Hydrological, Biogeochemical and Landscape Controls on Mercury Distribution and Mobility in a Boreal Shield Soil Landscape

by

Claire Jocelyn Oswald

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Geography
University of Toronto

© Copyright by Claire Jocelyn Oswald, 2011
Hydrological, Biogeochemical and Landscape Controls on Mercury Distribution and Mobility in a Boreal Shield Soil Landscape

Claire Jocelyn Oswald
Doctor of Philosophy
Department of Geography
University of Toronto
2011

Abstract

Mercury (Hg)-contaminated freshwater fisheries are a global toxicological concern. Previous research suggests that the slow release of Hg in runoff from upland soils may delay the recovery of Hg-contaminated aquatic systems. Four complementary studies were undertaken in a small boreal Shield headwater catchment as part of the Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S. (METAALICUS) to assess the controls on the retention and release of historically-deposited Hg (ambient Hg) and newly-deposited (spike Hg) in the soil landscape. In the first study, hydrometric and GIS-based methods were used to quantify thresholds in terrestrial water storage and their relationship to observed rainfall-runoff response. It was found that event-scale hydrologic response displayed a threshold relationship with antecedent storage in the terminal depression and predictions of event runoff improved when storage excesses from upslope depressions were explicitly routed through the catchment. In the second study, it was shown that the dominant source of ambient Hg to the lake was likely derived from shallow soil-water flowing through the lower, well-humified organic soil horizon. Throughout the catchment, ambient Hg to soil organic carbon (SOC) ratios increased with depth and the experimentally-applied spike Hg was concentrated in the surface litter layer, suggesting
that the vertical redistribution of $Hg$ in the soil profile is a function of the rate of decomposition of $SOC$. In the third study, canopy type was found to be a good predictor of ambient $Hg$ and spike $Hg$ stocks in the lower organic horizon, while drainage conditions were not, suggesting that vertical fluxes of $Hg$ dominate over lateral fluxes in topographically-complex landscapes. Lastly, it was shown that catchment discharge, antecedent depression storage and antecedent precipitation were the best predictors of dissolved organic carbon ($DOC$), ambient $Hg$ and spike $Hg$ concentrations in catchment runoff. A comparison of $DOC$, ambient $Hg$ and spike $Hg$ dynamics for two storm events showed that distinct shifts occurred in the concentration-discharge relationship as a result of differences in antecedent moisture conditions. Combined, the results of the four studies demonstrate the need to incorporate hydrological, biogeochemical and landscape controls into predictive models of terrestrial-aquatic $Hg$ export.
Acknowledgments

Research Acknowledgements

First and foremost, I extend special thanks to my supervisor, Dr. Brian A. Branfireun, in appreciation for the opportunities he has given me and for sharing his enthusiasm and insight for scientific research. Dr. Branfireun has supported me both professionally and personally during my graduate work, which has been invaluable for my academic development. I look forward to our future collaborations and continued friendship.

I am very grateful to colleagues at the Chesapeake Biological Laboratory (University of Maryland), specifically Dr. Andrew Heyes, Sarah Ghorpade and Elizabeth Jenny, for hosting me over the years to conduct analytical work, assisting with field campaigns and providing research-related advice.

I extend thanks to everyone at the Experimental Lakes Area who supported me throughout this project. In particular, I would like to thank Ken Sandilands and Justin Shead for extensive field assistance, Ken Beatty for hydrological resources, and Marnie Potter for keeping me nourished. Thank you as well to all the other staff and students who provided help over the years.

I would like to thank all members of the METAALICUS project for their collegiality and advice on my research. In particular, I would like to thank Dr. Dave Krabbenhoft and Mike Tate (U.S. Geological Survey, Madison, Wisconsin), Dr. Vince St. Louis, Dr. Jenny Graydon and Linnea Mowat (University of Alberta), and Dr. Cindy Gilmour and Georgia Riedel (Smithsonian Environmental Research Centre). It has been a pleasure to be involved in such an interesting and multi-disciplinary project.

I would also like to thank my colleagues from the University of Toronto who assisted me in the field, in the lab, and at various stages throughout the research process: Dr. Murray Richardson, Dan Fitzgerald, Almuth Klemenz, Steven Kim, Christopher Wellen, Dr. George Arhonditsis, Michelle Collins, Ashley Warnock, Britney Myers, Tom Ulanowski, Dr. Chris Eckley, Evan Malczyk and Dr. Carl Mitchell. Special thanks go to my supervisory and examination committee members, Dr. Brian Branfireun, Dr. Myrna Simpson, Dr. Tony Price, Dr. Scott
Munro, Dr. Nathan Basiliko, and Dr. Marie-Josée Fortin for their research advice over the years and their suggestions for the final version of my thesis. And very special thanks goes to Dr. Jamie Shanley (U.S. Geological Survey, Montpellier, Vermont) for making the trip to Toronto to be the external examiner for my final defense and for his invaluable comments on my thesis.

This research was not possible without generous financial assistance from the National Science and Engineering Research Council of Canada, the Ontario Graduate Scholarship program and the University of Toronto awards program.

**Personal Acknowledgements**

My husband, Peter Brown, has been a constant foundation of support throughout my years as a graduate student. There are no words to express how much his patience, advice and love mean to me. My mother, Heather Oswald, father, Daniel Oswald, and sister, Janet Oswald, have also been unconditionally supportive and I am eternally grateful to them for this. Thank you as well to my aunt, Susan Smith and grandmother, Marcelle Oswald, for their support and interest in my work.

Many friends and colleagues in the Department of Geography have been an integral part of my graduate experience at the University of Toronto. They are too many to name. I have deeply enjoyed our conversations and collaborating on extra-curricular activities. I wish them all the best in their future endeavours.
# Table of Contents

Abstract ........................................................................................................................................... ii

Acknowledgments .......................................................................................................................... iv

Table of Contents ............................................................................................................................ vi

List of Tables ................................................................................................................................. xii

List of Figures ............................................................................................................................... xiv

List of Appendices ........................................................................................................................ xix

Chapter 1 Introduction ..................................................................................................................... 1

1.1 Background Information ........................................................................................................ 1

1.2 Knowledge Gaps ........................................................................................................................ 3

1.2.1 Hydrological Processes .................................................................................................. 3

1.2.2 Vertical Distribution and Partitioning of \( Hg \) ................................................................. 3

1.2.3 Controls on the Spatial Distribution of \( Hg \) in the Soil Landscape ............................... 4

1.2.4 The Influence of Antecedent Moisture Conditions on Event-Scale \( Hg \) Fluxes....... 5

1.3 Objectives ............................................................................................................................... 5

1.4 General Research Approach .................................................................................................. 8

1.5 Thesis Structure and Publication Information ........................................................................ 9

1.5.1 Chapter 1 ...................................................................................................................... 9

1.5.2 Chapter 2 ...................................................................................................................... 9

1.5.3 Chapter 3 .................................................................................................................... 10

1.5.4 Chapter 4 .................................................................................................................... 10

1.5.5 Chapter 5 .................................................................................................................... 10

1.5.6 Chapter 6 .................................................................................................................... 10

Chapter 2 Water Storage Dynamics and Runoff Response of a Boreal Shield Headwater
Catchment ........................................................................................................................................ 12

2.1 Introduction ............................................................................................................................ 12
2.2 Study Area ................................................................................................................................. 15

2.3 Methods ......................................................................................................................................... 17
  2.3.1 Study Period ........................................................................................................................... 17
  2.3.2 Landscape Partitioning ........................................................................................................... 18
  2.3.3 Depth-To-Bedrock Mapping ................................................................................................. 19
  2.3.4 Hydrometric Measurements ............................................................................................... 21
  2.3.5 Graphical Hydrograph Separation ..................................................................................... 22
  2.3.6 Water Storage Calculation ................................................................................................. 23

2.4 Results and Discussion .................................................................................................................... 26
  2.4.1 Variability in Catchment Response Factors .......................................................................... 26
  2.4.2 Hydrologic Response Units (HRUs) ................................................................................... 32
  2.4.3 HRU Water Storage Dynamics ........................................................................................... 36
    2.4.3.1 General Hydrologic Behaviour .................................................................................. 36
    2.4.3.2 Water Storage Dynamics ......................................................................................... 38
  2.4.4 Storage-Discharge Relationships ....................................................................................... 38
    2.4.4.1 Piecewise Regression Models .................................................................................... 38
    2.4.4.2 Relationship to Storm Response ................................................................................. 43
    2.4.4.3 Storage Excess Routing ........................................................................................... 46
  2.4.5 Implications for Predicting the Hydrologic Behaviour of Boreal Shield Catchments .... 50

2.5 Conclusion .................................................................................................................................... 51

Chapter 3 Vertical Distribution of Ambient Mercury and Applied Mercury Isotope in Soil and Soil-Water in a Boreal Shield Soil Landscape ........................................................................... 53

3.1 Introduction .................................................................................................................................. 53

3.2 Methods ...................................................................................................................................... 55
  3.2.1 Site Description ..................................................................................................................... 55
  3.2.2 Application of Enriched \( Hg \) Isotope to the Lake 658 Uplands ........................................ 59
4.2.4 Chemical Analysis........................................................................................................99
4.2.5 Topographic Analysis................................................................................................101
4.2.6 Spatial Analysis .........................................................................................................102
  4.2.6.1 Data Preparation..............................................................................................102
  4.2.6.2 Surface Pattern Analysis .............................................................................103
  4.2.6.3 Testing for Deposition-Related Spatial Controls ........................................104
  4.2.6.4 Testing for SOC-Related Spatial Controls ..................................................105
  4.2.6.5 Testing for Translocation-Related Spatial Controls.......................................105
4.3 Results ..........................................................................................................................106
  4.3.1 Assessment of Spatial Patterns in Hg Data......................................................106
  4.3.2 Deposition-Related Controls on Spatial Variability .........................................111
  4.3.3 SOC-Related Controls on Spatial Variability ..................................................114
  4.3.4 Spatial Variability due to Translocation in Soil-Water .....................................122
4.4 Discussion.......................................................................................................................124
  4.4.1 Do SOC, ambient Hg, and spike Hg stocks, and the stoichiometry of the
        Hg:SOC relationship, in different soil horizons exhibit spatial patterns across
        the catchment? .........................................................................................................124
  4.4.2 Are spatial patterns in SOC, ambient Hg, and spike Hg stocks related to tree
        species type or canopy density? ...........................................................................125
  4.4.3 Is there a downslope increase in SOC and Hg in the soil profile? .....................126
  4.4.4 Do the concentrations of DOC, ambient Hg, and spike Hg in soil-water
        increase downslope? ............................................................................................127
4.5 Conclusion ......................................................................................................................128

Chapter 5 Antecedent Moisture Conditions Control Mercury and Dissolved Organic Carbon
Concentration-Discharge Dynamics in a Boreal Shield Catchment....................................130
5.1 Introduction ..................................................................................................................130
5.2 Methods .......................................................................................................................134
  5.2.1 Site Description ..............................................................................................134
  5.2.2 Study Period and Event Selection ..................................................................134
5.2.3 Hydrometric Measurements

5.2.4 Calculating Indices of Antecedent Moisture Conditions

5.2.5 Water Sample Collection and Chemical Analysis

5.2.6 Data Analysis

5.2.6.1 Estimating Event-Scale Solute Fluxes

5.2.6.2 2-Component and 3-Component Mixing Model Analysis

5.2.6.3 Statistical Analysis

5.3 Results

5.3.1 General Hydrologic Behaviour of the UP1 Catchment

5.3.2 $THg$, $^{200}Hg$, and DOC Dynamics

5.3.2.1 Concentration-Discharge Relationships for $THg$, $^{200}Hg$, and DOC

5.3.2.2 $THg$, $^{200}Hg$, and DOC Concentrations as a Function of Discharge and Antecedent Moisture Conditions

5.3.2.3 $THg$-DOC and $^{200}Hg$-DOC Relationships

5.3.3 Event-Scale $THg$, $^{200}Hg$, and DOC Export

5.3.4 Isotopic and Hydrochemical Hydrograph Separations

5.3.4.1 Two-Component Separations

5.3.4.2 Three-Component Separations

5.4 Discussion

5.4.1 Are $THg$, $^{200}Hg$, and DOC C-Q dynamics dependent on event characteristics and/or AMCs?

5.4.2 Are $THg$-DOC dynamics dependent on event characteristics and/or AMCs?

5.4.3 Do differences in water sources and/or flow pathways account for differences in C-Q or $Hg$-DOC dynamics?

5.4.4 Implications for watershed $Hg$ modelling

5.5 Conclusion

Chapter 6 Summary and Synthesis

6.1 Summary
6.1.1 Water storage thresholds and runoff generation in a boreal Shield catchment ...170
6.1.2 The vertical distribution of ambient mercury and applied mercury isotope in soil and soil-water in the soil landscape ..............................................................171
6.1.3 The spatial distribution of ambient mercury and applied mercury isotope across the soil landscape ......................................................................................172
6.1.4 The influence of antecedent moisture conditions on the concentration-discharge dynamics of ambient mercury, applied mercury isotope and dissolved organic carbon .................................................................174

6.2 Synthesis ...............................................................................................................................................175
6.2.1 Factors affecting the timing and magnitude of upland export of ambient mercury and applied mercury isotope ........................................................................175
   6.2.1.1 Runoff generation and hydrologic connectivity between landscape units ........................................................................................................176
   6.2.1.2 The development of the potentially-mobile DOC-bound Hg pool .......176
   6.2.1.3 Landscape controls on the spatial distribution of mercury ...............177
   6.2.1.4 The effect of antecedent moisture conditions on the balance between discharge- and concentration-driven fluxes ................................177
6.2.2 Future Research Directions.............................................................................................................178
   6.2.2.1 Long-term catchment inter-comparisons ............................................178
   6.2.2.2 Long-term monitoring of spike $^{200}$Hg in METAALICUS upland soils 179
   6.2.2.3 Further examination of landscape controls on mercury distribution in soil landscapes .......................................................................................179
   6.2.2.4 Mercury speciation, carbon quality, and climate change ..................179

References ...............................................................................................................................................181

Appendix 1. Spatial Statistics Results for Chapter 4 ..................................................................................190
List of Tables

Table 2-1 Soil properties of depression and midslope HRUs used to fit depth function for drainable porosity. *Used as estimates of $n_0$.  
Table 2-2 Total precipitation ($P$), total runoff ($R$), aggregated runoff ratio ($R/P$), mean event quick flow ratio ($QF/P$) (standard deviation in brackets), and number of events for the period May-August, 2001-2009.  
Table 2-3 Summary of areal, soil depth and storage characteristics of delineated HRUs. Disconnected upslope contributing area refers to the portion of the total upslope contributing area located downslope of any depression HRUs that may short-circuit flow due to storage deficits. Numbers in brackets under areal characteristics indicate % of total catchment area and under storage characteristics indicate % of total storage capacity. The total area of the catchment is 77493 m$^2$ (7.75 ha). Note that soil depth characteristics for Bedrock Upland/Ridge HRUs represent measurements in soil pockets.  
Table 2-4 Assessment of exponential and piecewise regression analysis (PRA) models ability to reproduce storage-discharge relationships in the UP1 catchment. $r^2$ is the coefficient of determination. PRA-derived breakpoints are shown as volumes and normalized to storage capacity for all S-Q relationships. The slope below ($\beta_1$) and above ($\beta_2$) the breakpoint is also given. The 97.5% confidence intervals (CI) for the breakpoints and slopes are reported.  
Table 3-1 Solid phase characteristics of Live/L/Of, F/H/Oh/Oh, and Ah/Bm soil layers in the UP1 catchment.  
Table 3-2 Solid phase characteristics with respect to HgS of Live/L/Of, F/H/Oh/Oh, and A/B soil layers in the UP1 catchment.  
Table 3-3 Slopes (b), correlation coefficient (r), significance level (p), and coefficient of determination ($r^2$) for HgS vs. SOC, HgD vs. DOC, HgD vs. $UV_{254}$, and HgD vs. SUVA.  
Table 3-4 Solution phase characteristics with respect to DOC based on shallow soil-water sampled from zero-tension lysimeters in the Live/L/Of and F/H/Oh/Oh layers, deep soil-water sampled from piezometers in the 20-80cm portion of the Ah/Bm layer, and runoff from the catchment outlet.  
Table 3-5 Solution phase characteristics with respect to HgD based on shallow soil-water sampled from zero-tension lysimeters in the Live/L/Of and F/H/Oh/Oh layers, deep soil-water sampled from piezometers in the 20-80cm portion of the Ah/Bm layer and water sampled in runoff at the catchment outlet.  
Table 4-1 Global Moran’s $I$ for Hg variables calculated for the original point data and 10-m resolution gridded data. Bolded values indicate $p<0.01$.  
Table 4-2 Relationships between SOC, ambient HgS, spike$^{200}$HgS, ambient HgS:SOC, spike$^{200}$HgS and LAI, LAI and canopy type, the 2006 cumulative spray release, $A$, and TWI for the litter, organic and mineral soil horizons based on Pearson’s correlation coefficients. $p$ values.
Table 4-3 Summary of multiple linear regression model selection based on higher $r$ value. Predictor variables for SOC, ambient HgS, and ambient HgS:SOC include LAI, canopy type, and TWI. Predictor variables for spike $^{200}$HgS and spike $^{200}$HgS:SOC include LAI, canopy type, 2006 cumulative spray release, and TWI. Significant ($p<0.05$) standardized partial regression coefficients are shown before each variable. Variables are listed in order of importance...........117

Table 5-1 Summary of multiple linear regression analysis applied to the concentrations of $THg$, $^{200}Hg$, and DOC. Independent variables that were input into the analysis were UPI catchment discharge ($Q_{UPI}$, m$^3$/h), antecedent precipitation ($AP_x$, mm), and antecedent mean storage in DEP_TERMINAL ($AS_x$, m$^3$). The subscript $x$ represents the number of antecedent days over which precipitation was summed and storage was averaged. Shaded values represent $p < 0.05$ (considered significant). * Standardized regression coefficients allow for a comparison of the relative contribution of each independent variable in the prediction of the dependent variable……………………………………………………………………….......................….146

Table 5-2 Summary of event characteristics including: event duration, total precipitation ($P_{TOT}$), mean precipitation rate ($P_{AVG}$), peak precipitation rate ($P_{MAX}$), total discharge ($R_{TOT}$), peak discharge rate ($R_{MAX}$), runoff ratio ($R_{TOT}/P_{TOT}$), antecedent precipitation ($AP_x$), mean antecedent water storage in DEP_TERMINAL ($AS_x$, m$^3$), and total event $THg$, $^{200}Hg$, and DOC fluxes. The subscript $x$ represents the antecedent number of days over which $AP_x$ is summed and $AS_x$ is averaged. The highlighted events are those with similar $R_{TOT}$, but different antecedent moisture conditions and solute fluxes…………………………………………...............................................………….148

Table 5-3 Summary of two-component and three-component hydrograph separations for the 25-May-2008 and 11-Oct-2008 storm events. Percent contributions are shown for event water ($Q_e$), pre-event water ($Q_p$), shallow soil-water flowing through the organic soil horizon (collected from zero-tension lysimeters in the upper west portion of the catchment; $Q_{ss}$), and deep soil-water flowing through mineral soil horizons (collected from 80 cm piezometers throughout the catchment; $Q_{ds}$)……………………………………………………………………………………………158
List of Figures

**Figure 1-1** Conceptual diagram of the links between the four research objectives in a hypothetical catchment...................................................................................................................7

**Figure 2-1** (a) Location (●) of the Experimental Lakes Area region in northwestern Ontario, Canada (Map source: The Atlas of Canada; http://atlas.nrcan.gc.ca; © 2001. Her Majesty the Queen in Right of Canada, Natural Resources Canada), (b) the UP1 catchment boundary overlaid on the shaded relief of the Lake 658 watershed, (c) UP1 topography as represented by slope and all hydrometric and gauging sites, (d) locations of depth-to-bedrock measurements and transects for elevation profiles, (e) map of soil depth, (f) frequency distribution of soil thicknesses (n=485), and (g) profiles of surface and bedrock elevation along west and east transects (vertical exaggeration is 5X)...................................................................................................................16

**Figure 2-2** (a) HGED-derived landscape elements overlaid on a shaded relief perspective of the UP1 DEM, landscape elements classified according to (b) mean gradient, (c) upslope contributing area, (d) leaf area index, (e) L/G index, (f) HRU types (note that boundaries between like elements are dissolved), and (g) classification and regression tree model for discriminating between bedrock ridge, bedrock upland, midslope, and depression HRUs.............20

**Figure 2-3** (a) Schematic illustration of mobile unsaturated water storage, mobile dynamic saturated water storage, and mobile residual saturated water storage, and (b) schematic illustration of the depth dependence of drainable porosity...........................................................24

**Figure 2-4** Relationships between (a) event runoff (R) and event precipitation (P), (b) the event runoff ratio (R/P) and P, (c) event quickflow (QF) and P, (d) the event quickflow ratio (QF/P) and P, (e) QF and R, (f) QF/P and R, (g) delayed flow (DF) and R, and (h) DF/P and R for 164 events occurring between 18 April and 29 October 2001-2009. Regression lines are included in (a), (c), (e), and (g) to indicate the general trend of the relationships........................................30

**Figure 2-5** Frequency distributions of R/P (a) and QF/P (b) for 164 events occurring between 18 April and 29 October 2001-2009. Note: R/P >> 1 in (a) are relatively small events with wet antecedent moisture conditions.............................................................31

**Figure 2-6** Monthly variations in (a) R/P and (b) QF/P for events occurring between 18 April and 29 October 2001-2009. Outliers are identified as: (75th percentile value) + 1.5 · (interquartile range)..............................................................................................................32

**Figure 2-7** Boxplot illustrating soil depths measured in bedrock upland/ridge (n=150), midslope (n=184), and depression (n=151) HRUs. Outliers are identified as: (75th percentile value) + 1.5 · (interquartile range)..............................................................................................................34

**Figure 2-8** Hydrologic overview of the 2008 study period. (a) Open precipitation, (b) catchment and west sub-catchment streamflow, and (c) shallow volumetric water content, (d) water table elevation with respect to the ground surface, (e) total storage, and (f) total storage normalized to storage capacity for all depression and midslope HRUs.................................................................37

**Figure 2-9** Storage-discharge relationships for the UP1 catchment and UP1 west-subcatchment. Relationships are shown for catchment discharge and total storage in (a) all depression and
midslope HRUs, (b) the midslope HRU, (c) all depression HRUs, (d) DEPTERMINAL, (e) DEPEAST, and discharge from the west-subcatchment and total storage in (f) DEPWEST. Exponential functions are plotted for each dataset (thin black line), as well as the segmented linear functions from the piecewise regression analysis (PRA). Note that total storage normalized to the storage capacity of the HRU or combination of HRUs in question is shown on the upper x-axis.

**Figure 2-10** Event runoff ratios \((R/P)\) as a function of (a) total event precipitation and (b) antecedent storage in all HRUs, (c) the midslope HRU, (d) all depression HRUs and (e) DEPTERMINAL. (f) \(R/P\) as a function of maximum event storage in DEPTERMINAL. Open circles represent events with \(R/P \leq 0.1\) and relatively small antecedent storage. Closed circles represent events with \(R/P > 0.1\) and relatively large antecedent storage. The upper x-axis in (b)-(f) denote storage normalized to the total storage capacity of the HRU or combination of HRUs. The dashed line in (b)-(f) marks the PRA-derived breakpoint in the S-Q relationship (see Fig. 9). Note that only events with greater than 10 mm of total precipitation are shown.

**Figure 2-11** A comparison of two events with similar inputs, but with varying antecedent storage \((S_{ANTECEDENT})\) in the terminal depression (DEPTERMINAL). (a) Hyetograph and hydrograph for an early autumn event with relatively small \(S_{ANTECEDENT}\) in DEPTERMINAL, (b) storage-discharge (S-Q) dynamics for the storm in (a) overlaid on the modeled S-Q relationship for DEPTERMINAL, (c) hyetograph and hydrograph for a late spring event with relatively large \(S_{ANTECEDENT}\) in DEPTERMINAL, and (d) S-Q dynamics for the storm in (c) overlaid on the modeled S-Q relationship for DEPTERMINAL. The upper x-axis in (b) and (d) denotes storage normalized to the total storage capacity of DEPTERMINAL.

**Figure 2-12** (a) Conceptual model of storage excess routing through the catchment. Runoff response factors, \(R/P\) and \(QF/P\), as a function of storage excess \((S_{EXCESS})\) in DEPTERMINAL (b) and \(S_{EXCESS}\) for all depressions using explicit routing (c). Runoff \((R)\) and quick flow \((QF)\) as a function of \(S_{EXCESS}\) in DEPTERMINAL (d) and \(S_{EXCESS}\) for all depressions using explicit routing (e).

**Figure 3-1** (a) The UP1 catchment boundary overlaid on the shaded relief of the Lake 658 watershed, (b) UP1 topography as represented by slope and all soil and water sample sites, and (c) map of soil depth.

**Figure 3-2** Boxplots showing the median (bar), interquartile range (25\(^{th}\) to 75\(^{th}\) percentiles; box), 10\(^{th}\) to 90\(^{th}\) percentiles (whisker), and outliers (circles) of (a) the concentration of ambient \(Hg_5\) and spike \(^{200}Hg_5\), (b) the areal mass of ambient \(Hg_5\) and spike \(^{200}Hg_5\), (c) soil organic carbon content \((SOC)\), and (d) ambient \(Hg_5:SOC\) and spike \(^{200}Hg_5:SOC\) for the surface organic soil layer (Live/L/Of), lower, humified organic soil layer (F/H/Ohm/Oh), and the mineral soil layer (Ah/Bm). Note the log\(_{10}\) scale on some y axes, and different ranges for ambient \(Hg_5\) and spike \(^{200}Hg_5\).

**Figure 3-3** Relationships between (a) ambient \(Hg_5\) and soil organic carbon \((SOC)\) and (b) spike \(^{200}Hg_5\) and \(SOC\) for the surface organic soil layer (Live/L/Of), lower, humified organic soil layer (F/H/Ohm/Oh), and the mineral soil layer (Ah/Bm). Only significant \((p < 0.05)\) linear fits are shown (lines).

**Figure 3-4** Boxplots showing the median (bar), interquartile range (25\(^{th}\) to 75\(^{th}\) percentiles; box), 10\(^{th}\) to 90\(^{th}\) percentiles (whisker), and outliers (circles) of (a) the concentration of ambient \(Hg_5\) and spike \(^{200}Hg_5\).
HgD and spike $^{200}$HgD, (b) the concentration of dissolved organic carbon (DOC), (c) UV absorbance at 254 nm (UV$_{254}$), and (d) specific UV absorbance (SUVA) for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Note the log$_{10}$ scale on some y axes, and different ranges for ambient HgD and spike $^{200}$HgD. ...........................................................................................................77

Figure 3-5 Boxplots showing the median (bar), interquartile range (25$^{th}$ to 75$^{th}$ percentiles; box), 10$^{th}$ to 90$^{th}$ percentiles (whisker), and outliers (circles) of (a) ambient HgD:DOC and spike $^{200}$HgD:DOC, (b) ambient HgD:UV$_{254}$ and spike $^{200}$HgD:UV$_{254}$, and (c) ambient HgD:SUVA and spike $^{200}$HgD:SUVA for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Note the log$_{10}$ scale on some y axes, and different ranges for ambient HgD and spike $^{200}$HgD. ...........................................................................................................................................82

Figure 3-6 Relationships between (a) ambient HgD and dissolved organic carbon (DOC) and (b) spike $^{200}$HgD and DOC for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Only significant ($p < 0.05$) linear fits are shown (lines).................................85

Figure 3-7 Relationships between (a) ambient HgD and UV absorbance at 254 nm (UV$_{254}$) and (b) spike $^{200}$HgD and UV$_{254}$ for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Only significant ($p < 0.05$) linear fits are shown (lines).................................86

Figure 4-1 Maps of the UP1 catchment showing (a) soil sampling and well locations overlaid on a map of slope, (b) leaf area index, (c) dominant canopy types, and (d) the 2006 cumulative spray release...........................................................................................................................................97

Figure 4-2 Maps showing (a) upslope contributing area, (b) downslope gradient, (c) topographic wetness index, and (d) HRU types in the UP1 catchment. (a)-(c) are at a 10-m cell resolution....................................................................................................................................102

Figure 4-3 Maps of point SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Note that the legends shown for the litter layer apply to all layers........................................................................................................................................107

Figure 4-4 Maps of interpolated SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Note that different ranges are used for each horizon to allow for comparison of spatial patterns.........................................................................................................................108

Figure 4-5 Moran’s I spatial correlograms for SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Correlograms were generated using point data. Note the different y-axis ranges. Circled values are statistically significant ($p<0.05$)..........................................................................................................................110

Figure 4-6 Moran’s I spatial correlograms for SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Correlograms were generated using 10-m cell resolution interpolated data. Note the different y-axis ranges. Circled values are statistically significant ($p<0.05$)..........................................................................................................................111

Figure 4-7 Boxplot comparing the distribution of leaf area index (LAI) in old growth and deciduous dominated areas of the UP1 catchment...........................................................................................................................................112

xvi
Figure 4-8 Boxplots comparing the distribution of SOC, ambient \( Hg_S \) and spike \(^{200}Hg_S \) stocks in the litter, organic and mineral soil horizons under old growth and deciduous canopies. Note the different y-axes scales for ambient \( Hg_S \) and spike \(^{200}Hg_S \) and for the different soil horizons...

Figure 4-9 Relationships between ambient \( Hg_S \) and spike \(^{200}Hg_S \) stocks, and SOC stocks in the litter, organic and mineral soil horizons. Note that both x and y axes vary depending on horizon.

Figure 4-10 Boxplots showing the median (bar), interquartile range (25\(^{th}\) to 75\(^{th}\) percentiles; box), 10\(^{th}\) to 90\(^{th}\) percentiles (whisker), and outliers (circles) of soil organic carbon (SOC; kg m\(^{-2}\)) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.

Figure 4-11 Boxplots showing the median (bar), interquartile range (25\(^{th}\) to 75\(^{th}\) percentiles; box), 10\(^{th}\) to 90\(^{th}\) percentiles (whisker), and outliers (circles) of ambient \( Hg_S \) and spike \(^{200}Hg_S \) (\( \mu g \) m\(^{-2}\)) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.

Figure 4-12 Boxplots showing the median (bar), interquartile range (25\(^{th}\) to 75\(^{th}\) percentiles; box), 10\(^{th}\) to 90\(^{th}\) percentiles (whisker), and outliers (circles) of ambient \( Hg_S \):SOC and spike \(^{200}Hg_S \):SOC (\( \mu g \) gC\(^{-1}\)) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.

Figure 4-13 HRU boxplots for (a) DOC concentrations, (b) ambient \( Hg_D \) and spike \(^{200}Hg_D \) concentrations, and (c) ambient \( Hg_D \):DOC and spike \( Hg_D \):DOC in individual depression and midslope HRUs.

Figure 5-1 Map of the study catchment showing, slope, the UP1 catchment boundary, the UP1_WEST subcatchment boundary, the location of the ephemeral stream at the bottom of the catchment, the location of estimated flow pathways, and the locations of hydrometric sites (well, piezometer nest, and shallow soil moisture), zero-tension lysimeters, and the two gauged weirs.

Figure 5-2 Flow duration curve for discharge from the UP1 catchment outlet during the study period (note that early snowmelt is not included). Points on the line represent the streamwater samples collected during the study period (\( n = 163 \)). Note the log\(_{10}\) scale on the y-axis.

Figure 5-3 Hydrologic summary of the study period (1-31 October 2007 and 24 April 2008 to 27 October 2008) including (a) hourly precipitation, (b) hourly discharge measured at the UP1 outlet, (c) antecedent precipitation (\( AP_x \)), and (d) antecedent mean storage in DEPTERMINAL (\( AS_x \)). \( x \) is the number of antecedent days over which precipitation was summed and storage was averaged. The individual events that were investigated for this study are shaded in (b). * denotes the events used for detailed concentration-discharge analysis. Note the break in the x-axis separating the 2007 and 2008 study periods.

Figure 5-4 Concentration-discharge relationships for (a) \( THg \), (b) \(^{200}Hg \), and (c) DOC for samples obtained at the UP1 catchment outlet between the periods 9-Oct-2007 and 27-Oct-2008. Linear regression lines, correlation coefficients and p-values are shown. \( p < 0.05 \) is considered significant.
Figure 5-5 Relationships between (a) THg concentration and DOC concentration, and (b) $^{200}$Hg concentration and DOC concentration, for samples collected at the UP1 catchment outlet......147

Figure 5-6 Relationships between total event solute export and total event water export for (a) THg, (b) $^{200}$Hg, and (c) DOC..............................................................................................................................149

Figure 5-7 Relationships between (a) total event THg export and total event DOC export, and (b) total event $^{200}$Hg export and total event DOC export..................................................................................................150

Figure 5-8 Hourly precipitation ($P$), discharge ($Q$), pre-event component of discharge ($Qp$), and concentrations of THg, $^{200}$Hg, and DOC for the 25-May-2008 event (a, c, e, g, i) and the 11-October-2008 event (b, d, f, h, j). Both sample concentrations and modeled concentrations are shown. Note the different y-axis for the two events for all variables........................................152

Figure 5-9 Concentration-discharge dynamics for the 25-May-2008 event with relatively wet antecedent moisture conditions (AMCs) and the 12-October-2008 event with relatively dry AMCs, for (a) THg, (b) $^{200}$Hg, and (c) DOC. Arrows indicate the direction of hysteresis if applicable....................................................................................................................................154

Figure 5-10 THg-DOC concentration dynamics for the 25-May-2008 event with relatively wet antecedent moisture conditions (AMCs) and the 12-October-2008 event with relatively dry AMCs, for (a) THg and (b) $^{200}$Hg. Arrows indicate the direction of hysteresis if applicable...155

Figure 5-11 Boxplots showing the differences in THg, $^{200}$Hg, and DOC concentrations between the 25-May-2008 and 11-Oct-2008 storms for streamwater, shallow soil-water, and baseflow collected just prior to the event. All differences are statistically significant ($p < 0.05$) except for baseflow.................................................................156

Figure 5-12 Component mixing diagrams using Ca$^{2+}$ and DOC as tracers for (a) the entire study period, (b) the 25-May-2008 event and (c) the 11-Oct-2008 event. Mean values of the end-members are shown with error bars representing ±1 standard deviation.................................160
List of Appendices

Appendix 1. Spatial Statistics Results for Chapter 4.................................................................190
Chapter 1
Introduction

1.1 Background Information

Anthropogenic emissions from industrial activities have increased mercury ($Hg$) in the environment and wildlife over the past 150 years (Fitzgerald et al. 1991; Morel et al. 1998). Industrial activities that directly use $Hg$ and those who indirectly produce $Hg$, for example through the combustion of $Hg$-containing fossil fuels, are responsible for the majority of present-day $Hg$ emissions (Driscoll et al. 2007). The atmospheric lifetime of elemental $Hg$ ranges from 0.5 to 2 years, which is enough time for global-scale atmospheric transport from point sources to remote areas (Mason et al. 1994; Selin et al. 2008). In remote regions, $Hg$ levels 2 to 5 times preindustrial levels have been reported (Lindberg et al. 2007). In natural waters, inorganic $Hg$ occurs in different forms including elemental mercury ($Hg^0$) and ionic mercury ($Hg^+, Hg^{2+}$). Following deposition, $Hg^{2+}$ may be converted by bacteria in anoxic sediments to a more bioavailable form, methylmercury ($CH_3Hg^+$, $(CH_3)_2Hg$, or more commonly $MeHg$) (Ravichandran 2004). $MeHg$ bioaccumulates in fish and can reach levels at the top of aquatic food webs that are toxic to humans and wildlife that consume fish (Munthe et al. 2007).

Efforts to regulate atmospheric $Hg$ emissions are underway in Canada (Canadian Environmental Protection Act, 1999) and internationally (UNEP, 2009). However, these efforts have been challenged by uncertainties in the magnitude and timing of the response of fish $MeHg$ levels to changes in deposition (Driscoll et al. 2007). While the general consensus amongst $Hg$ researchers is that $MeHg$ concentrations in fish do respond to changes in atmospheric $Hg$ inputs to lakes and watersheds, the environmental processes that control the magnitude and timing of the response are less certain (Harris et al. 2007; Munthe et al. 2007). 150 years of anthropogenic $Hg$ emissions have left a legacy of historically-deposited $Hg$ in soils, even in relatively remote areas Canada. Current research suggests that the transport of newly-deposited mercury from terrestrial to aquatic systems is delayed, whereas older historically-deposited $Hg$ is exported at a relatively constant rate (Harris et al. 2007; Munthe et al. 2007). Hence, the
terrestrial $Hg$ pool has the potential to delay the recovery of boreal lakes after emission reductions because of the slow release of $Hg$ in runoff to receiving waters (Munthe et al. 2007).

Upland environments have been recognized as a dominant source of $Hg$ to receiving waters, such as wetlands and lakes, in many watersheds (Harris et al. 2007; Grigal, 2002). Previous studies have shown that the major input of $Hg^{2+}$ to soils in boreal regions is bound to natural organic matter ($OM$) in litterfall and throughfall under old-growth coniferous canopy (Graydon et al. 2008). Upland soils retain the majority of deposited $Hg$ and this retention is coupled to the strong interaction between $Hg^{2+}$ and natural $OM$ (Grigal, 2003). Natural $OM$ affects the speciation, mobility, and bioavailability of mercury through the formation of very strong ionic bonding between $Hg^{2+}$ and reduced sulfur sites in soil organic matter ($SOM$) and dissolved organic matter ($DOM$) (Ravichandran 2004). A common assumption amongst $Hg$ scientists and modelers is that the lifetime and turnover of $Hg$ are determined by the lifetime and turnover of $SOM$ (Meili, 1991; Munthe et al. 2007; Smith-Downey et al. 2010), since the release of $Hg$ in runoff has been shown to be tightly linked to the mobility of particulate organic matter ($POM$) and/or $DOM$ (Mierle and Ingram, 1991; Grigal, 2002). While $DOM$ can be derived from different sources, for example, inputs of plant litter, root exudates, decomposition of $SOM$, and microbial biomass (Kalbitz et al. 2000), the magnitude and timing of the release of $Hg$ from soils is thought to be controlled by the decomposition of the $SOM$ pool (Munthe et al. 2007). In this way, it is believed that $Hg$ becomes potentially-mobile in the soil when it is bound to $POM$ or $DOM$ (Grigal, 2002). Previous studies have shown that $POM$- and $DOM$-bound $Hg$ are mainly exported from uplands during high flow events, such as snowmelt and summer storms (e.g. Shanley et al. 2008; Babiarz et al. 1998, Schuster et al. 2008).

Based on the current conceptual understanding of $Hg$ cycling in uplands, in order to predict the timing and magnitude of $Hg$ fluxes from a particular watershed it is necessary to understand the factors that influence both the soil-water concentrations of $Hg$, $POM$ and $DOM$, and runoff dynamics. To do so, we must understand how $Hg$ is distributed in the soil landscape, where in the soil profile it is released into the solution phase and is potentially-mobile, what the dominant hydrological processes are that connect different parts of the landscape and generate runoff, and the role of hydroclimatic conditions on the concentration-discharge relationship.
1.2 Knowledge Gaps

To accurately predict the ecological consequences of $Hg$ contamination in a particular watershed, knowledge of the dominant hydrological processes occurring in the watershed and knowledge of the distribution, cycling and export of $Hg$ in runoff are required.

1.2.1 Hydrological Processes

Many previous studies have furthered our understanding of runoff generation processes in boreal Precambrian Shield landscapes (e.g. Spence and Woo, 2002, 2003, 2006; Allan and Roulet, 1994; Branfireun and Roulet, 1998; Frisbee et al. 2007; Buttle et al. 2004). The findings of these studies and others clearly point towards the role of variable water storage capacity, dictated by bedrock topography and variations in soil depth, as a primary control on hydrologic connectivity and runoff generation. Studies that have examined storage-discharge relationships in large catchments (e.g. Spence, 2007; Spence et al. 2010) have demonstrated the need to improve our ability to represent water storage-discharge dynamics quantitatively within predictive modelling frameworks. In small, yet topographically-complex, boreal Shield headwater catchments, no direct examinations of the storage-discharge relationship yet exist. Predictive models of $Hg$ export from boreal Shield uplands will benefit immensely from a quantitative understanding of water storage dynamics and variations in runoff response.

1.2.2 Vertical Distribution and Partitioning of $Hg$

Despite a large body of literature describing the strong relationship between $Hg$ and $OM$ (e.g. Grigal, 2002; Schuster et al. 2008; Shanley et al. 2008, Demers et al. 2007; Dittman et al. 2010), relatively few studies have examined the vertical distribution of $Hg$ and the degree with which it partitions between the solid and dissolved phases in different soil layers in boreal soil landscapes. Knowledge of the overall distribution and degree of partitioning of $Hg$ in different soil horizons in a catchment should give an indication of the location and size of the potentially-mobile $Hg$ pool, especially when compared between sites. A recent Swedish study found that solid-phase (i.e. $SOM$-bound) and solution-phase (i.e. $DOM$-bound) $Hg$ to carbon ratios were similar in the near-surface organic soil horizons at two different sites, which suggested a simple
mobilization mechanism with negligible fractionation (Akerblom et al. 2008). However, the study did not involve a comparison of different soil horizons at a single site. A recent modelling study identified the need to determine whether Hg binds to and partitions from all soil horizons with equal affinity (Smith-Downey et al. 2010). To the best of my knowledge, no previous studies have examined the sources of potentially-mobile mercury in a soil landscape by quantifying the vertical distribution and partitioning of historically- and newly-deposited Hg in different soil horizons. This information, coupled with knowledge of the relative contributions of soil-water from different horizons to runoff that is delivered to the stream will undoubtedly improve our ability to understand and model terrestrial-aquatic Hg fluxes.

1.2.3 Controls on the Spatial Distribution of Hg in the Soil Landscape

There continues to be little published research on the horizontal spatial variability of Hg in different soil horizons and the potential controls on these patterns (Grigal, 2003; Munthe et al. 2007). While several recent studies have examined spatial patterns of MeHg in wetland systems (e.g. Branfireun et al. 1996; Mitchell et al. 2008), much less is known about Hg spatial variability in upland forested catchments. It was suggested by Grigal (2003) that landscape characteristics that lead to differential SOM accumulation, such as variations in topography, drainage, and vegetation, are responsible for spatial variations in Hg accumulation. Several studies have examined coarse spatial patterns of Hg in relation to drainage conditions and topographic position (e.g. Grigal et al. 1994; Gladkova and Malinina, 1999); however, their results were not conclusive. Based on the literature and our current understanding of Hg cycling in upland forested systems, other spatial controls potentially include those related to deposition patterns, to the translocation of DOM-bound Hg in runoff, and to the physical and biogeochemical characteristics of the soil. There is a distinct lack of knowledge on whether or not these potential controls apply to catchment-scale Hg spatial patterns, particularly in boreal Shield regions, which are characterized by complex, heterogeneous landscapes. Knowledge of this kind, when combined with knowledge of variable hydrological source areas and hydrologic connectivity, is critical for understanding how much of the soil landscape actually contributes Hg to receiving waters.
1.2.4 The Influence of Antecedent Moisture Conditions on Event-Scale Hg Fluxes

Previous studies in the northeastern United States (e.g. Bushey et al. 2008; Dittman et al. 2010; Schelker et al. 2010) that have examined Hg and DOC concentration-discharge dynamics during periods of high flow have found evidence of seasonal variations in the concentration-discharge relationship and hysteresis in the concentration-discharge and Hg-DOC relationships. These findings suggest that antecedent moisture conditions, which vary seasonally, may be a controlling factor in the magnitude of Hg fluxes in runoff. Although a lot of research has been conducted on Hg export from uplands in boreal catchments (e.g. Bishop et al. 1995a,b; St. Louis et al. 1996; Branfireun et al. 1996; Allan et al. 2001), no examination of the role of antecedent moisture conditions on historically- and newly-deposited Hg concentration-discharge dynamics and seasonal variability in the Hg-DOC relationship have been carried out. There are also few studies that make use of isotopic and geochemical methods of hydrograph separation in conjunction with measurements of event Hg and DOC fluxes to discern the role of variable flow pathways. Previous studies have predicted that there will be a decrease in DOC inputs to freshwater aquatic ecosystems under warmer and drier hydroclimatic conditions due to a decrease in runoff (Schindler, 2009; Schindler and Smol, 2006). Given the strong relationship between DOC and Hg, it follows that Hg fluxes to freshwater aquatic systems should also decrease with climate warming; however, this assumes that discharge has a primary and predictable control on Hg concentrations. In reality, there is no research to suggest that this is the case in all systems and it is certainly unclear if this hypothesis applies in boreal forested regions.

1.3 Objectives

The research presented in this thesis was carried out to improve our understanding of the hydrological, biogeochemical and landscape controls on Hg transport in boreal Shield uplands by specifically addressing the knowledge gaps described in the previous section. The results of this research will help to inform future predictions of Hg export from boreal uplands and the associated impacts of changes in hydroclimatic conditions. The general research objectives were as follows:
1. To improve our understanding of how the water storage dynamics of topographically-defined landscape units influence the variable rainfall-runoff response of a small boreal Shield headwater catchment.

2. To examine the vertical distribution of $Hg$ in soil and soil-water in different soil horizons across a boreal Shield soil landscape.

3. To examine the controls on the spatial distribution of $Hg$ in soil and soil-water across a boreal Shield soil landscape.

4. To investigate the influence of antecedent moisture conditions on event-scale $Hg$ concentration-discharge dynamics in boreal Shield headwater catchment.

Figure 1-1 shows conceptually how these four objectives relate to one another and to the overall goal of the dissertation. More detailed research objectives, questions, and hypotheses are outlined at the end of the introductions of Chapters 2 through 5.
Figure 1-1 Conceptual diagram of the links between the four research objectives in a hypothetical catchment.
1.4 General Research Approach

This research was conducted as part of the Mercury Experiment To Assess Atmospheric Loading to Canada and the United States (METAALICUS; Hintelmann et al. 2002; Harris et al. 2007). METAALICUS is a whole-ecosystem manipulation experiment designed to address the relationship between atmospheric mercury deposition and mercury accumulation in fish. A study watershed was established at the Experimental Lakes Area (ELA) in northwestern Ontario, which lies within the boreal Shield ecozone. This is the largest of Canada’s ecozones and lies at the intersection of the boreal forest and the Canadian Shield, which is characterized by large areas of exposed Precambrian granite bedrock. In the METAALICUS study catchment, different enriched stable $Hg(II)$ isotope “spikes” were loaded to different watershed compartments (lake, uplands and wetland) from 2001 and 2006 to simulate elevated atmospheric deposition of mercury. The research in this thesis was conducted after 2006 during the METAALICUS ‘recovery phase’, which was, and currently is, focused on determining the magnitude and timing of the response of fish $MeHg$ concentrations to a decrease in loading. The dynamics of $Hg$ mobility and speciation in different ecosystem compartments and the interactions and transfers between compartments could only be investigated when the whole ecosystem was observed at once. Another unique aspect of the METAALICUS study, which has been particularly useful in this research, was the ability to follow newly-deposited stable isotopes of $Hg$ separately from ambient $Hg$ that was already in the catchment.

The research in this thesis was carried out in one of the upland catchments in the METAALICUS watershed. Discharge from the 7.75 ha catchment had been monitored since 2001 by members of the METAALICUS project from the US Geological Survey and hence there was a useful historical dataset of discharge and rainfall measurements. These data are particularly useful for the hydrological investigation described in Chapter 2 of this thesis. In this study, a combination of field-based hydrometric monitoring and GIS-based terrain analysis methods was used to examine water storage dynamics and variations in runoff response. Of particular usefulness for the topographic analysis was a high-resolution digital elevation model that was derived from a Light Detection and Ranging (LiDAR) survey of the catchment in 2006. Chapters 3 and 4 of this thesis focused on the vertical distribution and partitioning of $Hg$ in different soil horizons and landscape controls on the spatial distribution of $Hg$ across the soil landscape, respectively. Both of these chapters made use of samples collected from a spatially-extensive soil survey and water samples collected from the distributed network of hydrometric
sites. The research presented in these chapters involved significant analytical work, the majority of which was conducted by the author, GIS-based mapping, and statistical analyses. Chapter 4, in particular, made extensive use of current methods in the field of spatial statistics to establish the existence and nature of the lateral spatial distribution of $\text{Hg}$ in the catchment. Lastly, Chapter 5 made use of hydrometric, isotopic, and geochemical analyses to examine the contributions of different areas of the catchment and flow pathways to discharge during different storm events. Chapter 5 drew heavily from the knowledge generated in the previous three chapters to interpret the results of the different mixing analyses. It is also important to point out that the stable isotope of $\text{Hg}$ that was applied to the uplands was used extensively in Chapters 3, 4, and 5. It was an invaluable tool used to distinguish differences in the retention and release of historically- and newly-deposited $\text{Hg}$.

1.5 Thesis Structure and Publication Information

1.5.1 Chapter 1

Chapter 1 provides an overall introduction to the thesis as a whole, identifies the knowledge gap that the research addresses, outlines the general objectives of the thesis, describes the overall research approach, and describes the thesis structure.

1.5.2 Chapter 2

Chapter 2 focuses specifically on measuring and modeling the dominant hydrological processes operating in the research catchment. Chapter 2 is currently in press at *Hydrological Processes* (DOI: 10.1002/hyp.8036). The co-authors on the paper are Murray C. Richardson and Brian A. Branfireun. MCR coded and carried out the hydrogeomorphic edge detection landscape partition analysis on the research catchment, coded the graphical hydrograph separation, and contributed to editing. BAB contributed to the development of research questions and editing.
1.5.3 Chapter 3

Chapter 3 focuses on the vertical distribution of mercury in soil and soil-water in different soil horizons. Chapter 3 will be shortened substantially for submission to the journal *Environmental Science & Technology*. Co-authors on this paper will be Andrew Heyes (Chesapeake Biological Laboratory – University of Maryland) and Brian A. Branfireun. The majority of analytical work for this paper was carried out under the supervision of AH at the Chesapeake Biological Lab. AH also contributed to the development of research questions and editing. BAB contributed to the development of research questions and editing.

1.5.4 Chapter 4

Chapter 4 focuses on the spatial distribution of mercury in soil and soil-water and the landscape characteristics that best explained the observed spatial variations. Potential journals to which Chapter 4 could be submitted include *Environmental Science & Technology*, *Journal of Geophysical Research*, *Ecological Applications*, or *Science of the Total Environment*. The co-author on this paper will be Brian A. Branfireun, who contributed to the development of research questions and editing.

1.5.5 Chapter 5

Chapter 5 focuses on mercury concentration-discharge dynamics and the role of antecedent hydrological conditions on event-scale fluxes of mercury from the research catchment. It is anticipated that Chapter 5 will be submitted to the journal *Water Resources Research*. The co-author on this paper will be Brian A. Branfireun, who contributed to the development of research questions and editing.

1.5.6 Chapter 6

Chapter 6 provides an overall summary and synthesis of the thesis. The synthesis section identifies some of the key factors controlling the magnitude and timing of upland export of
ambient $Hg$ and applied $Hg$ isotope. It also addresses future research needs identified during this study.
Chapter 2
Water Storage Dynamics and Runoff Response of a Boreal Shield Headwater Catchment

2.1 Introduction

Headwater catchments in boreal, bedrock-dominated landscapes are highly sensitive to inter- and intra-annual variability in precipitation and temperature regimes, leading to dramatic differences in seasonal and annual runoff to streams, wetlands and lakes (Allan and Roulet, 1994; Buttle et al. 2004). These differences can, in turn, impact lake levels, wetland stability, and water quality, causing dramatic variations in the renewable freshwater supply available for humans and ecosystems alike (Schindler, 2009; Schindler and Lee, 2010). Projections for future precipitation and temperature patterns in the Canadian Boreal Shield ecozone differ spatially, but generally point towards smaller winter snow packs, greater summer rainfalls and higher annual temperatures (Natural Resources Canada, 2009). While widespread impacts are expected (Schindler 2009), the implications of these changes on runoff response and downstream water quantity and quality are still poorly understood, particularly at the watershed scale. Quantifying the mechanistic relationships among precipitation and temperature regimes, hillslope water storage capacity, and catchment runoff response is an important step in reducing the uncertainty surrounding the hydrology of these important catchments in the future.

Previous empirical studies that have furthered our understanding of physiographic controls on runoff generation processes on the Precambrian Shield have been undertaken around Yellowknife, Northwest Territories (Spence and Woo, 2002, 2003, 2006; Mielko and Woo, 2006; Spence et al., 2010), at the Experimental Lakes Area in northwestern Ontario (Allan and Roulet, 1994; Branfireun and Roulet, 1998), northeast of Thunder Bay, Ontario (Frisbee et al., 2007), and near Dorset, Ontario (Peters et al., 1995; Devito et al., 1996; Buttle and Peters, 1997; Buttle and Turcotte, 1999; Buttle et al., 2004). Results from these studies, and others in different geographic regions (e.g. Tromp-van Meerveld and McDonnell, 2006; Uchida et al.,
provide a foundation from which to explore spatially variable water storage dynamics and their relationship to catchment hydrologic response.

The differing abilities of landscape units to generate runoff and the variable nature of hydrologic connectivity between adjacent units in bedrock-dominated watersheds were addressed by Allan and Roulet (1994). They observed the quick generation of runoff from bedrock surfaces, but the relatively large storage capacity and the antecedent moisture status of downslope forested soil deposits controlled the transmission of flow further downslope. Similar spatial variations in storage and transmission ability have been observed in other catchments and attributed to variations in bedrock topography, soil thickness and ground frost (Spence and Woo, 2003; Buttle et al., 2004). Spence and Woo (2003) found that storage deficits in specific landscape units determined the minimum input required for interflow to spill over subsurface bedrock sills. Frisbee et al. (2007) reported similar findings in two Shield catchments where sill-controlled connections between soil-filled depressions and riparian areas were dependent on internal water storage deficits.

The above findings clearly point towards the role of variable water storage capacity, dictated by bedrock topography and variations in soil depth, as a primary control on hydrologic connectivity and runoff response. These findings reflect the concept of partial area storm runoff (Betson, 1964) whereby contributing areas can develop in any location where storage capacity is surpassed. This contrasts the commonly accepted idea that contributing areas begin in downslope saturated areas and expand upslope (Hewlett and Hibbert, 1967; Dunne and Black, 1970). Partial area theory was the first to explain the nonlinear behaviour of many hydrologic relationships. As a means of conceptualizing hydrologic thresholds for flow generation the fill-and-spill flow mechanism has been proposed (Spence and Woo, 2003; Tromp van Meerveld and McDonnell, 2006). Fundamental to the fill-and-spill concept is that storage deficits in relatively discrete landscape units must be satisfied before subsurface or surface flow can continue downslope. The presence of bedrock sills are common features in the Precambrian Shield landscape that, depending on their elevation and orientation, can interrupt flow until the water table rises above internal topographic thresholds and subsurface or surface flow cascades downslope. Each unit will have a unique storage capacity and hydrological behaviour (storing,
contributing and/or transmitting). Implicit in this element threshold concept is that units with low thresholds relative to available water are the first to contribute to adjacent units; however, flow may be depleted to satisfy downslope storage deficits dictated in part by antecedent moisture conditions (AMCs; Spence and Woo, 2006). The $T^3$ template (typology, topology and topography) set forth by Buttle (2006) echoes the important results of the above studies by reinforcing the need for information on the internal hydrologic behaviour of drainage basins. Given the results of these field-based and conceptual studies, physically-based estimates and mapping of the spatial and temporal variability in water storage across the hillslope or catchment appear to be useful approaches for classifying the typology and topology of a catchment.

The hydrological science community has expressed a need for a set of organizing principles that underlie landscape heterogeneity and process complexity and provide fundamental frameworks for scale-adaptive catchment classification (Sivapalan, 2003; McDonnell and Woods, 2004; Buttle, 2006; McDonnell et al., 2007; Tetzlaff et al., 2010; Spence 2010). McDonnell and Woods (2004) noted that underlying concepts of catchment classification must integrate fluxes, storages, and runoff response times, and suggested that the response time of the dominant catchment storage unit could be an appropriate metric. Storage-discharge relationships are a simple example of an underlying principle that is scalable and tied to process descriptions at smaller scales (Sivapalan, 2003; McDonnell and Woods, 2004; Uchida et al., 2006; Spence, 2007; McDonnell et al., 2007; Kirchner, 2009; Spence et al., 2010; Spence 2010). Several studies in relatively large catchments have directly examined the storage-discharge relationship. Spence (2007) reported hysteretic patterns in the storage-discharge relationship for several reaches of a 55 ha Prairie catchment and inferred that this represented the transition between storing and contributing hydrologic functionality (Spence, 2007). Similarly, Spence et al. (2010) found that the spatial distribution of storage in a 165 km$^2$ subarctic Shield watershed controlled the efficiency of the catchment to convert inputs to runoff. The important findings of these studies demonstrate the need to improve our ability to represent storage-discharge dynamics quantitatively within predictive modelling and management frameworks. This is especially true in systems where topographic complexity is likely to result in nonlinear hydrologic response, for example, in small Boreal Shield headwater catchments where no direct examinations of the storage-discharge relationship yet exist.
The goal of this study was to improve our understanding of how the water storage dynamics of topographically-defined landscape units influence the variable rainfall-runoff response of a small Boreal Shield headwater catchment. Specifically, the objectives of this study were to:

1. Assess the variability in runoff response within and between years with varying precipitation input magnitude and timing;
2. Apply a recently developed GIS-based method for landscape partitioning to define hydrological response units;
3. Calculate saturated and unsaturated water storage for defined hydrological response units;
4. Develop a model for the relationship between catchment runoff and water storage that could be used to generate insights into the controls on runoff generation and water quality under both current and future conditions.

2.2 Study Area

This study was conducted in the 7.75-ha UP1 catchment of the Lake 658 experimental watershed, located in the Experimental Lakes Area (ELA) in north-western Ontario (49° 40’ N, 93° 43’ W; Fig. 2.1a and 2.1b). Lake 658 is 8-ha in surface area and is surrounded by a 43-ha watershed. The climate of the study area is boreal cold temperate. Average monthly air temperatures range from -16.5 °C for January to +20.1 °C for July, mean annual air temperature is 2.8 °C and mean annual precipitation is 708 mm, 75% of which is rain (based on 1970-2009 climate normals; pers. comm. K. Beaty, Central & Arctic Region, Fisheries and Oceans Canada, Winnipeg, MB).
Figure 2-1 (a) Location (●) of the Experimental Lakes Area region in northwestern Ontario, Canada (Map source: The Atlas of Canada; http://atlas.nrcan.gc.ca; © 2001. Her Majesty the Queen in Right of Canada, Natural Resources Canada), (b) the UP1 catchment boundary overlaid on the shaded relief of the Lake 658 watershed, (c) UP1 topography as represented by slope and all hydrometric and gauging sites, (d) locations of depth-to-bedrock measurements and transects for elevation profiles, (e) map of soil depth, (f) frequency distribution of soil thicknesses (n=485), and (g) profiles of surface and bedrock elevation along west and east transects (vertical exaggeration is 5X).
The UP1 catchment is south-facing with a mean slope of 12° and a difference in elevation from the outflow datum to the watershed divide of 63 m. The local topography is highly variable and includes a sequence of soil-filled bedrock depressions separated by near-vertical bedrock ridges in the western half of the catchment, while the eastern half exhibits a more continuously sloping morphology (Fig. 2.1c). The catchment lacks a well-defined drainage network; however, it is drained by a short, ephemeral stream into Lake 658, with high flows during spring snowmelt and early summer and fall rain storms. UP1 is underlain by granitic bedrock and over approximately 40% of the catchment the bedrock is either exposed (16%; mainly in the upper portion and along cliff edges) or covered with very shallow soil patches with a mean soil depth of 23 cm \((n=124)\). In the remaining areas, soils range in depth from 0 to 242 cm with a mean depth of 54 cm \((n=344);\) Fig. 2.1e). The soils are acidic brunisols, are texturally classified as silt loams, and are likely of a glaciolacustrine origin (Allan and Roulet, 1994; Brunskill and Schindler, 1971). The sandy mineral horizon is overlain by an organic layer with a mean thickness of 10.1 cm \((n=117)\).

A 6-ha section in the northwest portion of the Lake 658 watershed, part of which falls within the UP1 catchment, was logged in 1978 (pers. comm. K. Beaty, Central & Arctic Region, Fisheries and Oceans Canada, Winnipeg, MB) and now supports a deciduous forest of red maple \((Acer rubrum)\) and paper birch \((Betula papyrifera)\). The portion (~ 85%) of UP1 that was not logged is dominated by mature black spruce \((Picea mariana)\) and balsam fir \((Abies balsamea)\). Lichens (e.g. \(Cladina stellaris\) and \(Peltigera aphthosa\)), mosses (e.g. \(Polytrichum piliferum\) and \(Pleurozium schreberi\)), and juniper \((Juniperus virginiana)\) grow on the bedrock outcrops. In depressional areas the organic horizon is relatively thick and the surface vegetation is dominated by \(Sphagnum\) spp. with some shrubs such as Labrador tea \((Ledum groenlandicum)\).

### 2.3 Methods

#### 2.3.1 Study Period

Discharge from the UP1 catchment has been monitored since 2001 by the U.S. Geological Survey (USGS) as part of METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S.) project, which is examining mercury fluxes in upland runoff.
and the relative role of uplands as sources of mercury to lakes and fish (Harris et al., 2007). Detailed hydrologic measurements within the UP1 catchment were initiated in July 2007 (undertaken specifically for this study). Discharge from the west sub-catchment of UP1, groundwater levels, and soil moisture data presented in this paper were collected between 26 July (Day of Year (DOY) 207) and 31 October (DOY 304) 2007, and 19 May (DOY 140) and 29 October (DOY 303) 2008, and 10 May (DOY 130) and 28 October (DOY 301) 2009.

2.3.2 Landscape Partitioning

The physiographic variability of boreal headwater catchments plays an important role in governing runoff generation and terrestrial fluxes of contaminants and nutrients to surface waters (Branfireun et al., 1996; Dillon and Molot, 1997; Devito et al. 1997). High-resolution digital topographic data and hydrologically-meaningful methods for partitioning the landscape have advanced our understanding of runoff processes in these systems (Lindsay and Creed, 2004; Buttle, 2006; Tetzlaff et al., 2008; Richardson et al., 2009). In order to provide a framework for our hydrological analysis, we carried out a landscape partitioning and classification exercise on the complex topography of the UP1 catchment. The ground returns from a LiDAR survey flown in 2006 were used to generate a 1m resolution digital elevation model (DEM) of the Lake 658 watershed using inverse distance weighted (IDW) interpolation. IDW interpolation was chosen because it uses a variable search window and the algorithm can be forced to use a certain number of neighbouring points. This feature eliminates problems with NoData values in areas of lower ground return density, which could be problematic with a fixed search window. Richardson et al. (2009) demonstrated that hydrogeomorphic edge detection (HGED), based on the downslope drainage index (Hjerdt et al., 2004), applied to high resolution DEMs is a successful tool for delineating landscape units that may serve as basic hydrologic response units (HRUs) (Pomeroy et al., 2007). HGED was applied to the LiDAR DEM to delineate functionally homogenous landscape elements (Fig. 2.2a). Four physiographic indices – mean gradient (Fig. 2.2b), upslope contributing area (Fig. 2.2c), leaf area index (derived from the LiDAR survey; Fig. 2.2d), and the flowpath length over gradient \( L/G \) index of mean transit time (McGuire et al., 2005; Fig. 2.2e) - were computed for all HGED polygons at the UP1 catchment. A classification and regression tree analysis (CART) was then used to determine
thresholding parameters for the classification of bedrock uplands and ridges, midslopes, and saturation-prone depressions based on the four physiographic indices (Fig. 2.2g). Adjacent landscape elements with the same HRU classification were merged (Fig. 2.2f). The HGED approach to delineating landscape elements and the subsequent classification into HRU types using geomorphic and physiographic parameters is consistent with the idea that hydrological gradients typically correspond to geomorphic gradients (Richardson et al., 2009). It also presents a step beyond the status quo of using pixel-based topographic indices (e.g. the Topographic Wetness Index (Beven and Kirkby, 1979)) to evaluate hydrologic patterns and includes the delineation of more than just wetland and depression areas alone (Richardson et al., 2009).

2.3.3 Depth-To-Bedrock Mapping

In order to improve our estimates of water storage we required a detailed map of soil thickness for the UP1 catchment. A spatially extensive depth-to-bedrock (DBR) survey (n=485) was carried out over approximately 3 days using a 2.5 m-long steel hammer probe to determine spatial patterns in soil thickness (Fig. 2.1d). At locations where the probe was hammered all the way to the ground the soil thickness was recorded as 2.5 m, despite the possibility that the soil depth could have been larger. The frequency distribution of DBR measured in the catchment demonstrates the variability in soil thickness in UP1 (Fig. 2.1f). The point measurements of DBR were then used to create a spatially-interpolated map of DBR for the entire catchment using inverse-distance weighting (ArcMap, ESRI; Fig. 2.1e). Soft breaklines were included along the bedrock ridges so that values on either side of these extreme topographical transitions were not considered as neighbours and interpolation did not occur between them. Two cross-sections of the catchment (marked on Fig. 2.1d) were generated using surface and bedrock elevations relative to an arbitrary datum to better visualize the cascade of depression HRUs in the western half of the catchment and the more continuous soil thickness in the eastern half (Fig. 2.1g).
Figure 2-2 (a) HGED-derived landscape elements overlaid on a shaded relief perspective of the UP1 DEM, landscape elements classified according to (b) mean gradient, (c) upslope contributing area, (d) leaf area index, (e) L/G index, (f) HRU types (note that boundaries between like elements are dissolved), and (g) classification and regression tree model for discriminating between bedrock ridge, bedrock upland, midslope, and depression HRUs.
2.3.4 Hydrometric Measurements

A distributed network of hydrometric instrumentation was designed to represent the range of HRU types found in the UP1 catchment (Fig. 2.1c). In June 2007, we instrumented 15 recording and 7 manual sites to represent each of the classified HRU types: depressions, midslopes, and bedrock uplands/ridges. In total, 22 groundwater wells were installed to refusal in these units and surveyed relative to the datum at the USGS flume. The wells were 1.5 m long and were installed to depths ranging between 0.5 and 1.2 m. At the recording sites, 15-minute average water table levels were continuously recorded for the duration of the study period using 1.5 m capacitance water level loggers (Odyssey®, Dataflow Systems, NZ). At the manual sites, the water table was measured manually on a weekly basis during spring, early summer and autumn. The wells were constructed of 2.5 cm i.d., slotted PVC pipe and were screened (250 μm NITEX®) over their entire length. At each site, the groundwater level was calculated relative to the mean surface elevation within a 5-metre radius buffer around each well to account for variations in microtopography. We supplemented the 15 recording sites with soil moisture sensors (Odyssey, Dataflow Systems, NZ) installed ~0.2 m below the surface within 2 m of the wells. The Odyssey Soil Moisture Probe uses the measurement of the dielectric constant of the moist soil to determine the volumetric water content of the soil and provides a continuous record (15-min interval) of soil moisture content in the shallow subsurface. A two-point calibration of the sensors was implemented using a factory default calibration for dry soil and multiple gravimetric calibrations for field soils. The sensors were installed by delicately digging a hole to just below the beginning of the mineral horizon and inserting the sensor into the side of the hole across the organic-mineral horizon interface at a 45° angle to prevent water from running down the side of the sensor. The soil was then replaced into the hole in the same order in which it was excavated and lightly tamped to maintain the bulk density of the original soil profile.

Discharge from UP1 to Lake 658 ($Q_{UP1}$) (Fig. 2.1c) has been monitored from mid-April to late-October since 2001 by the USGS using a trapezoidal flume equipped with a bubble water level recorder. The stage-discharge relationship for the $Q_{UP1}$ flume was previously established by the USGS (Harris et al. 2007). Open precipitation has also been monitored for the same time period by the USGS using a tipping bucket rain gauge located near the $Q_{UP1}$ flume. Since July 2007, discharge from the upper west subcatchment of UP1 ($Q_{UP1-West}$) (Fig. 2.1c) has been monitored...
during the same seasons using a 60° V-notch weir-box equipped with a CS615 pressure transducer (Campbell Scientific Inc.®, Canada) to measure stage height behind the weir. Short diversion walls were built to further constrain the already existing convergence of surface flow over an exposed bedrock sill. The stage-discharge relationship for the Q\textsubscript{UPl-WEST} weir-box was developed through manual bucket gauging and stage records throughout the 2007 field season and encompassed the full range of discharge measured at this site over the study period, such that the rating curve did not need to be extrapolated. In addition to our hydrometric measurements, we estimated daily potential evaporation with a modified Penman-Monteith equation using measurements of net radiation, air temperature, horizontal wind speed and relative humidity at a meteorological station located in the UP1 catchment. CR10X and CR23X dataloggers (Campbell Scientific, Canada) were used to collect and store data at the gauging and meteorological sites.

15-minute average values were output for all hydrometric and meteorological instrumentation and hourly and daily means were calculated for further analysis. Linear interpolation was used to fill missing data for time periods less than 3 hours (< 5 % of all data). Missing data over longer periods was modeled based on relationships between adjacent sites.

2.3.5 Graphical Hydrograph Separation

The 2001-2009 streamflow hydrographs were classified into event and non-event periods automatically using the USGS HYSEP minimum flow routine (Sloto and Crouse, 1996) executed in R software for statistical computing. The script defined events as the period from the initial rise in discharge from a local minimum in the hydrograph to the next local minimum. The quick flow and delayed flow components of the hydrograph were separated by the line connecting the local minima. The event quickflow volume (\(QF\)), delayed flow volume (\(DF\)), and runoff volume (\(R = QF + DF\)), all in mm, were calculated by summing hourly values over the identified event period. The gross event precipitation volume (\(P\)) was calculated as the sum of hourly precipitation values over the event period, as well as any precipitation that fell within 24 hours prior to the event. Only events with greater than 0.5 mm of runoff were retained for further analysis. The fraction of \(P\) yielded as \(R \ (R/P)\) and \(QF \ (QF/P)\), as well as the fraction of \(R\) that is \(QF \ (QF/R)\) and \(DF \ (DF/R)\) were calculated to examine the hydrologic behavior of the
catchment (Hewlett and Hibbert, 1967). $Q_F$ was also calculated for a subset of storms ($n = 15$) using the constant slope method of Hewlett and Hibbert (1967) and was found to be in close agreement ($\pm 5\%$) with the local minimum method described above.

2.3.6 Water Storage Calculation

Previous studies in Boreal Shield landscapes have recognized that water is not stored evenly throughout the soil landscape and that spatial variability in bedrock topography and soil depth are first-order controls on this heterogeneity (e.g. Buttle et al. 2004). The spatial variability in water stores is integral to the discontinuous hydrologic connectivity and nonlinear runoff response often observed in topographically complex catchments (Spence 2010). Water storage dynamics are often represented by measurements of water table elevation and often do not include unsaturated storage or account for the retention of capillary and hydroscopic water that is effectively immobile. Our use of HGED and CART methods to delineate hydrologic response units in UP1 allows us to constrain our calculations of water storage based on the actual geomorphology and physiography of the catchment. In this study we calculated water storage in midslope and depression HRUs using the landscape partitioning results, depth-to-bedrock map, and measurements of volumetric water content and groundwater level described above. Storage was not calculated for bedrock upland/ridge HRUs in part due to the difficulty of installing hydrometric instrumentation in these areas and the assumption that storage in small bedrock depressions and soil-filled pockets is relatively transient and only represents a small portion of the total volume of water stored in the catchment at any given time.

The total amount of water in storage in an HRU, $S_{TOTAL} [L^3]$, is given as:

$$S_{TOTAL} = \left[ (S_U + S_{S_{dynamic}}) \cdot A_{HRU} \right] + \left[ S_{S_{residual}} \cdot A_{residual} \right]$$  \hspace{1cm} (2.1)

where $S_U [L]$ is the depth of water in storage in the unsaturated zone, $S_{S_{dynamic}} [L]$ is the depth of water in storage in the saturated zone within the dynamic range of water table fluctuations, $A_{HRU}$
$[L^2]$ is the surface area of the HRU derived from the HGED delineation, $S_{\text{residual}} [L]$ is the depth of water in storage in the residual saturated zone, and $\bar{A}_{\text{residual}} [L^2]$ is the mean area of the HRU in the residual volume (Fig. 2.3a). The calculation of each of these terms is described below.

Figure 2-3 (a) Schematic illustration of mobile unsaturated water storage, mobile dynamic saturated water storage, and mobile residual saturated water storage, and (b) schematic illustration of the depth dependence of drainable porosity.

As we were concerned with the relationship between water storage and discharge we focused conceptually on identifying the mobile water content that is available for drainage and flow. Therefore we make use of a depth function for drainable porosity to calculate mobile storage in the saturated zone and only consider water storage in the unsaturated zone that is above the water content at field capacity (Fig. 2.3a,b). Drainable porosity is defined as the difference between the saturated water content and the water content at field capacity. Field observations have shown that drainable porosity usually declines with depth due to changes in the soil structure (Weiler and McDonnell, 2006). Hence, $S_{\text{dynamic}}$ is given as:

$$S_{s_{\text{dynamic}}} = \int_{z_{\text{WT}}}^{z_{\text{WTmin}}} n_d(z) dz = n_0 \cdot m \left[ \exp \left( \frac{-z_{\text{WT}}}{m} \right) - \exp \left( \frac{-z_{\text{WTmin}}}{m} \right) \right] \quad (2.2)$$
where $n_d(z)$ is the depth function for drainable porosity of the form $n_d(z) = n_0 \exp\left(-\frac{z}{m}\right)$ (Weiler and McDonnell, 2006) whose integral is evaluated between the minimum water table depth recorded during the study period in the HRU, $z_{WT_{\text{min}}}$ [L], and the current water table depth, $z_{WT}$ [L]. In (2), $n_0$ is the drainable porosity at the soil surface and $m$ is a depth scale. Table 1 summarizes the relevant soil properties that were used to estimate $n_0$ and determine $m$ for depression and midslope HRUs. Values for total porosity ($n$) were estimated based on profile measurements of volumetric water content ($VWC$) under saturated conditions for the litter and organic soil horizons. $n$ for mineral soil horizons was estimated based on the relation between $n$, bulk density ($\rho_b$), and particle density ($\rho_p$, commonly valued at 2650 kg m$^{-3}$), $n = 1 - \frac{\rho_b}{\rho_p}$.

Bulk density values are arithmetic means based on an extensive survey ($n = 190$) of soils in the catchment. Drainable porosity was calculated by subtracting $VWC$ at field capacity from the total porosity. Field capacity was estimated as the $VWC$ at which the rate of decline during drainage conditions became insignificant. $S_u$, is given as:

$$S_u = (\theta_U - \theta_{fc}) \cdot z_{WT}$$  

(2.3)

where $\theta_U$ is the near-surface volumetric water content measured every 15 minutes and $\theta_{fc}$ is the volumetric water content at field capacity. $S_{\text{residual}}$ was calculated for each HRU by estimating the volume of soil below $z_{WT_{\text{min}}}$, $V_{\text{residual}}$ [L$^3$], and multiplying this value by the mean drainable porosity for that portion of the profile. The Cut/Fill tool in ArcMap 9.3 (ESRI), which calculates the areas and volumes of change between two surfaces, was used to estimate $V_{\text{residual}}$.

The Cut/Fill tool was also used to evaluate the change in $A_{HRU}$ with depth within the dynamic range of water table elevation to determine if a constant value was acceptable. It was determined that the areas of all depression HRUs can be considered constant to a depth consistent with the deepest water table position recorded; however, a logarithmic depth function for the midslope area was required to accurately reflect the subsurface morphology of this unit.
In order to normalize our storage estimates we also estimated the total storage capacity of an HRU by summing \( S_{\text{residual}} \) and \( S_{\text{dynamic}} (z_{WT} = 0) \).

### Table 2-1 Soil properties of depression and midslope HRUs used to fit depth function for drainable porosity. *Used as estimates of \( n_0 \).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Bulk Density, ( \rho_b ) (g cm(^{-3}))</th>
<th>Total Porosity, ( n )</th>
<th>Drainable Porosity, ( n_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Depression</td>
<td>Midslope</td>
<td>Depression</td>
</tr>
<tr>
<td>LFH</td>
<td>0.14</td>
<td>0.18</td>
<td>0.89</td>
</tr>
<tr>
<td>Organic</td>
<td>0.17</td>
<td>0.17</td>
<td>0.75</td>
</tr>
<tr>
<td>Mineral</td>
<td>1.25</td>
<td>1.45</td>
<td>0.49</td>
</tr>
</tbody>
</table>

We calculated several metrics at the event-scale in order to characterize the relationships between storage estimates, discharge, and runoff response. The start and end of an event were defined using the automated graphical hydrograph separation routine. A volumetric antecedent storage (\( S_{\text{ANTECEDENT}} \)) metric, a volumetric maximum storage (\( S_{\text{MAXIMUM}} \)) metric, and a storage excess (\( S_{\text{EXCESS}} \)) metric were calculated for all HRUs. \( S_{\text{ANTECEDENT}} \) was taken as the hourly storage value in a specific HRU or combination of HRUs three hours prior to the start of an event and \( S_{\text{MAXIMUM}} \) is the largest hourly storage value estimated for the event. \( S_{\text{EXCESS}} \) is described in more detail in section 2.4.4.3, but in general, is a lumped value that takes into consideration \( S_{\text{ANTECEDENT}} \), total event precipitation, the fill-and-spill behaviour of depressional landscape units, and hydrological connections between these units.

### 2.4 Results and Discussion

#### 2.4.1 Variability in Catchment Response Factors

Variability in runoff response for the UP1 catchment was calculated using several common catchment response factors. \( QF/P \) indicates how the catchment controls the precipitation it
receives on an event scale, while $R/P$ does the same but also reflects the antecedent hydrologic status of the catchment by incorporating $DF$. $QF/R$ and $DF/R$ indicate how the catchment controls its total water yield at the event scale, through its partitioning of hydrologic inputs into storage and runoff (Hewlett and Hibbert, 1967).

Aggregate precipitation and streamflow records for the summer months May through August (period with continuous measurements in all years) were used to examine inter-annual (2001-2009) differences in the runoff response of the UP1 catchment (Table 2.2). Total precipitation inputs from May to August ranged from 226 mm in 2009 to twice this amount in 2001. The fraction of total precipitation yielded as runoff for the same period ranged from 0.05 in 2003 to 0.89 in 2007. The graphical hydrograph separation routine, applied to streamflow and precipitation records between 18 April and 29 October 2001-2009, resulted in the identification of 164 events. Inputs during snowmelt and rain-on-snow events were not considered. The mean $QF/P$ for all events identified by the separation analysis between May and August ranged from 0.11 in 2003 to 0.28 in 2007. Both $R/P$ and $QF/P$ increased with $P$, however, linear regressions were not statistically significant ($R/P$: $r^2 = 0.23$, $p < 0.19$; $QF/P$: $r^2 = 0.39$, $p < 0.07$; plots not shown). The increase in $R/P$ and $QF/P$ with increasing $P$ has implications for how much runoff we should expect if summer precipitation increases in the future as predicted for this region. The years with the largest response factors did not necessarily have the largest number of events (Table 2.2), from which we infer that an increase in more extreme events, but not the number of events, may have the same effect on catchment yield as a widespread increase in precipitation.
Table 2-2 Total precipitation ($P$), total runoff ($R$), aggregated runoff ratio ($R/P$), mean event quick flow ratio ($QF/P$) (standard deviation in brackets), and number of events for the period May-August, 2001-2009.

<table>
<thead>
<tr>
<th>Year</th>
<th>$P$ (mm)</th>
<th>$R$ (mm)</th>
<th>$R/P$</th>
<th>Mean Event $QF/P$</th>
<th>No. of Events</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>452.6</td>
<td>216.6</td>
<td>0.48</td>
<td>0.19 (0.13)</td>
<td>23</td>
</tr>
<tr>
<td>2002</td>
<td>419.8</td>
<td>212.2</td>
<td>0.51</td>
<td>0.24 (0.23)</td>
<td>16</td>
</tr>
<tr>
<td>2003</td>
<td>284.4</td>
<td>12.9</td>
<td>0.05</td>
<td>0.11 (0.04)</td>
<td>7</td>
</tr>
<tr>
<td>2004</td>
<td>376.6</td>
<td>193.0</td>
<td>0.51</td>
<td>0.20 (0.20)</td>
<td>17</td>
</tr>
<tr>
<td>2005</td>
<td>360.7</td>
<td>158.3</td>
<td>0.44</td>
<td>0.24 (0.19)</td>
<td>12</td>
</tr>
<tr>
<td>2006</td>
<td>235.9</td>
<td>18.7</td>
<td>0.08</td>
<td>0.12 (0.07)</td>
<td>5</td>
</tr>
<tr>
<td>2007</td>
<td>403.5</td>
<td>358.8</td>
<td>0.89</td>
<td>0.28 (0.24)</td>
<td>15</td>
</tr>
<tr>
<td>2008</td>
<td>352.7</td>
<td>215.8</td>
<td>0.61</td>
<td>0.21 (0.16)</td>
<td>20</td>
</tr>
<tr>
<td>2009</td>
<td>226.2</td>
<td>140.0</td>
<td>0.62</td>
<td>0.19 (0.14)</td>
<td>13</td>
</tr>
</tbody>
</table>

When all 164 events identified by the separation analysis were pooled we found that $R$ increased approximately linearly with $P$ ($r^2 = 0.62$); however, scatter in the relationship was apparent when $P$ exceeded 20 mm (Fig. 2.4a). $R/P$ was extremely variable when $P$ was less than 10 mm, due in part to the sensitivity of $R/P$ to changes in $P$ when $R$ was small, and also due to higher sensitivity to antecedent moisture conditions in the soil and differences in water storage in the canopy before the event (Fig. 2.4b). $QF$ increased approximately linearly with $P$ ($r^2 = 0.66$; Fig. 2.4c), and residuals increased with increasing $P$. $QF/P$ generally increased with increasing $P$; however, there was a large amount of scatter throughout the relationship (Fig. 2.4d). We found a strong ($r^2 = 0.96$) linear relationship between $QF$ and $R$ (Fig. 2.4e), and relatively large variability in $QF/R$ when $R$ was less than 10 mm (Fig. 2.4f). The relationship between $DF$ and $R$ was best explained with a logarithmic function ($r^2 = 0.68$; Fig. 2.4g) and the relationship between $DF/R$ and $R$ was the inverse of Figure 4f (Fig. 2.4h). The delayed flow component of the streamflow hydrograph is usually presumed to be flow from groundwater aquifers (Hewlett and Hibbert, 1967). As the UP1 catchment is underlain by bedrock (unfractured) and has a relatively thin, discontinuous soil cover, the delayed flow component that was separated in our
analysis was unlikely derived from deep groundwater flow. Future studies are required to test whether or not it delayed flow is attributable to slow drainage through mineral horizon flow pathways from the terminal depression and/or from the midslope area on the eastern side of the catchment closest to the outlet. The frequency distributions of the catchment response factors indicated that the majority of events had $R/P$ values less than 0.5 (Fig. 2.5a) and $QF/P$ less than 0.2 (Fig. 2.5b). If it is assumed that $QF/P$ is representative of the effective contributing area of the catchment, we may infer that for the majority of storms less than 20% of the total catchment area contributed to streamflow. Despite the obvious issues with this assumption such as the presence of significant subsurface contributions to $QF$ (Hewlett and Hibbert, 1967), it does give us an indication of the variability in and limits to hydrologic connectivity within the catchment.
Figure 2-4 Relationships between (a) event runoff ($R$) and event precipitation ($P$), (b) the event runoff ratio ($R/P$) and $P$, (c) event quickflow ($QF$) and $P$, (d) the event quickflow ratio ($QF/P$) and $P$, (e) $QF$ and $R$, (f) $QF/R$ and $R$, (g) delayed flow ($DF$) and $R$, and (h) $DF/R$ and $R$ for 164 events occurring between 18 April and 29 October 2001-2009. Regression lines are included in (a), (c), (e), and (g) to indicate the general trend of the relationships.
Figure 2-5 Frequency distributions of $R/P$ (a) and $QF/P$ (b) for 164 events occurring between 18 April and 29 October 2001-2009. Note: $R/P >> 1$ in (a) are relatively small events with wet antecedent moisture conditions.

Monthly median $R/P$ values exhibited seasonal patterns with larger values in spring and early summer (Apr, May, Jun), smaller values in mid to late summer (Jul, Aug), and larger values again in early autumn (Sep, Oct; Fig. 2.6a). Monthly median $QF/P$ values exhibited weaker seasonal patterns; however, the same seasonality as $R/P$ was evident from the 75-th percentile values in Figure 2.6b. This intra-annual variability is similar to that reported by Buttle et al. (2004) for a Boreal Shield site in central Ontario and likewise reflects the relatively large evapotranspiration demands in mid-summer that resulted in precipitation inputs being allotted to satisfy storage deficits. In light of the potential changes in precipitation and temperature regimes predicted for this region, the intra- and inter-annual differences in runoff response described above and their dependence on seasonal and annual hydroclimatic conditions reinforce the need to quantify first-order controls on the variability in hydrologic response for predictive evaluations of future hydrologic functioning.
Figure 2-6 Monthly variations in (a) R/P and (b) QF/P for events occurring between 18 April and 29 October 2001-2009. Outliers are identified as: (75th percentile value) + 1.5 · (interquartile range).

2.4.2 Hydrologic Response Units (HRUs)

In total, 42 landscape units were delineated and classified using the HGED routine and CART model classification (Fig. 2.2a). After dissolving adjacent units with the same classification these units were reduced to 16 HRUs: four depressional units, one midslope unit, six bedrock upland units, and five bedrock ridge units (Fig. 2.2f). Table 2.3 summarizes the areal, soil depth and storage capacity characteristics of the delineated HRUs. Note that bedrock upland and ridge HRUs are presented together for the remainder of the paper since we assume their behaviour is similar hydrologically.

The delineation and classification of HRUs were used to conduct some initial quantitative estimates of the potential threshold-dominated changes in catchment contributing area in relation to storage-discharge dynamics of discrete landscape units. Depressional HRUs make up
22% of the total catchment area ($A_{UP1}$), the midslope HRU makes up 37% and the remaining 41% is classified as bedrock uplands and ridges. Of the four depression HRUs that cover less than one quarter of the catchment (see Fig. 2.2f for depression HRU labels), DEPEAST is the largest covering almost 10% of the area of the catchment, followed by DEPTERMINAL at almost 7% of the total area. DEPWEST and DEPUPWEST are both close to 3% of the area of the catchment. The total upslope contributing areas for the depression HRUs range from 93% of the total catchment area for DEPTERMINAL to 18% for DEPUPWEST. We also delineated a disconnected upslope contributing area, defined as the upslope contributing area that is located downslope of other depression HRUs. This area is meaningful when storage deficits in upstream depressions prevent flow downslope and hence only applies to DEPTERMINAL and DEPWEST, which both have depression HRUs located directly upstream. Hence, if flow from DEPWEST to DEPTERMINAL ceases, the upslope contributing area for DEPTERMINAL is effectively reduced from 93% to just under 10% of $A_{UP1}$. Likewise, the upslope contributing area for DEPWEST is reduced from 43% to 21% of $A_{UP1}$ when flow from DEPUPWEST stops. Together, the disconnected upslope contributing area for DEPTERMINAL, estimated at 9.6 %, and the area of DEPTERMINAL itself, estimated at 6.9 % (Table 2.3), could account for the contributing area of the majority of events as described in the previous section.

Based on our extensive depth-to-bedrock survey ($n=485$) soil depths ranged from 0 m on exposed bedrock to 2.42 m in DEPTERMINAL. Mean soil depth ranged from 0.23 m for soil pockets in bedrock/upland HRUs to 0.29 m for the midslope HRU to approximately 1 m for DEPTERMINAL and DEPEAST. As an independent assessment of the ability of the HRUs to better capture relative differences in storage capacity throughout the landscape, the distribution of soil depths for each HRU type were compared (Fig. 2.7). Results of an ANOVA indicated that the differences in median soil depth for the three HRU types were significant ($p < 0.01$). The ranges of soil depths in the bedrock upland/ridge and midslope HRUs were very similar, which may have been an artifact of preferential sampling of soil pockets in bedrock upland/ridge HRUs. The fact that the $HG_{ED}$ method was able to capture significant differences in soil depth between HRU types holds promise for predictive soil mapping to better capture relative differences in storage capacity throughout the landscape. Further examination of this application of $HG_{ED}$ and comparison to other predictive soil mapping methods (e.g. Dahlke et al. 2009) is recommended.
Figure 2-7 Boxplot illustrating soil depths measured in bedrock upland/ridge \((n=150)\), midslope \((n=184)\), and depression \((n=151)\) HRUs. Outliers are identified as: \((75^{th}\) percentile value) + 1.5 \cdot (interquartile range).

The midslope HRU had the largest storage capacity, followed by DEPEAST, DEPTERMINAL, DEPUPWEST, and DEPWEST. Interestingly, the residual storage capacities of the midslope and DEPUPWEST HRUs were very small portions of the total capacity (1.3% and 5.8%, respectively) compared to the other depression HRUs, which ranged from 17.7% to 27.2% of their respective total capacities. These differences reflect differences in the slope, bedrock topography, and soil depth of depressions and midslopes and should be considered when examining differences in storage-discharge relationships for different HRUs.
Table 2-3 Summary of areal, soil depth and storage characteristics of delineated HRUs. Disconnected upslope contributing area refers to the portion of the total upslope contributing area located downslope of any depression HRUs that may short-circuit flow due to storage deficits. Numbers in brackets under areal characteristics indicate % of total catchment area and under storage characteristics indicate % of total storage capacity. The total area of the catchment is 77493 m² (7.75 ha). Note that soil depth characteristics for Bedrock Upland/Ridge HRUs represent measurements in soil pockets.

<table>
<thead>
<tr>
<th>HRU(s)</th>
<th>Areal Characteristics</th>
<th>Soil Depth Characteristics</th>
<th>Storage Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area (m²)</td>
<td>Total upslope contributing area (m²)</td>
<td>Disconnected upslope contributing area (m²)</td>
</tr>
<tr>
<td>DEPTERMINAL</td>
<td>5375 (6.9)</td>
<td>72118 (93.1)</td>
<td>7463 (9.6)</td>
</tr>
<tr>
<td>DEPWEST</td>
<td>1825 (2.4)</td>
<td>33254 (42.9)</td>
<td>16458 (21.2)</td>
</tr>
<tr>
<td>DEPUPEWEST</td>
<td>2425 (3.1)</td>
<td>14194 (18.3)</td>
<td>Not applicable</td>
</tr>
<tr>
<td>DEPEAST</td>
<td>7400 (9.5)</td>
<td>22424 (28.9)</td>
<td>Not applicable</td>
</tr>
<tr>
<td><strong>All Depressions</strong></td>
<td>17025 (22.0)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Midslope</td>
<td>28890 (37.3)</td>
<td>Not estimated</td>
<td>Not applicable</td>
</tr>
<tr>
<td><strong>All Depressions and Midslope</strong></td>
<td>45915 (59.3)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Bedrock Upland/Ridge</td>
<td>31578 (40.7)</td>
<td>Not estimated</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>
2.4.3 HRU Water Storage Dynamics

2.4.3.1 General Hydrologic Behaviour

Our inter-annual comparison of runoff response (Table 2.2) indicated that 2008 was a year of average precipitation inputs. For 2008, as an average year, the seasonality of the hydrologic regime was evident (Fig. 2.8). Following snowmelt, baseflow was high and numerous events in the late spring and early summer generated quickflow (Fig. 2.8a,b). In late summer, there were fewer large events and baseflow ceased in the west sub-catchment by early August when potential evaporation was largest. August was the only month when potential evaporation exceeded precipitation. Baseflow from the catchment outlet continued until early September, after which several large events were unable to generate flow. A sequence of large events in early to mid October finally generated flow at both gauged sites; however, early season baseflow levels were not restored.

The midslope tended to be the driest of the five HRUs with \( VWC \) less than 40% and the water table below 40 cm depth the majority of the time (Fig. 2.8c, d). In the depressions, shallow \( VWC \) responded rapidly to event inputs; however, was relatively constant during the wetter seasons (Fig. 2.8c). Of the four depression HRUs, only DEP\(_{\text{TERMINAL}}\) exhibited a water table at or above the surface for extended periods of time in the spring/early summer and autumn seasons (Fig. 2.8d). DEP\(_{\text{TERMINAL}}\) also had the most dynamic patterns of water table depth, ranging from surface inundation to 60 cm below the surface. In contrast, DEP\(_{\text{WEST}}\) exhibited the most persistent water table, very near the surface during the spring/early summer and autumn seasons, with a range of only 40 cm over the entire study period. The deepest water tables were observed in DEP\(_{\text{UPWEST}}\), while DEP\(_{\text{EAST}}\) exhibited intermediate depths and dynamics. During the study period water tables never dropped below the depth of the \textit{recording} wells; however, at most of the \textit{manual} well sites, located in midslope and bedrock upland HRU sites higher up in the catchment, the water table frequently dropped below the bottom of the well during dry periods. Hence, these sites were not used in the storage calculations.
Figure 2-8 Hydrologic overview of the 2008 study period. (a) Open precipitation, (b) catchment and west sub-catchment streamflow, and (c) shallow volumetric water content, (d) water table elevation with respect to the ground surface, (e) total storage, and (f) total storage normalized to storage capacity for all depression and midslope HRUs.
2.4.3.2 Water Storage Dynamics

In the spring and early summer seasons storage deficits were relatively small and storage excesses, when the water table was at or above the ground surface, were evident in DEP\textsubscript{TERMINAL} (Fig. 2.8e). In terms of relative magnitude, DEP\textsubscript{TERMINAL} and DEP\textsubscript{EAST} exhibited the largest $S_{TOTAL}$ throughout the study period. $S_{TOTAL}$ in the midslope exhibited the greatest range and during several spring and early summer events it approached the same volume as DEP\textsubscript{TERMINAL}. $S_{TOTAL}$ in DEP\textsubscript{WEST} and DEP\textsubscript{UPWEST} was relatively small, reflecting the smaller areas of these depressions. DEP\textsubscript{TERMINAL}, DEP\textsubscript{WEST}, and DEP\textsubscript{EAST} were near their respective storage capacities during the wet seasons, whereas DEP\textsubscript{UPWEST}, and to a much larger degree the midslope area, consistently maintained a storage deficit (Fig. 2.8f). The timing of storage deficits throughout the catchment was consistent with periods of reduced precipitation inputs and relatively high potential evaporation.

Our use of an exponential depth function for drainable porosity for each HRU that is constrained by field measurements, instead of a single value for the entire catchment, better reflects the role of soil characteristics on water storage. Future studies focused on quantifying spatial (lateral and vertical) variability in drainable porosity in relation to the HRU classifications are warranted. Storage in the bedrock uplands/ridge HRUs was not estimated in this study due to limitations in instrumentation and uncertainty in the extent of small soil pockets in these areas. The assumption that storage in bedrock uplands/ridges is small relative to storage in depression and midslope HRUs needs to be verified in subsequent studies. Nevertheless, we believe that the application of HG\textsubscript{ED} to other catchments will facilitate decisions regarding instrumentation and estimation of water storage for different landscape elements, such that element water budgets may be fully examined and compared.

2.4.4 Storage-Discharge Relationships

2.4.4.1 Piecewise Regression Models

In order to investigate threshold behaviour in the hydrologic functioning of the catchment, we examined the relationship between water storage ($S$) and catchment discharge ($Q$), hereafter referred to as the S-Q relationship. We examined catchment discharge as a function of total

in the spring and early summer seasons storage deficits were relatively small and storage excesses, when the water table was at or above the ground surface, were evident in DEP\textsubscript{TERMINAL} (Fig. 2.8e). In terms of relative magnitude, DEP\textsubscript{TERMINAL} and DEP\textsubscript{EAST} exhibited the largest $S_{TOTAL}$ throughout the study period. $S_{TOTAL}$ in the midslope exhibited the greatest range and during several spring and early summer events it approached the same volume as DEP\textsubscript{TERMINAL}. $S_{TOTAL}$ in DEP\textsubscript{WEST} and DEP\textsubscript{UPWEST} was relatively small, reflecting the smaller areas of these depressions. DEP\textsubscript{TERMINAL}, DEP\textsubscript{WEST}, and DEP\textsubscript{EAST} were near their respective storage capacities during the wet seasons, whereas DEP\textsubscript{UPWEST}, and to a much larger degree the midslope area, consistently maintained a storage deficit (Fig. 2.8f). The timing of storage deficits throughout the catchment was consistent with periods of reduced precipitation inputs and relatively high potential evaporation.

Our use of an exponential depth function for drainable porosity for each HRU that is constrained by field measurements, instead of a single value for the entire catchment, better reflects the role of soil characteristics on water storage. Future studies focused on quantifying spatial (lateral and vertical) variability in drainable porosity in relation to the HRU classifications are warranted. Storage in the bedrock uplands/ridge HRUs was not estimated in this study due to limitations in instrumentation and uncertainty in the extent of small soil pockets in these areas. The assumption that storage in bedrock uplands/ridges is small relative to storage in depression and midslope HRUs needs to be verified in subsequent studies. Nevertheless, we believe that the application of HG\textsubscript{ED} to other catchments will facilitate decisions regarding instrumentation and estimation of water storage for different landscape elements, such that element water budgets may be fully examined and compared.

2.4.4 Storage-Discharge Relationships

2.4.4.1 Piecewise Regression Models

In order to investigate threshold behaviour in the hydrologic functioning of the catchment, we examined the relationship between water storage ($S$) and catchment discharge ($Q$), hereafter referred to as the S-Q relationship. We examined catchment discharge as a function of total
storage in all depression and midslope HRUs, as well as, total storage in individual HRUs. Nonlinearities in the S-Q relationship were clearly evident regardless of the predictor variable used (Fig. 2.9). Exponential functions were a good fit for the S-Q relationship when storage in all HRUs was combined (Fig. 2.9a) and when only storage in the midslope HRU was considered (Fig. 2.9b). However, an exponential function did not fully capture the abrupt increase in discharge at high storage volumes when only depression HRUs were considered (Fig. 2.9c-f). In these cases, the relationship was partitioned into two responses, for which a separate linear function could be fit to each interval. Piecewise regression analysis (PRA) was carried out to further examine the threshold behaviour of the S-Q relationship for all storage predictors. Piecewise regression models are ‘broken-stick’ models, where two or more lines unite at unknown point(s), called breakpoint(s), which represent the threshold(s) in the relationship (Toms and Lesperance, 2003). The PRA was performed in WinBUGS, an interactive Windows program for Bayesian analysis of complex statistical models using Markov chain Monte Carlo techniques (Lunn et al. 2000). From the PRA, we estimated a breakpoint in the S-Q relationship, with respect to the predictor variable, above which a large increase in discharge is associated with a small increase in storage. Figure 2.9 shows the observed S-Q relationships, exponential fits, and PRA-derived models for select predictor variables. A comparison of efficiency criteria for the exponential and PRA models, the PRA-estimated breakpoints and slopes below ($\beta_1$) and above ($\beta_2$) the breakpoint, as well as 97.5 % confidence intervals (CIs; Toms and Lesperance, 2003) are summarized in Table 2.4.
Figure 2-9 Storage-discharge relationships for the UP1 catchment and UP1 west-subcatchment. Relationships are shown for catchment discharge and total storage in (a) all depression and midslope HRUs, (b) the midslope HRU, (c) all depression HRUs, (d) DEPTERNIAL, (e) DEPEAST, and discharge from the west-subcatchment and total storage in (f) DEPWEST. Exponential functions are plotted for each dataset (thin black line), as well as the segmented linear functions from the piecewise regression analysis (PRA). Note that total storage normalized to the storage capacity of the HRU or combination of HRUs in question is shown on the upper x-axis.
Table 2-4 Assessment of exponential and piecewise regression analysis (PRA) models ability to reproduce storage-discharge relationships in the UP1 catchment. $r^2$ is the coefficient of determination. PRA-derived breakpoints are shown as volumes and normalized to storage capacity for all S-Q relationships. The slope below ($\beta_1$) and above ($\beta_2$) the breakpoint is also given. The 97.5% confidence intervals (CI) for the breakpoints and slopes are reported.

<table>
<thead>
<tr>
<th>Response Variable</th>
<th>Predictor Variable</th>
<th>Total Storage in...</th>
<th>Exponential</th>
<th>Piecewise Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r^2$</td>
<td>$r^2$ Breakpoint</td>
</tr>
<tr>
<td>$Q_{\text{UP1}}$</td>
<td>All HRUs</td>
<td></td>
<td>0.46 0.63 6279 (6060,6423) 46.6</td>
<td>0.03 (0.02,0.04)</td>
</tr>
<tr>
<td></td>
<td>All SPDAs</td>
<td></td>
<td>0.43 0.79 4976 (4962,4994) 92.4</td>
<td>0.06 (0.05,0.07)</td>
</tr>
<tr>
<td></td>
<td>Midslope</td>
<td></td>
<td>0.45 0.57 1167 (963,1246) 14.4</td>
<td>0.07 (0.05,0.09)</td>
</tr>
<tr>
<td>$Q_{\text{UP1}}$</td>
<td>$\text{DEP}_{\text{TERMINAL}}$</td>
<td></td>
<td>0.55 0.85 1702 (1698,1705) 97.9</td>
<td>0.14 (0.12,0.16)</td>
</tr>
<tr>
<td></td>
<td>$\text{DEP}_{\text{WEST}}$</td>
<td></td>
<td>0.16 0.45 455 (438,468) 90.3</td>
<td>0.73 (0.03,1.14)</td>
</tr>
<tr>
<td>$Q_{\text{UP1}}$</td>
<td>$\text{DEP}_{\text{UPWEST}}$</td>
<td></td>
<td>0.23 0.69 518 (504,544) 71.8</td>
<td>0.34 (0.20,0.48)</td>
</tr>
<tr>
<td></td>
<td>$\text{DEP}_{\text{EAST}}$</td>
<td></td>
<td>0.37 0.59 2275 (2263,2281) 93.9</td>
<td>0.14 (0.11,0.17)</td>
</tr>
<tr>
<td>$Q_{\text{UP1,WEST}}$</td>
<td>$\text{DEP}_{\text{WEST}}$</td>
<td></td>
<td>0.59 0.42 452 (443,457) 89.7</td>
<td>0.24 (0.07,0.40)</td>
</tr>
<tr>
<td>$Q_{\text{UP1,WEST}}$</td>
<td>$\text{DEP}_{\text{UPWEST}}$</td>
<td></td>
<td>0.52 0.71 557 (544,562) 77.3</td>
<td>0.16 (0.12,0.20)</td>
</tr>
</tbody>
</table>
The coefficient of determination ($r^2$) values for the exponential fits ranged between 0.16 and 0.55 for different HRUs and combinations of HRUs (Table 2.4). The largest $r^2$ was obtained when $S_{TOTAL}$ for DEP_{TERMINAL} was used as the predictor variable. $r^2$ values for the exponential functions describing the S-Q relationship for the UP1 west-subcatchment were similar in magnitude with the largest value of 0.59 obtained when $S_{TOTAL}$ for DEP_{WEST} was used as the predictor variable (Table 2.4). $r^2$ values derived from the PRA models ranged between 0.45 and 0.85 for $Q_{UP1}$ and 0.42 and 0.71 for $Q_{UP1\text{-WEST}}$ (Table 2.4). In these cases, the largest $r^2$ values were obtained when $S_{TOTAL}$ for DEP_{TERMINAL} and DEP_{UPWEST} were used as predictor variables for $Q_{UP1}$ and $Q_{UP1\text{-WEST}}$, respectively. The PRA-derived breakpoints ranged between 14.4% of $S_{CAPACITY}$ for the midslope HRU and 97.9% of $S_{CAPACITY}$ for DEP_{TERMINAL} (Table 4). DEP_{WEST} and DEP_{EAST} also both have breakpoints above 90% of $S_{CAPACITY}$; however, DEP_{UPWEST} falls between the other depressions and midslope values at 71.8% of $S_{CAPACITY}$. For all predictor variables but one, coefficient of determinations were higher for the PRA model fits than those for the exponential model fits. The breakpoint CIs were largest when storage in all HRUs and only the midslope HRU were used as predictor variables in the PRA. The smallest CIs were achieved when storage in DEP_{TERMINAL} was used as the predictor variable (Table 2.4). These results suggest that storage in DEP_{TERMINAL} has the most ‘power’ to precisely detect a breakpoint in the S-Q relationship and hence is the strongest predictor of rapid changes in discharge. For all models, the slope below the breakpoint was at least one order of magnitude smaller than the slope above the breakpoint. Based on the range of possible slopes indicated by the CIs for $\beta_1$ and $\beta_2$, the combined storage variable was the most powerful at detecting changes in discharge. This precision was reflected in the CI range for the midslope HRU, but surprisingly the CI range for DEP_{TERMINAL} and DEP_{EAST} were relatively large.

Strong nonlinearities were evident in the S-Q relationships in the UP1 catchment (Fig. 2.9). Exponential functions reasonably described these relationships at low storage and discharge values; however, they were not adequate at capturing the abrupt increase in discharge at large storage values, in particular when only storage in depressional HRUs was considered. The estimation of a breakpoint in the relationship, with separate linear regressions explaining the change in discharge with storage above and below this value, was an objective means of quantifying the transition between the two distinct hydrologic regimes in this catchment. The magnitudes of the PRA-derived breakpoints varied considerably between the midslope and
depressional HRUs, with larger values (expressed as % of storage capacity) for depressions. Likewise, the slope of the regression above the breakpoint was larger for depression HRUs than the midslope HRU. These differences bode well for our assumption that the HGED landscape partitioning captures significant differences in hydrologic functioning for different landscape elements. By taking into consideration storage in individual landscape units and combinations of units we can clearly see how the S-Q relationship varies across scales. The relationship is strongest when only storage in DEPTERMINAL is considered, from which we infer that antecedent moisture conditions (i.e. storage) in the terminal depression directly influence catchment discharge.

2.4.4.2 Relationship to Storm Response

Of the 164 events identified in the hydrograph separation analysis, the 43 events that occurred between July 2007 and October 2009 were used to examine the relationship between storage metrics and runoff response. Since runoff ratios were more sensitive to changes in $P$ when $R$ values were small, we constrained our analysis to events when $P$ was greater than 10mm ($n = 27$). We recognize that this may exclude storm events whose runoff response was influenced by storage deficits in the canopy.

The relationship between $R/P$ and total event precipitation diverged with increasing $P$ (Fig. 2.10a), suggesting an influence of antecedent moisture conditions (i.e. storage) on catchment response. Hence, we examined event $R/P$ values as a function of $S_{ANTECEDENT}$ in combinations of HRUs and individual HRUs and found evidence of threshold-like change over a relatively small change in storage (Fig. 2.10b-e). In general, events with $R/P \leq 0.1$ (represented by open circles in Fig. 2.10) were preceded by relatively low storage in both depression and midslope HRUs. Exponential functions best explained the pattern of increasing runoff response with $S_{ANTECEDENT}$; however, this was only the case when depression HRUs were incorporated in the predictor metric with $r^2$ values ranging between 0.76 for all HRUs and 0.86 for DEPTERMINAL (Fig. 2.10b,d,e). A power function was best at explaining the relationship between runoff response and $S_{ANTECEDENT}$ for the midslope HRU ($r^2 = 0.75$) (Fig. 2.10c). We also examined runoff response as a function of $S_{MAXIMUM}$ during the storm period (Fig. 2.10f) and found that $R/P$ increased exponentially with $S_{MAXIMUM}$ ($r^2 = 0.62$). Although the fit resulted in a lower $r^2$ than
for $S_{ANTECEDENT}$ (Fig. 2.10e), the residuals were reduced as $S_{MAXIMUM}$ increased, suggesting that $R/P$ may be better described as a function of both $S_{ANTECEDENT}$ and $S_{MAXIMUM}$. The PRA-derived breakpoints (indicated by dashed lines in Fig. 2.10b-f) were significantly larger than the apparent thresholds in the storage-response relationship. From this we inferred that antecedent storage was an important indication of potential runoff response, but that event input dynamics needed to be considered when attempting to explain the large variability in response in and around the breakpoint value.

To further illustrate the combined effects of $S_{ANTECEDENT}$ and $S_{MAXIMUM}$ on $R/P$, we compared the hourly storage-discharge dynamics of two events relative to the PRA model using storage in DEPTERMINAL as the predictor (Fig. 2.11). Approximately 30 mm of rainfall was recorded for both events; however, there was an order of magnitude difference in $R/P$. The 5-October-2007 event (Fig. 2.11a) was preceded by a period of small inputs and large evaporative demand and as a result $S_{ANTECEDENT}$ in DEPTERMINAL was relatively low. Over the course of the event storage in DEPTERMINAL increased, but did not exceed the breakpoint in the S-Q model (Fig. 2.11b), resulting in a low $R/P$. In contrast, the 9-June-2008 event (Fig. 2.11c) was preceded by a period with significant baseflow and large inputs. $S_{ANTECEDENT}$ was already close to the breakpoint for DEPTERMINAL (Fig. 2.11d), hence there was a small storage deficit to be satisfied and inputs were translated quickly to runoff at the outlet. With such a large volume of water in storage prior to the event, saturation overland flow would have been a major component of the hydrograph. The slight counter clockwise hysteresis that was evident in the event-scale S-Q dynamics for these two storms was also evident in many of the other storms we examined and often to a greater extent. Spence (2010) noted that S-Q hysteresis is likely linked to patterns between storage and flow at smaller scales, for example, the nonlinear and hysteretic relationship between pressure head, water content and hydraulic conductivity. The hysteresis may also be indicative of temporal variability in contributing areas due to changes in connectivity and activation of faster flow pathways that bypass the terminal depression. Further analysis of the relationships between storm characteristics, depression and midslope storage, and catchment discharge are warranted.
Figure 2-10 Event runoff ratios ($R/P$) as a function of (a) total event precipitation and (b) antecedent storage in all HRUs, (c) the midslope HRU, (d) all depression HRUs and (e) DEP_TERMINAL. (f) $R/P$ as a function of maximum event storage in DEP_TERMINAL. Open circles represent events with $R/P \leq 0.1$ and relatively small antecedent storage. Closed circles represent events with $R/P > 0.1$ and relatively large antecedent storage. The upper x-axis in (b)-(f) denote storage normalized to the total storage capacity of the HRU or combination of HRUs. The dashed line in (b)-(f) marks the PRA-derived breakpoint in the S-Q relationship (see Fig. 9). Note that only events with greater than 10 mm of total precipitation are shown.
Figure 2-11 A comparison of two events with similar inputs, but with varying antecedent storage ($S_{ANTECEDENT}$) in the terminal depression ($DEP_{TERMINAL}$). (a) Hyetograph and hydrograph for an early autumn event with relatively small $S_{ANTECEDENT}$ in $DEP_{TERMINAL}$, (b) storage-discharge (S-Q) dynamics for the storm in (a) overlaid on the modeled S-Q relationship for $DEP_{TERMINAL}$, (c) hyetograph and hydrograph for a late spring event with relatively large $S_{ANTECEDENT}$ in $DEP_{TERMINAL}$, and (d) S-Q dynamics for the storm in (c) overlaid on the modeled S-Q relationship for $DEP_{TERMINAL}$. The upper x-axis in (b) and (d) denotes storage normalized to the total storage capacity of $DEP_{TERMINAL}$.

2.4.4.3 Storage Excess Routing

The final step in our examination of how storage conditions influence the runoff response of the catchment was to calculate a volumetric storage excess metric, $S_{EXCESS}$, which takes into account $S_{ANTECEDENT}$, total event inputs ($P_{TOTAL}$), the threshold behaviour of the depression HRUs, and their arrangement in the catchment. Each depression HRU was designated as either a head depression, defined as having no upslope depressions, or a receiving depression, defined as having one or more upslope depressions. $S_{EXCESS}$ for head depressions was calculated as:
\[ S_{\text{EXCESS(Head Depression)}} = S_{\text{ANTECEDENT}} + P_{\text{TOTAL}} - S_{\text{BREAKPOINT}} \]  

(2.4)

where \( S_{\text{BREAKPOINT}} \) is the breakpoint in the S-Q relationship quantified for the specific HRU using the PRA, and is expressed volumetrically. Since receiving depressions have other depressions located upslope they can potentially receive \( S_{\text{EXCESS}} \) from these units, hence equation (4) was modified for receiving depressions as:

\[ S_{\text{EXCESS(Receiving Depression)}} = S_{\text{ANTECEDENT}} + P_{\text{TOTAL}} - S_{\text{BREAKPOINT}} + \sum S_{\text{EXCESS(Upslope Depressions)}} \]  

(2.5)

Once \( S_{\text{EXCESS}} \) was calculated for each depression, it was explicitly routed through all depressions in the catchment based on their topological arrangement. The conceptual model for this explicit routing (Fig. 2.12a) was based on both field observations and topographic estimates of flow pathway routing. Other routing directions may exist that we have not incorporated into our calculation of \( S_{\text{EXCESS}} \), for example, a direct connection from DEP\text{EAST} to the stream outlet. We also have not included the midslope in the routing due to the highly variable nature of \( S_{\text{EXCESS}} \) in this HRU.

We examined how the incorporation of hydrologic connections between depression HRUs affected our ability to explain the observed runoff response by comparing \( S_{\text{EXCESS}} \) calculated for DEP\text{TERMINAL} only (Fig. 2.12b) to the explicitly routed \( S_{\text{EXCESS}} \) (Fig. 2.12c). The explicit routing of \( S_{\text{EXCESS}} \) through all depressions resulted in a decrease in the residual values for both \( R/P \) and \( QF/P \). When the same comparison was made for \( R \) and \( QF \) (Fig. 2.12d,e), the slope of the linear functions fit to the relationships with \( S_{\text{EXCESS}} \) decreased from 6.22 to 2.32 for \( R \) and from 3.96 to 1.40 for \( QF \) (1:1 lines are shown in Fig. 2.12d,e for reference). Based on the slope of 1.40 for the \( QF \) versus \( S_{\text{EXCESS(All Depressions)}} \) function, we infer that storage excess in the depressions and precipitation onto the depressions accounted for approximately 71% of \( QF \). Furthermore, this suggests that only 22% of the total catchment area (all depressions; see Table 2.3) accounted for the majority of the \( QF \) and that this fraction was not influenced by the total event.

We examined how the incorporation of hydrologic connections between depression HRUs affected our ability to explain the observed runoff response by comparing \( S_{\text{EXCESS}} \) calculated for DEP\text{TERMINAL} only (Fig. 2.12b) to the explicitly routed \( S_{\text{EXCESS}} \) (Fig. 2.12c). The explicit routing of \( S_{\text{EXCESS}} \) through all depressions resulted in a decrease in the residual values for both \( R/P \) and \( QF/P \). When the same comparison was made for \( R \) and \( QF \) (Fig. 2.12d,e), the slope of the linear functions fit to the relationships with \( S_{\text{EXCESS}} \) decreased from 6.22 to 2.32 for \( R \) and from 3.96 to 1.40 for \( QF \) (1:1 lines are shown in Fig. 2.12d,e for reference). Based on the slope of 1.40 for the \( QF \) versus \( S_{\text{EXCESS(All Depressions)}} \) function, we infer that storage excess in the depressions and precipitation onto the depressions accounted for approximately 71% of \( QF \). Furthermore, this suggests that only 22% of the total catchment area (all depressions; see Table 2.3) accounted for the majority of the \( QF \) and that this fraction was not influenced by the total event.
precipitation. Although we did not calculate $S_{EXCESS}$ for the midslope and bedrock-dominated HRUs, we hypothesize that they account for the remaining 29 % of $QF$. Future studies will focus on methods to route water from the midslope and bedrock HRUs into neighbouring depressions. Given the complicated shape, likelihood of preferential flow pathways, and variability in soil depth in the midslope HRU, it may need to be subdivided into smaller landscape units to facilitate flow routing. Methods also need to be developed to accurately estimate $S_{EXCESS}$ from bedrock HRUs where $S_{CAPACITY}$ is relatively small.
Figure 2-12 (a) Conceptual model of storage excess routing through the catchment. Runoff response factors, $R/P$ and $QF/P$, as a function of storage excess ($S_{EXCESS}$) in $DEP_{TERMINAL}$ (b) and $S_{EXCESS}$ for all depressions using explicit routing (c). Runoff ($R$) and quick flow ($QF$) as a function of $S_{EXCESS}$ in $DEP_{TERMINAL}$ (d) and $S_{EXCESS}$ for all depressions using explicit routing (e).
2.4.5 Implications for Predicting the Hydrologic Behaviour of Boreal Shield Catchments

The study watershed is topographically-complex yet we believe that many catchments may exhibit similar nonlinear relationships because of transmissivity feedback and/or organic layer interflow mechanisms. Based on our field observations of bedrock topography in the UP1 catchment, the nonlinear relationship between discharge and depressional storage is consistent with the fill-and-spill flow mechanism (Spence and Woo, 2003). However, our hydrometric analysis alone provides no information on the presence or absence of preferential flow pathways that potentially bypass the terminal depression and/or quickly route water through adjoining midslope areas. Further analysis of the geochemistry and isotopic signatures of water in the catchment is expected to provide evidence for additional testing of these hypotheses and to examine whether or not all water exiting the catchment has flowed (and mixed) through the terminal depression.

The identification of thresholds in catchment S-Q relationships is a simple approach for understanding runoff response at multiple scales and relating response to hydrologic processes at smaller scales. As suggested by McDonnell and Woods (2004), catchment classification must integrate fluxes and storages, and the response of the dominant catchment storage unit could be an appropriate metric. This study presents new findings that may help to implement this conceptual framework in predictions of the hydrologic behaviour of Boreal Shield catchments. Specifically, this study demonstrates that topographic-based landscape delineation can be used to partition the landscape into hydrologic response unit types that have significantly different soil depths and hydrologic functioning, and hence can be used to constrain estimates of water storage. Furthermore, it demonstrates that storage-discharge dynamics in the dominant storage unit, in this case the terminal depression, control the runoff response of the catchment by regulating whether or not upslope runoff is used to satisfy storage deficits. However, the explicit routing of storage excesses from upslope depressions improves our ability to account for the quantity of runoff quickly routed to the stream outlet. Hence, efforts to use S-Q relationships to predict discharge and runoff response should include an integration of storage metrics, particularly antecedent storage, total event input, the storage breakpoint, and upslope storage excess. Further-refined estimates of the spatial distribution of water storage in depression HRUs and storage-discharge breakpoints have the potential to be used directly in
physically-based rainfall-runoff models and biogeochemical models to explore hydrological controls on solute transport. Given present concerns over potential changes in water quantity and quality with changing precipitation and temperature regimes, further examination of how storage-discharge thresholds relate to hydrologic source areas and flow pathways is clearly warranted.

2.5 Conclusion

In this study of the relationship between storage-discharge dynamics of topographically-defined landscape units and rainfall-runoff response, we found that for the majority of rainfall events, less than 20% of precipitation inputs were translated into quick flow. This suggests that for the majority of events less than 20% of the catchment area contributes to streamflow and that hydrologic connectivity in the catchment is usually limited.

This work has shown how the use of a novel landscape partitioning approach coupled to high-frequency hydrometric measurements can be an effective way to partition the landscape into physically-based HRUs, and assess water storage dynamics at the catchment scale. We believe that for hydrological systems that have non-linear storage-discharge relationships and display distinct thresholds or breakpoints, piecewise regression analysis is a useful tool to model the relationship and to objectively quantify the breakpoint in the relationship. The storage breakpoint allows for two distinct hydrologic regimes at both the HRU and catchment scales to be quantitatively distinguished. In the UP1 catchment, water storage dynamics in the terminal depression were the strongest predictor of catchment runoff.

Our results showed that both the storage conditions just prior to an event, and the total event input as indicated by the maximum storage achieved during the event, were important predictors of potential runoff response. However, our inclusion of storage excesses from upslope depressions that were explicitly routed through the catchment is the piece that significantly improved our ability to predict runoff response. We showed that approximately 71% of the event quick flow was generated by depression HRUs that cover only 22% of the total area of the UP1 catchment. These findings are among the first to quantitatively support other conceptual models of hydrological behaviour in Boreal Shield landscapes that indicate that runoff
This work contributes to the advancement of our understanding of, and ability to quantify, thresholds in runoff response. The storage-discharge curve is a quantitative means of classifying the hydrologic function and sensitivity of a catchment and, when coupled to geochemical and isotope tracer data, will provide even greater insights into runoff source areas and flow pathways.
3.1 Introduction

There is substantial evidence that concentrations of mercury ($\text{Hg}$) in the environment have increased over the past 150 years due to an increase in anthropogenic mercury emissions (e.g. Fitzgerald et al. 1991; Morel et al. 1998). Even in remote ecosystems, $\text{Hg}$ concentrations have increased between 2- and 5-fold over preindustrial levels because of the long residence time of $\text{Hg}$ in the atmosphere (Lucotte et al. 1995; Lorey and Driscoll, 1999; Lindberg et al. 2007). Transformation of inorganic $\text{Hg}^{2+}$ by bacteria to methylmercury ($\text{MeHg}$) and the subsequent biomagnification through food webs has resulted in human health concerns worldwide. The general consensus among $\text{Hg}$ researchers is that $\text{MeHg}$ concentrations in fish respond to changes in atmospheric inputs of $\text{Hg}$ to lakes and watersheds (Munthe et al. 2007). The magnitude and the timing of the response will vary depending on factors such as the timing and extent of loading, the efficiency of the terrestrial system in delivering atmospherically deposited $\text{Hg}$ to receiving waters and zones of methylation, and the availability of $\text{MeHg}$ to the food web.

The Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) project underway at the Experimental Lakes Area (ELA) in northwestern Ontario is investigating the mobility and bioavailability of atmospherically-deposited $\text{Hg}$ through the application of enriched stable $\text{Hg}^{2+}$ isotopes (spike $\text{Hg}$) to different compartments (lake, wetland, upland) of an experimental watershed (Harris et al. 2007). This approach allows METAALICUS scientists to distinguish added spike $\text{Hg}$ from ambient $\text{Hg}$ that was resident in the watershed, and thus the fates of the spikes can be tracked through the ecosystem. The first three years of experimental results showed a rapid increase in fish $\text{MeHg}$ concentration exclusively because of the $\text{Hg}$ loaded to the lake. In contrast, <1% of the $\text{Hg}^{2+}$ isotope deposited to the uplands was exported to the lake despite the overwhelming importance of watershed derived $\text{Hg}$ to the lake $\text{Hg}$ budget (Harris et al. 2007). This finding confirmed an earlier pilot study by Hintelmann et al. (2002) and indicates that a significant lag exists between
Hg deposition to uplands and the delivery of Hg to adjacent lakes. This slow release of Hg from the soil pool may mask or delay the recovery of fish MeHg levels when emission controls are enacted and Hg deposition declines, and thus a quantitative means of predicting the time and magnitude of watershed responses is needed (Munthe et al. 2007).

The entry of Hg to most ecosystems is via interaction with vegetation. Hg is deposited onto vegetation via wet or dry deposition, is incorporated into foliage and is deposited to the ground via litterfall or foliage wash off (Graydon et al. 2008). Further movement of Hg occurs as a result of the decomposition and leaching of natural organic matter, whereby Hg bound to dissolved organic matter (DOM) and/or particulate organic matter (POM) is mobilized in storm runoff or snow melt and makes its way to streams, the lake and sites of methylation. The retention of Hg in watershed soils is strongly coupled to soil organic matter (SOM) and our conceptual understanding of the release of Hg in runoff is that it is dependent on the rate of decomposition of the SOM pool (Meili, 1991; Grigal, 2002, 2003; Munthe et al. 2007).

Despite a relatively large body of literature describing the correlation between Hg and natural organic matter, which suggests that upland soils are a delayed source of Hg to downstream aquatic ecosystems (Ravichandran, 2004; Munthe et al. 2007; Grigal, 2002; Harris et al. 2007; Demers et al. 2007), data on the distribution of SOM-bound and DOM-bound Hg in different soil horizons in boreal soil landscapes are lacking. Both of these factors contribute to our uncertainty surrounding the effects of terrestrial ecosystems on the timing and magnitude of the delivery of atmospherically-deposited Hg to aquatic ecosystems. The distribution and concentration of DOM-bound Hg within the soil profile provides an indication of the location and size of the potentially mobile pool of Hg (Akerblom et al. 2008; Smith-Downey et al. 2010). Differences in the concentration of DOM-bound Hg between horizons are important to know given the distinct hydrologic functioning in boreal regions that is often dominated by interflow through near-surface organic soil horizons (Frisbee et al. 2007; Allan and Roulet, 1994). Furthermore, once Hg moves deep enough in boreal soils, lateral movement becomes increasingly less probable. A recent study in Sweden found that solid-phase and solution-phase Hg to carbon ratios were similar for the near-surface organic horizon at two different sites, from which the authors inferred a simple mobilization mechanism with negligible fractionation (Akerblom et al. 2008). Additionally, a recent global modelling study that describes the lifetime and turnover of Hg in soils based on the lifetime and turnover of the soil carbon pool to which it
is bound identifies the need to determine whether \( Hg \) binds to all soil pools (e.g. organic and mineral pools) with equal affinity (Smith-Downey et al. 2010). While several other studies have made use of stable isotopes of \( Hg \) to examine the mobility and methylation of newly deposited \( Hg \) in lake water, sediments, and fish (Gilmour et al. 1998; Orihel et al. 2006; Patterson et al. 2006;), wetland soils (Branfireun et al. 2005), upland soils at the plot-scale (Hintelmann et al. 2002), and vegetation (Graydon et al. 2009), to the best of our knowledge, no other study has made use of \( Hg \) isotopes as tracers of \( SOM \)- and \( DOM \)-bound \( Hg \) distribution in boreal uplands at the catchment-scale.

Here we examine the sources of potentially mobile mercury in a boreal shield catchment by quantifying the vertical distribution of \( SOM \)- and \( DOM \)-bound ambient \( Hg \) and spike \( Hg \) in different soil layers. Our study is carried out in the METAALICUS experimental watershed; hence we make use of the stable isotope of mercury that was applied to the uplands (spike \( ^{200}Hg \)) as a tracer of newly-deposited mercury mobility in the soil profile. The main objective of this research is to provide insight into the dynamics of \( Hg \) retention and release from soils in a boreal shield landscape. This chapter addresses the following specific research questions:

1. Does the vertical distribution of \( SOM \)-bound spike \( Hg \) reflect that of ambient \( Hg \)?

2. Does the vertical distribution of \( DOM \)-bound spike \( Hg \) reflect that of ambient \( Hg \)?

3. Can we attribute the \( DOM \)-bound \( Hg \) leaving the catchment in runoff to a particular soil layer?

### 3.2 Methods

#### 3.2.1 Site Description

This study was conducted in the METAALICUS experimental watershed, located in the Experimental Lakes Area (ELA) in north-western Ontario (49° 40’ N, 93° 43’ W). The climate of the study area is boreal cold temperate. Average monthly air temperatures range from -16.5 °C for January to +20.1 °C for July, mean annual air temperature is 2.8 °C and mean annual precipitation is 708 mm, 75% of which is rain (based on 1970-2009 climate normals; pers comm. K. Beaty).
The UP1 study area is a 7.75 ha headwater catchment that drains into Lake 658 (L658) (Fig. 3.1a). The UP1 catchment is south-facing with a mean slope of 12° and a difference in elevation from the outflow datum to the watershed divide of 63 m. The local topography is highly variable and includes a sequence of soil-filled bedrock depressions separated by near-vertical bedrock ridges in the western half of the catchment, while the eastern half exhibits a more continuously sloping morphology (Fig. 3.1b). UP1 lacks a well-defined drainage network; however it is drained by a short, ephemeral stream into L658, with high flows during spring snowmelt and early summer and fall rain storms.

UP1 is underlain by unfractured, granitic bedrock and over approximately 40% of the catchment the bedrock is either exposed (16 %; mainly in the upper portion and along cliff edges) or covered with very shallow soil patches (mean depth is 23 cm). In the remaining areas, soils range in depth from 0 to 242 cm with a mean value of 54 cm (Fig. 3.1c). The soils are acidic brunisols, are texturally classified as silt loams, and are likely of a glaciolacustrine origin (Allan and Roulet, 1994; Brunskill and Schindler, 1971). At the surface of the soil profile, folic or sphagnic surface organic layers dominate depending on drainage conditions. For the purposes of this study, this soil horizon is labeled $Live/L/Of$ since some live mosses and grasses were included with the accumulated organic matter during sampling. Beneath the $Live/L/Of$ horizon, is a relatively thin, well-humified organic horizon, which for the purposes of this study is labeled $F/H/Oh$, thereby representing partly decomposed and decomposed organic matter derived from both folic ($F/H$) and sphagnic ($Oh$) sources. Beneath the $F/H/Oh$ horizon is a thin $Ah$ mineral horizon characterized by an accumulation of organic matter expressed morphologically by a darkening of the soil. Beneath the $Ah$ horizon is a $B$ mineral horizon characterized by enrichment of organic matter and clay in some areas of the catchment, but mainly a relatively uniform browning due to oxidation of iron ($Bm$). The mineral horizons that were sampled were sandy with < 30% organic matter, and for the purposes of this study are labeled $Ah/Bm$, since samples were generally not obtained from deeper than 15 cm into the mineral layer. All soil horizons were classified according to The Canadian System of Soil Classification (Soil Classification Working Group, 1998).

A 6-ha section in the northwest portion of the Lake 658 watershed, part of which falls within the UP1 catchment, was logged in 1978 (pers comm. K. Beaty) and now supports a deciduous forest of red maple ($Acer rubrum$) and paper birch ($Betula papyrifera$). The portion of UP1 that was
not logged is dominated by mature black spruce (*Picea mariana*) and balsam fir (*Abies balsamea*). Lichens (e.g. *Cladina stellaris* and *Peltigera aphthosa*), mosses (e.g. *Polytrichum piliferum* and *Pleurozium schreberi*), and juniper (*Juniperus virginiana*) grow on and from shallow fractures in the bedrock outcrops. In depressional areas the organic horizon is relatively thick and the surface vegetation is dominated by *Sphagnum* spp. with some shrubs such as Labrador tea (*Ledum groenlandicum*).
Figure 3-1 (a) The UP1 catchment boundary overlaid on the shaded relief of the Lake 658 watershed, (b) UP1 topography as represented by slope and all soil and water sample sites, and (c) map of soil depth.
3.2.2 Application of Enriched Hg Isotope to the Lake 658 Uplands

At the ELA, most of the mercury is atmospheric in origin, with approximately 0.1-0.3 \( \mu g \cdot m^{-2} \) estimated to be derived from geologic weathering (St. Louis et al. 2001). The average wet deposition rate of \( Hg \) at the ELA is 3.6 \( \mu g \cdot m^{-2} \cdot y^{-1} \) (Graydon et al. 2008), which is low compared to other more contaminated sites in the United States and Europe (St. Louis et al. 1995; Lindberg et al. 2007). At the ELA, inorganic \( Hg^{2+} \) load to the entire L658 catchment was experimentally increased to levels observed in more polluted regions by adding three different enriched stable \( Hg^{2+} \) isotopes at an average addition rate of 20.1 \( \mu g \cdot m^{-2} \cdot y^{-1} \) (approx. 6 times the wet deposition rate; Harris et al. 2007). The lake, wetland and upland portions of the L658 watershed were expected to respond differently to \( Hg^{2+} \) loadings; hence a different isotope was added to each of these compartments by fixed-wing aircraft and shoreline spraying (upland and wetland) and by boat during the open-water season (lake). The upland spike \( ^{200}Hg \) (80.45% enriched) was added each year (2001-2006) between mid-May and mid-August during light rain events. The average application rate for the uplands was 18.51 \( \mu g \cdot m^{-2} \) (Sandilands et al. 2008).

3.2.3 Depth-to-Bedrock Mapping

A spatially extensive depth-to-bedrock (DBR) survey (\( n=485 \)) was carried out using a 2.2 m-long steel hammer probe to determine spatial patterns in soil thickness. At locations where the probe was hammered all the way to the ground the soil thickness was recorded as 2.2 m, despite the possibility that the soil depth could have been larger. The frequency distribution of DBR measured in the catchment points to the variability in soil thickness in UP1 (not shown). The point measurements of DBR were then used to create a spatially-interpolated map of DBR for the entire catchment (\textit{ArcMap, ESRI}; Fig. 3.1c). The interpolation method used was inverse-distance weighting with soft breaklines inserted along the bedrock cliffs that run in a generally east-west direction across the catchment to avoid having the interpolation cross these extreme topographical gradients.
3.2.4 Soil Sampling

A total of 528 soil samples were collected at 190 sites throughout the UP1 catchment in October 2007 and June 2008 (Fig. 3.1b). Samples were taken at approximately 5 m intervals along transects that followed topographic contours in soil-filled areas. In areas covered mainly by exposed bedrock, samples were taken from soil pockets located in shallow bedrock depressions. Every attempt was made to sample evenly over the full extent of the catchment, however due to the increased presence of exposed bedrock in its northern reaches; fewer samples were collected higher in the catchment. A subset of the samples involved strategic sampling near zero-tension lysimeters and wells installed throughout the catchment (Fig. 3.1b). Samples were collected using standard clean procedures for mercury analysis (EPA Method 1631) to avoid Hg contamination. Samples were taken either with an auger (4.8 cm i.d.) equipped with a sharpened edge to cut through roots or a sharp knife. Where possible, soil samples were removed intact so that their dimensions could be measured to calculate bulk density ($\rho_b = m_{soil} / V_{sample}$). At each site, where possible, a sample was taken from the surface organic horizon (folic: $L/F$ and sphagnic: $O_f$), lower humified organic horizon (folic: $H$ and sphagnic: $O_m/Oh$) and the mineral horizons ($Ah$ and $Bm$). In some cases (e.g. at bedrock sites) only a surface organic horizon was present and in other cases (e.g. in deep soil-filled depressions) multiple organic layer and mineral samples were collected. In all cases, live surface vegetation (including mosses, lichens, and short grasses; excluding small and large shrubs) and litter were collected as part of the surface organic samples.

Soil samples were air dried at room temperature (24-72 h), sieved through stainless steel mesh (2 mm), milled (A11 Analytical Grinding Mill, IKA Works Inc., U.S.A.), and stored in polypropylene containers prior to chemical analysis. Wet weight-dry weight conversions were obtained by weighing prior to and following the drying. A subset of samples was tested before the entire survey was dried to ensure no significant change in Hg concentration occurred as a result of air drying.

3.2.5 Soil-Water and Catchment Runoff Sampling

Soil-water was sampled from wells and piezometers between May and October 2008, and from zero-tension lysimeters and the catchment outlet between May 2006 and October 2008. All
water samples were collected in the field using ultraclean trace metal protocols according to US EPA Method 1631 to prevent Hg contamination. Immediately after sampling, bottles were double-bagged and samples were transported to the ELA laboratory for filtering and aliquots were separated for total dissolved Hg analysis (acidified to 0.5 % v/v), and dissolved organic carbon (DOC) analysis.

Soil-water in the surface and lower humified organic layers, hereafter defined as shallow soil-water, was collected from zero-tension lysimeters located at 15 different sites throughout the catchment (Fig. 3.1b). Lysimeters were made of 4” i.d. PVC pipe with 250 μm NITEX mesh to filter out coarse material. One end of the pipe was sharpened so that the lysimeters were easily installed into the organic layer with minimal disturbance to the soil structure. Lysimeter sites were located in areas with sufficiently large slope to allow for lateral installation into the surface soil layer. Soil-water samples were collected into new 500 mL PETG bottles connected to the lysimeters by Teflon tubing and placed downslope in opaque containers to shield samples from sunlight and prevent heating. Samples (n = 417) were collected during and immediately after periods when subsurface runoff, as a result of snowmelt and/or rainfall events, occurred in the organic horizon. Samples that sat in the field longer than 3 days were discarded.

Wells were located at 24 sites (Fig. 3.1b), were slotted over their entire length, and extended 0.5 to 1.5 m below the ground. Piezometers were nested at 14 of the sites with wells, were slotted over their lower 20 cm, and extended 40, 60 and 80 cm below the ground. Hence well samples represent the integrated signal of water from the entire soil profile, while piezometer samples represent water located mostly in the mineral horizons, although at some sites the shallowest piezometer may have intersected the very bottom of the lower organic horizon. In this paper, we have pooled all 80 cm piezometer results to represent deep soil-water. Samples were collected from wells and piezometers using a Teflon line attached to a peristaltic pump (GeoPump Inc, New York). The Teflon line was rinsed with 0.5 % v/v HCl and DI water prior to each sample being collected and sample was allowed to pass through the line fully before being collected into new PETG bottles. Deep soil-water samples (n = 56) were collected from piezometers during surveys in late June, late August, and late October of 2008.

Catchment outlet runoff samples were collected from the stream emptying the UP1 catchment (Fig. 3.1b). Samples were collected by hand, using ultraclean protocol, into 500 mL PETG bottles that were pre-rinsed with sample water to environmetalize the bottle. Catchment outlet
samples \((n = 259)\) were collected during snowmelt, rainfall events, and low flow periods. Both soil-water and catchment runoff sampling were limited in midsummer when the water table fell into the mineral horizon at most sites and during the winter and early snowmelt periods when the ground was frozen.

### 3.2.6 Chemical Analysis

For the analysis of \(Hg\) in the soil samples, approximately 0.5 g of dry, homogenized soil sample was digested in 30:70 HSO\(_4\);HNO\(_3\) and allowed to reflux on a hot plate at 250 °F until vapours lost their distinct brown colour (~4 h). Once cool, the mixture was diluted with 18.2 MΩ DI water and brominated for at least 12 h with 0.5 % v/v BrCl. The soil digestate was then diluted to approximately 50 ml with 18.2 MΩ deionized water and all \(Hg\) was oxidized to \(Hg^{2+}\) by adding 0.5 ml of BrCl. For the analysis of \(Hg\) in soil-water, high-purity BrCl equivalent to 1% of volume was added to samples at least 24 h prior to analysis (Hintelmann and Harris 2004). Diluted soil digestate and soil-water samples were analyzed for \(Hg\) using a cold vapour atomic fluorescence (CVAFS) system equipped with an autosampler (Tekran 2600 automatic mercury analyzer, Tekran Inc., Toronto) connected directly to an inductively coupled plasma mass spectrometer (ICP-MS; Hewlett Packard 4500, Agilent Technologies, USA). In CVAFS analysis, \(Hg^{2+}\) is converted to cold \(Hg^0\) vapour using SnCl\(_2\) as a reductant, concentrated using dual gold-trap amalgamation, and introduced to the detector on a stream of argon. The exhaust from the CVAFS system is then delivered to the ICP-MS, which we use to distinguish historically-deposited ambient \(Hg\) from the experimentally applied spike \(^{200}Hg\) (Hintelmann and Evans 1997). To calculate concentrations of ambient \(Hg\) we used an isotope that was not experimentally applied to the L658 uplands \((^{202}Hg)\) as an ambient \(Hg\) surrogate. All concentrations of soil \(Hg\) are expressed on a mass of \(Hg\) per soil dry mass basis (ng g\(^{-1}\)), while concentrations of \(Hg\) in water are expressed on a mass per volume basis (ng L\(^{-1}\)).

For each batch of samples, a suite of quality control and assurance (QA/QC) measures including initial and ongoing precision recovery, analysis of blanks (equipment, field, laboratory, and method), duplicates, matrix spikes, and standard reference material (SRM) were analyzed. We used IAEA-405 estuarine sediment as the SRM for solid-phase total \(Hg\) (\(THg\)), which had an expected dry weight \(THg\) concentration of 0.81 ± 0.04 ng g\(^{-1}\) \((n = 60)\). Our mean \(THg\) recovery
from the SRM was within the 95% confidence interval of THg and concentrations reported. All our analyses showed good reproducibility. The limit of detection (LOD) for ambient Hg in soil was 0.35 ng g\(^{-1}\) and in water was 0.09 ng L\(^{-1}\). The LOD for the spike \(^{200}\)Hg does not depend on the absolute detection limit of the ICP-MS system, but rather on the precision with which isotope ratios can be measured and the concentration of ambient Hg in the sample (Hintelmann and Evans, 1997). Using the techniques described above, to detect an applied isotope with certainty, it had to have a concentration >0.5-1.5% of the ambient Hg concentration of a sample. Our LOD for spike \(^{200}\)Hg in soil ranged from 0.05 to 2.2 ng g\(^{-1}\) (median = 0.70 ng g\(^{-1}\)) and in water ranged from 0.02 to 0.24 ng L\(^{-1}\) (median = 0.07 ng L\(^{-1}\)). Soil and water samples with ambient and/or spike Hg concentrations below detection were assigned a value of (LOD/2).

Soil samples were also analyzed for SOM and soil organic carbon (SOC) content. SOM was estimated from loss-on-ignition at 550 °C (LOI\(_{550}\)) at the University of Toronto and for a subset of samples SOM and SOC were also measured using the Walkley-Black method and combustion method, respectively, at the University of Guelph Agriculture and Food Laboratory. We calculated the SOC:SOM for this subset, which was comparable to other studies (Konen et al. 2002; Périé and Ouimet, 2007), to the samples that were not analyzed for SOC. Water samples were also analyzed for DOC using a TOC-TN IL-550 high-temperature combustion system (Lachat Instruments Inc.) and following US EPA Method 415.3. In this method, water samples are pre-acidified to pH 2 and purged with oxygen prior to automated injection and combustion. The character of DOC in water samples was assessed by measuring the ultraviolet absorbance at a wavelength of 254 nm (UV\(_{254}\)) on a full spectrum spectrophotometer (NanoDrop 1000, Thermo Fisher Scientific, USA), which is an established proxy measure of percent aromaticity (Weishaar et al. 2003; Chin et al. 1994). We also calculated the specific ultraviolet absorbance at a wavelength of 254 nm (SUVA\(_{254}\)) by dividing the UV\(_{254}\) for a sample by the concentration of DOC in the sample (units of L mg\(^{-1}\) m\(^{-1}\)).

### 3.2.7 Statistical Analysis

All statistical analyses were performed using Statistica version 8.0 software (StatSoft Inc.). Data were tested for normality using the Shapiro-Wilk \(W\) test and subsequently tested for skewness and kurtosis if \(W\) was significant \((p < 0.05)\). Most variables were not normally
distributed and were right-skewed; hence the data were natural log transformed. Analysis of variance (ANOVA) and the Tukey post hoc multiple comparison test were used to compare the mean values of different groups of variables. Relationships between mercury concentration and other variables were investigated using simple linear regression and the correlation coefficient and coefficient of determination are reported. In cases where the distribution of the residuals is non-normal, the dependent data were transformed according to skewness as described above. Normality of residuals was confirmed for all variables after transformation for simple linear regression analysis. Analysis of covariance (ANCOVA) and calculation of the q statistic were used to compare the regressions slopes of different groups of data. Relationships were considered statistically significant at \( p < 0.05 \).

3.3 Results and Discussion

In this paper we distinguish between the historically-deposited, ambient \( Hg \) and the experimentally-applied spike \( ^{200}Hg \). We also distinguish between mercury bound to SOM or solid-phase \( (Hg_S) \) and mercury that is bound to DOM in porewater and runoff or solution-phase \( (Hg_D) \).

3.3.1 Soil Characteristics

Table 3.1 summarizes the solid phase characteristics of the three general soil layers that were sampled in the UP1 catchment. The mean ± standard error (SE) thicknesses of the surface organic layer \( (Live/L/Of) \), lower organic layer \( (F/H/Om/Oh) \), and mineral layer \( (Ah/Bm \) and underlying mineral soil to bedrock) are 3.5 ± 0.1 cm, 11.4 ± 0.5 cm, and 63.3 ± 4.4 cm, respectively, which are typical of the shallow, weakly-developed soils in this region (Soil Classification Working Group, 1998). Mean ± SE soil bulk density \( (\rho_b) \) ranges from 0.15 ± 0.02 g cm\(^{-3}\) at the surface to 1.26 ± 0.07 g cm\(^{-3}\) in the upper mineral layer. These bulk densities are consistent with values reported in other boreal forest studies in northwestern Ontario \( (~ 0.08 \text{ g cm}^{-3} \) for near surface soils and \( ~ 0.42 \text{ g cm}^{-3} \) for shallow mineral soils; Westbrook and Devito, 2004) Québec \( (~ 0.2 – 2.0 \text{ g cm}^{-3}; \) Périé and Ouimet, 2008) and the Northwest Territories \( (~ 0.11 \text{ g cm}^{-3} \) for near-surface soils; Spence \textit{et al.} 2010). Mean ± SE SOC content ranges from
48.0 ± 0.2 % at the surface to 3.4 ± 0.2 % in the upper mineral layer. These values are similar to those reported for near-surface soils (25.6 – 49.9 %) and deeper mineral soils (~ 1.9 – 2.5 %) in the boreal forests of Sweden (Akerblom et al. 2008), as well as B horizon soils (~ 1.9 – 11.6 %) in boreal forests in Québec (Périé and Ouimet, 2008).
Table 3-1 Solid phase characteristics of Live/L/Of, F/H/Om/Oh, and Ah/Bm soil layers in the UP1 catchment.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (cm)</th>
<th>( \rho_b ) (g cm(^{-3} ))</th>
<th>SOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Min-Max</td>
<td>Median</td>
</tr>
<tr>
<td>Live/L/Of</td>
<td>190</td>
<td>0.5-10</td>
<td>3.0</td>
</tr>
<tr>
<td>F/H/Om/Oh</td>
<td>190</td>
<td>2-35</td>
<td>10.0</td>
</tr>
<tr>
<td>Ah/Bm</td>
<td>190</td>
<td>0-205</td>
<td>41.4</td>
</tr>
</tbody>
</table>

SE: standard error of the mean; \( \rho_b \): bulk density; SOC: soil organic carbon.
3.3.2 Vertical Distribution of Solid-Phase Mercury Concentrations

*Ambient Hg* and *spike*\(^{200\text{Hg}}\) concentrations in the UP1 catchment exhibit different vertical distributions (Table 3.2; Figure 3.2a). The mean ± SE concentration of *ambient Hg* is largest in the lower, humified organic layer (242.5 ± 7.5 ng g\(^{-1}\)), followed by the surface organic layer (111.0 ± 3.0 ng g\(^{-1}\)), and the mineral layer (32.7 ± 2.3 ng g\(^{-1}\)). Our concentrations for the surface and lower, humified organic layer are at the low end of values reported in studies of more contaminated organic soils (e.g. ~350 ng g\(^{-1}\) for the mor layer and ~310 to 390 ng g\(^{-1}\) for O horizon soils in southern Sweden (Akerblom *et al.* 2008) and ~39 to 57 ng g\(^{-1}\) for leaf litter and ~261 to 413 ng g\(^{-1}\) for O horizon soil in the northeastern United States (Demers *et al.* 2007)), but similar to or slightly larger than in areas with potentially lower atmospheric Hg loads (e.g. ~68 to 127 ng g\(^{-1}\) in litter and ~100 to 300 ng g\(^{-1}\) in O horizon soils and ~8.8 to 25.2 ng g\(^{-1}\) in mineral soils in northern Saskatchewan (Friedli *et al.* 2007) and ~240 to 260 ng g\(^{-1}\) for O horizon soils in northern Sweden (Akerblom *et al.* 2008)). Our values for the mineral layer are mostly from samples collected in the upper portion of this horizon. At several sites we collected samples from deeper in the mineral layer (maximum depth 52.5 cm) and found that the *ambient Hg* concentration declines slightly with depth; however our sample size is too small to speculate as to whether or not this pattern is widespread over the soil-filled areas of the catchment. In contrast to *ambient Hg*, the mean concentration of *spike*\(^{200\text{Hg}}\) is largest in the surface organic layer (11.1 ± 0.7 ng g\(^{-1}\)), followed by the lower organic layer (3.3 ± 0.4 ng g\(^{-1}\)) and the mineral layer (0.3 ± 0.02 ng g\(^{-1}\)). To test for significant differences between mean Hg concentrations for the three soil layers, an ANOVA was performed on the natural log transformed data. For both *ambient Hg* and *spike*\(^{200\text{Hg}}\) the null hypothesis that mean concentrations are equal for all layers was rejected. Results of a Tukey post hoc multiple comparison test indicate that significant \((p < 0.05)\) differences exist between the mean *ambient Hg* and *spike*\(^{200\text{Hg}}\) concentrations for all soil layers.

The vertical distribution of *ambient Hg* that we observe in the UP1 catchment is consistent with other studies that find the largest concentration in well-humified organic layers, followed by the surface organic layer, and the smallest concentrations in deeper mineral layers (Obrist *et al.* 2009; Akerblom *et al.* 2008; Grimaldi *et al.* 2008; Demers *et al.* 2007; Friedli *et al.* 2007; Grigal, 2003; Hintelmann *et al.* 2002). It is generally accepted that patterns of Hg concentration with depth mirror changes in SOM (Grigal, 2003). Our finding that the *spike*
$^{200}Hg_S$ concentration is largest in the surface organic layer suggests that the integration of newly-deposited $Hg$ into the soil profile occurs over timescales that are longer than the period between the onset of spiking and sample collection for this study (~ 7 years). Previous studies at this site have found that litterfall generally represents the largest input of total $Hg$ to the landscape on an annual basis, followed by atmospheric particulate $Hg$ that is washed off foliage during rain events and deposited as throughfall (Graydon et al. 2008). Hence, upon entering the soil profile the majority of $Hg$ is already bound to $SOM$. If we assume that the ambient $Hg_S$ distribution we observe represents steady-state, then we should expect that the spike $^{200}Hg_S$ distribution will assume the ambient distribution over a time period that is consistent with $SOM$ turnover rates. It is important to note, however, that not all $SOM$ degrades at the same rate, so differential rates of $SOM$-bound spike $^{200}Hg_S$ redistribution in the soil profile will likely occur.
Table 3-2 Solid phase characteristics with respect to $Hg_S$ of Live/L/Of, F/H/Om/Oh, and Ah/Bm soil layers in the UP1 catchment.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Hg$_S$</th>
<th>Concentration of Hg$_S$ (ng g$^{-1}$)</th>
<th>Areal Mass of Hg$_S$ (µg m$^{-2}$)</th>
<th>Hg$_S$:SOC (µg g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Min-Max</td>
<td>Median</td>
<td>Mean±SE</td>
</tr>
<tr>
<td>Live/L/Of</td>
<td>Amb</td>
<td>169</td>
<td>39.7-287.8</td>
<td>106.9</td>
</tr>
<tr>
<td></td>
<td>Spk</td>
<td>169</td>
<td>0.5-70.2</td>
<td>9.2</td>
</tr>
<tr>
<td>F/H/Om/Oh</td>
<td>Amb</td>
<td>186</td>
<td>31.0-615.3</td>
<td>233.0</td>
</tr>
<tr>
<td></td>
<td>Spk</td>
<td>186</td>
<td>0.2-49.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Ah/Bm</td>
<td>Amb</td>
<td>141</td>
<td>4.0-139.3</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Spk</td>
<td>141</td>
<td>0.2-1.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

SE: standard error of the mean; SOC: soil organic carbon.
Figure 3-2 Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of (a) the concentration of ambient $\text{Hg}_S$ and spike $^{200}\text{Hg}_S$, (b) the areal mass of ambient $\text{Hg}_S$ and spike $^{200}\text{Hg}_S$, (c) soil organic carbon content (SOC), and (d) ambient $\text{Hg}_S$:SOC and spike $^{200}\text{Hg}_S$:SOC for the surface organic soil layer (Live/L/Of), lower, humified organic soil layer (F/H/Om/Oh), and the mineral soil layer (Ah/Bm). Note the log$_{10}$ scale on some y axes, and different ranges for ambient $\text{Hg}_S$ and spike $^{200}\text{Hg}_S$. 
3.3.3 Vertical Distribution of Solid-Phase Mercury Areal Mass

Although larger \( HgS \) concentrations are usually associated with larger \( SOM \) concentrations, \( \rho_b \) and \( SOM \) are inversely related (Périé and Ouimet, 2008) and hence an emphasis on concentration can distort our view of \( HgS \) abundance (Grigal, 2003). This often leads to the paradox that soil horizons with large \( HgS \) concentrations have small mass per unit area. Accordingly, we examined the areal mass of ambient \( HgS \) and spike \( HgS \) for the three soil layers (Figure 2b). The mean ± SE areal mass of ambient \( HgS \) is largest in the mineral layer (32318.6 ± 3839.6 \( \mu g \) m\(^{-2}\)), followed by the lower, humified organic layer (8892.3 ± 419.5 \( \mu g \) m\(^{-2}\)), and the surface organic layer (273.4 ± 13.7 \( \mu g \) m\(^{-2}\)). Differences between mean ambient \( HgS \) for all layers are significant (ANOVA, Tukey post hoc test, all \( p <0.05 \)). The relatively large \( \rho_b \) of the mineral layer accounts for the difference between the pattern of concentration and areal mass with depth, despite the mineral layer having the smallest ambient \( HgS \) concentration. Estimates of the areal mass of \( HgS \) in forest floor organic soil layers and mineral layers in Sweden, the USA, and Germany vary considerably depending on the thickness of soil that is considered (~ 500 to 4000 \( \mu g \) m\(^{-2}\) in forest floor organic soil layers and ~ 3000 to 10000 \( \mu g \) m\(^{-2}\) in the upper mineral layers (as described in Grigal, 2003)). Our value for the surface organic layer falls on the low end of these estimates, while our values for the lower, humified organic layer and mineral layer are substantially larger. One likely reason why our mineral layer values are so large is that we extrapolated the concentrations that were measured near the top of the mineral layer over its entire thickness. While this probably represents an overestimate of \( HgS \) abundance in the mineral soil given our observations at several sites that \( HgS \) concentration decreases with depth in this layer, it does represent the maximum amount of \( HgS \) that could be stored in the mineral horizon and accounts for the possibility that \( Hg \) may be transported to deeper soil layers along preferential flow pathways (Grigal, 2002). Similar to the vertical pattern of ambient \( HgS \), the mean areal mass of spike \( HgS \) is largest in the mineral layer (397.8 ± 48.8 \( \mu g \) m\(^{-2}\)), followed by the lower organic layer (55.5 ± 13.7 \( \mu g \) m\(^{-2}\)) and the surface organic layer (29.3 ± 2.4 \( \mu g \) m\(^{-2}\)). Differences between mean spike \( HgS \) for all layers are significant (ANOVA, Tukey post hoc test, all \( p <0.05 \)). Despite relatively small concentrations of spike \( HgS \) in the lower organic and mineral layers, the areal masses of both are relatively large due to the increase in \( \rho_b \) with depth. It is important to note that our estimates of areal mass are only applicable to areas of the catchment that are soil-filled (~ 84 %). We suggest caution when reporting and/or comparing areal mass values for different sites,
especially for the mineral horizon, and believe that further investigation of HgS concentrations in deep mineral horizons is warranted.

3.3.4 Vertical Distribution of HgS:SOC

The strong relationship between Hg and SOC is well established (Aastrup et al. 1991; Johansson et al. 1991; Meili, 1991; Grigal, 2002, 2003) and therefore, it is crucial to our understanding of Hg storage in terrestrial ecosystems that we study the distribution of Hg in soil in relation to these substances. In this paper we focus on the relationship between HgS and SOC, as opposed to SOM, since we measured DOC in soil-water and compare the vertical distributions of HgS:SOC and Hg0:DOC. As expected, mean ± SE percent SOC content was largest in the surface organic layer (48.0 ± 0.2 %) and decreased with depth in the lower, humified organic layer (35.5 ± 0.7 %) and mineral layer (3.4 ± 0.2 %) (Table 3.1; Figure 3.2c). Differences among the three soil layers were significant (ANOVA, F2,∞, Tukey post hoc test, p < 0.05). Mean ± SE ambient HgS:SOC increases with depth in the soil profile (0.23 ± 0.01 µg g⁻¹ for the surface organic layer, 0.71 ± 0.02 µg g⁻¹ for the lower organic layer, and 2.00 ± 0.44 µg g⁻¹ for the mineral layer) with significant (ANOVA, F2,∞, Tukey post hoc test, p < 0.05) differences between the three soil layers (Table 3.2; Fig. 3.2d). These results are lower than values reported for mor layers at two Swedish sites (~ 0.54 to 0.93 µg g⁻¹), which may be due to higher Hg deposition in Sweden compared to northwestern Ontario, but are within the range of values reported for the lower organic (~ 0.37 to 1.51 µg g⁻¹) and mineral (~ 1.2 to 1.7 µg g⁻¹) layers (Akerblom et al. 2008). In contrast, the distribution of spike²⁰⁰HgS:SOC is largest in the mineral layer (0.03 ± 0.004 µg g⁻¹), followed by the surface organic layer (0.02 ± 0.002 µg g⁻¹), and the lower organic layer (0.009 ± 0.001 µg g⁻¹). The difference in spike²⁰⁰HgS:SOC was significant between the surface organic and lower organic layers and the mineral and lower organic layers (ANOVA, F2,∞, Tukey post hoc test, p < 0.05), but not between the surface organic and mineral layers (p = 0.66). Based on the strong relationship between Hg and SOC, we might expect that patterns of HgS concentration with depth should mirror changes in SOC, and hence that HgS:SOC ratios are the same for all soil layers. Such a finding would suggest that the vertical translocation of HgS and SOC are occurring at the same rate and possibly due to similar processes, for example the leaching of organic matter during infiltration. However, the pattern of increasing ambient HgS:SOC that we observe implies that less HgS than SOC is lost as
organic matter degrades and is incorporated deeper into the soil profile (Grigal, 2003). The fact that the spike $^{200}\text{Hg}_S:\text{SOC}$ ratios do not exhibit these patterns and are relatively similar in the different layers suggests that any $^{200}\text{Hg}_S$ that has been incorporated deeper into the soil profile has likely done so solely as a result of in situ vertical translocation and that any enrichment of the soil with $^{200}\text{Hg}_S$ as a result of organic matter degradation is not yet detectable.

### 3.3.5 Relationship between $\text{Hg}_S$ and SOC

Simple linear regression was also used to examine the relationship between ambient $\text{Hg}_S$ and SOC and spike $^{200}\text{Hg}_S$ and SOC in the different soil layers (Fig. 3.3). For ambient $\text{Hg}_S$ only the lower organic ($r^2 = 0.16$) and mineral layer ($r^2 = 0.48$) regressions were significant and for spike $^{200}\text{Hg}_S$ only the lower organic ($r^2 = 0.09$) layer regression was significant ($p < 0.05$) (Table 3.3). However, for both ambient $\text{Hg}_S$ and spike $^{200}\text{Hg}_S$, the slope ($b$) of the regression with SOC was significantly different amongst all soil layers (ANCOVA, $q_{2,\alpha}$ statistic multiple comparison test, $p < 0.05$). Despite these significant differences the ambient $\text{Hg}_S$, $b \pm \text{SE}$ are quite similar for the lower organic ($0.53 \pm 0.10$) and mineral layers ($0.70 \pm 0.06$) relative to the litter layer ($0.025 \pm 0.144$). This pattern was not evident among the spike $^{200}\text{Hg}_S$ to SOC relationships. Previous studies have found similar relationships as the ones we have identified for ambient $\text{Hg}_S$, for example, positive linear relationships between $\text{Hg}_S$ and SOC for pooled mineral and organic soil layers and inverse relationships for pooled organic and litter layers were reported at four Sierra Nevada forest sites (Grigal, 2003; Obrist et al. 2009). Hence, several studies have suggested that in order to model the lifetime and turnover of $\text{Hg}$ in the soil pool we must do so on the basis of the lifetime and turnover of the carbon pool (Meili, 1991; Smith-Downey et al. 2010). It is interesting to note that SOC becomes a stronger predictor of ambient $\text{Hg}_S$ concentration with depth in the soil profile. The relatively small $r^2$ values for the surface and lower organic layers may reflect spatial variability in $\text{Hg}$ deposition related to heterogeneity in canopy density and vegetation type, as well as large variations in the source and quality of SOC in near surface soil horizons relative to deeper soil horizons.
Figure 3-3 Relationships between (a) ambient HgS and soil organic carbon (SOC) and (b) spike $^{200}$HgS and SOC for the surface organic soil layer (Live/L/Of), lower, humified organic soil layer (F/H/Om/Oh), and the mineral soil layer (A/h/Bm). Only significant ($p < 0.05$) linear fits are shown (lines).
Table 3-3 Slopes (b), correlation coefficient (r), significance level (p), and coefficient of determination (r²) for Hg₅ (μg m⁻²) vs. SOC (%), Hg_D (ng L⁻¹) vs. DOC (mg L⁻¹), Hg_D vs. UV₂₅₄ (m⁻¹), and Hg_D vs. SUVA (L mgC⁻¹ m⁻¹).

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Soil Layer or Water Source</th>
<th>b ± SE</th>
<th>r²</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Hg₅ vs. SOC</td>
<td>Live/L/Of</td>
<td>0.02 ± 0.14</td>
<td>0.00</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>F/H/Om/Oh</td>
<td>0.53 ± 0.10</td>
<td>0.16</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Ah/Bm</td>
<td>0.70 ± 0.06</td>
<td>0.48</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Spike²⁰⁰Hg₅ vs. SOC</td>
<td>Live/L/Of</td>
<td>0.031 ± 0.037</td>
<td>0.00</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>F/H/Om/Oh</td>
<td>0.015 ± 0.004</td>
<td>0.09</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Ah/Bm</td>
<td>-0.001 ± 0.001</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Ambient Hg_D vs. DOC</td>
<td>Shallow Soil-Water</td>
<td>0.66 ± 0.02</td>
<td>0.65</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>0.52 ± 0.08</td>
<td>0.42</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>0.77 ± 0.04</td>
<td>0.62</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Spike²⁰⁰Hg_D vs. DOC</td>
<td>Shallow Soil-Water</td>
<td>0.028 ± 0.002</td>
<td>0.35</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>0.002 ± 0.001</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>0.006 ± 0.001</td>
<td>0.30</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Ambient Hg_D vs. UV₂₅₄</td>
<td>Shallow Soil-Water</td>
<td>193.7 ± 10.1</td>
<td>0.59</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>79.1 ± 14.1</td>
<td>0.38</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>225.7 ± 10.6</td>
<td>0.71</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Spike²⁰⁰Hg_D vs. UV₂₅₄</td>
<td>Shallow Soil-Water</td>
<td>7.21 ± 0.80</td>
<td>0.24</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>0.05 ± 0.21</td>
<td>0.00</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>1.85 ± 0.13</td>
<td>0.51</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Ambient Hg_D vs. SUVA</td>
<td>Shallow Soil-Water</td>
<td>-4046.0 ± 1915.4</td>
<td>0.02</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>1368.7 ± 450.1</td>
<td>0.15</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>2586.6 ± 1952.4</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Spike Hg_D vs. SUVA</td>
<td>Shallow Soil-Water</td>
<td>-363.3 ± 110.7</td>
<td>0.04</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Deep Soil-Water</td>
<td>-4.9 ± 5.8</td>
<td>0.01</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>Catchment Outlet</td>
<td>23.9 ± 19.0</td>
<td>0.01</td>
<td>0.21</td>
</tr>
</tbody>
</table>

SE: standard error of the mean; DOC: dissolved organic carbon; SUVA: specific UV absorbance

3.3.6 Vertical Distribution of DOC, UV₂₅₄, SUVA in Soil-Water

As expected, the mean ± SE concentration of DOC was significantly (p < 0.05) larger in shallow soil-water (29.7 ± 0.9 mg L⁻¹) than in deeper soil-water (11.9 ± 0.8 mg L⁻¹; Table 3.4; Fig. 3.4a). Interestingly, the concentration of DOC in catchment outlet runoff (24.0 ± 0.4 mg L⁻¹) was very similar to that in shallow soil-water. Our mean DOC concentration for catchment outlet runoff is ~ 2 to 8 times larger than mean annual concentrations reported for seven headwater boreal shield catchments in south-central Ontario (~ 3.0 to 13.6 mg L⁻¹) but is only slightly larger than the mean summer value reported for one of the catchments (21.3 mg L⁻¹; Eimers et al. 2008). In addition to DOC concentration, previous studies have also measured UV₂₅₄ as an index of the...
aromaticity of DOC, which has been shown to be an important indicator of DOC interactions with inorganic species such as mercury (Weishaar et al. 2003; Schuster et al. 2008; Dittman et al. 2009). Since $UV_{254}$ generally increases proportionally with DOC concentration (Dittman et al. 2009), SUVA is often also calculated as a measure of DOC quality. Our $UV_{254}$ results showed the same pattern with the largest value in shallow soil-water ($0.109 \pm 0.004$ m$^{-1}$), followed by outlet runoff ($0.087 \pm 0.002$ m$^{-1}$), and deep soil-water ($0.051 \pm 0.005$ m$^{-1}$; Table 3.4; Fig. 3.4b). However, we were unable to detect statistically significant differences in mean SUVA for shallow and deep soil-water and outlet runoff (Fig. 3.4c).
Figure 3-4 Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of (a) the concentration of dissolved organic carbon (DOC), (b) UV absorbance at 254 nm, and (c) specific UV absorbance (SUVA) for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Note the log₁₀ scale on some y axes.
Table 3-4 Solution phase characteristics with respect to DOC based on shallow soil-water sampled from zero-tension lysimeters in the Live/L/Of and F/H/Ohm/Oh layers, deep soil-water sampled from piezometers in the 20-80cm portion of the Ah/Bm layer, and runoff from the catchment outlet.

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Concentration DOC (mg L⁻¹)</th>
<th>UV Absorbance (λ = 254 nm; m⁻¹)</th>
<th>SUVA (L mg⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Min-Max</td>
<td>Median</td>
</tr>
<tr>
<td>Shallow Soil-Water</td>
<td>383</td>
<td>7.2-168.2</td>
<td>24.9</td>
</tr>
<tr>
<td>Deep Soil-Water</td>
<td>56</td>
<td>3.0-28.8</td>
<td>10.4</td>
</tr>
<tr>
<td>Catchment Outlet</td>
<td>276</td>
<td>5.0-48.5</td>
<td>23.1</td>
</tr>
</tbody>
</table>

SE: standard error of the mean; DOC: dissolved organic carbon; SUVA: specific UV absorbance
3.3.7 Vertical Distribution of Hg<sub>D</sub> Concentration, Hg<sub>D</sub>:DOC, Hg<sub>D</sub>:UV<sub>254</sub>, and Hg<sub>D</sub>:SUVA

In order to address the extent to which Hg partitions from the solid- to solution-phase in different soil layers, we measured ambient Hg<sub>D</sub> and spike<sup>200</sup>Hg<sub>D</sub> concentrations in shallow and deep soil-water. We also measured Hg<sub>D</sub> concentration in catchment runoff since it represents the integrated signal of these two potential sources. The mean ± SE concentration of ambient Hg<sub>D</sub> concentration is largest in shallow soil-water that is flowing through near-surface and lower organic soil horizons (21.0 ± 1.0 ng L<sup>-1</sup>), followed by the catchment runoff (16.7 ± 0.4 ng L<sup>-1</sup>), and deep soil-water flowing through the mineral layer (11.5 ± 1.0 ng L<sup>-1</sup>; Table 3.5; Fig. 3.5a).

Our mean ambient Hg<sub>D</sub> concentration for shallow soil-water is very close to the mean Hg<sub>D</sub> concentration reported in O-horizon zero-tension lysimeters in northern Sweden (21.8 ng L<sup>-1</sup>), but smaller than the mean concentration reported at a more contaminated site in southern Sweden (47.0 ng L<sup>-1</sup>; Akerblom et al. 2008). Our mean ambient Hg<sub>D</sub> concentration for deep soil-water is much lower than the 32.2 ng L<sup>-1</sup> reported for E-horizon tension lysimeters at the same site in southern Sweden (Akerblom et al. 2008). Our concentration of ambient Hg<sub>D</sub> in catchment runoff is at the high end of values reported at other sites (e.g. 10.2 ng L<sup>-1</sup> for runoff from a headwater catchment in south-central Ontario, Canada (Mierle and Ingram, 1991), 10.4 ng L<sup>-1</sup> for plot-scale runoff during a METAALICUS pilot study (Hintelmann et al. 2002), and < 6 ng L<sup>-1</sup> at three northern forested watersheds in New Hampshire, Vermont, and New York, U.S.A. (Dittman et al. 2010)). Similar to ambient Hg<sub>D</sub>, our mean concentration of spike<sup>200</sup>Hg<sub>D</sub> is largest in shallow soil-water (0.3 ± 0.05 ng L<sup>-1</sup>), but is at the limit of detection in catchment runoff and deep soil-water (0.07 ± 0.01 ng L<sup>-1</sup>; Table 3.5; Fig. 3.5a). A plot-scale METAALICUS pilot study found a similar concentration of experimentally-applied Hg isotope in runoff (0.05 ng L<sup>-1</sup>; Hintelmann et al. 2002). To the best of our knowledge, no other research has investigated the prevalence of experimentally-applied Hg isotope tracers in upland soil-water and runoff. Results of an ANOVA and Tukey post hoc multiple comparison test indicate that significant (p < 0.05) differences exist between the mean ambient Hg<sub>D</sub> concentrations in shallow and deep soil-water, and deep soil-water and outlet runoff, but that the concentration of Hg<sub>D</sub> in shallow soil-water is not statistically different from that in outlet runoff. In contrast, results of the multiple comparison tests on spike<sup>200</sup>Hg<sub>D</sub> concentrations indicate that shallow and deep soil-water, and deep soil-water and outlet runoff, are not significantly different, but that shallow soil-water and outlet runoff concentrations are significantly different.
Mean ± SE ambient HgD:DOC values are significantly ($p < 0.05$) smaller in shallow soil-water (0.67 ± 0.01 ng mg$^{-1}$) than in deep soil-water (0.95 ± 0.05 ng mg$^{-1}$; Table 3.5; Fig. 3.5b). Ambient HgD:DOC in outlet runoff (0.70 ± 0.02 ng mg$^{-1}$) is not statistically dissimilar to shallow soil-water (ANOVA, Tukey post hoc test, $p < 0.05$). Our HgD:DOC values for shallow and deep soil-water are in the range of other boreal sites (e.g. 0.54 ng mg$^{-1}$ in O-horizon in northern Sweden, 0.73 ng mg$^{-1}$ in O-horizon in southern Sweden, and 1.11 ng mg$^{-1}$ in E-horizon in southern Sweden (Akerblom et al. 2008)). Spike $^{200}$HgD:DOC values decreased slightly from shallow (0.008 ± 0.001 ng mg$^{-1}$) to deep soil-water (0.007 ± 0.001 ng mg$^{-1}$) and were smaller still in outlet runoff (0.003 ± 0.001 ng mg$^{-1}$; Table 3.5; Fig. 3.5b). All differences in spike $^{200}$HgD:DOC were significant (ANOVA, Tukey post hoc test, $p < 0.05$). Mean ± SE ambient HgD:UV$_{254}$ values followed the same pattern as HgD:DOC and differences were significant for all layers (Fig. 3.5c). As well, significant differences amongst layers were measured for spike $^{200}$HgD:UV$_{254}$ with largest value measured in the lower organic horizon, followed by the surface organic horizon and the mineral horizon. Mean ± SE ambient HgD:SUVA was largest in shallow soil-water, followed by catchment runoff and then deep soil-water, however significant differences were only found between shallow and deep soil-water and deep soil-water and catchment runoff (Fig. 3.5d). Spike $^{200}$HgD:SUVA patterns differed in that the mean value was largest for shallow soil-water, followed by deep soil-water and then catchment runoff with a significant difference only between shallow soil-water and catchment runoff (Fig. 3.5d).
Table 3-5 Solution phase characteristics with respect to Hg\textsubscript{D} based on shallow soil-water sampled from zero-tension lysimeters in the \textit{Live/L/Of} and \textit{F/H/Om/Oh} layers, deep soil-water sampled from piezometers in the 20-80cm portion of the \textit{Ah/Bm} layer and water sampled in runoff at the catchment outlet.

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Hg\textsubscript{D} Concentration (ng L\textsuperscript{-1})</th>
<th>Hg\textsubscript{D}:DOC (ng mg\textsuperscript{-1})</th>
<th>Hg\textsubscript{D}:UV\textsubscript{254} (ng L\textsuperscript{-1} m)</th>
<th>Hg\textsubscript{D}:SUVA (ng L\textsuperscript{-1} mg m L\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow Amb</td>
<td>343 3.1-154.3 15.4 21.0±1.0 331 0.20-2.23 0.63 0.67±0.01 261 49.1-619.0 157.7 171.0±4.2 260 677.3-55380.8 3698.8 5169.2±356.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil-Water Spk</td>
<td>343 0.02-12.0 0.04 0.3±0.05 331 0.000-0.161 0.002 0.008±0.001 261 0.1-36.4 0.5 1.8±0.2 260 3.7-5235.0 10.3 89.8±22.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep Amb</td>
<td>67 4.7-57.2 9.6 11.5±1.0 56 0.31-1.93 0.91 0.95±0.05 54 59.2-951.5 234.0 280.6±24.6 54 950.3-6426.7 2304.5 2739.6±175.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil-Water Spk</td>
<td>67 0.02-0.27 0.03 0.07±0.01 56 0.001-0.022 0.006 0.007±0.001 54 0.14-13.8 1.51 2.3±0.40 54 3.2-84.2 13.3 20.9±2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catchment Amb</td>
<td>253 5.0-33.8 15.9 16.7±0.4 250 0.36-2.5 0.63 0.70±0.02 186 92.0-416.0 185.8 18.6±4.0 185 1247.9-9108.8 3890.3 4459.7±155.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet Spk</td>
<td>253 0.02-0.4 0.04 0.07±0.01 250 0.001-0.016 0.002 0.003±0.000 186 0.23-3.19 0.5 0.7±0.04 185 3.8-104.4 11.3 18.8±1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-5 Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of (a) ambient HgD and spike $^{200}$HgD concentrations, (b) ambient HgD:DOC and spike $^{200}$HgD:DOC, (c) ambient HgD:UV$_{254}$ and spike $^{200}$HgD:UV$_{254}$, and (d) ambient HgD:SUVA and spike $^{200}$HgD:SUVA for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Note the log$_{10}$ scale on all y axes, and different ranges for ambient HgD and spike $^{200}$HgD.
3.3.8 Relationship between \(Hg_D\) and DOC, \(Hg_D\) and \(UV_{254}\), \(Hg_D\) and SUVA

We also used simple linear regression to examine the relationships between the concentrations of ambient \(Hg_D\) and DOC, spike \(^{200}Hg_D\) and DOC (Fig. 3.6), ambient \(Hg_D\) and \(UV_{254}\) and spike \(^{200}Hg_D\) and \(UV_{254}\) (Fig. 3.7). There is a significant \((p < 0.05)\) positive correlation between ambient \(Hg_D\) and DOC concentration in shallow soil-water \((r^2 = 0.65)\), deep soil-water \((r^2 = 0.42)\), and outlet runoff \((r^2 = 0.62)\). There is also a significant \((p < 0.05)\) positive correlation between ambient \(Hg_D\) and \(UV_{254}\) absorbance for both shallow and deep soil-water and outlet runoff, but \(UV_{254}\) was only a stronger predictor than DOC of ambient \(Hg_D\) concentration for outlet runoff \((r^2 = 0.71; \text{Table 3.3})\). Similarly, Dittman et al. (2009) found that \(UV_{254}\) was a stronger predictor of total \(Hg_D\) concentrations in streamwater at three forested watersheds in the northeastern U.S.A. For spike \(^{200}Hg_D\), we found a significant \((p < 0.05)\) positive correlation with DOC concentration in shallow soil-water \((r^2 = 0.35)\) and outlet runoff \((r^2 = 0.30)\), but not in deep soil-water \((r^2 = 0.04, p = 0.19)\). There are also significant \((p < 0.05)\) positive correlations between spike \(^{200}Hg_D\) and \(UV_{254}\) for both shallow soil-water and outlet runoff, and again \(UV_{254}\) was only a stronger predictor than DOC of spike \(^{200}Hg_D\) concentration for outlet runoff \((r^2 = 0.51; \text{Table 3.3})\). Similar to findings from the Sleepers River watershed in the northeastern U.S.A. (Schuster et al. 2008), SUVA is not a strong predictor of either ambient \(Hg_D\) or spike \(^{200}Hg_D\) in soil-water and catchment runoff \((r^2 \sim 0.01\) to 0.15). For ambient \(Hg_D\), the slope of the regression line with DOC was significantly different (ANCOVA, \(q\) statistic multiple comparison test, \(p < 0.05\)) for shallow \((0.66 \pm 0.02)\) and deep \((0.52 \pm 0.08)\) soil-water and deep soil-water and outlet runoff \((0.77 \pm 0.04)\). However we could not reject the shallow soil-water and outlet runoff slopes being equal. This was not the case for the spike \(^{200}Hg_D\) to DOC relationships where the regression slopes were significantly different amongst all pools. The relationship between \(Hg_D\) and DOC is well documented (e.g. Mierle and Ingram, 1991; Schuster et al. 2008; Shanley et al. 2008; Dittman et al. 2009) and relationships from sites around the northern hemisphere report similar slopes of \(\sim 0.2\) to \(0.4\) ng mgC\(^{-1}\) for streamflow and \(\sim 0.40\) ng mgC\(^{-1}\) for interflow through organic and mineral horizons (Grigal, 2002; Shanley et al. 2008). Our slopes for catchment runoff are higher than those reviewed by Grigal (2002) and reported by Shanley et al. (2008), except for exceptionally high values measured in Colorado. For ambient \(Hg_D\), the slope of the regression line with \(UV_{254}\) was significantly different (ANCOVA, \(q\) statistic multiple comparison test, \(p < 0.05\)) for shallow \((193.7 \pm 10.1)\) and deep \((79.1 \pm 14.1)\).
soil-water and deep soil-water and outlet runoff (225.7 ± 10.6). As with \( DOC \), we could not reject the shallow soil-water and outlet runoff slopes being equal. Again, this was not the case for the \( spike^{200Hg_D} \) to \( UV_{254} \) relationships where the regression slopes were significantly different amongst all pools.

There seem to be differences in the literature as to how the relationships between \( Hg_S \) and \( SOC \) and \( Hg_D \) and \( DOC \) are expressed. In some cases, the ratios for individual samples are pooled to calculate basic statistics (e.g. mean ± SE; Akerblom \textit{et al.} 2008), but in many others the slope of the best-fit line describing the relationship between these parameters is used (sometimes with the intercept and sometimes without; see Grigal, 2003). Using our dataset, we found that these two approaches can produce differences in the \( Hg:OC \) ratios that are larger than the differences between pools (e.g. soil layers or soil-water and runoff) using a single approach. For example, the mean ± SE ambient \( Hg_D:DOC \) ratio using pooled samples is 0.95 ± 0.05 ng mg\(^{-1}\) for deep soil-water, but the equation of the linear regression line is \( \text{ambient } Hg_D = (0.52 ± 0.05)DOC + 3.90 \) \((n = 56, r^2 = 0.42, p < 0.05)\). Here we see a difference in \( Hg_D:DOC \) of ~ 0.43 ng mg\(^{-1}\), which is larger than the differences in ratios or slopes amongst all the other pools. This may present a problem when comparing \( Hg_D \) to \( DOC \) relationships among sites and studies if different approaches are being used.
Figure 3-6 Relationships between (a) ambient $Hg_D$ and dissolved organic carbon (DOC) and (b) spike $^{200}Hg_D$ and DOC for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Only significant ($p < 0.05$) linear fits are shown (lines).
Figure 3-7 Relationships between (a) ambient $Hg_D$ and UV absorbance at 254 nm ($UV_{254}$) and (b) spike $^{200}Hg_D$ and $UV_{254}$ for shallow soil-water, deep soil-water, and runoff collected at the catchment outlet. Only significant ($p < 0.05$) linear fits are shown (lines).
3.3.9 Does the vertical distribution of SOM-bound spike Hg reflect that of ambient Hg?

Our finding that the concentration of spike $^{200}$Hg is significantly larger in the surface organic horizon compared to lower horizons, whereas the concentration of ambient Hg is largest in the lower organic horizon suggests that newly-deposited Hg is not immediately incorporated into the soil profile and has not been substantially vertically translocated after seven years. Since the majority of Hg is already bound to organic matter when it enters the soil profile (i.e. via litterfall), and stability constants for Hg-DOM complexes are very high (Ravichandran, 2004), it is logical to assume that Hg will remain bound to SOM and/or DOM throughout its lifetime in the soil pool. Thus, its mobility, turnover, and lifetime will determined by the mobility, turnover, and lifetime of natural organic matter. Based on the turnover rate of soil organic carbon, Meili (1991) estimated the half-time of Hg recovery in soils to be on the order of 1000 years and Smith-Downey et al. (2010) estimate the mean present day soil Hg turnover time with respect to respiration for boreal forests at 560 years. In our study, the spike $^{200}$Hg had only been in the ecosystem for ~7 years when soil and water samples were collected. Thus, we infer that the spike $^{200}$Hg has not been in the ecosystem long enough to have had the effects of SOM decomposition and leaching move it deeper into the soil profile. That said, there are certain locations in the catchment where we observed higher concentrations of spike $^{200}$Hg in the lower organic horizon and even some in the mineral layer. Locations where spike $^{200}$Hg has made its way into the lower organic horizon are generally well-drained and hence may be sites with relatively high decomposition rates. Locations where spike $^{200}$Hg has made its way into the mineral horizon are generally in areas of flowpath convergence, for example just upslope of the catchment outlet, and hence may be sites where deeper flowpaths exist in the upper portion of the mineral layer. Also, since SOM cycles at different rates depending on its source (e.g. folic vs. sphagnum), locations with deeper penetration of spike $^{200}$Hg may contain less recalcitrant SOM. The relationship between differential SOM cycling rates and Hg mobility is a limitation in our current state of knowledge and warrants further study. The spatial patterns of ambient Hg and spike $^{200}$Hg in the catchment and their relationships with topography, drainage conditions, and soil and vegetation characteristics are examined in Chapter 4.
3.3.10 Does the vertical distribution of DOM-bound spike Hg reflect that of ambient Hg?

The degree of release of Hg from the solid- to solution-phase can be represented by the ratio of $H_{\text{D}}:\text{DOC}$ to $H_{\text{S}}:\text{SOC}$ (e.g. Akerblom et al. 2008). When $H_{\text{D}}:\text{DOC}/H_{\text{S}}:\text{SOC}$ nears unity, it suggests that the $H_{\text{D}}$ is bound to a pool of potential DOM (Kalbitz et al. 1999) that is in equilibrium with the SOC it is derived from. It also suggests that there is negligible fractionation (or concentrating effect) of Hg in the transition from solid to dissolved phase (Akerblom et al. 2008). Our comparison of $H_{\text{D}}:\text{DOC}/H_{\text{S}}:\text{SOC}$ ratios for ambient and spike Hg and for different soil layers shows that $H_{\text{D}}:\text{DOC}/H_{\text{S}}:\text{SOC}$ is close to unity for both spike and ambient only from the lower humified organic layer to shallow soil water. Whereas, $H_{\text{D}}:\text{DOC}/H_{\text{S}}:\text{SOC}$ for surface organic to shallow soil-water for spike is only 14% of the value for ambient and for mineral soil to deep soil-water the spike value is only 49% of ambient.

From these findings we infer that newly-deposited Hg exhibits nearly the same degree of release from the lower organic horizon to shallow soil-water as ambient Hg. However, newly-deposited Hg is released from the surface organic soil layer into soil-water and from the mineral soil layer into deep soil-water to a lesser degree than ambient Hg. The logical explanation for our claim again rests in the idea of the mobility of Hg being tightly coupled to organic matter. Any newly-deposited spike Hg that makes it into shallow soil-water is doing so because it has is now bound to OM that is small enough to be mobile (Kalbitz et al. 1999). Previous studies have shown that the dominant source of DOM to shallow soil-water and mineral soils is from the lower humified horizon and not the overlying surface organic layer or the underlying mineral layer (Fröberg et al. 2003; Fröberg et al. 2007). Hence, it makes sense that $H_{\text{D}}:\text{DOC}/H_{\text{S}}:\text{SOC}$ will be close to unity for the spike only in the lower humified layer, but will be less than the ambient ratio in the other two layers since there is less DOM (and hence Hg) being contributed from these layers. Our ambient results support the idea that the lack of fractionation between phases bodes well for simple Hg leaching model formulations based on DOC production and mobility (Akerblom et al. 2008); however, our spike results indicate that this only applies to the portion of the Hg soil pool that is bound to the ‘potential’ DOC pool, i.e. not newly-deposited Hg.
3.3.11 Can we attribute the DOM-bound Hg leaving the catchment in runoff to a particular soil layer?

Our data suggest that the soil layers we examined in this study (surface organic, lower organic and mineral) retain and release historically-deposited and newly-deposited Hg to varying degrees. As discussed in the previous section, our finding that both ambient and spike \( \text{HgD:DOC/HgS:SOC} \) are closest to unity for the lower humified organic soil horizon suggests that this horizon is the dominant source of Hg to soil-water. Previous studies have suggested that the flow pathway that water takes through a catchment, and how this varies under different hydroclimatic conditions, will determine the concentration and quality of DOC leaving the catchment in runoff. We extend this idea to the concentration of Hg leaving the catchment in runoff. In our study we found that ambient \( \text{HgD:DOC} \) was more similar for shallow soil-water and catchment runoff than for deep soil-water and catchment runoff (Table S4), which suggests that shallow soil-water is the likely source of \( \text{HgD} \) in catchment runoff. And based on the \( \text{HgD:DOC/HgS:SOC} \) values discussed above, we go further in suggesting that the lower humified organic soil horizon is the dominant source of \( \text{HgD} \) being exported to the lake in runoff. This important finding is consistent with the current understanding of the dominant hydrological flowpaths in this catchment being through the relatively conductive organic soil horizon.

3.4 Conclusion

In this study, the sources of potentially mobile mercury in a boreal shield catchment were investigated by quantifying the vertical distribution of ambient and spike mercury in soil and soil-water in different soil horizons. The results of an extensive soil survey showed that mean ambient and spike Hg concentrations had distinctly different vertical distributions in the soil profile. While ambient Hg concentrations were highest in the lower, humified organic soil horizon, spike Hg concentrations were highest in the surface organic horizon composed mainly of fresh and partially-decomposed litter and mosses. These statistical differences imply that the integration of newly-deposited Hg into the soil profile occurs over a period greater than 7 years, which is the period of time between the onset of experimental loading and sample collection. For both ambient and spike Hg, concentrations were significantly different between all soil horizons suggesting that the movement of Hg through the soil profile is related to processes involved in the degradation and leaching of SOC. Ambient Hg:SOC increased with depth,
suggesting that less Hg than SOC is lost as SOM decomposes and is incorporated deeper into the soil profile; however, spike Hg:SOC did not show the same pattern.

The results of an extensive soil-water survey showed that solution-phase ambient and spike Hg concentrations are highest in shallow soil-water collected from zero-tension lysimeters. Interestingly, the mean ambient Hg concentration in shallow soil-water was not statistically different than the concentration in runoff collected at the catchment outlet; however, the mean spike Hg concentration in catchment runoff was statistically lower than in shallow soil-water. When Hg concentration was normalized to DOC concentration, the vertical patterns in soil-water reversed, such that ambient Hg:DOC was higher in deep soil-water compared to shallow soil-water and catchment runoff which had similar mean values. These results were used in conjunction with the solid-phase Hg:SOC distributions to assess the release of Hg from solid- to solution-phase by examining the ratio of HgD:DOC to HgS:SOC. This ratio was only close to unity for both ambient and spike Hg when values from the lower, humified organic soil horizon and shallow soil-water were used, suggesting that the dominant source of DOM-bound Hg to shallow soil-water is from the lower, humified organic soil horizon.

Overall, the results of our study suggest that there are variations in the retention and release of historically-deposited and newly-deposited Hg between soil horizons. Given the findings that the well humified organic soil horizon is the dominant source of ambient and spike Hg to soil-water and that the concentrations of ambient Hg in shallow soil-water and catchment runoff are not statistically different, it is likely that the lower organic horizon is also the dominant source of ambient Hg to catchment runoff and the lake. This is also evidence that shallow subsurface flow pathways through the highly conductive organic soil horizon may be the dominant flow pathway by which runoff generated further up in the catchment reaches the lake. However, further research is required to determine the depth to which Hg penetrates into the mineral layer and whether or not it is ever released into solution and mobilized along deeper flow pathways.
4.1 Introduction

Following deposition onto terrestrial landscapes, mercury ($Hg$) may be reemitted to the atmosphere or retained in vegetation and soil. Terrestrial systems are an important indirect source of $Hg$ to aquatic systems via runoff; however, only a fraction of the atmospheric inputs are exported to receiving waters (Grigal, 2003; Driscoll et al. 2007; Harris et al. 2007). The soil landscape is a significant reservoir of atmospherically-deposited $Hg$, containing many times the annual flux from the atmosphere (Mason et al. 1994). Previous estimates of the mass of $Hg$ stored in near-surface forest soils range from 0.5 to 4 $\mu$g m$^{-2}$ in near-surface organic horizons and 3 to 10 $\mu$g m$^{-2}$ in mineral horizons, although the estimate of the $Hg$ pool in mineral soils can be much higher depending on the depth that is considered (Grigal, 2003). The lifetime of $Hg$ in these compartments is strongly related to the turnover of soil organic matter ($SOM$), to which $Hg$ readily binds (Meili, 1991; Skyllberg et al. 2000). Over time, $Hg$ moves downward through the soil profile as a result of the decomposition of $SOM$ and leaching of dissolved organic matter ($DOM$) from surface organic horizons (Grigal, 2003). The redistribution of $SOM$ and the mobility of $DOM$ are integral to the movement of $Hg$ through the terrestrial environment to receiving waters. Recent studies have examined the vertical distribution of $Hg$ in the soil profile and in soil-water (Chapter 3; Akerblom et al. 2008); however, there continues to be little research concerning the horizontal spatial patterns of $Hg$ in different soil horizons and their potential relationships with topographic- and deposition-related variables (Grigal, 2003; Munthe et al. 2007). While a few recent studies have examined spatial patterns of $Hg$ and methylmercury ($MeHg$) in wetland systems (Branfireun et al. 1996; Mitchell et al. 2008), much less is known about spatial variability in upland forested catchments even though it may play an important role in the timing and magnitude of $Hg$ fluxes to aquatic ecosystems (Munthe et al. 2007).
Describing the spatial variability of Hg in upland soil landscapes is essential to furthering our understanding of the role of variable hydrologic source areas and hydrologic connectivity on the export of Hg from terrestrial systems. In boreal forested uplands, the presence and transport of Hg in soil solution is closely related to the development and mobility of DOM (Mierle and Ingram, 1991; Grigal, 2002). The potentially mobile pool of DOM (Kalbitz et al. 2000) builds up in the lower, humified organic horizon and when subsurface flow occurs the DOM is flushed and transported in runoff. However, flushing of the organic horizon does not occur everywhere and usually only part of the watershed contributes to streamflow. Hydrologic source areas vary in size depending on antecedent moisture conditions in the soil and event (e.g. snowmelt, storm) dynamics. The timing and magnitude of flow and the path that it takes through the catchment are highly dependent on topographically-driven thresholds and hydrologic connectivity through the system (Spence and Woo, 2006, Buttle et al. 2004). The extent to which hydrologic source areas overlap with areas where the potentially mobile DOM-bound Hg pool has developed may play a critical role in the magnitude and timing of terrestrial Hg export. For example, near-stream areas of the watershed or depressional areas where saturated conditions persist are generally high in SOM and have large upslope contributing areas. These two factors could combine to make them areas where Hg concentrates in the soil and is then easily mobilized to streams during high flow periods. Assessment of spatial variability in Hg, both its concentration and mass, and the stoichiometry of the Hg-SOM relationship will not only aid in the overall description of Hg dynamics in the soil landscape, but also improve our understanding of the dual roles of organic matter turnover and hydrology as they relate to Hg fluxes to receiving waters.

The potential spatial controls on Hg distribution fall into four categories that are not mutually exclusive: (i) controls related to deposition, (ii) controls related to the accumulation of SOM, (iii) controls related to the translocation of DOM-bound Hg in runoff, and (iv) controls related to the physical and biogeochemical characteristics of the soil. Regional-scale differences in Hg levels in soil are often related to differences in atmospheric deposition and proximity to point sources (e.g. Akerblom et al. 2008) and to the extent of forest cover (Driscoll et al. 2007). The type of forest cover can also affect the amount of Hg that reaches the forest floor. In the METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S.) watershed in northwestern Ontario (the same site as the present study), Graydon et al. (2008) reported higher concentrations of total Hg (THg) in throughfall and litterfall under an upland old
growth balsam fir/black spruce canopy compared to concentrations under an upland fire-
regenerated jack pine canopy, an upland deciduous red maple/birch canopy, a wetland black
spruce/alder canopy, and in open area precipitation. Based on these findings we expect that
these patterns extend into the soil profile since litterfall and throughfall are the dominant input
of Hg to the forest floor (Graydon et al. 2008). A unique aspect of the METAALICUS study
was the application of different enriched stable $Hg^{2+}$ isotopes to different watershed
compartments (lake, wetland, uplands) to distinguish newly-deposited Hg from the historically-
deposited ambient pool. In Chapter 3 it was shown that newly-deposited Hg in the
METAALICUS catchment is retained in the litter horizon. It is likely then that the distribution
of the newly-deposited Hg will be related to spatial patterns in the aerial loading of the isotope.

It has been suggested that landscape conditions that lead to differential SOM accumulation, such
as variation in landscape position, drainage, and vegetation, are likely to lead to differential Hg
accumulation (Grigal, 2003). At some forested and agricultural sites, Hg has been shown to
increase downslope in relation to an increase in poorly-drained soils and hence a build-up of
SOM (Gladkova and Malinina, 1999; Grigal et al. 1994; Dudas and Pawluk, 1977). The
suggestion that poorly-drained areas have higher levels of Hg because of the accumulation of
SOM means that in well-drained areas with equivalent Hg loadings, Hg levels should be lower
because Hg is lost in the process of SOM decomposition, presumably either via evasion to the
atmosphere or via flushing of DOM-bound Hg and subsequent transport downslope. While
some Hg is known to volatilize from soils soon after input (Schluter et al. 1995), it is more
likely that as SOM degrades or becomes solubilized, eventually contributing to the potential
DOM pool (Kalbitz et al. 2000), Hg is flushed from the pool bound to DOM. If DOM-Hg
translocation does occur, the complex will be transported towards more poorly-drained areas of
the catchment, a process which would contribute to higher Hg levels in these areas along with
SOM accumulation.

The redistribution of Hg due to translocation in the solution phase is difficult to tease apart from
SOM-related controls since Hg is transported in runoff bound mainly to DOM, whose quantity is
likely correlated to the SOM content of nearby soils. Several studies have examined spatial
patterns of solution-phase Hg and MeHg and have noticed that it tends to be higher in areas of
flow convergence and poor-drainage. Grigal et al. (1994) found higher levels of Hg in soil-
water in toeslope positions at a forested site in Minnesota, which they speculated may have
resulted from the translocation of organic-\textit{Hg} complexes by runoff; however, they also found higher soil-water \textit{Hg} at shoulder slope positions, which they could not explain. Branfireun \textit{et al.} (2005) found that a stable mercury isotope applied to an experimental plot in a boreal wetland migrated vertically downward below the water table and traveled several meters horizontally in the direction of shallow subsurface flow. Mitchell \textit{et al.} (2009) related zones of high \textit{MeHg} accumulation at peatland-upland interfaces with larger upslope contributing areas and geomorphic form. Whether or not the majority of \textit{DOM}-bound \textit{Hg} that moves laterally through upland systems is always mobile or mobile in only certain areas is unknown. If the latter is more likely, then the ability to detect relationships between \textit{Hg} and drainage conditions may be quite difficult since \textit{SOM}-related controls may cloud the relationship.

As described above, previous studies that describe the distribution of \textit{Hg} in soils have mainly focused on wetland systems or have examined regional-scale patterns related to differences in deposition. Studies examining smaller-scale patterns, for example at the scale of individual landscape features, in forested landscapes are lacking. In this study, we investigated some of the controls on the spatial distribution of \textit{spike Hg} (newly-deposited) and \textit{ambient Hg} (historically-deposited) in soil and soil-water across an upland catchment in the METAALICUS watershed. Specifically, we seek answers to four research questions that address deposition-, \textit{SOM}-, and translocation-related spatial controls:

1. Do soil organic carbon (\textit{SOC}), ambient \textit{Hg}, and spike \textit{Hg} stocks (\textit{i.e.} areal masses), and the stoichiometry of the \textit{Hg:SOC} relationship, in different soil horizons exhibit spatial patterns laterally across the catchment?

2. Are spatial patterns in \textit{SOC}, ambient \textit{Hg}, and spike \textit{Hg} stocks related to tree species type or canopy density?

3. Are spatial patterns in \textit{SOC}, ambient \textit{Hg}, and spike \textit{Hg} stocks related to the surface topography of the catchment?

4. Are spatial patterns in dissolved organic carbon (\textit{DOC}), ambient \textit{Hg}, and spike \textit{Hg} concentrations in soil-water related to the surface topography of the catchment?

Based on previous studies in the METAALICUS watershed, we hypothesized that the amounts of spike and ambient \textit{Hg} would be higher in the litter and well-humified organic soil horizons.
under old growth coniferous canopy compared to under deciduous canopy and that the amounts of $Hg$ in these horizons would be positively correlated to canopy density. We also expected that spatial patterns of spike $Hg$ would be positively correlated with the patterns of aerial loading. Lastly, we hypothesized that areas of the catchment where flow converges, such as downslope depressional areas, would contain higher amounts of $SOC$ and $Hg$ in the well-humified organic and mineral horizons and a higher concentration of $DOC$ and $Hg$ in soil-water. As detailed studies of the patterns of $Hg$ in boreal upland soil landscapes are rare we believe this study provides a valuable initial assessment that can be used to better understand controls on the timing and magnitude of $Hg$ fluxes to aquatic ecosystems.

4.2 Methods

4.2.1 Study Area

This study was conducted in the METAALICUS experimental watershed, located in the Experimental Lakes Area (ELA) in north-western Ontario (49° 40’ N, 93° 43’ W). The UP1 study area is a well-characterized 7.75 ha headwater catchment that drains into Lake 658 (L658). The UP1 catchment is south-facing with a mean slope of 12° (Fig. 4.1a) and a difference in elevation from the outflow datum to the watershed divide of 63 m. The local topography is highly variable and includes a sequence of soil-filled bedrock depressions separated by near-vertical bedrock ridges in the western half of the catchment, while the eastern half exhibits a more continuously sloping morphology. UP1 lacks a well-defined drainage network; however it is drained by a short, ephemeral stream into L658, with high flows during spring snowmelt and early summer and fall rain storms.

UP1 is underlain by unfractured, granitic bedrock and over approximately 40% of the catchment the bedrock is either exposed (16 %; mainly in the upper portion and along cliff edges) or covered with very shallow soil patches (mean depth is 23 cm). In the remaining areas, soils range in depth from 0 to 242 cm with a mean value of 54 cm. The soils are acidic brunisols, are texturally classified as silt loams, and are likely of a glaciolacustrine origin (Allan and Roulet, 1994; Brunskill and Schindler, 1971). At the surface of the soil profile, folic or sphagnic
surface organic layers dominate depending on drainage conditions. For the purposes of this study, this soil horizon is labeled ‘litter’ and represents the Live/L/Of horizons (Soil Classification Working Group, 1998), since some live mosses and grasses were included with the accumulated organic matter during sampling. Beneath the litter layer, is a relatively thin, well-humified organic horizon, which for the purposes of this study is labeled ‘organic’ and represents the F/H/Oh/Oh horizons (Soil Classification Working Group, 1998), thereby representing partly decomposed and decomposed organic matter derived from both folic (F/H) and sphagnic (Oh/Oh) sources. Beneath the organic horizon is a thin Ah mineral horizon characterized by an accumulation of organic matter expressed morphologically by a darkening of the soil. Beneath the Ah horizon is a B mineral horizon characterized by enrichment of organic matter and clay in some areas of the catchment, but mainly a relatively uniform browning due to oxidation of iron (Bm). The mineral horizons that were sampled were sandy with < 30% organic matter, and for the purposes of this study are labeled ‘mineral’. All soil horizons were classified according to The Canadian System of Soil Classification (Soil Classification Working Group, 1998).

The UP1 catchment supports forest cover of varying density. Leaf area index ranges from 0 to 9.1 (Fig. 4.1b). A 6-ha section in the northwest portion of the Lake 658 watershed, part of which falls within the UP1 catchment (Fig. 4.1c), was logged in 1978 (pers comm. K. Beaty) and now supports a deciduous forest of red maple (Acer rubrum) and paper birch (Betula papyrifera). The portion of UP1 that was not logged is dominated by mature black spruce (Picea mariana) and balsam fir (Abies balsamea). Lichens (e.g. Cladina stellaris and Peltigera aphthosa), mosses (e.g. Polytrichum piliferum and Pleurozium schreberi), and juniper (Juniperus virginiana) grow on and from shallow fractures in the bedrock outcrops. In depressional areas the organic horizon is relatively thick and the surface vegetation is dominated by Sphagnum spp. with some shrubs such as Labrador tea (Ledum groenlandicum).
Figure 4-1 Maps of the UP1 catchment showing (a) soil sampling and well locations overlaid on a map of slope, (b) leaf area index, (c) dominant canopy types, and (d) the 2006 cumulative spray release.

4.2.2 Application of Enriched Hg Isotope to the Lake 658 Uplands

At the ELA, most of the mercury is atmospheric in origin, with approximately 0.1-0.3 $\mu$g·m$^{-2}$ estimated to be derived from geologic weathering (St. Louis et al. 2001). The average wet deposition rate of Hg at the ELA is 3.6 $\mu$g·m$^{-2}$·y$^{-1}$ (Graydon et al. 2008), which is low compared to other more contaminated sites in the United States and Europe (St. Louis et al. 1995; Lindberg et al. 2007). At the ELA, inorganic Hg$^{2+}$ load to the entire L658 catchment was
experimentally increased to levels observed in more polluted regions by adding three different enriched stable $Hg^{2+}$ isotopes at an average addition rate of $20.1 \mu g \cdot m^{-2} \cdot y^{-1}$ (approx. 6 times the wet deposition rate; Harris et al. 2007). The lake, wetland and upland portions of the L658 watershed were expected to respond differently to $Hg$ loadings, hence a different isotope was added to each of these compartments by either fixed-wing aircraft and shoreline spraying (upland and wetland) and by boat during the open-water season (lake). The upland isotope ($spike^{200}Hg; 80.45\%$ enriched) was added each year (2001-2006) between mid-May and mid-August during light rain events (Fig. 4.1d). The average application rate for the uplands was $18.51 \mu g \cdot m^{-2}$ (Sandilands et al. 2008).

4.2.3 Soil and Soil-Water Sampling

A total of 528 soil samples were collected from both organic (folic and sphagnic) and mineral soil horizons at 190 sites (Fig. 4.1a) throughout the UP1 catchment in October 2007 and June 2008. The mean ± standard deviation distance between soil sampling sites was $11.3 \pm 5.9 \text{ m}$ (range: 1.4 to 36.3 m). Exact locations of sampling sites were mapped using a Trimble Geo XT handheld field computer with a built-in submeter GPS receiver. A Trimble Hurricane GPS antenna was connected to the handheld unit to increase measurement accuracy beneath the canopy. Samples were taken at approximately 5 m intervals along transects that followed topographic contours in soil-filled areas. In areas covered mainly by exposed bedrock, samples were taken from soil pockets located in shallow bedrock depressions. Every attempt was made to have the survey evenly cover the full extent of the catchment, however due to the increased presence of exposed bedrock in its northern reaches; fewer samples were collected higher in the catchment.

Samples were collected using standard clean procedures for mercury analysis (Method 1631) to avoid $Hg$ contamination. Samples were taken either with an auger (4.8 cm i.d.) equipped with a sharpened edge to cut through roots or a sharp knife. Where possible, soil samples were removed intact so that their dimensions could be measured to calculate bulk density ($\rho_b = \frac{m_{soil}}{V_{sample}}$). At each site, where possible, a sample was taken from the litter, organic and mineral horizons. In some cases (e.g. at bedrock sites) only a surface organic horizon was present and in
other cases (e.g. in deep soil-filled depressions) multiple organic horizon and mineral samples were collected.

Soil samples were air dried at room temperature (24-72 h), sieved through stainless steel mesh (2 mm), milled (A11 Analytical Grinding Mill, IKA Works Inc., U.S.A.), and stored in polypropylene containers prior to chemical analysis. A subset of samples was test dried first to ensure no significant change in Hg concentration occurred as a result of air drying. Wet weight-dry weight conversions were obtained by weighing prior to and following the drying. A subset of samples was tested first to ensure no significant change in Hg concentration occurred as a result of air drying.

Soil-water was sampled from wells between May and October 2008. All water samples were collected in the field using ultraclean trace metal protocols according to US EPA Method 1631 to prevent Hg contamination. Samples were collected from wells by means of a Teflon line attached to a peristaltic pump (GeoPump Inc, New York). The Teflon line was rinsed with 0.5 \% v/v HCl and DI water prior to each sample being collected and sample was allowed to pass through the line fully before being collected into clean PETG bottles. Immediately after sampling, bottles were double-bagged and samples were transported to the ELA laboratory for filtering and aliquots were separated for total dissolved Hg analysis (acidified to 0.5 \% v/v), and DOC analysis. Wells were located at 24 sites (Fig. 4.1a), were slotted over their entire length, and extended 0.5 to 1.5 m below the ground. Hence, well samples represent the integrated signal of water from the entire soil profile.

### 4.2.4 Chemical Analysis

For the analysis of Hg in the soil, approximately 0.5 g of dry, homogenized soil sample was digested in 30:70 HSO₄:HNO₃ and allowed to reflux on a hot plate at 250 °F until vapours lost their distinct brown colour (~4 h). Once cool, the mixture was diluted with 18.2 MΩ DI water and brominated for at least 12 h with 0.5 \% v/v BrCl. The soil digestate was then diluted to approximately 50 ml with 18.2 MΩ deionized water and all Hg was oxidized to Hg²⁺ by adding 0.5 ml of BrCl. For the analysis of Hg in soil-water, high-purity BrCl equivalent to 1\% of volume was added to samples at least 24 h prior to analysis (Hintelmann and Harris 2004). Diluted soil digestate and soil-water samples were analyzed for Hg using a cold vapour atomic
fluorescence (CVAFS) system equipped with an autosampler (Tekran 2600 automatic mercury analyzer, Tekran Inc., Toronto) connected directly to an inductively coupled plasma mass spectrometer (ICP-MS; Hewlett Packard 4500, Agilent Technologies, USA). In CVAFS analysis, $Hg^{2+}$ is converted to cold $Hg^0$ vapour using SnCl$_2$ as a reductant, concentrated using dual gold-trap amalgamation, and introduced to the detector on a stream of argon. The exhaust from the CVAFS system is then delivered to the ICP-MS, which we use to distinguish ambient $Hg$ from the experimentally applied enriched spike $^{200}Hg$ (Hintelmann and Evans 1997). To calculate concentrations of ambient $Hg$ we used an isotope that was not experimentally applied to the L658 uplands ($^{202}Hg$) as an ambient $Hg$ surrogate. All concentrations of soil $Hg$ are expressed on a mass of $Hg$ per soil dry mass basis (ng g$^{-1}$), while concentrations of $Hg$ in water are expressed on a mass per volume basis (ng L$^{-1}$).

For each batch of samples, a suite of quality control and assurance (QA/QC) measures including initial and ongoing precision recovery, analysis of blanks (equipment, field, laboratory, and method), duplicates, matrix spikes, and standard reference material (SRM) were analyzed. We used IAEA-405 estuarine sediment as the SRM for solid-phase total $Hg$ ($THg$), which had an expected dry weight $THg$ concentration of $0.81 \pm 0.04$ ng g$^{-1}$ ($n = 60$). Our mean $THg$ recovery from the SRM was within the 95 % confidence interval of $THg$ and concentrations reported. All our analyses showed good reproducibility. The limit of detection (LOD) for ambient $Hg$ in soil was 0.35 ng g$^{-1}$ and in water was 0.09 ng L$^{-1}$. The LOD for the spike $^{200}Hg$ does not depend on the absolute detection limit of the ICP-MS system, but rather on the precision with which isotope ratios can be measured and the concentration of ambient $Hg$ in the sample (Hintelmann and Evans, 1997). Using the techniques described above, to detect an applied isotope with certainty, it had to have a concentration >0.5-1.5 % of the ambient $Hg$ concentration of a sample. Our LOD for spike $^{200}Hg$ in soil ranged from 0.05 to 2.2 ng g$^{-1}$ (median = 0.70 ng g$^{-1}$) and in water ranged from 0.02 to 0.24 ng L$^{-1}$ (median = 0.07 ng L$^{-1}$). Soil and water samples with ambient and/or spike $Hg$ concentrations below detection were assigned a value of (LOD/2).

Soil samples were also analyzed for $SOM$ and $SOC$ content. $SOM$ was estimated from loss-on-ignition at 550 °C (LOI$_{550}$) at the University of Toronto and for a subset of samples $SOM$ and $SOC$ were also measured using the Walkley-Black method and combustion method, respectively, at the University of Guelph Agriculture and Food Laboratory. We calculated the SOC:SOM for this subset, which was comparable to other studies (Konen et al. 2002; Périé and
Ouimet, 2007), to the samples that were not analyzed for SOC. Water samples were also analyzed for DOC using a TOC-TN IL-550 high-temperature combustion system (Lachat Instruments Inc.) and following US EPA Method 415. In this method, water sample are pre-acidified to pH 2 and purged with oxygen prior to automated injection and combustion.

4.2.5 Topographic Analysis

The ground returns from a LiDaR (Light Detection and Ranging) survey were interpolated using inverse distance weighting to generate a sub-metre digital elevation model (DEM) of the L658 watershed. The DEM was resampled to coarser resolutions (1 m, 2.5 m, 5 m, 10 m) and several topographic and hydrologic descriptors were calculated at each resolution to determine the best resolution to use for the analysis. The 10 m resolution DEM was chosen and a smaller DEM for the UP1 catchment was extracted. The topographic index (TWI = ln(a/tanβ)) is computed from the specific upslope area (a in m; i.e. the upslope area (A in m²) per unit contour length), which is an index of the amount of water converging at a specific location; and the local slope (tanβ), which is a measure of the drainage potential of a specific location (Beven and Kirkby, 1979). TWI was calculated using the 10 m gridded elevation data and the triangular multiple flow direction algorithm for upslope area, which distributes the accumulated upslope area among all downslope directions using a weighting based on the gradients (Seibert and McGlynn, 2007).

As well, the downslope drainage index (tanα_d = d/L_d, where L_d is the distance to the nearest cell having a height of d length units (here set to 1 m) below the cell) was used as an alternative to the local slope (Hjerdt et al. 2004), as it accounts for the downslope topography and hence is a better estimate of drainage. In addition to TWI we used ln(A) as a separate predictor variable in our topographic analysis. All topographic analysis was conducted in the open-source SAGA GIS (Conrad, 2006).

In addition to the pixel-scale calculations of topographic indices, we used a hydrogeomorphologic edge detection method (Richardson et al. 2009) to partition the landscape into individual landscape element based on the downslope drainage gradient (Hjerdt et al. 2004). We then classified the elements into hydrologic response unit (HRU) types using several physiographic variables and dissolved adjacent elements with the same classification. The four types of HRUs classified in this study were bedrock ridges, bedrock uplands, midslope, and depressions. Since
bedrock ridges and uplands have relatively little soil cover, our HRU-scale spatial analysis was constrained to the midslope and depressions HRUs.

**Figure 4-2** Maps showing (a) upslope contributing area, (b) downslope gradient, (c) topographic wetness index, and (d) HRU types in the UP1 catchment. (a)-(c) are at a 10-m cell resolution.

### 4.2.6 Spatial Analysis

#### 4.2.6.1 Data Preparation

In this study we examined the spatial distributions of the following solid-phase variables: $SOC$ (kg m$^{-2}$), $ambient\ Hgs$ ($\mu g\ m^{-2}$), $spike^{200}Hgs$ ($\mu g\ m^{-2}$), $ambient\ Hgs:_SOC$ ($\mu g\ gC^{-1}$), and $spike^{200}Hgs:_SOC$ ($\mu g\ gC^{-1}$). Basic statistical analyses were performed on these variables using
Statistica version 8.0 software (StatSoft Inc.). The data were tested for normality using the Shapiro-Wilk W test and subsequently tested for skewness and kurtosis if W was significant ($p < 0.05$). Most variables were not normally distributed and were right-skewed; hence the data were natural log transformed. The independent variables that were examined are leaf area index ($LAI$), which was determined from the vegetation return of the LiDAR survey and is an index of canopy foliage density, canopy type (old growth coniferous and deciduous), which was determined from aerial photography and ground-truthed maps of the dominant tree species, the 2001-2006 cumulative $^{200}$Hg spray release ($\mu$g m$^{-2}$), and the topographic indices $A$ (m$^2$) and $TWI$. Although the dependent variables were measured at discrete sampling locations (i.e. point data), they are all spatially continuous phenomena, and hence each observation point is assumed to represent the space surrounding it. In order to have dependent data match the gridded independent data, all dependent variables were interpolated using inversed distance weighting with breaklines. Hard breaklines were used to represent major changes in slope (e.g. along bedrock ridges) which mark a significant change in surface continuity. The data interpolations took into consideration these breaklines by preventing values on opposite sides of a breakline from being considered as neighbours. The interpolated data were resampled to 1 m, 2.5 m, 5 m, and 10 m resolutions, so that the effects cell size could be examined. Ultimately, the 10 m cell size was chosen for further analysis for all variables since it most closely matched the mean distance between sample points (11.3 m). We also examined the spatial distributions of the following solution-phase variables: $DOC$ (mg L$^{-1}$), $ambient \ HgD$ (ng L$^{-1}$), $spike \ ^{200}HgD$ (ng L$^{-1}$), $ambient \ HgD:DOC$ (ng gC$^{-1}$), and $spike \ ^{200}HgD:DOC$ (ng gC$^{-1}$). The solution-phase dependent variables were not interpolated since they were measured in a limited number of locations from wells and the spatial analysis conducted on them was undertaken within the HRU framework, which is discussed in more detail in section 4.2.6.5.

### 4.2.6.2 Surface Pattern Analysis

Spatial autocorrelation in the dependent variables was assessed globally by calculating a single Moran’s $I$ statistic for the whole study area and constructing spatial correlograms using Moran’s $I$ coefficients at 10 distance classes. Moran’s $I$ has values that typically range from +1, representing complete spatial autocorrelation, to -1, representing complete negative spatial autocorrelation, and is the spatial equivalent of the correlation coefficient, $r$. A Moran’s $I$ value
of 0 is indicative of spatially independent variables. The spatial autocorrelation analysis was applied to both the original point data and the interpolated data at a 10 m grid size to illustrate the effects of interpolation on spatial autocorrelation.

4.2.6.3 Testing for Deposition-Related Spatial Controls

We examined deposition-related controls on $Hg_S$ in several ways; first, we looked for differences in LAI, and SOC, ambient $Hg_S$ and spike $^{200}Hg_S$ stocks depending on canopy type using analysis of variance (ANOVA). The traditional one-way ANOVA requires an assumption of equal variances for all groups. We tested all datasets for homogeneity of variances using either the Bartlett’s test or Levene’s test (when data were not normally distributed). When the variances were not equal across groups, and to compensate for our unbalanced design with respect to canopy type (i.e. larger $n$ for old growth canopy than for deciduous canopy), we used Welch’s variance-weighted ANOVA. This analysis was coded in R software environment for statistical computing (R Development Core Team, 2008). These comparisons directly test the hypothesis that $Hg_S$ stocks in all soil horizons are higher under old growth canopy as a result of the higher throughfall and litterfall fluxes (Graydon et al. 2008). Second, we examined the relationships between SOC, ambient $Hg_S$ and spike $^{200}Hg_S$ stocks, ambient $Hg_S$:SOC, and spike $^{200}Hg_S$:SOC in different soil horizons and LAI using spatial correlation analysis. We conducted this analysis using Spatial Analysis in Macroecology (SAM version 4.0) software, which allowed us to correct for the presence of spatial autocorrelation in our gridded data by reducing the number of degrees of freedom in the data (Dutilleul, 1993). This analysis tests the hypothesis that SOC and $Hg_S$ levels will increase with increasing LAI. Lastly, we examined the relationship between spike $^{200}Hg_S$ stocks and the cumulative areal mass of spike $^{200}Hg$ that was experimentally loaded to the uplands since 2006 using the same approach. This tests the hypothesis that the spatial variability in spike $^{200}Hg_S$ in all soil horizons will be mainly controlled by the spatial patterns of experimental loading. For all relationships the Pearson correlation coefficient was calculated, as well as the level of significance corrected for spatial autocorrelation. Normality of residuals was confirmed for all correlations.

We also conducted multiple linear regression analysis for a combination of deposition-related variables. Since canopy type was a categorical variable we coded it using dummy variables such that it could be used as a continuous variable in the multiple regressions. We used
Akaike’s Information Criterion (AIC) to select the best model for each dependent variable. All regression analyses were conducted in SAM.

4.2.6.4 Testing for SOC-Related Spatial Controls

We examined spatial controls on Hg levels related to the accumulation of SOC in several ways; first, we examined the relationship between ambient HgS and spike $^{200}$HgS stocks, and SOC stocks for each soil horizon using the spatial correlation module in SAM applied to the point data. This was done to ensure that the strong relationship between Hg and SOC reported in other studies (Grigal, 2003) also applied in our study. Second, we examined the relationships between the SOC, ambient HgS, and spike $^{200}$HgS stocks and the topographic indices also using the spatial correlation module in SAM, but applied to the 10m gridded data. These analyses test the hypothesis that if SOC accumulates downslope and there is a strong relationship between SOC and Hg, Hg will also accumulate downslope (Grigal, 2003). Based on this hypothesis, we also expected to see a downslope increase in SOC and Hg when looking at specific HRUs. Hence, we also examined differences in SOC and Hg stocks between individual depression and midslope HRUs using Welch’s variance-weighted ANOVA.

4.2.6.5 Testing for Translocation-Related Spatial Controls

We looked for evidence of downslope translocation of DOC, ambient HgD, and spike $^{200}$HgD at the HRU-scale by comparing the concentrations measured in soil-water between individual depression HRUs (DEPUPWEST, DEPWEST, DEPEAST, DEPTERMINAL, MIDSLOPE), and between HRU types (depression and midslope) using Welch’s variance-weighted ANOVA and Tukey HSD post-hoc multiple comparisons testing.
4.3 Results

4.3.1 Assessment of Spatial Patterns in Hg Data

Maps of SOC, ambient Hg$_S$, and spike$^{200}$Hg$_S$ stocks, which were generated by interpolating the original point measurements (Fig. 4.3), show some spatial patterning in all three soil horizons (Fig. 4.4). Despite less soil cover in the north and west corners of the catchment (see Fig. 4.1d) and thus fewer soil samples in these areas (see Fig. 4.1a), the interpolations were extended into these regions to give a sense of the patterns for the entire catchment.

Global Moran’s I values for the original point data were quite low and only the values for spike$^{200}$Hg$_S$ stocks in the litter horizon, ambient Hg$_S$ stocks in the organic horizon, and spike$^{200}$Hg$_S$ stocks in the mineral horizon were considered significant (p<0.05) (Table 4.1). Global Moran’s I values for the 10 m gridded data were much higher, ranging from 0.59 to 0.82, and were significant for all variables, indicating positive autocorrelation.

Spatial correlograms were generated for SOC, ambient Hg$_S$, and spike$^{200}$Hg$_S$ stocks using the original point data (Fig. 4.5). For SOC in all soil horizons, ambient Hg$_S$ in the litter and organic horizons, and spike$^{200}$Hg$_S$ in the mineral horizon, the spatial range was between 40 and 70 m, a distance at which Moran’s I values changed from positive to negative. The spatial range corresponds to the patch size in which there exists positive spatial autocorrelation. For ambient Hg$_S$ in the mineral horizon and spike$^{200}$Hg$_S$ in the litter and organic horizons the Moran’s I values oscillated along the zero value, signifying an absence of spatial autocorrelation. Spatial correlograms were also generated for the same variables using the 10-m cell resolution interpolated data (Fig. 4.6). For all variables, significant positive spatial autocorrelation was evident over a spatial range of approximately 90 to 110 m for the litter and organic soil horizons and 50 m for the mineral horizon. In most cases, Moran’s I values oscillated along the zero value at intermediate and larger distances, except for spike$^{200}$Hg$_S$ stocks in the litter and organic horizons, which showed negative spatial autocorrelation at intermediate distances and a return to positive spatial autocorrelation at larger distances.
Figure 4-3 Maps of point SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Note that the legends shown for the litter layer apply to all layers.
Figure 4-4 Maps of interpolated SOC, ambient HgS, and spike $^{200}$HgS stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Note that different ranges are used for each horizon to allow for comparison of spatial patterns.
Table 4-1 Global Moran’s I for Hg variables calculated for the original point data and 10-m resolution gridded data (interpolated). Bolded values indicate p<0.01.

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Variable</th>
<th>Global Moran’s I (point data)</th>
<th>Global Moran’s I (10m grid data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m⁻²)</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m⁻²)</td>
<td>0.08</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS (µg m⁻²)</td>
<td><strong>0.16</strong></td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC⁻¹)</td>
<td>0.10</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS:SOC (µg gC⁻¹)</td>
<td>0.09</td>
<td>0.61</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m⁻²)</td>
<td>0.03</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m⁻²)</td>
<td><strong>0.18</strong></td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS (µg m⁻²)</td>
<td>0.05</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC⁻¹)</td>
<td>0.08</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS:SOC (µg gC⁻¹)</td>
<td>0.03</td>
<td>0.69</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m⁻²)</td>
<td>0.10</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m⁻²)</td>
<td>0.02</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS (µg m⁻²)</td>
<td><strong>0.27</strong></td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC⁻¹)</td>
<td>-0.03</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Spike²⁰⁰HgS:SOC (µg gC⁻¹)</td>
<td>-0.07</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>SOC (kg m⁻²)</td>
<td>Ambient Hg₅⁺ (μg m⁻²)</td>
<td>Spike ^2⁰⁰Hg₅⁺ (μg m⁻²)</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>-----------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Litter</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>Organic</td>
<td><img src="image4.png" alt="Graph" /></td>
<td><img src="image5.png" alt="Graph" /></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>Mineral</td>
<td><img src="image7.png" alt="Graph" /></td>
<td><img src="image8.png" alt="Graph" /></td>
<td><img src="image9.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Figure 4-5** Moran's $I$ spatial correlograms for SOC, ambient Hg$_S$, and spike $^{200}$Hg$_S$ stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Correlograms were generated using point data. Note the different y-axis ranges. Circled values are statistically significant ($p<0.05$).
<table>
<thead>
<tr>
<th></th>
<th>SOC (kg m⁻²)</th>
<th>Ambient Hg₅ (µg m⁻²)</th>
<th>Spike²⁰⁰Hg₅ (µg m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Litter</strong></td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
<td><img src="image3" alt="Graph" /></td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td><img src="image4" alt="Graph" /></td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
</tr>
<tr>
<td><strong>Mineral</strong></td>
<td><img src="image7" alt="Graph" /></td>
<td><img src="image8" alt="Graph" /></td>
<td><img src="image9" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Figure 4-6** Moran’s I spatial correlograms for SOC, ambient Hg₅, and spike²⁰⁰Hg₅ stocks in the litter, organic and mineral soil horizons of the UP1 catchment. Correlograms were generated using 10-m cell resolution interpolated data. Note the different y-axis ranges. Circled values are statistically significant (p<0.05).

### 4.3.2 Deposition-Related Controls on Spatial Variability

We found no significant difference ($F_{1,\infty} = 2.70$, $p = 0.10$) in leaf area index (LAI) between the old growth- and deciduous-dominated areas of the catchment (Fig. 4.7). Using the point data, we generally found that mean SOC, ambient Hg₅, and spike²⁰⁰Hg₅ stocks were larger under old growth canopy than under deciduous canopy; however, only some of the differences were significant ($p < 0.05$; ANOVA; Fig. 4.8). SOC and ambient Hg₅ stocks were significantly higher under old growth canopy for the organic horizon, as were spike²⁰⁰Hg₅ stocks in the mineral horizon. We also looked for differences in the ratios ambient Hg₅:SOC and spike²⁰⁰Hg₅:SOC, and found that only ambient Hg₅:SOC in the mineral horizon was significantly higher under deciduous canopy than old growth canopy.
Figure 4-7 Boxplot comparing the distribution of leaf area index (LAI) in old growth and deciduous dominated areas of the UP1 catchment.

We then examined the relationship between SOC, ambient HgS, and spike $^{200}$HgS stocks, and ambient HgS:SOC and spike $^{200}$HgS:SOC and the independent variable LAI for all soil horizons. All of the correlations were very weak and only those for ambient HgS:SOC ($r=0.17$, $p=0.02$) and spike $^{200}$HgS:SOC ($r=0.16$, $p=0.01$) in the mineral horizon were significant ($p<0.05$; ANOVA) (Table 4.2). When canopy type was included in the regression model using a dummy variable, the majority of correlations improved and had slopes significantly higher than zero (Table 4.2). We also examined the relationships between the above spike variables and the 2006 cumulative spray release. Spike $^{200}$HgS stocks were positively correlated to the 2006 cumulative spray release in both the litter ($r=0.51$, $p<0.001$) and organic ($r=0.40$, $p=0.02$) soil horizons, as was the spike $^{200}$HgS:SOC relationship in the litter ($r=0.42$, $p<0.001$) and organic ($r=0.34$, $p=0.02$) horizons. The correlations for both spike variables were insignificant in the mineral horizon.
Figure 4-8 Boxplots comparing the distribution of SOC, ambient Hg$_S$ and spike $^{200}$Hg$_S$ stocks in the litter, organic and mineral soil horizons under old growth and deciduous canopies. Note the different y-axes scales for ambient Hg$_S$ and spike $^{200}$Hg$_S$ and for the different soil horizons.

Recall that we extended our interpolations of the original point data into areas of the catchment that are dominated by exposed bedrock and discontinuous, shallow soil cover. To account for the possibility that values in these parts of the catchment, which are based on relatively few sampling points, were weakening the above relationships, we repeated the regression analysis using only gridded data from the midslope and depression HRUs (see Fig. 4.2d). While the correlation coefficients for some relationships did improve, we did not find a systematic increase in $r$ when the gridded data were stratified into midslope and depression HRUs (Table A.4.1) or even when just depression HRUs were considered (Table A.4.2).
Table 4-2 Relationships between SOC, ambient HgS, spike $^{200}$HgS, ambient HgS:SOC, spike $^{200}$HgS and LAI, LAI and canopy type, the 2006 cumulative spray release, A, and TWI for the litter, organic and mineral soil horizons based on Pearson’s correlation coefficients. P values are given in brackets and bold indicates p<0.05. 10-m resolution gridded data were used (n=611).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>LAI</th>
<th>LAI and Canopy</th>
<th>2006 Cumulative Spray Release (g m$^{-2}$)</th>
<th>A (m$^2$)</th>
<th>TWI$_{d=1m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.07 (0.51)</td>
<td>0.22 (&lt;0.01)</td>
<td>-</td>
<td>0.08 (0.48)</td>
<td>0.14 (0.20)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.08 (0.40)</td>
<td>0.28 (&lt;0.01)</td>
<td>-</td>
<td>-0.14 (0.19)</td>
<td>-0.06 (0.62)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.05 (0.66)</td>
<td>0.14 (&lt;0.01)</td>
<td>0.51 (&lt;0.01)</td>
<td>0.03 (0.80)</td>
<td>0.11 (0.38)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.19 (0.10)</td>
<td>0.22 (&lt;0.01)</td>
<td>-</td>
<td>-0.23 (0.08)</td>
<td>-0.22 (0.10)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.00 (0.95)</td>
<td>0.00 (0.98)</td>
<td>0.42 (&lt;0.01)</td>
<td>-0.00 (0.97)</td>
<td>0.04 (0.71)</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.16 (0.12)</td>
<td>0.41 (&lt;0.01)</td>
<td>-</td>
<td>0.25 (0.03)</td>
<td>0.22 (0.06)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.18 (0.14)</td>
<td>0.25 (&lt;0.01)</td>
<td>-</td>
<td>0.19 (0.18)</td>
<td>0.24 (0.09)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.18 (0.06)</td>
<td>0.20 (&lt;0.01)</td>
<td>0.40 (0.02)</td>
<td>0.19 (0.09)</td>
<td>0.22 (0.04)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.03 (0.83)</td>
<td>0.33 (&lt;0.01)</td>
<td>-</td>
<td>-0.03 (0.80)</td>
<td>0.08 (0.58)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.10 (0.30)</td>
<td>0.11 (0.03)</td>
<td>0.34 (0.02)</td>
<td>0.08 (0.46)</td>
<td>0.13 (0.20)</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.04 (0.53)</td>
<td>0.18 (&lt;0.01)</td>
<td>-</td>
<td>0.11 (0.14)</td>
<td>0.11 (0.17)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.08 (0.17)</td>
<td>0.08 (0.12)</td>
<td>-</td>
<td>0.07 (0.28)</td>
<td>0.08 (0.27)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.04 (0.68)</td>
<td>0.46 (&lt;0.01)</td>
<td>0.05 (0.79)</td>
<td>0.18 (0.11)</td>
<td>0.02 (0.87)</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.17 (0.02)</td>
<td>0.34 (&lt;0.01)</td>
<td>-</td>
<td>-0.00 (0.96)</td>
<td>0.12 (0.15)</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.16 (0.01)</td>
<td>0.20 (&lt;0.01)</td>
<td>0.04 (0.61)</td>
<td>0.10 (0.14)</td>
<td>0.13 (0.07)</td>
</tr>
</tbody>
</table>

4.3.3 SOC-Related Controls on Spatial Variability

Using the point data, we examined the relationship between HgS and SOC stocks in different soil horizons (Fig. 4.9). In the litter horizon, we found positive correlations between both ambient HgS stocks ($r=0.80, p<0.01$) and spike $^{200}$HgS stocks ($r=0.61, p<0.01$), and SOC stocks. In the organic horizon, we found a positive correlation between ambient HgS and SOC stocks ($r=0.78, p<0.01$) and a weak positive correlation between spike $^{200}$HgS and SOC stocks ($r=0.44, p<0.01$). The relatively strong positive correlation between ambient HgS and SOC stocks extended into the mineral horizon ($r=0.72, p<0.01$), but the correlation between spike $^{200}$HgS and SOC stocks was very weak and the slope was not significantly different than zero ($r=-0.07, p=0.45$). All relationships exhibited some heteroscedasticity with increasing SOC.
Correlations between SOC, ambient Hgs, and spike$^{200}$Hgs stocks, and the topographic variables $A$ and TWI, were generally weak (Table 4.2). There were significant positive correlations between SOC and $A (r=0.25, p=0.03)$ and between spike$^{200}$Hgs and TWI ($r=0.22, p=0.04$) in the organic horizon; however, all other correlations were insignificant ($p>0.05$). When only data from midslope and depression HRUs (Table A.4.1) and just depression HRUs (Table A.4.2) were considered there was an increase in the number of significant correlation coefficients, but there was no systematic increase in $r$ values for all variables.

We also examined the combined effects of the deposition-related and topographic variables using multiple linear regression analysis applied to the entire gridded datasets (Table A.4.3), only the depression and midslope HRUs (Table A.4.4), and finally only the depressions HRUs (Table A.4.5). The models yielding the highest $r$ values are summarized in Table 4.3. In general, $r$ values increased when all predictor variables were considered as opposed to only individual variables. The elimination of data in bedrock-dominated areas from the multiple regression analysis further improved the $r$ values for all variables in the litter horizon, ambient Hgs in the organic horizon, and for all variables except spike$^{200}$Hgs in the mineral horizon. However, despite higher $r$ values for these variables, the Akaike weights did not necessarily follow suit.
<table>
<thead>
<tr>
<th></th>
<th>Ambient $\text{Hg}_S$ ($\mu g \text{ m}^{-2}$)</th>
<th>Spike $^{200}\text{Hg}_S$ ($\mu g \text{ m}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Litter</strong></td>
<td><img src="image1" alt="Ambient Hg$_S$ vs SOC" /></td>
<td><img src="image2" alt="Spike $^{200}\text{Hg}_S$ vs SOC" /></td>
</tr>
<tr>
<td></td>
<td>$r = 0.80, p &lt; 0.001$</td>
<td>$r = 0.61, p &lt; 0.001$</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td><img src="image3" alt="Ambient Hg$_S$ vs SOC" /></td>
<td><img src="image4" alt="Spike $^{200}\text{Hg}_S$ vs SOC" /></td>
</tr>
<tr>
<td></td>
<td>$r = 0.78, p &lt; 0.001$</td>
<td>$r = 0.44, p &lt; 0.001$</td>
</tr>
<tr>
<td><strong>Mineral</strong></td>
<td><img src="image5" alt="Ambient Hg$_S$ vs SOC" /></td>
<td><img src="image6" alt="Spike $^{200}\text{Hg}_S$ vs SOC" /></td>
</tr>
<tr>
<td></td>
<td>$r = 0.72, p &lt; 0.001$</td>
<td>$r = 0.07, p = 0.45$</td>
</tr>
</tbody>
</table>

**Figure 4-9** Relationships between ambient $\text{Hg}_S$ and spike $^{200}\text{Hg}_S$ stocks, and SOC stocks in the litter, organic, and mineral soil horizons. Note that both x and y axes vary depending on horizon.
Table 4-3 Summary of multiple linear regression model selection based on higher $r$ value. Predictor variables for SOC, ambient HgS, and ambient HgS:SOC include LAI, canopy type, and TWI. Predictor variables for spike $^{200}$HgS and spike $^{200}$HgS:SOC include LAI, canopy type, 2006 cumulative spray release, and TWI. Significant ($p<0.05$) standardized partial regression coefficients are shown before each variable. Variables are listed in order of importance.

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variables with Significant Partial Regression Coefficients</th>
<th>Multiple $r$</th>
<th>Akaike Weight*</th>
<th>HRUs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.24Canopy -0.17LAI</td>
<td>0.32</td>
<td>0.37</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.31Canopy -0.30TWI</td>
<td>0.40</td>
<td>0.49</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.45Spray -0.30Canopy -0.19TWI -0.12LAI</td>
<td>0.57</td>
<td>0.43</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.32TWI -0.20Canopy -0.27LAI</td>
<td>0.41</td>
<td>0.87</td>
<td>Mid+Dep</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.50Spray -0.23TWI -0.15Canopy</td>
<td>0.60</td>
<td>0.47</td>
<td>Dep</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.37Canopy +0.17TWI +0.09LAI</td>
<td>0.44</td>
<td>0.81</td>
<td>All</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.24TWI -0.20Canopy +0.10LAI</td>
<td>0.37</td>
<td>0.67</td>
<td>Mid+Dep</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.36Spray +0.14TWI -0.05Canopy</td>
<td>0.42</td>
<td>0.33</td>
<td>All</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.33Canopy +0.09TWI</td>
<td>0.34</td>
<td>0.59</td>
<td>All</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.34Spray +0.08Canopy +0.07TWI</td>
<td>0.36</td>
<td>0.33</td>
<td>All</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.37Canopy</td>
<td>0.39</td>
<td>0.40</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.10TWI</td>
<td>0.12</td>
<td>0.28</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>-0.46Canopy</td>
<td>0.46</td>
<td>0.28</td>
<td>All</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.67Canopy</td>
<td>0.67</td>
<td>0.36</td>
<td>Dep</td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.38Canopy -0.17Spray</td>
<td>0.40</td>
<td>0.41</td>
<td>Dep</td>
</tr>
</tbody>
</table>

* The Akaike weight is an indication of the strength of the best model given the entire set of models (i.e. all combinations of predictor variables).

In addition to examining these relationships pixel-by-pixel, we looked for evidence of a downslope increase in SOC, ambient HgS, and spike $^{200}$HgS stocks at the HRU scale. Table A.4.6 summarizes the results of the Welch’s variance-weighted ANOVA performed on the dependent variables for individual HRUs and grouped depression and midslope HRUs. Significant differences between grouped depression HRUs and the midslope HRU were found in all three soil horizons for certain variables. In the litter horizon, the mean ± SE (standard error) SOC stock in the depression HRUs ($1.28 \pm 0.09$ kg m$^{-2}$) was significantly higher than in the midslope HRU ($1.02 \pm 0.08$ kg m$^{-2}$). As well, the mean ± SE ambient HgS stock in the depression HRUs ($297.2 \pm 22.7$ µg m$^{-2}$) was significantly higher than in the midslope HRU ($234.4 \pm 17.8$ µg m$^{-2}$). In the organic horizon, the mean ± SE spike $^{200}$HgS stock in the depression HRUs ($121.6 \pm 16.4$ µg m$^{-2}$) was significantly higher than in the midslope HRU ($78.0 \pm 11.7$ µg m$^{-2}$). This was also
the case in the mineral horizon where spike$^{200}$Hg$_S$ stock in the depression HRUs (85.0 ± 9.1 µg m$^2$) was significantly higher than in the midslope HRU (55.1 ± 5.1 µg m$^2$).

Significant differences between individual depression and midslope HRUs were found for certain variables in the litter and mineral soil horizons, but none were found in the organic horizon. In the litter horizon, SOC stocks were significantly higher in DEP$_{EAST}$ (1.56 ± 0.13 kg m$^2$) than the midslope HRU (1.02 ± 0.08 kg m$^2$) (Fig. 4.10a). No significant differences in SOC stocks were found in the organic horizon (Fig. 4.10b), but in the mineral horizon SOC was significantly higher in DEP$_{TERMINAL}$ (7.83 ± 1.37 µg m$^2$) than in DEP$_{UPWEST}$ (1.03 ± 0.37 µg m$^2$) (Fig. 4.10c). Significant differences between HRUs for other variables were only found in the litter horizon (Fig. 4.11 and 4.12; Table A.4.6). In litter, ambient Hg$_S$ stocks were significantly higher in DEP$_{EAST}$ (375.5 ± 35.1 µg m$^2$) than both DEP$_{TERMINAL}$ (237.9 ± 35.2 µg m$^2$) and the midslope (234.4 ± 17.8 µg m$^2$) (Fig. 4.11a). Spike$^{200}$Hg$_S$ stocks were significantly higher in DEP$_{EAST}$ (47.1 ± 6.0 µg m$^2$) than in DEP$_{TERMINAL}$ (24.0 ± 5.4 µg m$^2$), in the midslope (26.7 ± 3.9 µg m$^2$), and in DEP$_{WEST}$ (17.5 ± 5.4 µg m$^2$) (Fig. 4.11a). These differences were also evident when spike$^{200}$Hg$_S$ was normalized to SOC, such that spike$^{200}$Hg$_S$:SOC was significantly higher in DEP$_{EAST}$ (0.030 ± 0.003 µg gC$^{-1}$) than in DEP$_{TERMINAL}$ (0.018 ± 0.002 µg gC$^{-1}$), in the midslope (0.025 ± 0.003 µg gC$^{-1}$), and in DEP$_{WEST}$ (0.015 ± 0.002 µg gC$^{-1}$) (Fig. 4.12a).
Figure 4-10 Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of soil organic carbon (SOC; kg m\(^{-2}\)) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.
Figure 4-11 Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of ambient HgS and spike $^{200}\text{Hg}$S ($\mu$g m$^{-2}$) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.
Figure 4-12: Boxplots showing the median (bar), interquartile range (25th to 75th percentiles; box), 10th to 90th percentiles (whisker), and outliers (circles) of ambient Hg$_{S}$:SOC and spike $^{200}$Hg$_{S}$:SOC ($\mu$g gC$^{-1}$) for individual depression and midslope HRUs for (a) the litter horizon, (b) the organic horizon, and (c) the mineral horizon.
4.3.4 Spatial Variability due to Translocation in Soil-Water

Differences between individual and grouped HRUs were also examined for Hg-related properties in soil-water (Fig. 4.13; Table A.4.7). We found no significant differences in DOC, ambient HgD and spike $^{200}$HgD concentrations, or ambient HgD:DOC and spike $^{200}$HgD:DOC for the grouped comparison of depressions and midslope. The only significant difference we found for individual HRUs was a higher concentration of ambient HgD in DEPEAST (25.7 ± 6.5 ng L$^{-1}$) than the midslope (11.1 ± 0.9 ng L$^{-1}$; Fig. 4.13b).
Figure 4-13 HRU boxplots for (a) DOC concentrations, (b) ambient $Hg_D$ and spike $^{200}Hg_D$ concentrations, and (c) ambient $Hg_D$:DOC and spike $Hg_D$:DOC in individual depression and midslope HRUs.
4.4 Discussion

4.4.1 Do SOC, ambient Hg, and spike Hg stocks, and the stoichiometry of the Hg:SOC relationship, in different soil horizons exhibit spatial patterns across the catchment?

In this study, we expected that SOC, ambient Hgs, and spike Hgs stocks would exhibit some spatial pattern as a result of deposition- and topographic-related controls. Based on a visual inspection of the maps of the interpolated data for each soil horizon (Fig. 4.4), we can see that for all variables and soil horizons, regions with higher SOC, ambient Hgs, and spike Hgs stocks are clearly visible. While we are confident in the patterns we see lower in the catchment and more specifically, in depression and midslope HRUs where the majority of point samples were taken (Fig. 4.2), we are less confident in the spatial patterns generated from the interpolation in the northern reaches of the catchment in areas dominated by exposed bedrock. These areas are characterized by discontinuous soil cover, and fewer and more widely-spaced samples were taken, hence interpolated values may not be as accurate as areas with higher sample density.

The low global Moran’s I values for all variables using point data (Table 4.1) are indicative of little spatial autocorrelation across the catchment; however, upon inspection of the Moran’s I spatial correlograms in Fig. 4.5, we see that some significant positive spatial autocorrelation occurs for certain variables and layers in the spatial range of 40 to 70 m. The mean distances between our sampling points was 11.3 m, thus we expect that in depression and midslope areas we have collected our data at the appropriate spatial scale. The global Moran’s I values for all variables and layers using the 10-m resolution interpolated data were all significant and relatively high, indicating positive spatial autocorrelation in this dataset (Table 4.1). The spatial correlograms for the gridded data indicated positive spatial autocorrelation over a spatial range nearly twice the size of point correlograms. This difference between the point and grid data was expected, and consequently, in addition to an examination of the relationships between the dependent variables and catchment characteristics using the interpolated data for the entire catchment, we also examined these relationships for data constrained to depression and midslope HRUs combined, and just the depression HRUs. In future studies, spatial autocorrelation in the dependent variables should also be assessed locally by mapping a Moran’s
I local indicator of spatial association (LISA). In this way, ‘hot’ or ‘cool’ spots in the spatial patterns can be distinguished from outliers.

4.4.2 Are spatial patterns in SOC, ambient Hg, and spike Hg stocks related to tree species type or canopy density?

Canopy density, as represented by leaf area index, was not well correlated to SOC, ambient HgS, or spike \(^{200}\text{Hg}\) stocks in any soil horizon in the UP1 catchment, and the relationships did not improve substantially when ambient HgS and spike \(^{200}\text{Hg}\) stocks were normalized to SOC content. However, our ANOVA and multiple linear regression results suggest an important dependence of all variables on tree species type. We generally found higher mean values of SOC, ambient HgS, and spike \(^{200}\text{Hg}\) stocks in the portion of the catchment dominated by old growth coniferous canopy; however, the fact that these differences were only significant for SOC and ambient HgS in the organic horizon and spike \(^{200}\text{Hg}\) in the mineral horizon was surprising. Based on the fact that higher loadings of Hg in litterfall and throughfall have been recorded beneath old growth coniferous canopy compared to deciduous canopy (Graydon et al. 2008), we expected the differences to extend into the soil profile and to be most pronounced in the litter horizon. This expectation was also founded on the findings of St. Louis et al. (2001) who reported the highest \(^{2}\text{THg}\) stocks under old growth coniferous (mainly Jack Pine) stands, as well as the highest \(^{2}\text{THg}\) concentrations in litter composed of conifer needles, in the same region as the present study. Since we did not find a significant difference between the mean LAI of the deciduous area and of the coniferous area, a possible explanation for why we did not see the difference we expected in the litter layer is higher litterfall mass fluxes under deciduous compared to coniferous canopy, which would counteract higher Hg concentrations in conifer needles.

As expected, we found relatively strong, positive correlations between the spatial patterns of spike \(^{200}\text{Hg}\) stocks and the 2001-2006 cumulative \(^{200}\text{Hg spray release}\). The correlations were strongest in the litter horizon and became progressively weaker with depth. Similar to the findings reported in Chapter 3, these results reflect the fact that relatively small amounts of spike \(^{200}\text{Hg}\) were found in the organic and mineral horizons.
4.4.3 Is there a downslope increase in SOC and Hg in the soil profile?

The catena concept of increasing SOC downslope was not strongly evident from our regression analysis between SOC stocks and \( A \), or \( TWI \). Although we did find a significant increase in SOC in the organic horizon with increasing upslope contributing area, the relationship was weak and was not evident in the litter or mineral horizons. The catena concept of increasing SOC downslope was also not strongly evident from our results comparing mean values in grouped and individual depression and midslope HRUs. While we did find higher SOC stocks in depressions in the litter layer, the results appear to have been driven by higher values in just DEPEAST. Our expectation was that the highest SOC would be measured in DEPTERMINAL, due to the presence of poorly-drained soils and a water table at or near the surface most of the year. We also expected that the other depression HRUs would have higher SOC than the midslope area for the same reason; but that their SOC content would decrease the further upslope they were located in relation to contributing area size. Although we did find that SOC was generally lower in DEPUWEST than depression HRUs further downslope, the difference was only significant in comparison to DEPTERMINAL in the mineral horizon.

As expected, we found strong correlations between ambient \( Hg_S \) and SOC stocks in all soil horizons, which are consistent with our ambient \( Hg_S \) concentration findings in Chapter 3 and other studies that have examined this relationship (Grigal, 2003). The weaker, yet significant, correlations between spike \( ^{200}Hg_S \) stocks and SOC stocks in the litter and organic horizon were also expected based on our findings in Chapter 3 that the spike \( ^{200}Hg \) had penetrated into these horizons. The very weak relationship in the mineral soil suggests that the experimentally-applied \( ^{200}Hg \) has not been in the system long enough to become equilibrated in the soil profile like the ambient \( Hg_S \).

Based on the above findings and the absence of a downslope increase in SOC stocks we doubted that we would measure a downslope increase in \( Hg_S \) stocks as originally hypothesized. These doubts were confirmed by the weak and mostly insignificant correlations between all \( Hg_S \) variables and \( A \), or \( TWI \). However, in light of the lower SOC stocks found in DEPUWEST relative to the other HRUs and the strong relationship between \( Hg_S \) and SOC described above, it was expected that ambient \( Hg_S \) and spike \( ^{200}Hg_S \) stocks would also be lowest in DEPUWEST. DEPUWEST is dominated by a red maple/birch canopy and a previous study in the UP1 catchment found that \( THg \) deposition to the forest floor via throughfall and litterfall in areas
with deciduous canopy were nearly half the amount measured under old growth canopy (Graydon et al. 2008). Surprisingly, DEP_{UPWEST} did not have significantly lower ambient \( Hg_S \) or spike \( ^{200}Hg_S \) stocks, regardless of whether or not they were normalized to SOC. In fact, there were no significant differences in any of the \( Hg_S \) variables between individual HRUs in either the organic or mineral horizons. However, we did find significantly higher ambient \( Hg_S \) and spike \( ^{200}Hg_S \) stocks in DEP_{EAST} relative to several other HRUs. DEP_{EAST} is characterized by a low mean \( LAI \), more large conifers, and more fallen trees, compared to the other HRUs. Previous studies on the spatial distribution of SOC stocks (e.g. Spielvogel et al. 2008) have reported strong relationships with the spatial distribution of fallen logs. Given the strong relationship between SOC and \( Hg_S \), this may be a partial explanation for the higher ambient \( Hg_S \) and spike \( Hg_S \) stocks in the litter layer in DEP_{EAST}. Duplicate wood samples from fallen logs in DEP_{EAST} were taken during the soil survey for this study and were found to have relatively high concentrations of ambient \( Hg_S \) (\( \sim 33 \, \mu g \, kg^{-1} \)) compared to values reported in the literature (\( \sim 1 \) to \( 13 \, \mu g \, kg^{-1} \); Grigal, 2003). Future studies would benefit from a small-scale sampling design focused on proximity to large fallen logs to ascertain whether or not the spatial distribution of \( Hg_S \) is related to the distribution of large deadfall.

Our findings related to the distribution of soil-bound ambient and spike \( Hg_S \) suggest that the topographic controls found in other studies are not applicable in the topographically-complex Canadian Shield landscape. Discontinuous soil cover and threshold-driven hydrologic connectivity are typical characteristics of this landscape and likely favour the vertical movement of SOC and \( Hg_S \) through the soil profile, as opposed to lateral translocation downslope due to erosion and hydrologic transport.

### 4.4.4 Do the concentrations of DOC, ambient Hg, and spike Hg in soil-water increase downslope?

Given the limited number of widely-spaced wells from which water samples were obtained, our investigation into a potential downslope increase in the concentrations of DOC, ambient \( Hg_D \), and spike \( ^{200}Hg_D \) was conducted at the HRU-scale. We initially expected that we would find higher concentrations of all variables in depression soil-water relative to midslope soil-water and that concentration in the depressions would increase downslope as more decomposed organic matter was mobilized. However, our results showed no significant differences between
the two HRU types. We did generally find that mean concentrations in \( \text{DEP}_{\text{EAST}} \) were higher than the other HRUs, but the difference was only significant between \( \text{DEP}_{\text{EAST}} \) and the midslope HRU for \( \text{ambient } Hg_D \). Considering that \( \text{DEP}_{\text{EAST}} \) also had significantly higher \( \text{SOC} \) and \( \text{ambient } Hg_S \) in the litter layer, our soil-water results are not surprising. Overall, our results give no indication of a downslope increase in \( \text{DOC} \) or \( Hg_D \) concentrations in depression soil-water. There is the possibility that a downslope dilution effect is taking place in the catchment, but it seems more likely that the spatial distribution of \( \text{DOC} \) and \( Hg_D \) concentrations in soil-water are related to the distributions of \( \text{SOC} \) and \( Hg_S \) in the soil profile, particularly in the well-humified organic horizon.

4.5 Conclusion

At our boreal Canadian Shield catchment, \( \text{SOC} \), \( \text{ambient } Hg_S \), and \( \text{spike }^{200}Hg_S \) stocks are not randomly distributed across the landscape. However, the spatial variability in these stocks cannot be systematically attributed to spatial patterns in topography or drainage conditions. Areas of the catchment with larger upslope contributing area and/or higher topographic wetness index did not necessarily contain the largest stocks, regardless of whether the relationships were examined at a 10-m pixel scale or at the scale of pre-determined hydrologic response units. In our topographically complex catchment, canopy type was the strongest predictor of \( \text{SOC} \) and \( \text{ambient } Hg_S \) distributions at the 10-m pixel scale, and a combination of canopy type and mean \( \text{LAI} \) were the most determining factors at the HRU scale. In general, mean \( \text{SOC} \), \( \text{ambient } Hg_S \) and \( \text{spike }^{200}Hg_S \) stocks were higher under old growth coniferous canopy; however, the statistical significance of the differences depended on the soil horizon. At the HRU-scale, we found that the depression with the smallest \( \text{LAI} \) and largest amount of deadfall had the highest \( \text{SOC} \), \( \text{ambient } Hg_S \) and \( \text{spike }^{200}Hg_S \) stocks in the litter layer. However, the strongest determining factor for the \( \text{spike }^{200}Hg_S \) distribution in the litter and organic horizons was the spatial distribution of the \( 2001-2006 \) cumulative \( ^{200}Hg \) spray release.

Future studies are needed to refine our understanding of the spatial controls on soil \( Hg \) stocks in upland systems at multiple scales, for example, at smaller scales of hummocks and hollows or vegetation features such as fallen trees, and at larger landscape-scales where comparisons between catchments with different topographic forms can be made. This multi-scale framework
should be designed *a priori* based on the spatial patterns of the catchment characteristics of interest. Focus also needs to be placed on evaluating the relative importance of vertical and horizontal $Hg$ fluxes in soil-water across different landscape features. We expect that in systems that are less topographically-complex and that contain more continuous soil cover, the spatial distribution of $Hg$ in the soil landscape will be more strongly related to drainage conditions. Knowing the average rate of $DOC$-bound $Hg$ movement through different soil horizons in different topographic settings would help inform watershed $Hg$ export models.
Chapter 5
Antecedent Moisture Conditions Control Mercury and Dissolved Organic Carbon Concentration-Discharge Dynamics in a Boreal Shield Catchment

5.1 Introduction

Mercury-contaminated fisheries are a global toxicological concern and efforts are underway to reduce inorganic mercury (Hg) inputs and mobility in the environment in order to reduce fish Hg concentrations (Munthe et al. 2007). Terrestrial upland environments have been recognized as a dominant source of Hg to aquatic ecosystems, such as wetlands and lakes, in many watersheds (Harris et al. 2007; Grigal, 2002). A lack of knowledge about the dynamics of Hg release from soil landscapes is a major source of uncertainty in quantitative predictions of the timing and magnitude of the effects of a change in Hg load on Hg levels in fish (Munthe et al. 2007). The timing and magnitude of forested upland Hg contributions to aquatic ecosystems depend on many processes; in general, these processes include: (i) the deposition of atmospheric Hg onto vegetation and the forest floor, (ii) the loss of previously-deposited Hg back to the atmosphere, (iii) the retention of Hg bound to organic matter (OM) in vegetation and soil, (iv) the vertical redistribution of Hg in the soil profile as soil organic matter (SOM) decomposes, and (v) the lateral redistribution and export of Hg bound to particulate organic matter (POM) and/or dissolved organic matter (DOM) in runoff. As a result of the affinity of Hg to bind to reduced sulfur sites within natural OM (Skyllberg et al. 2000; Haitzer et al. 2003), the development of a potentially-mobile Hg pool in the soil landscape is strongly related to the turnover of SOM, and specifically the development of a potentially-mobile DOM pool (Kalbitz et al. 2000; Smith-Downey et al. 2010). Potential DOM exists as part of the SOM pool and is replenished by inputs of plant litter, root exudates, SOM, and microbial biomass (Kalbitz et al. 2000). The hydrologic transport of Hg through a catchment is closely coupled with the movement of both dissolved and particulate OM (Schuster et al. 2008; Shanley et al. 2008). DOM-bound Hg, which is of greater importance in this study, is transported to receiving waters when flow is generated in areas where the potentially-mobile DOM pool has accumulated and hydrological
connectivity exists between these areas and the catchment outlet. Hence, the magnitude and timing of $Hg$ fluxes from uplands should be dependent on both the biogeochemical processes that control the build-up of the potentially-mobile $DOM$-bound $Hg$ pool and the hydrological processes that deliver this pool to receiving waters.

Elevated fluxes of $Hg$ and $DOM$ usually occur episodically during high flow events such as snowmelt and summer storms (Scherbatskoy et al. 1998; Schuster et al. 2008; Shanley et al. 2008; Bushey et al. 2008; Dittman et al. 2010; Schelker et al. 2011). In areas with relatively high amounts of snowfall, the spring snowmelt period often represents the largest portion of annual water and solute fluxes; however, some summer storms can make up a large portion of the annual $Hg$ and $DOC$ export (e.g. Babiarz et al. 1998; Shanley et al. 2008). In the same catchment as the present study, Harris et al. (2007) found that $\sim 54 \%$ of the annual $THg$ loading to the lake was from the uplands, which was more than two times the annual loadings from direct atmospheric deposition to the lake. These findings highlight the importance of uplands as the dominant inorganic $Hg$ source to the lake; however, little is known about the hydrological and biogeochemical processes that control the timing and magnitude of upland $Hg$ fluxes (Krabbenhoft et al. 2006; Munthe et al. 2007).

Analyses of concentration-discharge ($C-Q$) dynamics are a useful way to assess the balance between hydrological and biogeochemical controls on streamwater solute concentrations (Huntington et al. 1994). In general, a decrease in concentration with an increase in discharge suggests that dilution is occurring, whereas an increase in concentration near peak discharge suggests that flushing is occurring (Ocampo et al. 2006). Flushing is usually referred to as a hydrological process; however, Burns (2005) highlights the need to also consider the biogeochemical processes that act to accumulate solutes in catchments. In the case of $Hg$, therefore, it is important to consider not only the hydrological processes by which $DOM$-bound $Hg$ is mobilized in the soil landscape and transported to the stream, but also the biogeochemical processes that result in $DOM$-bound $Hg$ accumulating in the soil landscape. A short-term shift in the $Hg$ $C-Q$ relationship (i.e. event-scale) away from the long-term $Hg$ $C-Q$ relationship (i.e. seasonal, annual, or multi-annual) would suggest that the size of the potentially-mobile $DOM$-bound $Hg$ pool has changed as a result of biogeochemical processes. Hysteresis in the $Hg$ $C-Q$ relationship at the event-scale may indicate that different components of flow (e.g. throughfall, groundwater, shallow subsurface flow) with different concentrations contribute at different
times over the hydrograph. Hysteresis could also suggest that different parts of the landscape (e.g. depressions, midslope) are flushing at different times over the hydrograph as a result of variable source areas and the development of hydrologic connectivity.

Much of the previous research on $Hg$ export from uplands has taken place in boreal catchments (e.g. Bishop et al. 1995a, b; St. Louis et al. 1996; Branfireun et al. 1996; Allan et al. 2001) and catchments in the northeastern USA (e.g. Schuster et al. 2008; Bushey et al. 2008; Dittman et al. 2010; Schelker et al. 2011). Previous boreal upland $Hg$ research has focused on methylmercury ($MeHg$) production and transport in catchments containing significant wetlands. However, at the Experimental Lakes Area in northwestern Ontario, Allan et al. (2001) also examined $Hg$ and total organic carbon ($TOC$) dynamics for two summer storms in an upland catchment dominated by exposed bedrock and soil-filled depressions. They found that $Hg$ concentrations generally increased with discharge and speculated that temporal variations in concentration were a result of changes in the proportions of runoff coming from different catchment components. Common themes amongst the studies from the northeastern USA were examinations of $THg$ and/or $MeHg$ concentration-discharge dynamics and $THg$-$DOC$ and $MeHg$-$DOC$ dynamics during periods of high flow, such as snowmelt and summer storms.

Schuster et al. (2008) found that an important $Hg$ transport mechanism from their catchment in Vermont, USA, was summer storms, especially those preceded by a prolonged dry period. They found that $THg$ concentrations rose very rapidly prior to peak discharge and that the total flux for the storm was about 10% greater than the total flux during peak snowmelt for an equivalent time period. Similarly, in the Adirondack region of New York, USA, Bushey et al. (2008) found that $THg$ concentration peaked prior to the peak in discharge, but that $DOC$ concentration peaked later. They reported clockwise and counter-clockwise hysteresis in event-scale $THg$ and $DOC$ concentration-discharge relationships, respectively, which they attributed to an initial rapid delivery of throughfall $THg$ followed by inputs of $THg$ and $DOC$ from the soil pool. They concluded that event-scale $THg$ fluxes from the forested catchment were controlled by discharge, but that $THg$ concentrations had a weak, insignificant relationship with discharge and $DOC$ concentration. However, in the same watershed, Dittman et al. (2010) found that filtered $THg$ concentration was positively linearly correlated to discharge, as well as to $DOC$. The difference between these two studies may be the temporal scale at which measurements were taken. Bushey et al. (2008) examined these relationships over individual events, whereas Dittman et al. (2010) pooled data that were collected over a 24 month period. Dittman et al.
(2010) also found seasonal differences in both *OM* and *THg* concentrations per unit discharge, with greater regression slopes during the growing season. They attributed these differences to higher temperatures during the growing season driving biological activity, increasing decomposition of *OM*, and increasing the solubility of *DOC*. In a snowmelt study in the same watershed, Demers et al. (2010) used end-member mixing analysis (EMMA) to show that shifts in hydrologic source areas and flow pathways that influence the source and quality of *DOC* influenced the transport of *Hg* from uplands to receiving waters. Similarly, Schelker et al. (2011) were able to explain a large part of the variation of *THg* concentrations from a headwater catchment in the Adirondack Mountains in New York, USA with the dynamics of TOPMODEL-simulated saturated area and soil storage deficits. Interestingly, they found that *THg-DOC* dynamics varied seasonally suggesting that variable hydrologic conditions result in variable mobilization behaviour.

The findings of the above studies highlight the importance of including detailed hydrologic processes over a range of hydroclimatic conditions in predictions of *THg* export from forested uplands. To the best of our knowledge, this has not been done for boreal Shield regions where discontinuous soil cover and sporadic hydrologic connectivity complicate *Hg* export models. Previous studies have predicted that there will be a decrease in *DOC* inputs to freshwater aquatic ecosystems in boreal regions under warmer and drier climatic conditions due to a decrease in runoff (Schindler, 2009; Schindler and Smol, 2006). By association, these predictions should also apply to *Hg* inputs; however, a lack of knowledge on the relative importance of hydrological controls versus biogeochemical controls on *DOM* and *Hg* fluxes contributes uncertainty to our predictions. Despite the important findings of previous *Hg* C-Q studies, there remains a lack of knowledge on the role of antecedent moisture conditions (AMCs) on the *Hg* C-Q relationship, especially in the boreal ecozone. Consequently, in this study we investigated the role of hydrological controls on the mobilization of *THg* and *DOC* during elevated runoff events in a topographically-complex boreal Shield headwater catchment. Specifically, we sought answers to three research questions:

1. Are *THg*, *200Hg*, and *DOC* C-Q dynamics dependent on event characteristics and/or AMCs?

2. Are *THg-DOC* dynamics dependent on event characteristics and/or AMCs?
3. Do differences in water sources and/or flow pathways account for differences in C-Q or Hg-DOC dynamics?

In addition to addressing the above questions, we discuss the implications of our results for conceptual models of boreal Shield upland Hg export and for predictions of future Hg export in a warmer, drier climate.

5.2 Methods

5.2.1 Site Description

This study was conducted in the 7.75 ha UP1 catchment of the Lake 658 watershed, located in the Experimental Lakes Area (ELA) in north-western Ontario (49° 40’N, 93° 43’W) (Fig. 5.1). The climate, topography, hydrology, soil, and vegetation characteristics of the catchment are described in detail in Section 2.2 of this thesis.

5.2.2 Study Period and Event Selection

Discharge from the UP1 catchment, precipitation, and hydrometric measurements presented in this paper were collected between 1 October 2007 (Day of Year (DOY) 274) and 26 October 2007 (DOY 299), and 24 April 2008 (DOY 115) and 27 October 2008 (DOY 301). Although most hydrological measurements began prior to and continued after this period as described in Section 2.3.1, it was during this period that intensive water sampling from the catchment outlet and the hydrometric network occurred.

As described in Section 2.3.5 of this thesis, streamflow hydrographs were classified into event and non-event periods automatically using the USGS HYSEP minimum flow routine (Sloto and Crouse, 1996) executed in R software for statistical computing. Events chosen for further analysis in this paper were those identified by the graphical separations that were also sampled over all or a portion of the event period.
5.2.3 Hydrometric Measurements

A detailed description of the distributed network of hydrometric instrumentation used in this study is given in Section 2.3.4 of this thesis. The location of the weir where catchment discharge was measured is marked at the southeast tip of the catchment in Figure 5.1, as well as the location of a midslope weir, the locations of all hydrometric stations (well, piezometer nest, soil moisture probe), and the locations of all shallow zero-tension lysimeters. Also marked on Figure 5.1 are the location of the ephemeral stream that drains the UP1 catchment and the locations of flow pathways that were estimated using a high-resolution digital elevation model derived from a Light Detection and Ranging (LiDaR) survey.
5.2.4 Calculating Indices of Antecedent Moisture Conditions

Two different indices of antecedent moisture conditions (AMCs) were calculated for this study, antecedent precipitation ($AP_x$) and antecedent mean storage in the bottommost depression in the catchment, DEPTerminAl (see Fig. 2.2f), ($AS_x$), where $x$ is the antecedent number of days over which precipitation was summed and storage was averaged. $AP_x$ and $AS_x$ were calculated for $x = 7$ days, $x = 14$ days, and $x = 28$ days. The calculation of water storage in DEPTerminAl is described in detail in Section 2.3.6 of this thesis.

5.2.5 Water Sample Collection and Chemical Analysis

In addition to the hydrometric methods presented above and in Chapter 2, hydrochemical methods were used to estimate water age, sources areas, and flow pathways in the catchment. Water samples were also collected for $THg$, $^{200}Hg$, and $DOC$ analyses. Snow samples were collected throughout the catchment ($n=38$) and snowmelt samples ($n=28$) were collected at the UP1 outlet weir in late April 2008 before the weir was completely unfrozen and instrumentation was installed for the season. Rain was sampled from a standard rain gauge located in an open area of the UP1 catchment and/or at the ELA field station located approximately 7.5 km south of the catchment during and immediately after an event. Over the study period, streamwater ($n=163$) was collected with greater frequency during high flow periods (Fig. 5.2), with the overall sampling schedule depending to a large degree on logistical factors (e.g. unpredictability of high flows, availability of personnel, ability to safely travel to site by all-terrain vehicle or boat during inclement weather). Well ($n=75$), piezometer ($n=67$), and lysimeter ($n=256$) samples were collected less frequently, but still cover the same range of flow conditions as the streamwater samples (not shown in Fig. 5.2). Higher flow periods were targeted since previous studies have shown that solute (e.g. $Hg$ and $DOC$) concentrations usually increase with increasing discharge and flow through shallow organic soils (e.g. Babiarz et al. 1998; Schuster et al. 2008; Shanley et al. 2008).
Figure 5-2 Flow duration curve for discharge from the UP1 catchment outlet during the study period (note that early snowmelt is not included). Points on the line represent the streamwater samples collected during the study period ($n=163$). Note the log$_{10}$ scale on the y-axis.

All water samples were filtered (0.7 μm), preserved, and analyzed for THg and the experimentally-applied $^{200}\text{Hg}$ isotope. Samples collected for Hg analyses were done so using clean protocols and standard EPA methods. Filtered splits were taken before acidification and analyzed for DOC, ultraviolet absorbance at 254 nm ($\text{UV}_{254}$), and major ions. Previous studies at the ELA have found that DOC accounts for >94% of the total carbon export in forested upland systems (Allan et al. 1993). In this study, the filters from a subset of samples collected over a range of flow conditions were analyzed for particulate-bound THg and $^{200}\text{Hg}$. For all samples, particulate THg concentrations were <5% of dissolved concentrations and particulate $^{200}\text{Hg}$ concentrations were below detection limit. Details of the application of the enriched Hg isotope to the Lake 658 uplands, soil-water and catchment runoff sampling, and chemical analyses for THg, $^{200}\text{Hg}$, DOC, and $\text{UV}_{254}$ are given in Sections 3.2.2, 3.2.5, and 3.2.6, respectively. Concentrations (mg/L) of Chloride ($\text{Cl}^{-}$), Nitrate ($\text{NO}_3^{-}$), Phosphate ($\text{PO}_4^{3-}$), Sulfate ($\text{SO}_4^{2-}$), Sodium ($\text{Na}^{+}$), Ammonium ($\text{NH}_4^{+}$), Potassium ($\text{K}^{+}$), Magnesium ($\text{Mg}^{2+}$), and Calcium ($\text{Ca}^{2+}$) were determined using a Dionex® ICS-1600 ion chromatography system at the University of Toronto Mississauga Ecohydrology Laboratory. The analytical detection limits for $\text{Cl}^{-}$, $\text{NO}_3^{-}$, $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{Na}^{+}$, $\text{NH}_4^{+}$, $\text{K}^{+}$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}$ were 0.05 mg/L, 0.08 mg/L, 0.08
mg/L, 0.07 mg/L, 0.04 mg/L, 0.02 mg/L, 0.03 mg/L, 0.07 mg/L, and 0.06 mg/L, respectively. The ion measurements were used with DOC to assess the relative contributions of different source areas and flow pathways in the catchment.

Water samples were also collected for stable water isotope analysis to assess the relative contributions of event and pre-event water to runoff at the UP1 outlet. Only a subset (n=300) of the total number of samples were analyzed for water isotopes. Water samples for isotope analysis were collected unfiltered and unpreserved in clean 20 mL borosilicate glass vials with air displacement caps and stored at room temperature. Samples were analyzed for 18-oxygen ($^{18}\text{O}$) at the Catchment Research Facility in the Department of Biology at the University of Western Ontario using a Los Gatos® liquid water isotope analyzer. Isotopic composition was reported as the relative deviation of the isotopic ratio ($^{18}\text{O}/^{16}\text{O}$) from that of Standard Mean Ocean Water (SMOW) ($\delta^{18}\text{O}$) in units per mil (‰). Analytical accuracy of $\delta^{18}\text{O}$ values was ±0.1‰.

5.2.6 Data Analysis

5.2.6.1 Estimating Event-Scale Solute Fluxes

In order to calculate $\text{THg}$, $^{200}\text{Hg}$ and DOC fluxes on an hourly basis, it was necessary to model the concentrations of these solutes for the hours between sample collections. To do this, missing concentrations were modeled based on a linear relationship between concentration and discharge for all samples obtained at the UP1 stream outlet. Residuals values were calculated as the difference between the predicted and observed concentrations. Linear interpolation was used to fill in missing residual values and then the modeled and residual concentration values were added together to obtain a final concentration. This composite method (Aulenbach and Hooper, 2006; Huntington et al. 1994) incorporates the portion of the concentration that is unexplained by the discharge regression model and represents a combination of unexplained shifts in the C-Q relationship due to biogeochemical and hydrological processes that are not accounted for, changes in the C-Q relationship over time, and measurement errors (Aulenbach
and Hooper, 2006). The final modeled concentrations were then multiplied by discharge at the catchment outlet to obtain hourly fluxes and were summed over the duration of the event to obtain a total event flux.

### 5.2.6.2 2-Component and 3-Component Mixing Model Analysis

A two-component mixing model was used to separate UP1 outlet runoff into event and pre-event components according to the following equations,

\[ C_t Q_t = C_p Q_p + C_e Q_e \]  \hspace{1cm} (5.1)

\[ X = \frac{(C_t - C_e)}{(C_p - C_e)} \]  \hspace{1cm} (5.2)

where \( C \) is the isotope concentration; \( Q \) is discharge; the subscripts \( t, p, \) and \( e \) represent total outlet runoff, the pre-event component of runoff, and the event component of runoff, respectively; and \( X \) is the pre-event fraction of streamflow. The assumptions related to this type of mixing analysis, outlined in Buttle (1994), were taken into consideration.

Three-component hydrograph separations with two tracers were used to calculate the relative contributions of event water, shallow soil-water from the organic soil horizon, and deeper soil-water from the mineral soil horizon to stream discharge according to the following equations,

\[ C_t Q_t = C_1 Q_1 + C_2 Q_2 + C_3 Q_3 \]  \hspace{1cm} (5.3)

\[ Q_1 = \frac{(C_t^1 - C_1^1) - (C_2^1 - C_1^1)(C_3^2 - C_3^1)}{(C_1^1 - C_3^1) - (C_2^1 - C_1^1)(C_3^2 - C_3^1)} Q_t \]  \hspace{1cm} (5.4)
\[
Q_2 = \frac{C_{t}^{1} - C_{t}^{3}}{C_{1}^{1} - C_{3}^{1}} Q_t - \frac{C_{t}^{1} - C_{t}^{3}}{C_{1}^{1} - C_{3}^{1}} Q_1 \tag{5.5}
\]

\[
Q_3 = Q_t - Q_1 - Q_2 \tag{5.6}
\]

where \( Q \) is discharge, \( C \) is concentration, the subscripts \( t, 1, 2, \) and \( 3 \) refer to stormflow, event water, shallow soil-water, and deep soil-water, respectively, and the superscripts \( 1 \) and \( 2 \) refer to the two different tracers used in the study. Note that equation 5.3 is applied to both tracers in order to solve equation 5.4-5.6. In this study, we tried different separation scenarios using different combinations of tracers, in the end deciding on \( DOC \) and \( Ca^{2+} \). The process of choosing these tracers and their applicability as conservative tracers is described and discussed in Section 5.4.3.2.

### 5.2.6.3 Statistical Analysis

All statistical analyses were performed using Statistica version 8.0 software (StatSoft® Inc.). All relationships were considered statistically significant if \( p < 0.05 \). Multiple linear regression analysis was used to assess the ability of various hydrological variables (e.g. catchment discharge and the indices of \( AMCs \) described in Section 5.2.4) to explain variations in \( THg \), \( ^{200}Hg \), and \( DOC \) concentrations. The strength of the multiple regression models was assessed using an adjusted \( r^2 \) value. The adjusted \( r^2 \) value is a better index of the fit of the regression equation to the data, since \( r^2 \) always increases when an additional predictor variable is added to the regression model, but adjusted \( r^2 \) will only increase if an added predictor variable results in an improved fit of the regression equation to the data. Model residuals were assessed for normality, bias, and the influence of outliers.
5.3 Results

5.3.1 General Hydrologic Behaviour of the UP1 Catchment

Discharge from the UP1 catchment has been monitored since 2001 by the US Geological Survey (USGS) as part of the METAALICUS project. The inter- and intra-annual variability in precipitation and runoff response factors for the growing season over the years 2001 – 2009 were described in detail in Section 2.4.1 of this thesis. In comparison to other years, October 2007 was relatively wet, whereas the 2008 study period had average precipitation inputs. The seasonality of the hydrologic regime is clearly evident in Figure 5.3, where following snowmelt (period not shown) baseflow was relatively high and numerous events in late spring and early summer generated stormflow (Fig. 5.3a,b). In late summer 2008, there were fewer large events and baseflow ceased by early August when potential evaporation was highest. Several large events in September did not generate significant flow and instead satisfied storage deficits in the soil landscape. In mid-October a sequence of large rain events finally generated flow from the catchment; however, spring baseflow levels were not restored (Fig. 5.3b). The indices of antecedent moisture conditions ($AP_x$ and $AS_x$) calculated for the study period also exhibit these seasonal patterns (Fig. 5.3c,d).
Figure 5-3 Hydrologic summary of the study period (1-31 October 2007 and 24 April 2008 to 27 October 2008) including (a) hourly precipitation, (b) hourly discharge measured at the UP1 outlet, (c) antecedent precipitation ($AP_x$), and (d) antecedent mean storage in DEP_TERMINAL ($AS_x$). $x$ is the number of antecedent days over which precipitation was summed and storage was averaged. The individual events that were investigated for this study are shaded in (b). * denotes the events used for detailed concentration-discharge analysis. Note the break in the x-axis separating the 2007 and 2008 study periods.
5.3.2 \( \text{THg}, \text{\textsuperscript{200}Hg}, \) and \( \text{DOC} \) Dynamics

5.3.2.1 Concentration-Discharge Relationships for \( \text{THg}, \text{\textsuperscript{200}Hg}, \) and \( \text{DOC} \)

The \( \text{THg}, \text{\textsuperscript{200}Hg}, \) and \( \text{DOC} \) C-Q relationships using all data from the study period were modeled using linear functions (Fig. 5.4). The regression models developed explained only an extremely small portion of the variation in concentrations, with model \( r^2 \) values of 0.004 for \( \text{THg} \) and \( \text{DOC} \) and 0.05 for \( \text{\textsuperscript{200}Hg} \). It is obvious from Figure 5.4 that C-Q shifts occurred for all three solutes over the study period, particularly for \( \text{DOC} \) (Fig. 5.4c), where two distinct trends are discernible. For the three solutes, but in particular \( \text{THg} \), there was a larger range in concentrations during low flow conditions (<15 m\(^3\)/h) and concentration increased slightly with increasing discharge; however, the linear correlations were not strong and the only slope significantly different than zero was for \( \text{\textsuperscript{200}Hg} \) (Fig. 5.4b). In all three cases, model residuals were nearly symmetrical, although all showed some skewness to the right, especially \( \text{\textsuperscript{200}Hg} \). The residual distributions for \( \text{THg} \) and \( \text{DOC} \) were platykurtic (flat with short tails), while the distribution for \( \text{\textsuperscript{200}Hg} \) was highly leptokurtic (narrow peak with long tails). All residuals showed some bias with respect to discharge.

5.3.2.2 \( \text{THg}, \text{\textsuperscript{200}Hg}, \) and \( \text{DOC} \) Concentrations as a Function of Discharge and Antecedent Moisture Conditions

In this study, we hypothesized that shifts in the \( \text{THg}, \text{\textsuperscript{200}Hg}, \) and \( \text{DOC} \) C-Q relationships would be related to differences in antecedent moisture conditions that in turn affect biogeochemical conditions in the soil and the development of the potentially-mobile \( \text{DOC} \)-bound \( \text{Hg} \) pool. Catchment discharge, \( AP_x, \) and \( AS_x, \) for \( x = 7 \) days, \( x = 14 \) days, and \( x = 28 \) days, were included as predictor variables in a multiple regression analysis to determine whether or not the C-Q relationships described in the previous section could be improved upon. We assessed the multiple regression model both with and without the removal of outliers (>2 and <-2 * standard deviation of the residuals) and found some improvement in the strengths of the models with the few outliers removed. We also assessed autocorrelation in the \( AP_x, AS_x \) and \( Q_{UP1} \) variables. Since significant autocorrelation was found between several combinations of variables (mainly the \( AP_x \) variables), we re-ran the multiple regression analysis using only the three highest rated
variables, in terms of the standardized regression coefficients, that were not significantly autocorrelated. Table 5.1 summarizes the results of the final multiple regression analysis. In general, we found that the inclusion of $AP_x$ and $AS_x$ variables with $Q_{UP1}$ greatly improved the prediction of $THg$, $^{200}Hg$, and $DOC$ concentrations in streamwater. The multiple regression model for $THg$ concentration was strongest (adjusted $r^2 = 0.77$) when $AS_7$, $AP_{28}$, and $Q_{UP1}$ were included as predictor variables. The multiple regression model for $^{200}Hg$ was relatively weak (adjusted $r^2 = 0.49$) compared to $THg$ using the same predictor variables. $DOC$ concentration was best explained by a model using $AS_7$, $Q_{UP1}$, and $AP_7$ (adjusted $r^2 = 0.58$). For all models, the distribution of residuals did not depart significantly from normality.

### 5.3.2.3 $THg$-DOC and $^{200}Hg$-DOC Relationships

Pooling all streamwater data from the study period, there was a strong positive correlation between $THg$ and $DOC$ concentration ($r^2 = 0.69$) and a weaker positive correlation between $^{200}Hg$ and $DOC$ concentration ($r^2 = 0.29$). As reported in Section 3.3.8 of this thesis, these correlations improved slightly when the ultraviolet absorbance at 254 nm ($UV_{254}$) was used as a predictor variable. $UV_{254}$ is an established proxy measure of percent aromaticity of $DOC$ (Weishaar et al. 2003; Chin et al. 1994) and has been shown in previous studies to be a better predictor of $Hg$ concentrations (Dittman et al. 2009).
Figure 5-4 Concentration-discharge relationships for (a) $THg$, (b) $^{200}Hg$, and (c) $DOC$ for samples obtained at the UP1 catchment outlet between the periods 9-Oct-2007 and 27-Oct-2008. Linear regression lines, correlation coefficients and p-values are shown. p < 0.05 is considered significant.
Table 5-1 Summary of multiple linear regression analysis applied to the concentrations of THg, $^{200}\text{Hg}$, and DOC. Independent variables that were input into the analysis were UP1 catchment discharge ($Q_{UP1}$, m$^3$/h), antecedent precipitation ($AP_x$, mm), and antecedent mean storage in DEP$_{TERMINAL}$ ($AS_x$, m$^3$). The subscript $x$ represents the number of antecedent days over which precipitation was summed and storage was averaged. Shaded values represent $p < 0.05$ (considered significant). * Standardized regression coefficients allow for a comparison of the relative contribution of each independent variable in the prediction of the dependent variable.

<table>
<thead>
<tr>
<th>Dependent Variable</th>
<th>Independent Variables</th>
<th>Standardized Regression Coefficients*</th>
<th>Intercept</th>
<th>Multiple R</th>
<th>Multiple $R^2$</th>
<th>Adjusted $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THg</td>
<td>$Q_{UP1}$</td>
<td>+0.27</td>
<td>+73.58</td>
<td>0.88</td>
<td>0.78</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>$AP_{28}$</td>
<td>+0.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$AS_7$</td>
<td>-0.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{200}\text{Hg}$</td>
<td>$Q_{UP1}$</td>
<td>+0.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$AP_{28}$</td>
<td>+0.21</td>
<td>+0.45</td>
<td>0.72</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>$AS_7$</td>
<td>-0.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>$Q_{UP1}$</td>
<td>+0.42</td>
<td>+86.44</td>
<td>0.77</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$AP_7$</td>
<td>-0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$AS_7$</td>
<td>-0.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3.3 Event-Scale THg, 200Hg, and DOC Export

Event-scale THg, 200Hg, and DOC loads were estimated for nine events that differed in duration, precipitation inputs, and total water export (Table 5.2). We compared total event flux values for five of these storms to ones calculated using a flow-weighted bulk concentration obtained and analyzed by the USGS for the same site. Total event fluxes for 5 storms differed 2-29 %, which we found to be an acceptable difference given the limitations of our dataset for two of the storms and hence the limitation of the composite method. Event-scale variations in THg, 200Hg, and DOC export were strongly related to event water export ($r^2$ ranges from 0.93 to 0.95) (Fig. 5.6). There were also strong relationships between THg and DOC export and 200Hg and DOC export (Fig. 5.7).
Table 5-2 Summary of event characteristics including: event duration, total precipitation ($P_{TOT}$), mean precipitation rate ($P_{AVG}$), peak precipitation rate ($P_{MAX}$), total discharge ($R_{TOT}$), peak discharge rate ($R_{MAX}$), runoff ratio ($R_{TOT}/P_{TOT}$), antecedent precipitation ($AP_x$), mean antecedent water storage in DEPTERMINAL ($AS_x$), and total event $THg$, $^{200}Hg$, and $DOC$ fluxes. The subscript $x$ represents the antecedent number of days over which $AP_x$ is summed and $AS_x$ is averaged. The highlighted events are those with similar $R_{TOT}$, but different antecedent moisture conditions and solute fluxes.

<table>
<thead>
<tr>
<th>Event Period</th>
<th>Duration (days)</th>
<th>$P_{TOT}$ (mm)</th>
<th>$P_{AVG}$ (mm h$^{-1}$)</th>
<th>$P_{MAX}$ (mm h$^{-1}$)</th>
<th>$R_{TOT}$ (mm)</th>
<th>$R_{MAX}$ (mm h$^{-1}$)</th>
<th>$R_{TOT}/P_{TOT}$</th>
<th>AP$_7$ (mm)</th>
<th>AP$_{14}$ (mm)</th>
<th>AP$_{28}$ (mm)</th>
<th>AS$_7$ (m$^3$)</th>
<th>AS$_{14}$ (m$^3$)</th>
<th>AS$_{28}$ (m$^3$)</th>
<th>THg ($\mu$g)</th>
<th>$^{200}Hg$ ($\mu$g)</th>
<th>DOC (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-15 Oct 2007</td>
<td>7.8</td>
<td>32.8</td>
<td>0.8</td>
<td>6.3</td>
<td>11.0</td>
<td>12.7</td>
<td>0.36</td>
<td>32.3</td>
<td>42.5</td>
<td>69.6</td>
<td>908.0</td>
<td>859.4</td>
<td>743.2</td>
<td>15713</td>
<td>37.8</td>
<td>24618</td>
</tr>
<tr>
<td>18-26 Oct 2007</td>
<td>8.1</td>
<td>98.0</td>
<td>0.7</td>
<td>26.3</td>
<td>34.9</td>
<td>0.6</td>
<td>0.36</td>
<td>0.0</td>
<td>63.2</td>
<td>-</td>
<td>1601.2</td>
<td>1442.2</td>
<td>-</td>
<td>48145</td>
<td>235.5</td>
<td>72923</td>
</tr>
<tr>
<td>25-28 May 2008</td>
<td>3.2</td>
<td>13.0</td>
<td>0.4</td>
<td>2.7</td>
<td>5.5</td>
<td>7.9</td>
<td>0.42</td>
<td>0.2</td>
<td>23.1</td>
<td>39.9</td>
<td>1589.4</td>
<td>-</td>
<td>-</td>
<td>3452</td>
<td>7.8</td>
<td>7234</td>
</tr>
<tr>
<td>30 May – 3 Jun 2008</td>
<td>4.5</td>
<td>6.4</td>
<td>0.4</td>
<td>1.8</td>
<td>7.2</td>
<td>0.1</td>
<td>1.1</td>
<td>13.0</td>
<td>15.1</td>
<td>36.1</td>
<td>1608.7</td>
<td>-</td>
<td>-</td>
<td>6125</td>
<td>22.3</td>
<td>9744</td>
</tr>
<tr>
<td>6-8 Jun 2008</td>
<td>2.6</td>
<td>21.3</td>
<td>1.3</td>
<td>6.2</td>
<td>7.0</td>
<td>13.8</td>
<td>0.33</td>
<td>8.2</td>
<td>22.4</td>
<td>45.5</td>
<td>1648.0</td>
<td>1628.6</td>
<td>-</td>
<td>9341</td>
<td>20.5</td>
<td>11649</td>
</tr>
<tr>
<td>9-11 Jun 2008</td>
<td>2.9</td>
<td>32.5</td>
<td>1.0</td>
<td>7.1</td>
<td>12.5</td>
<td>30.5</td>
<td>0.39</td>
<td>24.2</td>
<td>33.4</td>
<td>66.8</td>
<td>1667.1</td>
<td>1646.7</td>
<td>-</td>
<td>16080</td>
<td>54.7</td>
<td>22290</td>
</tr>
<tr>
<td>12-17 Jun 2008</td>
<td>6.0</td>
<td>33.3</td>
<td>0.5</td>
<td>9.9</td>
<td>19.9</td>
<td>0.2</td>
<td>0.60</td>
<td>53.7</td>
<td>63.1</td>
<td>80.0</td>
<td>1705.6</td>
<td>1673.6</td>
<td>-</td>
<td>22193</td>
<td>97.9</td>
<td>30349</td>
</tr>
<tr>
<td>27 Jun – 4 Jul 2008</td>
<td>7.0</td>
<td>63.5</td>
<td>1.8</td>
<td>19.3</td>
<td>26.3</td>
<td>0.6</td>
<td>0.41</td>
<td>7.9</td>
<td>21.6</td>
<td>101.0</td>
<td>1670.0</td>
<td>1694.9</td>
<td>1689.4</td>
<td>30071</td>
<td>157.1</td>
<td>42937</td>
</tr>
<tr>
<td>11-16 Oct 2008</td>
<td>4.8</td>
<td>56.6</td>
<td>0.5</td>
<td>6.9</td>
<td>5.0</td>
<td>0.1</td>
<td>0.09</td>
<td>10.7</td>
<td>12.5</td>
<td>55.6</td>
<td>1245.1</td>
<td>1304.5</td>
<td>1235.5</td>
<td>10851</td>
<td>56.7</td>
<td>13476</td>
</tr>
</tbody>
</table>
Figure 5-6 Relationships between total event solute export and total event water export for (a) THg, (b) $^{200}$Hg, and (c) DOC.
Comparisons of solute concentrations in stream water between events were made for events with nearly equivalent discharge, since on shorter time-scales concentration is strongly related to discharge. The two smallest events, in terms of total discharge, which started on 25-May-2008 (DOY 146) and 11-Oct-2008 (DOY 285), had similar amounts of runoff (~ 5 mm), but very different amounts of precipitation and THg, 200Hg, and DOC export (Fig. 5.6; Table 5.2). The 25-May event was preceded by a period of relatively low precipitation inputs; however, water storage in DEPTERMINAL was high, likely due to the snowmelt-driven recharge earlier in the month and low evaporative demand (Fig. 5.3; Table 5.2). Baseflow was relatively high preceding and during the 25-May event, and as a consequence, the 13.0 mm of low intensity rainfall over ~ 1.5 days resulted in significant runoff generation \( \frac{R_{TOT}}{P_{TOT}} = 0.42 \) (Fig. 5.8a,c). No samples were collected on the rising limb of this event; however, several samples were collected in and around peak flow, and a sample was also collected on the falling limb of the hydrograph. THg concentrations increased slightly by ~ 1 ng/L around peak flow and were highest (8.40 ng/L) just after maximum flow (Fig. 5.8e). Meanwhile, 200Hg concentrations were below detection limit for all samples taken during the event (Fig. 5.8g). Surprisingly, DOC concentrations decreased slightly right at peak flow, but otherwise were relatively constant (~ 17 mg/L). The estimated total event export of THg, 200Hg, and DOC for the 25-May-2008 event.
was 3452 μg, 7.8 μg, and 7234 mg, respectively. The 11-Oct event was preceded by a period of low precipitation inputs and high evaporative demand, which resulted in large storage deficits in DEPTERMINAL (Fig. 5.3; Table 5.2). Baseflow was extremely low preceding, throughout, and after the 11-Oct event. Rain fell fairly consistently over ~2 days resulting in a total input of 56.6 mm and a total output of 5.0 mm ($R_{TOT}/P_{TOT} = 0.09$; Fig. 5.8b,d). Extensive manual and automated sampling occurred over nearly the entire hydrograph for the 11-Oct event. $THg$ concentrations increased rapidly during the initial flush from ~17.5 ng/L to ~32.5 ng/L, were relatively constant around peak flow, and declined steadily over the recession limb to ~24.5 ng/L (Fig. 5.8f). Meanwhile, $^{200}Hg$ concentrations were somewhat erratic over the course of the event with some samples falling below detection limit and other samples reaching as high as 0.39 ng/L near peak flow (Fig. 5.8h). However, the overall the trend appeared similar to $THg$ with an initial flush followed by a gradual decrease in concentrations. $DOC$ concentrations more closely followed the same pattern as $THg$, increasing from ~29.6 mg/L to ~43.6 mg/L during the initial flush, followed by a slight decrease, and then another increase to ~43.3 mg/L coincident with peak flow, and gradually declining to ~26.7 mg/L over the recession limb (Fig. 5.8j). The estimated total event export of $THg$, $^{200}Hg$, and $DOC$ for the 11-Oct-2008 event was 10851 μg, 56.7 μg, and 13476 mg, respectively. The 11-Oct $THg$, $^{200}Hg$, and $DOC$ loads were 3.1, 7.3, and 1.9 times larger, respectively, than for the 25-May event despite both events having nearly the same total discharge (Table 5.2).

Streamwater samples collected during two other storms, beginning on 30-May-2008 and 6-June-2008, also had nearly equivalent total discharge (~7 mm); however, the $THg$, $^{200}Hg$, and $DOC$ loads for these events were much more similar than for the smaller events described above (Table 5.2). The 30-May and 6-Jun were both preceded by periods of moderate rainfall, high water storage in DEPTERMINAL, and high baseflow (Fig. 5.3).
Figure 5-8 Hourly precipitation ($P$), discharge ($Q$), pre-event component of discharge ($Q_p$), and concentrations of $THg$, $^{200}Hg$, and $DOC$ for the 25-May-2008 event (a, c, e, g, i) and the 11-October-2008 event (b, d, f, h, j). Both sample concentrations and modeled concentrations are shown. Note the different y-axis for the two events for all variables.

Variations in $THg$, $^{200}Hg$, and $DOC$ export between events having similar total water export were likely due to differences in the C-Q relationship (Fig. 5.9). For all three solutes, concentration was relatively constant despite increasing discharge for the 25-May-2008 event and concentration increased with increasing discharge for the 11-Oct-2008 event. Hysteresis in the C-Q relationship was evident for all three solutes for the 11-Oct event, with higher concentrations of $THg$ and $DOC$ on the recession limb (counter-clockwise). The pattern of
hysteresis was less evident for $^{200}\text{Hg}$ given the erratic concentrations measured over the hydrograph; however, concentrations did end up lower than they began (clockwise). The $THg$-$DOC$ and $^{200}\text{Hg}$-$DOC$ concentration relationships for the 25-May-2008 and 11-Oct-2008 (Fig. 5.10) were similar in that they both fall along the continuum shown in Figure 5.5; however, clockwise hysteresis was evident for both $THg$ and $^{200}\text{Hg}$ for the 11-Oct event. It is important to note that for both Figure 5-9b and 5-10b, the minimum $^{200}\text{Hg}$ values differ between events since the detection limit of $^{200}\text{Hg}$ depends in part on the concentration of $THg$ in the sample.

The differences in streamwater $THg$, $^{200}\text{Hg}$, and $DOC$ concentrations between the 25-May and 11-Oct event are also evident in shallow soil-water collected from zero-tension lysimeters throughout the catchment (Fig. 5.11). In shallow soil-water, $THg$, $^{200}\text{Hg}$, and $DOC$ concentrations for the 11-Oct event were significant higher ($p < 0.05$) than for the 25-May event. However, concentrations were not significantly different between storms for baseflow collected during the week prior to each event (Fig. 5.11).
Figure 5-9 Concentration-discharge dynamics for the 25-May-2008 event with relatively wet antecedent moisture conditions (AMCs) and the 12-October-2008 event with relatively dry AMCs, for (a) \( \text{THg} \), (b) \( ^{200}\text{Hg} \), and (c) \( \text{DOC} \). Arrows indicate the direction of hysteresis if applicable. Note that the method detection limit for \( ^{200}\text{Hg} \) depends on the concentration of \( \text{THg} \), hence the difference in minimum values between events in (b).
Figure 5-10 THg-DOC concentration dynamics for the 25-May-2008 event with relatively wet antecedent moisture conditions (AMCs) and the 12-October-2008 event with relatively dry AMCs, for (a) THg and (b) $^{200}Hg$. Arrows indicate the direction of hysteresis if applicable. Note that the method detection limit for $^{200}Hg$ depends on the concentration of THg, hence the difference in minimum values between events in (b).
Figure 5-11 Boxplots showing the differences in $THg$, $^{200}Hg$, and $DOC$ concentrations between the 25-May-2008 and 11-Oct-2008 storms for streamwater, shallow soil-water, and baseflow collected just prior to the event. All differences are statistically significant ($p < 0.05$) except for baseflow.
5.3.4 Isotopic and Hydrochemical Hydrograph Separations

5.3.4.1 Two-Component Separations

For both the 25-May-2008 and the 11-Oct-2008 storms, $\delta^{18}O$ ratios in rainfall were significantly different than pre-event waters in the soil and stream. Pre-event $\delta^{18}O$ was represented by baseflow $\delta^{18}O$ prior to the event, which had similar $\delta^{15}O$ values to pre-event soil-water. Results of the two-component hydrograph separations using $\delta^{18}O$ and equation 5.2 showed total pre-event water contributed 63.6 % and 51.7 % to total stormflow for the 25-May and 11-Oct events, respectively (Table 5.3; Fig. 5.8c,d). For the 25-May event, pre-event water initially contributed ~ 95 % to stormflow, but gradually decreased to ~ 36 % over the course of the event. For the 11-Oct event, pre-event water contributed ~ 60 % to stormflow during the initial flush, then decreased to ~ 40 % around peak flow, and ranged between ~ 42 to 67 % on the recession limb. The proportion of event water for the 25-May storm did not correspond with precipitation intensity; however, the proportion of event water for the 11-Oct storm reached a maximum shortly after peak rainfall intensity.
Table 5-3 Summary of two-component and three-component hydrograph separations for the 25-May-2008 and 11-Oct-2008 storm events. Percent contributions are shown for event water \((Q_e)\), pre-event water \((Q_p)\), shallow soil-water flowing through the organic soil horizon (collected from zero-tension lysimeters in the upper west portion of the catchment; \(Q_{ss}\)), and deep soil-water flowing through mineral soil horizons (collected from 80 cm piezometers throughout the catchment; \(Q_{ds}\)).

<table>
<thead>
<tr>
<th>Event</th>
<th>Source</th>
<th>Contribution (%)</th>
<th>Total</th>
<th>Min - Max</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two-components</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-May-2008</td>
<td>(Q_e)</td>
<td>36.4</td>
<td></td>
<td>4.6 - 63.6</td>
</tr>
<tr>
<td></td>
<td>(Q_p)</td>
<td>63.6</td>
<td></td>
<td>36.4 - 95.4</td>
</tr>
<tr>
<td>11-Oct-2008</td>
<td>(Q_e)</td>
<td>48.3</td>
<td></td>
<td>32.6 - 62.7</td>
</tr>
<tr>
<td></td>
<td>(Q_p)</td>
<td>51.7</td>
<td></td>
<td>37.3 - 67.4</td>
</tr>
<tr>
<td>Three-components</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-May-2008</td>
<td>(Q_e)</td>
<td>67.7</td>
<td></td>
<td>64.6 - 76.6</td>
</tr>
<tr>
<td></td>
<td>(Q_{ss})</td>
<td>23.1</td>
<td></td>
<td>18.6 - 24.6</td>
</tr>
<tr>
<td></td>
<td>(Q_{ds})</td>
<td>9.2</td>
<td></td>
<td>0.0 - 12.7</td>
</tr>
<tr>
<td>11-Oct-2008</td>
<td>(Q_e)</td>
<td>17.1</td>
<td></td>
<td>0.0 - 39.4</td>
</tr>
<tr>
<td></td>
<td>(Q_{ss})</td>
<td>60.3</td>
<td></td>
<td>40.6 - 79.4</td>
</tr>
<tr>
<td></td>
<td>(Q_{ds})</td>
<td>22.6</td>
<td></td>
<td>11.3 - 59.4</td>
</tr>
</tbody>
</table>

5.3.4.2 Three-Component Separations

All streamwater ion and DOC data for the study period were used to generate matrix solute-solute plots for all combinations of solutes (not shown). Mixing diagrams were checked for outliers and curvature, which indicates non-conservative behaviour. Potential end-members were plotted on the same graphs to evaluate possible mixing models. The flow pathways shown in Figure 5.1 were ground-truthed on several occasions and were observed to be a combination of surface flow over saturated areas during wet relatively wet hydrologic conditions, diffuse subsurface flow (e.g. through depressions), and more convergent subsurface flow in areas with a relatively steep gradient, which in some locations spills over exposed bedrock ridges. These observations helped inform decisions on potential end-members for our mixing analysis. Potential end-members included rainwater, water from a seep located partway up the slope on the eastern side of the UP1 catchment, water collected at the weir draining the west sub-catchment, deep soil-water collected from the 80 cm piezometers throughout the catchment, baseflow collected from the outlet weir, shallow soil-water collected from zero-tension lysimeters on the east, west, and upper west sides of the catchment, as well as all lysimeters.
combined, and a depth-integrated soil-water end-member collected from the network of wells. The variability of the end-members was assessed.

A principal components analysis (PCA) using a correlations matrix was also conducted to reduce the dimensionality of the dataset and estimate the number of end-members required. The results of the PCA indicated that the first two components, the only ones explaining > 16 % of the total variance (i.e. 1/# of solutes), explained 78 % of the total variance. The variable contributions, based on correlations, were highest for \( \text{DOC} \), \( \text{SO}_4^{2-} \), \( \text{Mg}^{2+} \), and \( \text{Ca}^{2+} \). Instead of continuing with a full end-member mixing analysis, we carried out a three-component mixing analysis using \( \text{DOC} \) and \( \text{Ca}^{2+} \) as tracers. The solute-solute plot for these two solutes for all samples showed no curvature and contained few outliers (Fig. 5.12a). \( \text{DOC} \) is not widely used as a tracer in geochemical hydrograph separation; however, it has been used to separate contributions from organic soil horizons at the event-scale (e.g. Carey and Quinton, 2005). \( \text{DOC} \) may be a useful tracer in boreal Shield catchments where complex topography and variable hydrologic connectivity often forces water tables to rise into near-surface organic soil horizons, resulting in the mobilization of \( \text{DOC} \). \( \text{Ca}^{2+} \) is more commonly used as a tracer in hydrograph separation. Its levels are much higher in deep soil-water than shallow soil-water due to contact with mineral soil and bedrock (Allan et al. 1993).

For streamwater samples collected over the entire study period, three end-members stood out as sufficiently bounding the streamwater samples (Fig. 5.12a). The three end-members were rainwater, deep soil-water collected from the 80 cm piezometers throughout the catchment, and shallow soil-water collected from lysimeters located in the upper west part of the catchment. The 25-May-2008 and 11-Oct-2008 events are also shown separately (Fig. 5.12b,c) with the same end-members marked. Flow contributions from the three-component analysis using \( \text{DOC} \) and \( \text{Ca}^{2+} \) are summarized in Table 5.3 for comparison with the two-component separation. The 25-May hydrograph was dominated by event water (~ 68 %), followed by shallow subsurface flow (~ 23 %), and deeper subsurface flow (~ 9 %). In contrast, the 11-Oct hydrograph was dominated by shallow subsurface flow (~ 60 %), followed by deep subsurface flow (~ 23 %), and event water (~ 17 %). These results are dramatically different than the event and pre-event contributions based on the two-component \( \delta^{18} \text{O} \) separations. The pre-event contribution for the 25-May storm using the two-component separation (63.6 %) is approximately twice the contribution based on the three-component separation (32.3 %) and the pre-event contribution
for the 11-Oct storm based on the two-component separation (82.9%) is approximately 1.5 times the two-component contribution (51.7%).

Figure 5-12 Component mixing diagrams using $Ca^{2+}$ and DOC as tracers for (a) the entire study period, (b) the 25-May-2008 event and (c) the 11-Oct-2008 event. Mean values of the end-members for the entire study period are shown with error bars representing ±1 standard deviation on each plot.
5.4 Discussion

5.4.1 Are $THg$, $^{200}Hg$, and $DOC$ C-Q dynamics dependent on event characteristics and/or AMCs?

Although the linear regression models of the C-Q relationships for $THg$, $^{200}Hg$, and $DOC$ were strong at the event-scale, they had little predictive ability when determined for the entire study period, and were in essence predicting the mean concentration of the samples, especially for $THg$ and $DOC$. The bias we observed in the residuals with respect to discharge suggests that the residuals did not just represent measurement error, but that they represented changes in the C-Q relationship due to changes in the pool of potentially-mobile solutes. The composite method incorporated these shifts in the C-Q relationship into the load estimates. However, as we did not follow a fixed interval sampling frequency over the study period there are some instances where interpolation was required over longer periods, during which the composite method may have failed to capture the true magnitude of the residuals (Aulenbach and Hooper, 2006). In future studies the sampling design should include a combination of fixed interval and high flow sampling. The data set could then be divided up into months or seasons so that stronger discharge models could be determined. It would also be wise to continue this type of sampling over multiple years so that the C-Q relationship could be examined over a range of hydroclimatic conditions. Most of the data collected for this study was collected in 2008, which fortunately was a year of average precipitation inputs and runoff outputs, and therefore may be fairly representative of the long-term C-Q relationship.

The inclusion of various indices of AMCs as predictor variables along with catchment discharge in a multiple regression analysis greatly improved the prediction of $THg$, $^{200}Hg$, and $DOC$. The relatively low adjusted $r^2$ value for $^{200}Hg$ may be related to the fact that most samples were near the analytical detection limit. For $THg$, $^{200}Hg$, and $DOC$, $Q_{UP1}$ and $AS_7$ were strong predictors of concentration. The standardized regression coefficients for $Q_{UP1}$ were all positive, indicating that concentrations increase with increasing discharge. This is likely related to the relationship between increases in discharge and the rise of the water table into shallow organic soils where most of the potentially-mobile $THg$, $^{200}Hg$, and $DOC$ are stored. The standardized regression coefficients for $AS_7$ were all negative, indicating that as antecedent storage in $DEP_{TERMINAL}$ increases (i.e. wetter AMCs), concentrations decrease. Short-term wet AMCs are likely
concurrent with enhanced flow through shallow organic soils, which would deplete the potentially-mobile $THg$, $^{200}Hg$, and $DOC$ pools.

At the event-scale, the strong relationships between total $THg$, $^{200}Hg$, and $DOC$ export and total event discharge were not surprising given the strong C-Q relationships we found at shorter timescales. Over the study period, only two sets of two events were captured that had similar total event export. Of these, only the two smallest in terms of discharge, 25-May-2008 and 11-Oct-2008, had very different AMCs allowing for a true comparison of solute export (Huntington $et$ $al.$ 1994). Since events with relatively large total water export usually occur during wetter periods, it may be difficult to find multiple large events with equivalent discharge and different AMCs to compare solute fluxes between. The $THg$, $^{200}Hg$, and $DOC$ dynamics of the 25-May and 11-Oct events were similar in their overall pattern, but very different in terms of their ranges in concentration. For the 25-May event, a slight flushing effect is evident for $THg$; however, it is a relatively small change ($\sim 1$ ng/L) in concentration compared to the 11-Oct event when $THg$ concentration jumped $\sim 15$ ng/L before peak discharge. Although samples were not collected on the rising limb of the 25-May event, two samples collected at the stream outlet two days prior to the event during baseflow conditions had concentrations within the range of the samples collected during the event. The difference in the magnitude of the initial concentration change for the two events is all the more impressive considering that baseflow samples collected one week prior to the 11-Oct event during very low flow conditions had the same concentrations as the 25-May antecedent baseflow samples. While $^{200}Hg$ remained relatively constant for the 25-May event, we do see a slight increase in $^{200}Hg$ concentrations at the beginning of the 11-Oct event, which suggests that some $^{200}Hg$ is flushed from organic soils after extended dry periods. The erratic pattern of $^{200}Hg$ concentrations during this event may be a consequence of the spatial variability of $^{200}Hg$ in soil-water and variable flow pathways. Surprisingly, for the 25-May event, $DOC$ decreased slightly around peak flow, which may indicate a slight dilution effect; however, there are too few samples prior to the event to be sure. During the 11-Oct event, $DOC$ increased by $\sim 14$ mg/L exhibiting the same pattern as $THg$, which suggests that the same flushing mechanism was co-mobilizing $THg$ and $DOC$. The higher overall $THg$, $^{200}Hg$, and $DOC$ loads for the 11-Oct event compared to the 25-May event, despite similar discharge, are most likely related to the differences in antecedent moisture conditions, which resulted in a difference in the C-Q relationship. Although precipitation dynamics were very different for the two events, we do not have evidence to suggest that there was an increase in the $POC$ load due
to more intense rainfall during the 11-Oct event. In future studies, it will be worthwhile to examine differences in $THg$ and $DOC$ in throughfall for storms of varying rainfall intensity to determine whether or not this could explain some of the differences in streamwater concentrations.

The change in the C-Q relationship between the 25-May-2008 and 11-Oct-2008 events and the corresponding difference in shallow soil-water concentrations suggests that a biogeochemical shift occurred in the soil that resulted in an increase in mobilizable $THg$, $^{200}Hg$, and $DOC$. An increase in the shallow soil-water concentrations of $THg$, $^{200}Hg$, and $DOC$ after the relatively dry, warm period prior to the 11-Oct event indicates that the pools of these solutes are dynamic and are responsive to hydrologic conditions. Kalbitz et al. (2000) described how the size of the potentially-mobile DOM pool grows during warm, dry periods as a result of enhanced decomposition; and as a perceptual model, we propose that by association the same should apply to $THg$ and $^{200}Hg$. The foundation of this perceptual model is that $DOC$ accumulates in shallow, organic surface soils during warm, dry periods and soil-water concentrations increase rapidly until sufficient precipitation inputs allow for flow to connect through surface soils, thereby flushing $DOC$-bound $THg$ and $^{200}Hg$. During extended wet periods, the continuous flushing mechanism will result in lower soil-water and streamwater concentrations as the potentially-mobile solute pools are continually depleted.

5.4.2 Are $THg$-$DOC$ dynamics dependent on event characteristics and/or AMCs?

Since similar patterns in the C-Q relationship were evident for $THg$ and $DOC$ and given the strong relationship we have already shown in the preceding chapters, it was not surprising that the $THg$-$DOC$ relationship was very strong. The positive linear relationship we found between $THg$ and $DOC$ is similar to previous studies; however, the mass of $THg$ per unit mass of $DOC$ (~ 0.82) was higher than many studies (e.g. ~ 0.2 ng $Hg$/mg $DOC$ on average for a range of catchments (Grigal, 2002); ~ 0.24 to 0.37 ng $Hg$/mg $DOC$ in catchments across the U.S.A., not including one in Colorado with ~ 2.94 ng $Hg$/mg $DOC$ (Shanley et al. 2008)). The relationship with $DOC$ was not as strong for $^{200}Hg$, which as discussed in Chapter 3, is likely due to the short amount of time that $^{200}Hg$ has been in the catchment (~ 7 years at the time of sampling) relative to the lifetime of $SOM$ in the soil landscape. Hence, the $^{200}Hg$, which is mainly retained in the
litter layer, has not migrated downwards into the zone of potential $\text{DOM}$ that is readily mobilized. The strong relationship between $\text{THg}$ and $\text{DOC}$ concentrations was also evident at the event scale for total event export and the poor $^{200}\text{Hg}-\text{DOC}$ relationship was greatly improved at the event-scale because of the influence of discharge in the flux calculation. As we can see in Figure 5.7, the two smallest events for which we examined the role of AMCs on the C-Q relationship appear collinear, suggesting that AMCs and event characteristics do not affect the $\text{THg}-\text{DOC}$ relationship. However, this may not be the case for $^{200}\text{Hg}$, which exhibits slightly more scatter than $\text{THg}$ in Figure 5.7. In Figure 5.10, we can see that although the $\text{THg}-\text{DOC}$ relationship for the two events fall on the overall $\text{THg}-\text{DOC}$ continuum, there is more hysteresis evident in the 11-Oct event. The clockwise hysteresis in the $\text{Hg}-\text{DOC}$ relationship for the 11-Oct event suggests that dry AMCs and subsequent re-wetting may result in variations in flow pathways and source areas throughout the storm. The same applies to the $^{200}\text{Hg}-\text{DOC}$ relationship, but to a lesser degree.

### 5.4.3 Do differences in water sources and/or flow pathways account for differences in C-Q or Hg-DOC dynamics?

While differences in total event export of $\text{THg}$, $^{200}\text{Hg}$, and $\text{DOC}$ appear to be related to differences in AMCs, it is not entirely clear if the differences are due solely to AMCs affecting the biogeochemical conditions in the soil and hence the size of the potentially-mobile pool, or if AMCs also affect the location of flow pathways and hydrologically connected source areas with different potential pools, thereby changing the contribution of different sources. The counter-clockwise hysteresis evident in the C-Q relationships for $\text{THg}$ and $\text{DOC}$ for the 11-Oct storm suggests that additional sources of runoff contributed higher concentrations of these solutes after the initial flush at the beginning of the event. Whereas, the relatively weak clockwise hysteresis in the $^{200}\text{Hg}$ C-Q relationship may suggest that the potentially-mobile $^{200}\text{Hg}$ pool in the near-surface organic soil horizon was depleted soon after peak water table levels and flow or that more dilute sources were invoked later in the hydrograph. The lack of hysteresis for all solutes for the 25-May event suggests that the sources and flow pathways of runoff remained constant throughout the event.

The results of the two-component isotopic hydrograph separation indicated a greater proportion of event water on the recession limb of the 25-May storm compared to the 11-Oct storm, which
may have been due to the wetter conditions in the catchment prior to the 25-May event. However, the two-component contributions of event and pre-event water were quite different than those obtained from the three-component hydrochemical separation. Based on these separations, streamwater appeared to be a mixture of shallow soil-water and event water for both storms. Since the stream channel near the base of the catchment is quite small, it is unlikely that the event contribution represented direct precipitation onto the channel. It is more likely that the event contribution was due to inputs onto saturated depressional areas where it was rapidly delivered as saturation overland flow (SOF) to the stream channel and outlet. For the 25-May event the deep soil-water contribution is relatively small and the hydrograph is dominated by event water. This makes more sense than the results of the two-component separation since wet AMCs are more likely to result in SOF. The deep soil-water contribution for the 11-Oct event is slightly higher than the event water contribution, but the hydrograph is dominated by shallow soil-water. This result could suggest that as water tables rise into shallow soil layers after drier periods, the highly permeable layer allows for rapid flow of water and it isn’t until later in the event once soils are saturated that the event water contribution increases. This explanation is corroborated by our calculations that the event contribution increased from 0 to 38% of total discharge over the course of the storm.

In terms of the delivery of THg, \(^{200}\text{Hg}\), and DOC to the catchment outlet, our results suggest that the relatively constant concentrations measured during the 25-May event are due to the dominant contribution of event water, as well as the continuous flow through the organic soil layer prior to the event. For the 11-Oct event, our results suggest that THg, \(^{200}\text{Hg}\), and DOC were initially low due to the contribution from deep soil-water that was shown to be low in all three solutes in Chapter 3. Around peak flow, THg, \(^{200}\text{Hg}\), and DOC were flushed from the organic soil layer as the water table rose and the contribution of shallow soil-water increased as hydrological connectivity was established throughout the catchment. A complicating factor, however, is the obvious spatial variability in the shallow soil-water end-members, which indicates that different parts of the catchment may be contributing different concentrations of Hg and DOC at different times during the event. The most logical scenario for the 11-Oct event that our three-component model and hydrometric data supports is that the initial contribution was from deeper flow pathways through the mineral soil and then the shallow organic soil in the eastern portion of the catchment where Hg:DOC ratios were shown to be higher (see Chapter 4), thus corroborating the clockwise hysteresis we observe in the THg-DOC relationship. As the
event continued and rainfall intensity increased, the sequence of soil-filled depressions in the western part of the catchment surpassed their storage thresholds and the shallow soil-water contribution from this side of the catchment, where THg-DOC ratios are slightly lower, increased. Later in the event, the increasing contribution from event water flowing over saturated areas likely diluted streamwater concentrations. These findings highlight the importance of understanding when and where hydrological connectivity is established in a catchment and how this relates to the spatial variability in Hg:DOC ratios and overall concentrations in soil and soil-water. Further examination and refinement of the shallow soil-water end-member in the UP1 catchment is warranted.

5.4.4 Implications for watershed Hg modelling

The observed net THg and 200Hg retention in the UP1 catchment indicates that even under the wettest conditions the majority of atmospherically-deposited Hg is not exported (Harris et al. 2007). The results of this study suggest that under dry conditions, potentially-mobile DOC, THg, and 200Hg can be temporarily retained in surface soil horizons and soil-water and later flushed when these flowpaths become hydrologically active and connected to the catchment outlet. Any DOC-bound Hg that comes into contact with deeper mineral soil horizons will likely be adsorbed and become unresponsive to changes in hydrologic conditions. Our results support the primary role of surface soils in the control of DOC, THg, and 200Hg fluxes in the UP1 catchment.

Changes in both streamwater and soil-water chemistry in response to variations in antecedent moisture conditions have implications for predicting terrestrial upland Hg export. Models must incorporate the potential for large and rapid changes in soil-water Hg concentrations in response to hydrologic conditions, otherwise they may be difficult to calibrate. For example, in the L658 uplands, a model calibrated to soil-water Hg concentrations following dry periods would result in the selection of different model parameters than a model calibrated to soil-water Hg concentrations following periods with average or above average hydrologic conditions. Model predictions based on the higher Hg concentrations measured during dry periods would indicate higher Hg fluxes than predicted with the model calibrated to lower Hg concentrations given the same discharge patterns. Ideally, upland Hg models need to include a calibration period that is long enough to incorporate intra- and inter-annual hydroclimatic variations. The dynamic
behaviour of the surface soil seen in this study and reported in Chapter 3, emphasizes that models should use multiple soil horizons to accurately predict water quality. Finally, since streamwater Hg concentrations are dependent on antecedent hydrologic conditions it is important to use time steps that are sufficiently small to capture variations in hydrologic conditions and flow routing parameters that may be masked with monthly or annual time steps. The significance of the responsiveness of DOC and Hg concentrations to antecedent hydrologic conditions is highlighted by the potential for climate warming to alter the amount and distribution of precipitation.

A common assumption is that as catchments become drier in a warmer climate there will be less upland runoff and hence less DOC will reach the freshwater aquatic systems (Schindler, 2009). By this reasoning, Hg fluxes should also decrease; however, these assumptions are based on the idea that discharge dominates flux calculations, such that the Hg C-Q relationship is as close to linear as possible. However, our results have shown that the size of the pool of potentially-mobile DOC and Hg grows as catchments become drier and that there are distinct shifts in the Hg and DOC C-Q relationships that are dependent on discharge and antecedent moisture conditions. Therefore, only considering runoff is too simplistic and correct predictions of the effects of climate warming on lake chemistry must consider the balance between runoff generation and the development of the potential DOC and Hg pools on longer time scales.

5.5 Conclusion

In this study we found that variations in THg, $^{200}$Hg, and DOC concentrations were not well explained by discharge over the entire study period, but were on shorter time-scales. However, the inclusion of various indices of antecedent moisture conditions significantly improved the relationships. We also found that variations in total event THg, $^{200}$Hg, and DOC export were controlled by total event runoff and changes in the C-Q relationship. The change in the C-Q relationship appears to be a result of the accumulation of potentially-mobile DOC-bound THg and $^{200}$Hg in well-humified organic soil horizons during dry and warm periods, an increase in soil-water concentrations, and subsequent release during wetter periods. In contrast, events with relatively wet antecedent moisture conditions export less THg, $^{200}$Hg, and DOC because the potentially-mobile pools have been depleted as water continually flows through transmissive
organic soil horizons. In the UP1 catchment, flow appears to be a mixture of shallow soil-water and event water falling on saturated areas. Our two-component and three-component mixing analyses were inconsistent in terms of the proportion of event water contribution to total discharge; however, the results of the three-component analysis are the most consistent with our hydrometric-based understanding of the hydrology of the catchment. They also provide a realistic explanation for the \( \text{THg}, \text{\textsuperscript{200}Hg} \), and \( \text{DOC} \) dynamics that we measured under different antecedent moisture conditions. A greater proportion of event water in the storm with wet antecedent moisture conditions may be partly responsible for lower solute concentrations, whereas a greater contribution of shallow soil-water during the event with dry antecedent moisture conditions likely enhances the flushing of the potentially-mobile solute pools. Spatial variability in the shallow soil-water end-member warrants further investigation.

Hydrologic control of variations in \( \text{THg}, \text{\textsuperscript{200}Hg} \), and \( \text{DOC} \) streamwater concentrations and fluxes indicate that the development of temporally-robust concentration-discharge models for estimation of mass flux must be calibrated over a range of hydroclimatic conditions. The assessment of trends in streamwater quality and watershed \( Hg \) retention require long-term studies to adequately characterize watershed response to variation in hydrologic conditions. The study period should cover a broad range of antecedent moisture conditions and the entire range of discharge. Predictive models of upland \( Hg \) export should also consider the linkage between climate warming and potential upland \( Hg \) export because of the responsiveness of soil-water and streamwater to hydroclimatic variation.
Chapter 6
Summary and Synthesis

6.1 Summary

The overarching goal of this dissertation was to improve our understanding of the hydrological, biogeochemical and landscape controls on Hg transport in boreal Shield uplands. All research presented in this thesis was carried out in a small headwater catchment in northwestern Ontario at the Experimental Lakes Area as part of the METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S.) project. The METAALICUS project was designed to investigate the magnitude and timing of the response of fish MeHg levels to changes in atmospheric-Hg deposition. A unique approach of the METAALICUS project was the use of stable Hg isotopes applied to different watershed compartments to track the mobility and speciation of newly-applied Hg separately from historically-applied ambient Hg. The research presented in this thesis made extensive use of the Hg isotope applied to the watershed uplands. Quantitative analyses of the dominant hydrological processes in the catchment were an essential starting point that provided context for the subsequent work on the distribution of Hg in different soil layers and the role of antecedent moisture conditions on event-scale Hg fluxes.

The general objectives of the four complementary studies carried out for this dissertation were to:

1. Improve our understanding of the relationship between water storage dynamics in topographically-defined landscape units and variations in the event-scale rainfall-runoff response of the catchment;

2. Examine the vertical distribution of Hg in soil and soil-water in different soil horizons;

3. Examine deposition- and topographic-related controls on the spatial distribution of Hg in soil and soil-water across the catchment;

4. Investigate the relationship between antecedent moisture conditions and event-scale Hg and DOC concentration-discharge dynamics.
In the following sections, the major results of the four studies are summarized and some of the factors controlling the timing and magnitude of upland export of ambient \(Hg\) and applied \(Hg\) isotope are discussed.

### 6.1.1 Water storage thresholds and runoff generation in a boreal Shield catchment

Boreal Shield catchments are often characterized by a topographically-complex landscape with variable soil depth and a relatively large proportion of exposed bedrock. Previous studies in boreal regions have noted that these characteristics lead to variable water storage capacity and hydrological connectivity, both of which are important controls on rainfall-runoff response. While several studies in large catchments containing multiple aquatic systems have examined storage-discharge dynamics, no studies have directly quantified the storage-discharge relationship in a headwater catchment. This was identified as an important step towards understanding and predicting the hydrological controls on terrestrial-aquatic solute transport in the METAALICUS uplands.

In Chapter 2, the relationship between water storage dynamics in topographically defined landscape units and variations in rainfall-runoff response were examined using a combination of high-frequency hydrometric monitoring, GIS-based landscape delineation, and piecewise regression analysis. Firstly, precipitation and discharge data collected in the study catchment since 2001 were used to examine inter- and intra-annual variability in rainfall-runoff response. Interestingly, it was found that for the majority of rainfall events less than 20% of precipitation was translated into quick flow, which suggested that for the majority of events less than 20% of the catchment area contributed to runoff and that hydrological connectivity was limited more often than not. The historical rainfall-runoff analysis also showed that 2008, the year of intensive hydrometric monitoring and water storage calculations, had average precipitation inputs and runoff response compared to other years. This was very fortunate as the analysis could then be considered representative of average conditions.

A novel landscape partitioning and classification approach was used to delineate physically-based hydrologic response units (depressions, midslopes, bedrock uplands/ridges), for which water storage was then calculated using a depth function for drainable porosity. The storage-
discharge relationships for depression and midslope HRUs were best modeled using piecewise regression analysis that was able to capture the distinct threshold or breakpoint in the relationship. The storage breakpoint was found to separate two distinct hydrologic regimes at both the HRU- and catchment-scale. In the study catchment, water storage dynamics in the terminal depression were the strongest predictor of catchment runoff. However, the inclusion of storage excesses from upslope depressions that were explicitly routed through the catchment significantly improved the ability to predict runoff response. One of the most important findings of this study was that approximately 71% of event quick flow was generated by depression HRUs that cover only 22% of the total catchment area. This study is among the first to quantitatively support previous conceptual models of hydrological behaviour in boreal Shield catchments that have runoff generation controlled by connectivity between discrete landscape units and that suggest the largest and/or terminal storage element will control the rainfall-runoff response of the entire catchment. This chapter was a useful foundation for all of the subsequent studies because it provided important information about the hydrogeomorphology of the catchment and the hydrological behaviour of potentially important biogeochemical source areas.

6.1.2 The vertical distribution of ambient mercury and applied mercury isotope in soil and soil-water in the soil landscape

In Chapter 3, the vertical distribution of ambient and spike Hg in soil and soil-water was examined in different horizons. While Hg$_{DOC}$:DOC to Hg$_{SOC}$:SOC ratios have been used in other studies to compare Hg release into solution between distant sites, this approach has not been applied to compare the differences between soil horizons for both historically- and newly-deposited Hg in a single catchment. In the METAALICUS watershed, there was a unique opportunity to make use of the stable Hg isotope applied to the uplands to investigate how new Hg moves through the soil in comparison to ambient Hg.

Extensive soil sampling from the surface organic, lower organic and mineral soil layers across the study catchment showed that mean solid-phase ambient Hg concentration was highest in the lower, humified organic soil horizon; however, mean spike Hg concentration was highest in the surface litter layer and decreased with depth. This result was not unexpected as the spike Hg had only been in the soil profile for ~7 years before samples were collected. A related finding was that ambient Hg:SOC increased with depth, suggesting that less Hg than SOC is lost as
SOM decomposes and is incorporated deeper into the soil profile. However, spike Hg:SOC was relatively constant with depth, suggesting that any enrichment of the soil with spike Hg as a result of decomposition had not occurred after 7 years. In order to examine the degree of release of Hg into solution, soil-water samples were collected from a network of shallow zero-tension lysimeters and deep piezometers throughout the catchment. Both ambient and spike Hg concentrations were highest in shallow soil-water, and more importantly, the mean ambient Hg concentration in shallow soil-water was not statistically different than the concentration in runoff collected at the catchment outlet. This was not the case for mean spike Hg, whose concentration in catchment runoff was statistically lower than in shallow soil-water. Similar to ambient Hg:SOC, ambient Hg:DOC was higher in deep soil-water compared to shallow soil-water and catchment runoff which had similar mean values.

Finally, the ratio of Hg\textsubscript{D}:DOC to Hg\textsubscript{S}:SOC was only close to unity for both ambient and spike Hg when values from the lower, humified organic soil horizon and shallow soil-water were used. This important result suggests that the dominant source of DOM-bound Hg to shallow soil-water is from the lower, humified organic soil horizon. Given that the lower organic soil horizon is likely the dominant source of ambient Hg to soil-water and that ambient Hg concentrations and its ratio to DOC in shallow soil-water and catchment runoff are not statistically different, it is likely that ambient Hg is transported to the lake along flow pathways through the highly conductive organic soil horizon. The results of this study will be potentially useful for parameterizing predictive models of upland Hg export that differentiate soil horizons.

### 6.1.3 The spatial distribution of ambient mercury and applied mercury isotope across the soil landscape

In Chapter 4, the extensive soil survey used to study the vertical distribution of Hg in the soil profile was used to examine the horizontal distribution of solid- and solution-phase organic carbon, ambient Hg and spike Hg stocks in different soil layers across the study catchment. In some landscapes, studies have suggested that factors that lead to differential SOM accumulation, such as landscape position, drainage, and vegetation characteristics, also lead to differential Hg accumulation. In boreal regions, spatial patterns of Hg in soils have been investigated mainly in wetlands and on regional scales; however, studies examining spatial patterns at the scale of individual landscape features are lacking. In order to accurately estimate the proportion of a
catchment that contributes to \( Hg \) in runoff, it is important to know both when and where hydrological contributing areas form and which soil horizons contribute the majority of \( Hg \). However, it is also important to know where \( Hg \) concentrations in the soil and soil-water are highest in the catchment, so that these areas can be assigned a relatively high source-strength value when they become hydrologically connected to the catchment outlet.

A spatial statistical analysis revealed that \( SOC \), \( ambient \ Hgs \), and \( spike \ ^{200} \ Hgs \) stocks are not randomly distributed across the landscape. Several deposition- and topographic-related variables were included in a multiple regression analysis to try to explain the spatial patterns. Relationships were examined using both interpolated data at the 10-m pixel scale and data that were aggregated for each of the HRUs delineated in Chapter 2. Topography and drainage conditions, as represented by the topographic wetness index, did not provide strong explanations for spatial variations in stocks. Areas of the catchment with larger upslope contributing area and/or higher topographic wetness index did not necessarily contain the largest stocks, regardless of the scale of study. Instead, canopy type was the most determining factor for \( SOC \) and \( ambient \ Hgs \) distributions at the 10-m pixel scale, and a combination of canopy type and mean \( LAI \) were the most determining factors at the HRU scale. In general, mean \( SOC \), \( ambient \ Hgs \) and \( spike \ ^{200} \ Hgs \) stocks were higher under old growth coniferous canopy compared to under deciduous canopy. This finding is consistent with previous studies in the catchment that found that \( Hg \) inputs to the forest floor were highest under old growth coniferous canopy and is also a potentially useful way to estimate the \( Hg \) source-strength of a watershed using remote sensing data to detect vegetation types. At the HRU-scale, depressions with the smallest \( LAI \) and largest amount of deadfall had the highest \( SOC \), \( ambient \ Hgs \) and \( spike \ ^{200} \ Hgs \) stocks in the litter layer. This is an important finding that warrants further study of the influence of deadfall on \( Hg \) concentrations in the soil. Lastly, the strongest determining factor for the \( spike \ ^{200} \ Hgs \) distribution in the litter and organic horizons was the spatial distribution of the \( 2001-2006 \ cumulative \ ^{200} \ Hg \) spray release. This finding was not unexpected given the relatively short amount of time the spike had been in the system at the time of sample collection and highlights the importance of continuing to monitor the lateral redistribution of the spike through the soil landscape for evidence of translocation in runoff.
6.1.4 The influence of antecedent moisture conditions on the concentration-discharge dynamics of ambient mercury, applied mercury isotope and dissolved organic carbon

A common assumption amongst aquatic scientists is that DOC inputs to freshwater systems will decrease in a warmer, drier climate as a result of a decrease in the amount of runoff. In such a scenario, DOC concentrations would be relatively constant and DOC fluxes would be controlled by the amount of discharge. Given the strong interaction between DOC and Hg, these assumptions should also apply to terrestrial-aquatic Hg fluxes. However, previous work in the northeastern USA found seasonal differences in both DOC and Hg concentrations per unit discharge. These important findings suggest that the Hg concentration-discharge relationship is dependent on antecedent moisture conditions (AMCs) and the impact these have on the development of the potentially-mobile DOM-bound Hg pool in the soil. However, there is also the possibility that differences in AMCs affect the flow pathways that water takes through the catchment, thereby connecting different areas of the catchment or different soil layers with differing degrees of Hg partitioning. There is currently a lack of knowledge, especially in boreal uplands, on the extent to which AMCs explain variations in DOC and Hg concentrations in runoff. It is also uncertain whether or not the avenue of AMCs influence is via changes in the biogeochemical conditions in the soil that affect decomposition and the growth of the potentially-mobile pool or via changes in flow pathways that connect different parts of the catchment or different soil layers or both.

In Chapter 5, these questions were addressed by examining ambient Hg, spike Hg and DOC concentration-discharge (C-Q) dynamics over several months and at the event-scale. The C-Q relationship for ambient Hg, spike Hg and DOC using all samples collected over the study period was very weak and based on the residual analysis there were obvious seasonal shifts in the relationship. When several common indices of AMCs were included with discharge in a multiple regression analysis, the amount of variation in the C-Q relationship explained by the model increased dramatically. Both discharge at the catchment outlet and mean antecedent storage over the previous week in the terminal depression were the strongest predictors of variations in concentration. This important result bodes well for including indices of AMCs in predictive models of upland Hg fluxes. However, it also stresses the need to calibrate these models over a range of hydroclimatic conditions, including both very dry and very wet years.
At the event-scale, total ambient Hg, spike Hg and DOC export was strongly correlated to total event water export; however, the two smallest events had significantly different solute loads despite nearly the same water export. Concentrations of ambient Hg, spike Hg and DOC in shallow soil-water also exhibited the same differences with higher values during the autumn event with relatively dry AMCs compared to the spring event with relatively wet AMCs. An examination of the C-Q relationships for these two events showed two distinctly different patterns. For the event with wet AMCs, solute concentrations remained relatively constant, but for the event with dry AMCs, solute concentrations increased with discharge indicating a flushing mechanism. The results of a three-component hydrograph separation showed that the event with wet AMCs had a higher contribution of event water and that the event with dry AMCs was dominated by shallow soil-water. Therefore, it is difficult to discern whether or not the effect of different AMCs on Hg and DOC export was as a result of enhanced development of the potentially-mobile pool in the organic soil horizon or if it was due to differences in end-member contributions. It is likely that both factors played a role; however, further examination of spatial variations in the shallow soil-water end member and changes in decomposition rates in the soil are warranted.

6.2 Synthesis

6.2.1 Factors affecting the timing and magnitude of upland export of ambient mercury and applied mercury isotope

The four studies presented in this dissertation address important questions that face Hg scientists interested in understanding and modelling the key environmental processes controlling Hg cycling and transport in boreal watersheds. While the research in this dissertation did not directly estimate the lifetime of Hg in the upland soil landscape, it did point towards the importance of incorporating watershed-specific information on hydrologic source areas and the extent to which they overlap with areas with a relatively large pool of potentially-mobile Hg into predictive models of Hg transport in upland environments. In addition, this research points toward the need to calibrate hydro-biogeochemical models of Hg transport over a range of hydroclimatic conditions to ensure that shifts in Hg concentration-discharge dynamics are
accounted for. The following sections provide brief syntheses of more specific factors that are likely to affect the timing and magnitude of upland Hg export in boreal Shield watersheds, as supported directly or indirectly by some of the key findings of this dissertation research.

6.2.1.1 Runoff generation and hydrologic connectivity between landscape units

Hydrologic connectivity in the study catchment is variable in space and time due to the complex topography, variable soil depth, and arrangement of soil-filled bedrock depressions. The hydrograph separation results presented in Chapter 2 implied that flow is generated from less than 20% of the catchment the majority of the time (i.e. limited hydrologic connectivity) and the results of the explicit routing exercise suggested that this 20% is the area covered by soil-filled bedrock depressions. However, the spatial analysis undertaken in Chapter 4 showed that the depressions were not necessarily where Hg concentrations in soil and soil-water were the highest. In Chapter 5, the results of a three-component hydrograph separation suggested that for storms with relatively dry AMCs deeper flow pathways along the more continuously-sloping eastern side of the catchment contribute water faster than water that fills and spills over the western depression-dominated side of the catchment. While the majority of this water was likely flowing through the deeper mineral soil horizon, it is important to keep in mind that the eastern depression had relatively high Hg$_S$:SOC and Hg$_D$:DOC ratios compared to the other depressions in the catchment. These findings point towards the need to improve our ability to make predictive maps of hydrological contributing areas and biogeochemical contributing areas (i.e. areas with a relatively large potentially-mobile DOC and Hg pools) over a range of hydroclimatic conditions.

6.2.1.2 The development of the potentially-mobile DOC-bound Hg pool

Two important findings in Chapter 3 were that the dominant source of ambient Hg to the lake was soil-water from the lower humified organic horizon and that the majority of experimentally-applied spike Hg was still retained in the surface litter layer after 7 years. While we were not able to estimate the time it took for ambient Hg to reach the lower organic horizon, the results suggested that the dominant mechanism by which Hg moves into the lower organic layer is
through the degradation of SOC, since $Hg_{S}:SOC$ ratios increased with depth throughout the catchment. Therefore, one could expect that the hydroclimatic and biogeochemical factors that affect the turnover rate and solubility of SOC may be considered as primary controls on the movement of Hg vertically through the soil profile and the development of the potentially-mobile DOC-bound Hg pool.

### 6.2.1.3 Landscape controls on the spatial distribution of mercury

In Chapter 4, canopy type was highlighted as a primary control on the spatial distribution of ambient Hg in the lower organic soil horizon, which is supported by previous findings in the METAALICUS watershed that showed higher concentrations of Hg in litterfall and throughfall under coniferous old growth canopy. Maps of tree species type derived from remote sensing or logging data have the potential to be used to estimate the areal extent of the potentially-mobile Hg soil pool. While no strong topographic controls on Hg in soil and soil-water were found in this study, it is more likely that they exist in more continuously sloping catchments. In the boreal Shield landscape, discontinuous soil cover and threshold-driven hydrologic connectivity likely favour the vertical movement of SOC and Hg through the soil profile the majority of time. However, in years with above average precipitation and wetter soil conditions, lateral translocation downslope due to erosion and hydrologic transport may increase. In time, the spike Hg applied to the uplands will serve as a tracer of the balance between these two modes of transport.

### 6.2.1.4 The effect of antecedent moisture conditions on the balance between discharge- and concentration-driven fluxes

The results presented in Chapter 5 call into question the common assumption that DOC, and by association Hg, terrestrial-aquatic fluxes will decrease in a warmer, drier climate. Climate change could have dramatic consequences for the hydrological cycle, particularly in regions where runoff is dominated by snowmelt. Reductions in winter precipitation falling as snow, shifts in the timing of peak flow and variations in soil conditions could result in major changes to water quantity and quality for northern freshwater ecosystems. Climate change predictions for the boreal Shield ecozone suggest that there will not be a significant change in the total
annual amount of precipitation, but that temporal shifts will occur with less wintertime precipitation and more summer storms. If this is the case, given the results of this study, we should expect the slope of the C-Q relationship to increase and the annual export of $Hg$ to increase in average to wet years. The extent to which high flow periods follow warm dry periods may be an important control on the magnitude and timing of $Hg$ export and total annual loading to the lake.

6.2.2 Future Research Directions

6.2.2.1 Long-term catchment inter-comparisons

The quantification of catchment-scale storage-discharge dynamics, hydrologic connectivity, flow pathways, and residence times remains a challenging problem for hydrologists interested in issues of water quantity and quality. In boreal regions, the role of temporally and spatially varying snowfall and ground ice add an extra layer of complexity to these challenges. While progress has been made in this and related studies, the field would benefit from watershed intercomparison studies that explore common features of watershed response across multiple temporal and spatial scales. As part of these, the role of winter hydroclimatic conditions on runoff response for a range of catchments that vary in size and hydrogeomorphic characteristics could be studied. At the ELA, landscape delineation could be easily applied in other areas of the L658 watershed and to other watersheds in the region to determine the areal coverage of different HRU types. Catchments of similar size, but with different HRU arrangements could then be monitored at the same time to determine whether or not the same hydrological controls on $Hg$ fluxes apply when topographic and soil depth patterns differ. Particular attention should be paid to careful characterization of the end-members that contribute to catchment discharge. In Chapter 5, the results of a three-component hydrograph separation were not conclusive due to spatial variability in the shallow soil-water end-member. Through catchment intercomparison, some of these complexities may be clarified.
6.2.2.2 Long-term monitoring of spike $^{200}\text{Hg}$ in METAALICUS upland soils

In the METAALICUS watershed, it is expected that the upland spike will slowly make its way into deeper mineral soils and be redistributed downslope in runoff once it has reached the lower organic soil horizon; however, this may occur over timescales longer than the average funding period. It will be important to maintain a modest sampling program in the METAALICUS uplands for as long as possible, so that the rate of spike $\text{Hg}$ movement can be estimated. As well, further research is required to determine the depth to which both ambient and spike $\text{Hg}$ penetrate into the mineral layer and whether or not these pools are able to partition into solution and move along deeper flow pathways.

6.2.2.3 Further examination of landscape controls on mercury distribution in soil landscapes

Future studies are needed to refine our understanding of the spatial controls on soil $\text{Hg}$ stocks in upland systems at multiple scales, for example, at smaller scales of hummocks and hollows or vegetation features such as fallen trees, and at larger landscape-scales where comparisons between catchments with different topographic forms can be made. This multi-scale framework should be designed \textit{a priori} based on the spatial patterns of the catchment characteristics of interest, for example canopy type. Focus also needs to be placed on evaluating the relative importance of vertical and horizontal $\text{Hg}$ fluxes in soil-water across different landscape features. We expect that in systems that are less topographically-complex and that contain more continuous soil cover, the spatial distribution of $\text{Hg}$ in the soil landscape will be more strongly related to drainage conditions. Knowing the average rate of DOC-bound $\text{Hg}$ movement through different soil horizons in different topographic settings would help inform watershed $\text{Hg}$ export models.

6.2.2.4 Mercury speciation, carbon quality, and climate change

Upland $\text{Hg}$ research should expand to investigate the role of perennially-saturated upland areas as possible sources of methylmercury ($\text{MeHg}$) to surface waters. Wetlands are a major source of $\text{MeHg}$ to lakes, however many upland topographic depressions that contain thick, saturated
organic soils also produce MeHg. It is still uncertain whether or not this MeHg is mobile and contributes to the MeHg found in lakes and fish.

The role of dissolved organic carbon quality on Hg mobility and bioavailability for methylation should also be examined further in boreal Shield uplands. Recent unpublished work has found that molecular weight of DOM in runoff changes as flow progresses downslope and affects the amount of Hg reaching the lake relative to source areas. A systematic analysis of carbon quality at the stream outlet over a range of hydrologic conditions may be a useful approach to determine the extent that carbon characteristics affect Hg transport.

Climate change has the potential to increase SOM decomposition leading to an increase in terrestrial-aquatic DOC and Hg export. The presence of DOC has been shown to increase the complexation and solubility of Hg. Few studies have directly investigated the process-level relationships between soil decomposition rates, climate-induced changes in soil biogeochemistry, and Hg mobilization in runoff. To start, these relationships could be examined through in situ soil warming experiments that are designed to ascertain the combined effects of changes in temperature and wetness on the quality and mobility of dissolved organic carbon in forested landscapes.
References


Demers, J. D. et al. (2007). “Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA.” Ecological Applications 17(5): 1341-1351.


Kalbitz, K. et al. (2000). “Controls on the dynamics of dissolved organic matter in soils:


Tetzlaff, D. et al. (2010). “Catchment processes and heterogeneity at multiple scales – benchmarking observations, conceptualization and prediction.” Hydrological


Appendix 1. Spatial Statistics Results for Chapter 4

Table A.4.1 Relationships between SOC, ambient HgS, spike $^{200}$HgS, ambient HgS:SOC, spike $^{200}$HgS and LAI, LAI and canopy type, the 2006 cumulative spray release, upslope area ($A$), and the topographic wetness index (TWI) for the litter, organic and mineral soil horizons based on Pearson’s correlation coefficients. $p$ values are given in brackets and bold indicates $p<0.05$. Only data from midslope and depression HRUs are included ($n$=387).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variable(s)</th>
<th>LAI</th>
<th>LAI and Canopy</th>
<th>2006 Cumulative Spray Release (µg m$^{-2}$)</th>
<th>A (m$^2$)</th>
<th>TWI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.08 (0.45)</td>
<td>0.20 (&lt;0.01)</td>
<td>-</td>
<td>0.06 (0.63)</td>
<td>0.20 (0.13)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.09 (0.39)</td>
<td>0.28 (&lt;0.01)</td>
<td>-</td>
<td>-0.12 (0.28)</td>
<td>-0.03 (0.83)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.02 (0.88)</td>
<td>0.22 (&lt;0.01)</td>
<td>0.46 (0.02)</td>
<td>-0.03 (0.81)</td>
<td>0.10 (0.45)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.26 (&lt;0.01)</td>
<td>0.30 (&lt;0.01)</td>
<td>-</td>
<td>-0.25 (0.02)</td>
<td>-0.33 (0.01)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.11 (0.08)</td>
<td>0.00 (0.98)</td>
<td>0.36 (0.03)</td>
<td>-0.08 (0.46)</td>
<td>-0.01 (0.91)</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.20 (0.12)</td>
<td>0.39 (&lt;0.01)</td>
<td>-</td>
<td>0.30 (0.05)</td>
<td>0.33 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.20 (0.13)</td>
<td>0.32 (&lt;0.01)</td>
<td>-</td>
<td>0.19 (0.27)</td>
<td>0.31 (0.09)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.17 (0.09)</td>
<td>0.22 (&lt;0.01)</td>
<td>0.33 (&lt;0.01)</td>
<td>0.17 (0.14)</td>
<td>0.30 (0.02)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.04 (0.67)</td>
<td>0.13 (0.05)</td>
<td>-</td>
<td>-0.05 (0.70)</td>
<td>0.06 (0.65)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.04 (0.68)</td>
<td>0.05 (0.63)</td>
<td>0.26 (0.01)</td>
<td>0.01 (0.92)</td>
<td>0.11 (0.27)</td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.01 (0.92)</td>
<td>0.25 (&lt;0.01)</td>
<td>-</td>
<td>0.14 (0.15)</td>
<td>0.13 (0.26)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.04 (0.58)</td>
<td>0.05 (0.59)</td>
<td>-</td>
<td>0.10 (0.23)</td>
<td>0.10 (0.31)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.04 (0.67)</td>
<td>0.44 (&lt;0.01)</td>
<td>0.03 (0.85)</td>
<td>0.25 (0.04)</td>
<td>0.10 (0.46)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.16 (0.07)</td>
<td>0.40 (&lt;0.01)</td>
<td>-</td>
<td>-0.04 (0.73)</td>
<td>0.10 (0.37)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.18 (0.01)</td>
<td>0.19 (&lt;0.01)</td>
<td>-0.02 (0.75)</td>
<td>0.09 (0.25)</td>
<td>0.15 (0.09)</td>
<td></td>
</tr>
</tbody>
</table>
Table A.4.2  Relationships between SOC, ambient HgS, spike $^{200}$HgS, ambient HgS:SOC, spike $^{200}$HgS and LAI, LAI and canopy type, the 2006 cumulative spray release, upslope area (A), and the topographic wetness index (TWI) for the litter, organic and mineral soil horizons based on Pearson’s correlation coefficients. $p$ values are given in brackets and bold indicates $p<0.05$. Only data from depression HRUs are included ($n=138$).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variable(s)</th>
<th>LAI</th>
<th>LAI and Canopy</th>
<th>2006 Cumulative Spray Release ($\mu$g m$^{-2}$)</th>
<th>A (m$^2$)</th>
<th>TWI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.23 (0.06)</td>
<td>0.30 (&lt;0.01)</td>
<td>-</td>
<td>-0.12 (0.45)</td>
<td>-0.06 (0.72)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.24 (0.08)</td>
<td>0.30 (&lt;0.01)</td>
<td>-</td>
<td>-0.27 (0.14)</td>
<td>-0.22 (0.19)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>-0.24 (0.07)</td>
<td>0.27 (&lt;0.01)</td>
<td>0.45 (0.03)</td>
<td>-0.25 (0.16)</td>
<td>-0.25 (0.12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.09 (0.40)</td>
<td>0.09 (0.56)</td>
<td>-</td>
<td>-0.28 (0.02)</td>
<td>-0.28 (0.02)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.15 (0.22)</td>
<td>0.16 (0.18)</td>
<td>0.55 (&lt;0.01)</td>
<td>-0.30 (0.07)</td>
<td>-0.35 (0.02)</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.15 (0.28)</td>
<td>0.28 (&lt;0.01)</td>
<td>-</td>
<td>0.21 (0.10)</td>
<td>0.18 (0.16)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.15 (0.29)</td>
<td>0.30 (&lt;0.01)</td>
<td>-</td>
<td>-0.04 (0.80)</td>
<td>-0.02 (0.90)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>-0.03 (0.80)</td>
<td>0.05 (0.86)</td>
<td>0.14 (0.36)</td>
<td>0.00 (0.99)</td>
<td>-0.01 (0.96)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.06 (0.49)</td>
<td>0.08 (0.64)</td>
<td>-</td>
<td>-0.26 (0.02)</td>
<td>-0.20 (0.09)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.01 (0.89)</td>
<td>0.23 (0.03)</td>
<td>0.17 (0.31)</td>
<td>-0.12 (0.38)</td>
<td>-0.16 (0.22)</td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.07 (0.59)</td>
<td>0.38 (&lt;0.01)</td>
<td>-</td>
<td>0.13 (0.42)</td>
<td>0.20 (0.18)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.08 (0.46)</td>
<td>0.09 (0.61)</td>
<td>-</td>
<td>0.07 (0.59)</td>
<td>0.09 (0.43)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS (µg m$^{-2}$)</td>
<td>0.02 (0.89)</td>
<td>0.17 (0.13)</td>
<td>-0.26 (0.10)</td>
<td><strong>0.35 (0.01)</strong></td>
<td>0.11 (0.39)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.24 (0.09)</td>
<td><strong>0.66 (&lt;0.01)</strong></td>
<td>-</td>
<td>-0.13 (0.50)</td>
<td>-0.09 (0.62)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spike $^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.14 (0.26)</td>
<td><strong>0.36 (&lt;0.01)</strong></td>
<td>-0.10 (0.50)</td>
<td>0.03 (0.80)</td>
<td>-0.03 (0.81)</td>
<td></td>
</tr>
</tbody>
</table>
Table A.4.3 Summary of multiple linear regression model selection using weighted Akaike’s Information Criterion. Predictor variables for SOC, ambient HgS, and ambient HgS:SOC include LAI, canopy type, and TWI. Predictor variables for spike$^{200}$HgS and spike$^{200}$HgS:SOC include LAI, canopy type, 2006 cumulative spray release, and TWI. Significant ($p<0.05$) standardized partial regression coefficients are shown before each variable. Variables are listed in order of importance. All gridded data used in analyses (n=611).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variables with Significant Partial Regression Coefficients</th>
<th>Multiple r</th>
<th>Akaike Weight*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Litter</strong></td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.2Canopy +0.13TWI</td>
<td>0.25</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.27Canopy -0.07LAI</td>
<td>0.28</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>0.52Spray -0.09Canopy -0.08LAI</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.19TWI -0.13Canopy -0.1LAI</td>
<td>0.27</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.44Spray -0.10LAI</td>
<td>0.43</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.37Canopy +0.17TWI +0.09LAI</td>
<td>0.44</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.20TWI -0.16Canopy +0.09LAI</td>
<td>0.30</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>0.36Spray +0.14TWI -0.05Canopy</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.33Canopy +0.09TWI</td>
<td>0.34</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.34Spray +0.08Canopy +0.07TWI</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td><strong>Mineral</strong></td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.17Canopy + 0.11TWI</td>
<td>0.20</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.07LAI</td>
<td>0.09</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>-0.46Canopy</td>
<td>0.46</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.30Canopy +0.14LAI +0.08TWI</td>
<td>0.34</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.15LAI -0.11Canopy</td>
<td>0.20</td>
<td>0.35</td>
</tr>
</tbody>
</table>

* The Akaike weight is an indication of the strength of the best model given the entire set of models (i.e. all combinations of predictor variables).
Table A.4.4 Summary of multiple linear regression model selection using weighted Akaike’s Information Criterion. Predictor variables for SOC, ambient HgS, and ambient HgS:SOC include LAI, canopy type, and TWI. Predictor variables for spike$^{200}$HgS and spike$^{200}$HgS:SOC include LAI, canopy type, 2006 cumulative spray release, and TWI. Significant ($p<0.05$) standardized partial regression coefficients are shown before each variable. Variables are listed in order of importance. Only midslope and depression HRU gridded data used in analyses (n=387).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variables with Significant Partial Regression Coefficients</th>
<th>Multiple r</th>
<th>Akaike Weight*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.17 TWI -0.15Canopy</td>
<td>0.25</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (μg m$^{-2}$)</td>
<td>-0.27Canopy -0.08LAI</td>
<td>0.28</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (μg m$^{-2}$)</td>
<td>0.46Spray -0.16Canopy -0.10LAI</td>
<td>0.49</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (μg gC$^{-1}$)</td>
<td>-0.32TWI -0.20Canopy -0.27LAI</td>
<td>0.41</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (μg gC$^{-1}$)</td>
<td>0.39Spray -0.13LAI</td>
<td>0.39</td>
<td>0.29</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.28Canopy +0.25TWI +0.09LAI</td>
<td>0.44</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (μg m$^{-2}$)</td>
<td>0.24TWI -0.20Canopy +0.10LAI</td>
<td>0.37</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (μg m$^{-2}$)</td>
<td>0.26Spray +0.22TWI</td>
<td>0.40</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (μg gC$^{-1}$)</td>
<td>0.13Canopy +0.08TWI</td>
<td>0.14</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (μg gC$^{-1}$)</td>
<td>0.26Spray</td>
<td>0.27</td>
<td>0.31</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.24Canopy + 0.09TWI</td>
<td>0.26</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (μg m$^{-2}$)</td>
<td>0.10TWI</td>
<td>0.11</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (μg m$^{-2}$)</td>
<td>-0.44Canopy</td>
<td>0.44</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (μg gC$^{-1}$)</td>
<td>0.39Canopy +0.14TWI +0.11LAI</td>
<td>0.42</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (μg gC$^{-1}$)</td>
<td>0.17LAI +0.10TWI -0.09Canopy</td>
<td>0.22</td>
<td>0.23</td>
</tr>
</tbody>
</table>

* The Akaike weight is an indication of the strength of the best model given the entire set of models (i.e. all combinations of predictor variables).
Table A.4.5 Summary of multiple linear regression model selection using weighted Akaike’s Information Criterion. Predictor variables for SOC, ambient HgS, and ambient HgS:SOC include LAI, canopy type, and TWI. Predictor variables for spike$^{200}$HgS and spike$^{200}$HgS:SOC include LAI, canopy type, 2006 cumulative spray release, and TWI. Significant ($p<0.05$) standardized partial regression coefficients are shown before each variable. Variables are listed in order of importance. Only depression HRU gridded data used in analyses (n=138).

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Response Variable</th>
<th>Predictor Variables with Significant Partial Regression Coefficients</th>
<th>Multiple r</th>
<th>Akaike Weight*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.24Canopy -0.17LAI</td>
<td>0.32</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.31Canopy -0.30TWI</td>
<td>0.40</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>0.45Spray -0.30Canopy -0.19TWI -0.12LAI</td>
<td>0.57</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.29TWI -0.13Canopy</td>
<td>0.30</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.50Spray -0.23TWI -0.15Canopy</td>
<td>0.60</td>
<td>0.47</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.13Canopy</td>
<td>0.31</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>-0.30Canopy</td>
<td>0.31</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>0.14Spray</td>
<td>0.15</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>-0.23TWI</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.21Canopy +0.13Spray</td>
<td>0.27</td>
<td>0.20</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>-0.37Canopy</td>
<td>0.39</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.10TWI</td>
<td>0.12</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>-0.25Canopy</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.67Canopy</td>
<td>0.67</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>0.38Canopy -0.17Spray</td>
<td>0.40</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* The Akaike weight is an indication of the strength of the best model given the entire set of models (i.e. all combinations of predictor variables).
Table A.4.6 Results of Welch’s variance-weighted analysis of variance applied to point data for individual depression and midslope HRUs and for grouped depression HRUs versus the midslope HRU. Results of the Tukey Unequal N HSD post-hoc multiple comparisons test are given for individual HRUs. $F$ values are given with $p$ value in brackets. Bold indicates $p<0.05$.

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Variable</th>
<th>$F$ (p) (individual HRUs)</th>
<th>Results of Tukey Unequal N HSD (p) (individual HRUs)</th>
<th>$F$ (p) (grouped HRUs)</th>
<th>Result (grouped HRUs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter</td>
<td>SOC (kg m$^{-2}$)</td>
<td>3.08 (0.04)</td>
<td>DEP$^{EAST}$ &gt; MID (0.02)</td>
<td>5.24 (0.02)</td>
<td>DEP &gt; MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>3.13 (0.04)</td>
<td>DEP$^{EAST}$ &gt; DEP$^{TERMINAL}$ (0.04) DEP$^{EAST}$ &gt; MID (0.02)</td>
<td>4.74 (0.03)</td>
<td>DEP &gt; MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>3.34 (0.03)</td>
<td>DEP$^{EAST}$ &gt; DEP$^{TERMINAL}$ (0.03) DEP$^{EAST}$ &gt; MID (0.03) DEP$^{EAST}$ &gt; DEP$^{WEST}$ (0.04)</td>
<td>0.84 (0.36)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>1.02 (0.42)</td>
<td>-</td>
<td>0.57 (0.45)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>4.17 (0.01)</td>
<td>DEP$^{EAST}$ &gt; DEP$^{TERMINAL}$ (0.03) DEP$^{EAST}$ &gt; MID (0.03) DEP$^{EAST}$ &gt; DEP$^{WEST}$ (0.04)</td>
<td>0.50 (0.48)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Organic</td>
<td>SOC (kg m$^{-2}$)</td>
<td>0.94 (0.47)</td>
<td>-</td>
<td>2.34 (0.13)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.91 (0.47)</td>
<td>-</td>
<td>2.27 (0.13)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>1.54 (0.21)</td>
<td>-</td>
<td>4.65 (0.03)</td>
<td>DEP &gt; MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>0.12 (0.97)</td>
<td>-</td>
<td>0.01 (0.93)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>1.26 (0.32)</td>
<td>-</td>
<td>0.26 (0.61)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Mineral</td>
<td>SOC (kg m$^{-2}$)</td>
<td>18.04 (&lt;0.001)</td>
<td>DEP$^{TERMINAL}$ &gt; DEP$^{UPWEST}$ (0.05)</td>
<td>0.32 (0.57)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS (µg m$^{-2}$)</td>
<td>0.76 (0.56)</td>
<td>-</td>
<td>0.09 (0.76)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS (µg m$^{-2}$)</td>
<td>2.36 (0.09)</td>
<td>-</td>
<td>8.20 (0.005)</td>
<td>DEP &gt; MID</td>
</tr>
<tr>
<td></td>
<td>Ambient HgS:SOC (µg gC$^{-1}$)</td>
<td>1.59 (0.22)</td>
<td>-</td>
<td>0.36 (0.55)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td></td>
<td>Spike$^{200}$HgS:SOC (µg gC$^{-1}$)</td>
<td>2.15 (0.12)</td>
<td>-</td>
<td>1.33 (0.25)</td>
<td>DEP = MID</td>
</tr>
</tbody>
</table>
Table A.4.7 Results of analysis of variance (ANOVA) on DOC and HgD variables for individual depression and midslope HRUs and for grouped depression and midslope HRUs. *F* values are given with *p* value in brackets. Results of the Tukey HSD post-hoc multiple comparisons test are given for individual HRUs. Bold indicates *p*<0.05.

<table>
<thead>
<tr>
<th>Variable</th>
<th>F (p) (individual HRUs)</th>
<th>Results of Tukey HSD (p) (individual HRUs)</th>
<th>F (p) (grouped HRUs)</th>
<th>Result (grouped HRUs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg L⁻¹)</td>
<td>1.90 (0.12)</td>
<td>-</td>
<td>0.30 (0.59)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Ambient HgD (ng L⁻¹)</td>
<td>2.53 (0.05)</td>
<td><strong>DEP</strong>&lt;sub&gt;EAST&lt;/sub&gt; <strong>&gt;</strong> MID (0.05)</td>
<td>2.98 (0.09)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Spike²⁰⁰HgD (ng L⁻¹)</td>
<td>0.90 (0.47)</td>
<td>-</td>
<td>1.61 (0.21)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Ambient HgD:DOC (ng gC⁻¹)</td>
<td>1.65 (0.18)</td>
<td>-</td>
<td>1.78 (0.19)</td>
<td>DEP = MID</td>
</tr>
<tr>
<td>Spike²⁰⁰HgD:DOC (ng gC⁻¹)</td>
<td>1.54 (0.20)</td>
<td>-</td>
<td>0.95 (0.34)</td>
<td>DEP = MID</td>
</tr>
</tbody>
</table>