Catchment-scale Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield

Brian A. Branfireun

Department of Geography
McGill University, Montréal.
January, 1999

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

0-612-50321-6

Abstract

The role of catchment hydrology and biogeochemistry in the production and transport of methylmercury (MeHg) was studied in a headwater catchment in the low boreal forest zone of the Precambrian Shield. A simple, catchment-scale model found that peatlands were large sources of MeHg, and lakes were large sinks. Sensitivity analysis revealed that the volume of runoff delivered to the peatland by the upland, peatland size, and pore water MeHg concentration in the peatland are important controls on catchment MeHg yield. Contemporary atmospheric deposition of MeHg was found to be insignificant compared to the sources of MeHg within the catchment.

Sulfate addition experiments were undertaken to examine the controls on MeHg production in peatlands, and it was found that the *in situ* addition of sulfate to peat and peat pore water resulted in an increase in pore water MeHg concentrations by a factor of 3 to 4.

A supporting hydrological study found that the annual catchment hydrologic regime is strongly influenced by the volume and timing of precipitation inputs. For example, a 19% smaller than average snowpack and a dry April in 1995 resulted in the absence of a spring melt runoff event. This finding, coupled with 30% less summer rainfall in 1995 than in 1996, produced low antecedent moisture conditions in the upland soils, 68% less total runoff and reversals of hydraulic gradients.

Concentrations of MeHg in pore water were variable across the catchment, with the highest found in the peatland (up to 3.02 ng/l). The delivery of sulfate, carbon quality and temperature appear to influence the production of MeHg at a variety of scales. The mass flux of MeHg within and from the catchment is dependent upon the mass flux of water and the placement of landscape units in the catchment hydrologic cascade. In the two study years, the total mass flux of MeHg over the study period was 8.65 mg and 25.9 mg in 1995 and 1996 respectively.

Résumé

Le rôle de l'hydrologie et de la biogéochemie d'un bassin versant sur la production et le transport de méthylmercure (MeHg) a été étudié dans un bassin versant d'amont dans la zone de la forêt boréale des basses-terres du bouclier précambrian. Un modéle simple à l'échelle du bassin versant a révélé que les tourbières étaient des sources importantes de MeHg et les lacs de grands puits. L'analyse de sensibilité a révélé que le volume d'eau de ruissellement que les hautes terres déversent vers les tourbières, la taille de la tourbière et la concentration de MeHg de l'eau porale de la tourbière sont d'importants facteurs qui influent sur le rendement du bassin versant en matière de MeHg. On a constaté que les dépôts atmospheriques contemporains de MeHg sont negligeables par rapport aux sources de MeHg trouvement du bassin versant.

On a réalisé des expériences d'ajout de sulfate pour examiner les facteurs qui influent sur la production de MeHg dans les tourbières et l'on a constaté qui l'ajout de sulfate in situ à la tourbe et a l'eau porale de la tourbe entraînait une accroissement d'un facteur de 3 ou 4 des concentrations de MeHg dans l'eau porale.

Une étude hydrologique simultaneé a permis de découvrir que le régime hydrologique annuel d'un bassin versant depénd fortement du volume et du moment des précipitations. Par exemple, un manteau nival inférieur de 19% à la moyenne et un mois d'avril sec en 1995 ont entraîné l'absence de ruisellement dû à fonte des neiges printanières. Cette observation, combineé à des précipitations estivales inférieurs de 30% en 1995 par rapport à 1996, a produit des conditions d'humidité antécédente faibles dans les sols des hautes terres, une baisse de 68% du ruissellement total et une inversion des gradients hydrauliques.

Les concentrations de MeHg dans l'eau porale étaient variables dans tout le bassin versant, les plus fortes concentrations se retrouvement dans la tourbière (jusqu'à 3,02 ng/l). L'apport de sulfate, la qualité de carbone et la température semblent exercer une influence sur la production de MeHg à diverses échelles. Le

flux massique de MeHg à l'interieur et à partir du bassin versant dépend du flux massiqu de l'eau et la cascade hydrologique de bassin versant. Au cours des années de l'étude, le flux massique total du MeHg a été respectivement de 8,65 mg et 25.9 mg en 1995 et 1996.

Acknowledgments

I would like to thank Dr. Andrew Heyes for his substantial influence in my development as a scientist, without whom my work in the study of methylmercury would not have happened. I will fondly recall our time spent sharing confined space, both personally and professionally, while conducting our research at the Experimental Lakes Area (there's nothing like an 18 hour day in a white box). At the same time, I look forward to fruitful future collaboration and friendship.

My thanks to the staff and research scientists at the Experimental Lakes Area, in particular: hydrologists Mark Lyng and Ken Beaty for assistance with the design of hydrometric installations, the provision of data on a moments notice and aid in equipment monitoring and data collection; Mike Stainton, Eva Schindler and ELA/FWI Chemistry Lab staff for sulfate analysis, and; Gord Taylor for scotch, music, Kenora, John Hammond and grounding.

For other assistance and support, my thanks to: Blair Stevenson for a summer as a dedicated field assistant; Trish Sellers for her lab camaraderie and patience in teaching me about MeHg analysis; Dr. Robert Flett of Flett Research, Winnipeg, for his expert advice and troubleshooting of the CVAFS Hg analytical system; Neil Comer for friendship, videotaping while I was in the field and unfailing technical help; Dr. Vince St. Louis for sampling and intellectual input; Mike Dalva for DOC analysis; Paul Humenchuk for sharing space and equipment, general hilarity, and introducing me to "agar"; Jan Slavacek, machinist extraordinaire, for the construction of the custom peat 'sipper' and ultra-clean modifications to automated water samplers; Paula Kestelman for inventory control, and; my parents Liz and Brian Fowle and in-laws Shirley and Ken Preston for their unwavering support, and in the case of the Prestons, for allowing me to use their home as a hotel and warehouse.

I am grateful to my co-authors and colleagues: Dr. David Hilbert for introducing me to dynamic modelling, and; Drs. Carol Kelly and John Rudd for my

inclusion in ELARP and their substantial contributions to my understanding of the way things (biological) work.

I am indebted to my supervisor, Dr. Nigel Roulet for steadfast supervision and unquestioning intellectual, financial and logistical support over our six year history. I consider him a role-model for my future academic career and most importantly, I have learned from him that there is much more to being a good scientist than just doing good science. My thanks to the other members of my committee, Drs. Tim Moore, Alfonso Mucci and Michel Lapointe for their intellectual input and comments on this thesis.

All of my love and endless thank-yous to Marnie Branfireun, my wife and colleague, whose intellectual and emotional support, critical evaluation of my work, and field and laboratory assistance were essential to the completion of this thesis. The sharing of our interests in science and life sustains me through times like these!

Table of Contents

Abstract i

Résumé ii

Acknowledgments iv

List of Figures x

List of Tables xiii

Statement of Manuscript Format xiv

Statement Regarding the Role of Co-Authors xv

Copyright Waiver xvii

Original Contributions to Knowledge xviii

Chapter 1: Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield 1

1.1 INTRODUCTION 1

1.2 RESEARCH OBJECTIVES 3

1.3 RESEARCH SITE DESCRIPTION 5

1.4 PROCEDURES FOR METHYLMERCURY SAMPLING AND ANALYSIS 8

Chapter 2: Hydrology and Methylmercury Biogeochemistry: A Review of the Literature 10

2.1 CATCHMENT-SCALE HYDROLOGY AND BIOGEOCHEMISTRY 10

2.2 THE CATCHMENT AS A SOURCE OF METHYLMERCURY 12

2.3 MERCURY METHYLATION PROCESSES 14

Preface to Chapter 3 16

Chapter 3: Sources and Sinks of Methylmercury in a Boreal Catchment...17

3.1 INTRODUCTION....17

3.2 MODEL DESCRIPTION....18
3.2.1 Hydrology Sub-Model....19
3.2.2 Methylmercury Sub-Model....21
3.2.3 The Role of MeHg Sources and Sinks....22

3.3 RESULTS....23
3.3.1 Scenario 1....24
3.3.2 Scenario 2....26
3.3.3 Sensitivity Analysis....27

3.4 DISCUSSION....31
3.4.1 Possible Sources and Sinks of Methylmercury....33

3.5 SUMMARY....33

Preface to Chapter 4....35

Chapter 4: *In situ* Sulfate Stimulation of Mercury Methylation in a Boreal Peatland: Towards a Link Between Acid Rain and Methylmercury Contamination in Remote Environments....36

4.1 INTRODUCTION....36

4.2 METHODS....38
4.2.1 Twenty Times Sulfate Addition....38
4.2.2 Two Times Sulfate Addition....40

4.3 RESULTS....40
4.3.1 Twenty Times Sulfate Addition....40
4.3.2 Two Times Sulfate Addition....43

4.4 DISCUSSION....45

4.5 IMPLICATIONS....48

Preface to Chapter 5....50

Chapter 5: Hydrology of a Small Boreal Forest Catchment: The Effects of Inter-annual Variability in Precipitation on Water Yield and Hillslope Flowpaths....51

5.1 INTRODUCTION....51

5.2 SITE DESCRIPTION....52

5.3 METHODS....54
5.3.1 Precipitation....55
5.3.2 Soil Moisture and Water Table....55
5.3.3 Soil Characteristics....56
5.3.4 Surface Flow....56
5.3.5 Groundwater Flow....56

5.4 RESULTS....57
5.4.1 Precipitation....57
5.4.2 Upland Soil Moisture and Water Table Development....58
5.4.3 Lower Hillslope and Peatland Water Table Development....60
5.4.4 Surface Flow....62
5.4.5 Groundwater Flow....64

5.5 DISCUSSION....65

5.6 CONCLUSION....68

Preface to Chapter 6....69

Chapter 6: Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield....70

6.1 INTRODUCTION....70

6.2 SITE DESCRIPTION....71

6.2 METHODS....72
6.2.1 Hydrology....72
6.2.2 Geochemistry....73

6.3 RESULTS....74
6.3.1 Spatial Distribution and Temporal Variability of Methylmercury Concentrations in the Catchment....74
6.3.1.1 Uplands....74
6.3.1.1 Peatland....76
6.3.3 Methylmercury Concentrations in Surface Waters....85
6.3.4 Catchment-scale Methylmercury Fluxes....89

6.4 DISCUSSION....92
6.4.1 Pools of Methylmercury....92
6.4.2 Transport of Methylmercury Through the Catchment....96

6.5 CONCLUSION....98

Chapter 7: Conclusion **100**

References **104**

List of Figures

Figure 1.1: Location of the Experimental Lakes Area in North America. 6

Figure 1.2: Map of the 632 Catchment in the Experimental Lakes Area, Northwestern Ontario, Canada. 6

Figure 1.3: Oblique aerial photograph of the 632 catchment, ELA. View is to the northwest. The south ridge is in the foreground, with the peatland and central pond clearly visible in the middle of the image. Photograph by the author. 7

Figure 1.4: Overhead aerial photograph of the 632 catchment, ELA. North is at the top of the image. Photograph by AirQuest Resource Survey, Inc...........................7

Figure 3.1: Schematic diagram of the model reservoirs and fluxes............................18

Figure 3.2 MeHg concentrations in the three reservoirs for a model run *without* net MeHg sinks and sources..25

Figure 3.3: MeHg concentrations in the three reservoirs for a model run *with* net MeHg sinks and sources..26

Figure 3.4: Results of peatland area sensitivity analysis. Peatland area was varied from 0.1 ha to 4 ha and upland and pond areas were constant at 20 ha and 0.8 ha respectively..28

Figure 3.5: Results of upland area sensitivity analysis. Upland area was varied from 5 ha to 400 ha and peatland and pond areas were constant at 4 ha and 0.8 ha respectively..29

Figure 3.6: Results of precipitation MeHg sensitivity analysis. The precipitation MeHg used in the model based on ELA records was varied by a factor of 0 to 15 to simulate various degrees of loading...30

Figure 3.7: Results of peat porewater MeHg concentration sensitivity analysis. 31

Figure 4.1: Schematic diagram of the reference and experimental collars inserted into the poor fen of the 632 peatland, Experimental Lakes Area, northwestern Ontario. 39

Figure 4.2: Reference and experimental collar methylmercury, sulfate and DOC concentrations and pH for the 20x experiment. Vertically-drawn dashed line indicates times of experimental irrigations at t = 0 hrs and t = 24 hrs..................42

Figure 4.3: Reference and experimental collar methylmercury and sulfate concentrations for the 2x experiment. Dashed line indicates time of experimental irrigation at t = 0 hrs. 44

Figure 5.1: Left panel: Map of the 632 catchment, Experimental Lakes Area, Northwestern Ontario. The dashed box indicates the location of the instrumented hillslope/peatland subcatchment (right panel). Right panel: Light grey areas are wetlands; dark grey areas are zones of bedrock exposure. Contour interval is 0.25 m. Elevation is above an arbitrary datum..53

Figure 5.2: Monthly (1994-1996) and mean (1970-1996) precipitation for the Experimental Lakes Area, October, 1994 to December, 1996..............................57

Figure 5.3: Rainfall for the study period in 1995 and 1996...58

Figure 5.4: Volumetric soil moisture and water table elevation at TDR sites A and B, 1995 and 1996...59

Figure 5.5: Water table elevation measured in two lower hillslope wells as a peatland well over the study period, 1995 and 1996..61

Figure 5.6: Surface flow as measured at the upland weir, the peatland inflow stream and the catchment outflow. All values are instantaneous discharges in L/s, averaged over 15 minutes for the upland weir, 30 minutes for the peatland inflow stream and 24 hours for the catchment outflow. 62

Figure 5.7: Equipotential lines relative to an arbitrary datum and arrows indicating groundwater flow for the IF 1-6 piezometer transect in the 632 peatland, Experimental Lakes Area, (a) May 26, 1995, and (b) May 27, 1996. 64

Figure 6.1: Map of sampling areas in the 632 Catchment, northwestern Ontario.....72

Figure 6.1: MeHg concentration profiles in a poor fen hollow, 1995-1996................77

Figure 6.2: MeHg concentration profiles in a bog hollow, 1995-1996.......................77

Figure 6.3: Concentrations of methylmercury and sulfate in three piezometer nests, 632 peatland, August 1, 1995 79

Figure 6.4: Methylmercury concentrations at various locations at, and 25 cm below the water table in the 632 poor fen zone, June 14, 1996 (n=2 for each sample site and depth, analyzed in duplicate) 80

Figure 6.5: Profiles of methylmercury, sulfate, dissolved organic carbon (DOC) and pH from a typical poor fen hollow, a poor fen 'black' hollow and a raised bog hollow, July 18, 1996. 81

Figure 6.6: Sulfate versus methylmercury concentration in surface and groundwaters in the 632 catchment. 83

Figure 6.7: DOC and sulfate versus methylmercury concentrations in surface and groundwaters in the 632 catchment. 84

Figure 6.8: Methylmercury concentrations in surface waters at the upland weir, peatland inflow stream, pond and catchment outflow in 1995 and 1996. 85

Figure 6.9: Relationships between daily discharge and methylmercury concentrations for the peatland inflow stream and the catchment outflow, 1995-1996 88

Figure 6.10: Cumulative daily discharge and mass of methylmercury for the peatland inflow stream, 1995-1996. 90

Figure 6.11: Cumulative daily discharge and mass of methylmercury flux for the catchment outflow stream, 1995-1996 90

List of Tables

Table 3.1: Actual and modelled catchment MeHg depositions and yields. Model results are means and standard errors from a 30 run Monte Carlo simulation in which all randomly generated parameters were varied independently and randomly........24

Table 5.1: Total rainfall, total surface discharge and runoff ratios for the catchment and it's compartments from day 130 to 250, 1995-1996........63

Table 6.1: MeHg concentrations in upland soils and porewaters (n=3 for each sample)........75

Table 6.2: MeHg fluxes for the peatland inflow stream and catchment outflow, Day 130-250, 1995-1996........91

Table 6.3: Comparison of catchment MeHg yields from this study with others reported in the literature........92

Statement of Manuscript Format

Candidates have the option of including, as part of the thesis, the text of a paper(s) submitted or to be submitted for publication, or the clearly duplicated text of the published paper(s). These texts must be bound as an integral part of the thesis.

If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory**. The thesis must be written in such as way that is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.

The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparation". The Thesis must include: A Table of Contents, an abstract in English and French, an introduction which clearly states the rationale and objectives of the study, a comprehensive review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.

Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent**. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidates interest to make perfectly clear the responsibilities of all of the authors of the co-authored papers. **Under no circumstances can a co-author of any component of such a thesis serve as an examiner for that thesis**.

Statement Regarding the Role of Co-Authors

One of the papers included in this thesis has been published in a peer-reviewed journal, and one has been submitted for publication: Branfireun, B.A., D. Hilbert and N.T. Roulet, 1998, Sinks and Sources of Methylmercury in a Boreal Catchment, **Biogeochemistry**, **41(3)**, 277-291, 1998: (Chapter 3), and; Branfireun, B. A., N.T. Roulet, C.A. Kelly and J.W.M. Rudd, In Situ Sulfate Stimulation of Mercury Methylation in a Boreal Peatland: Towards a Link between Acid Rain and Methylmercury Contamination, Global Biogeochemical Cycles, submitted (Chapter 4). Although the manuscript is neither submitted or in press, co-authors are listed for Chapter 5 and Chapter 6, in order to adequately acknowledge their collaboration and input in anticipation of future publication of these results. The published and submitted manuscripts are reproduced here in full, in a format which is consistent with the rest of the thesis.

In accordance with the McGill University Faculty of Graduate Studies and Research guidelines, I declare here that the research presented in these papers is work of my conception and execution undertaken with the input and/or assistance of the listed co-authors. The role of the listed co-authors in the production of these papers is elaborated on below.

Chapter 3: Sinks and Sources of Methylmercury in a Boreal Catchment:

Dr. David Hilbert (now at CSIRO Tropical Forest Research Station, Atherton, Australia) assisted in the development of the heuristic model reported here while he was at McGill University as a Post-Doctoral Fellow in the Centre for Climate and Global Change Research (1995-1996). Dr. Hilbert introduced me to dynamic modelling, provided technical instruction in the computer software used to construct the model (STELLA II) and suggested simplifications and refinements to model code. I solely developed, and validated the model's logical structure. Dr. Nigel Roulet advocated the heuristic modelling approach and advised on the structure of the hydrology sub-model. Both co-authors provided intellectual comments on the drafts of the manuscript.

Chapter 4: Sulfate Stimulation of Mercury Methylation in a Boreal Peatland: Linking Acid Rain and Methylmercury Contamination

Discussion with Dr. Nigel Roulet led to my original idea of the sulfate-stimulation experiment and the larger link between "acid rain" and enhanced mercury methylation in peatlands. Dr. Carol Kelly (Department of Microbiology, University of Manitoba, and Department of Fisheries and Oceans - Freshwater Institute) and Dr. John Rudd (Department of Fisheries and Oceans - Freshwater Institute) advised on the microbiology of sulfate-reducing and mercury methylating bacteria, and on the execution of the field experiments. All of the co-authors provided intellectual comments on the drafts of the manuscript.

Chapter 5: Hydrology of a Small Boreal Forest Catchment: The Effects of Inter-annual Variability in Precipitation on Water Yield and Hillslope Flowpaths

Discussion with Dr. Nigel Roulet aided in the implementation of the hydrometric instrumentation and the interpretation of the data acquired. Mark Lyng and Ken Beaty of the Department of Fisheries and Oceans - Freshwater Institute/Experimental Lakes Area collected, analyzed and provided the 632 watershed catchment outflow data, and the precipitation data (current and historical) for the 632 catchment and the Experimental Lakes Area.

Chapter 6: Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield

This chapter resulted from the synthesis of the hydrological modelling and experimental studies presented in Chapters 3 through 5 and a catchment-scale biogeochemical study. The synthetic views expressed in this final paper have emerged over the last year's discussions between myself and Dr. Nigel Roulet.

Copyright Waiver

With regard to the research presented in Chapter 3, published previously as Branfireun, B. A., D. Hilbert and N.T. Roulet, Sinks and sources of methylmercury in a boreal catchment, **Biogeochemistry**, **41(3)**, 277-291, 1998:

With reference to your request to reprint material on which Kluwer Academic Publishers control the copyright, our permission is granted, free of charge, for the use indicated in your enquiry.

This permission

- allows you non-exclusive reproduction rights throughout the World.
- excludes use in an electronic form. Should you have a specific project in mind, please reapply for permission.

Full credit (Kluwer Academic Publishers book/journal title, volume, year of publication, page, chapter/article title, name(s) of author(s), figure number(s), original copyright notice) is given to the publication in which the material was originally published, by adding: with kind permission from Kluwer Academic Publishers.

Permission free of charge on this occasion does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.

best regards,

B.van Straalen

Kluwer Academic Publishers
Rights and Permissions Department
P.O.Box 17
3300 AA Dordrecht, The Netherlands
Fax: +31-78-6392 254

Original Contributions to Knowledge

The work presented in this dissertation makes original contributions in the areas of the catchment-scale modelling of methylmercury, the biogeochemistry of mercury methylation, the hydrology of a heterogeneous boreal landscape, and the relations amongst the production and flux of methylmercury and catchment hydrology and other biogeochemistry.

Chapter 3 presents a model which examines the principal controls on catchment yield of methylmercury. This simple 'grey box' model, although intended to heuristically address questions about the role of peatlands and mass flux of water in controlling catchment yields of methylmercury presents, to my knowledge, the first published modelled data that elucidate the importance of internal cycling of methylmercury (and potentially other important chemical species) within the catchment units, the relative unimportance of atmospheric methylmercury deposition, and the interrelationship amongst catchment size, water yield and methylmercury flux.

Chapter 4 is the first reported experimental data demonstrating sulfate stimulation of mercury methylation in peatlands, building on previous hypotheses and research in the literature (e.g. Gilmour and Henry, 1991; Gilmour *et al.*, 1992; Winfrey and Rudd, 1990; Heyes, 1996). Previous work in estuaries and lakes suggested that a link between sulfate deposition in 'acid rain' and mercury methylation may exist because sulfate reducing bacteria have been implicated as principal methylators of mercury in the environment. However this finding could not be validated in some lakes (e.g. in the boreal forest zone; see Winfrey and Rudd, 1990). The results from the research presented here suggest that atmospheric deposition of sulfate on peatlands may enhance the production of methylmercury *in situ*.

Chapter 5 reports on the sensitivity of boreal zone catchment hydrologic response and water yield to inter-annual climatic variability. The data presented illustrate the difficulty in making general statements regarding catchment hydrology in this landscape, and the impact that this extreme variability may have on biogeochemical cycles.

Chapter 6 links this hydrologic data with water chemistry to report for the first time: the conditions required for increased mercury methylation in peatlands; the variability in methylmercury concentrations at the meso and micro-scale in the catchment and peatland, and; the catchment-scale hydrologic controls on methylmercury yield. These data represent one of the first attempts to look inside the 'black box' of catchment-scale water and methylmercury budgets, which first demonstrated that peatlands were large sources of methylmercury to the downstream environment.

Chapter I: Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield

1.1 INTRODUCTION

Increased mercury (Hg) loading of freshwater ecosystems and its subsequent impacts on ecosystem and human health have become major research foci in environmental biogeochemistry in the 1990s, as 'acid rain' was in the 1970s and 80s. The deleterious effects of mercury pollution on natural aquatic ecosystems are not quite so obvious as they are for 'acid rain', but the impacts on health at the higher levels of the food chain, including fish, predatory wildlife and humans, are serious and well documented (e.g. Harada, 1995; Porcella *et al.*, 1995 - Part 1).

Atmospheric Hg, which is the major source of Hg to remote or 'pristine' ecosystems, is predominantly in the inorganic form (Hg^0 and Hg^{2+}) in both vapour and particulate phases (Iverfelt *et al.*, 1995; Keeler *et al.*, 1995; Lucotte *et al.*, 1995; Lindberg and Stratten, 1998; Lindberg *et al.*, 1998; Schroder and Munthe, 1998). MeHg comprises over 90% of Total-Hg in fish (Bloom, 1992), with the vast majority of the fish MeHg burden acquired from their ingestion of MeHg-laden organisms, as opposed to directly from the dissolved or particulate phases (Bodaly *et al.*, 1997). This large proportion of MeHg found in fish tissue occurs despite the fact that less than 10% of all Hg in most natural ecosystems is in the methyl form (Kelly *et al.*, 1995). The amount of direct methylmercury (MeHg) deposition that does occur appears to be insufficient to account for the amount found in lake biota (Gilmour and Henry, 1991), suggesting that methylation of atmospherically or terrestrially-derived inorganic Hg is occurring in the catchment. This MeHg is acquired from the dissolved and particulate phases by bacteria and zooplankton, and is biomagnified up the food chain. In view of these findings, knowledge about the processes of methylation and demethylation of Hg in the natural environment, preferential sites of methylation in the landscape, and how MeHg is transported within catchments to downstream systems is essential for a better understanding of MeHg cycling.

Recent research indicates that Boreal/Precambrian Shield catchments containing peatlands export considerably more MeHg to the downstream aquatic system than those which have strictly upland catchments (St. Louis *et al.*, 1994; 1996) and that peatlands are sources of MeHg (St. Louis *et al.*, 1994, 1996; Bishop *et al.*, 1995; Rudd, 1995; Hurley *et al.*, 1995; Krabbenhoft *et al.*, 1995; Branfireun *et al.*, 1996), although the specifics of Hg transformation processes in peatlands are not understood. Thus peatlands represent an important link between the terrestrial/semi-aquatic landscape and the aquatic food-web where the effects of MeHg are magnified.

The same work that determined that peatlands are sources of MeHg show that there is considerable spatial and temporal variation among upland terrains with respect to MeHg export (St. Louis *et al.*, 1994, 1996; Branfireun *et al.*, 1996). This variability appears to be related to the presence of pockets of organic soil in the upland portion of the catchment (i.e. upland 'wetlands'). The episodic transport of MeHg during storm events makes up a large proportion of the total amount of MeHg delivered downstream in some landscapes (Branfireun *et al.*, 1996).

Although the role of catchment processes in Hg cycling are receiving increased attention, there has yet to be an attempt to study, or model, the coupling of hydrology and MeHg dynamics at the catchment scale. Also, no research has clearly delineated the sources of MeHg in catchments (i.e. zones of methylation) or determined site-specific relationships among contributing area, runoff, hydrologic flowpaths and MeHg concentrations and export.

1.2 RESEARCH OBJECTIVES

The study of catchment-scale MeHg biogeochemistry is still in the very early stages. Although recent data indicate that peatlands are sources of MeHg, a number of fundamental questions need to be answered:

- What are the biogeochemical controls on Hg methylation?
- How does hydrology influence the production of MeHg in anoxic organic sediments?
- How does the hydrology of a catchment influence the movement of MeHg?

From these questions, four main objectives have been developed:

1) Build a catchment-scale model to examine the role of catchment hydrology, MeHg stores and fluxes, and net methylation on the catchment yield of MeHg from a small boreal headwater catchment containing a peatland. The model will test the following hypotheses:

> a) The peatland is a large source of MeHg relative to the annual MeHg input via precipitation;
>
> b) *In situ* production of MeHg in the peatland is a major controlling factor in the magnitude of the downstream flux of MeHg, and;
>
> c) The yield of MeHg from the catchment is highly dependent on the hydrologic connectivity among the upland, peatland and pond.

2) Examine the biogeochemical controls on Hg methylation in peatlands. As indicated previously, catchment-scale MeHg budgets constructed for catchments at the ELA have indicated that catchments containing peatlands export more MeHg than their purely upland counterparts and that the total MeHg yield exceeds the amount of MeHg arriving in the peatlands via precipitation and runoff, indicating an intra-peatland source of MeHg (St. Louis *et al*, 1994). Given that sulfate-reducing bacteria have been implicated as prime methylators of Hg^{2+}, an *in situ* experiment will be undertaken to test the following hypothesis:

Sulfate-stimulation of Hg methylation is a significant mechanism of MeHg production in this (and other) boreal peatlands, suggesting that atmospheric and groundwater delivery of sulfate may increase catchment MeHg yields.

3) Gain a more complete understanding of the continuous and transient hydrologic flow systems that link upland mineral hillslopes and peatlands to explain MeHg delivery to the downstream systems and the role of hydrology in determining the methylating environments in soil/sediment. This involves the characterization of the hydrologic interactions amongst catchment compartments (i.e. upland hillslopes, peatland, lake and streams) and their spatial and temporal variability.

4) Synthesize the catchment hydrological data with MeHg and other biogeochemical data to explain the movement of MeHg within and from the catchment. This requires the determination and delineation of:

a) sites of potential net methylation through the measurement of MeHg concentrations, and;

b) the MeHg concentrations associated with the various active components of the catchment hydrologic system, such as:

i) pore water of upland mineral and organic soils, and peat,

ii) runoff from upland subcatchments,

iii) runoff from peatland, and

iv) runoff from the catchment.

Previous work (Branfireun *et al.*, 1996; Branfireun and Roulet, 1998) on both the hydrology and MeHg dynamics of this site provided important insight and background data.

1.3 RESEARCH SITE DESCRIPTION

This research was conducted on a small (41.6 ha) Precambrian Shield headwater catchment (Basin 632) located in the Experimental Lakes Area (ELA) (49°40' N, 93°43' W) near Kenora, Ontario, Canada (Figure 1.1; Figure 1.2; Figure 1.3; Figure 1.4). The climate of the study area is classified as low boreal, cold temperate. Average monthly air temperatures based on data from 1969-1989 ranged from -16.5°C for January to 20.1°C for July, and average total annual precipitation for 1969-1996 was 690.6 mm, 27% of which fell as snow (Data courtesy of M. Lyng and K. Beaty, 1998). The peatland is bounded to the north and south by steep ridges, with a more gently sloping inflow area to the west. The catchment can be topographically divided into three major subcatchments: the north subcatchment (7.0 ha) dominated by an exposed bedrock ridge; the west subcatchment (15.4 ha) which is the major contributing area to catchment runoff, and; the south subcatchment (13.5 ha), which primarily delivers runoff to the outflow zone of the peatland (Figure 1.2). The lowest elevations of the catchment are occupied by a small peatland (4.7 ha) with a central pond (1.0 ha). Catchment areas may be different from those reported in previous papers (e.g. Branfireun *et al.*, 1996, 1998; St. Louis *et al.*, 1996) as a new map was digitized and areas calculated specifically for this study.

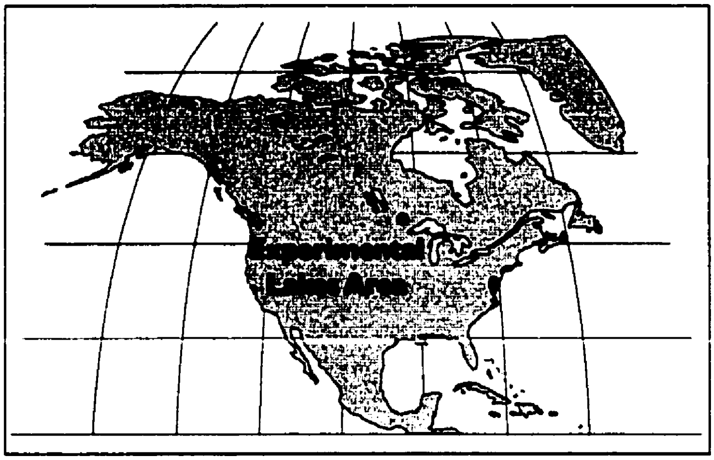


Figure 1.1: Location of the Experimental Lakes Area in North America.

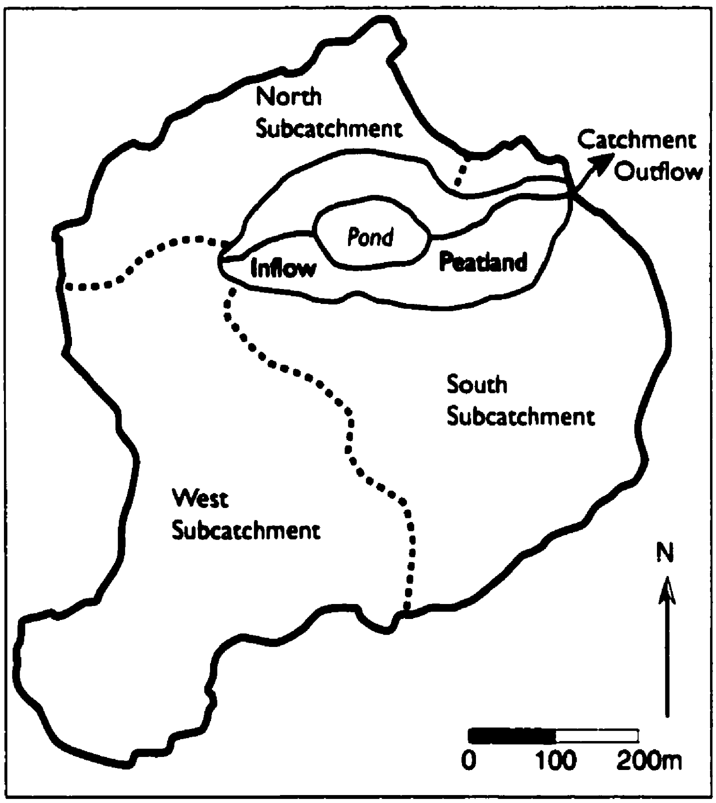


Figure 1.2: Map of the 632 Catchment in the Experimental Lakes Area, Northwestern Ontario, Canada.

Figure 1.3: Oblique aerial photograph of the 632 catchment, ELA. View is to the northwest. The south ridge is in the foreground, with the peatland and central pond clearly visible in the middle of the image. Photograph by the author.

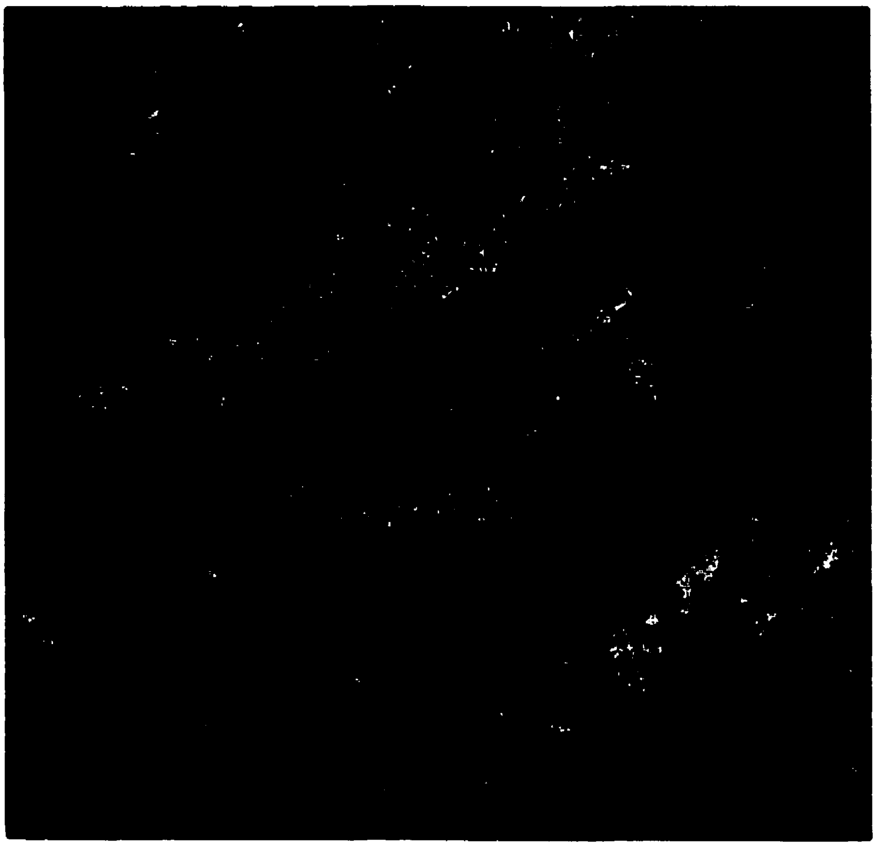


Figure 1.4: Overhead aerial photograph of the 632 catchment, ELA. North is at the top of the image. Photograph by AirQuest Resource Survey, Inc.

The bedrock geology of the catchment is typical of the Precambrian Shield - largely unfractured granite. Soils in the upland portion of the catchment are dominated by silty-loams of glacio-lacustrine origin. Below the peatland, bedrock was overlain by well sorted sand and gravel greater than 1m in depth in the inflow area, and fine silts and clay in the deeper central depression. Above the inorganic sediments, there is peat accumulation of between 7 m (near pond margins) and less than 1 m (at hillslope-peatland interface), with an average depth of approximately 2 m. A surficial accumulation of dead *Sphagnum* spp. overlain by living *Sphagnum* spp. was nearly ubiquitous across the terrestrial portion of the peatland. The peatland overstorey is open and comprised almost entirely of black spruce (*Picea mariana*) with scattered tamarack (*Larix laricina*).

Upland vegetation comprises an overstorey of jackpine (*Pinus banksiana*) and black spruce (*Picea mariana*) with scattered paper birch (*Betula papyrifera*) (J. Bubier, personal communication, 1995). Bedrock outcrops are colonized by lichens (both foliose and fruticose forms), juniper (*Juniperus virginiana*) and mosses (*Racomitrium* spp.). Peatland surface vegetation is dominated by *Sphagnum* spp. (*S. angustifolium*; *S. fuscum*; *S. magellanicum*) with shrubs such as Labrador tea (*Ledum groenlandicum*) and leatherleaf (*Chamedaphne calyculata*) in the more ombrotrophic area, and grasses and sedges (*Oligosperma* spp. and *Carex* spp.) in the more mineral-poor fen zones around seeps and streams (J. Bubier, personal communication, 1995).

1.4 PROCEDURES FOR METHYLMERCURY SAMPLING AND ANALYSIS

The sampling and analytical procedure for MeHg is specialized and merits description here. MeHg samples were almost exclusively taken and analysed by the author. Ultra-clean sampling protocol was followed at all times. Vinyl gloves were worn at all times and the sample bottle was protected from contamination by double-bagging with two polyethylene bags and placing it in a clean transport container. One field worker handled potentially contaminated sampling articles while another handled the sample bottle only. All Teflon® sampling gear (bottles, peat sippers and piezometers) were pre-cleaned with hot nitric acid and deionized water.

Samples for pore water MeHg analyses were either passed immediately through a sterile 0.45 µm filter (Nalgene® cellulose nitrate) and frozen in Teflon® bottles. Stream and surface water samples were not filtered, but samples were rejected if visible particles were present. MeHg analysis was performed at ELA in a mercury clean room and at the University of Manitobausing a technique modified from Bloom and Fitzgerald (1988) and Horvat *et al.*, (1993). Humics were removed from the samples using a sub-boiling distillation (Horvat *et al.*, 1993). The Hg in the distillate was then ethylated and purged with nitrogen onto Tenax®. The Tenax® was flash heated in a stream of helium releasing the mercury, which was speciated chromatographically, combusted to Hg^0 and measured using atomic fluorescence (Bloom and Fitzgerald, 1988). The detection limit averaged 0.01 ng/l as Hg. All MeHg concentrations are presented in ng/l as Hg.

Chapter 2: Hydrology and Methylmercury Biogeochemistry: A Review of the Literature

2.1 CATCHMENT-SCALE HYDROLOGY AND BIOGEOCHEMISTRY

A large volume of knowledge exists about the nature of water flow through soil and bedrock. Groundwater flow may significantly affect the water balance, surface water chemistry and runoff processes of some catchments, but the source areas and pathways by which this water is delivered are often much more easily determined than that of hillslope (soil) water because of its relatively longer residence time and stable discharge patterns. The movement of water through hillslope soils tends to be more difficult to study given its highly transient nature and dependence upon antecedent moisture conditions. Even though difficult to investigate, hillslope runoff processes in small catchments have been the focus of many hydrologic investigations because of the influence of the soil matrix on downslope water quality and quantity.

Catchment soil characteristics strongly control how precipitation moves through small catchments and becomes streamflow. Motivated largely by the need to understand catchment stormflow response to rainfall and snowmelt, research in this area has progressed from the definition of fundamental ideas such as the 'variable source-area concept' (e.g. Hewlett and Hibbert, 1967) to very detailed process-based studies which are beginning to shed light on specific flow pathways (e.g. macropore flow) under various moisture conditions in a wide variety of landscapes (e.g. Bevan and Germann, 1982). Fundamental principles of soil physics can be used to explain water movement through a relatively homogeneous soil matrix, but more recent studies, utilizing geochemical and isotopic measurements, convincingly demonstrate that Darcian flow is not able to explain subsurface flow volumes and response times in many catchments (e.g. Renzetti *et al.*, 1992). These studies suggest that preferential flow paths occur in most catchments, providing a means to rapidly deliver soil water to streams and thus control the catchment stormflow response. The mechanisms of these subsurface preferential flow pathways are not yet fully understood, nor are the ways to determine 'event' and 'pre-event' water mixing in the soil matrix or macropores which ultimately controls water chemistry.

Although the literature reports studies in hillslope hydrology from many different geographic and physiographic settings, relatively few mechanistic studies of hillslope runoff processes have been undertaken in the boreal/Precambrian Shield zone of North America (some exceptions being Roberge and Plamondon, 1987; Maulé and Stein, 1990; Renzetti *et al.*, 1992; Hinton *et al.*, 1993; Allan and Roulet, 1994) even though the surface waters of this region may be some of the most strongly affected by acid precipitation and other atmospherically deposited contaminants. This susceptibility to contamination is largely due to rapid runoff as a result of shallow/non-existent soils overlying impermeable bedrock and relatively low buffering/binding capacity of the soils. Generally, hydrologic studies in this region have found that runoff mechanisms (e.g. subsurface stormflow vs. saturation overland flow) (Allan and Roulet, 1994), and pathways (e.g. interstitial vs. preferential flow) (Renzetti *et al.*, 1992; Roberge and Plamondon, 1987; Maulé and Stein, 1990) are strongly dependent on antecedent soil moisture conditions in hillslope soils/soil pockets, and to a lesser degree, rainfall intensity and duration. My own research at the Experimental Lakes Area has shown that under wet antecedent moisture conditions, rainfall may produce 8 to 10-fold more stream discharge than that from dry conditions (Branfireun and Roulet, 1998). Very little work has been done to attempt to relate this highly dynamic hillslope hydrologic system and their changing flowpaths to water chemistry, even though the degree of interaction of incoming water with the soil matrix may strongly influence stream and lake water quality.

The lack of information about runoff processes in peatlands, which are common features of catchments in the boreal/Precambrian Shield zone of North America, also limits our understanding of surface water chemistry in the region since they are most often found between uplands and the downstream aquatic system, perfectly situated to further modify the chemistry of water as it passes from the terrestrial to aquatic sphere. Although a body of literature exists on the influence of wetlands on downstream water chemistry such as the release of organic acids, the sequestering of metals and the uptake of nutrients and cations (see Urban *et al.*, 1995), there appears to be little or no information regarding the *specific* flow pathways of water through peat and/or associated changes in water chemistry as a result of those pathways. It is understood that the behaviour of streamflow from wetlands is a function of the amount and intensity of precipitation, antecedent conditions, the nature of the peat profile, the location of the wetland within the landscape and the topographic forms within the wetland (e.g. Verry *et al.*, 1988), but the pathways of water from the peatland to the stream as the water table rise through the peat profile are not well known. Because of the extreme heterogeneity of peat and the multitude of potentially 'preferential' flowpaths, it is possible that the use of relatively large representative elementary volumes and macro-scale measures of porosity are most appropriate (i.e. approaches like hillslope flowpath analysis are not applicable in wetlands). However, even though 'simple' storm runoff mechanisms in wetlands are conceptually understood based on a few empirical studies (e.g. Bay, 1969; Verry *et al.*, 1988), the mechanistic underpinnings are still vague.

2.2 THE CATCHMENT AS A SOURCE OF METHYLMERCURY

Before it was known that total-Hg data failed to adequately explain concentrations of Hg (mostly as MeHg) in fish and other animals, total-Hg was often the only type of Hg sampled and analyzed in field studies of Hg cycling in catchments. This was also the result of inadequate analytical techniques for detecting MeHg at trace (sub-ppt) concentrations. Catchment-scale total-Hg research largely concentrated on mineral hillslopes. Meili (1991) suggested that, in Sweden, shallow soils overlying igneous bedrock favored the transport of mercury-laden organic matter to surface waters, and that the short residence time of water in the shallow soils leads to the rapid transport of mercury to lakes. Aastrup *et al.* (1991) modelled mercury transport from a forested upland catchment which contained a treeless bog and estimated that of a total flux of 3.4

g km^{-2} yr^{-1}; 75% of mercury transport occurred in the top 20 cm of the soil. No work of this type has yet been undertaken for MeHg.

Now that it has been established that total-Hg concentrations and MeHg concentrations in natural systems are independent (Kelly *et al.*, 1995), and behave quite differently during episodic events (e.g. Krabbenhoft *et al.*, 1995; Bishop *et al.*, 1995a), mercury researchers who are concerned about it's toxic effects in the food web have begun to concentrate their efforts on catchment MeHg dynamics.

Much of the initial catchment-scale research on MeHg that has been reported is based upon input-output budget analysis (e.g. St. Louis *et al.*, 1994; Hultberg *et al.*, 1995). Recent work that has taken a more process-based approach (i.e. attempting to define internal MeHg reservoirs and fluxes, for example Bishop *et al.* (1995a,b); Krabbenhoft *et al.* (1995); Lee *et al.* (1995); Branfireun *et al.* (1996)), has revealed that many of the processes involved in MeHg cycling are very spatially and temporally variable and appear to operate at a sub-catchment scale not considered using a catchment-scale budget approach. Even these studies, although advancing our understanding of MeHg processing within the catchment, have only begun to identify key intra-catchment processes.

Some of this research (Driscoll *et al.*, 1994, 1998; St. Louis *et al.*, 1994, 1996; Rudd, 1995; Bishop *et al.*, 1995a,b; Krabbenhoft *et al.*, 1995; Branfireun *et al.*, 1996) has demonstrated that peatlands are important sources of MeHg and may also contain sites of methylation. While the presence of peatlands result in increased export of MeHg, the pathways by which the MeHg enters the downstream systems are not well known. Aside from biotic uptake and relocation, the transport of MeHg must be linked to surface water or groundwater flow, and may be highly dependent upon flow pathways, and how they link zones of MeHg production in the catchment.

2.3 MERCURY METHYLATION PROCESSES

The methylation of inorganic Hg has been linked to the activity of strictly anaerobic sulfate-reducing bacteria (SRB); specifically *Desulfovibrio desulfuricans* LS (e.g. Compeau and Bartha, 1984, 1985; Gilmour and Henry, 1991; Gilmour *et al.*, 1992). More recent studies have shown that *D. desulfuricans* LS methylates Hg^{2+} via cobalamin (vitamin B_{12}), and that methylation is an enzymatically catalyzed process (Choi and Bartha, 1993; Choi *et al.*, 1994 a,b). Other bacteria are capable of Hg methylation, but have been found to be ineffective methylators at environmental concentrations.

Increased sulfate availability has been linked to increased rates of Hg methylation (e.g. Gilmour *et al.*, 1992), but other work has shown that the Hg methylating activity of SRB is maximum only when sulfate is limiting and fermentable organic substrates are available (e.g. Compeau and Bartha, 1985). The inconclusiveness of many of these experiments on Hg methylation is likely the result of large additions of (often radio-labelled) Hg (up to 25 times background) to experimental samples.

Recent lake studies (e.g. Watras *et al.*, 1995) have shown that hypolimnetic zones of MeHg enrichment were transition zones for sulfate and sulfide, supporting the hypothesis that sulfate reduction and Hg methylation are linked biogeochemically in anoxic hypolimnetic water and littoral sediments. Some research has also shown that SRB can demethylate Hg via oxidative degradation, although the addition of $[^{14}C]$MeHg, substantially increasing pore water MeHg concentrations, raises the question of whether or not oxidative demethylation takes place at trace levels (Oremland *et al.*, 1995). Data from the Experimental Lakes Area (ELA) have shown that abiotic photodegradation of MeHg in open water may exceed biotic demethylation by orders of magnitude, thus possibly diminishing the importance of the oxidative demethylation pathway (Sellers *et al.*, 1996)

Recent work at the ELA (Branfireun *et al.*, 1996; Heyes, 1996), has found extremely elevated MeHg pore water concentrations in the anoxic zone of both natural and impounded peatlands, particularly in areas of groundwater discharge. Other recent studies have found elevated MeHg concentrations in peat pore water (Krabbenhoft *et al.*, 1995; Bishop *et al.*, 1995a), particularly in groundwater discharge zones (Krabbenhoft *et al.*, 1995), suggesting that nutrient delivery by groundwater and persistent anoxia at such sites may enhance Hg methylation. Incubation experiments (Heyes, 1996) using peat from a peatland groundwater discharge zone without addition of Hg has shown that the addition of sulfate stimulates Hg methylation, suggesting that methylation processes in anoxic peat pore water may be similar to those reported for bacterial cultures, anoxic lake sediments and hypolimnetic water, although they seem, on average, to result in much higher MeHg equilibrium concentrations.

Preface to Chapter 3

In this chapter, a simple, catchment-scale, cascade model is presented that was used to assess the importance of sinks and sources of methylmercury (MeHg) in a boreal catchment that contains a forested upland, lowland peatland and a small lake (i.e. to represent the study catchment ELA 632). The three compartment model was run using realistic flow rates and atmospheric loading of MeHg. Tthe model was constrained by observed concentrations of MeHg in each compartment. This model was used to test the hypotheses outlined in Chapter 1 (see page 3).

Chapter 3: Sources and Sinks of Methylmercury in a Boreal Catchment*

3.1 INTRODUCTION

There is a debate on the role that catchment physiography plays in methylmercury (MeHg) production. Although it is not contested that demethylation processes (e.g. oxidation, complexation, binding) are at work in the terrestrial portions of catchments, there are differences in opinion regarding the importance of methylation. Some researchers suggest that MeHg in precipitation is sufficient to account for catchment yields of MeHg in runoff in some landscapes; hence by inference Hg methylation in the catchment soils/water is unimportant or insignificant relative to the atmospheric deposition (e.g. Hultberg, *et al.*, 1995). St. Louis *et al.* (1994) observe similar or higher MeHg catchment yields in Northern Ontario to that of southern Sweden but atmospheric inputs of MeHg are much smaller. St. Louis *et al.* (1994) and Branfireun *et al.* (1996) conclude that *in situ* methylation processes contribute significantly to catchment MeHg output and that peatlands appear to be a locus of MeHg production. This conclusion is supported by other recent work (Bishop *et al.*, 1995a,b; Krabbenhoft *et al.*, 1995; Hurley *et al.*, 1995).

"Black box" catchment input-output budgets may indicate that atmospheric MeHg inputs account for a significant proportion of MeHg outputs. However, sources and sinks of MeHg within the catchment may be very large, but go unnoticed if the net within-catchment budget is comparable to other inputs. The results of recent covered-catchment experiments have attempted to dismiss the latter (e.g. Hultberg, *et al.*, 1995), but the results have not been definitive.

Our objective in the present study is to develop a simple hydrology model and use it as a heuristic tool to test the relative importance of wet MeHg

---

*This research, originally published in **Biogeochemistry**, **41(3)**, 277-291, 1998, is reproduced here in a format consistent with the thesis with kind permission from Kluwer Academic Publishers.

deposition and internal sinks and sources of MeHg on variations in MeHg yield for a low boreal headwater catchment.

3.2 MODEL DESCRIPTION

The model comprises two coupled sub-models, hydrologic volumes and fluxes and net MeHg sinks and sources (Figure 3.1[*]).

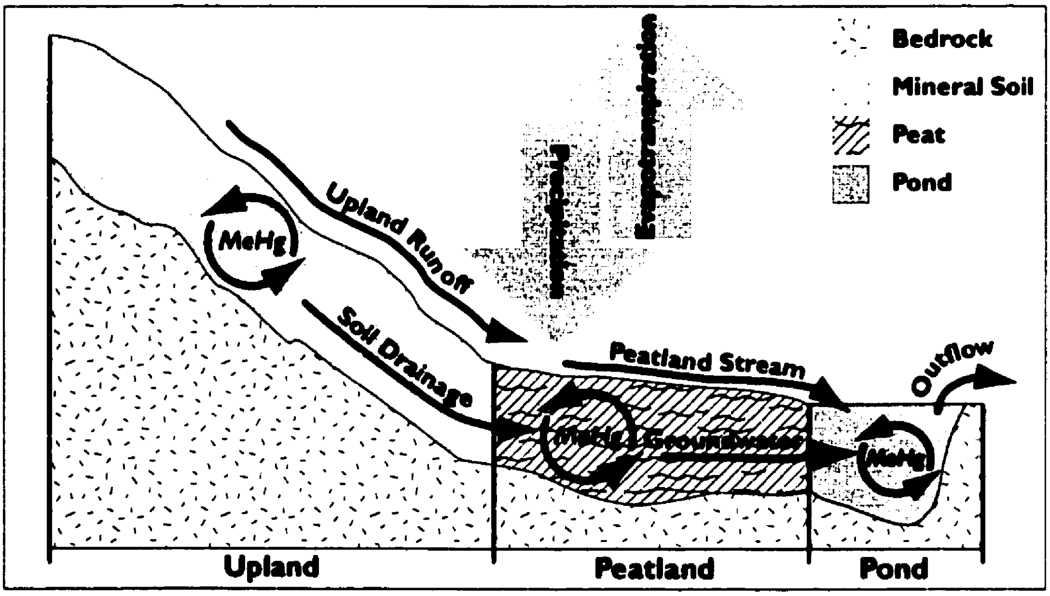


Figure 3.1: Schematic diagram of the model reservoirs and fluxes.

The model operates on a daily time step and simulations are one year long. The model simulation starts after the end of snowmelt and assumes saturated conditions at the beginning of the open water season and zero flow during the winter. The catchment simulated was based on a small headwater catchment (632) in the Experimental Lakes Area, northwestern Ontario, Canada which is a site of ongoing research into boreal catchment hydrology and MeHg dynamics (Branfireun *et al.*, 1996; Branfireun and Roulet, 1998a).

[*] Figures and table order in this chapter correspond to the order in the original publication (e.g. Figure 3.1 is Figure 1 in Branfireun et al., 1998).

The hydrology sub-model is a simple cascading reservoir system with precipitation, and evapotranspiration and catchment outflow as the major input and outputs, respectively, to three sub-catchment reservoirs (upland, peatland and pond). The sub-model considers each catchment unit as a "bucket" which flows into the next sub-catchment compartment at a rate determined by the drainage coefficient D, and the amount of water in the "bucket". The sub-model's data requirements are the volume of each catchment reservoir and it's saturated volumetric soil moisture, which are set at the beginning of each run. All other values are generated by the model (e.g. precipitation; net radiation) and are tailored to field data from the reference catchment. This limits the model's application to the reference catchment but this simple structure simulates this catchment's hydrologic response, storage volumes, and fluxes between the catchment units reasonably well, therefore satisfying our desire to capture the hydrology and to test our hypotheses about the importance of sources and sinks of MeHg.

The MeHg sub-model uses net MeHg production, which encompasses a wide variety of (largely unknown) biotic and abiotic processes, as the input and output of MeHg to each reservoir which are sufficient to maintain equilibrium concentrations. The equilibrium concentrations are based on field data from the reference catchment and are set at the beginning of each model run. This approach was taken because of the absence of information in the literature regarding *in situ* methylation and demethylation processes in terrestrial and wetland environments.

3.2.1 Hydrology Sub-Model

As discussed above, the hydrology sub-model is a simple cascading reservoir system with all units in m^3 of water. The upland was allocated an area of 20 ha with 75% soil cover at 1 m depth (allowing for exposed bedrock areas). The peatland was assigned an area of 2 ha with 100% organic soil coverage (peat) at a depth of 2 m. The pond was given an area of 0.8 ha with a depth of 1 m. Initial volumes of water in the reservoirs are based on field data and assume saturated conditions. These volumes are 67500 m^3 for the upland (assuming a uniform 45% volumetric soil moisture), 32000 m^3 for the peatland (assuming a uniform 80% volumetric soil moisture), and 8000 m^3 for the pond.

Precipitation is generated using a subroutine based on the probability of rain on a given day (p=0.22; determined from ELA precipitation records). If rain is selected, then a storm magnitude (based on monthly averages from the ELA) is determined randomly within a specified range weighted towards smaller, 'normal' magnitude storms. Daily total evapotranspiration over the upland and peatland surfaces, and evaporation over the pond is calculated as:

$$E = \frac{\frac{Q^* + Q_G}{1+\beta}}{L_v} \qquad (1)$$

where E is the mass of water evaporated (Kg m^{-2} d^{-1}), Q^* is the net radiation incident at the surface (MJ d^{-1}), Q_G is the ground heat flux (MJ d^{-1}), β is the Bowen Ratio (unitless), and L_v is the latent heat of vaporization. Potential Q^* is generated as a function of latitude (Charles-Edwards, 1982). Random variability ("cloud effect") in Q^* is introduced which varies Q^* by 0 to 90% on any given day. On days with rain, Q^* is reduced by 50%. Modelled Q^* agrees well with actual Q^* data from field studies at the ELA catchment (Roulet, unpublished data, 1993). Q_G is set at 10% of Q^* for the forested upland and peatland, and 0% of Q^* for the pond, except for in the spring when Q_G is set to 30% of Q^* for the pond to account for heating of the water (Roulet *et al.*, 1997). β was determined from representative values from the literature (Oke, 1987; Roulet *et al.*, 1997) and set at 0.2 for the pond, 0.4 for the peatland and 0.6 for the forested upland. It is assumed that evapotranspiration from the upland occurs from the soil covered areas only, and that no evapotranspiration occurs on days when it rains.

Changes in the amount of water in a state variable is determined as:

$$V_{H_2O}(t) = V_{H_2O}(t-dt) + (I_1 + I_2 + I_3 ... - O_1 - O_2)dt \qquad (2)$$

where $V_{H_2O}(t)$ is the volume of water in the state variable at time t, $V_{H_2O}(t-dt)$ is the volume of water in the state variable at the previous time interval and I_x and O_x are inputs and outputs to the state variable, respectively.

The source of water to the model catchment is precipitation. This is the same as that in the study catchment at ELA since there is no inter-basin transport of groundwater. Evapotranspiration and catchment outflow are the two outputs. Fluxes from the upland to the peatland are upland surface runoff and soil drainage, and from the peatland to the pond are a peatland stream and groundwater. Fluxes within the catchment may generally be described as:

$$F(t) = (V_{H_2O}(t) - V_{sat})D \qquad (3)$$

where $F(t)$ is the magnitude of the flux at time t (m_3 d^{-1}), V_{sat} is the volume of the 'full' reservoir and D is the drainage coefficient which ranges between 0.001 and 0.8 for all fluxes (smaller for slow, insensitive fluxes such as peatland groundwater; larger for responsive, episodic fluxes such as overland flow (see Branfireun and Roulet, in press)) and determines the rate at which excess water in each reservoir may drain via that pathway. D was determined by trial and error, manually calibrating the hydrograph responses and magnitudes of the model fluxes to approximate those of the study catchment (632). Fluxes via upland runoff, peatland streamflow and catchment outflow pathways are only permitted to occur when the volume of their corresponding state variables exceeds V_{sat}, and upland soil drainage may only occur uninhibited if volumetric soil moisture in the upland soils is in excess of 20%.

3.2.2 Methylmercury Sub-Model

The sub-model for MeHg is nearly identical in form to that of the hydrology sub-model, with the exception that the units for this sub-model are mass of MeHg (ng), the fluxes are controlled by MeHg concentration in free porewater (mass of

MeHg in the reservoir multiplied by the volume of water in the reservoir; all water in the reservoirs is assumed to be mobile and completely mixed) and the magnitude of the flux of water, with reservoir volumes and water fluxes being determined by the hydrology sub-model. Inputs of MeHg by precipitation are determined using [MeHg] data for the ELA area from St. Louis *et al.* (1995), with storm concentrations allowed to vary randomly between 0.010 and 0.179 ng L^{-1}. The equilibrium MeHg concentration of each reservoir is variable to allow for the testing of relative importance of each state variable in determining final pond concentrations.

The model is run to resolve the MeHg export from the basin, and the initial model runs are constrained by the known concentrations of MeHg in each reservoir. This allows us to determine the net sinks/sources of MeHg needed to maintain observed MeHg concentrations in the reservoirs when the initial conditions are set to that representative of measured field values and assumed to be in steady-state.

The analysis of the potential role of sources/sinks of MeHg, the impact of MeHg in precipitation, and the effects of upland and peatland size are examined using two different model scenarios and sensitivity analysis.

3.2.3 The Role of MeHg Sources and Sinks

To determine the role of MeHg sources and sinks in the catchment compartments, two different model scenarios are used. In scenario 1, the model is run with wet deposition of MeHg as the sole MeHg input. Initial MeHg concentrations for the three reservoirs are set at 0.2 ng L^{-1} [MeHg], 2.0 ng L^{-1} [MeHg] and 0.2 ng L^{-1} [MeHg] for the upland, peatland and pond respectively, representing concentrations measured in the field (Branfireun, *et al.*, 1996; A. Heyes, unpublished data, 1995; B. Branfireun, unpublished data, 1996). In reality these concentrations would not be distributed evenly throughout the volume of water in each reservoir given the heterogeneity of MeHg in the landscape, but these values represent an estimated average concentration. 2.0 ng/L represents a very conservative estimate for MeHg concentrations in the peat porewater, as concentrations in excess of 7 ng/L have been measured at this site (Branfireun *et al.*, 1996).

In scenario 2, net MeHg sinks/sources are added to scenario 1, in which MeHg will be removed/added based on the assumption that the amount of MeHg in each reservoir will remain relatively stable over the model run (i.e. the concentration of MeHg in each compartment is in 'steady-state'). If the MeHg concentration in the reservoir at time t is different from the equilibrium concentration, then:

$$Net\_Sink/Source_t = K_{MeHg}(MeHg_{eq} - MeHg_{t-dt}) \qquad (4)$$

where $Net\_Sink/Source_t$ is the amount of MeHg (ng) added to, or removed from, the system at time t, K_{MeHg} is the rate constant for MeHg production/destruction, $MeHg_{eq}$ is the equilibrium mass of MeHg in the reservoir (ng) which is set at the beginning of the model run (the same concentrations as used in scenario 1), and $MeHg_{t-dt}$ is the amount of MeHg in the reservoir at the previous time step (ng). K_{MeHg} is set to 0.5 to simulate the relatively rapid equilibration of porewater MeHg concentrations observed in the field (Heyes, unpublished data, 1995).

3.3 RESULTS

For all of the model scenarios, the simulated mean contribution of MeHg by wet deposition to the entire catchment was 0.0004 mg ha^{-1} d^{-1} [MeHg], which is comparable to that reported by St. Louis *et al.* (1994). Modelled and measured MeHg yields for precipitation and catchment yields from the different model scenarios are found in Table 3.1. Simulation results in Table 3.1 are mean values derived from a 30 run Monte Carlo simulation in which all randomly generated parameters were independently and randomly varied. These include 4 parameters which control rainfall occurrence and magnitude, 2 parameters which control cloud cover and Q* and 1 parameter which controls the concentration of MeHg in rainfall.

	Mean Deposition or Yield of MeHg (mg/ha/d)	*Standard Error*	*Yields/Annual Precip. Input*
Actual Precipitation[1]	0.0004	-	-
Modelled Precipitation	0.0004	0.00002	-
Actual Catchment Yield (upland dominated)[2]	0.0009	-	2.25
Actual Catchment Yield (peatland dominated)[2]	0.0036	-	9.00
Modelled Catchment Yield (scenario 1)	0.0052	0.00038	12.75
Modelled Catchment Yield (scenario 2)	0.0026	0.00036	6.51
Modelled Upland Net MeHg Source	0.0007	0.00009	1.73
Modelled Peatland Net MeHg Source	0.1065	0.00879	259
Modelled Pond Net MeHg Sink	-0.2215	0.01466	-539

[1] Data from St. Louis *et al.*, 1995. [2] Data from St. Louis *et al.*, 1994.

Table 3.1: Actual and modelled catchment MeHg depositions and yields. Model results are means and standard errors from a 30 run Monte Carlo simulation in which all randomly generated parameters were varied independently and randomly.

3.3.1 Scenario 1

With the initial concentrations set at 'realistic' levels, concentrations of MeHg in the upland showed little variation, with a maximum occurring at the height of the summer period when fluxes out of the reservoir were at a minimum (Figure 3.2). Concentrations dropped to below initial levels by the end of the model year.

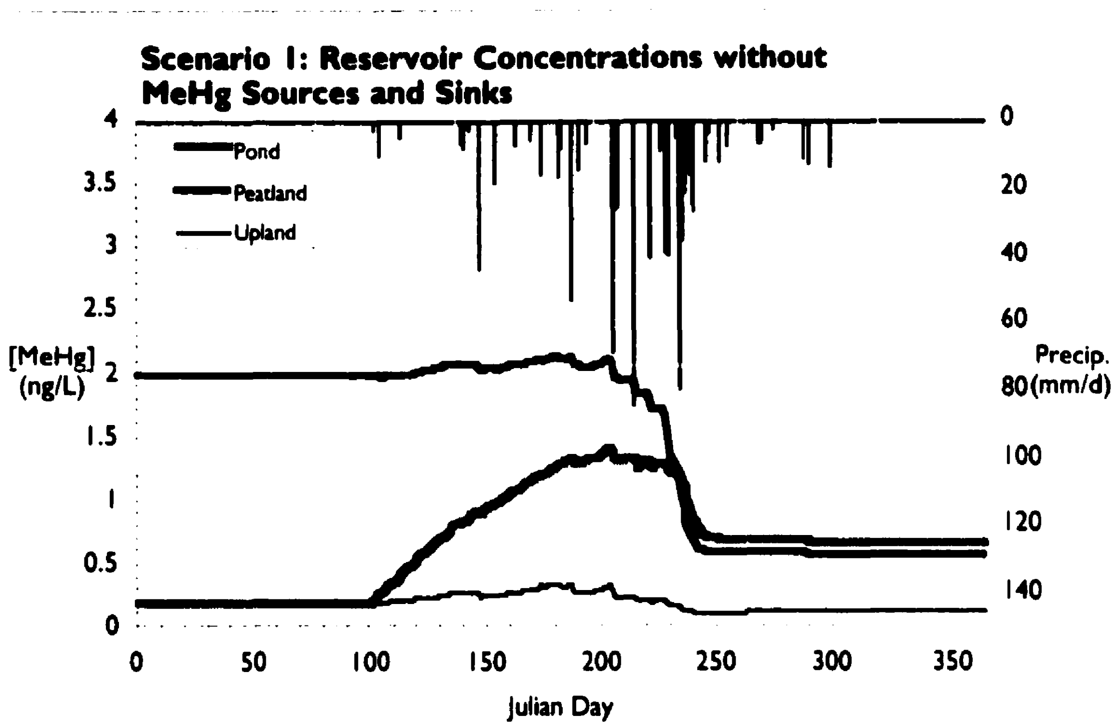


Figure 3.2 MeHg concentrations in the three reservoirs for a model run *without* net MeHg sinks and sources.

Peatland MeHg concentration behaved quite differently. The initial concentration of 2.0 ng L^{-1} was maintained until mid-summer, after which the concentration rapidly dropped to a minimum of 0.56 ng L^{-1}. Subsequent undocumented model runs revealed that MeHg concentration above approximately 0.75 ng L^{-1} could not be sustained, suggesting that production of MeHg *in situ* may be important. MeHg export appeared to be controlled by high runoff events with substantial decreases in concentration coinciding with large storms during high water table conditions.

Pond MeHg concentration increased rapidly at the beginning of the model run, stabilizing at between 1 and 1.4 ng L^{-1}, nearly an order of magnitude above the initial concentration and measured field values. This suggests that demethylation processes may significantly control pond concentrations. The catchment yield of MeHg calculated from the outflow flux was 0.0062 mg ha^{-1} d^{-1} [MeHg].

3.3.2 Scenario 2

Sink and source fluxes were added to the upland, peatland and pond, as defined in equation 4, to maintain concentrations at or about the initial levels. The source and sink fluxes regulated the amounts of MeHg in the upland, peatland and pond quite effectively, allowing for normal fluctuation as a result of dilution and flushing effects, particularly due to large storms (e.g. day 240; Figure 3.3).

Peatland concentration reached a maximum of 2.88 ng/L at mid-summer, whereas upland and pond concentrations were maintained about their initial values. The catchment yield of MeHg calculated from the outflow flux was 0.0031 mg ha^{-1} d^{-1} [MeHg].

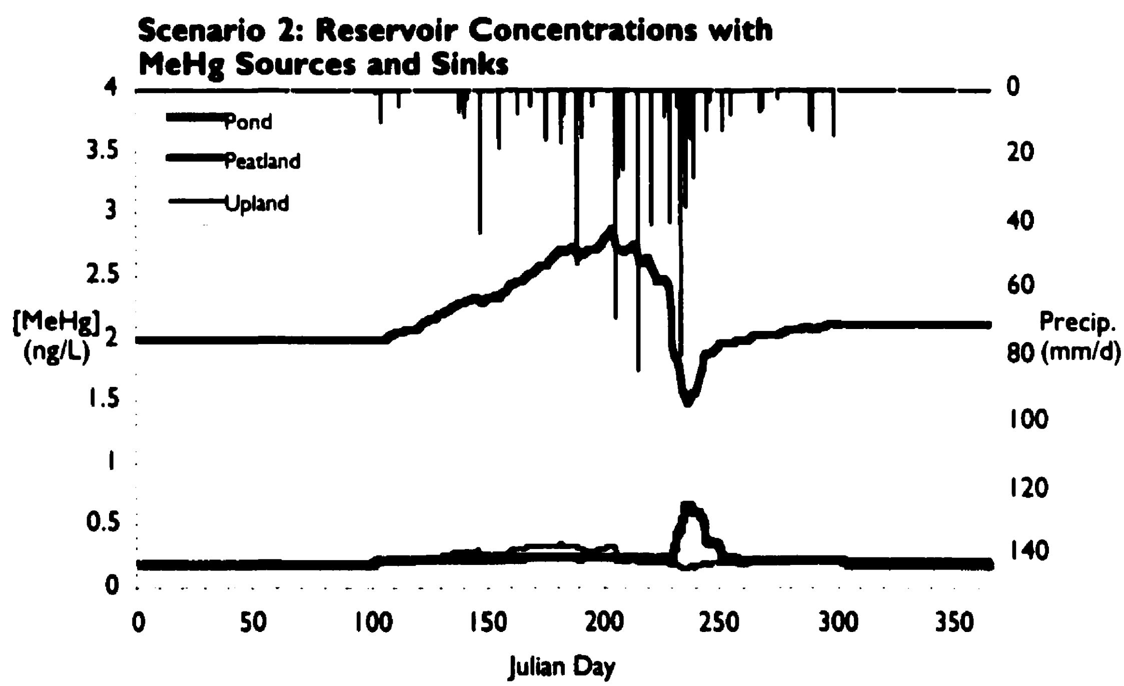


Figure 3.3: MeHg concentrations in the three reservoirs for a model run *with* net MeHg sinks and sources.

The results presented in Table 3.1 indicate that when sources and sinks of MeHg are included in the model, the upland and peatland are mean net sources of MeHg (0.0007 and 0.1065 mg ha^{-1} d^{-1}) which are 1.73 and 259 times larger than the simulated atmospheric input of MeHg to the entire catchment. The pond is a mean net sink for MeHg (-0.2215 mg ha^{-1} d^{-1}) which is 539 times larger than the atmospheric input.

3.3.3 Sensitivity Analysis

Sensitivity analyses were performed to determine the effects on catchment yield of upland and peatland size, the magnitude of atmospheric MeHg deposition, and the equilibrium concentrations of MeHg in the peatland reservoir, since the results of scenario 2 indicate that it is the primary source of MeHg in the catchment. All sensitivity analyses were performed using the scenario 2 model structure (i.e. sinks and sources of MeHg were included, and where catchment yield = 0.0031 mg ha^{-1} d^{-1} under initial conditions).

The catchment MeHg yield is sensitive to changes in peatland area relative to the rest of the catchment (Figure 3.4). In this sensitivity analysis, the upland and pond areas were unchanged while the peatland area was varied from 0.2 to 4 ha. Catchment yields were largest with relatively large peatland areas, and decreased with increasing upland area-peatland area ratio.

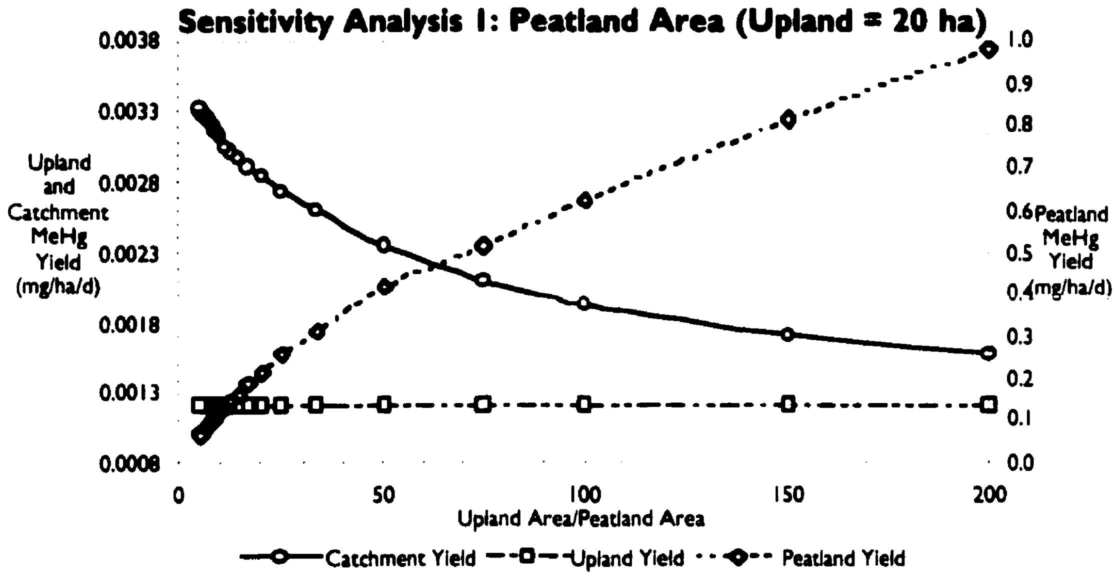


Figure 3.4: Results of peatland area sensitivity analysis. Peatland area was varied from 0.1 ha to 4 ha and upland and pond areas were constant at 20 ha and 0.8 ha respectively.

Upland yield was constant at 0.0012 mg/ha/d, whereas peatland yield increased markedly with increasing upland area- peatland area ratio as a result of the increased flushing rate of the smaller peatland volume relative to the upland. The catchment yield decreases with increasing upland area-peatland area ratio in spite of this since the size of the pond MeHg sink remains constant, offsetting the increased yield from a relatively smaller peatland area.

Similarly, the catchment yield is sensitive to the size of the upland relative to the peatland (Figure 3.5).

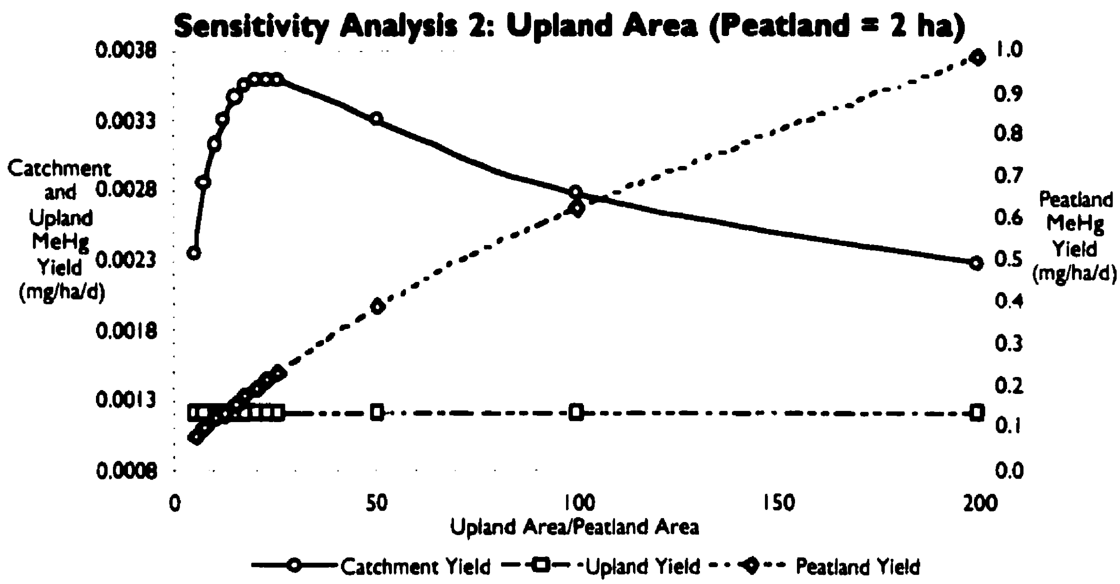


Figure 3.5: **Results of upland area sensitivity analysis. Upland area was varied from 5 ha to 400 ha and peatland and pond areas were constant at 4 ha and 0.8 ha respectively.**

Catchment yield increases rapidly with increasing upland area (peatland area held constant at 2 ha) with a maximum yield of approximately 0.0036 mg ha^{-1} d^{-1} occurring with an upland area-peatland area ratio of 20:1, and decreases with increasing ratio. Peatland and upland yields are similar to those observed in the previous sensitivity analysis, and decreasing catchment yield at higher upland area-peatland area ratios suggests that the relatively much larger uplands are capable of delivering large volumes of low MeHg runoff which counteract the influence of the higher MeHg peatland runoff contributions. Both of the above scenarios become somewhat implausible at higher upland area-peatland area ratios, as the overall basin physiography would not be expected to scale proportionally, particularly with regard to pond characteristics. For example, very large catchments would be expected to have larger, deeper lakes associated with them which could represent much larger sinks for MeHg, thus regulating the catchment yields significantly.

Sensitivity analysis in which the amount of MeHg deposited in precipitation over the catchment was varied by factors of 0 to 15 times ELA deposition revealed that catchment yield remained virtually unchanged (0.0031 mg ha^{-1} d^{-1}), even at 15 times deposition (Figure 3.6). This model suggests that contemporary deposition of MeHg plays an insignificant role in influencing the magnitude of catchment yield in catchments containing peatlands.

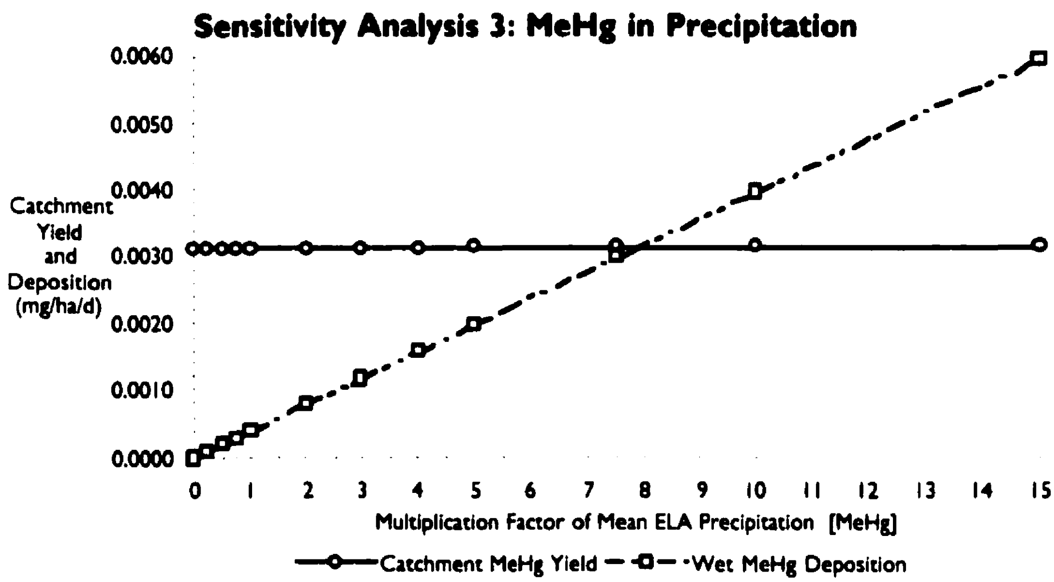


Figure 3.6: Results of precipitation MeHg sensitivity analysis. The precipitation MeHg used in the model based on ELA records was varied by a factor of 0 to 15 to simulate various degrees of loading.

Catchment yield is also extremely sensitive to the concentrations of MeHg found in the peatland reservoir (Figure 3.7). Realistic yields are only found between 2 and 4 ng L^{-1} for this simulation which agrees with measured field concentrations. This finding suggests that accurate quantification of the 'active' pool of MeHg in peatlands is important if it is to be incorporated into catchment-scale budgets or process-based models.

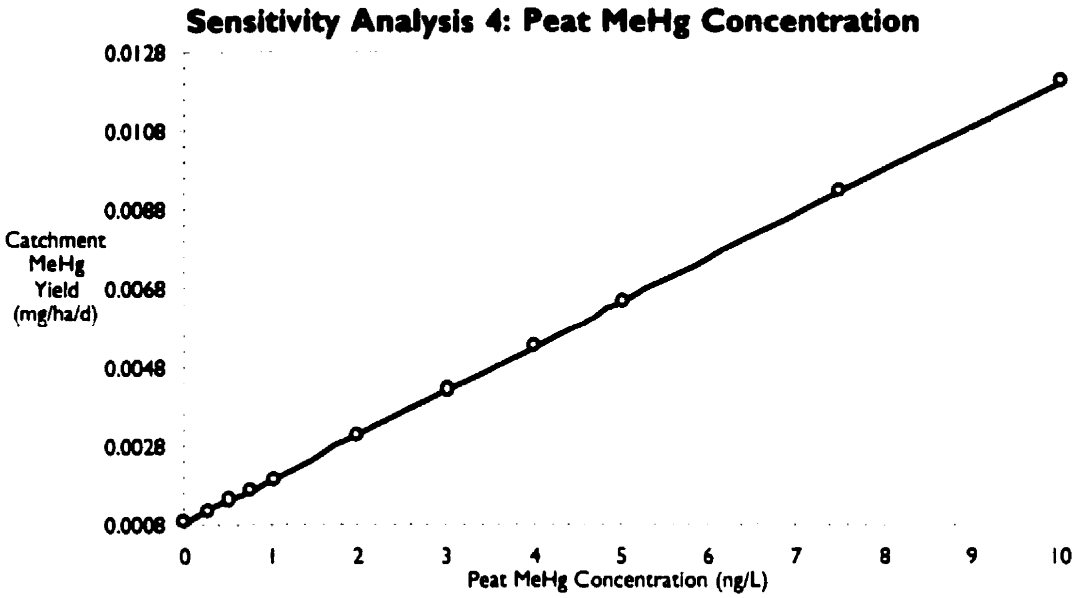


Figure 3.7: Results of peat porewater MeHg concentration sensitivity analysis.

3.4 DISCUSSION

When realistic initial concentrations of MeHg are used and no net MeHg sinks/sources are included (as in scenario 1), concentrations in the upland generally vary between 0.20 and 0.40 ng L^{-1}, which is consistent with measured field concentrations (Branfireun, unpublished data, 1995). This finding suggests that net methylation in this type of environment may be about zero (i.e. methylation and demethylation processes are either negligible or roughly in balance).

A much different situation is found in the peatland and pond. The peatland reservoir is incapable of maintaining the initial concentrations of MeHg likely as a result of flushing with low MeHg upland runoff, particularly during large runoff events. The conclusion of this simulation is that if concentrations are to be maintained at the observed level in the peatland, there needs to be an additional source of MeHg to the system. Conversely, the relatively high volume, high concentration fluxes entering the pond elevate pond concentrations to nearly seven times the observed concentrations, indicating that MeHg must be removed from the pond. The mean catchment yield calculated in scenario 1 (0.0052 mg ha^{-1} d^{-1}) is 1.69 times larger than that found by St. Louis *et al.* (1994) for the catchment on which this model is based (0.0036 mg ha^{-1} d^{-1}), but is not unreasonable. However, the behaviour of reservoir MeHg concentrations render this simulation implausible.

In scenario 2, the model was inverted to ask, "What are the net sources and/or sinks needed in the various compartments of the catchment to maintain the reservoir concentrations and basin yield, given the observed atmospheric loading?". This scenario confirms that a source of MeHg (0.1065 mg ha^{-1} d^{-1}) to the peatland over 250 times the MeHg input by precipitation (Table 3.1) exists, according to the model. Even given gross errors in the model parameterization, there is clearly a large source of MeHg to the peatland area. This scenario also indicates that MeHg is being removed from the pond reservoir (0.2215 mg ha^{-1} d^{-1}), at a rate over 500 times that of MeHg input by precipitation. The mean catchment yield of 0.0026 mg ha^{-1} d^{-1} is within 30% of that found by St. Louis *et al.* (1994), and is subject to variability in precipitation volume and timing, and MeHg concentration. What is important is that the catchment yields are in rough agreement while preserving a realistic concentration regime in the three reservoirs through the addition of methylation and demethylation fluxes.

Sensitivity analyses confirm the importance of the peatland reservoir as a source of MeHg to the system (Figure 3.4 and 3.7). The upland portion of the catchment is also important, not as a source of MeHg, but as a source of runoff which serves to flush high MeHg water from the peatland to the pond (Figure 3.5). Most importantly, this simulation clearly indicates that contemporary atmospheric deposition of MeHg has little or no influence on catchment MeHg yield in catchments containing peatlands because of the magnitude of the sources and sinks found within the catchment.

These results are limited by the assumptions made in the formulation of the model. The assumptions that MeHg concentrations are in equilibrium in the reservoirs, and that MeHg is transferred conservatively between compartments of the catchment are potentially the greatest sources of error in this study. To relax these assumptions to allow for *in situ* methylation, demethylation and the mobility of MeHg through oxic, anoxic, mineral and organic soils in the model structure requires greater understanding of the factors that control the transport and transformation of (Me)Hg than is currently found in the literature.

3.4.1 Possible Sources and Sinks of Methylmercury

MeHg in the porewater of peatlands may be derived from the methylation of *in situ* inorganic Hg in decaying organic matter, and/or the equilibration of porewater MeHg concentrations with MeHg in the plant tissues and organic sediment. The store of inorganic Hg in peatland vegetation and pore water is more than sufficient to provide enough Hg^{2+} for *in situ* methylation (Moore *et al.*, 1995), and porewater MeHg concentrations have been found to rapidly equilibrate with the high concentrations of MeHg in plant tissue and sediments, likely through diffusion (Heyes, unpublished data, 1995). We hypothesize that biotic methylation may be a major source of MeHg in peatlands, as suggested by previous research (e.g. Branfireun *et al.*, 1996).

The large sink of MeHg in the pond may be attributed to a variety of demethylation processes including oxidation, and uptake by sediments and/or plants and biota (biodilution). More importantly, lakes have recently been found to be large sinks of MeHg via an abiotic photodegradive pathway (Sellers *et al.*, 1996). This model simulation independently confirms this finding, and further testing of this model incorporating the empirically derived rates of MeHg photodegradation from Sellers *et al.* (1996) would be valuable.

3.5 SUMMARY

The results of this preliminary model suggest that cycling of Hg species may be going on at a tremendous rate ***within the catchment***, and interpretations regarding the role of the landscape in methylation/demethylation processes must be made with great care.

It is difficult to draw comparisons between the results found here and field data derived elsewhere because of differences in catchment characteristics and our assumptions regarding the behaviour of MeHg in natural systems, but the model results indicate that, although the catchment yield found under a no net methylation scenario may be realistic, the internal concentration regime is inconsistent with that observed in the study catchment in the ELA. The model results indicate that: the peatlands must be a large source of MeHg (consistent with St. Louis *et al.*, 1994; Branfireun *et al.*,1996); the amount of MeHg which must be destroyed by demethylation in the pond system to maintain measured field concentrations is consistent with the large photodegradive MeHg sink found by Sellers *et al.* (1996) and; contemporary atmospheric deposition of MeHg is not a significant component of MeHg budgets in catchments containing peatlands. This suggests that post-industrial MeHg contamination of "pristine" lakes may be the result of the enhancement of Hg methylation or inhibition of MeHg demethylation by the deposition of some other atmospherically-derived industrial pollutant (e.g. SO_4^{-2}; see Gilmour and Henry, 1991) or through some change in the bioavailability of the large volumes of inorganic mercury which are held in the catchment soils and sediments. Work is ongoing to elucidate these mechanisms. This simulation does not consider the impact of atmospheric deposition of inorganic Hg, which must also contribute to the pool of Hg methylated *in situ*. The importance of this atmospheric Hg in the catchment Hg cycle is unknown.

These large internal sources and sinks indicate a need for improved understanding of the mechanisms of Hg cycling within catchments before conclusions regarding sinks or sources of MeHg may be drawn. This finding also has more wide ranging implications for those modelling any biogeochemical system using a "black box" input-output approach, where the potential for internal transformations larger than the inputs and outputs combined may exist.

Preface to Chapter 4

Recent studies have found that 'pristine' peatlands have high peat and pore water methylmercury (MeHg) concentrations, and that peatlands may act as large sources of MeHg to the downstream aquatic systems, depending upon the degree of hydrologic connectivity and catchment physiography. Model results presented in Chapter 3 also suggest that this flux of MeHg is highly sensitive to the concentrations of MeHg found in the peatland reservoir. Sulfate-reducing bacteria have been implicated as principal methylators of inorganic mercury in many environments with previous research focussed primarily on mercury methylation in aquatic sediments. The work presented in Chapter 4 attempts to explain the high concentrations of MeHg found in peatlands by demonstrating that they are attributable to the activity of sulfate-reducing bacteria which methylate inorganic mercury as a by-product of sulfate metabolism.

Chapter 4: *In situ* Sulfate Stimulation of Mercury Methylation in a Boreal Peatland: Towards a Link Between Acid Rain and Methylmercury Contamination in Remote Environments

4.1 INTRODUCTION

Atmospheric inorganic mercury is the major source of mercury to 'pristine' ecosystems, but it is methylmercury (MeHg, an organic species) which enters the food chain, bioaccumulates and constitutes nearly all of the mercury found in fish (Bloom, 1992). Atmospheric deposition of MeHg is seldom sufficient to account for the MeHg found in biota (Fitzgerald *et al.*, 1990). Levels of MeHg in fish and catchment export of MeHg vary even though levels of atmospheric deposition of inorganic mercury are similar (Gilmour and Henry, 1991), suggesting that MeHg is derived from in-lake, and in-catchment processes.

Previous research showed that one possible source of MeHg in lakes is the in-lake transformation of inorganic Hg to MeHg, predominantly in anoxic sediments. Recent studies (e.g. St. Louis *et al.*, 1994; Rudd, 1995; Hurley *et al.*, 1995; St. Louis *et al.*, 1996; Branfireun *et al.*, 1996; Branfireun *et al.*, 1998) have indicated that peatlands are sources of MeHg to downstream lakes and streams. St. Louis *et al.* (1994) found a 4 to 15-fold greater yield of MeHg from catchments containing some peatlands than from upland catchments with no peatlands. They suggest that the contribution of MeHg per unit area of wetland terrain is 26-79 times greater than that from upland terrain. Hurley *et al.* (1995) found that, in Wisconsin, MeHg yields were highest from catchments containing wetlands, and that percent wetland surface area in a catchment was positively correlated with MeHg yield.

Following from mass-balance studies, Branfireun *et al.* (1996) undertook a detailed study of a small headwater peatland in northwestern Ontario and found high concentrations of MeHg in peat pore water relative to other catchment waters. In particular, zones of highest MeHg concentrations in peat pore water corresponded to areas of groundwater upwelling in the wetland, suggesting that these MeHg 'hot spots' could be sites of enhanced microbial methylation of inorganic mercury.

Fish in lakes affected by acid deposition have been noted to be particularly susceptible to increased MeHg contamination. Gilmour and Henry (1991) suggested that since sulfate-reducing bacteria had been identified as strong methylators of mercury (e.g. Compeau and Bartha, 1985), sulfate deposited as a component of 'acid rain' may stimulate MeHg production by enhancing the activity of sulfate-reducing bacteria in lacustrine sediments. Gilmour *et al.* (1992) found that experimental additions of sulfate to anoxic sediment slurries or lake water above intact sediment cores resulted in increased production of MeHg from added inorganic mercury, supporting the hypothesis that increased sulfate deposition provides a possible mechanism for increased MeHg loading to lakes from their underlying sediments. In contrast, the conclusions of Winfrey and Rudd (1990) indicated that experimentally elevated sulfate concentrations in boreal forest lakes resulted in no change in fish MeHg concentrations, making the link between in-lake MeHg production and sulfate unclear.

While the direct stimulation of in-lake Hg methylation by sulfate is being debated in the literature, it is clear that the presence of wetlands is an important factor in determining catchment MeHg yield, and evidence is mounting that sulfate-reducing bacteria are responsible, as least in part, for Hg methylation at 'natural' concentrations. From this, it is of interest to determine if a relationship exists between peatland MeHg production and sulfate deposition. We suggest that elevated levels of MeHg in peatlands are the result of an *in situ* geochemistry which provides suitable conditions for mercury methylation and the accumulation of MeHg. Following from the hypotheses of Gilmour and Henry (1991) and Gilmour *et al.* (1992), we hypothesize that elevated peat and pore water MeHg concentrations in peatlands are the result of sulfate stimulation of mercury methylation by sulfate-reducing bacteria.

The objective of this study was to investigate whether the *in situ* addition of sulfate to peat and peat pore water in a 'pristine' peatlands in northwestern Ontario had an effect on pore water MeHg concentrations.

4.2 METHODS

Experiments were undertaken in a small headwater peatland (Catchment 632) in the Experimental Lakes Area (ELA), located in northwestern Ontario (49°40' N, 93°43' W). Physiographic and hydrologic details of this 'poor fen' are reported in Branfireun *et al.*, (1996) and Branfireun and Roulet (1998). Experiments were undertaken in early September, 1996 and September, 1997.

At the ELA site, two collars (0.2 m deep with an area of 0.16 m^2) (Figure 4.1) made from Plexiglas® and lined with Teflon® were inserted into a flat, relatively homogeneous lawn in the 'poor fen' zone of the peatland dominated surficially by *Sphagnum angustifolium* and underlain by approximately 1 m of peat. The collars were left in the peatland for approximately one week prior to the first sulfate addition.

Previous sampling in the 'poor fen' zone indicated that there were large within and between year variations in both sulfate and MeHg concentrations in porewater in the 30 cm of peat below the water table. The average MeHg concentration between 0 and -30 cm from 1993 to 1996 was 2.31 ng/l (S.D.=1.03; n=9), and the average sulfate concentration for the same depth and time was 0.37 mg/l (S.D.=0.13; n=12). Sulfate and MeHg concentrations were somewhat related, in that higher concentrations of sulfate and MeHg were mutually exclusive.

4.2.1 Twenty Times Sulfate Addition

Twenty times the average monthly deposition of sulfate was applied in a two day period in the initial experiment in September, 1996. A first application of 10 times the monthly average deposition of sulfate was made to see the effect of one addition. A second application of the same amount was made after 24hrs to determine if a subsequent addition elicited any further responses.

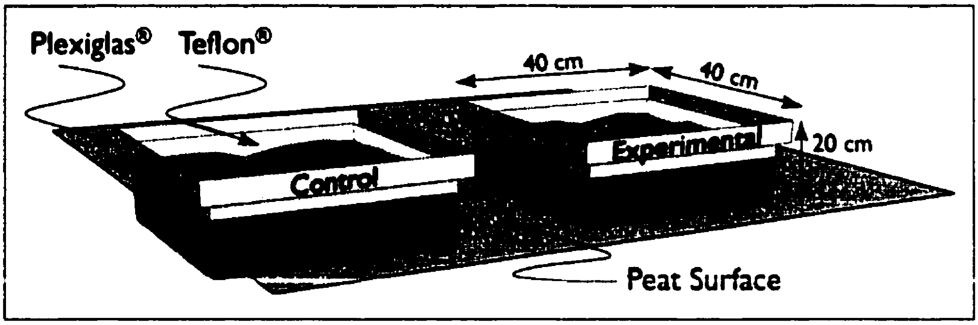


Figure 4.1: Schematic diagram of the reference and experimental collars inserted into the poor fen of the 632 peatland, Experimental Lakes Area, northwestern Ontario.

The 'reference' collar was irrigated at time=0 and time=24h with 1 liter of distilled, deionized water (pH=6.78). The 'experimental' collar was irrigated at time=0 and time=24h with 230 mg of SO_4^{-2}, applied as 1 liter of 430 mg/l K_2SO_4 solution (pH=5.86) at each time. The sulfate was applied as K_2SO_4 (as opposed to sulfuric acid) to prevent confounding effects. This amount of experimentally applied sulfate was determined by taking the mean monthly deposition of sulfate for ELA in the summer months [1500 mM m^{-2}; Linsey *et al.*, (1987)], and multiplying it by 10, resulting in an experimental addition equivalent to 1.4 mg m^{-2} or 14 kg ha^{-1} applied twice. No appreciable inorganic mercury was added to the collars.

Both collars were sampled at t=0 hrs (prior to the first sulfate addition), 24 hrs (prior to the second sulfate addition), 48 hrs, 72 hrs and 110 hrs at 0, -5 and -10 cm from the water table. The water table was within 5 cm of the ground surface at all times during the experiment. Ultra-clean sampling protocol was used at all times (see Branfireun *et al.*, 1996). Samples were taken using a custom-fabricated stainless-steel profile sampler with 0.5 mm intakes every 5 cm. The sampler was inserted randomly into the peat in the collars at each time interval. Samples were drawn through a teflon sampling tube into a teflon transfer container and then transferred into 125ml teflon bottles for MeHg analyses, and into 20ml glass scintillation with zero-headspace caps for sulfate, DOC and pH analyses. All samples were filtered within 4 hours of sampling (0.45 mm cellulose-nitrate) and had pH measured at that time. Samples for MeHg analysis were immediately frozen in the teflon bottles, and the vials for sulfate and DOC were refrigerated until analysis could be completed.

4.2.2 Two Times Sulfate Addition

The second experiment in September 1997 used a single 2 times sulfate addition to see if a lower, more realistic level of deposition would result in a detectable change in the pore water MeHg concentrations. 46 mg of SO_4^{-2} (0.28 mg m^{-2} or 2.8 kg ha^{-1}) was applied as 1 litre of 86 mg/l K_2SO_4 solution at time=0 hrs. Analyses were performed for MeHg and sulfate only. Samples for MeHg and sulfate were taken at t=0 hrs (initial), 24 hrs, 48 hrs and 120 hrs, with all other procedures as described above.

MeHg analysis was performed using a technique modified from Bloom and Fitzgerald (1988) and Horvat *et al.* (1993) (see Branfireun *et al.*, 1996). Sulfate was measured using suppressed ion chromatography at Department of Fisheries and Oceans-Freshwater Institute Laboratories, Winnipeg, and DOC was measured using a Shimadzu TOC-5050 analyzer.

4.3 RESULTS

4.3.1 Twenty Times Sulfate Addition

Reference Plot: MeHg concentrations, sulfate concentrations, DOC concentration and pH over the course of the experiment are presented in Figures 4.2a-d. MeHg concentrations ranged from 0.20 to 2.6 ng/l, generally decreased with depth and were relatively consistent over the course of the experiment. Sulfate concentrations ranged from 0.04 to 0.71 mg/l with little variability over depth or time. DOC concentrations were quite variable, ranging from 24.5 to 39.9 mg/l. Control plot pH was stable over time, ranging from 4.7 to 5.5, with the lowest pH occurring at the water table (0 cm).

Experimental Plot: Initial concentrations of MeHg, sulfate and DOC from the experimental plot (Figures 2e-h) were similar to those of the reference plot. However, after the initial application of sulfate, MeHg, sulfate and DOC data from the experimental plot varied considerably and with some consistent patterns, with the exception of pH.

MeHg concentrations (Figure 2e) increased markedly at 24 hours, reaching concentrations of between 3.46 ng/l at the water table and 5.13 ng/l at -10 cm. After the second sulfate application, MeHg concentrations continued to increase at -5 cm to 6.07 ng/l while the other depths showed a slight decline. After 110 hours, concentrations at 0 cm and -10 cm had returned to initial levels (1.94 and 0.82 ng/l respectively), while -5 cm exhibited the highest concentration measured over the course of the experiment (9.19 ng/l).

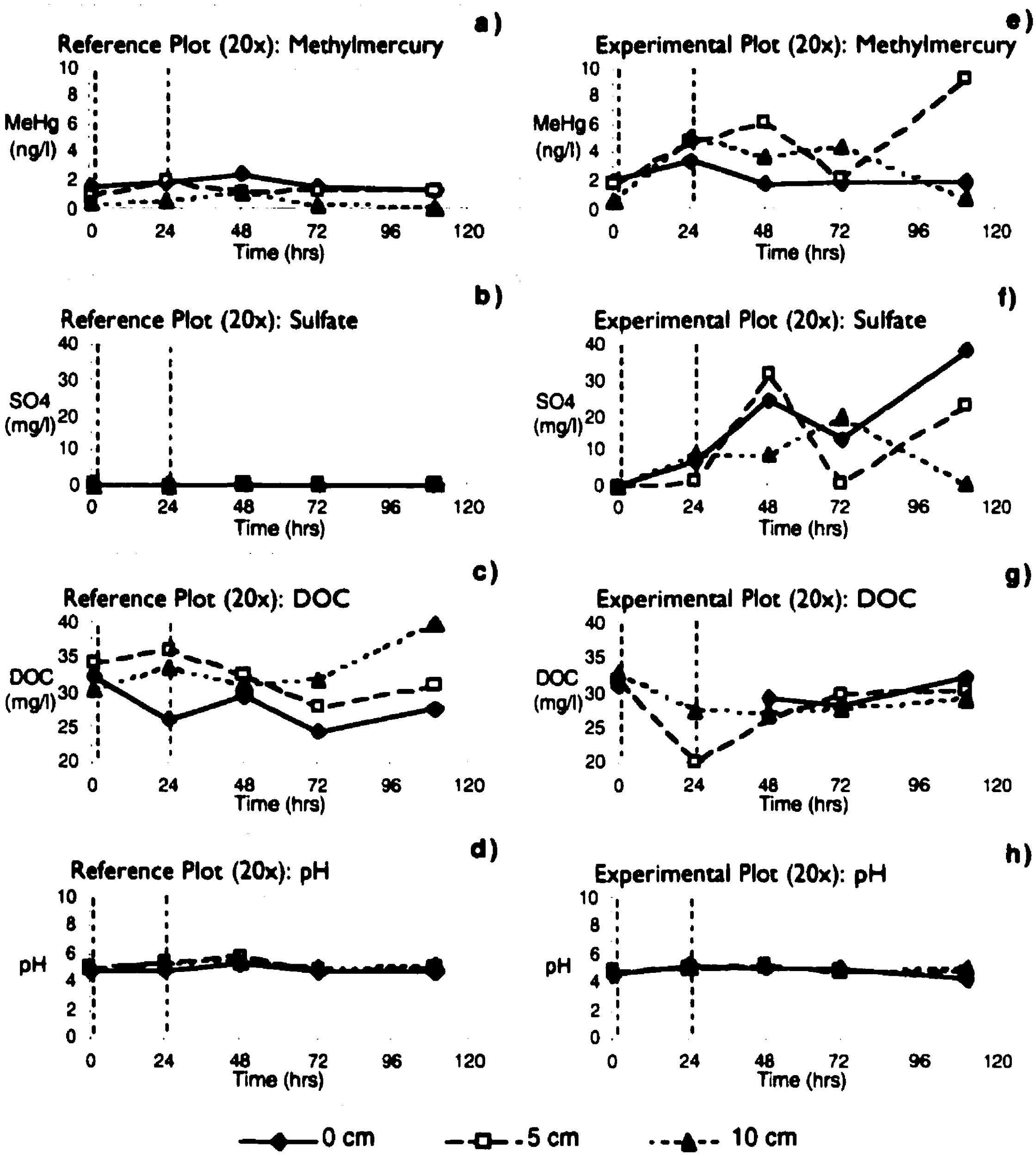


Figure 4.2: Reference and experimental collar methylmercury, sulfate and DOC concentrations and pH for the 20x experiment. Vertically-drawn dashed line indicates times of experimental irrigations at t = 0 hrs and t = 24 hrs.

Sulfate concentrations (Figure 2f) rose to over 9 mg/l at -10 cm after the first sulfate application, and then increased much more sharply after the second application, with peaks at 0 cm and -5 cm reaching 24.3 and 31.5 mg/l respectively. After 110 hours, sulfate concentrations had returned to initial levels at -10 cm, but were still very high relative to background at 0 cm and -5 cm (39.0 and 22.5 mg/l respectively).

DOC concentrations (Figure 2g) generally ranged between 27 and 33 mg/l with the exception of -5 cm at t=24h, which dropped to 20.1 mg/l. A vial broken in transport unfortunately deprived us of the DOC concentration at 0 cm for that same sampling time.

pH (Figure 2h) for the experimental plot ranged between 4.33 and 5.17 with a general increase with depth. These values are similar to those of the reference plot and did not vary considerably over the course of the experiment, indicating that the additions of water and sulfate did not produce a shift in pH, neither through the addition itself, nor any resultant biogeochemical process.

4.3.2 Two Times Sulfate Addition

Reference Plot: At t=0 hrs, MeHg concentrations from the control plot, ranged from 0.35 to 0.65 ng/l (lower than those found in 1996) with concentrations decreasing with depth (Figure 4.3a). Throughout the experiment, reference plot MeHg concentrations ranged from 0.28 to 0.98 ng/l with the highest concentrations always found at the water table (0 cm). A slight increase in concentration at 0 cm at t= 24hrs and 48 hrs, and a decrease at 120 hrs was noted. Any relatively small changes in MeHg concentration at a depth can easily be accounted for by spatial and analytical variability, and cannot be considered significant.

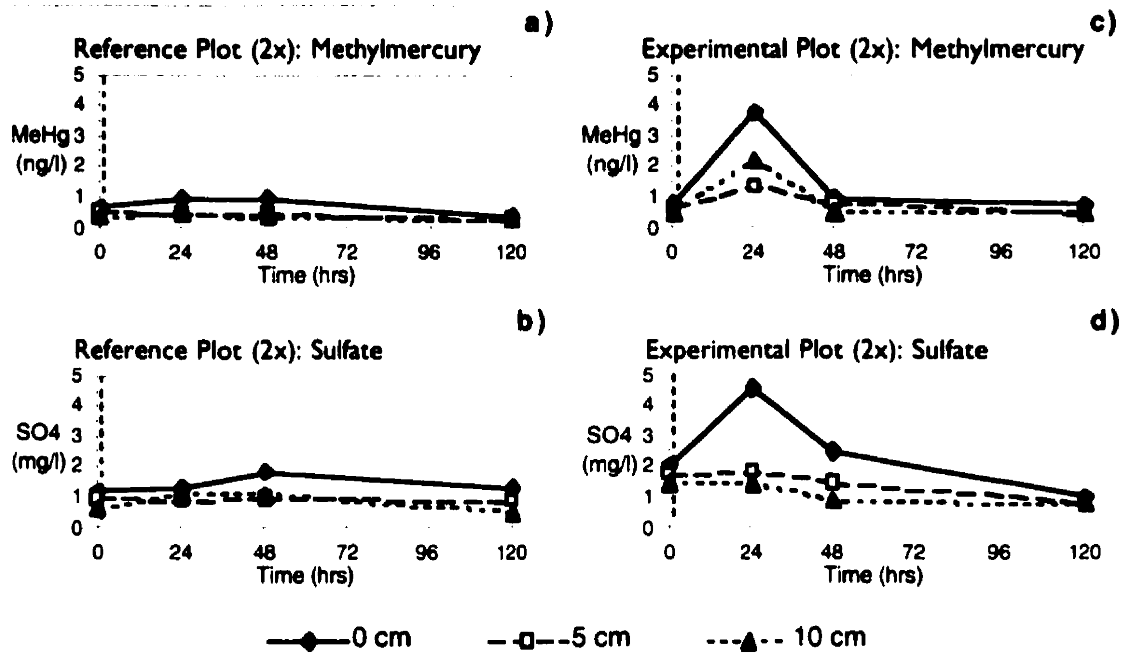


Figure 4.3: **Reference and experimental collar methylmercury and sulfate concentrations for the 2x experiment. Dashed line indicates time of experimental irrigation at t = 0 hrs.**

Sulfate concentrations were on average 2.7 to 3.0 times higher in the reference plot in 1997 as compared to 1996, ranging from 0.49 to 1.89 mg/l over the course of the experiment (Figure 3b). A slight increase in concentration was noted at 0 cm at 48 hrs and 120 hrs.

Experimental Plot: Initial MeHg concentrations in the experimental plot were similar to those of the reference plot, ranging between 0.83 ng/l at 0 cm and 0.52 ng/l at -5 cm (Figure 3c). Twenty four hours after the 2x sulfate application, MeHg concentrations increased markedly, with the greatest increase at 0 cm (3.83 ng/l) followed by -10 cm (2.27 ng/l) and -5 cm (1.36 ng/l). By t=48 hrs, MeHg concentrations had returned to values comparable to those at the beginning of the experiment.

Initial sulfate concentrations were somewhat higher in the experimental plot than in the reference plot, ranging between 2.09 mg/l (0 cm) and 1.46 mg/l (-

10 cm) (Figure 3d). Twenty four hours after the sulfate application, concentrations at 0 cm were still high (4.61 mg/l), while at -5 and -10 cm, sulfate concentrations had either returned to their initial values, or never changed to begin with. All sulfate concentrations continued to decrease for the remainder of the experiment, with the high concentrations at 0 cm returning to somewhat lower than initial values by t=120 hrs.

4.4 DISCUSSION

The response of the experimental plot to both the 20 times and 2 times sulfate additions is clear; the *in situ* addition of sulfate to the peat and peat pore water resulted in increases in pore water MeHg concentrations. After 24 hours, both experiments resulted in an increase in pore water MeHg concentrations by a factor of 3 to 4 (Figure 2e; 3c). However, the five-fold greater amount of sulfate applied initially in the 20 times experiment (compared to the 2 times experiment) did not result in a proportionally greater increase in MeHg concentrations. The fact that no proportional increase in MeHg concentrations was observed suggests that the increased MeHg concentrations are not the result of ion exchange through the addition of the K_2SO_4. The 20 times experiment ultimately resulted in the highest measured pore water MeHg concentration (9.19 ng/l), but the maximum concentration measured over the course of the 20 times experiment is not close to being a factor of 10 greater than that seen in the 2 times addition.

If sulfate-reducing bacteria are responsible for the consumption of sulfate and the production of MeHg in this soil, then their activity could have been limited early in the 20 times experiment by population and/or by the availability of organic substrate for the sulfate reduction reaction. Also, production of sulfide might limit methylation, either physiologically, or through the complexation of available Hg^{2+} into an unavailable HgS precipitate (Berman and Bartha, 1986; Gilmour *et al.*, 1992; Choi and Bartha, 1994). Research indicates that there are sulfate and sulfide concentrations at which certain species of sulfate-reducing bacteria will optimally methylate mercury in lake sediments (Gilmour *et al.*, 1992; Gilmour *et al.*, 1998). Peat chemistry will not necessarily behave similarly to lake sediments, but the higher MeHg concentrations in the 20 times experiment suggests that the 2 times experiment was not the optimal condition.

In both the 20 times and the 2 times experiment, sulfate reduction appears to be strongest at -10 cm, suggesting that the peat sediments may not be sufficiently anoxic above this depth to permit strong sulfate reduction. Certainly, very high concentrations of sulfate remained in pore water at the water table after 5 days in the 20 times experiment. If the added sulfate solutions were assumed to perfectly mix with the pore water throughout the volume of the 0-10 cm layer of peat (assuming 80% volumetric soil moisture), then one could expect a final sulfate concentration of 38 mg/l throughout if no sulfate reduction had occurred. This is, coincidentally or not, the sulfate concentration at the water table at the end of the 20 times experiment. At -5 cm, this concentration drops to around 50% of this value, and further decreases to background at -10 cm. Similarly, in the 2 times experiment, sulfate concentrations at the water table after 24 hours (4.6 mg/l) are comparable to a 'well-mixed' sulfate concentration of 5.7 mg/l in a no reduction scenario, suggesting weak reduction, whereas at -5 and -10 cm, sulfate concentrations are comparable to initial values.

The high degree of variability in sulfate and MeHg concentrations over the course of the 20 times experiment confounds interpretation of these data. This variability could be due to spatial variability in zones of oxia/anoxia, bacterial communities, flowpaths in the peat matrix which preferentially channelled the added sulfate solution, or some combination of these. The much more consistent trends seen in both MeHg and sulfate concentrations over the course of the 2 times experiment could indicate that the variability seen in the 20 times experiment is not an artifact of the sampling methodology, but is an actual indication of the dynamic *in situ* methylation, demethylation, and sulfate reduction and oxidation. For example, Gilmour *et al.* (1998) suggested that variability in sulfate reduction profiles in some sediments of the Florida Everglades may reflect strong internal cycling of sulfur, mediated by the transport of oxygen through root systems of emergent macrophytes. Oxygenation of near surface anoxic peat by vascular plants could be occurring in this environment as well. Only a more spatially and temporally intensive sampling regime in future experiments will reveal more information about the cycling of sulfur in these soils. Certainly, the ambiguity of the sulfate data do not take away from the finding that the addition of sulfate resulted in an increase in MeHg concentrations.

The finding that the strongest sulfate reduction occurred at -10 cm fails to explain why the highest MeHg concentrations were found at -5 cm during the 20 times experiment, and at the water table during the 2 times experiment, if sulfate reduction and mercury methylation are presumed to be associated. We believe that the answer lies in the understanding of the hydrology of the experimental site. The experimental collars are in a zone of groundwater discharge where previous studies have found rates of upwelling of up to 6 cm per day at 50 cm below the surface of the peat (Branfireun *et al.*, 1996) It is plausible that the highest concentrations of MeHg found at 0 to -5 cm in both the 20 times and 2 times experiments are simply the result of mass transport from the zone of greatest sulfate reduction and mercury methylation at some depth below. This mass flux of MeHg may also explain the coincidence of higher concentrations of MeHg *and* sulfate, particularly in the 2 times experiment. The MeHg may be produced in the anoxic sediment where sulfate reduction is evident, then migrates upwards into more oxic sediments where the sulfate persists. This hypothesis assumes that MeHg is stable in oxic waters, at least in the short term.

Other sources of variability include processes which 'remove' MeHg in solution, such as demethylation, complexation and binding in both the oxic and anoxic peat. The MeHg concentrations found in peat pore water must represent an equilibrium between mercury methylation and demethylation. Unfortunately, the experiments discussed here represent some measure of "net methylation" and no information about the complexation or solid phase-liquid phase partitioning.

The removal of MeHg from pore water by any one, or combination of the aforementioned processes is clear in the 2 times experiment, where pore water concentrations returned to background within 48 hours. The continued production of MeHg due to the availability of sulfate in the 20 times experiment precluded the observation of this effect, but could also go towards explaining the high variability. The finding that 'new' MeHg 'disappears' after a short amount of time suggests a transient impact of the sulfate stimulation of mercury methylation. However, we would expect that chronic deposition of elevated levels of sulfate would result in a gradual shift in the solid-phase and liquid-phase MeHg equilibrium concentrations to accommodate the higher rates of MeHg production.

4.5 IMPLICATIONS

The major implication of the findings described here is that the atmospheric deposition of sulfate in 'acid rain' onto peatlands could contribute to the MeHg contamination of lakes which are hydrologically connected to those peatlands. This may be particularly important in the boreal and sub-boreal zones where peatlands are very common landscape features. The literature presents confounding results regarding the importance of sulfate stimulation of in-lake mercury methylation. The potential significance of the link between acid deposition and MeHg production in peatlands may provide an explanation for increased MeHg in fish in acid-impacted lakes in landscapes containing peatlands. Certainly, the concentrations of MeHg found in the pore water of, and runoff from, peatlands far exceeds those found in lakes, thereby having the potential for a more significant impact in some environments. Assumptions underlying this hypothesized implication are: the peatlands(s) and lake(s) must be part of a hydrologically connected system; all peatlands behave similarly to the one studied here in terms of sulfate and MeHg dynamics (i.e. bacterial communities are similar), and; chronic elevated deposition of sulfate results in a permanent upward shift in the equilibria between the solid-phase and liquid-phase MeHg in peat and peat pore water.

In addition, if the boreal forest zone of North America becomes warmer and drier as a result of global warming, then the lowering of wetland water tables and reoxidation of a large store of reduced sulfur to sulfate could also result in the sulfate stimulation of higher rates of mercury methylation in the future. This reoxidation of reduced sulfur to sulfate has been observed in wetlands on the Precambrian Shield during dry summers when water table drawdown is pronounced (e.g. Devito and Hill, 1997). Confounding factors such as increasingly oxic sediment as a result of decreased precipitation and increased evapotranspiration, changing peat temperatures and changing flowpaths make this potential effect of global change a complex argument in need of more research.

More work is required on the processes of mercury methylation and demethylation *in situ*, particularly in peatlands, in order to unravel the complex relationship amongst the supply of sulfate and it's effect on mercury methylation, sulfide inhibition of methylation, available carbon, and bacterial metabolism (e.g. Choi and Bartha, 1994). In particular, it is essential that microbial ecologists explore the *in situ* community structure of MeHg "hot spots" in the landscape (e.g. Devereux *et al.*, 1996). More detailed catchment-scale research is required into the hydrologic connections among the terrestrial catchment, peatlands and the downstream aquatic systems. Finally, links between sulfate deposition and MeHg concentrations should be explored in other sites experimentally, and by looking at unmanipulated sites in landscapes with differing levels of atmospheric sulfate deposition.

Preface to Chapter 5

Catchments containing peatlands have been shown to yield far greater amounts of MeHg than purely upland catchments, indicating that peatlands are sources of MeHg in the catchment. Previous studies (e.g. St. Louis *et al.*, 1996) and the model results presented in Chapter 3 have shown that this catchment MeHg yield is quite variable, and is highly dependent upon catchment water yield. This chapter investigates the effects of inter-annual variability of precipitation on the hydrology of the study catchment and its subcatchments; specifically changes in water yield and runoff mechanisms which influence the quantity and quality of water leaving the catchment.

Chapter 5: Hydrology of a Small Boreal Forest Catchment: The Effects of Inter-annual Variability in Precipitation on Water Yield and Hillslope Flowpaths

5.1 INTRODUCTION

Catchments of the Canadian Precambrian Shield are frequently characterized by thin soils (often till dominated) overlying massive granitic bedrock, ephemeral water flow and transient runoff regimes. There are a number of studies which have focussed on the hydrologic response of till-dominated catchment hillslopes on the Canadian Precambrian Shield, many of which have been innovative in their use of geochemical and/or isotopic tracers (e.g. Moore, 1989; Wels *et al.*, 1990; Peters *et al.*, 1995), and hydrometric instrumentation (e.g. Renzetti, 1992). These studies have made significant contributions to the literature such as the importance of subsurface flow in the delivery of storm runoff downslope (e.g. McDonnell and Taylor, 1987; Roberge and Plamondon, 1987), the delivery of "pre-event" water in stormflow (e.g. Maulé and Stein, 1990) and biogeochemical cycles in this landscape, particularly with respect to the susceptibility of Precambrian Shield catchments to acidification (Bottomley *et al.*, 1984, 1986; Maulé and Stein, 1990)

Although the amount of literature on this fairly specific topic appears generous, a large number of these studies have been undertaken in southerly sites on the Precambrian Shield with mixed hardwood forests and in places with quite deep till-dominated soils (>2.5m (Hinton *et al.* 1993)). This landscape is very different from the pine and spruce forested, bedrock dominated, thin glacio-lacustrine soiled (< 1m) Precambrian Shield Boreal catchments which cover a vast swath of the Precambrian Shield landscape.

A few studies have looked at the hydrology of the more heterogeneous, bedrock-dominated boreal Precambrian Shield catchments (e.g. Allan and Roulet, 1994; Branfireun and Roulet, 1998), but these studies were mainly limited to zero-order catchments dominated by overland flow processes, and peatland hydrology, respectively. There has been no work to date regarding the inter-annual variability of boreal catchment hydrology and the effects of changes in precipitation input on the hydrologic cascade or water quality.

The objectives of this study are:

1) to examine the inter-annual variability in the hydrologic responses of the catchment and sub-catchment units, and;

2) to explain this variability in terms of the hydrologic flowpaths and the hydrologic coupling of landscape units.

5.2 SITE DESCRIPTION

This study was conducted in a small (41.6 ha) Precambrian Shield headwater catchment (Basin 632) located in the Experimental Lakes Area (ELA) (49°40' N, 93°43' W) near Kenora, Ontario, Canada (Figure 5.1). The catchment contains a peatland (4.7 ha) with a small central lake (1.0 ha). A hydrologic study of this peatland has been reported previously (Branfireun and Roulet, 1998). The catchment uplands may be topographically divided into three subcatchments, west (15.4 ha), south (13.5 ha) and north (7.0 ha).

The uppermost portions of the south subcatchment are bedrock dominated with isolated, vegetated, soil-filled depressions called "treed islands" (Allan and Roulet, 1994). The hydrology of this landscape type was previously reported in Allan and Roulet (1994). Runoff is dominated by Hortonian overland flow, and antecedent moisture conditions in the soil-filled depressions strongly control runoff response through saturation overland flow processes by varying the total runoff contributing area (Allan and Roulet, 1994).

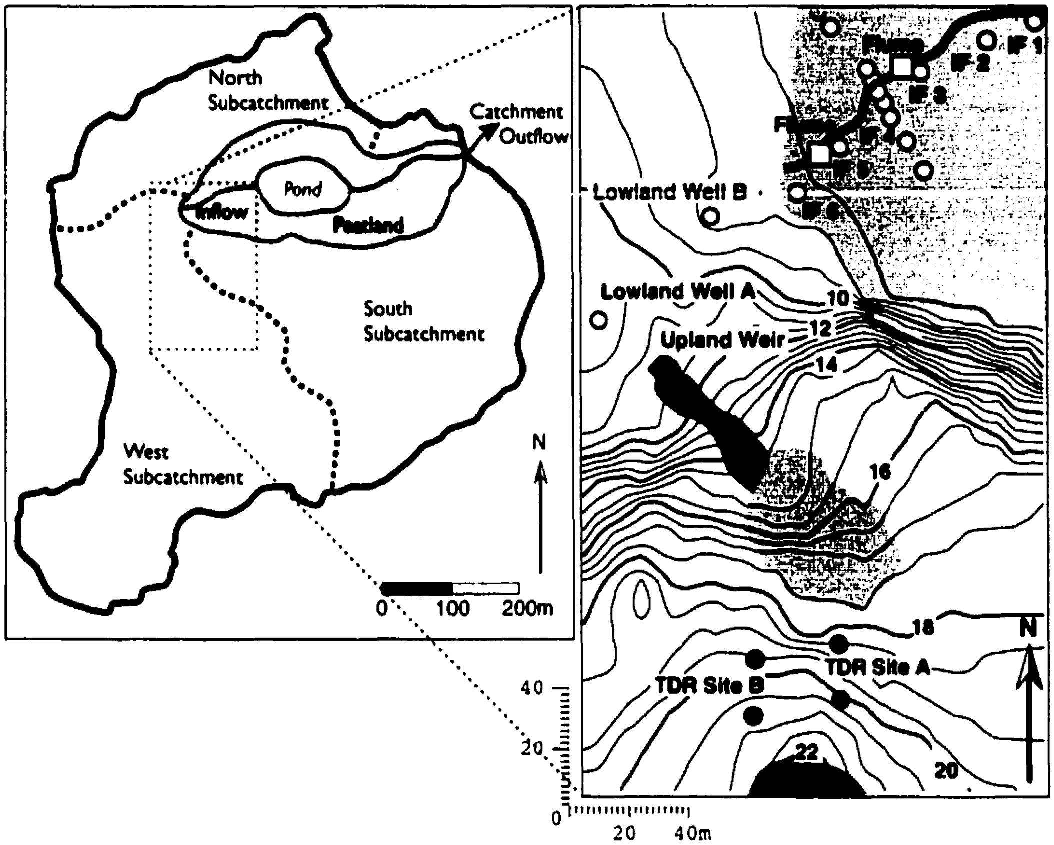


Figure 5.1: Left panel: Map of the 632 catchment, Experimental Lakes Area, Northwestern Ontario. The dashed box indicates the location of the instrumented hillslope/peatland subcatchment (right panel). Right panel: Light grey areas are wetlands; dark grey areas are zones of bedrock exposure. Contour interval is 0.25 m. Elevation is above an arbitrary datum.

Mid-slopes of the south subcatchment are steep with soil covered (< 1m) bedrock steps. The north subcatchment of the study site is dominated by a steep bedrock cliff which delivers water rapidly to a peatland sand unit (E. Mewhinney, personal communication, 1994). The catchment recharge area is dominated by the west subcatchment, the mid-slopes of which are soil covered with bedrock outcroppings. Soil depths range from 0 cm on steep bedrock exposures to over 1.5 m in some deep valley bottom depressions.

Average soil depth on the upland slopes is approximately 40 cm but varies considerably over short distances. Soils are composed of an assemblage of glacio-fluvial/lacustrine deposits which are well sorted in some locations, containing erratic cobbles and boulders. These humo-ferric podsols and dystric brunisols (T. R. Moore, personal communication, 1998) are underlain in most of the upland by a basal layer of coarse sand/fine gravel. Details of the peatland soils and vegetation are reported elsewhere (Branfireun *et al.*, 1996).

The upland portion of the study plot in west subcatchment (Figure 5.1) is overlain by a mineral soil which varies in depth from 20 to 75 cm. Downslope of the true mineral upland occupying a slight break of slope is a small "upland wetland", dominated by a surficial layer of living *Sphagnum* spp. with a largely unconsolidated, fibrous peat layer (up to 30 cm deep) overlying a bouldery gravel basal layer (20-30 cm deep). Overland flow generated by this upland terrain during some storm events is channeled over a bedrock pavement. Between the open bedrock pavement and the peatland proper is a flat, deeper soiled (up to 1.5 m) lowland transition zone.

5.3 METHODS

Measurements of precipitation input, volumetric soil moisture, upland and lowland water table elevation, upland overland flow and peatland and catchment streamflow were made as continuously as possible during the ice free seasons of 1995 and 1996. Large breaks in the measurement record were due to unanticipated technical problems with the time domain reflectometry (TDR) system in 1995 and lightning damage to electronic equipment in 1996. Smaller interruptions were largely the result of equipment damage by animals. Surface topography of the instrumented areas was surveyed using a Nikon DTM-430 Total Station.

5.3.1 Precipitation

Rainfall was measured over the study period using two automated tipping bucket raingauges located in the lower part of the southwest subcatchment near the other upland hydrologic instrumentation, and near the catchment divide on the south bedrock upland. Precision of both gauges was 0.2 mm. Annual rainfall and snowfall was recorded at the Experimental Lakes Area/Environment Canada Meteorological Station.

5.3.2 Soil Moisture and Water Table

Volumetric soil moisture was measured at 4 upland sites along two transects (Figure 5.1) by time domain reflectometry using a Tectronix 1502B cable tester and 3 rod, unbaluned 30 cm probes. At each site, a small pit was excavated to bedrock, the probes were inserted into the upslope clean face and the pit backfilled. Three probes were inserted at depths corresponding with each major soil horizon (at the base of the surficial organic horizon (denoted "Organic" in subsequent figures), in the sandy-silt middle horizon ("Sand-Silt") and in the basal coarse sand-gravel horizon ("Basal"). Volumetric soil moisture content was calculated using a version of the equation presented by Topp *et al.* (1980). Measurements were stored by a Campbell Scientific datalogger and taken frequently (every 30 minutes) in order to detect diurnal changes as a result of evaporation and slow drainage, and transient changes due to rainfall inputs.

Near each TDR installation, a 10 cm ID well perforated along its entire length was installed to bedrock to measure the development of transient water tables in the upland soils. Water table elevation in the upland, transition zone and peatland was monitored continuously downslope using float-potentiometers in a series of 10 cm ID wells. Measurements were taken with a frequency of 15 minutes to 1 hour, depending upon the location and stored in Campbell Scientific dataloggers.

5.3.3 Soil Characteristics

Upland mineral soil saturated hydraulic conductivity was measured using a Guelph Permeameter at several sites. Grab samples of upland soil were returned to the lab for sand-silt-clay content analysis using a gravimetric technique in order to derive various soil hydraulic parameters.

5.3.4 Surface Flow

Episodic overland flow generated in the upland was gauged at a 90° V-notch weir ("Upland Weir") installed in a small wooden retaining structure built on the exposed bedrock pavement (Figure 5.1). Height of water in the V-notch was measured continuously in the small pond of water held behind the retaining structure in the same manner as described for the water table wells. Discharge was calculated using a standard equation for relating the elevation of the water surface (Z_w) to discharge (Dingman, 1994; eq. F-15). Surface streamflow on the peatland was measured in two flumes. Stage was related to discharge using the velocity-area method.

5.3.5 Groundwater Flow

Patterns of groundwater flow were measured in piezometers installed in two perpendicular transects in the inflow zone of the peatland (Figure 5.1). This installation was in place from a previous study and details of this network may be found in Branfireun and Roulet (1998).

5.4 RESULTS

All comparative hydrological statistics and relationships are calculated for the period from day 130 to day 250, the length of the shortest duration streamflow record over the two years (1995 and 1996), and will be referred to as "the study period" henceforth. All water table elevations are presented with respect to the ground surface.

5.4.1 Precipitation

Precipitation input to the catchment was variable between years (Figure 5.2). In 1995, a total of 603.1 mm was delivered to the catchment, 33.2% (200.4 mm) of which was delivered as snow. In 1996, total precipitation was 1018.1 mm, 29.0% (295.6) of which was snow. 1995 total precipitation was 12.6% below the 1970-1996 mean of 690.6 mm, and 1996 total precipitation was 47.4% higher than the mean, and was the highest recorded annual precipitation over the 26 year record. Total snow accumulation for the winters of 1994-5 and 1995-6 (November to April) was 134 mm and 202 mm (water equivalent), respectively.

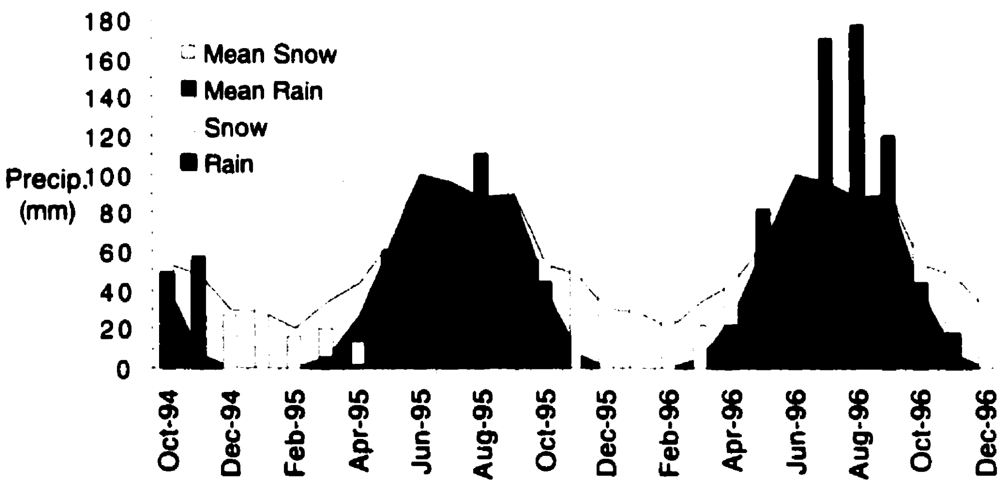


Figure 5.2: Monthly (1994-1996) and mean (1970-1996) precipitation for the Experimental Lakes Area, October, 1994 to December, 1996.

Total rainfall during the study period was 349 mm in 1995 and 496 mm in 1996. Figure 5.3a and 5.3b illustrate the pattern of hourly rainfall for the two study years. The total and event-scale catches of the upper and lower catchment raingauges agreed well; only the upper gauge data are presented here as the record is more complete.

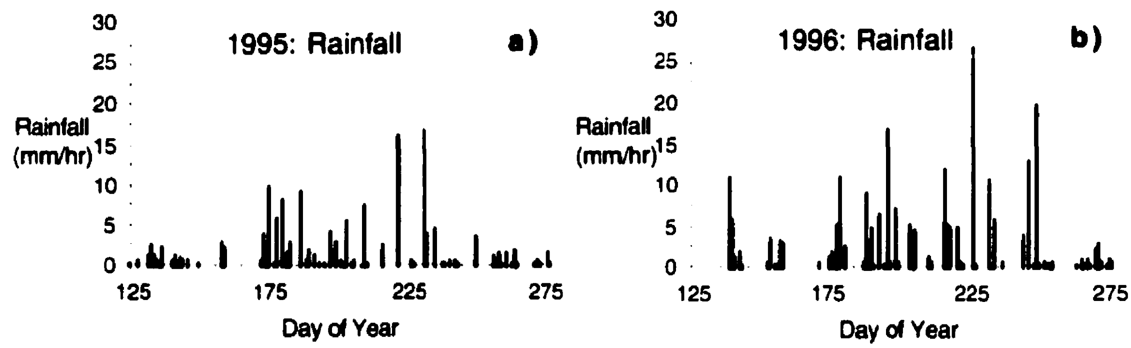


Figure 5.3: Rainfall for the study period in 1995 and 1996.

5.4.2 Upland Soil Moisture and Water Table Development

Although there are large breaks in the record for both 1995 and 1996, measurements of volumetric soil moisture indicate that moisture in the upper hillslope varied as a function of location, soil horizon and year (Figure 5.4a-h). In 1995, volumetric soil moistures generally ranged from 15-30%, with measurements at all three depths within a narrow range of values (Figure 5.4a,c,e,g). The upslope profiles at Sites A and B both showed a greater retention of water in the thick sandy-silt horizon (Figure 5.4a,e) with lower moisture contents at the surface and in the (presumably well drained) basal sand-gravel layer. Downslope (Figure 5.4c,g), the sandy-silt horizon and the basal layer had similar moisture contents within each site. Site A showed no measurable water table development at any time over the measurement period except for one extremely transient response to a storm in late August (Figure 5.4a) At Site B, there was the occurrence of a water table, with transient zones of saturation at one time greater than 20 cm thick developing above the bedrock (Figure 5.4g).

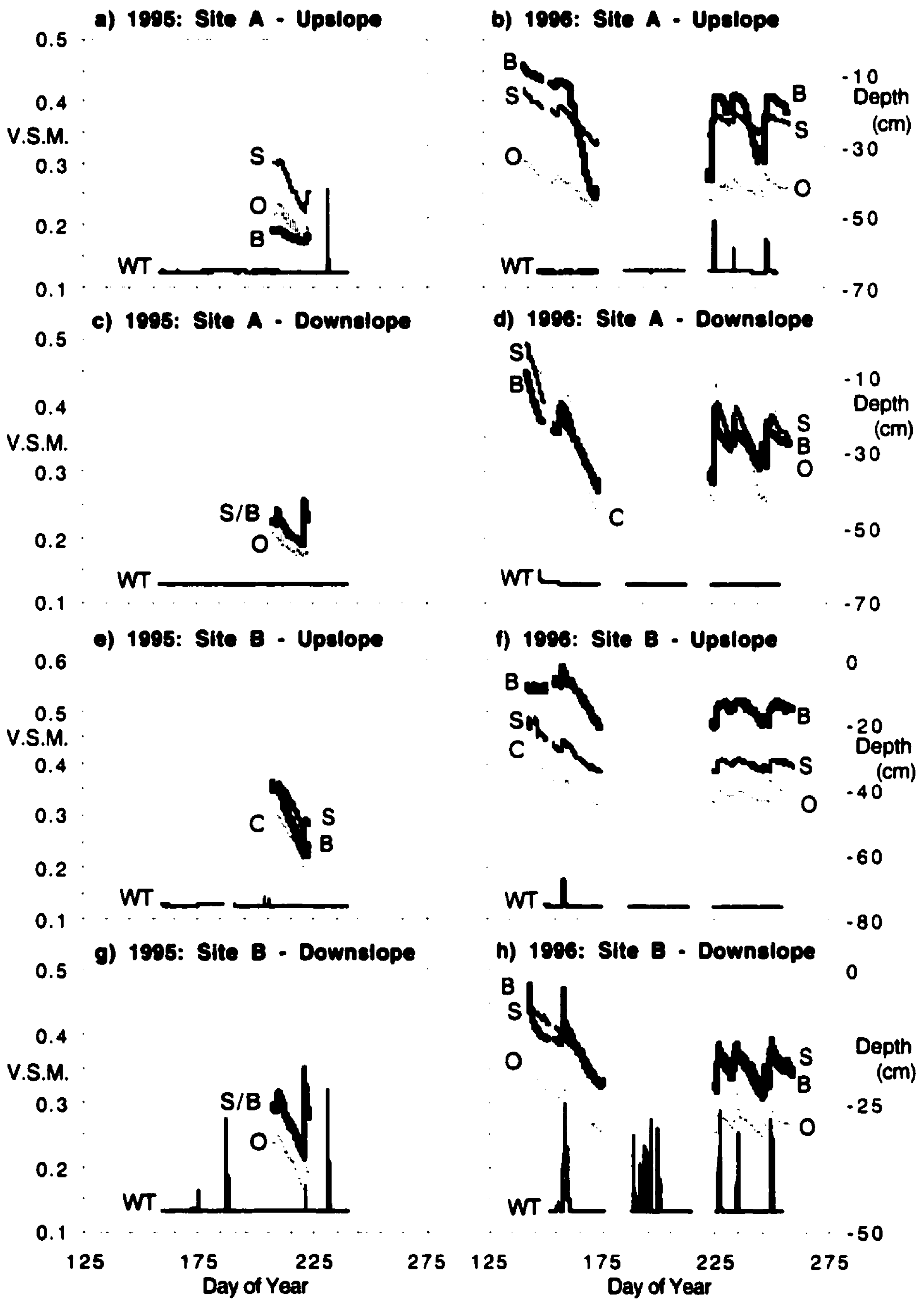


Figure 5.4: Volumetric soil moisture and water table elevation at TDR sites A and B, 1995 and 1996.

In 1996, volumetric soil moistures were higher than in 1995, but Site A soils again appear to be more susceptible to strong drying/draining, especially in the upslope basal layer (Figure 5.4 b). It is also more prone to the development of a transient water table as a result of large late summer storms than the downslope soil profile at Site A (Figure 5.4 b,d). In 1996, Site B upslope remains wetter in the basal layer than Site A, even though it is marginally higher topographically (Figure 5.4f,h). Site B downslope again shows the greatest propensity for water table rise, with transient zones of saturation between 15 and 20 cm thick developing eight times over the 1996 study period.

5.4.3 Lower Hillslope and Peatland Water Table Development

Two wells located downslope of the upland weir site also exhibited strong inter-seasonal variability. Lower hillslope well A showed no water table over the study period in 1995 (Figure 5.5a). Lower hillslope well B exhibited significant episodic changes in water table elevation in 1995, with single events producing greater than 50 cm rise (Figure 5.5c).

In 1996, water tables were recorded at all wells. Lower hillslope well A, developed a saturated zone in excess of 70 cm thick above bedrock (Figure 5.5b). Lower Hillslope well B had a permanent zone of saturation above bedrock in 1996, ranging from less than 5 cm to nearly 50 cm in thickness (Figure 5.5d).

Water table depth for a well in the middle of the peatland is representative of the inter-season variability in peatland water table position (Figure 5.5e,f; see Branfireun and Roulet, 1998). In 1995, the water table was consistently below the peat surface. In contrast, the water table was at or above the peat surface most of the time in 1996. There was in excess of 15 cm of flooding during early spring storms.

Lower hillslope well A reflects the pattern of the upland water table measurements at TDR sites A and B, while lower hillslope well B appears to reflect the expansion of the saturated wedge at the base of the hillslope. The range of water table fluctuation in both of the lower hillslope wells is large relative to the other sites in the catchment.

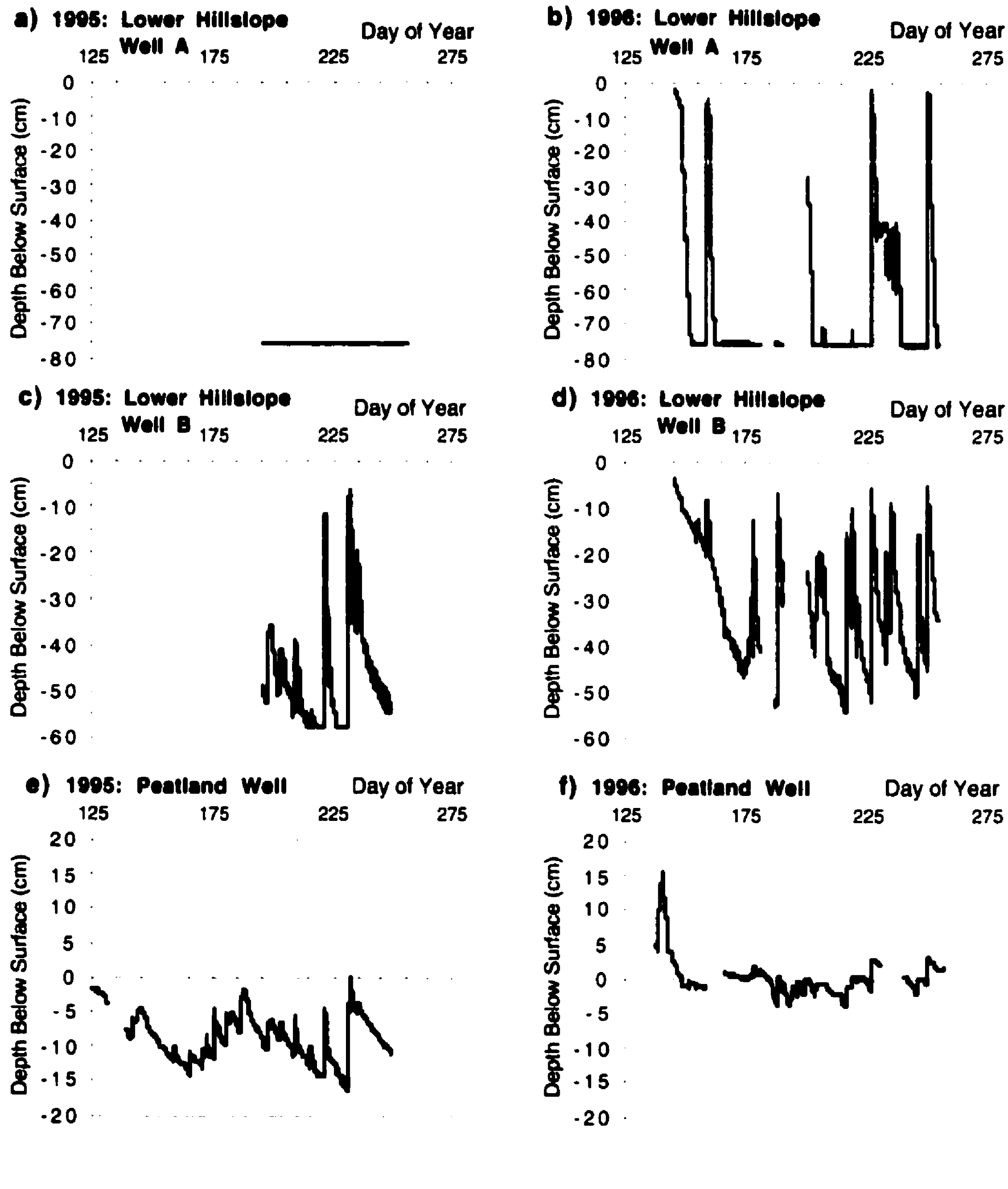


Figure 5.5: Water table elevation measured in two lower hillslope wells as a peatland well over the study period, 1995 and 1996.

5.4.4 Surface Flow

The discharge for the west subcatchment, the inflow stream from the peatland to the lake, and for the catchment outflow were respectively 10.8, 4.8 and 3.6 times greater in 1996 (7531, 50543 and 75384 m^3) than in 1995 (696, 10440, 24304 m^3) (Figure 5.63-f). The proportional contribution to total discharge of the west subcatchment and the inflow stream to total catchment outflow was also greater in 1996 than in 1995: 3 and 43% in 1995 compared to 10 and 67% in 1996.

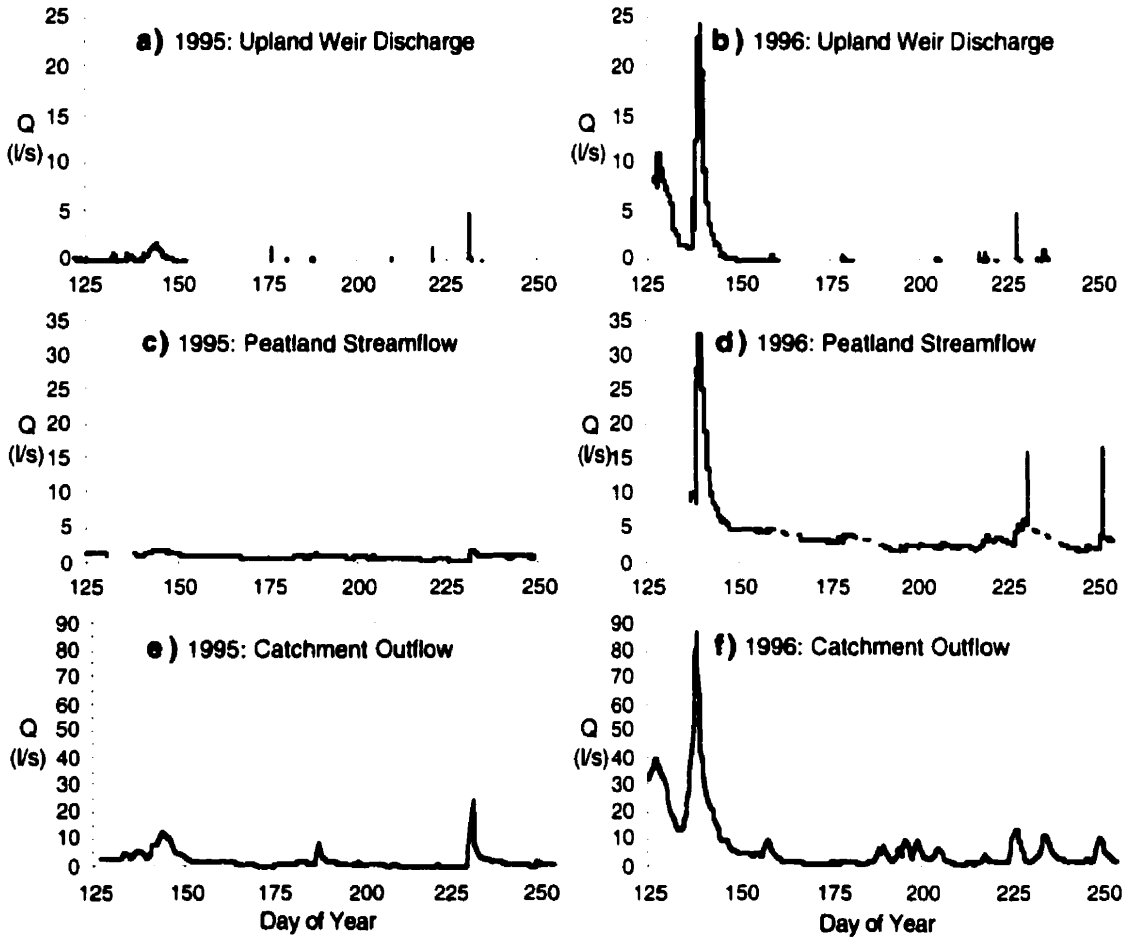


Figure 5.6: Surface flow as measured at the upland weir, the peatland inflow stream and the catchment outflow. All values are instantaneous discharges in L/s, averaged over 15 minutes for the upland weir, 30 minutes for the peatland inflow stream and 24 hours for the catchment outflow.

An analysis of runoff ratios for the various catchment compartments illustrates significant differences in the partitioning of incoming water to runoff between 1995 and 1996 (Table 5.1).

	Area (ha)	Year	Total Rainfall (m^3)	Total Surface Discharge (m^3)	Runoff Ratio (%)
West Upland Subcatchment	15.4	1995	53746	696	1
		1996	76384	7531	10
Inflow Stream Subcatchment*	18.2	1995	63518	10440	16
		1996	90272	50543	56
Whole Catchment	41.6	1995	145184	24304	17
		1996	206336	75384	37

*Includes the west subcatchment plus approximately 40% of the north subcatchment (2.8 ha) which contributes subsurface flow to the inflow portion of the peatland (1.0 ha).

Table 5.1: Total rainfall, total surface discharge and runoff ratios for the catchment and it's compartments from day 130 to 250, 1995-1996.

The west upland subcatchment surface runoff over the study period was only equivalent to 1% of precipitation in 1995, but increased to 10% in 1996, with the majority of it occurring in the late spring post-snowmelt period. Runoff from the peatland inflow stream subcatchment, which includes part of the north subcatchment and the inflow portion of the peatland, was equivalent to 16% of precipitation in 1995, increasing to 56% in 1996. Runoff ratios for the entire catchment were 17% in 1995 and 37% in 1996.

Peatland inflow stream discharge comprises overland flow from the west subcatchment during high flow events, subsurface flow from the upland hillslopes of the west and north subcatchments, and runoff from the peatland area adjacent to the stream. The volume of water delivered via overland flow pathways from the west subcatchment in both 1995 and 1996 was small relative to the peatland inflow stream flow. This, along with the small peatland contributing area indicate that subsurface flow from the upland hillslopes are an important hydrologic process in this catchment.

5.4.5 Groundwater Flow

In addition to the surface water regime, the groundwater regime is significantly affected by changes in the timing and amount of precipitation in a given year. Figure 5.7 depicts hydraulic head measured in late May, 1995 and 1996, along the IF 1-6 transect in the inflow zone of the peatland (Figure 5.1).

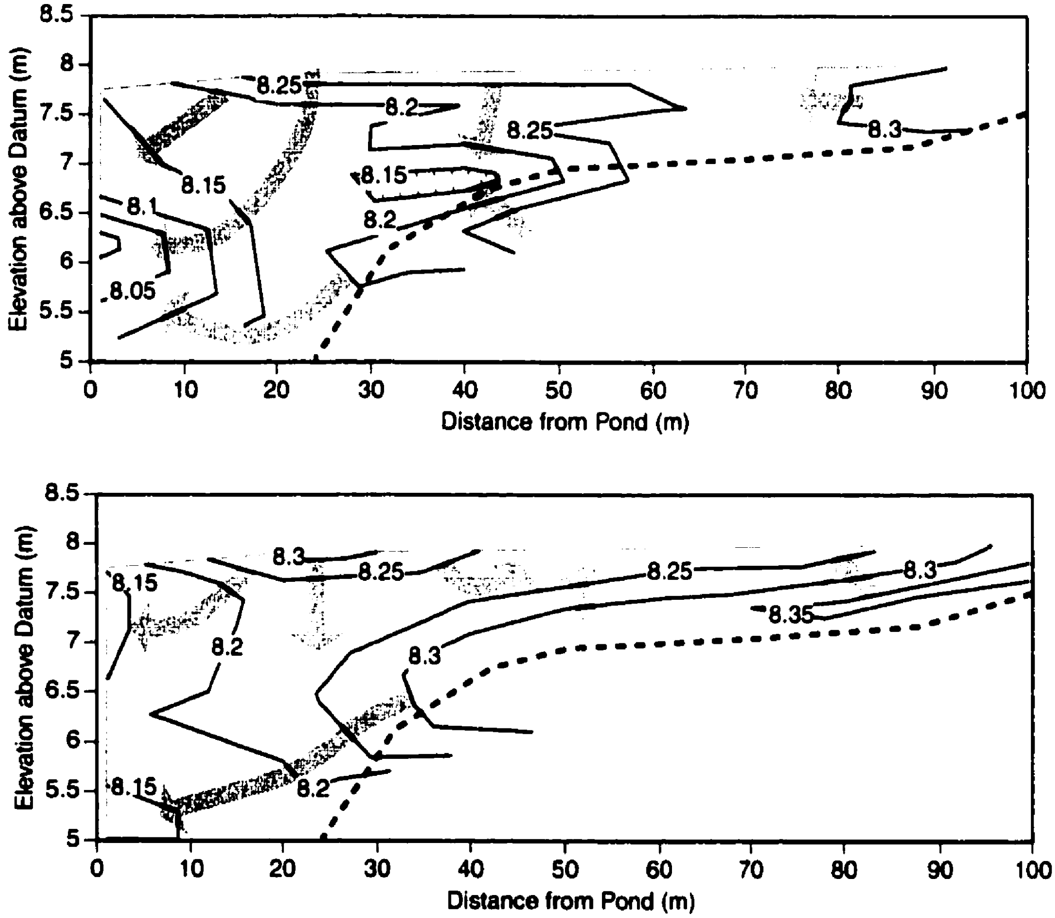


Figure 5.7: Equipotential lines relative to an arbitrary datum and arrows indicating groundwater flow for the IF 1-6 piezometer transect in the 632 peatland, Experimental Lakes Area, (a) May 26, 1995, and (b) May 27, 1996.

The pattern of hydraulic head for 1996 (Figure 5.7b) is similar to that reported previously for this site during normal to wet conditions (see Branfireun and Roulet, 1998) with the general pattern of flow dominated by a zone of high hydraulic potential in the sand unit/deep peat between 40 and 80 m from the pond edge. Water in this zone is presumably supplied by seepage from the adjacent hillslope, and discharges to areas of lower potential at the surface, and at the littoral zone of the pond (Figure 5.7b). During the dry spring of 1995, this typical pattern of flow breaks down completely, likely due to the drying of the hillslope soils which provide the deeper flow system with water. Hydraulic gradients are generally weak to non-existent, with the only distinct flow pattern being a zone of discharge to the deep littoral zone of the pond. A weak zone of lower hydraulic potential between 25 and 45 m from the pond suggests a zone of stagnation, and reversal of the groundwater flow direction in a known zone of groundwater discharge in the peatland, changing it to a zone of recharge.

5.5 DISCUSSION

The annual hydrologic regime of this catchment and it's compartments is strongly influenced by changes in water input via snow and rain. A snowpack 19% smaller than average in the winter of 1994-95, and a very dry April (93% less rain and 33% less snow than average) resulted in the complete absence of the typical spring runoff event which dominates the hydrology of most temperate forested catchments, and which is evident in 1996 (Figures 5.6 a,d,f). Thirty percent lower rainfall during the study period in 1995 than in 1996 resulted in a significantly dampened streamflow response to rainfall, low water tables in the peatland and in the uplands immediately adjacent to the peatland, and effectively no measurable water tables in the true upland soils. The clear control on this 'dry' versus 'wet' year response is the antecedent moisture content of the upland mineral soils.

In 1995, the lack of water table in the wells at the TDR sites (Figure 5.4 a,c,e,g) (except Site B - Downslope) and in Lower hillslope well A (Figure 5.5a) indicates that the dry upland soils had a large unsaturated capacity to retain water inputs. Based on estimates of soil moisture characteristic curves and unsaturated hydraulic conductivity (Cosby *et al.*, 1984; Clapp and Hornberger, 1978; Dingman, 1994) using the particle size analysis for the upland sand-silt soil at soil moistures of 20% to 30% such as those typically found in the upland soils in 1995, very high matric tensions of up to nearly 1000 cm, along with unsaturated hydraulic conductivities of between 1.6×10^{-7} and 3.0×10^{-5} cm s^{-1} would have occurred. It is unlikely that there would be significant movement of water downslope through the sandy-silt soil horizon given these strong retentive forces.

This large storage capacity results in little transfer of water from the upland hillslope to the peatland, as indicated by the lack of water table in the upland hillslopes (Figure 5.4 a,c,e,g; Figure 5.5 a,c), the small amount of overland flow from the west subcatchment (Figure 5.6a) and de-coupling of the inflow groundwater flow system from the west and north upland subcatchments (Figure 5.7a). The decreased input of water to the peatland from the upland soils and rainfall results in a water table drawdown (Figure 5.5e), increased water storage capacity of the peatland soils, decreased surface runoff from the peatland via the inflow stream, and decreased catchment outflow (Figure 5.6g). The significant changes in groundwater flow patterns in the peatland found here as a result of short term drought (e.g. flow reversals) have also been reported for northern peatlands (Siegel *et al.*, 1995; Devito *et al.*, 1997). These combined observations suggest that water table elevations and streamflow were sustained by direct precipitation on the peatland and pond, and subsurface flow contributions from the lower upland hillslopes only.

In contrast, under 'wet' conditions such as those observed in 1996, volumetric moisture contents of between 0.35 and 0.50 would result in matric tensions of between 65 and 10 cm respectively, and unsaturated hydraulic conductivities of between 2.0×10^{-4} and 2.0×10^{-2} cm s^{-1} respectively. These values represent a much lower storage capacity than under 'dry' conditions, and produce conditions conducive to vertical and lateral movement of water through the sandy-silt horizon, and the development of a transient saturated zone at the base of the soil profile (Figure 5.4h). This transient saturated zone, in combination with the much higher hydraulic conductivity of this coarse sand-gravel horizon (estimated to be 1.0×10^{-1} to 10 cm s^{-1}; Freeze and Cherry, 1979) suggest the rapid conductance of water downslope via a saturated "basal flow" process (Renzetti, 1992). Increased inputs of water from the upland hillslope soils via subsurface seepage during baseflow and stormflow maintain the pattern of groundwater flow in the inflow zone of the peatland observed in other years (Branfireun *et al.*, 1996; Branfireun and Roulet, 1998), as well as high water table conditions in the peatland (Figures 5.5f) and higher baseflow discharges (Figure 5.6d,f). During stormflow conditions, basal flow from the uplands, saturation overland flow generated in the peatland, and occasionally saturation/Hortonian overland flow from the west subcatchment produce more peaked, higher magnitude hydrographs more frequently than under 'dry' conditions.

In addition to these runoff mechanisms, the transient and large (50-70 cm) water table fluctuation in both of the lower hillslope wells relative to other sites in the catchment suggest that 'groundwater mounding' may be another possible runoff process (e.g. Abdul and Gillam, 1984, 1989). If there was a thick capillary fringe in the deeper valley bottom soils which becomes saturated with a small input of water, a water table rise at the base of the hillslope could result in a transient shift in the local hydraulic gradients, rapidly discharging hillslope water to the peatland inflow stream seeps. Although no data regarding the height of the capillary fringe or the air-entry tension exist for these soils, the height of capillary rise for the upland sand-silt soil horizon could be as much as 1.5 m, based on measured and estimated particle and pore sizes of the sandy-silt soils.

These calculations coupled with the pattern of water table elevation and the presence of ***Sphagnum*** spp. on the lower hillslopes where the water table is generally well below the ground surface suggest that groundwater mounding through the saturation of a thick capillary fringe is a plausible runoff mechanism under ***wet antecedent conditions***, further adding to the complexity of this catchment's hydrology.

5.6 CONCLUSION

Catchments in the boreal forest are subject to highly variable hydrologic responses at a variety of scales, depending upon precipitation input. One year of lower than average precipitation, marked by a particularly dry spring resulted in the complete modification of the catchment hydrologic system with tangible physical effect. In wetter years, runoff ratios and mechanisms of runoff production are markedly different than in drier years. The high degree of inter-annual variability in hydrologic interaction among the catchment units demands careful consideration in any short-term study of not only catchment hydrology, but also biogeochemical cycling in the boreal landscape.

Preface to Chapter 6

This chapter links the hydrological information presented in Chapter 5 with a spatially and temporally diverse MeHg dataset coupled with other geochemical information to explain: the spatial variability in MeHg pore water concentrations throughout the catchment; hydrological and geochemical controls on MeHg pore water concentrations; controls on catchment MeHg yield; and the relative importance of the various catchment compartments on the flux of MeHg from this small boreal catchment.

Chapter 6: Hydrology and Methylmercury Biogeochemistry in the Low Boreal Forest Zone of the Precambrian Shield

6.1 INTRODUCTION

Methylmercury as a global pollutant continues to demand great attention as a persistent toxin in the food chain, particularly with respect to it's bioaccumulation in fish. Considerable time and effort has gone into the study of the effects of methylmercury (MeHg) on humans and other mammals, *in vitro* studies of methylating bacteria, industrial Hg emissions to the atmosphere, MeHg point-source contamination of lakes and rivers, and the MeHg dynamics of perturbed ecosystems (e.g. hydroelectric reservoirs). Ecosystem-scale investigations are more rare, and the vast majority of these have tended to focus on lakes. Relative to the large body of MeHg literature on these topics, studies focussing on whole system MeHg dynamics in 'pristine' (i.e. non-point source impacted) boreal/temperate catchments are few (notable exceptions include Krabbenhoft *et al.*, 1995; Heyes, 1996; St. Louis *et al.*, 1996; Driscoll *et al.*, 1998). The lack of studies at the catchment-scale in systems which are relatively 'pristine' leaves us with little for comparison to catchments directly impacted by Hg pollution.

The catchment studies which do exist have tended to be "black box" investigations of MeHg budgets for different types of catchments. This work has provided significant insight into the role of the catchment in MeHg cycling, particularly with respect to the role of wetlands. For example, St. Louis *et al.* (1994) first demonstrated a clear relationship between the presence of wetlands and increased methylmercury yield from boreal catchments. Hurley *et al.* (1995) also found a positive relationship utilizing GIS techniques between percent wetland coverage and methylmercury yield. Although these studies indicate that wetlands are sites of Hg methylation resulting in elevated catchment yields, they do not provide information about the distribution of MeHg within the catchment, or the mechanisms by which the MeHg is moved among the various landscape units.

The objective of this paper is to link the results of a hydrologic investigation in the low boreal forest zone of the Precambrian Shield with a MeHg dataset to couple hydrology, MeHg pools and fluxes and other water chemistry at the catchment-scale. This information will be used to explain the spatial and temporal variability in catchment MeHg concentrations and fluxes, and determine the role of the different landscape types in catchment MeHg dynamics.

6.2 SITE DESCRIPTION

This study was conducted between spring 1995 and autumn 1996 in a small (41.6 ha) Precambrian Shield headwater catchment (Basin 632) located in the Experimental Lakes Area (ELA) (49°40' N, 93°43' W) near Kenora, Ontario, Canada. The catchment contains a peatland (4.7 ha) and a small lake (1 ha) (Figure 6.1). Major sampling sites are shown on Figure 6.1 and include four sites routinely sampled for surface water MeHg (upland weir, inflow stream, pond, catchment outflow), and others where pore water chemistry was sampled (upland wetland, poor fen and raised bog). The poor fen is fed by precipitation and is a zone of groundwater discharge originating from the adjacent uplands, while the raised bog is a zone of groundwater recharge supplied solely by precipitation (Branfireun and Roulet, 1998).

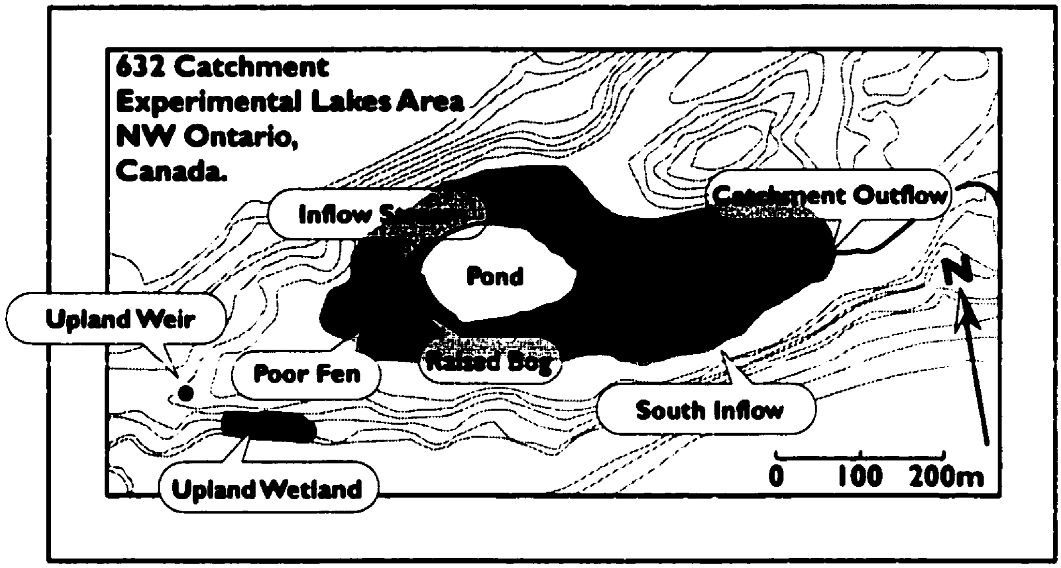


Figure 6.1: Map of sampling areas in the 632 Catchment, northwestern Ontario.

6.2 METHODS

6.2.1 Hydrology

Water table elevation in the upland hillslopes and the peatland was monitored continuously downslope via a series of 10 cm ID wells with measurements stored in dataloggers. Episodic overland flow generated in the upland was gauged at a 90° V-notch weir ("Upland Weir") installed in a small wooden retaining structure built on the exposed bedrock pavement. Height of water in the V-notch was measured continuously in the small pond of water held behind the retaining structure in the same manner as described for the water table wells. Discharge was calculated using a standard equation for relating the elevation of the water surface behind the weir (Z_w) to discharge (Dingman, 1994; eq. F-15). Surface streamflow on the peatland was measured in two flumes. Stage was related to discharge using the velocity-area method. Catchment outflow was gauged at a 90° V-notch weir monitored by ELA staff.

Patterns of groundwater flow in the peatland were measured in piezometers installed in two perpendicular transects in the inflow zone of the peatland. This installation was in place from a previous study and details of this network can be found in Branfireun and Roulet (1998). Delineation of catchment and subcatchment areas was accomplished through the estimation of within-catchment surface divides using 1:16000 maps generated from aerial photographs, and the digitizing of areas.

6.2.2 Geochemistry

Both soil and pore water samples were taken for MeHg analysis in 1995 and 1996 in an attempt to characterize the spatial distribution and temporal variability of MeHg concentrations within this small catchment. Pore water and surface water samples were taken from the peatland on several occasions from a variety of locations as the peatland has been identified as a locus of MeHg production in this catchment and was an area of specific interest (Branfireun *et al.*, 1996; Branfireun *et al.*, 1998). Upland soil water was more difficult to obtain due to the extremely episodic development of upland water table (see Chapter 5) and samples were temporally limited to late summer 1996. Upland soil samples for solid phase MeHg analysis were taken from the surficial organic and sand-silt horizons of the dominant upland humo-ferric podsols, and from the thin peat layer of the small upland wetland. Surface waters were sampled at the upland weir, in the peatland inflow stream, in the central pond and at the catchment outflow.

Ultra-clean protocol was used at all times for MeHg sampling. All sampling equipment was hot HNO_3-washed Teflon®, vinyl gloves were worn at all times and care was taken to not allow the sampling bottle to come in contact with anything but the sample. MeHg samples were handled and processed in different ways, depending upon location. Surface water samples were taken by completely submerging the bottle and rinsing three times before the sample was taken. Pore water samples were drawn either from PVC piezometers or a teflon or teflon/stainless steel 'sipper' attached to a Teflon sampling tube, Teflon transfer container and a peristaltic pump (see Branfireun *et al.*, 1996; Heyes, 1996 for details). Sample bottles were protected by double polyethylene bags, and were stored in a dark cooler in the field until they could be returned to the laboratory for processing (not more than 2 hours). Surface water samples were not filtered though samples with visible particles were rejected, assuming that the dissolved and small particulate phase comprised the total flux. Pore water samples were passed through a sterile 0.45 micron nitrocellulose-acetate filter immediately upon return to the lab. All samples were frozen until analyses could be performed. MeHg analysis was performed using a cold vapour atomic fluorescence technique modified from Bloom and Fitzgerald (1988) and Horvat *et al.* (1993) (see Branfireun *et al.*, 1996). All water samples were analyzed in duplicate, and solids in triplicate for MeHg. Sulfate was measured using suppressed ion chromatography at Department of Fisheries and Oceans-Freshwater Institute Laboratories, Winnipeg, and DOC was measured using Shimadzu TOC-5050 analyzer. Sediment samples being analyzed for MeHg were subjected to an overnight acid digestion prior to distillation (Heyes, 1996).

6.3 RESULTS

6.3.1 Spatial Distribution and Temporal Variability of Methylmercury Concentrations in the Catchment

6.3.1.1 Uplands

Concentrations of MeHg in upland soil and pore water samples varied widely and appeared to relate to organic content and site wetness (Table 6.1). These data are spatially and temporally limited to triplicate samples taken in late summer, 1996, and do not necessarily reflect the potential spatial and temporal variability MeHg concentrations throughout the entire upland terrain.

Location	Water MeHg (ng/l)	Sediment MeHg (ng/g d.w.)
[illegible]	[illegible]	0.23 (S.D. 0.02)
Upper Hillslope (Mineral)	-	0.04 (S.D. 0.01)
Upland Wetland	0.28 (S.D. 0.09)	6.99 (S.D. 3.01)
Lower Hillslope	0.11 (S.D. 0.05)	-

Table 6.1: MeHg concentrations in upland soils and porewaters (n=3 for each sample).

In the upper hillslope, water table development was so ephemeral, that no free water samples were extractable from wells installed to bedrock. Tension lysimeters were not used for MeHg sampling due to potential contamination problems and concerns about representativeness of pore water samples extracted under negative pressure. Pore water MeHg concentrations in the small 'upland wetland' organic sediments averaged 0.28 ng/l, within the range of concentrations found in other wetlands (e.g. Krabbenhoft *et al.*, 1995; Branfireun *et al.*, 1996; Heyes 1996), but MeHg concentrations in the upland wetland were lower than surface and near-surface MeHg concentrations in the main peatland at this site (see Branfireun *et al.*, 1996; this Chapter). In the lower hillslope which tended to be wetter with some surficial *Sphagnum* growth on top of approximately 1 m of mineral soils, water samples extracted from piezometers in the mineral soil had a mean concentration of 0.11 ng/l.

MeHg concentrations of upland sediments varied over two orders of magnitude, with the highest found in the upland wetland peat (mean 6.99 ng/g dry weight). The dry upland humo-ferric podsols showed a clear discontinuity in MeHg concentration between the predominantly organic surficial horizon (mean 0.23 ng/g d.w.) and the lower sand-silt horizon (mean 0.04 ng/g d.w. or 17% that of the organic horizon).

6.3.1.1 Peatland

All profile data presented in this section express the depth relative to the water table at the specific sample site. MeHg concentration profiles from fen and bog hollows emphasize the spatial variability in MeHg concentrations, both across the landscape and down the peat profile (Figure 6.1, Figure 6.2). Regardless of time, the concentration profiles in the poor fen exhibited a characteristic maximum concentration at or near the water table and decreasing sharply with depth, as found in previous work (Branfireun *et al.*, 1996; Heyes, 1996) (Figure 6.1). In the poor fen, concentrations ranged from a maximum of 3.02 ng/l at the water table (July 18, 1996) to a minimum of 0.22 ng/l at -100 cm (May 28, 1996). These near-surface values are not as high as those reported for the same location in previous years of study (up to 7 ng/l - Branfireun *et al.*, 1996; Heyes, 1996) suggesting that there is substantial inter-annual variability. The location of the peak concentration in the profile is somewhat of an artifact of the sampling resolution at the different times, but in 1995, the maximum MeHg concentration in the profile is below the water table, whereas in 1996, it tended to be at the water table.

Methylmercury concentrations in the raised bog profile show similar patterns to those in the poor fen, but the maximum concentrations are lower (Figure 6.2).

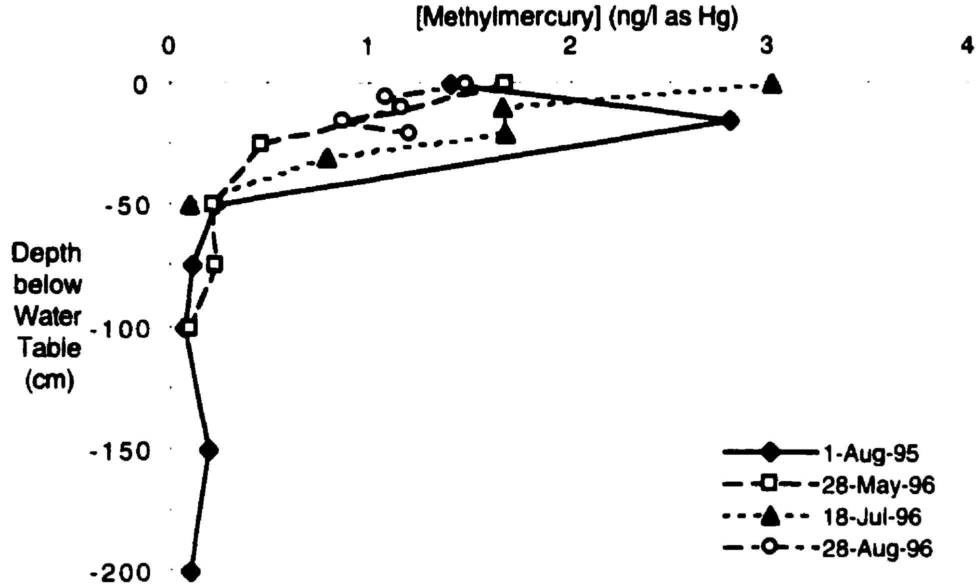


Figure 6.1: MeHg concentration profiles in a poor fen hollow, 1995-1996.

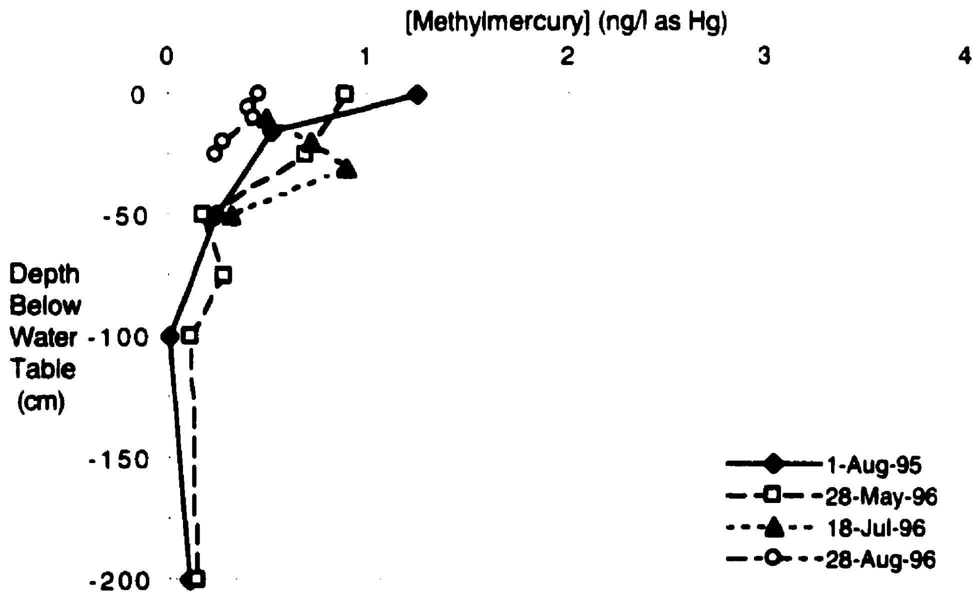


Figure 6.2: MeHg concentration profiles in a bog hollow, 1995-1996.

The lowest concentration (1995, -100 cm) was below the limit of detection (<0.01 ng/l as Hg). As in the poor fen, the depth of the highest concentration varied over time, with maxima at the water table on August 1, 1995 and on May 28, 1996, and at 30 cm below the water table on July 18, 1996.

For a number of profiles in the peatland inflow area, other water quality parameters were measured concurrently with MeHg concentrations. On August 1, 1995, sulfate in pore water was measured along with MeHg in an attempt to discern geochemical differences between MeHg 'hot spots' in the poor fen and lower MeHg sites in the raised bog found in a previous study (Branfireun *et al.*, 1996). Sulfate is a biogeochemically significant chemical in the MeHg cycle as it fuels the methylation of Hg(II) by sulfate reducing bacteria (e.g. Chapter 3; Gilmour and Henry, 1991).

Profiles taken in three piezometer nests throughout the inflow area on August 1, 1995 show considerable variability in sulfate concentrations with depth (Figure 6.3a and 6.3b). The poor fen area has water delivered by precipitation and groundwater upwelling; the raised bog by precipitation only (see Branfireun *et al.*, 1996; Branfireun and Roulet, 1998).

Concentration profiles for MeHg in the poor fen show the MeHg maxima of between 2.42 and 2.81 ng/l at -25 cm below the water table with concentrations decreasing with depth (Figure 6.3a). Concentration profiles for sulfate show a slight elevation at the water table (0.32 to 0.58 mg/l), minima of between 0.15 and 0.22 mg/l between -25 and -75 cm, and then a significant increase in concentrations to between 3.29 and 3.63 mg/l between -100 and -200 cm. The highest concentrations of sulfate occur at the interface between the underlying sand unit and the peat strata where groundwater is moving vertically upwards into the peat (Branfireun et al, 1996; Branfireun and Roulet, 1998; Chapter 5).

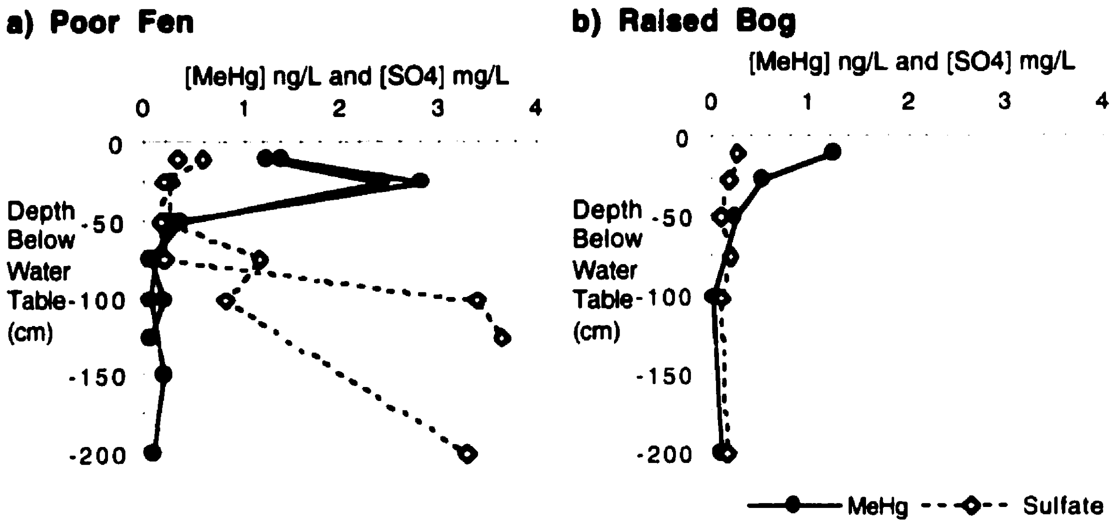


Figure 6.3: Concentrations of methylmercury and sulfate in three piezometer nests, 632 peatland, August 1, 1995.

Concentrations of MeHg in the raised bog profile are maximum (1.24 ng/l) at the water table, but lower than those observed in the poor fen, and concentrations drop off rapidly with depth. Sulfate concentrations are extremely low throughout the profile, decreasing with depth from a maximum of 0.25 mg/l at the water table to a minimum of 0.08 mg/l at -100 cm (Figure 6.3b).

The concentrations of MeHg among sites in the poor fen were highly variable. A survey of dissolved MeHg concentrations in peatland microtopographical features in the poor fen zone of the 632 peatland serves to illustrate this finding (Figure 6.4). MeHg concentrations at the water table ranged from below 1 ng/l in 'black' hollows and beneath hummocks, to over 3.5 ng/l in water pooled in the bottoms of poor fen hollows. This range in MeHg concentrations is evident between sampling sites only a few meters apart and even between similar microtopographical features. For example, 'black' hollows had significantly lower surficial MeHg concentrations than 'typical' hollows. The so called 'black' hollows were different from 'typical' hollows in that they were characterized by steeper sides, *Sphagnum* spp. on their sides which were black in colour (possibly stained by the precipitation of FeS species; Heyes, 1996) and had a slimy algal/bacterial mat at the bottom. These 'black' hollows appeared only in the poor fen zone and appeared to be distributed randomly with an occurrence of approximately 1 in 10 relative to normal hollows. MeHg concentrations of the 'black' *Sphagnum* were found to be higher than those of *Sphagnums* in similar locations elsewhere (Heyes, 1996). At -25 cm, the range in concentrations is much smaller (between 0.36 and 1.28 ng/l) with no clear trend between microtopographic features.

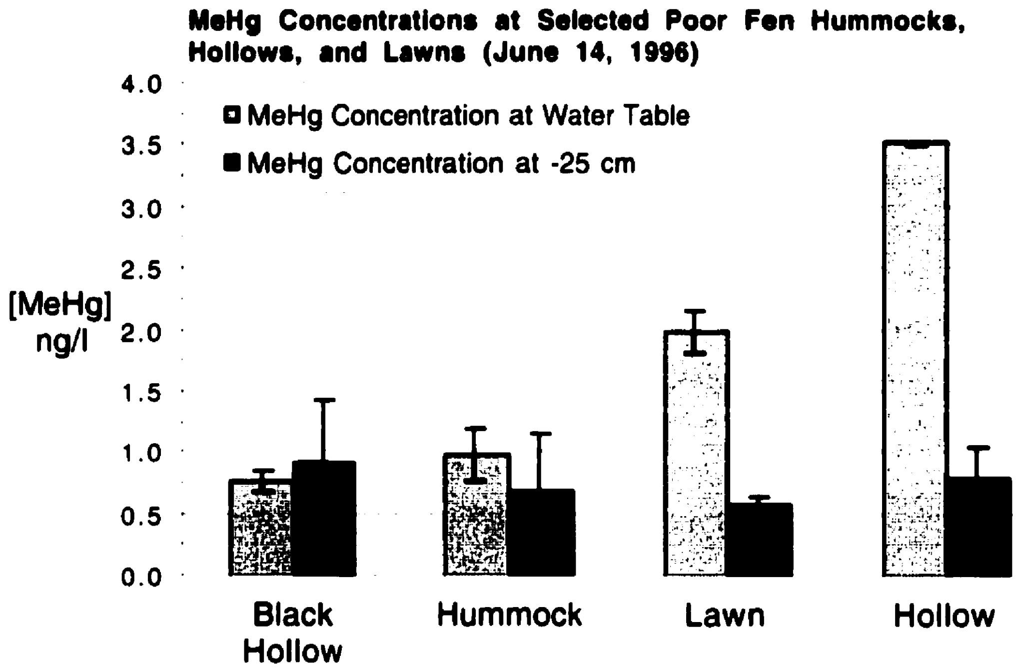


Figure 6.4: Methylmercury concentrations at various locations at, and 25 cm below the water table in the 632 poor fen zone, June 14, 1996 (n=2 for each sample site and depth, analyzed in duplicate).

Figure 6.5a-c display higher resolution profiles from 0 to -50 cm for the two types of hollows ('typical' and 'black') found in the poor fen, and a raised bog hollow on July 18, 1996. These profiles illustrate the considerable variability in MeHg and other chemistry between adjacent peatland microtopography, and between similar features in the poor fen and the raised bog.

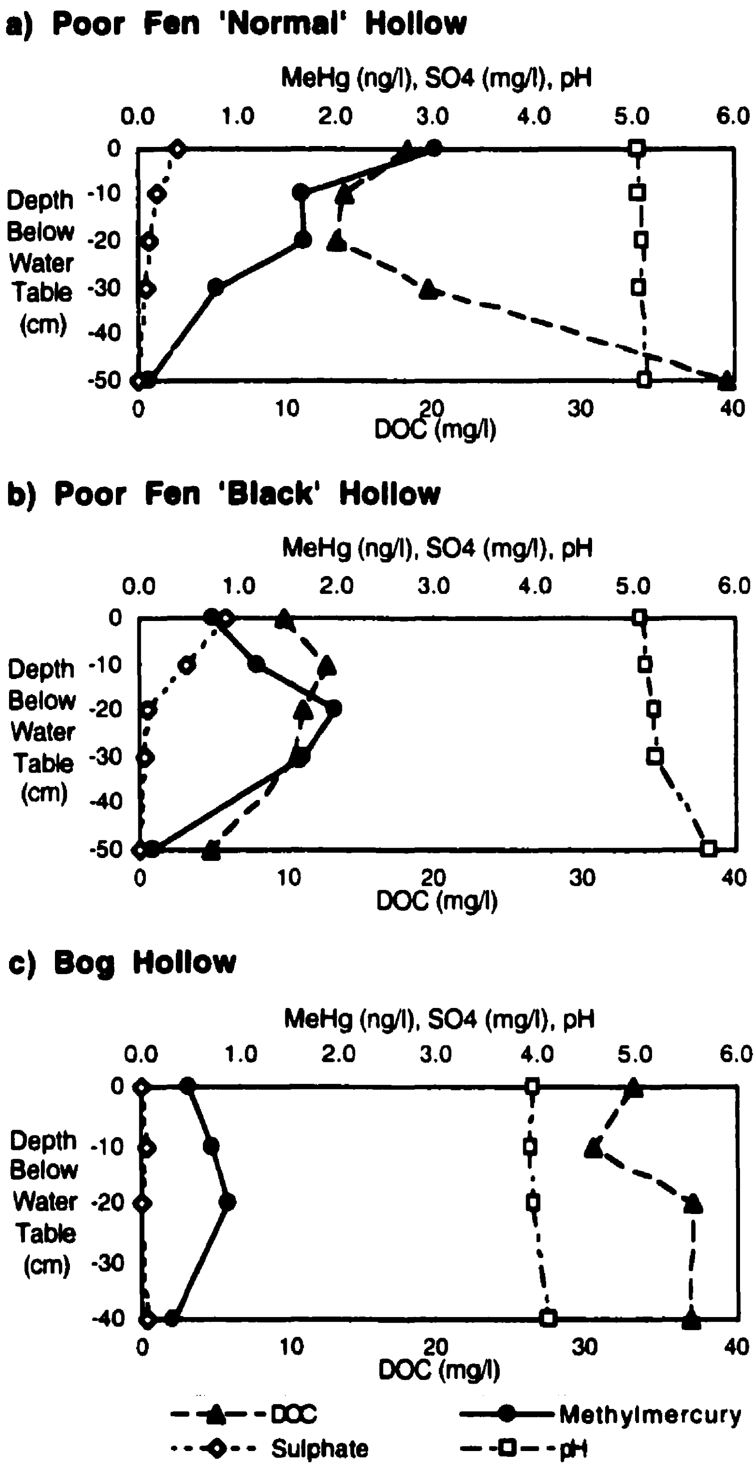


Figure 6.5: Profiles of methylmercury, sulfate, dissolved organic carbon (DOC) and pH from a typical poor fen hollow, a poor fen 'black' hollow and a raised bog hollow, July 18, 1996.

In the 'typical' poor fen hollow (Figure 6.5a), the maximum MeHg concentration is found at the water table (3.02 ng/l), is 1.67 ng/l between -10 cm and -20 cm, and then decreases sharply to a minimum of 0.09 ng/l at -50 cm. Sulfate concentrations in this profile show a steady decrease with depth, from a maximum at the water table of 0.41 mg/l to <0.01 mg/l (detection limit) at -50 cm. DOC concentrations at the water table are 18.1 mg/l, decrease to between 13.7 and 13.3 mg/l between -10 and -20 cm, and then increased sharply with depth to a maximum of 39.5 mg/l. pH was nearly constant with depth, increasing only slightly from 5.03 at the water table to 5.12 at -50 cm.

In an adjacent 'black' fen hollow, profiles are quite different from those in the 'typical' fen hollow (Figure 6.5b). MeHg concentrations are relatively lower at the water table (0.76 ng/l), increase to a maximum of 1.97 ng/l at -20 cm and then decrease with depth to a minimum of 0.12 ng/l at -50 cm. The sulfate concentration profile is similar to that of the 'typical' fen hollow, but exhibits higher concentrations at the surface (up to 0.88 mg/l). DOC concentrations are low relative to the 'typical' fen hollow and follow a similar pattern to that of MeHg; 9.61 mg/l at the surface, a maximum of 12.6 mg/l at -10 cm, then decreasing with depth to a minimum of 4.79 mg/l at -50 cm. The pH profile shows an increase with depth, from 5.08 at the surface to 5.74 at -50 cm, with the greatest increase between -30 cm (pH = 5.23) and -50 cm (pH = 5.74).

In the raised bog, MeHg concentrations were below 1 ng/l throughout the profile, with the maximum of 0.89 ng/l at -30 cm (Figure 6.5c). Sulfate was extremely low, being at or about the detection limit (0.01 mg/l) at all depths with a maximum of only 0.05 mg/l at -20 and -50 cm. DOC concentrations decreased from -10 cm (33.2 mg/l) to -20 cm (30.5 mg/l), and then increased to 37.0 mg/l at -40 cm and 36.9 mg/l at -50 cm. pH was lower than that found at the poor fen sites, averaging 4.0 with a very slight increase with depth.

The relationship between MeHg and sulfate concentrations is of interest, given the role of sulfate-reducing bacteria in the methylation of Hg, and the efficacy of these bacteria in methylating Hg under varying sulfate concentrations (e.g. Gilmour *et al.*, 1998). For the surface and groundwaters in this catchment, there is a negative non-linear relationship (r^2 = 0.76) between MeHg and sulfate concentrations in surface water throughout the catchment and over the study period (Figure 6.6). This relationship breaks down when samples from the raised bog are included, where both sulfate and MeHg concentrations are low, resulting in an insignificant (r^2 = 0.02) best fit for all data.

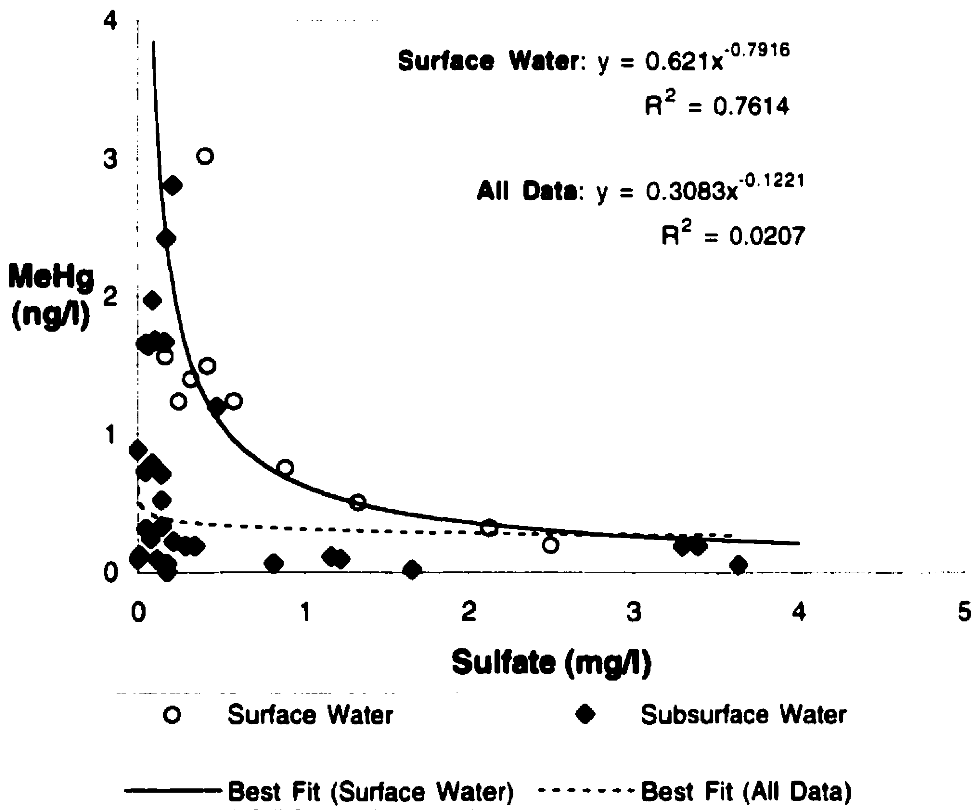


Figure 6.6: Sulfate versus methylmercury concentration in surface and groundwaters in the 632 catchment.

Confounding these findings are relationships amongst other variables such as DOC concentrations and temperature. No temperature data exist for examination, but relations among MeHg, sulfate and DOC concentrations suggest that the highest MeHg concentrations are found at sites with sulfate concentrations greater than 0 but less than 0.5 mg/l, and DOC concentrations between 10 and 20 mg/l (Figure 6.7).

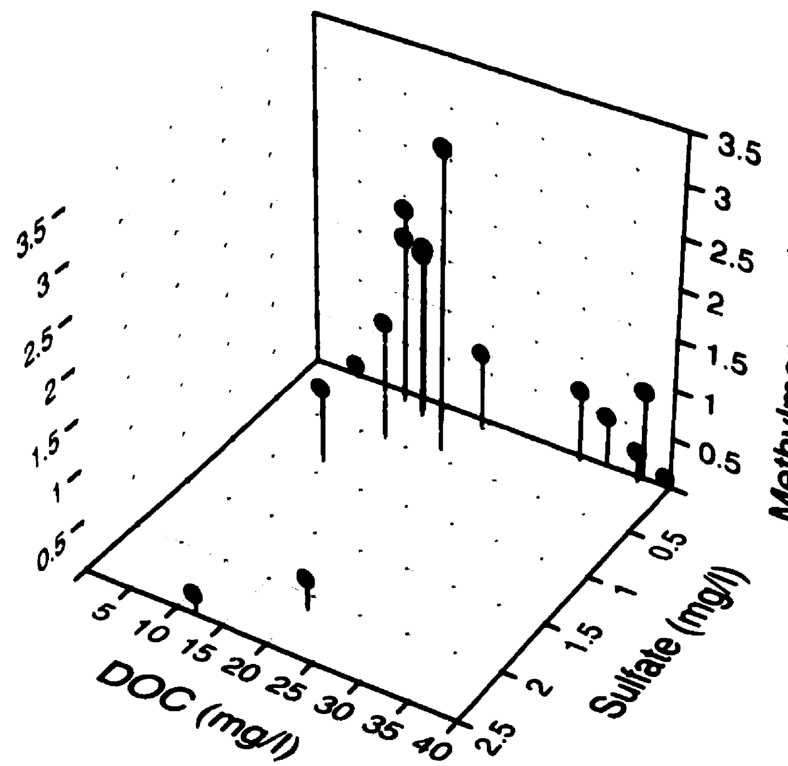


Figure 6.7: DOC and sulfate versus methylmercury concentrations in surface and groundwaters in the 632 catchment.

6.3.3 Methylmercury Concentrations in Surface Waters

Samples taken from surface waters throughout the catchment over the two study years show marked within and between year variability in MeHg concentrations, particularly in the inflow and outflow streams (Figure 6.8a and 6.8b).

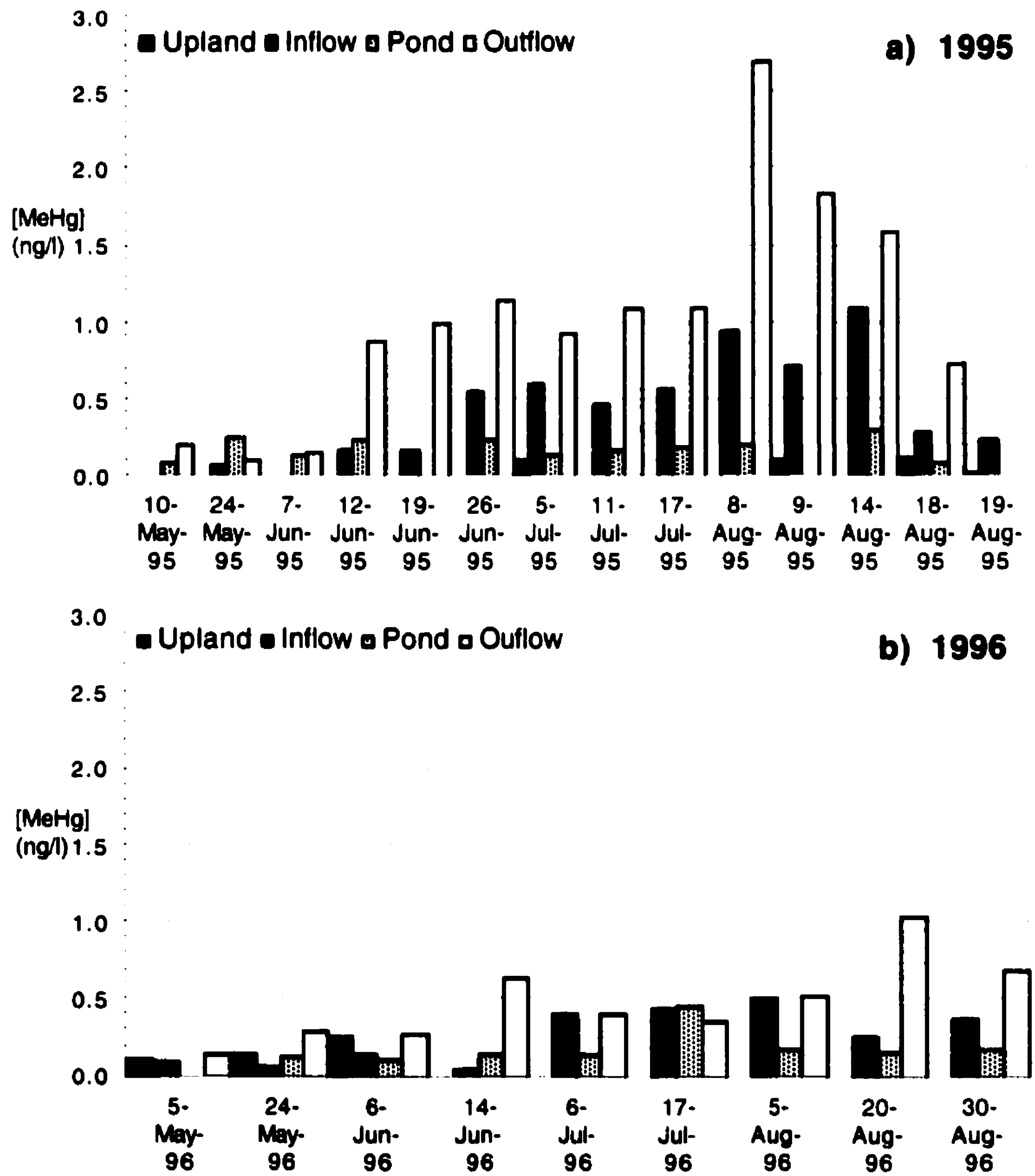


Figure 6.8: Methylmercury concentrations in surface waters at the upland weir, peatland inflow stream, pond and catchment outflow in 1995 and 1996.

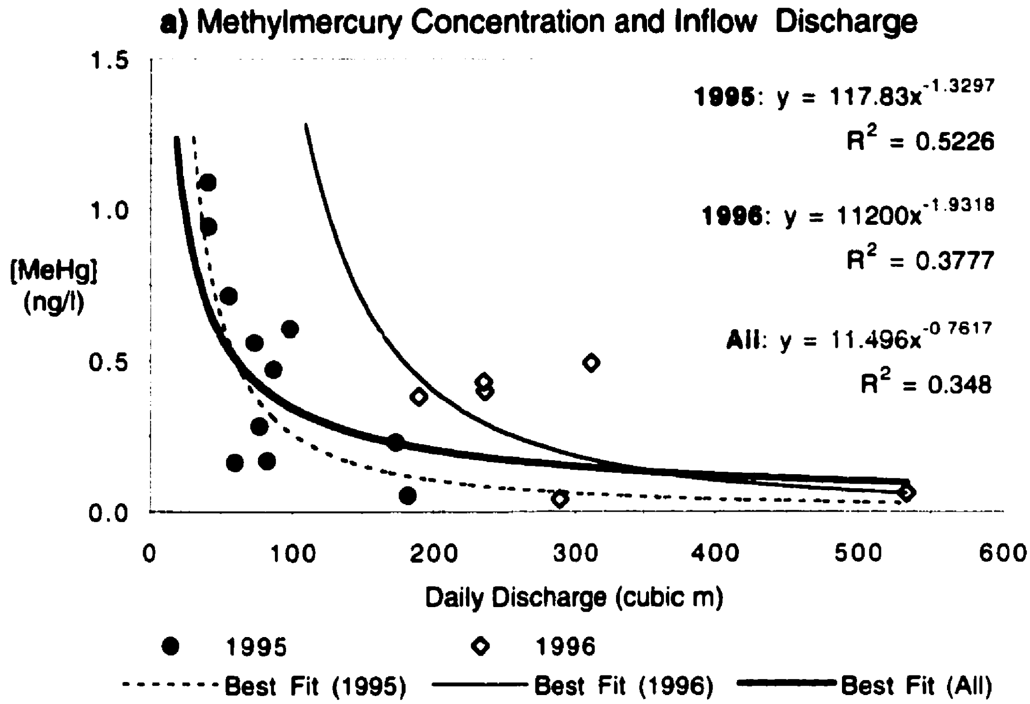
The upland weir records overland flow generated in the west subcatchment (15.4 ha). The inflow stream flume box dominantly gauges overland flow and seep contributions to the inflow portion of the peatland from the west subcatchment and the outflow weir gauges surface and groundwater contributions from the entire catchment (41.6 ha). In 1995 (a drier, low flow year), flow from the upland weir was extremely episodic (see Chapter 5), and MeHg concentrations were always less than 0.12 ng/l (Figure 6.8a). This is in contrast with previously reported data (Branfireun *et al.*, 1996) which found concentrations in excess of 0.3 ng/l to occur in some years. When no values for the upland weir are reported in Figure 6.6, it means that there was no flow over the weir at that sampling time. The peatland inflow stream had MeHg concentrations of less than 0.2 ng/l until June 26, 1995 when concentrations began to increase, reaching a maximum of 1.09 ng/l by August 14, 1995. A similar pattern is seen in the catchment outflow data where after June 9, 1995, MeHg concentration begin increasing markedly until August 8, 1995, when it reached a maximum of 2.70 ng/l, the highest concentration recorded at this site. Pond concentrations varied little in comparison to the concentrations in the inflow and outflow streams, ranging between 0.09 and 0.30 ng/l.

In 1996 (a wet, high flow year), surface water MeHg concentration trends were quite different from those seen in 1995 (Figure 6.8b). A more sustained late spring runoff resulted in a longer period of discharge from the upland weir which was accompanied by higher MeHg concentrations than those seen in 1995 (up to 0.26 ng/l). MeHg concentrations in the inflow stream were lower than in 1995, never exceeding 0.49 ng/l. MeHg concentrations at the catchment outflow saw a small increase in concentration until mid-June as was seen in 1995, but maximum MeHg concentrations near the end of the summer (August 20, 1996 [1.04 ng/l]) never approached those values measured in 1995. Pond MeHg concentrations in 1995 were similar to those in 1995, although a mid-season increase to 0.45 ng/l (July 17, 1996) above the mean of the rest of the season of 0.15 ng/l is noted.

In 1995, the concentration of MeHg was measured in runoff from the south subcatchment at the point where it enters the peatland (south inflow). This water was not in contact with any wetland soils before reaching the peatland, and it was deemed important to determine the MeHg concentrations of this input. Water flowed over exposed bedrock and through a steep forested hillslope soil before reaching the margin of the peatland as overland flow and then infiltrating, entering the peatland subsurface flow system. MeHg concentrations in these waters were below the level of detection of the instrument (0.01 ng/l) on all occasions in 1995.

MeHg shows a negative non-linear relationship with instantaneous discharge for both the inflow (Figure 6.9a) and outflow (Figure 6.9b) streams in both 1995 and 1996. For the inflow stream, the form of this relationship is quite different between 1995 and 1996, reflecting the very different hydrologic regime between those years. The goodness of fit (particularly the 1996 relationship) may be compromised by the small sample size (N=11, 1995; N=6, 1996), and both years suffer from a lack of data at the extremes of their distributions (high discharges in 1995 and low discharges in 1996). The result is a best fit for all of the inflow data with less explanatory power (r^2=0.35), given the inter-year variability.

The catchment outflow stream relationship explains over 50% and 72% of the variation in 1995 and 1996 respectively, even though the hydrologic years were considerably different (Figure 6.9b). The mean best fit for all data maintains an r^2 of nearly 50% and a form close to those of the individual years, suggesting that more data could produce a relationship with significant predictive power for the catchment outflow.



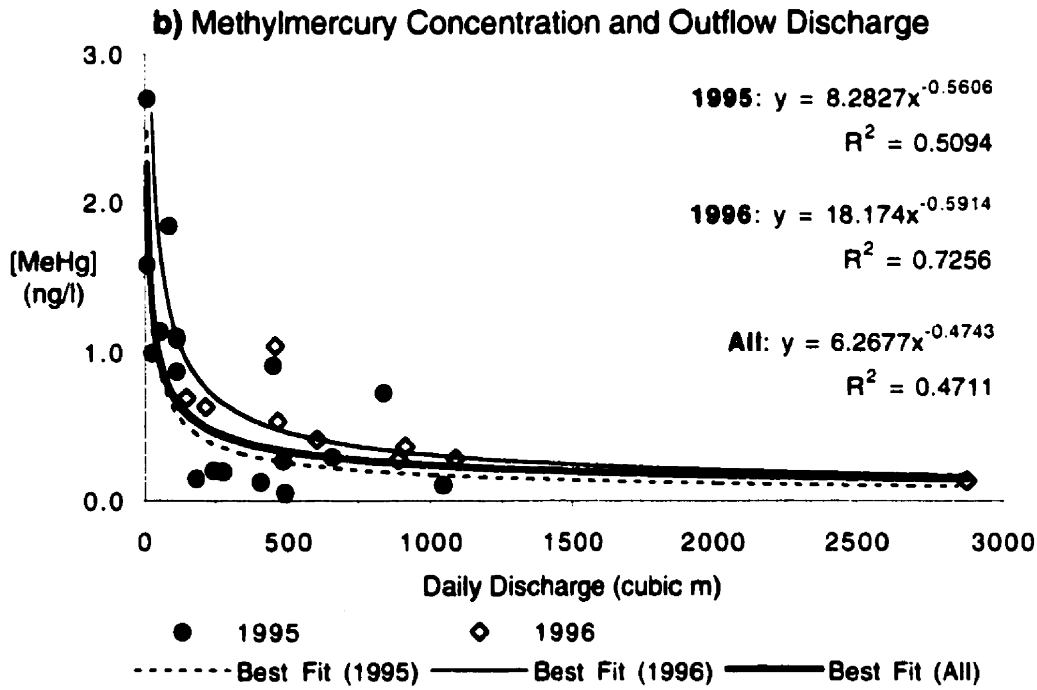


Figure 6.9: Relationships between daily discharge and methylmercury concentrations for the peatland inflow stream and catchment outflow, 1995-1996.

6.3.4 Catchment-scale Methylmercury Fluxes

Flux values were determined using the equations presented in Figure 6.9 to calculate predicted MeHg concentration from daily discharge. Although the length of record varies for the two streams and between years, the values presented are expressed for the 120 day late spring-summer period between day 130 and day 250, the length of the shortest record (1995 inflow stream). Cumulative daily MeHg flux for the inflow stream (Figure 6.10) and catchment outflow (Figure 6.11) for the 1995 and 1996 seasons show marked between year variation. For the inflow stream, 1995 total discharge over the study period (Day 130 - 250) was 10440 m^3, which transported 3.35 mg of MeHg (Figure 6.10a). Since streamflow was extremely low but constant over this season, no marked changes in the cumulative MeHg flux are apparent. In 1996, total discharge was nearly five-fold greater than in 1995 (50543 m^3) with a total mass flux of MeHg slightly greater than 2 times that of 1995 (6.77 mg) (Figure 6.10b). Notable trends include the rapid cumulative increase in discharge during the late spring runoff period of 1996, accompanied by a more gradual increase in MeHg owing to a dilution effect.

For the catchment outflow, total discharge over the study period in 1995 was also low (24304 m^3), with a total MeHg mass flux of 8.65 mg (Figure 6.10a). Small incremental increases in cumulative discharge starting at Day 143 and Day 230 were accompanied by corresponding increases in the cumulative MeHg flux. Similar increases in cumulative MeHg flux with increasing cumulative discharge are apparent in 1996 (Figure 6.10b) and is particularly notable during the late spring runoff period. Total discharge and MeHg flux for the catchment outflow in 1996 were 75384 m^3 and 25.9 mg respectively. No strong MeHg dilution is apparent for the catchment outflow in 1996 as it is for the inflow stream.

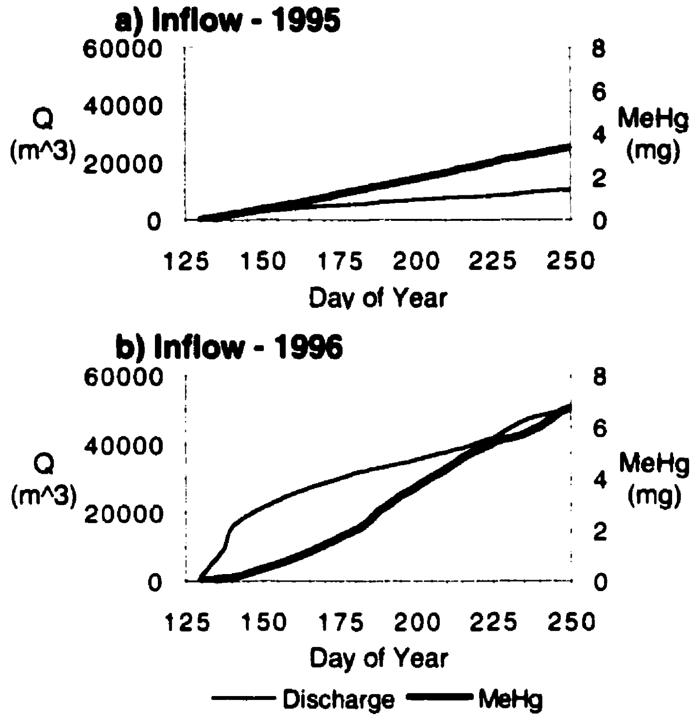


Figure 6.10: Cumulative daily discharge and methylemercury flux for the peatland inflow stream, 1995-1996.

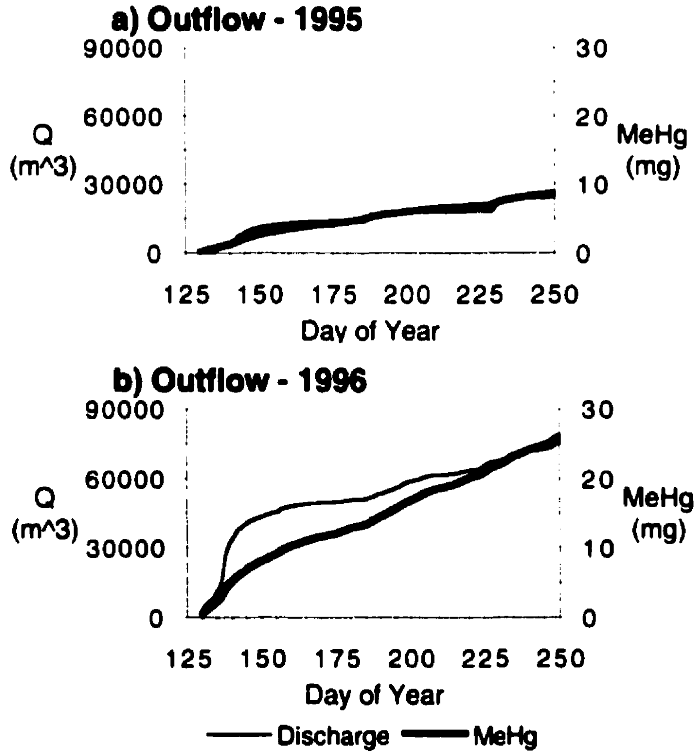


Figure 6.11: Cumulative daily discharge and methylemercury flux for the catchment outflow stream, 1995-1996.

Average daily, minimum daily, maximum daily, total and per unit area fluxes for the peatland inflow stream and catchment outflow are summarized in Table 6.2.

	Average Daily Flux (mg/d)	Minimum Daily Flux (mg/d)	Maximum Daily Flux (mg/d)	Total Flux (mg)	MeHg Yield (mg/ha/d)
Inflow - 1995	0.028	0.021	0.036	3.35	0.0018
Inflow - 1996	0.056	0.007	0.142	7.03	0.0038
Outflow - 1995	0.072	0.021	0.241	8.65	0.0017
Outflow - 1996	0.214	0.085	0.700	25.8	0.0052

Table 6.2: MeHg fluxes for the peatland inflow stream and catchment outflow, Day 130-250, 1995-1996.

If the mean daily yields are prorated over the ice-free season (assumed April 1 - November 1: 214 days) then the total yearly flux of MeHg from the inflow stream to the pond would be 5.97 and 12.6 mg for 1995 and 1996 respectively. This is substantially less than the total flux reported by Branfireun *et al.* (1996) for this same stream in 1993 (0.133 mg/ha/d, or 24.1 mg total flux, calculated as above). Total yearly flux for the catchment outflow would be 15.4 and 46.0 mg for 1995 and 1996 respectively. Catchment MeHg yields presented above are similar to those reported elsewhere in the literature (Table 6.3), to yields reported for the same catchment in a previous study for the years 1990-1993 (St. Louis *et al.*, 1996).

Location	MeHg Yield ($\mu g\ ha^{-1}\ d^{-1}$)	Reference
Southern Sweden	3.3	Lee and Hultberg (1990)
Northern Sweden (Wetland)	2.2 - 4.4	Lee *et al.* (1995)
Wisconsin (Wetland Area Only)	6.0 - 15.0	Krabbenhoft *et al.* (1995)
Ontario ([illegible])	0.2	St. Louis *et al.*, (1996)
Ontario (Riverine Wetland)	0.3 - 0.9	St. Louis *et al.* (1996)
Ontario (Valley Bottom Wetland)	0.7 - 2.5	St. Louis *et al.* (1996)
Ontario (Basin Wetland)[1]	3.6 - 6.8	St. Louis *et al.* (1996)
New York (Wetland)	4.7	Driscoll *et al.* (1998)
Ontario (Whole Catchment)	**1.7 - 5.2**	**This Study**
Ontario (Wetland Outflow Area Only)[2]	29 - 86	This Study

[1]Yields from the "Ontario Basin Wetland" from St. Louis *et al.* (1996) are for the same catchment as studied here, with yields cited being the range reported over 1990-1993.
[2]Yield calculated per unit area of presumed contributing area of the post-pond peatland (2.5 ha) as per method of Krabbenhoft et al. (1995).

Table 6.3: Comparison of catchment MeHg yields from this study with others reported in the literature.

6.4 DISCUSSION

6.4.1 Pools of Methylmercury

The results of this study show the temporal variability and the spatial heterogeneity of MeHg stores and fluxes in this boreal headwater catchment. On the upland hillslopes, solid phase MeHg concentrations in the organic soil horizon and in 'upland wetland' sediments are high relative to concentrations elsewhere in the catchment. Similarly, the pore water concentrations are high in the upland wetland (Table 6.1). This suggests that conditions exist in the upland wetland conducive to methylation (i.e. anoxia, sulfate reduction, adequate supply of labile carbon). Potentially superior methylating conditions exist in the upland wetland relative to those of the lowland peatland (namely a direct supply of more labile allochthonous carbon; see Heyes, 1996). However, these favourable conditions for MeHg accumulation may be offset by a more shallow zone of anoxia and more extreme water table fluctuation than in the lowland (unreported data and observed drying of the soil) resulting in the oxidation of sediments during the summer, precisely when methylation would be at its peak.

The small amount of MeHg in the sand-silt may be affiliated with the small fraction of organics (3.9% by weight) in the form of fine root hairs and small organic particles mobilized from the surface horizon. There may also be some affinity of MeHg with inorganic particles both in the clay fraction which on average comprises 4.5% of the lower mineral horizon. Clay and other mineral oxides have a substantial ability to bind MeHg via inter-layer adsorption, and through surface complexation and surface precipitation respectively (see Desauziers *et al.*, 1997). Although no free water samples were extracted from the sand-silt sediments for MeHg analysis, one would expect to find extremely low concentrations of MeHg in pore water from these soils, given the very low solid phase concentration, and the partition coefficient between solid and liquid phase MeHg (see Heyes, 1996). One would also expect that MeHg would represent a very small fraction of the total-Hg species in the upland mineral soils, although no data were collected to further this point.

In the peatland, MeHg concentrations are variable across the landscape, and appear to be related in part to recharge-discharge function and microtopography. Figures 6.1 and 6.2 confirm the finding of earlier work (Branfireun *et al.*, 1996) showing that in the area of groundwater discharge ('poor fen'), MeHg concentrations are elevated at the surface (up to 3 ng/l) and decrease sharply with depth. In the area of groundwater recharge ('raised bog'), MeHg concentrations are not as high as in the poor fen, and lack the distinctive maxima in the near surface zone. When the poor fen and raised bog are exhibiting their expected discharge and recharge pattern (e.g. July 18, 1996), peak MeHg concentrations are at the water table in the poor fen (upward mass flux), and at -30 cm below in the raised bog (downward mass flux). During a dry summer when this expected discharge and recharge pattern can break down (e.g. August 1, 1995), the maximum MeHg concentrations are found below the water table in the poor fen due to a reversal of the normally upward gradient in groundwater flow. For the same time in the raised bog, the maximum MeHg concentrations remain at the water table due to small rainfall inputs and a significantly weakened downward hydraulic gradient (see Chapter 5). Interestingly, this hydrologic reversal did not appear to affect the maximum MeHg concentrations - within year variations were as large as between years. It is possible that net MeHg production was higher in 1996, but that the flushing rate was correspondingly higher given the wetter summer conditions and greater runoff, resulting in seemingly similar concentrations between years.

This pattern of MeHg concentration may be, in part, due to the delivery of sulfate via a groundwater flowpath in the poor fen zone (Figure 6.3). Slightly higher concentrations of sulfate are seen at depth in the poor fen and, in conjunction with vertical transport via groundwater upwelling, could supply the near surface peat and pore water with the sulfate required for Hg methylation (see Chapter 4). This interpretation is confounded by the presence of higher sulfate concentrations only at -75 cm and deeper, suggesting that sulfate is being reduced *before* it reaches the near surface zone of methylation. There are two potential explanations: It may not be that the sulfate is being reduced at depth, but that it was not being vertically transported by the drought-induced weak hydraulic gradients at the particular time of sampling in 1995, and/or; sulfate reduction and Hg methylation may be occurring at deeper depths than previously thought (<-30 cm). The second suggestion is supported by increasing MeHg burdens in plant materials in some litter bags at depths < -30 cm in the poor fen zone, indicating that active Hg methylators are present in deeper peat (M. Branfireun, unpublished data, 1998). Upwelling of groundwater may also serve to concentrate MeHg in the near surface zone by vertical advection.

In the raised bog, MeHg concentrations are much lower than in the poor fen, however sulfate concentrations at the water table are similar (0.25 mg/l in the raised bog compared to 0.32-0.58 mg/l in the poor fen). As water is downwelling in the raised bog, there is no source of sulfate other than precipitation to the near surface peat and pore water. The pore water sulfate concentrations at the water table in both the raised bog and poor fen likely reflect the concentrations of sulfate in precipitation plus the active recycling of sulfur species in the oxic-anoxic transition zone. The difference in MeHg concentrations between these sites may be related to temperature (proximity of the water table to the ground surface), and/or differences in the 'quality' of carbon available for metabolic processes (i.e. DOC is more labile in poor fen than in raised bog due to the presence of vascular plant litter and/or allochthonous DOC).

Spatial heterogeneity in pore water MeHg concentrations is also evident at a much smaller scale within the poor fen (Figure 6.4). This may be related to the quality of carbon delivered to the sites of methylation (i.e. more labile carbon from vascular plant litter in hollows versus more refractory compounds in decomposing *Sphagnum* spp. beneath hollows), and small-scale spatial variability in water geochemistry (i.e. the presence of FeS precipitates in some hollows and not others).

Sulfate and MeHg concentrations are significantly and negatively related in (near) surface waters throughout the catchment (Figure 6.6), supporting the hypothesis that sulfate reduction is a mechanism by which MeHg is produced, and that the highest MeHg concentrations are found where sulfate is present, but limited (e.g. Gilmour *et al.*, 1998). This relationship breaks down for subsurface waters where MeHg and sulfate concentrations are both low (i.e. lower profile in the raised bog; mid-profile in the poor fen). Figure 6.7 suggests that the sulfate - MeHg relationship is influenced by the presence of DOC, with the highest MeHg concentrations occurring at low concentrations of sulfate and DOC.

6.4.2 Transport of Methylmercury Through the Catchment

Surface water MeHg concentrations at the peatland inflow stream and catchment outflow were at their highest during the dry, low flow year of 1995. Pond MeHg concentrations were not markedly higher in 1995 than in 1996 largely because of the low mass flux of MeHg-laden runoff from the peatland to the pond in 1995. If the pond volume is estimated to be 10000 m^3 (1 ha x 1 m deep on average), then the turnover rate would have been approximately once in the study period, as compared to at least five times over the same time period in 1996. The low mass flux of peatland water also resulted in noticeably greater clarity and light penetration in this normally 'brown water' pond in 1995, potentially promoting greater photodegradation of MeHg and thus increasing the size of the pond sink (Sellers *et al.*, 1996). A weak positive correlation between the inflow stream and pond MeHg concentrations in 1996 (r^2 = 0.27), but not in 1995 (r^2 = 0.06) suggests that the inflow stream only influences pond MeHg concentrations under high flow regimes, whereas in low flow years, within pond processes probably dominate the pond MeHg cycle.

The finding that the overall relationship between MeHg concentration and discharge is negative is consistent with the findings of Bishop *et al.* (1995), but opposite to that of Branfireun *et al.* (1996) in which no dilution of MeHg in peatland inflow stream water was seen after a large summer storm. Although the overall relationship for the inflow stream appears to be negative, the correlation for 1996 is weaker than that of 1995, and in fact shows a slight positive relationship between daily discharges of 200 and 300 m^3. The difficulty in generating such relationships with biologically mediated species such as MeHg is that stream water concentrations may be as dependent on air/soil/water temperatures (as controls on methylation rates) as they are on discharge, and it is coincidental that the highest peak discharges in most years occur in the spring, which is also the time of the lowest rates of biological activity (methylation). Likewise, the highest rates of methylation (and highest stream concentrations) would occur in the mid to late summer period; the same time when stream flows are likely to be at their lowest. Thus, the apparent dilution effect may be, in part, an artifact of the annual pattern of biologically-mediated Hg methylation. Attempts to sample individual storm events to characterize this relationship were not successful for technical and logistical reasons.

Although catchment outflow concentrations were much higher in 1995 than in 1996, the total MeHg mass flux (Table 6.3) was extremely low as compared to 1996 and other studies (St. Louis *et al.*, 1996; Table 6.3), indicating the importance of the catchment hydrology in controlling the flux of MeHg from catchments. Measured catchment outflow MeHg concentrations were on average 2.5 times higher in 1995 than in 1996, yet the 1996 MeHg yield over the study period was 3 times higher than in 1995, controlled in large part by the 3 times greater total discharge in 1996 than in 1995. These findings suggest that flux of MeHg is discharge limited (e.g. 1995). This is in agreement with the findings of St. Louis *et al.* (1996) and Branfireun *et al.*, (1998) (Chapter 3) in which a heuristic model of this catchment indicated that the amount of runoff is a major control on MeHg flux. In the model, the sensitivity of the MeHg flux to volume of runoff was tested by varying the size of the upland contributing area; in reality it is controlled by the magnitude and pattern of annual precipitation and catchment antecedent moisture conditions.

Finally, it is apparent that the main peatland in this catchment is the dominant control on the supply of MeHg. The lack of a statistically significant relationship between pond and catchment outflow MeHg concentrations further suggests that it is only the approximately 300 m of peatland over which the outflow stream flows which controls the supply of MeHg to the outflow and governs catchment MeHg yield. Recalculating the catchment MeHg yields assuming that the entire 2.5 ha of post-pond peatland is the sole MeHg contributor gives a value of 29 - 86 μg/ha/d, or between 6.2 and 18.4 mg/ha over the ice-free season, much higher than other values reported in the literature, but consistent with the methodology of Krabbenhoft *et al.* (1995) (i.e. calculating yield over the presumed contributing area instead of the entire catchment).

These findings strongly indicate that the 'flux order' of the different landscape types within the catchment determines whether or not a catchment will be a net exporter of MeHg. In this case, there are a number of landscape units which are net sources of MeHg, including the upland wetland and the inflow portion of the peatland. However, between these landscape units and the downstream system, there are intervening landscape units which negate the influence of these zones of MeHg production at the catchment scale: in the case of the upland wetland, a portion of mineral hillslope which binds/demethylates MeHg, and; in the case of the inflow peatland, an open water body which mutes the peatland's influence through in-lake MeHg cycling. Thus, it is only the outflow peatland, which, given its place in the landscape, has some influence over the catchment MeHg yield. If this flux order was hypothetically different, and a mineral hillslope intervened between the peatland and the catchment outflow, then the role of the peatland on catchment MeHg yield would be significantly lessened. This concept is consistent with the 'ecotone' and 'landscape patch' concept (Naiman *et al.*, 1988; Naiman and Décamps, 1990) which suggests that it is difficult to apply traditional notions of continuum concepts to ecosystems where sharply defined zones exist naturally. The ecotones which encompass the terrestrial-aquatic interface (e.g. wetlands and riparian zones) have been identified as particularly critical in determining water quality (Naiman and Décamps, 1990), as has been found here.

6.5 CONCLUSION

Catchment hydrology is a strong control on the MeHg dynamics of this boreal headwater catchment, from the differences in MeHg burdens between upland mineral and peat soils, the form of MeHg profiles in the different peatland sub-types, 'micro'-scale variability in MeHg concentrations in peatland microtopographical landforms, and the yield of MeHg from the catchment. The water-borne flux of chemicals such as sulfate via surface and subsurface pathways are a control on *in situ* Hg methylation processes, and require an understanding of the hydrologic interaction between the landscape units (i.e. upland hillslopes and peatlands). The characterization of intra and inter-annual variability in catchment hydrologic response and water yield, and the evaluation of the catchment landscape flux order are important steps towards understanding catchment MeHg dynamics. Future work in this area must include more work on the *in situ* geochemical and biological controls on Hg methylation and demethylation. In addition, an evaluation of the relative importance of the different MeHg contributing areas by evaluating the strength of sources and sinks through the use of isotopes of Hg, as well as the hydrological connectivity of catchment compartments is critical in order to more clearly establish the relationship between MeHg production, hydrological flowpaths and catchment MeHg yield.

Chapter 7: Conclusion

The research presented in this dissertation has posed and answered a number of fundamental questions regarding the temporal variability and spatial distribution of MeHg in the boreal landscape, the hydrological and geochemical controls on MeHg production in peatlands and the delivery of that MeHg to the downstream system. This was accomplished by means on an heuristic model, *in situ* experimentation, and field-based empirical measurements.

The results of a simple cascading-reservoir model of a boreal headwater catchment suggest that: peatlands are large sources of MeHg to the downstream system and that lakes are large sinks of MeHg, consistent with the findings of previous research (St. Louis *et al.*, 1996; Sellers *et al.*, 1996 respectively), and; catchment yield of MeHg is sensitive to the concentrations of MeHg in the peatland reservoir and the amount of water flushing through that peatland from the surrounding uplands. Further, the model suggests that catchment MeHg yield is not sensitive to the amount of MeHg being delivered in rainfall.

The finding that the catchment MeHg yield is sensitive to the amount of MeHg in the peatland reservoir provided motivation to undertake an *in situ* experiment to determine the controls on MeHg production in peatlands. The addition of sulfate to peat and peat pore water was found to increase pore water MeHg concentrations, providing further evidence that sulfate-reducing bacteria are methylators of mercury in natural environments, and suggesting that the atmospheric deposition of anthropogenically-derived sulfate in 'acid rain' may contribute to enhanced Hg methylation and a concomitant increase in catchment MeHg yield.

The model finding that MeHg yield is highly dependent upon catchment water yield provided the impetus for a catchment-scale hydrological investigation. All aspects of the study catchment's hydrology were found to be susceptible to inter-annual variability in precipitation input, with the ice-free hydrologic response dominated by the character of the spring melt event. For a year in which the amount of snowmelt and summer precipitation input were below average (1995), catchment inflow and outflow discharges were 21 and 32% of those in a 'wet' year (1996). Along with this decreased streamflow, pond turnover times were five times longer in the drier year based on surface inflow. Accompanying the lower surface flow rates, groundwater recharge/discharge patterns were also affected, with the breakdown of normal patterns of groundwater flow during the dry year due to the disconnection of the upland hillslope soil reservoir from the peatland hydrological system. Of particular note was the occurrence of groundwater reversals in the poor fen zone which has consistently been a zone of groundwater discharge in all other study years, but was an area of recharge in the dry year (1995) due to the weakening of the zone of higher hydraulic head in the sub-peat sand unit. These changes in catchment hydrology have implications for the cycling of MeHg, which is controlled in part by catchment hydrology, both in terms of its production and its movement within and from the catchment.

MeHg concentrations were found to be variable over time and across the landscape at a variety of scales. The poor fen/groundwater discharge, raised bog/groundwater recharge pattern of high and low MeHg concentrations respectively were confirmed over the study years, even when the groundwater flow patterns were weakened or reversed, as was seen in 1995. This suggests a long residence time of the MeHg *in situ* once produced, a lag in the response of MeHg production to a change in hydrological conditions, or other geochemical controls which are not dependent upon the nature of the hydrological flowpaths.

Pore water MeHg concentrations were also found to be quite variable amongst peatland microtopographical features, with the highest concentrations found at the water table in normal hollows, followed by lawns, hummocks and 'black' hollows. Higher temperature (i.e. distance of the anoxic zone from the ground surface) and litter quality, although not quantified, appear to contribute to higher MeHg concentrations in pore water, although the 'black' hollows are a strong exception to this finding, with unique biogeochemical processes at work in the (near) surface zone which result in lower dissolved MeHg concentrations and highly elevated solid MeHg concentrations.

Field data confirmed that the presence of sulfate, as indicated by the experimental results of Chapter 3, is related to the occurrence of higher concentrations of MeHg in surface and near-surface waters. This was particularly apparent in the poor fen zone where the groundwater delivery of allochthonous sulfate to the surface peat may at least partially explain the higher MeHg concentrations found in this peatland sub-type.

Finally, the mass flux of MeHg within and from the catchment was strongly controlled by the mass flux of water. Although MeHg concentrations were much higher in surface waters in 1995 than in 1996, the fluxes of MeHg from the catchment were three times lower in 1995 than in 1996 due to the three times lower water yield. These findings indicate the importance of understanding the nature of catchment hydrology, both within and between years when attempting to unravel the complex behaviour of a reactive, biologically-mediated trace metal such as MeHg.

A number of questions remain to be answered with respect to the understanding of the sources, transport and fate of MeHg in Boreal, and other catchments. Of particular importance is the understanding of the processes of Hg methylation and demethylation *in situ*. Preliminary experimental incubations with additions of an isotope of MeHg have shown that peat from the study peatland has very strong demethylating potential (B. Branfireun and H. Hintelmann, unpublished data, 1996). These results suggest that high MeHg concentrations found in the poor fen are the result of high rates of Hg methylation. More work towards an understanding of the balance between Hg methylation and demethylation and the controls on these processes in catchment soils and waters is crucial to the predictive modelling of catchment-scale MeHg cycling.

Data on the specific mechanisms of movement of MeHg are also fundamental to the understanding of the processing of MeHg within the catchment. This study failed to address specific questions related to the event-scale behaviour of MeHg concentrations in surface waters. This type of data would provide clarification of the size of the MeHg pool within the catchment, and the resolution of the conflicting reports of a dilution effect at the annual scale (this work), but not at the event scale (Branfireun *et al.*, 1996). Further, the exploration of the biogeochemical function of landscape interfaces such as wetland-aquatic transitions and oxic-anoxic boundaries with respect to the speciation of Hg is of critical importance. Combining these types of information will permit the development of landscape-based predictive models to determine the susceptibility of an aquatic system to elevated MeHg loads through simple catchment landscape classification and analysis of the flux order of landscape types.

References

Aastrup, M., J. Johnson, E. Bringmark, I. Bringmark and Å. Iverfeldt, Occurrence and transport of mercury within a small catchment area, *Water, Air and Soil Pollution*, *56*, 155-167, 1991.

Abdul, A. S. and R. W. Gillam, Laboratory studies of the effects of the capillary fringe on streamflow generation, *Water Resources Research*, *10*, 691-698, 1984.

Abdul, A. S. and R. W. Gillam, Field studies of the effects of the capillary fringe on streamflow generation, *Journal of Hydrology*, *112*, 1-18, 1989.

Allan C. and N. T. Roulet, Runoff generation in zero-order Precambrian Shield catchments: the hydrologic stormflow response of a heterogeneous landscape, *Hydrological Processes* , 8, 369-388, 1994.

Bay, R. R., Runoff from small peatland watersheds, *Journal of Hydrology*, *9*, 90-102, 1969.

Berman, M. and R. Bartha, Control of the methylation process in a mercury polluted aquatic sediment. *Environmental Pollution*., *11*, 41-53, 1986.

Bevan, K. J. and P. Germann, Macropores and water flow in soils, *Water Resources Research*, *8*, 1311-1325, 1982.

Branfireun, B. A., A. Heyes and N. T. Roulet, The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland, *Water Resources Research*, *32*, 1785-1974, 1996.

Branfireun, B. A. and N. T. Roulet, The baseflow and stormflow hydrology of a Precambrian Shield headwater peatland. *Hydrological Processes*, *12*, 57-72, 1998.

Branfireun, B. A., D. Hilbert and N. T. Roulet, Sources and sinks of methylmercury in a boreal catchment, *Biogeochemistry*, *41*, 277-291, 1998.

Bishop, K., Y-H. Lee, C. Petterson and B. Allard, Methylmercury in runoff from the Svartberget catchment in northern Sweden during a stormflow episode. *Water, Air and Soil Pollution*, *80*, 221-224, 1995.

Bishop, K., Y-H. Lee, C. Petterson and B. Allard, Terrestrial sources of methylmercury in surface waters: the importance of the riparian zone on the Svartberget Catchment. *Water, Air and Soil Pollution*, *80*, 435-444, 1995.

Bloom, N. S. and W. F. Fitzgerald, Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold-vapor atomic fluorescence detection, *Anal. Chim. Acta*, *208*, 151-161, 1988.

Bloom, N. S., On the chemical form of mercury in edible fish and marine invertebrate tissue. *Canadian Journal of Fisheries and Aquatic Science*, *49*, 1010-1017, 1992.

Bodaly, R. A., V. L. St. Louis, M. J. Paterson, R. J. P. Fudge, B. D. Hall, D. M. Rosenberg and J. W. M. Rudd, Bioaccumulation of mercury in the aquatic food chain in newly flooded areas, in A. Sigel and H. Sigel (eds.), *Metal Ions in Biological Systems Volume 34: Mercury and Its Effects on Environment and Biology*, New York: Marcel Dekker Inc., pp. 259-287, 1997.

Bottomley, D. J., D. Craig and L. M. Johnston, Neutralization of acid runoff by groundwater discharge to streams in Canadian Precambrian Shield watersheds, *Journal of Hydrology*, *75*, 1-26, 1984.

Bottomley, D. J., D. Craig and L. M. Johnston, Oxygen-18 studies of snowmelt runoff in a small Precambrian Shield watershed: implications for streamwater acidification in acid-sensitive terrain, *Journal of Hydrology, 88*, 213-234, 1986.

Charles-Edwards, D. A., *Physiological determinants of crop growth.* Sydney: Academic Press, 161 pp., 1982.

Choi, S.-C. and R. Bartha, Cobalamin-mediated mercury methylation by *Desulfovibrio desulfuricans* LS, *Applied and Environmental Microbiology, 59*, 290-295, 1993.

Choi, S.-C. T. Chase and R. Bartha, Enzymatic catalysis of mercury methylation by *Desulfovibrio desulfuricans* LS, *Applied and Environmental Microbiology, 60*, 1342-1346, 1994.

Choi, S.-C. T. Chase and R. Bartha, Metabolic pathways leading to mercury methylation in *Desulfovibrio desulfuricans* LS, *Applied and Environmental Microbiology, 60*, 4072-4077, 1994.

Clapp, R. B. and G. M. Hornberger, Empirical equations for some soil hydraulic properties, *Water Resources Research, 14*, 601-604, 1978.

Compeau, G. C. and R. Bartha, Methylation and demethylation of mercury under controlled redox, pH and salinity conditions, *Applied and Environmental Microbiology, 48*, 1203-1207, 1984.

Compeau, G. C. and R. Bartha, Sulfate-reducing bacteria: principal methylators or mercury in anoxic estuarine sediment, *Applied and Environmental Microbiology, 50*, 498-502, 1985.

Cosby, B. J., G. M. Hornberger, R. B. Clapp and T. R. Ginn, A statistical exploration of the relationships of soil moisture characteristics to the physical properties of soils, *Water Resources Research, 20*, 682-690, 1984.

Desauziers, V., N. Castre and P. Le Cloirec, Sorption of methylmercury by clays and mineral oxides, *Environmental Technology, 18*, 1009-1018, 1997.

Devereaux, R., M. R. Winfrey, J. Winfrey and D. A. Stahl, Depth profile of sulfate-reducing bacterial ribosomal RNA and mercury methylation in an estuarine sediment, *FEMS Microbiological Ecology, 20*, 23-31, 1996.

Devito, K. J. and A. R. Hill, Sulphate dynamics in relation to groundwater-surface water interactions in headwater wetlands of the southern Canadian Shield, *Hydrological Processes, 11*, 485-500, 1997.

Devito, K. J., M. J. Waddington and B. A. Branfireun, Flow reversals in peatlands influenced by local groundwater systems, *Hydrological Processes, 11*, 103-110, 1997.

Dingman, S. L., *Physical Hydrology*, Prentice-Hall Inc., Englewood Cliffs. 574 pp.

Driscoll, C. T., C. Yen, C. L. Schofield, R. Munson and J. Holsapple, The chemistry and bioavailability of mercury in remote Adirondack lakes, *Environmental Science and Technology, 28*, 136A-143A, 1994.

Driscoll, C. T., J. Holsapple, C. L. Schofield and R. Munson, The chemistry and transport of mercury in a small wetland in the Adirondack region of New York, USA, *Biogeochemistry, 40*, 137-146, 1998.

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

Gilmour, C. C. and E. A. Henry, Mercury methylation in aquatic systems affected by acid deposition, *Environmental Pollution, 71*, 131-169, 1991.

Gilmour, C. C., E. A. Henry and R. Mitchell, Sulfate stimulation of mercury methylation in freshwater sediments, *Environmental Science and Technology, 26*, 2281-2287, 1992.

Gilmour, C. C., G. S. Riedel, M. C. Ederington, J. T. Bell, J. M. Benoit, G. A. Gill and M. C. Stordal, Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades, *Biogeochemistry, 40*, 327-345, 1998.

Harada, M., Minimata disease: Methylmercury poisoning in Japan caused by environmental pollution, *Critical Reviews in Toxicology, 25(1)*, 1-24, 1995.

Hewlett, J. D. and A. R. Hibbert, Factors affecting the response of small watersheds to precipitation in humid areas, In W. E. Sopper and H. W. Lull (eds.), *Forest Hydrology*, Pergamon, Oxford, pp. 275-290, 1967.

Heyes, A. *Methylmercury in Natural and Disturbed Wetlands*, PhD Dissertation, Montreal: McGill University Department of Geography, 1996.

Hinton, M. J., S. L. Schiff and M. C. English, Physical properties governing groundwater flow in a glacial till catchment, *Journal of Hydrology, 142*, 229-249, 1993.

Horvat, M., N. S. Bloom and L. Liang, Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part 1. Sediments, *Anal. Chim. Acta, 281*, 135-152, 1993.

Hultberg, H., J. Munthe and Å, Iverfelt, Cycling of methyl mercury and Mercury - responses in the forest roof catchment to three years of decreased atmospheric deposition, *Water, Air and Soil Pollution, 80*, 415-424, 1995.

Hurley, J. P., J. M. Benoit, C. L. Babiarz, M. M. Shafer, A. W. Andren, J. R. Sullivan, R. Hammond and D. A. Webb, Influences of watershed characteristics on mercury levels in Wisconsin rivers, *Environmental Science and Technology, 29*, 1867-1875, 1995.

Iverfelt, Å, J. Munthe, C. Brosset and J. Pacyna, Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia, *Water, Air and Soil Pollution, 80*, 227-233, 1995.

Keeler, G., G. Glinsorn and N. Pirrone, Particulate mercury in the atmosphere: Its significance, transport, transformation and sources, *Water, Air and Soil Pollution, 80*, 159-168, 1995.

Kelly, C. A., J. W. M. Rudd, V. L. St. Louis and A. Heyes, Is total mercury concentration a good predictor of methyl mercury concentrations in aquatic systems?, *Water, Air and Soil Pollution., 80*, 715-724, 1995.

Krabbenhoft, D. P., J. M. Benoit, , C. L. Babiarz, J. P. Hurley and A. W. Andren, Mercury cycling in the Allequash Creek watershed, northern Wisconsin, *Water, Air and Soil Pollution, 80*, 425-433, 1995.

Lee, Y-H, and H. Hultberg, Methylmercury in some Swedish surface waters, *Environmental Toxicology and Chemistry, 9*, 833-841, 1990.

Lee, Y. H., K. Bishop, C. Petterson, Å. Iverfelt and B. Allard, Subcatchment output of mercury and methylmercury at Svartberget in Northern Sweden, *Water, Air and Soil Pollution, 80*, 455-465, 1995.

Lindberg, S. E. and W. J. Stratton, Atmospheric mercury speciation - concentrations and behaviour of reactive gaseous mercury in ambient air, *Environmental Science and Technology, 32*, 49-57, 1998.

Lindberg, S. E., P. J. Hanson, T. P. Meyers and K. H. Kim, Air/surface exchange of mercury vapor over forests - the need for a reassessment of continental biogenic emission, *Atmospheric Environment*, 32, 895-908, 1998.

Linsey, G. A., D. W. Schindler and M. P. Stainton, Atmospheric deposition of nutrients and major ions at the Experimental Lakes Area in northwestern Ontario, 1970-1982, *Canadian Journal of Fisheries and Aquatic Science*, 44: 206-214, 1987.

Lovley, D. R. and M. J. Klug, Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations, *Applied and Environmental Microbiology, 45*, 187-192, 1983.

Lucotte, M., A. Mucci, C. Hillaire-Marcel, P. Pichet and A. Grondin, Anthropogenic mercury enrichment in remote lakes of northern Québec, Canada, *Water, Air and Soil Pollution*, *80*, 467-476, 1995.

McDonnell, J. J. and C. H. Taylor, Surface and subsurface water contributions during snowmelt in a small Precambrian Shield watershed, Muskoka, Ontario, *Atmosphere-Ocean*, *25*, 251-266, 1987.

Maulé, C. P. and J. Stein, Hydrologic flow path definition and partitioning of spring meltwater, *Water Resources Research*, *36(12)*, 2959-2970, 1990.

Meili, M., The coupling of mercury and organic matter in the biogeochemical cycle - towards a mechanistic model for the boreal forest zone, *Water, Air and Soil Pollution*, *56*, 333-347, 1991.

Moore, R. D., Tracing runoff sources with deuterium and oxygen-18 during spring melt in a headwater catchment, southern Laurentians, Quebec, *Journal of Hydrology*, *112*, 135-148, 1989.

Moore, T. R., J. L. Bubier, A. Heyes and R. J. Flett, Methyl and total mercury in boreal wetland plants, Experimental Lakes Area, northwestern Ontario. *Journal of Environmental Quality*, *24*, 845-850, 1995.

Naiman, R.J., M.M. Holland, H. Décamps and P.G. Risser, The potential importance of boundaries to fluvial ecosystems, *Journal of the North American Benthological Society*, *7*, 289-306, 1988.

Naiman, R.J., and H. Décamps (Eds.), *The Ecology and Management of Aquatic-Terrestrial Ecotones*, Paris: Unesco, 316 pp, 1990.

Oke, T. R., *Boundary Layer Climates* (2nd ed.). Methuen: London. 435 pp., 1987.

Oremland, R. S., L. G. Miller, P. Dowdle, T. Connell and T. Barkay, Methylmercury oxidative degradation potentials in contaminated and pristine sediments of the Carson river, Nevada, *Applied and Environmental Microbiology, 61*, 2745-2753, 1995.

Peters, D. L., J .M. Buttle, C. H. Taylor and B. D. LaZerte, Runoff production in a forested, shallow soil, Canadian Shield basin, *Water Resources Research, 31*, 1291-1304, 1995.

Porcella, D. B., J. W. Huckabee and B. Wheatley (eds.), Mercury as a global pollutant: Proceedings of the third international conference held in Whistler, British Columbia, July 10-14, 1994 (*Water, Air and Soil Pollution, 80*, 1995), Kluwer Academic Publishers, Dordrecht, The Netherlands. 1336 pp., 1995.

Renzetti, A. V. E., C. H. Taylor and J. M. Buttle, Subsurface flow in a shallow soil Canadian Shield watershed, *Nordic Hydrology, 23*, 209-226, 1992.

Roberge, J. and A. P. Plamondon, Snowmelt runoff pathways in a boreal forest hillslope, the role of pipe throughflow, *Journal of Hydrology*, 95, 39-54, 1987.

Roulet N. T., S. Munro and L. Mortsch, Wetlands. In: *Surface Climate of Canada*. Bayley, W., T. Oke and W. Rouse (eds.), McGill - Queens University Press., 1997.

Rudd, J. W. M., Sources of methyl mercury to freshwater ecosystems: a review, *Water, Air and Soil Pollution, 80*, 697-713, 1995.

Schroeder, W. H. and J. Munthe, Atmospheric mercury - an overview, *Atmospheric Environment, 32*, 809-822, 1998.

Sellers, P., W. M. Rudd, C. A. Kelly and A, Machutcheon, Photodegradation of methylmercury in lakes, *Nature, 380*, 694-697, 1996.

St. Louis, V. L., J. W. M. Rudd, C. A. Kelly, K. G. Beaty, N. S. Bloom and R. J. Flett, Importance of wetlands as sources of methyl mercury to boreal forest ecosystems, *Canadian Journal of Fisheries and Aquatic Science, 51*, 1065-1076, 1994.

St. Louis, V. L., J. W. M. Rudd, C. A. Kelly and L. A. Barrie, Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. *Water, Air and Soil Pollution*, *80*, 405-414, 1995.

St. Louis, V. L., J. W. M. Rudd, C. A. Kelly, K. G. Beaty, R. J. Flett and N. T. Roulet, Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands, *Environmental Science and Technology*, *30*, 2719-2729, 1996.

Topp, G. C., J. L. Davis and A. P. Annan, Electromagnetic determination of soil water content: Measurement in coaxial transmission lines, *Water Resources Research*, *16*, 579-582, 1980.

Urban, N. R., E. S. Verry and S. J. Eisenreich, Retention and mobility of cations in a small peatland: trends and mechanisms, *Water, Air and Soil Pollution*, *79*, 201-224, 1995.

Verry, E. S., K. N. Brooks and P. K. Barten, Streamflow response from an ombrotrophic mire, in *Proceedings of the International Symposium on the Hydrology of Wetlands in Temperate and Cold Regions - Vol. 1*, pp. 52-59, The Academy of Finland, Helsinki, 1988.

Watras, C. J., N. S. Bloom, S. A. Claas, K. A. Morrison, C. C. Gilmour and S. D. Craig, Methylmercury production in the anoxic hypolimnion of a diamictic seepage lake, *Water, Air and Soil Pollut*ion, *80*, 735-745, 1995.

Wels, C., R. J. Cornett and B. D. LaZerte, Groundwater and wetland contributions to stream acidification: an isotopic analysis, *Water Resources Research*, *26*, 2993-3003, 1990.

Winfrey, M. and J. W. M. Rudd, Environmental factors affecting the formation of methylmercury in low pH lakes: A review, *Environmental Toxicology and Chemistry, 12*, 2245-2264, 1990.