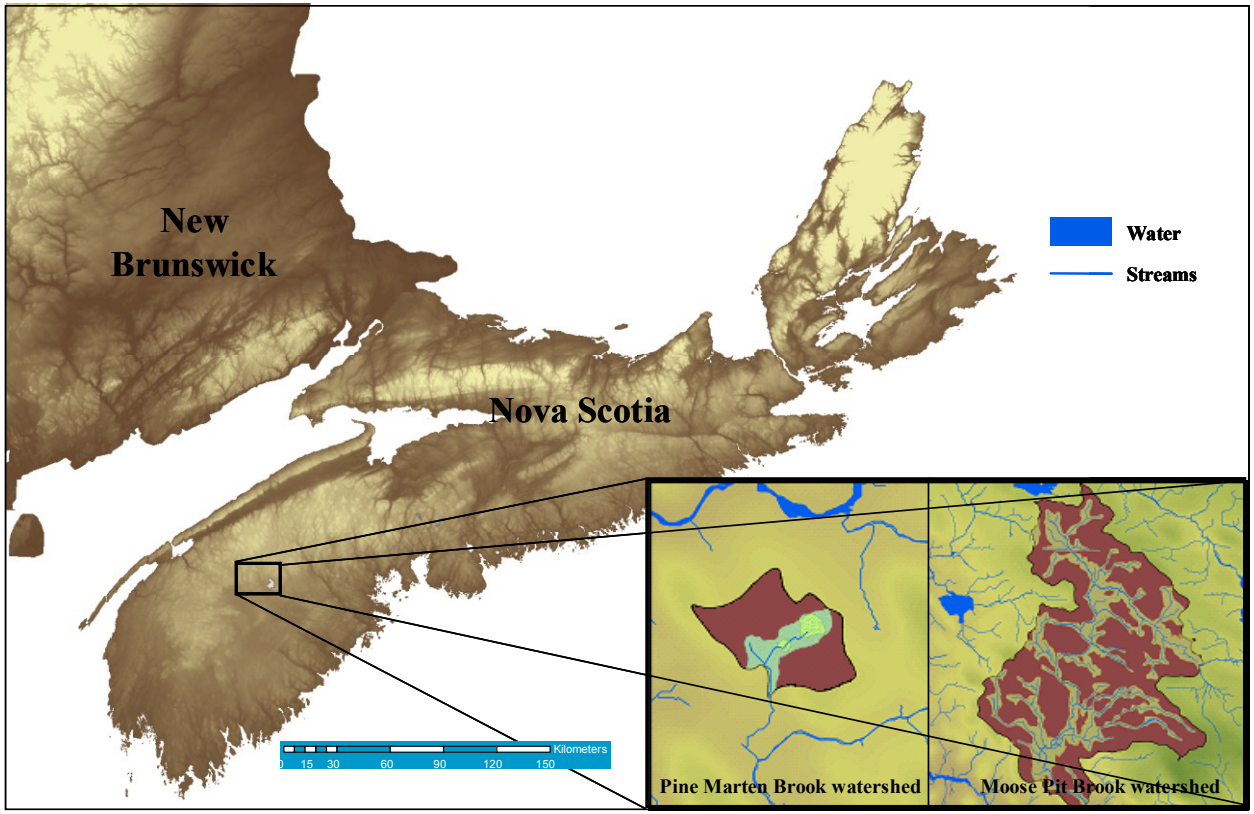

Figure 5.3 Location of Pine Marten Brook and Moose Pit Brook watersheds, Kejimkujik National Park, westcentral Nova Scotia. The inset gives the watershed distribution of upland (brown) to wetland area (light greenish-blue).

Table 5.2 Land covertype distribution; area (ha) and % dominance of watershed.

	Pine Marten Brook		**Moose Pit Brook**	
	Area (ha)	**%**	**Area** (ha)	**%**
Vegetation				
Hardwood	26.91	20.7	298.4	17.2
Softwood	61.49	47.3	955.2	55.2
Mixedwood	37.96	29.2	99.0	5.7
Regeneration	2.47	1.9	326.8	18.9
Others	1.17	0.9	50.9	2.9
Total	130	100	1730.4	100
Wetland	31.1	23.9	616.0	35.6

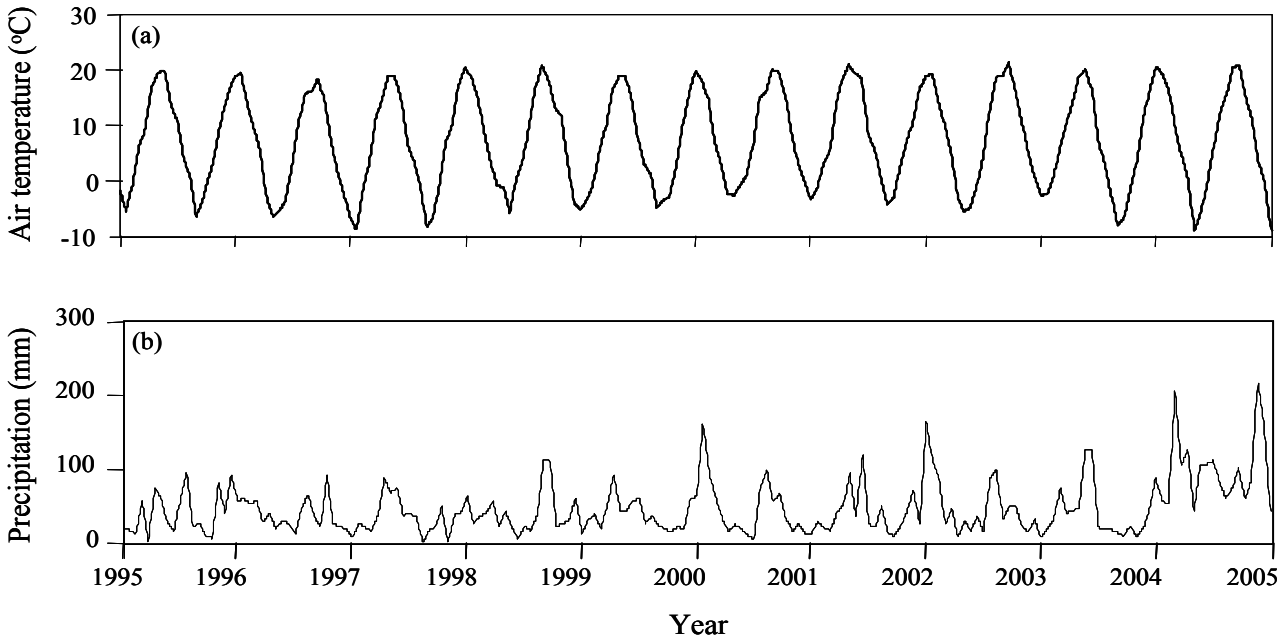

Figure 5.4 Park-monitored monthly air temperature (^{o}C; a) and total precipitation (mm; b). Timeseries serve as input to ForHyM2.

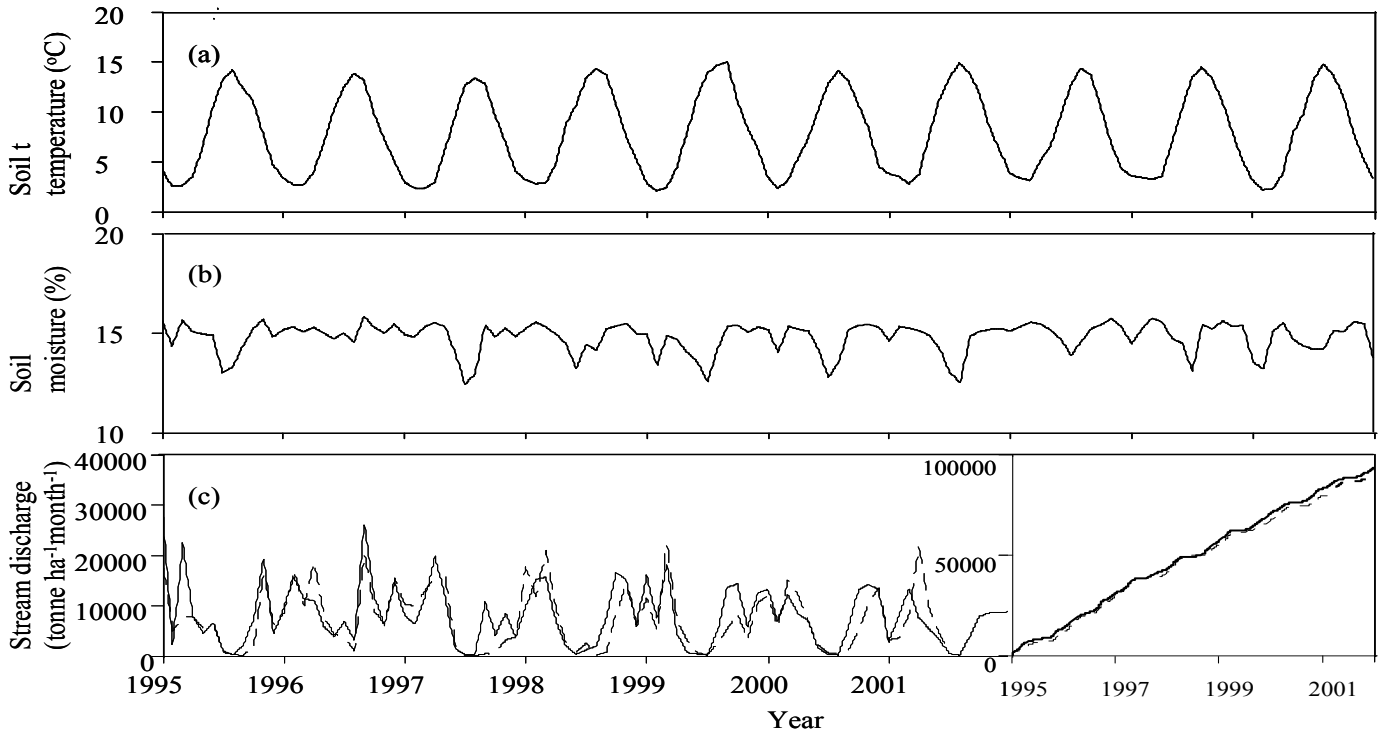

Figure 5.5 Simulated output from ForHyM2; (a) gives the simulated monthly average temperature (^{o}C) of the forest floor and A-horizon, (b) simulated monthly soil moisture (in % by volume); and (c) measured (dashed line) and simulated (continuous line) monthly stream discharge rate (tonne ha^{-1} month^{-1}). The inset to (c) gives the accumulation of stream discharge over the 1995-2001 period.

5.6 Model Calibration, Sensitivity Analysis, and Model Validation

In modelling monthly DOC concentrations, monthly soil temperature, moisture, and water discharge are obtained by averaging the daily output generated with ForHyM2. Figure 5.5 shows the simulated monthly soil temperature and moisture (average of the forest floor and A-horizon temperature and moisture), and measured and simulated stream discharge. Monthly stream DOC concentrations are derived by averaging the sampled weekly concentrations. ForHyM2 is calibrated with the stream discharge data from Moose Pit Brook. As Moose Pit and Pine Marten Brooks are in the same general location, water discharge for Pine Marten Brook is assumed to be a fraction of that of Moose Pit Brook to reflect differences in watershed surficial area (130 vs.1730 ha).

Organic-matter chemical composition of the leaf litter is determined from samples from the CIDET experiment (Trofymow and the CIDET working group, 1998) and fine-root OM-chemical composition is assumed to be the same as that for leaf litter. Partitioning of the leaf and root litter into the fast, slow, and very slow decomposing litter pools is based on species composition within individual watersheds (weighted by basal area). Leaf-fall mass is assumed constant over every consecutive autumn and fine-root input is assumed to be the same as that of leaf litter. The leaf litter fall are estimated from biomass data of the Province of Nova Scotia, showing that on average 3.16 and 2.65 tonne ha^{-1} is generated annually in coniferous and deciduous forests, respectively (Townsend, 2008), and litter input from ground

vegetation is estimated to be 25% of that of the trees (Wallace and Freedman, 1986). The initial litter mass in each litter pool is based on a mass-balance calculation.

5.6.1 Model Calibration, 1995-2000 Data

ForHyM2 is formulated in the STELLA™ environment (1998) and FLDM and DOC production and export models in ModelMaker™ (1999), both of which are visual-programming software. ModelMaker optimises model parameters automatically by minimising

$$x^2 = \sum \frac{(P_j - O_j)^2}{err^2}, \tag{5.15}$$

either with the Levenberg-Marquardt or Nelder-Mead simplex method. In the minimising function P_j and O_j are the individual calculated and observed values; err is the level of uncertainty in the data predetermined by the user.

The parameters determining the rate of litter decomposition, such as a_0, a_1, a_2, a_3, Ea, R, k_1, and k_3, are preset according to values used in Zhang et al. (2010a); P_{DOC1}, P_{DOC2}, and P_{DOC3}, which determine the rate of DOC leaching from the three litter pools, are set according to values reported in Currie and Arber (1997); b_{DOCu}, determines DOC release from upland soils and is estimated from Eckhardt and Moore (1990); T_{Lf} (leaf-fall time), b_Q, b_{DOCw}, and k_2, are calibrated directly by model optimisation (based on minimising Eq. 5.15) using field-based estimates of DOC

concentrations for the 1995-2000 period as target values. Parameter values and their sources are provided in Table 5.3.

Figure 5.6 provides a comparison of results generated with the calibrated model and field-based concentration measurements for Pine Marten and Moose Pit Brooks for 1995-2000. The comparison produces R^2-values of 0.61 and 0.72 for Pine Marten and Moose Pit Brook watersheds, respectively. P and Q values calculated based on an F-test and goodness-of-fit test are all < 0.001 (Table 5.4), indicating that the calibrated model captures seasonal variation in DOC concentrations for the two watersheds reasonably well.

5.6.2 Model Validation, 2000-2005 Data

Figure 5.7 compares the model results and field-based DOC concentrations for Pine Marten and Moose Pit Brook for 2000-2005. Coefficient of determinations (R^2) for the point-data comparisons between observed and modelled concentrations are 0.63 and 0.75 for Pine Marten Brook and Moose Pit Brook. As with the calibration, F and goodness-of-fit tests on both sets of results (modelled and field data) provide P and Q values < 0.001.

Table 5.3 Calibrated parameter values. Recalibration of parameters refers to an update of parameters initially used in Zhang et al. (2010a). Values in bracket provide the standard error of the estimate (SEE).

Parameter	Value (SEE)	Derived from
T_{Lf}	9	Calibration
R	8.314	Constant
a_0	-10.9	Zhang et al., 2010a
a_1	0.14	Zhang et al., 2010a
a_2	0.131	Zhang et al., 2010a
a_3	0.119	Zhang et al., 2010a
E_a	63392	Calibration
k_1	17.92	Zhang et al., 2010a
k_2	0.015	Calibration
k_3	0.35	Zhang et al., 2010a
p_{TJan}	20.7	Zhang et al., 2010a
sm_{max}	1	Constant
sm_{opt}	0.95	Zhang et al., 2010a
sm_{min}	0	Constant
P_{DOC1} (deciduous species)	0.048	Currie and Aber,1997
P_{DOC2} (deciduous species)	0.138	Currie and Aber,1997
P_{DOC3} (deciduous species)	0.199	Currie and Aber,1997
P_{DOC1} (coniferous species)	0.069	Currie and Aber,1997
P_{DOC2} (coniferous species)	0.212	Currie and Aber,1997
P_{DOC3} (coniferous species)	0.337	Currie and Aber,1997
b_{DOCu}	4.0	Estimated from Eckhardt and Moore, 1990
b_Q	1.014 (0.01)	Calibration
b_{DOCwa}	17.4 (3.2)	Calibration based on data from Pine Marten Brook
b_{DOCwb}	43.2 (5.4)	Calibration based on data from Moose Pit Brook

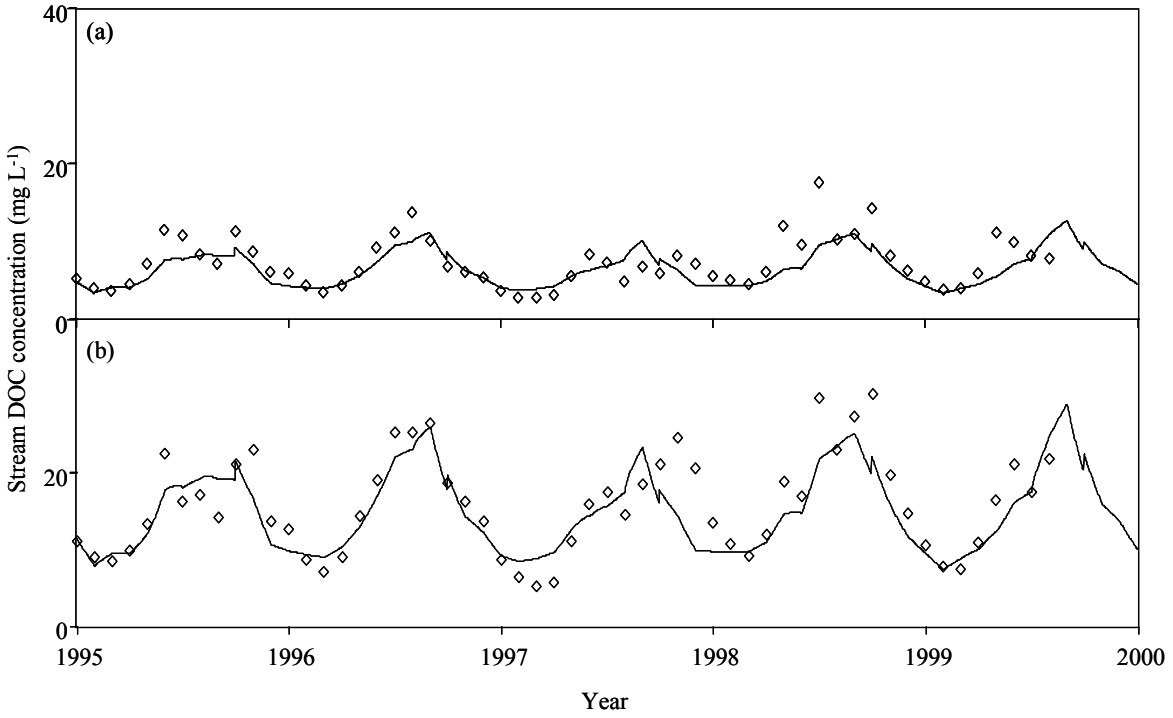

Figure 5.6 Results of model calibration with respect to in-stream DOC concentrations. The upper panel (a) gives concentrations at the stream outlet of Pine Marten Brook watershed for the 1995-2000 period and the lower panel (b), DOC concentrations at the stream outlet of Moose Pit Brook watershed. Symbols represent field-based concentrations and the lines, modelled concentrations.

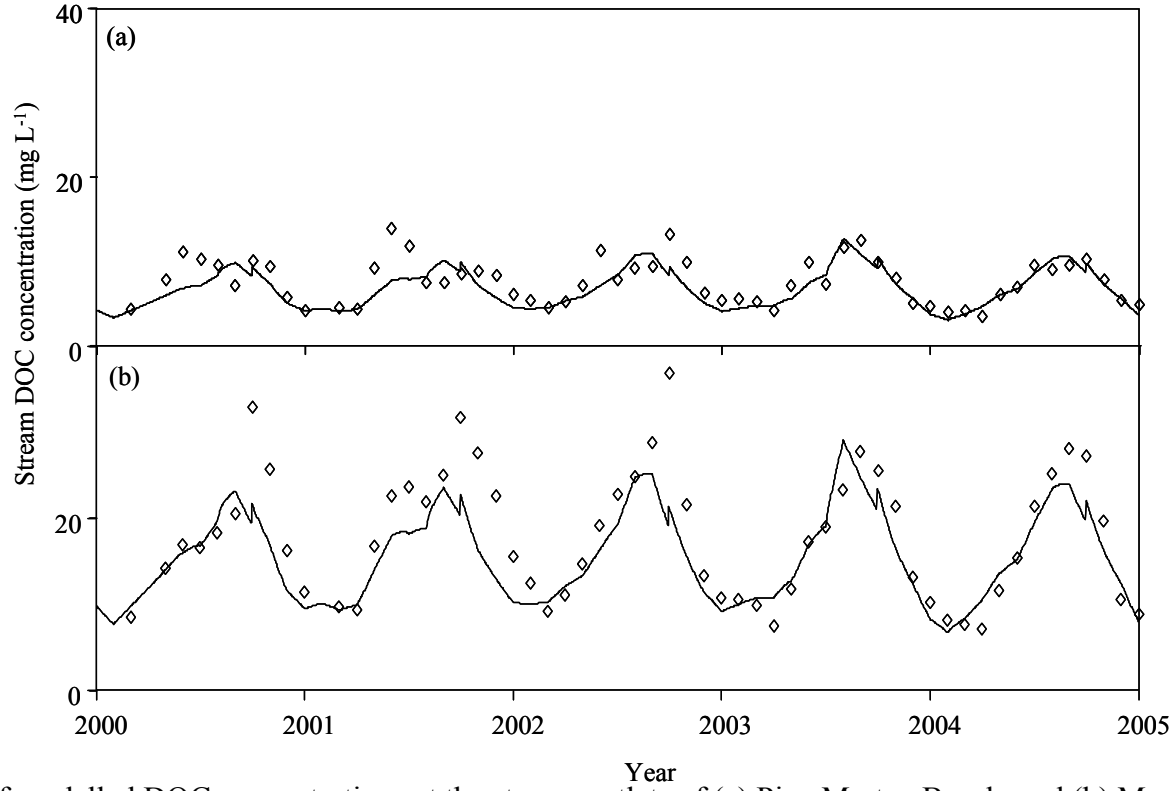

Figure 5.7 Validation of modelled DOC concentrations at the stream outlets of (a) Pine Marten Brook, and (b) Moose Pit Brook watersheds for the 2000-2005 period. Symbols represent field-based concentrations and the lines, modelled concentrations.

5.7 Discussion

5.7.1 Seasonal Stream DOC Concentration Dynamics and Litter Decomposition

Measured DOC concentrations follow a specific seasonal cycle; i.e., concentrations (i) peaks after leaves fall in the autumn, (ii) decrease to a minimum in April, (iii) gradually increase to a maximum in June, and (iv) then decrease to a second minimum the following April. Results show a small increase after leaf fall (Fig. 5.6 and 5.7). These changes reflect the timing and amount of litter fall and climate-induced variation in seasonal litter decomposition. The trend produced with the model is very much in agreement with field observations reported by Cronan and Aiken (1985), McDowell and Likens (1988), Hongve (1999), and Dai et al. (1996).

The modelled increase in DOC concentrations in autumn (Fig. 5.5) has been observed to occur in the field by McDowell and Likens (1998), Hinton et al. (1998), David et al. (1992), and Easthouse et al. (1992). From a modelling perspective, forest litter input is seen to be an important element in describing seasonal DOC-concentration dynamics (Futter et al., 2007). Also, the DOC-concentration peak in autumn is mostly associated with the short-term decomposition of the current year's litter in the fast decomposing litter pool, explaining why the peak may be large with deciduous forests (Hongve, 1999; Zhang et al., 2007).

5.7.2 Species Type versus DOC Production

DOC production from decomposing litter is a complicated process. There are contradicting opinions on the influence of tree species and deciduous vs. coniferous species on DOC production. Kuiters and Mulder (1993) found greater DOC production

with deciduous species. However, Currie and Aber (1997) and Strobel et al. (2001) obtained contradictory results, while Michalzik et al. (2001) and Don and Kalbitz (2005) found no difference between species type. From the work presented here, DOC production is not only determined by species type, but also by the amount of litter fall involved. Litter fall not only depends on forest age, but on the species composition of the forest. For different climate regions, the growth rate of deciduous and coniferous species is generally different (Bourque et al., 2010), resulting in differences in annual litter production (Zhang et al., 2010b).

5.7.3 Impact of Runoff on DOC Production

In-field surface DOC transport and water discharge has been observed to be positively correlated (Bobba and Lam, 1989; and Eckhardt and Moore, 1990). Trofymow et al. (2002) found that higher precipitation and associate runoff had the ability to leach more DOC from litterbags. In mineral soil, Neff and Asner (2001) found a linear relationship between DOC concentrations and water flow velocities. This result is consistent with the fact that DOC is released by runoff (addressed by way of b_Q) ~ 1.0 and, as a result, Δ [DOC] = Δ discharge; see Eq. (5.13) and (5.14).

5.7.4 DOC Absorption by Mineral Soil

Net DOC export is a function of forest litter decomposition and absorption by mineral soil (Moore, 1989). DOC absorption by mineral soil is an important process (Stevenson, 1994) that elevates soil-cation adsorption (Thurman, 1985). In this work, DOC absorption by mineral soil is assumed to be proportional to litter decomposition and DOC in the

mineral soil is in steady state. This assumption is supported by other researchers' work, e.g., Nodvin et al. (1986), Wigginton et al. (2000), and West and Six (2007).

For different soils, DOC absorption rates differ. For example, clayey soils tend to absorb more DOC than sandy soils (Gregorich et al., 1991; McInerney and Bolger, 2000). In addition to soil texture, soil depth, upland slope, and bedrock type, wet soils also exert a degree of control on the release of DOC from terrestrial sources (Eckhardt and Moore, 1990; Harris et al., 2005). In wetlands, dissolvation of polyvalent cations (e.g., Fe, Al, Ca, Mg; important DOC adsorbents), promotes the release of DOC to streams (Fiedler and Kalbitz, 2003; Müller, et al., 2009). From the results presented here, DOC export is approximately 73.9 kg ha^{-1} $year^{-1}$ from Pine Marten Brook watershed (65% originating from wetlands) and 177.1 kg ha^{-1} $year^{-1}$ from Moose Pit Brook watershed (91% from wetlands).

5.8 Concluding Remarks

DOC is generated from partly decomposed OM. Forest species and topography are important factors in the export of DOC from terrestrial sources to aquatic ecosystems. The monthly DOC production and export model developed in this study captures the seasonal dynamics of DOC export in two forest-dominated watersheds in westcentral Nova Scotia. Seasonal DOC-export dynamics observed are consistent with seasonal patterns modelled in forest litter decomposition. DOC production depends not only on forest species composition, but also on the amount of litter fall. Variation in litter fall is controlled to a large measure by climate and the age of the forest. In general, watersheds

with a larger amount of wetland tend to export more DOC to streams than watersheds with more upland (well-drained) area.

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CHAPTER 6 LONG-TERM MODEL SIMULATION OF SEASONAL MERCURY EXPORT FROM TWO SMALL FORESTED WATERSHEDS IN WESTCENTRAL NOVA SCOTIA, CANADA

Chengfu Zhang[a,b], Rob C. Jamieson[b], Fan-Rui Meng[a], Robert J. Gordon[c], Charles P.-A. Bourque[a,*]

[a] *Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada*
[b] *Department of Process Engineering and Applied Science, Dalhousie University, Halifax, NS, B3J 1Z1, Canada*
[c] *Ontario Agricultural College, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

Running title: Hg-concentration dynamics

[*] Corresponding author at: Faculty of Forestry and Environmental Management, 28 Dineen Drive, PO Box 4400, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada. Tel.: 1-506-453-4509; Fax.: 1-506-453-3538.
E-mail address: cbourque@unb.ca (C. P.-A. Bourque)

This Chapter has yet to be submitted as a scientific article.

6.1 Abstract

This Chapter presents a numerical model developed to simulate the seasonal export of total mercury (THg) from forest-dominated watersheds over two forest-growing cycles or rotations. This model is based on the observation that THg export from terrestrial to aquatic ecosystems occurs with the binding and subsequent in-stream transport of THg by dissolved organic carbon (DOC). In this work, DOC export is simulated with an integrated model consisting of several modelling components, including (i) a forest nutrient cycling and biomass growth component, (ii) a forest-floor litter decomposition component, (iii) a forest hydrology component, and (iv) a within-watershed delineation of wetland-area component. From the results generated with the integrated model, THg export follows two main trends; (i) an annual trend, associated with the seasonal dynamics in forest litter production, decomposition, and DOC production and export, and (ii) a multiple-year trend, associated with forest harvesting and re-growth patterns over the lifetime of the forest. In a single year, the integrated model predicts that THg concentration peaks after leaf fall in autumn, decreases to a minimum in April, increases to another maximum in June, and finally decreases to a second minimum just before leaf fall. This seasonal cycle is repeated every year. During a forest rotation, THg concentration decreases following clearcutting, reaches a minimum at about 15 years after forest regeneration, and then gradually increases with forest aging. Large debris pools left on site following clearcutting can provide a significant pulse in DOC production and within-watershed THg export during the first 2-3 years after harvest. Following the DOC-results of Zhang et al. (2010; Ecological Modelling, in review), conifer-species and wetland-dominated watersheds are anticipated to release a greater

amount of THg to aquatic ecosystems than deciduous and dryland-dominated watersheds. This claim needs to be confirmed with field-based measurements of THg concentrations.

Keywords: ecosystem modelling, forest rotation, seasonal stream Hg-concentrations, species effects, streamwater quality, systems modelling, wetland distribution.

6.2 Introduction

Mercury (Hg) pollution represents a significant threat to aquatic ecosystems, because environmental Hg biomagnifies up the food chain reaching high concentrations in longer-lived fish (Watras et al., 1998) and in humans. Rivers and lakes receive Hg from both direct atmospheric deposition and terrestrial sources (e.g., forests). The amount of Hg transferred to aquatic ecosystems from terrestrial sources generally exceeds the amount delivered directly by atmospheric deposition (Mason et al, 1991; Bishop et al., 1995; Branfireun et al., 1996; Allan and Heyes, 1998).

Normally, water systems in coastal areas exhibit higher Hg concentrations than inland areas (NESCAUM, 2003) because of (i) recurring inland advection of Hg-laden marine air masses and fog (Ritchie et al., 2006) and the subsequent scrubbing of the Hg by coastal forests (Allan et al., 2001), and (ii) presence of extensive coastal wetlands. Forests tend to filter a greater amount of in-air Hg than other vegetation types because of their greater surface area and canopy-surface roughness. Elevated canopy roughness causes mechanical mixing of the air next to the top of the forest to increase, causing deposition of Hg (in particulate or gaseous form) and other airborne materials to be high. Presence of wetlands along the coast is equally significant, because these wetlands serve as reservoirs of Hg released from upslope source areas (Rea et al., 2001; Driscoll et al., 2007).

Atmospheric Hg deposition to forest canopies is either absorbed by leaves (dry deposition) or transferred directly to the soil with its incorporation in precipitation (wet deposition; Iverfeldt, 1991; Lindberg et al., 1995). The untransferred portion of the Hg absorbed by leaves during the growing period eventually reaches the forest floor with leaf

drop in autumn. Once on the forest floor, Hg is (i) absorbed by plant roots, (ii) stored in the soil, or (iii) exported to aquatic ecosystems by interacting with surface water (Iverfeldt, 1991; Lindberg et al., 1995).

Numerical simulation of seasonal dynamics of Hg permits us to examine how vegetation and environmental conditions control Hg in watersheds. In the scientific literature there are three types of Hg models: (i) empirical models, (ii) steady-state models, and (iii) process-based models. Meng et al. (2005) developed a statistical model to elucidate the relationship between upstream DOC and Hg concentrations and the surrounding environment. It was found that in-stream DOC and Hg concentrations were reasonably correlated to stream and lake dimensions (e.g., width of streams, diameter of lake), water origin (surface or ground water), and water acidity (pH). Models proposed by Hope et al. (2005) and Ambrose et al. (2005) are steady-state models that simulate Hg cycling and accumulation in watersheds. The models successfully reproduce Hg transport related to (i) atmospheric deposition to and volatilisation from terrestrial surfaces (land and water), and (ii) accumulation in lake-bottom sediments. IEM-2M (United States Environmental Protection Agency, 1997) is a process-based model that simulates the processes associated with the annual transformation of Hg in watersheds, in particular, Hg^0 to Hg^{2+} and methyl Hg.

Empirical and steady-state models, because of their internal structure, are inherently unable to simulate seasonal Hg-export dynamics in waterways. IEM-2M simulates Hg export from watersheds as a process of soil erosion. Movement of Hg from terrestrial to aquatic ecosystems by soil erosion is considered unimportant in forested watersheds. Furthermore, IEM-2M operates on an annual timestep. In instances, when annual Hg-

concentration averages meet water-quality standards, it is entirely probable that individual monthly concentration during the year may in fact exceed the standard.

Mercury export from terrestrial ecosystems is largely controlled by the availability and passive transport of dissolved organic carbon (DOC) in watersheds (Mierle and Ingram, 1991; Watras and Huckabee, 1994; Rea et al., 1996; Allan and Heyes, 1998; Allan et al., 2001). Environmental conditions that favour enhanced DOC production in upland source areas of watersheds serve to raise Hg concentrations in streamwater further downslope (Mierle and Ingram, 1991; Kamman et al., 2004; Shanley et al., 2005). In this Chapter, seasonal export of total Hg (THg) is simulated as a linear function of in-stream DOC concentration predictions (Shanley et al., 2005; Dennis et al., 2005; Meng et al., 2005; Reddy et al., 2007). In this work, in-stream Hg concentrations are simulated at a monthly time resolution in order to define the seasonal concentration dynamics of the pollutant. In order to capture the influence of forest regeneration and re-growth on Hg concentrations, Hg-concentration is predicted over a 150-year period representing two forest-growing cycles or rotations, each of 75-year intervals.

6.3 Methods

In this study, THg export from forested watersheds is based on the observation that in-stream DOC and THg concentrations are linearly correlated (Schnoor, 1996; Meng et al., 2005; James et al., 2006), i.e., $y=\mu x$, where y and x are the THg and DOC concentrations (in ng L^{-1} and mg L^{-1}), and μ is a THg-to-DOC binding efficiency coefficient (ng mg^{-1}). DOC-THg export from forested watersheds is simulated with an existing DOC production and export model developed by Zhang et al. (2010a), described in Chapter 5. The DOC model is developed based on the hypothesis that DOC export is

positively correlated to (i) the rate at which forest litter decomposes; (ii) the extent organic matter (OM) is absorbed by upland and wetland soils; and (iii) the rate surface and shallow subsurface water moves through the watershed. Forest growth and litter production, litter decomposition, and watershed hydrology, in particular surface-runoff generation, are individually modelled with (i) **ForNBM** (**For**est **N**utrient cycling and **B**iomass growth **M**odel; Zhu et al., 2003; Zhang et al., 2010b), (ii) **FLDM** (**F**orest **L**itter **D**ecomposition **M**odel; Zhang et al., 2010b, 2010c), and (iii) **ForHyM2** (**For**est **Hy**drology **M**odel v. **2**; Meng et al., 1995; Balland, 2003; Figure 6.1).

ForNBM was developed with the aim to (i) simulate forest growth and C cycling; (ii) determine nutrient sustainability of forests based on nutrient cycling and soil-geochemical balances; and (iii) evaluate the effects of forest management on the environment, including streamwater quality (Zhu et al., 2003). ForNBM was modified by reformulating the original expression of foliage growth and litter fall to

$$M_{lf} = \mathrm{F_{lf1}} \mathrm{M_{wd}}^{\mathrm{F_{lf2}}} \tag{6.1}$$

$$F_{ltr} = \mathrm{F_{lf3}} \mathrm{M_{lf}} \text{ ; if } \varepsilon_{\mathrm{W}} \varepsilon_{\mathrm{T}} \varepsilon_{Age} < 0 \tag{6.2}$$

where M_{wd} and M_{lf} are the living stem and leaf biomass (tonne ha^{-1}), F_{ltr} is the annual litter fall mass (tonne ha^{-1}), and $F_{lf1,}$ $F_{lf2,}$ and F_{lf3} are model parameters (non-

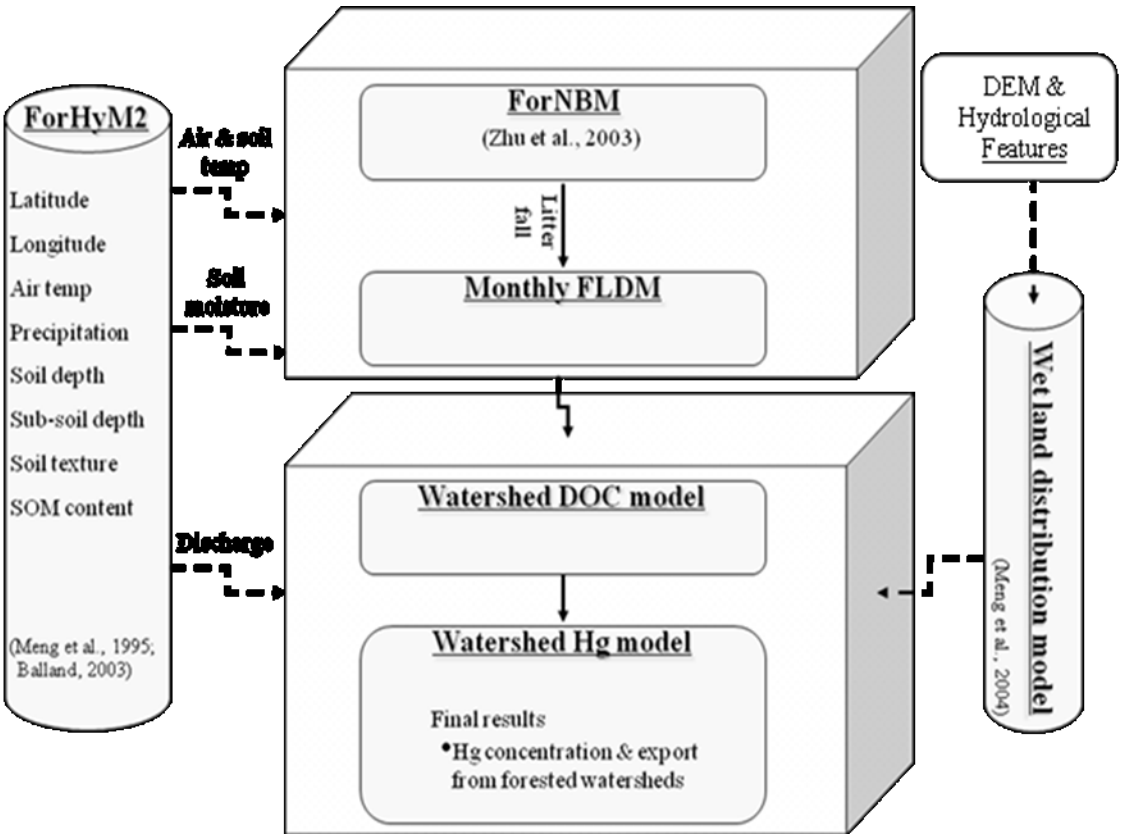

Figure 6.1 Structure of the in-stream DOC and Hg concentration model**.** ForHyM2 is used to simulate variation in soil temperature and moisture, and stream discharge. ForNBM is used to simulate forest growth and litter production. Monthly FLDM is used to simulate monthly litter decomposition. Output from FLDM is used as input to the DOC production and export model component.

dimensional); $\varepsilon_{\mathrm{W}}, \varepsilon_{\mathrm{T}}$, and ε_{Age} are soil moisture-, soil temperature-, and stand age-related variables (Zhu et al., 2003).

FLDM simulates litter decomposition with the assumption that litter is composed of three different chemical compounds (litter pools), which decompose independently and at different rates. Monthly litter decomposition is shown to be mostly controlled by monthly soil temperature, soil water content, and mean January soil temperature. January soil temperature is believed to control the over-wintering survival of decomposers and their level of activity in the following summer (Zhang et al., 2010c).

ForHyM2 is a daily process model (Figure 6.1), which simulates the hydrology and energy characteristics of forests, such as soil moisture, generation of surface and subsurface runoff, and soil temperature. The input variables of the model are daily mean air temperature and precipitation, either as rain or snow. In the model, soil and subsoil layers are treated as separate layers having their own chemical and physical characteristics (e.g., A, B, C mineral soil horizons, and 12 1-m subsoil layers). State variables, such as soil temperature, soil moisture, percolation, and lateral flow, are calculated for each soil layer (Meng et al., 1995; Balland, 2003).

6.4 Data

6.4.1 Site Description

All watershed characteristics (e.g., elevation, wetland-to-watershed area ratio) and field data (e.g., in-stream DOC concentrations, surface discharge) used in this study originate from the Pine Marten Brook and Moose Pit Brook watersheds of Kejimkujik National Park (KNP), westcentral Nova Scotia (NS), Canada (Figure 6.2). The two

watersheds are within 15 km of each other. Mean annual air temperature and precipitation within the area (Figure 6.2) are 6.4^{o}C and 1352 mm, respectively (Allen et al., 1992).

Main deciduous species present in the watersheds are red maple (*Acer rubrum*), American beech (*Fugus grandifolia*), and several birches (*Betula spp*), amounting to 44%, 38%, and 18% of the total hardwood basal area. Coniferous species include balsam fir (*Abies balsamea*), spruce (*Picea spp*), eastern white pine (*Pinus strobus*), and eastern hemlock (*Tsuga canadensis*), amounting to 35%, 33%, 15%, 13% of the softwood basal area.

As a coastal area, KNP is a biological Hg hotspot (Figure 6.2; Evers et al., 2005 and 2007). Locally- and remotely-emitted Hg, mostly from industrial sources, reach the area from atmospheric transport and deposition (Bullock and Brehme, 2002). A large component of the pollutant is carried during the summer by southwest winds from the United States. Once deposited locally, the Hg is re-distributed (exported downslope) according to the flow and DOC-production characteristics of the watershed (Mierle and Ingram, 1991; Allan et al., 2001).

6.4.2 Landscape Classification

Vegetation cover (coniferous, deciduous, mixedwood) and within-watershed upland and wetland areas were delineated to account for differences in land cover capacities to produce and transfer DOC, and thus translocate THg. Digital vegetation cover maps and elevation model (DEM) of the study area (consisting of the two study watersheds) were

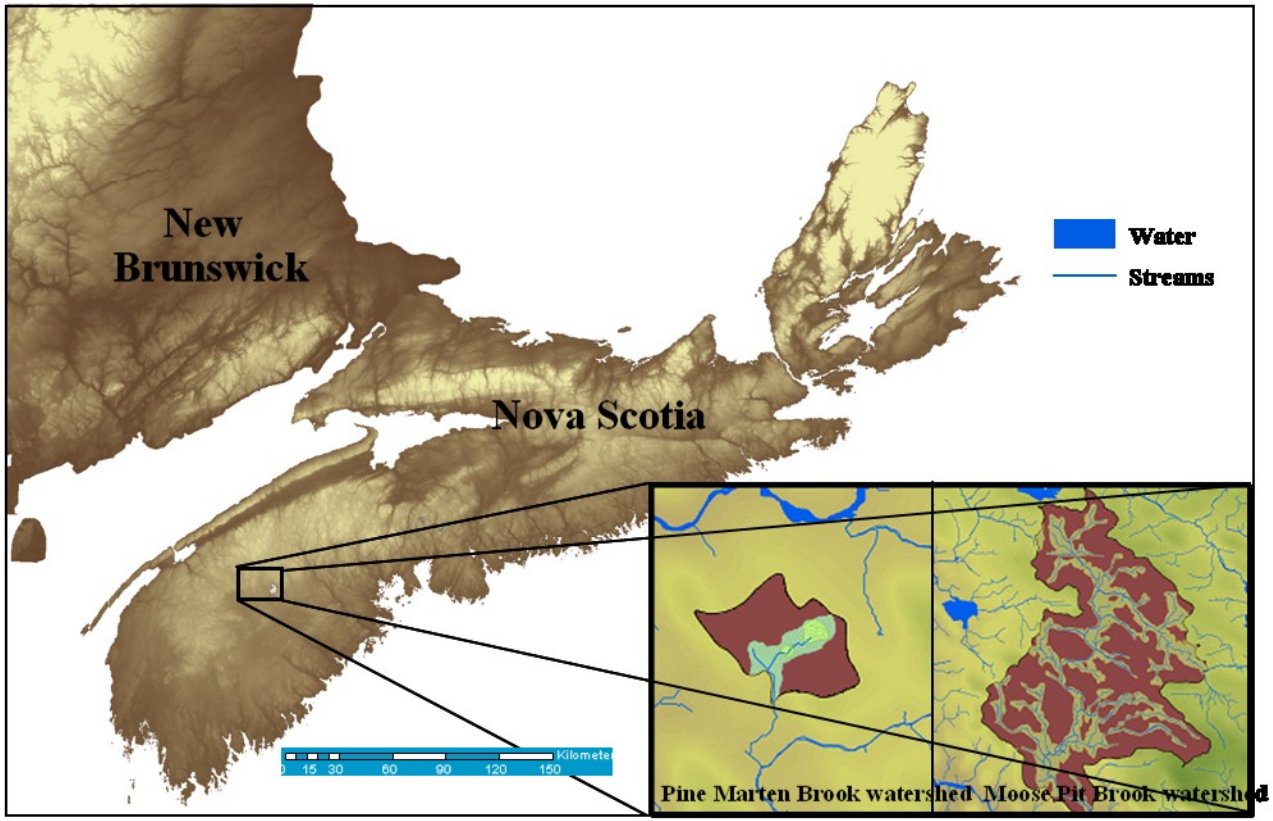

Figure 6.2 Location of Pine Marten Brook and Moose Pit Brook watersheds, Kejimkujik National Park, westcentral Nova Scotia. The inset gives the watershed distribution of upland (brown) to wetland area (light greenish-blue).

obtained from the NS Department of Natural Resources. Delineation of wetland areas (ha) were based on a depth to water table (DTW) threshold = 1.0 m (Figure 6.2; Meng et al., 2004). Vegetation- and wetland-delineated areas and their corresponding dominance as a % of total watershed area are given in Table 6.1 for both Pine Marten and Moose Pit Brook watersheds.

6.4.3 Climate and Stream Discharge Data

Daily average air temperature and precipitation were collected from a first-order climate station located in KNP for the 1990-2005 period. For the examination of multiple-year impact of forest-growth patterns on THg export, 15 years of weather data were cycled ten times to generate timeseries of simulated weather for 150 years. Stream discharge data for the 1996-2005 period were collected at the outlet of Moose Pit Brook watershed by Environment Canada personnel.

6.4.4 THg-to-DOC Binding Efficiency

The THg-to-DOC correlation for KNP was shown to be adequately represented by a mean binding-efficiency coefficient (μ) of 0.48±0.038 (in ng mg^{-1}; the value after the "±" gives the standard error of estimate) from a one-time collection of THg and DOC concentrations from 45 different stream sites across KNP (Meng et al., 2005), giving a coefficient of determination (R^2) of 0.75. Similar studies in KNP (e.g., Vaidya and Howell, 2002; Rencz et al., 2003) have produced equally high R^2-values, e.g., 0.85 and 0.87.

6.5 Model Integration

In the integrated model (Figure 6.1), ForHyM2 was constructed in STELLA™ (1998), while ForNBM, FLDM, and combined DOC-THg export model components were constructed in ModelMaker™ (1999). The soil texture data used in this study are from Eastern Ecological Services Ltd (1976). The daily forest soil temperature, soil moisture, and stream discharge simulated with ForHyM2 were averaged to provide monthly input to relevant model components.

OM-chemical composition of the leaf litter was determined from CIDET-experiment leaf-litter samples (Trofymow and the CIDET working group, 1998; and reported in Zhang et al., 2010c). Chemical composition of fine-root OM was assumed to be the same as that for leaf litter. Partitioning of the leaf and root litter into fast, slow, and very slow decomposing litter pools was based on within-watershed species composition, weighted according to species basal area. Initial partitioning of the litter mass to the three litter pools in FLDM was based on a mass-balance calculation. ForHyM2 was calibrated with stream discharge data (water amount ha^{-1}) from Moose Pit Brook. Normalised stream discharge (per ha) was assumed to be the same for both watersheds, given their similar climate and bio-geophysical characteristics.

Parameters in ForNBM, FLDM, and the combined DOC-THg model components were optimised in ModelMaker with either the Levenberg-Marquardt or Nelder-Mead simplex method. The parameters determining net primary productivity and leaf litter fall in ForNBM were derived from Zhang et al. (2001b), except for M_{max} (see Table 6.2).

Table 6.1 Land covertype distribution; area (ha) and % dominance of watershed.

	Pine Marten Brook		**Moose Pit Brook**	
	Area (ha)	**%**	**Area** (ha)	**%**
Vegetation				
Hardwood	26.91	20.7	298.4	17.2
Softwood	61.49	47.3	955.2	55.2
Mixedwood	37.96	29.2	99.0	5.7
Regeneration	2.47	1.9	326.8	18.9
Others	1.17	0.9	50.9	2.9
Total	130	100	1730.4	100
Wetland	31.1	23.9	616.0	35.6

Parameter values determining leaf litter decomposition in FLDM and DOC production in the combined DOC-THg export model were derived from Zhang et al. (2010a). Model parameter definition, values, and equation sources are provided in Table 6.2.

6.6 Results and Discussion

6.6.1 Seasonal In-Stream DOC and THg-Concentration Dynamics

Figure 6.3 gives the simulated seasonal Hg concentration dynamics at the outlets of Pine Marten Brook and Moose Pit Brook watersheds for mature overstorey canopies. As would be expected, seasonal THg-concentration dynamics are consistent with that of DOC. Differences in THg and DOC concentrations across years is a result of differences in litter fall and litter decomposition, mostly as a result of interannual variation in climate (Chapter 5). During a single year, THg concentrations tend to (i) peak after leaf fall in autumn, (ii) decrease to a minimum in April, (iii) increase to another maximum in June, and (iv) subsequently decrease to a second minimum just before leaf fall. This pattern is consistent with observations reported by Krabbenhoft et al. (1995) and Garcia et al. (2007).

6.6.2 Impact of Forest Age and Rotation Management on THg Export

6.6.2.1 Leaf Fall and Forest-Floor Residual Litter as a Function of Forest Growth

Figure 6.4 shows the projected leaf fall (a) and forest-floor litter dynamics (b) over two forest rotations (of 75-year duration) for Pine Marten Brook watershed. Following forest regeneration and re-growth, living leaf biomass reaches a maximum at about 40 years after harvest (at time zero and 75 years later).

Table 6.1 Parameter values of forest-floor litter mass decomposition and forest re-growth.

Process	Definition	Unit	Value	Eq. & Source	Derivation
Net primary productivity (NPP)					
M_{max}	Potential maximum NPP	tonne month^{-1}	1.8	1 , Zhu et al., 2003	Calibration
T_{max}	Maximum temperature, above which NPP will stop	^{o}C	40	2 , Zhu et al., 2003	Zhang et al., 2010b
T_{opt}	Optimum temperature, at which NPP will reach maximum	^{o}C	20	2 , Zhu et al., 2003	Zhang et al., 2010b
T_{min}	Minimum temperature, below which NPP will stop	^{o}C	5	2 , Zhu et al., 2003	Zhang et al., 2010b
sm_{max}	Maximum soil moisture, above which NPP will stop	% volume	1	4 , Zhu et al., 2003	Zhang et al., 2010b
sm_{Opt}	Optimum soil moisture, at which NPP will reach maximum	% volume	0.80	4 , Zhu et al., 2003	Zhang et al., 2010b
sm_{min}[a]	Minimum soil moisture, below which NPP will stop	% volume	0.16	4 , Zhu et al., 2003	Zhang et al., 2010b
P_{age0}	Determined by species biological characteristics	year^{-1}	0.016	7 , Zhu et al., 2003	Zhang et al., 2010b
P_{age1}	Determined by species biological characteristics	unitless	2.387	7 , Zhu et al., 2003	Zhang et al., 2010b
P_{age2}	Determined by species biological characteristics	year^{-1}	0.083	7 , Zhu et al., 2003	Zhang et al., 2010b
F_{lf1}	Parameter for deciduous forest	unitless	0.05	1 ,	Townsend, 2008
F_{lf1}	Parameter for coniferous forest	unitless	0.21	1 ,	Townsend, 2008
F_{lf2}	Parameter	unitless	0.67	1 , Zhang et al., 2010b	Zhang et al., 2010b
Litter fall					
F_{lf3}	Parameter for deciduous forest	unitless	1	2 ,	
F_{lf3}	Parameter for coniferous forest	unitless	0.33	2 , Zhang et al., 2010b	Zhang et al., 2010b
Litter decomposition					
a_0	Parameter for initialisation of litter decomposition	unitless	-10.9	8 , Zhang et al., 2010c	Zhang et al., 2010c
a_1	Parameter for initialisation of litter decomposition	unitless	0.14	8 , Zhang et al., 2010c	Zhang et al., 2010c
a_2	Parameter for initialisation of litter decomposition	unitless	0.13	8 , Zhang et al., 2010c	Zhang et al., 2010c
a_3	Parameter for initialisation of litter decomposition	unitless	0.119	9 , Zhang et al., 2010c	Zhang et al., 2010c

Table 6. 2 cont'd.

k_1	Decomposition ratio between the fast and slow decomposition litter pools	unitless	17.92	2 , Zhang et al., 2010c	Zhang et al., 2010c
k_2	Parameter for the slow decomposition litter pool	$month^{-1}$	0.015	3 , Zhang et al., 2010c	Zhang et al., 2010c
k_3	Decomposition ratio between the very slow and slow decomposition litter pool	unitless	0.35	4 , Zhang et al., 2010c	Zhang et al., 2010c
Ea	Constant, representing activation energy	J $mole^{-1}$	63392	11, Zhang et al., 2010c	Zhang et al., 2010a
R	Universal gas constant	J $mole^{-1}$ C^{-1}	8.31	11, Zhang et al., 2010c	Constant
p_{TJan}	Parameter for the impact of January temperature on litter decomposition	^oC	20.7	11, Zhang et al., 2010c	Zhang et al., 2010c
sm'_{max}	Maximum soil moisture, above which decomposition will stop	% volume	1.00	12, Zhang et al., 2010c	Zhang et al., 2010c
sm'_{opt}	Optimum soil moisture, above which decomposition will reach maximum	% volume	0.95	12, Zhang et al., 2010c	Zhang et al., 2010c
sm'_{min} [a]	Minimum soil moisture, below which decomposition will stop	% volume	0	12, Zhang et al., 2010c	Zhang et al., 2010c
DOC concentration					
P_{DOC1}	DOC release from the fast decomposing litter pool	mg $tonne^{-1}$	0.048	13, Zhang et al., 2010a	Currie and Aber,1997
P_{DOC2}	DOC release from the slow decomposing litter pool	mg $tonne^{-1}$	0.138	13, Zhang et al., 2010a	Currie and Aber,1997
P_{DOC3}	DOC release from the very slow litter decomposing pool	mg $tonne^{-1}$	0.199	13, Zhang et al., 2010a	Currie and Aber,1997
P_{DOC1}	DOC release from the fast decomposing litter pool	mg $tonne^{-1}$	0.069	13, Zhang et al., 2010a	Currie and Aber,1997
P_{DOC2}	DOC release from the slow decomposing litter pool	mg $tonne^{-1}$	0.212	13, Zhang et al., 2010a	Currie and Aber,1997
P_{DOC3}	DOC release from the very slow litter decomposing pool	mg $tonne^{-1}$	0.337	13, Zhang et al., 2010a	Currie and Aber,1997
b_Q	Parameter	unitless	1.014	14, Zhang et al., 2010a	Zhang et al., 2010a
b_{DOCu}	Parameter for DOC release from upland sites	unitless	4.0	14, Zhang et al., 2010a	Zhang et al., 2010a
b_{DOCa}	Parameter for DOC release from wetland sites	unitless	17.4	14, Zhang et al., 2010a	Zhang et al., 2010a
b_{DOCb}	Parameter for DOC release from wetland sites	unitless	43.2	14, Zhang et al., 2010a	Zhang et al., 2010a

[a] sm'_{min}, sm'_{max}, and sm'_{opt} for litter decomposition differ from sm_{min}, sm_{max}, and sm_{opt} for net primary productivity.

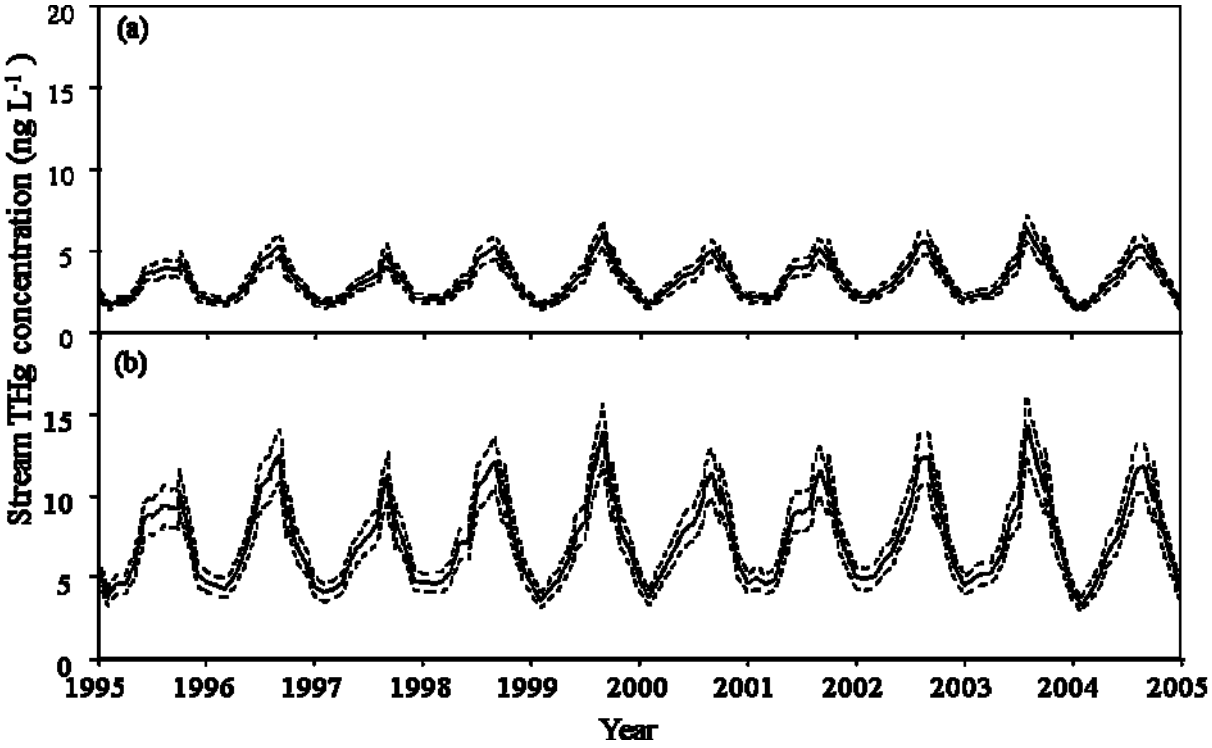

Figure 6.3 Projected stream THg concentrations for Pine Marten Brook (a) and Moose Pit Brook (b) watersheds. The dashed lines represent the variation-band about the mean prediction (solid line) based on a THg-to-DOC binding-efficiency coefficient (μ) of 0.48±0.038 (after Meng et al., 2005).

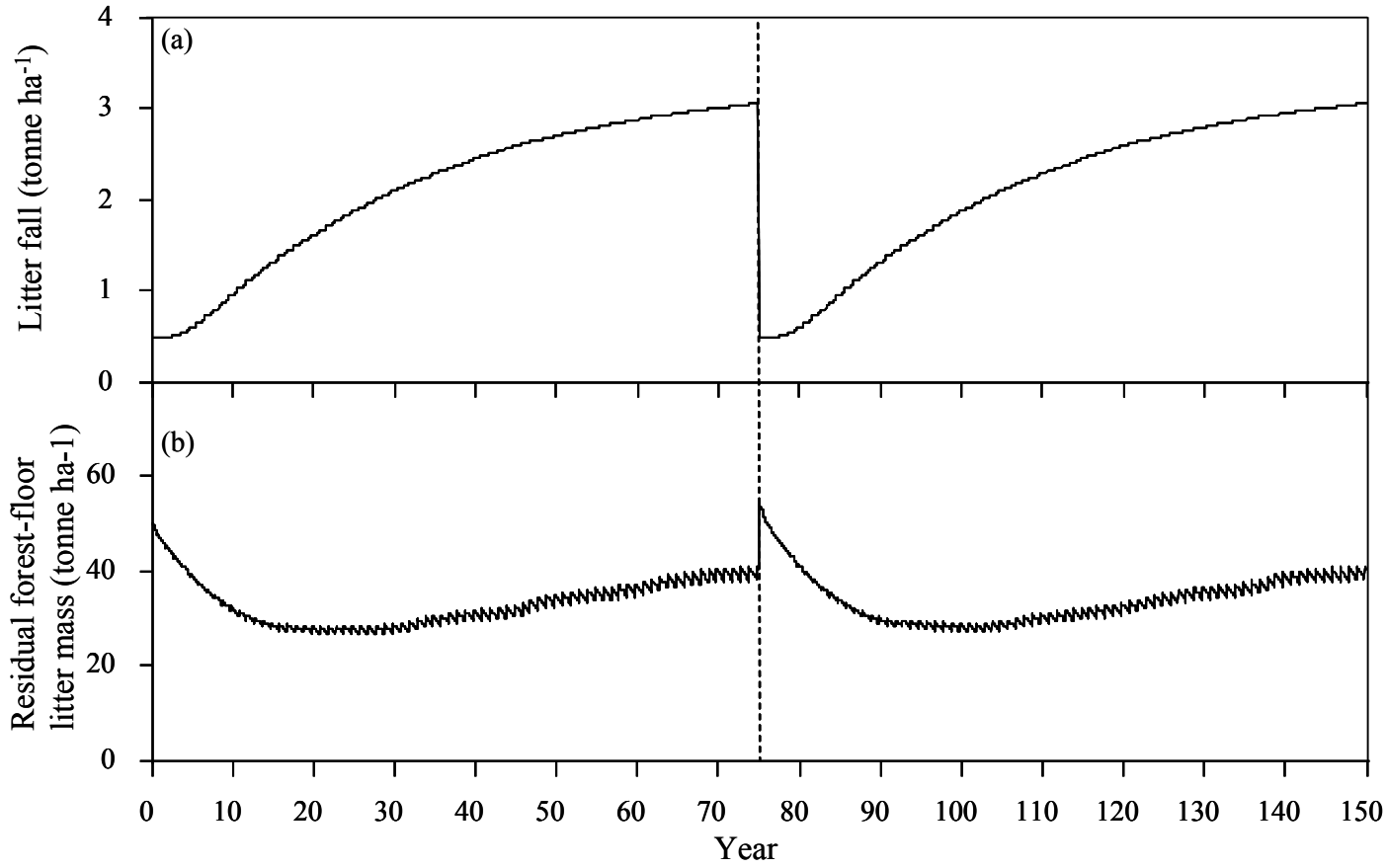

Figure 6.4 Projected mean forest litter fall (a) and forest-floor litter dynamics (b) 75 years after clearcutting; year=0-75 represents the first forest rotation and year=75-150, the second rotation; the two rotations are separated by the vertical dashed line.

Forest-floor residual litter mass initially decreases and reaches a minimum at about 15 years after harvest, and gradually increases and reaches a maximum just before the second harvest. The results presented are consistent with observations made by (i) Covington (1981), who showed with field data that the OM-content of the organic horizon in northern hardwood forests decreases to a minimum at about 15 years after clearcutting, and (ii) Aber et al. (1978), who showed with computer models that harvesting lowers OM in the forest floor during the first 15-30 years subsequent to cutting.

6.6.2.2 In-Stream DOC- and THg-Concentration Dynamics

Figures 6.5 and 6.6 show the projected stream DOC- and THg-concentration dynamics for the two study watersheds as a function of forest regeneration and re-growth after harvest. In-stream DOC (Figure 6.5) and THg concentrations (Figure 6.6) have similar dynamics, which vary according to the observed patterns in modelled leaf-litter production and forest-floor residual litter mass (Figure 6.4). Large debris pools left on site following harvesting provide a significant pulse in DOC production and within-watershed THg export during the first 2-3 years after stand initiation.

6.6.3 Impact of Vegetation Type and Topography on Stream DOC and THg Concentration

From a DOC-production and export point of view (Zhang et al., 2010a), conifers should produce more DOC than broadleaf species, as the litter in softwood species generally contain more very slow decomposing chemical compounds than hardwood

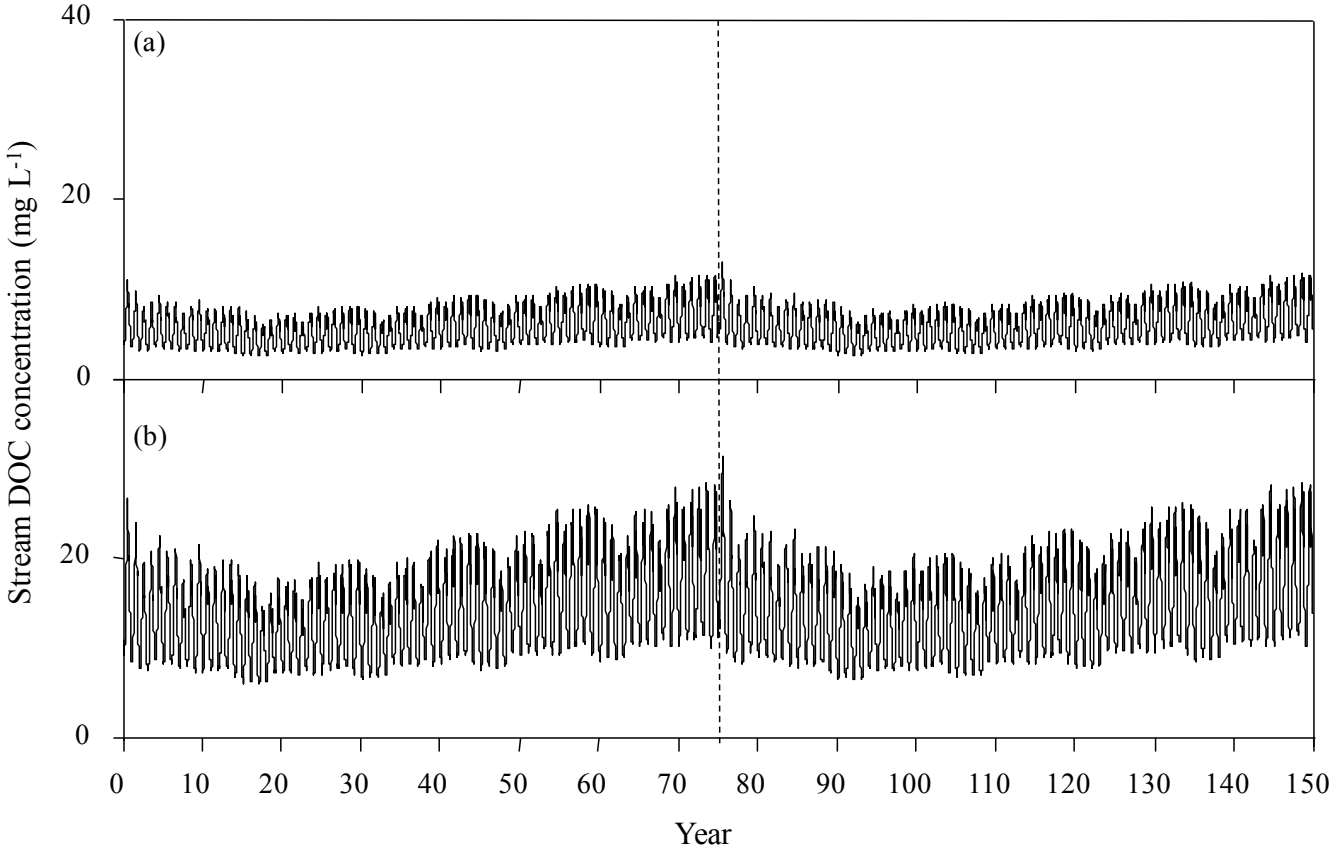

Figure 6.5 Projected mean DOC concentrations in Pine Marten Brook (a) and Moose Pit Brook (b) watersheds following monthly weather and forest re-growth patterns 75 years after clearcutting; year=0-75 represents the first forest rotation and year=75-150, the second rotation; the two forest rotations are separated by the vertical dashed line.

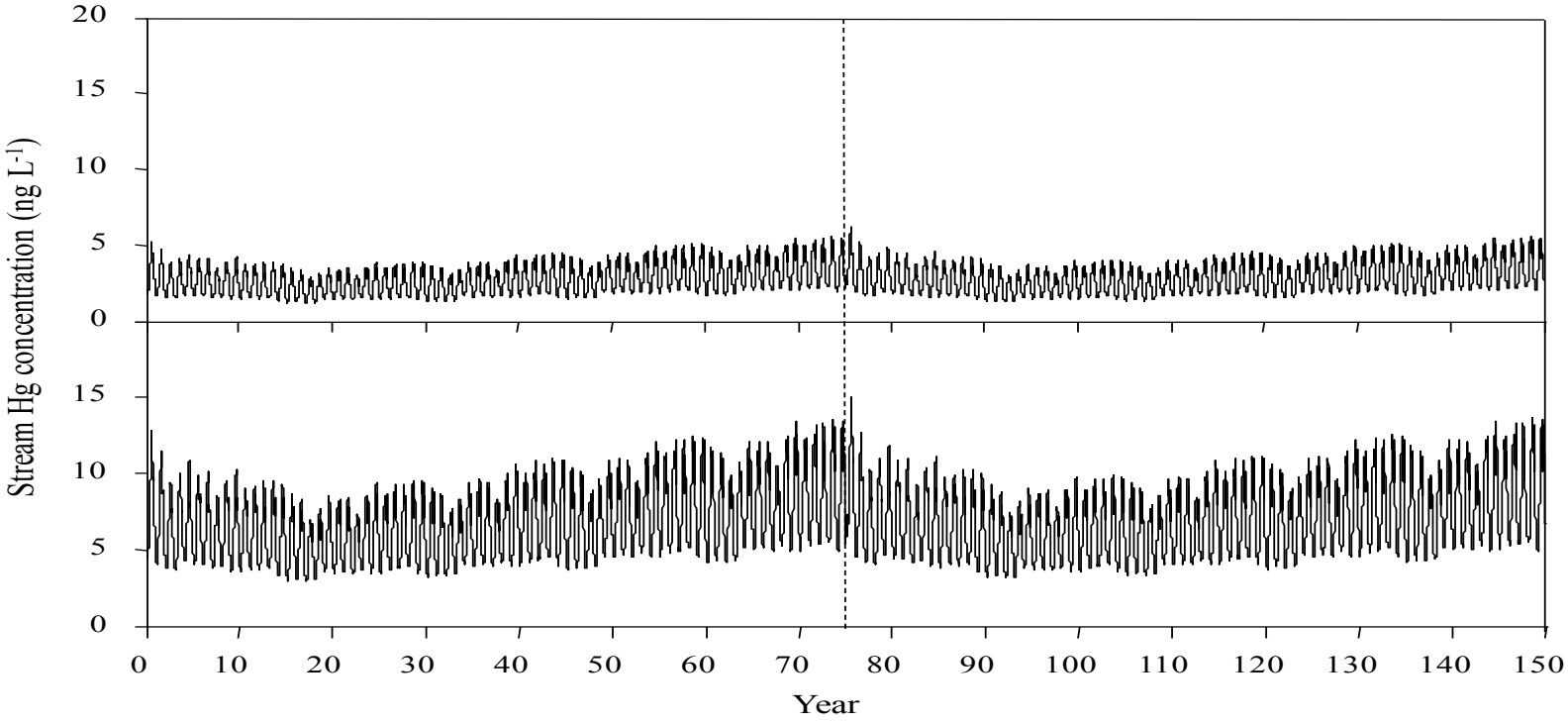

Figure 6.6 Projected mean THg concentrations in Pine Marten Brook (a) and Moose Pit Brook (b) watersheds following monthly weather and forest re-growth patterns 75 years after clearcutting; year=0-75, gives the first forest rotation and year=75-150, the second rotation; the two forest rotations are separated by the vertical dashed line.

litter (Zhang at el., 2007). As a result, for similar physiographic and environmental conditions, conifer-dominated watersheds should transfer more THg to streams than broadleaf-dominated watersheds. In wetlands, dissolvation of polyvalent cations (e.g., Fe, Al, Ca, Mg; all important DOC adsorbents), promotes the release of DOC to streams (Fiedler and Kalbitz, 2003; Müller, et al., 2009). Consequently, watersheds with a proportionally greater amount of wetland area would tend to export more DOC and THg to streams than dry, upland-dominated watersheds.

6.6.4 In-stream THg Concentration and Canadian Water Quality Guidelines for Aquatic Life

From *Canadian water quality guidelines for aquatic life*, inorganic Hg concentrations in freshwater should be < 26 ng L^{-1} (Canadian Council of Ministers of the Environment, 2003). At no time THg concentrations in the two watersheds are projected to exceed 26 ng L^{-1}.

6.6.5 THg Distribution Pattern and Efficient Water Quality Monitoring

From this study, it is determined that forest age, species composition, and wetland-to-watershed area ratio are important factors in defining DOC and THg export from terrestrial to aquatic ecosystems. Quantifying these variables spatially can facilitate the spatial representation of DOC and THg dynamics. DOC and THg concentrations peak in summer and after leaf fall, indicating when water samples should be taken to screen for high DOC and THg concentrations in low-ordered forest streams.

6.7 Concluding Remarks

This Chapter presents the simulation of seasonal stream THg-concentration dynamics as a function of (i) forest development and growth, litter production, and DOC production and export processes, and (ii) a THg-to-DOC binding-efficiency coefficient. To address the disparity in organic matter-absorption between the wet and dry portions of watersheds, the wetland-to-total-watershed-area ratio, based on a GIS-mapping of depth to water table, is used.

Simulations with the integrated model show that DOC and THg export from forested watersheds are sensitive to both short-term and long-term conditions of the forest (over one year vs. over the life span of the forest). Over a single year, DOC and THg exports increase simultaneously during spring following a gradual increase in temperature and reach their individual maxima in July. Following this, DOC and THg exports gradually decrease before leaf fall, perch to their maxima after leaf fall, and then decrease with the onset of cold fall-winter temperatures. DOC and THg exports are shown to (i) increase sharply in the first 2-3 years following clearcutting, (ii) decrease to their respective minima at about 15 years after stand initiation, and (iii) gradually increase thereafter.

Because conifers contain more very slow decomposing compounds and produce more DOC than deciduous forests (Zhang et al., 2010a), it is expected that coniferous forests should export a greater amount of THg to streams. Also, watersheds with a greater portion of wetlands are expected to produce more DOC and export more THg than watersheds with a reduced wetland cover.

6.8 Acknowledgements

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CHAPTER 7 CONCLUSION

7.1 Thesis Summary

Hg is a highly toxic metal, which affects the health of humans and animals alike. Hg toxicity increases by bioaccumulation and bioamplification. Forested watersheds have been long identified as significant deposition surfaces for airborne Hg and major sources of low-concentration Hg compounds to surrounding streams and lakes. Mercury export from forests is highly variable in both space and time. This spatiotemporal variation cannot be quantified accurately by field experiments alone. Mathematical models are required for improved representation.

The Thesis presents an integrated modelling approach to simulating seasonal THg-concentration dynamics for two small forest streams in westcentral Nova Scotia. In its calculation of THg dynamics, the model integrates principles of (i) forest hydrology, particularly as it relates to the calculation of soil temperature, soil moisture, and surface-runoff generation (via ForHyM2), (ii) forest nutrient cycling and biomass growth (ForNBM), (iii) forest-floor litter decomposition (FLDM), and (iv) DOC production and export. Results from the integrated model are compared against field measurements, including litterbag and *in-situ* residual litter mass, and watershed-outlet DOC concentrations. My Thesis addresses the following detail:

1) Chapter 1 reviews field experiments and models related to the circulation of Hg at the global to watershed scale. From the literature, (i) Hg exported from forested source areas define the spatiotemporal dynamics of Hg concentrations in aquatic ecosystems; and (ii) DOC is an important binding medium involved in transporting Hg from

terrestrial source areas to aquatic ecosystems. Accurate simulation of seasonal trends in in-stream Hg concentrations is best addressed with DOC-production process-based models that integrate ecosystem-scale DOC-transport processes.

2) Ecosystems are complex. To understand the characteristics of these systems, it often requires data acquired from multiple field experiments and modelling studies carried out at various spatiotemporal resolutions. Chapter 2 addresses the structure of the integrated DOC-THg export model, its spatiotemporal extent and resolution, and its overall input requirements and output.
3) Based on the fact that the annual FLDM cannot address seasonal trends in litter decomposition, the annual FLDM is modified to operate at a monthly time resolution. Chapter 3 addresses this modification and the subsequent comparison of the revised model's results against litterbag decomposition data. The revised model is shown to give similar calculations of residual mass and N concentrations as the original, annual model (R^2= 0.91, 0.78), albeit producing very different timeseries of decomposition over a 6-year simulation period.
4) Performance of FLDM (three-pool formulation) is compared against that of a single-pool forest litter decomposition formulation and *in-situ* measurements of forest-floor residual litter mass. In this effort, forest litter fall (an input to both litter-decomposition formulations) is simulated with the forest nutrient cycling and biomass growth model, ForNBM. Chapter 4 addresses this work.
5) Chapter 5 addresses the development of the DOC production and export model and its calibration and validation with field-based measurements of in-stream DOC concentrations. The DOC production and export model is developed based on the

concept that (i) DOC production is largely determined by forest-floor litter decomposition, and (ii) DOC export is determined by soil-absorption disparity between wetland and upland soils and extent of surface runoff. Comparisons for the two watersheds show that predicted monthly DOC concentrations are generally in good agreement with field-based concentrations, giving R^2-values of 0.61 and 0.63 for Pine Marten Brook watershed and 0.72 and 0.75 for Moose Pit Brook watershed for model calibration and validation, respectively.

6) In Chapter 6, monthly stream THg concentrations are simulated for two forested watersheds in westcentral Nova Scotia, integrating short-term (seasonal) and long-term (forest development) processes of modelled seasonal litter decomposition, DOC production and export, and forest removal and re-growth.

7.2 Contributions to Science

The integrated model (Figure 2.1) is used to predict the long-term impact of forest management on stream THg concentrations, which is of particular concern as a result of its impact on human and environmental health. Major contributions to the science of Hg-circulation in small forested watersheds are itemised according to Chapter.

1) **Chapter 3** - It is found that the average January air temperature has a special role in defining litter decomposition in the following summer by determining the over-winter survival of decomposers and their level of activity in the following summer. This finding highlights the importance of winter constraints and residual decomposer-communities on the summer litter-decomposition process. This is the first time this notion is applied in modelling litter decomposition. Other well-known monthly litter

decomposition models, such as CENTURY and SOMM overlook this important fact. From a modelling point of view, litter decomposition is independent of N mineralisation, while N mineralisation is dependent on decomposition. This Chapter has been published as an original research article in *Ecological Modelling*.

2) **Chapter 4** - Simulation of litter decomposition with a single-pool formulation underpredicts *in-situ* forest-floor residual litter mass when forests are younger than 65 years old. The three-pool formulation of FLDM resolves this underprediction, supporting the idea that the various litter types (defined by the amount of water-extractable, acid-hydrolysable, and ash content of the litter) be modelled separately. The underprediction of the single-pool formulation could potentially lead to an underprediction of DOC production and DOC and THg export from forested watersheds. From FLDM-based (three-pool) simulations applied to the Boreal Forest Transect Case Study (BFTCS) sites, it was shown that forest-floor litter mass is expected to increase (i) from cold to warm sectors of a climate gradient, and (ii) from low to high productivity sites. This model development is expected to gain greater importance in the study of forest-floor litter dynamics and C-stock (and DOC) fluctuations anticipated with climate change. This Chapter has recently been accepted for publication in Ecological Modelling.

3) **Chapter 5** - In this Chapter, a monthly, process-based DOC export model was developed and successfully calibrated and validated. The modelling work supports the idea that stream DOC concentrations are positively correlated to (i) wetland-to-watershed area ratio, (ii) monthly soil temperature, (iii) surface flow rates, and (iv) autumn leaf fall. Given the fact that a range of contaminants adhere to and are carried

by DOC, the current model may be used to simulate seasonal-concentration dynamics of nonmetals, such as phosphorus and other toxic metals, besides Hg.

4) **Chapter 6** - Simulation of seasonal THg exports is based on the fact that in-stream THg and DOC concentrations are highly correlated. This correlation led to the development of a THg-to-DOC binding-efficiency coefficient [0.48±0.038 (Standard error of estimate)] by relating one-time measurements of DOC and THg concentrations collected at 45 different stream sites across Kejimkujik National Park. The model simulates forest age and forest management impact on in-stream THg-concentrations. Over a single year, in-stream THg concentrations increase gradually from a minimum in April to a maximum in June, and then decrease. A small concentration peak forms after leaf fall. This seasonal pattern is consistent with field observations. Over a forest rotation, in-stream THg concentrations increase in the first 2-3 years following forest harvesting and then subsequently increase as the forest matures. Because conifers produce more DOC than deciduous forests, it is expected that coniferous forests should export a greater amount of THg to streams. Also, watersheds with a greater portion of wetlands are expected to export more DOC and THg than watersheds with a reduced wetland cover.

7.3 Application of the Model

1) Besides being used to simulate THg export from forested watersheds, the FLDM and DOC components of my work can be integrated in carbon and nutrient cycling models.

2) Simulation of seasonal THg concentrations as presented here can be used to establish more efficient monitoring programs of streamwater quality associated with DOC and THg effluxes. Such models can be used to identify the timing and extent of seasonal peaks in DOC and THg concentrations.

3) The integrated model has the potential to be used in assessing the long-term export of THg and DOC from forested terrestrial to aquatic ecosystems. This link between atmosphere Hg deposition and stream Hg concentration can be used to assess the impact of atmospheric Hg deposition on aquatic ecosystems at the watershed level.

4) The THg and DOC export model can be used to assess forest management strategies at the watershed level. Maintaining forest productivity and natural environments sustainable are key objectives of forest ecosystem managers. In highly polluted areas, hardwood forests should be grown in greater proportions as they export less DOC and THg to surrounding aquatic ecosystems than coniferous forests. To stabilise streamwater quality locally, regionalised forest management planning should account for differences in watersheds.

5) Species succession is a naturally occurring phenomenon in forests and other vegetation-dominated ecosystems. In temperate regions, vegetation undergoes succession, typically starting with pioneer species (e.g., grasses), switching to shrubs and hardwood forests, and eventually to tolerant softwood forests. Without naturally or anthropogenically induced disturbances, climax softwood species may persist for an indefinite period. From my work, mature and over-mature forests export the greatest amount of THg. To encourage low THg export over the long term, it is

suggested that disturbances (e.g., fire, insect-disease infestations) be allowed to occur unabated.

7.4 Recommendations for Future Work

1) For an improved implementation of a 'space trade for time' forest-C experiment, one should consider the effects of site quality (and potentially, site index) on forest-growth response, beyond the effects associated simply with forest age.
2) As the integrated model (Figure 2.1) is based on a parameterisation and validation centered on data from two watersheds from the same area and climate regime, the model is most likely site specific and unrepresentative of sites with vastly different biogeochemical and climatic conditions. For development of a more robust model, it is suggested that model parameter setting and validation be based on data acquired from a wider range of forest sites. Such data, to my knowledge, currently do not exist.
3) ForNBM considers the growth of forest biomass as a function of air temperature and soil moisture and ignores the influence of solar radiation on photosynthesis. Potential inaccuracies generated with this over-simplification should be considered when updating the model.
4) Effort should be expended in collecting field-based measurements of THg concentrations on a regular basis (possibly weekly) and at different stream locations, in order to validate the THg-export component of the integrated model (Figure 2.1) in a more direct and defensible manner.
5) The 20-year limitation on ForHyM2 simulations with STELLA™ constrains the level of information that can be produced with the model, especially for long-term

simulations. To circumvent this problem, 20-year time slices of simulated results are usually cycled repeatedly to cover the period of interest (e.g., over one forest rotation). This is highly undesirable and to resolve the time-constraint dilemma, it is suggested that ForHyM2 be re-written in a common computer language, such as C/C++, Visual Basic, or Visual Fortran. Enhanced flexibility gained with a well-structured, re-written code would far outweigh the time and resources used in re-writing it.

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